

Designing Water Resistant High Entropy Oxide Materials



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REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

Review

Authors' scientific findings provide the insights into the rational computational design of catalysts, capable of withstanding moisture-related industrial challenges/issues. I can recommend this submitted manuscript for publication, but only after revision. Please find my improving comments attached:

In this manuscript, the authors propose a concept of engineering entropy to design water-resistant oxide catalysts, inspired by the principle of high entropy-stabilized structures. They focus on the C₃H₆ oxidation reaction using spinel ACr₂O₄ catalysts (where A represents various metal ions such as Ni, Mg, Cu, Zn, and Co) as a model. The authors conducted DFT calculations to evaluate key factors affecting the catalyst performance. These factors include the adsorption energy of C₃H₆, the dissociation energy of molecular H₂O on the oxide surface, and the formation energy of oxygen vacancy. The DFT calculations suggested that higher configurational entropy could lead to improved catalyst performance. To validate their findings, the authors conducted experimental tests. They found that a high entropy oxide catalyst, specifically (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄, exhibited excellent water resistance, lasting for more than 100 hours in the C₃H₆ oxidation reaction. In contrast, binary oxides like NiCr₂O₄ and CoCr₂O₄ deactivated within 20 hours. The authors supported their experimental results with various characterization techniques such as H₂O-TPD, in-situ Raman spectroscopy, and in-situ FTIR. These analyses confirmed the low H₂O adsorption energy and strong hydrothermal stability of the high entropy oxide catalysts, attributed to their lower Gibbs free energy. Overall, the authors' work introduces a novel approach to designing water-resistant catalysts by leveraging the concept of high entropy-stabilized structures. Their findings provide insights into the rational design of catalysts capable of withstanding moisture-related challenges in industrial catalysis. I can recommend this manuscript for publication but only after revision. Please find my comments below.

1. First, the authors must provide original spectra (GC and/or GC-MS) with obtained product mixture over studied oxide catalysts. This information can be included in the Support Information file. Also, the authors should decrypt/label each intense/main peak observed on spectra.
2. The authors must present the product distribution over all studied catalysts with a calculation of corresponding product selectivity and/or yield in mol%.
3. What is the experimental error of the catalytic activity study (conversion, selectivity)? Did the authors check the reproducibility of the obtained experimental data? This information must be provided.

4. Did authors calculate total carbon balance? I think this general information must be presented.
5. Figure 6 should include much more details about reaction operating conditions.
6. The authors should provide the real/experimental composition of the synthesized catalysts and include it in Table S5. ICP-OES or XRF analyses can be useful.
7. Please provide information in detail about the utilized method for analysis of product mixture on GC.
8. Why were the baselines for Ni2p (Fig9a top) and Co2p (Fig9b bottom) shifted so low?
9. How were the adsorption energies of C₃H₆ and the dissociation energies of water calculated? Add the equations.
10. Expand the discussion on how each A = Ni, Mg, Cu, Zn, Co in ACr₂O₄ affects the adsorption of C₃H₆, the dissociation of water and the formation of an oxygen vacancy.
11. In the description of Figure 2 you state that the dissociation energies of molecular water are calculated and shown in the figure, but in each image you denoted the adsorption energies (E_{ad}) of OH – and not the dissociation energies of molecular water. Which one is correct?
12. Please rotate the images in Figure 3 so that the oxygen vacancy is clearly visible.
13. I suggest that you round the values of the calculated energies to two decimal places.
14. I suggest that the authors re-read the manuscript and correct the typos. In several places in the manuscript, spaces before brackets (between a word and a bracket) are missing.
15. There is a discrepancy between the use of DFT calculations and experimental work. On page 9 (and elsewhere) you state that experiments were carried out to validate the DFT results, but in the Methods section you claim that DFT calculations were performed to verify the experimental results. Please correct the discrepancy.
16. Manuscript conclusion section is missing. You can combine Discussion and Conclusion sections or rename the Discussion part to Conclusion portion.
17. “Meanwhile, Wang et al.[3] identified the favorable role of water in the hydrogenation of CO₂ to methanol, which strongly affected the selectivity and yield of methanol.” – Firstly, this is contrary to what most literature says, while secondly, the review of works here is indeed very poor. The effect of the water during the synthesis of methanol, as well as during the (reverse) water–gas shift reactions is very well documented, which cannot be traced from (authors’) presentation. Some initial points that should be mentioned/ duly referenced:
 - the mechanisms of the copper-based catalyst deactivation during the CO₂ reduction to methanol
 - the sulphur poisoning, water vapour and nitrogen dilution effects on the copper-based catalyst dynamics, stability and deactivation during the CO₂ reduction process reactions to methanol

- the reaction path analysis of the CO₂ reduction to the methanol through the multisite micro-kinetic modelling over Cu/ZnO/Al₂O₃ catalysts

Reviewer #2 (Remarks to the Author):

Zhang and coworkers investigate the effect of entropic stabilization on the water resistance and catalytic performance of chromate spinels towards the oxidation of propene. Through a combined computational and experimental approach, the authors examine a series of MCr₂O₄ spinel structures, where M is either a single metal (Ni, Co, Zn, Mg, Cu) or a random mixture of all five metals occupying the same crystallographic site (determined to be entropically stabilized). The authors conclude that the entropically-stabilized version of the catalyst shows higher hydrothermal stability than the formal ternary compounds and improved catalytic performance, suggested initially by DFT calculation and corroborated by experiment. On their face, the reported findings seem interesting (and aligned with other reports in the literature). However, the analysis/methodology presented in the current contribution is missing either some key explanatory details or additional, convincing control experiments to back up their claims.

My background is not in computation, so I cannot comment on the effectiveness of the calculations or the veracity of the authors' claims from that angle. I will leave the specifics of those experimental details to reviewers with more relevant expertise. My comments/questions are from an experimental materials perspective, and I think, point to the overall accessibility of the work for publication in a journal with a broad readership of scientists and engineers.

1/ Overall, I think the paper would benefit from some more clear explanations. The chosen materials are highly complex from an experimental and computational perspective. I find that the explanations given for both experimental and computational observations lacking, particularly in light of the complexity or messy-ness of the materials in question. As one example: the authors find that the dissociation energy of water on the surface of the high-entropy oxide is much higher than the single component spinels... why is that? What's the mechanism that's governing this switch? Why is it not just a simple combination of the single component materials?

2/ I have some questions about the calculations performed as part of the study: while the formal ternary structures (with a single M occupant on the +2 site in the spinel) have a regular, predictable structure that seems relatively straightforward to model, how is the inherent "randomness" of the M site handled by the computation for the multi-component M site (the entropically stabilized material)? The DFT-related figures seem to suggest well-defined composition on the surface and bulk sites, but that doesn't seem to be a rigorous model that comports with the reality of the complex sample (which will have, in principle a random occupancy of these sites). If a "randomness" term can't be well handled by the model, did the authors try multiple surface site compositions/permutations? What was the effect of this? Are the only things that matter the surface sites?

3/ The experimental aspects of the paper also raise a series of questions. Perhaps most critically,

related to control materials and materials characterization. Some thoughts:

- the characterization of the high-entropy material lacks the kind of spatial resolution and elemental composition data needed to draw sweeping conclusion about surface structure/bulk structure/entropic stabilization. The material seems to be agglomerated nanoscale crystallites and the elemental composition (using EDS mapping) is too low-resolution and low-count to make any assessment of the local composition in any nanoscale domain. EDS mapping is a visual representation of semi-quantitative data, but the composition of the metals (based on spectral data) aren't given. Is there batch-to-batch variability here? How well mixed are these oxides experimentally?

- The main controls use single component oxides (i.e., one M). Do 5 metals really need to be there? What about 3, or 2? Does this impact performance/structure?

- To make an appropriate/rigorous comparison, the materials and the control materials should be the same phase (minimally) and ideally, the same grain size/morphology/loading, etc. To wit, several of the "control" single metal spinels are not the correct phase by XRD (either a mixture of phases or unidentified other oxides. No TEM or other characterization is given for these samples. Are these the samples being used for catalytic testing? It is unclear that the catalytic samples were held at the very same testing conditions. Overall, it is difficult to assess the appropriateness of the comparisons between the high entropy material and the control materials without these details.

Reviewer #3 (Remarks to the Author):

The high-entropy oxide presented herein displays more efficient catalytic activity and higher resiliency to water degradation than current catalysts. Density functional theory, H₂O-temperature programmed desorption, raman spectroscopy, x-ray photoelectron spectroscopy, and x-ray diffraction were all used to characterize the water resistance and catalytic activity.

The manuscript is well written, dense with experimental findings, and timely: high-entropy oxides for robust catalysis is an exciting topic. There is also strong theory to support the conclusions. This work can be published in its current state but would be stronger with some revisions.

Recommendations:

1. It appears that the propylene molecules modeled in figure 1 are not consistently positioned between the models with and without water. It is unclear whether they migrated during relaxations or were placed intentionally.
2. It was mentioned that the lattice spacings found in the experimental results corresponded to the following crystal faces: (111), (311), and (220). However, it appears that the (111) face was not investigated with DFT. It is unclear why.
3. It is unclear which sites were used to model the oxygen vacancy in the high-entropy oxide, zinc, and cobalt structures. It would be helpful if they were highlighted with the yellow atom (O-vacancy) as was done for the other structures in figure 3.

Response to the reviewers' comments

Dear Reviewers,

We are very grateful for your professional review work on our article. These comments are valuable and very helpful in revising and improving our paper. According to your nice suggestions, we have made extensive corrections to our previous manuscript, a point-by-point response to the reviewers' comments is listed below. In this revised version, all changes to our manuscript are all highlighted in yellow color.

Reviewer: 1

Comments:

In this manuscript, the authors propose a concept of engineering entropy to design water-resistant oxide catalysts, inspired by the principle of high entropy-stabilized structures. They focus on the C_3H_6 oxidation reaction using spinel ACr_2O_4 catalysts (where A represents various metal ions such as Ni, Mg, Cu, Zn, and Co) as a model. The authors conducted DFT calculations to evaluate key factors affecting the catalyst performance. These factors include the adsorption energy of C_3H_6 , the dissociation energy of molecular H_2O on the oxide surface, and the formation energy of oxygen vacancy. The DFT calculations suggested that higher configurational entropy could lead to improved catalyst performance. To validate their findings, the authors conducted experimental tests. They found that a high entropy oxide catalyst, specifically $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$, exhibited excellent water resistance, lasting for more than 100 hours in the C_3H_6 oxidation reaction. In contrast, binary oxides like $NiCr_2O_4$ and $CoCr_2O_4$ were deactivated within 20 hours. The authors supported their experimental results with various characterization techniques such as H_2O -TPD, in-situ Raman spectroscopy, and in-situ FTIR. These analyses confirmed the low H_2O adsorption energy and strong hydrothermal stability of the high entropy oxide catalysts, attributed to their lower Gibbs free energy. Overall, the authors' work introduces a novel approach to designing water-resistant catalysts by leveraging the concept of high entropy-stabilized structures. Their findings provide insights into the rational design of catalysts capable of withstanding moisture-related challenges in industrial catalysis. I can recommend this manuscript for publication but only after revision. Please find my comments below.

1. First, the authors must provide original spectra (GC and/or GC-MS) with obtained product mixture over studied oxide catalysts. This information can be included in the Support Information file. Also, the authors should decrypt/label each intense/main peak observed on spectra.

Reply: Thanks for the constructive suggestion! The original GC spectra of obtained product mixture for studied oxide catalysts were important. This information was added in the **Support Information 2 (>300 pages)**. In addition, we labeled main peaks observed on the spectra. Please refer to the original GC data in **Support Information 2** for details.

2. The authors must present the product distribution over all studied catalysts with a calculation of corresponding product selectivity and/or yield in mol%. 4. Did authors calculate total carbon balance? I think this general information must be presented.

Reply:

Thanks for the constructive suggestion!

Initially, we have investigated many relevant literatures about how to calculate the conversion rate of volatile organic compounds (VOC) in the VOC combustion reaction.^[1~6] For example, a denary multi-element oxide catalyst showed high performance and superior stability for catalytic methane combustion over 100 hours (Nature Catalysis, **2021**, 4(1): 62-70.). The measurement of catalytic performance was as follows: Catalytic methane combustion was conducted in a fixed-bed flow reactor at atmospheric pressure. To determine the conversions of the reactants and the formation of products, a gas chromatograph (GC-2010 plus, Shimadzu) was employed, equipped with a silica capillary column (SH-Rt-Q-BOND) and a barrier ionization discharge detector. All of the lines between the reactor outlet and GC sampling loop inlet were heat-traced to 423K to prevent product condensation. Methane conversion was calculated as follows:

$$\text{CH}_4 \text{ conversion} = ([\text{CH}_4]_{\text{in}} - [\text{CH}_4]_{\text{out}}) / [\text{CH}_4]_{\text{in}} \times 100.$$

$[\text{CH}_4]_{\text{in}}$ and $[\text{CH}_4]_{\text{out}}$ represent the inlet and outlet amount of CH_4 .

For another example, a defective Pt/TiO_{2-x} catalyst was proposed to uncover the different catalytic mechanisms of C_3H_6 combustion (*Environ. Sci. Technol.* **2022**, 56, 5, 3245–3257). The reactant C_3H_6 in the outlet streams was analyzed using an online gas chromatograph (GC 2030). The C_3H_6 was detected using a flame ionization detector (FID) equipped with a FFAP capillary column. The conversion of C_3H_6 was calculated by the following equation:

$$\text{C}_3\text{H}_6 \text{ conversion} = (\text{C}_3\text{H}_6_{\text{in}} - \text{C}_3\text{H}_6_{\text{out}}) / \text{C}_3\text{H}_6_{\text{in}} \times 100\%.$$

$[\text{C}_3\text{H}_6]_{\text{in}}$ and $[\text{C}_3\text{H}_6]_{\text{out}}$ represent the inlet and outlet amount of C_3H_6 .

- [1] FANG Y, LI H, ZHANG Q, et al. Oxygen Vacancy-Governed Opposite Catalytic Performance for C_3H_6 and C_3H_8 Combustion: The Effect of the Pt Electronic Structure and Chemisorbed Oxygen Species [J]. Environmental Science & Technology, **2022**, 56(5): 3245-57
- [2] FANG Y, LI L, YANG J, et al. Engineering the Nucleophilic Active Oxygen Species in CuTiOx for Efficient Low-Temperature Propene Combustion [J]. Environmental Science & Technology, **2020**, 54(23): 15476-88.
- [3] NIE L, MEI D, XIONG H, et al. Activation of surface lattice oxygen in single-atom Pt/CeO₂ for low-temperature CO oxidation [J]. Nature, **2017**, 358(6369): 1419-23.
- [4] LI T, YAO Y, HUANG Z, et al. Denary oxide nanoparticles as highly stable catalysts for methane combustion [J]. Nature Catalysis, **2021**, 4(1): 62-70.
- [5] NIE L, MEI D, XIONG H, et al. Activation of surface lattice oxygen in single-atom Pt/CeO₂ for low-temperature CO oxidation [J]. Science, **2017**, 358(6369): 1419-23.

[6] HAO H, JIN B, LIU W, et al. Robust Pt@TiOx/TiO₂ Catalysts for Hydrocarbon Combustion: Effects of Pt-TiOx Interaction and Sulfates [J]. ACS Catalysis, **2020**, 10(22): 13543-8.

For the total oxidation of low concentration propylene in this work, the main product is carbon dioxide. The possible products include epoxy propylene and carbon monoxide. For total oxidation of propylene by as-made catalysts in this work, only carbon dioxide was observed in the chromatography (please refer to the original GC spectrum in **Support Information 2** for details). There was a small peak around 2.5min, which was the peak of trace air during swithing valve. This peak could be observed in the black run without catalysts (**Figure S59**), and the corresponding area can be ignored (Its area accounts for 0.029% of the propylene area). Moreover, the detection limit of this GC for CO was below 10ppm (**Figure S58**). If no peak of CO was visible on the chromatography, indicating that the concentration of CO was below 10ppm (Note that the initial C₃H₆ concentration is 10000ppm.).

To further find CO and other products in the propylene combustion reaction, the total propylene oxidation was followed by a mass spectrometry experiment. Only signals of propylene and CO₂ were detected in the mass spectrometry, and no signal of CO was detected (**Figure S6~7 in Support Information 2 file**). This result fully indicated that the product of the propylene combustion reaction was almost CO₂.

To observe CO₂ product, the chromatography in this work contained a conversion furnace with a Ni-based catalyst. Low-concentration CO₂ was converted into CH_x, which then entered the FID detector, and finally a signal would appear. To figure out the liner relationship between CO₂ concentration and GC peak area, we conducted namely the standard curve for low-concentration CO₂ (**Table S1 and Figure S3 in Support Information 2 file**), and the standard curve for high-concentration CO₂ (**Table S2 and Figure S4 in Support Information 2 file**). We found that there was a difference in the fitted formula between the low-concentration CO₂ standard curve and the high-concentration CO₂ standard curve (please refer to the original GC spectrum in Support Information 2 for details).

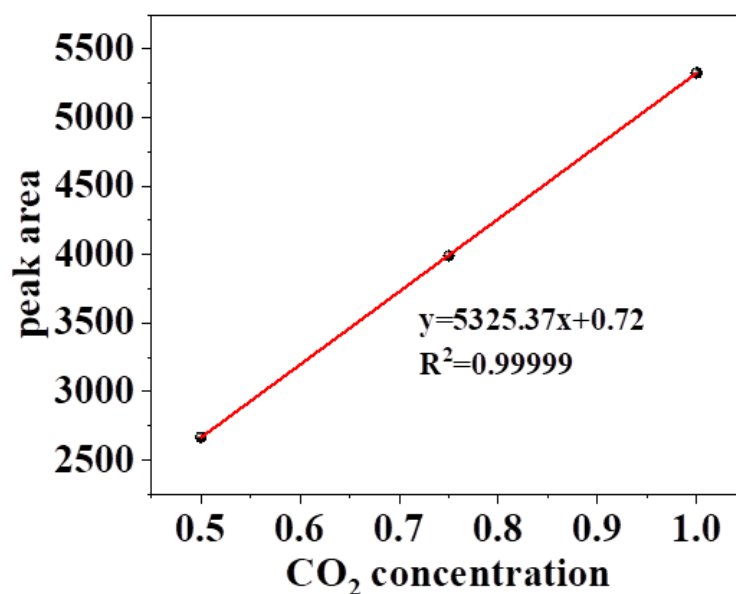


Figure S3 (in Support Information 2) CO₂ Standard curve (positive linear relationship between peak area and concentration) of 0.5%~1% CO₂

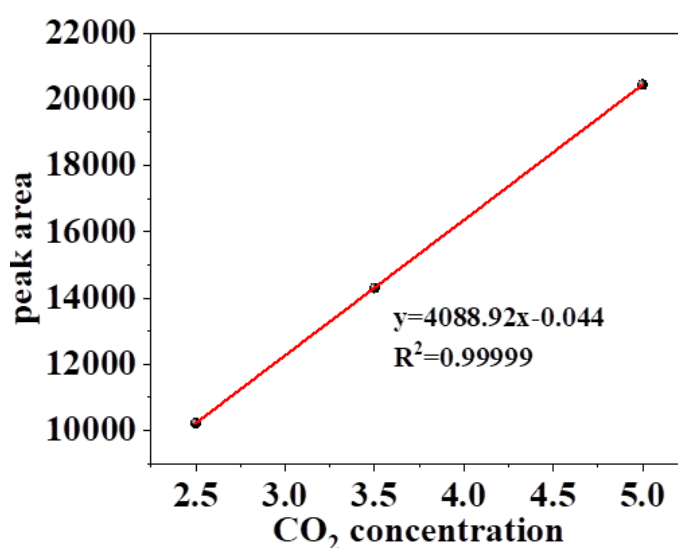


Figure S4 (in Support Information 2) CO₂ Standard curve (positive linear relationship between peak area and concentration) of 2.5%~5% CO₂

Therefore, we concluded that Ni-based conversion furnace cannot transform all CO₂ in time, and FID detectors cannot detect the true concentration of CO₂ generated. Because CO₂ concentration cannot be precisely determined, the calculation of product selectivity and carbon balance seems difficult in current system (**Figure S57**).

Based on those results and literature methods^[1~6], we calculated the conversion rate of propylene based on the ratio of the remaining concentration of propylene and the initial concentration of propylene, as follows:

$$\text{C}_3\text{H}_6 \text{ conversion} = ([\text{C}_3\text{H}_6]_{\text{in}} - [\text{C}_3\text{H}_6]_{\text{out}}) / [\text{C}_3\text{H}_6]_{\text{in}} \times 100.$$

$[C_3H_6]_{in}$ and $[C_3H_6]_{out}$ represent the inlet and outlet amount of C_3H_6 .

- [1] FANG Y, LI H, ZHANG Q, et al. Oxygen Vacancy-Governed Opposite Catalytic Performance for C_3H_6 and C_3H_8 Combustion: The Effect of the Pt Electronic Structure and Chemisorbed Oxygen Species [J]. Environmental Science & Technology, **2022**, 56(5): 3245-57
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- [3] NIE L, MEI D, XIONG H, et al. Activation of surface lattice oxygen in single-atom Pt/CeO₂ for low-temperature CO oxidation [J]. Nature, **2017**, 358(6369): 1419-23.
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- [6] HAO H, JIN B, LIU W, et al. Robust Pt@TiOx/TiO₂ Catalysts for Hydrocarbon Combustion: Effects of Pt-TiOx Interaction and Sulfates [J]. ACS Catalysis, **2020**, 10(22): 13543-8.

Revised:

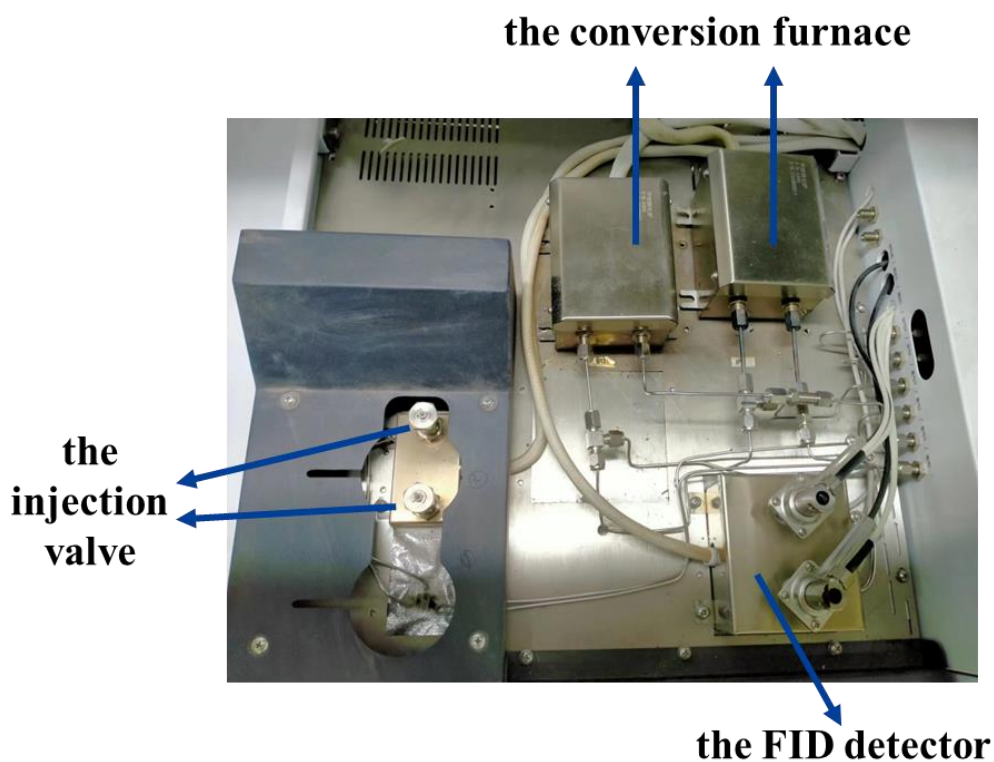


Figure S57. The Picture of experimental GC instrument in this work.

Revised:

Table S1 (in Support Information 2) Original data of CO₂ internal standard curve of 0.5%~1% range

CO ₂ concentration	peak area						average
0.5%	2684.3	2650.1	2656.3	2672.3	2659.9	2665.6	2664.75
0.75%	4224.7	3856	3976.8	4000.3	3976.8	3917.7	3992.05
1%	5326.9	5398.4	5314.5	5260.4	5332.8	5331.6	5327.43

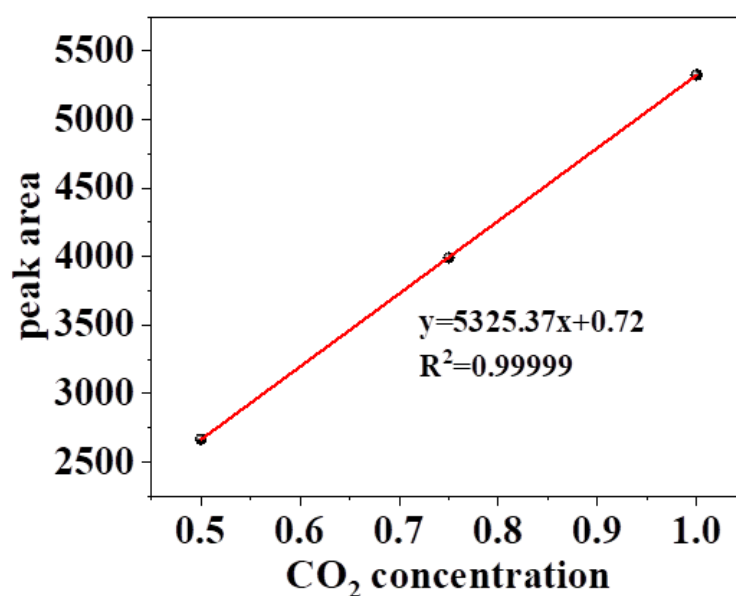


Figure S3 (in Support Information 2) CO₂ Standard curve (positive linear relationship between peak area and concentration) of 0.5%~1% CO₂

Table S2 (in Support Information 2) Original data of CO₂ internal standard curve of 2.5%~5% range

CO ₂ concentration	peak area						average
2.5%	10237	10542	10108	10266	10423	9778	10225.67
3.5%	14304	13973	14255	14577	14304	14420	14305.5
5%	21144	19813	19548	21522	21169	19485	20446.83

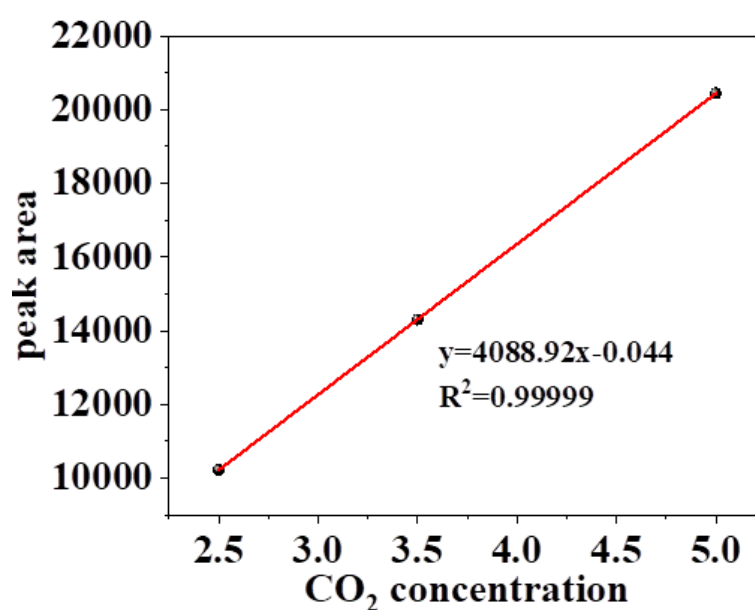


Figure S4 (in Support Information 2) CO₂ Standard curve (positive linear relationship between peak area and concentration) of 2.5%~5% CO₂

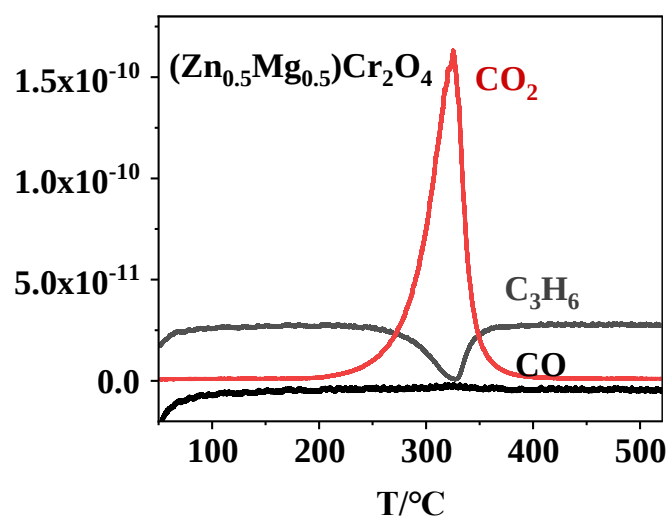


Figure S6 in Supporting Information 2 Mass spectrometry Spectrum in the catalytic C_3H_6 combustion by $(\text{Zn}_{0.5}\text{Mg}_{0.5})\text{Cr}_2\text{O}_4$ sample.

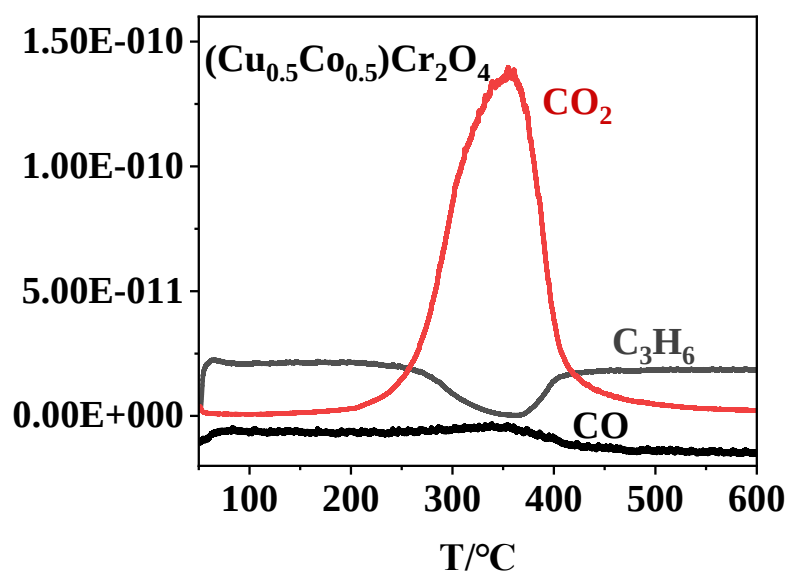
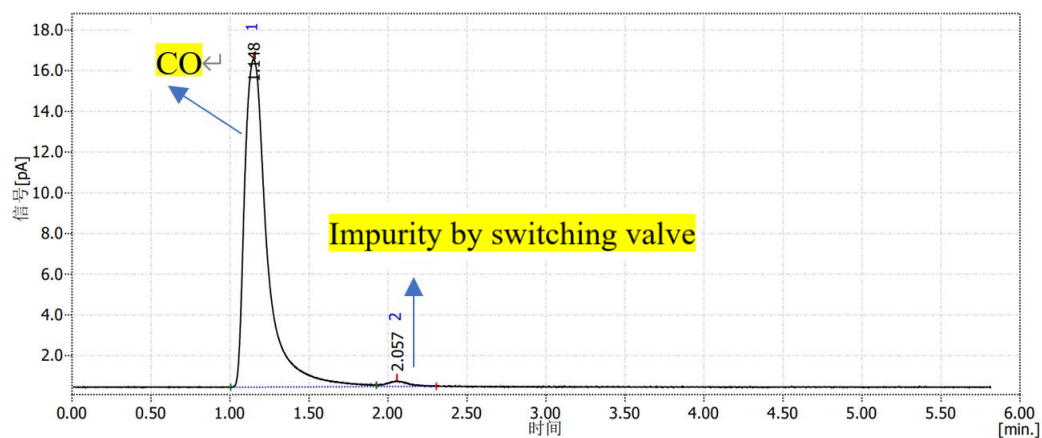
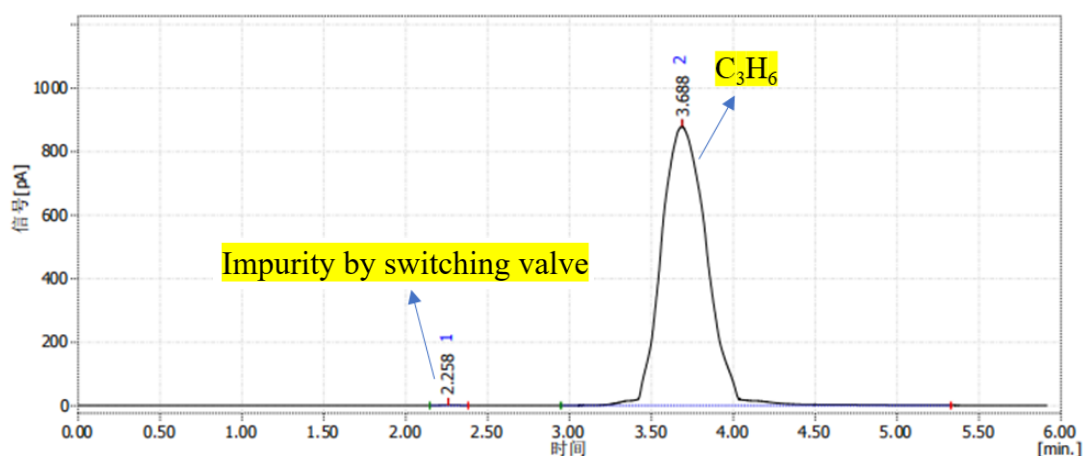


Figure S7 in Supporting Information 2 Mass spectrometry Spectrum for C_3H_6 combustion of $(\text{Cu}_{0.5}\text{Co}_{0.5})\text{Cr}_2\text{O}_4$ sample.



序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		1.1483	160.7037	0.0000	98.4144	
2		2.0567	2.5892	0.0000	1.5856	
总计			163.2930	0.0000	100	0.0000

Figure S58. Original GC spectrum (The raw gas contains 10ppm CO and the remaining is air. The small peak around 2.5min was the peak of trace air during switching valve).



序号	组份名称	保留时间 (min)	峰面积	浓度 ()	面积百分比	浓度百分比
1		2.2584	4.9733		0.0294	
2		3.6875	16896.4200		99.9706	
总计			16901.3900	0.0000	100	0.0000

Figure S59. Original GC spectra with no catalysts at 50°C (10 mL/min, Feed gas ratio: 1 vol % C₃H₆ and 99 vol % air) The small peak around 2.5min was the peak of trace air during switching valve.

3. What is the experimental error of the catalytic activity study (conversion, selectivity)? Did the authors check the reproducibility of the obtained experimental data? This information must be provided.

Reply:

Thanks for the constructive suggestion!

Initially, to study the experimental error of the $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ catalyst in C_3H_6 combustion, we figure out the influence of internal and external diffusion. Results suggested that there were no effects of internal and external diffusion for this catalytic combustion process (**Figure S18**).

Then, we agree with the reviewer that the reproducibility of current data is key. For this issue, the optimized high entropy component were prepared three times, and the samples were labeled as a- $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, b- $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, c- $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ respectively. Characterizations such as: XRD (**Figure S19**), SEM (**Figure S20**), and TEM (**Figure S21~32**) were added to find the reproducibility of high entropy oxides.

High entropy samples a- $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, b- $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, c- $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ all showed characteristic diffraction peaks of cubic phase spinel (JCPDS 80-1668), and no other diffraction peaks were observed. This result suggested the formation of single high entropy phase. In addition, the accurate content of each metal ions in a- $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, b- $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, c- $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ were determined through Inductance-coupled plasma (ICP) analysis (ICP-MS) respectively (**Table S7, Table S8, Table S9**). We found good repeatability and minimal variability in elemental contents among a- $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, b- $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, c- $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$. Moreover, high-resolution elemental composition (by using EDS spectra) demonstrated that the elemental distribution was uniform in the nanoscale for all high entropy samples. The SEM images of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ showed the morphology of aggregated nanoparticles with sizes of 10–30 nm (**Figure S20**), which matched well with the XRD result (**Figure S2**). The enlarged image showed that the surface of the particle contained smaller particles. Furthermore, the TEM images (**Figure S21~32**) revealed these HEOs were solid particles.

Finally, the catalytic activity of the three samples were measured in the same process. The variance in the C_3H_6 conversion rate of a- $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, b- $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, c- $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ was quite low. This result suggested the good reproducibility of as-made high entropy oxides in catalytic oxidation (**Figure S5 and Table S3 in Supporting Information 2**) (please refer to the original GC spectrum in **Support Information 2** for details).

Revised:

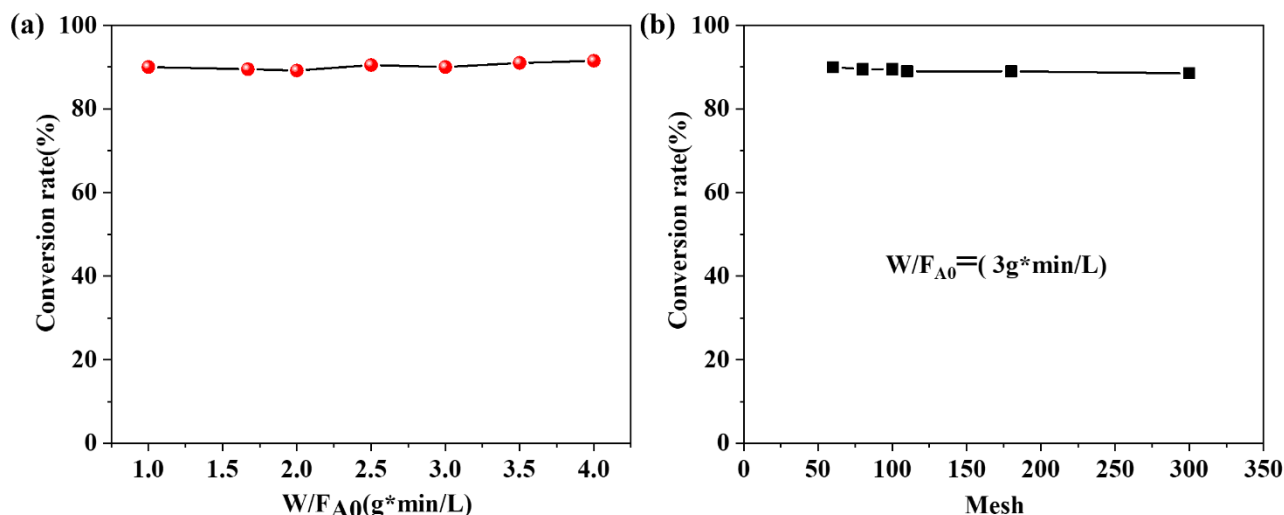


Figure S18. (a) The influence of external diffusion for C_3H_6 oxidation. (b) The influence of external diffusion C_3H_6 oxidation.

In addition, to study the catalytic performance of $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$ in C_3H_6 combustion, it was necessary to study the influence of internal and external diffusion. First, whether the existence of external diffusion or not was determined. For C_3H_6 combustion, 10mg, 20mg, 30mg, 40mg, and 50mg of catalysts were mixed with 30 mg of quartz sand for each measurement at a flow rate of 4 mLmin $^{-1}$, 10 mLmin $^{-1}$, 20 mLmin $^{-1}$ and 30 mLmin $^{-1}$). Then the conversion rate was measured at 265°C separately. As shown in **Figure S18a**, the test points all fall on the linear curve. This result indicated that the difference in linear velocity did not affect the reaction rate, thus excluding the external diffusion effect. Moreover, under the fixed W/F_{A0} parameters (30 mg catalyst mixed with 30 mg quartz sand was used for each measurement under a flow rate of 10 mL min $^{-1}$), the conversion rate at 265°C was almost unchanged by changing the mesh size of the $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$ catalyst. These results suggested that there was no effect of internal diffusion (**Figure S18b**).

Revised:

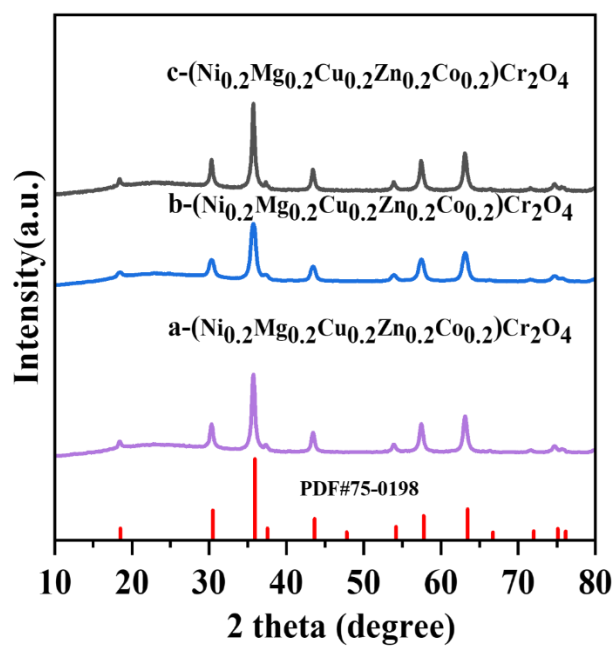


Figure S19. X-ray diffraction patterns of a-($\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2}$) Cr_2O_4 , b-($\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2}$) Cr_2O_4 and c-($\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2}$) Cr_2O_4 .

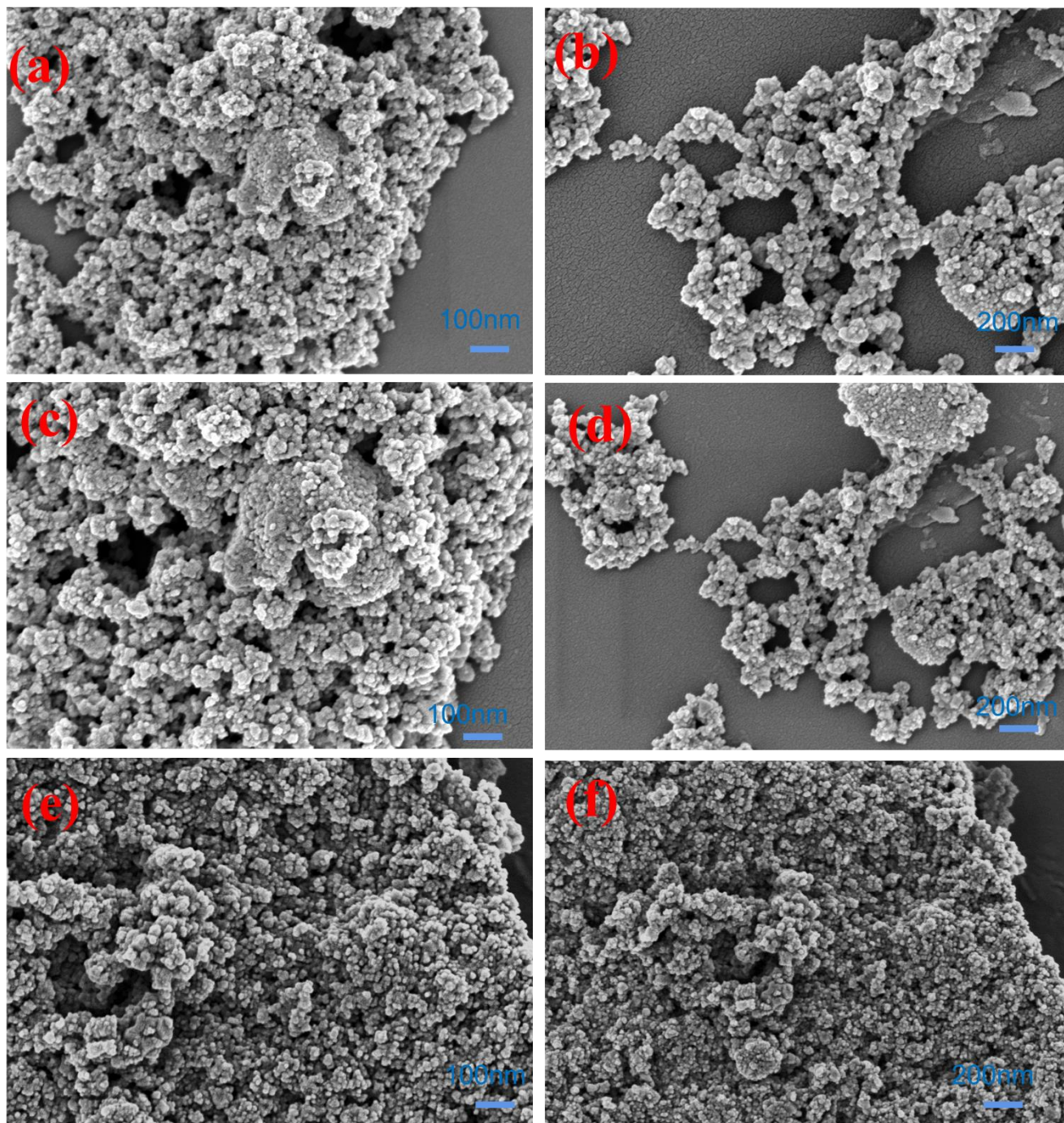


Figure S20. SEM images of (a, b) a-($\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2}$) Cr_2O_4 , (c, d) b-($\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2}$) Cr_2O_4 and (e, f) c-($\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2}$) Cr_2O_4 .

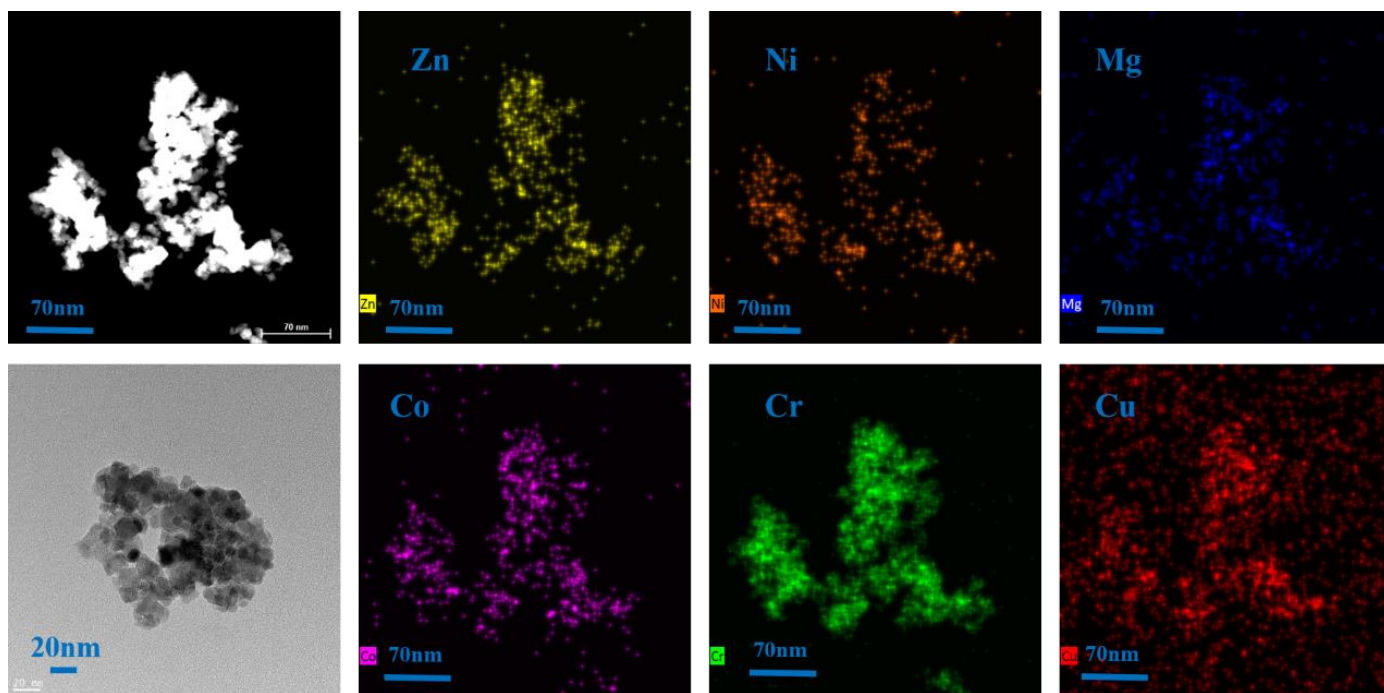


Figure S21 High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and energy-dispersive spectroscopy (EDS) elemental mapping images of a- $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ nanoparticles.

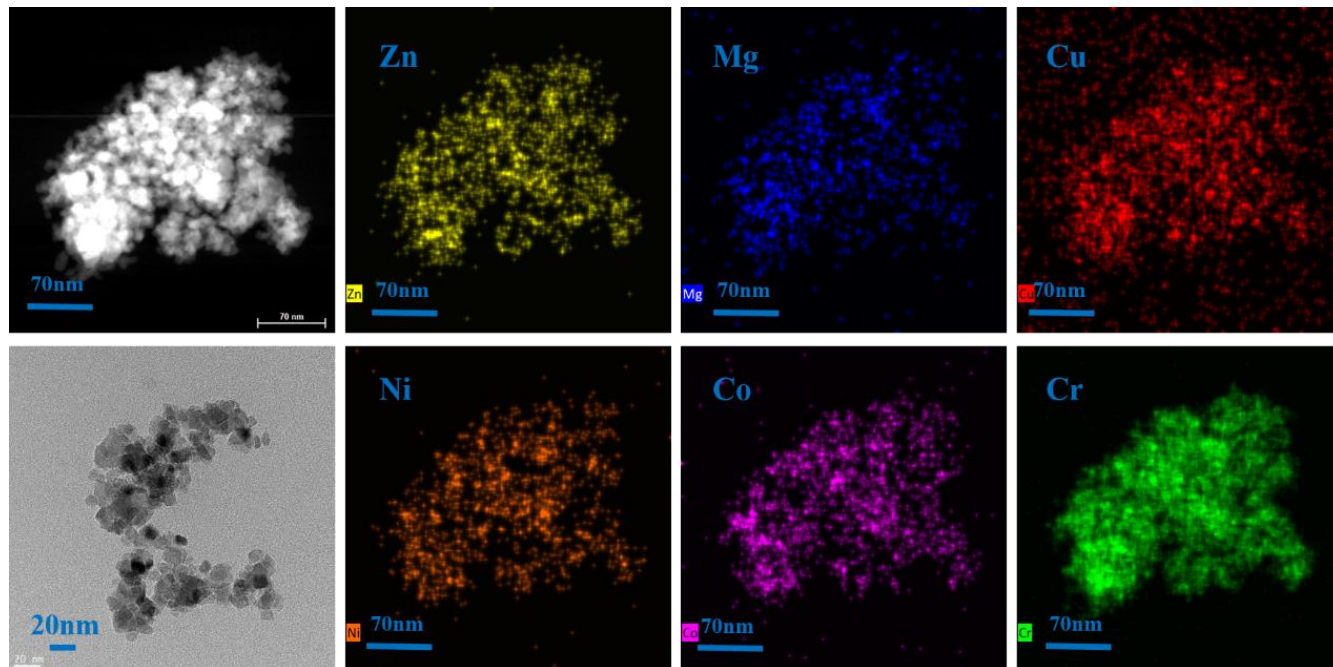
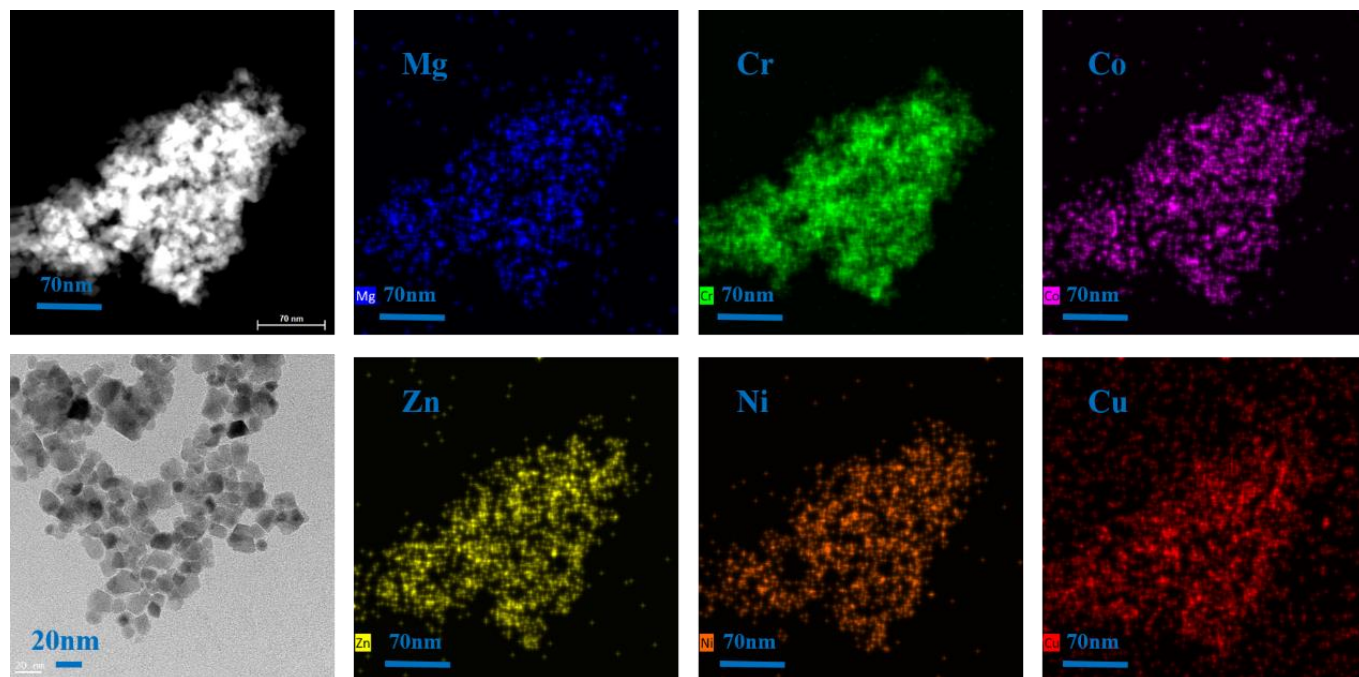


Figure S23 High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and energy-dispersive spectroscopy (EDS) elemental mapping images of b- $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ nanoparticles.



FigureS25 High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and energy-dispersive spectroscopy (EDS) elemental mapping images of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ nanoparticles.

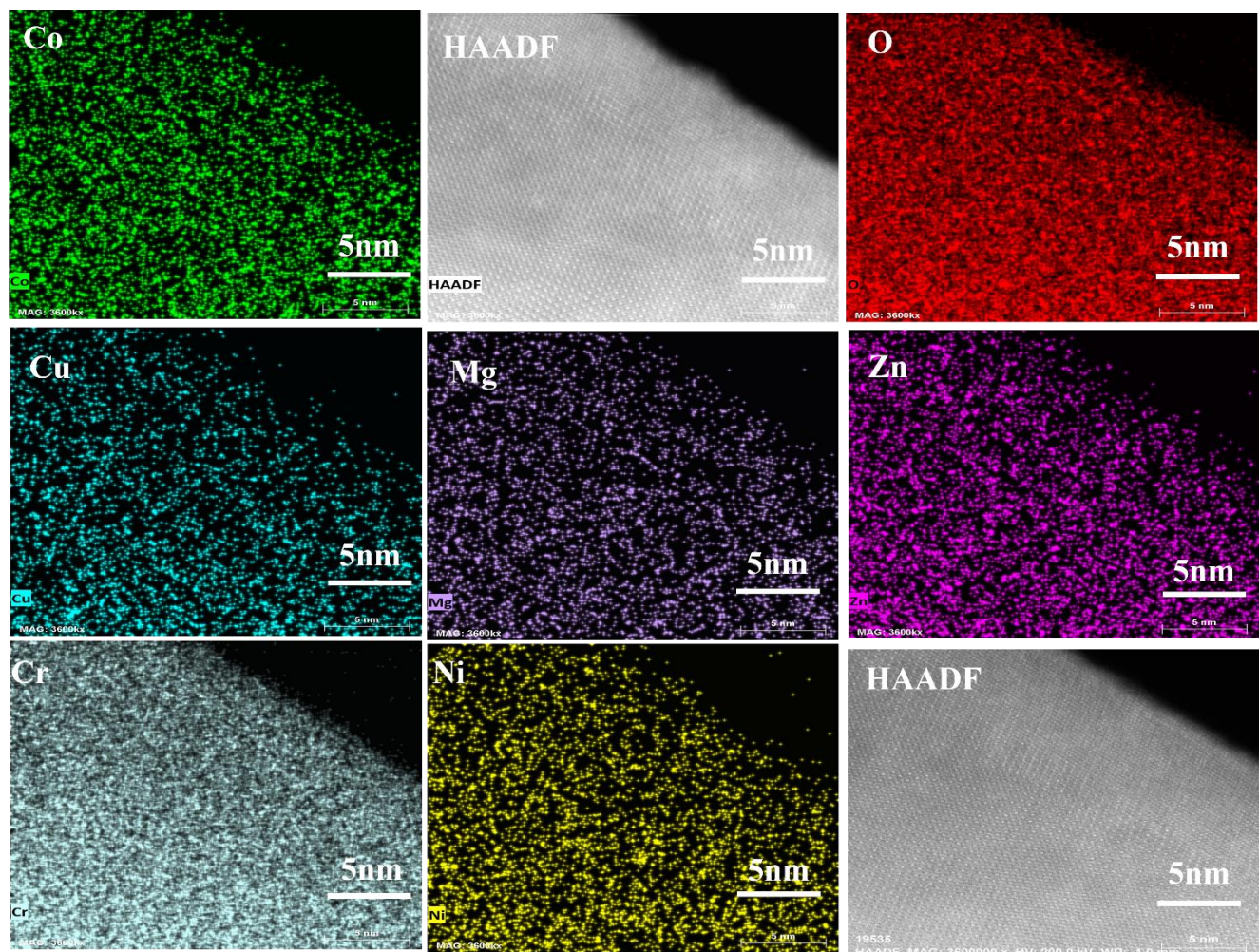


Figure S27.High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and energy-dispersive spectroscopy (EDS) elemental mapping images of a-($\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2}$) Cr_2O_4 nanoparticles.

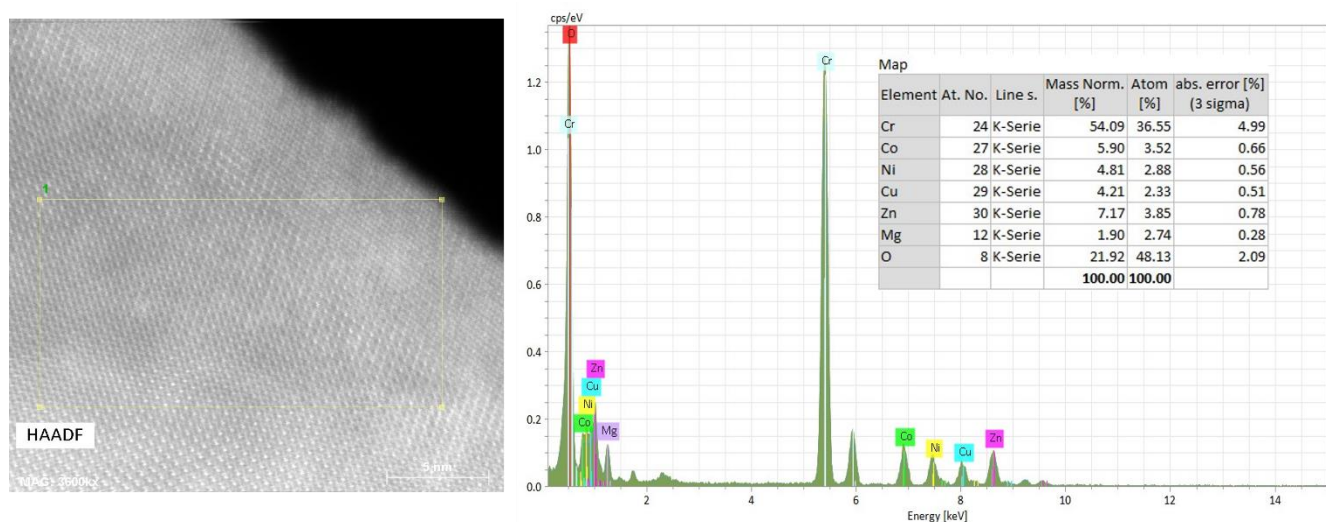


Figure S28.The qualitative analysis with composition of the metals (based on EDS mapping spectral data) of a-($\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2}$) Cr_2O_4 nanoparticles.

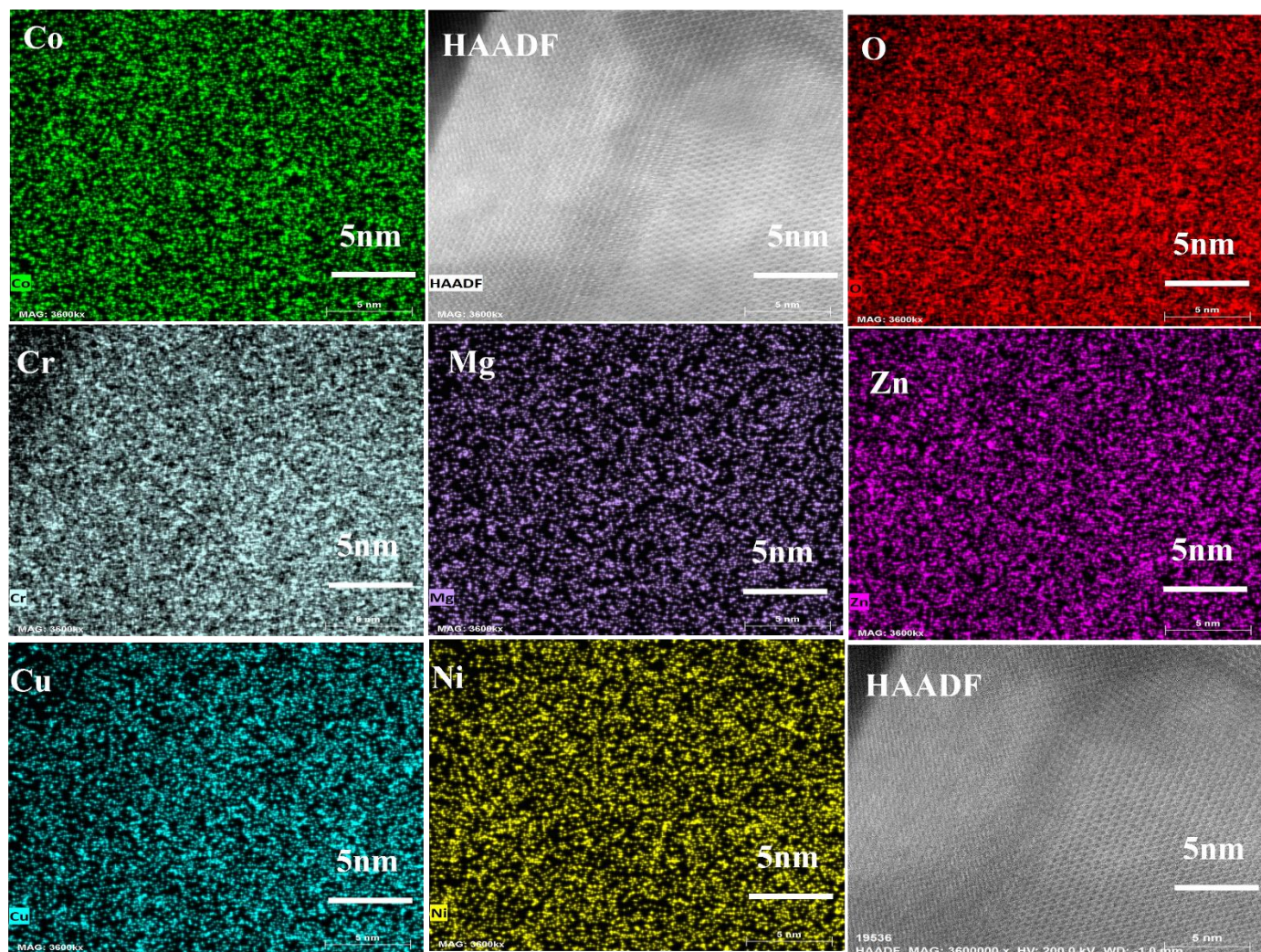


Figure S29. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaged and energy-dispersive spectroscopy (EDS) elemental mapping images of b- $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ nanoparticles.

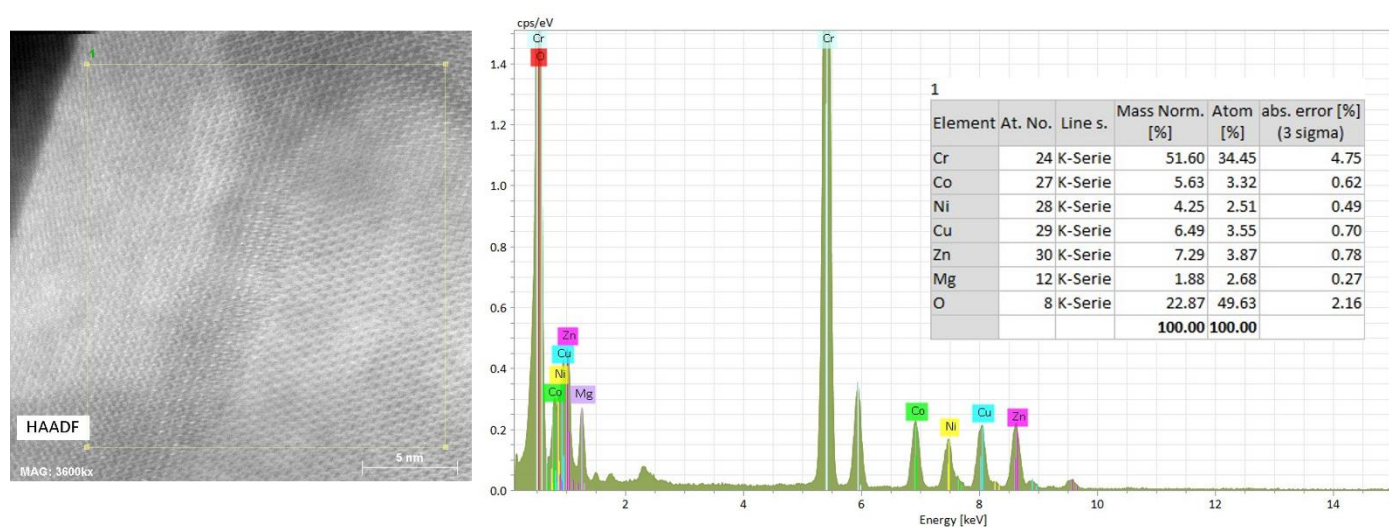


Figure S30. The qualitative analysis with composition of the metals (based on EDS mapping spectral data) of b- $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ nanoparticles.

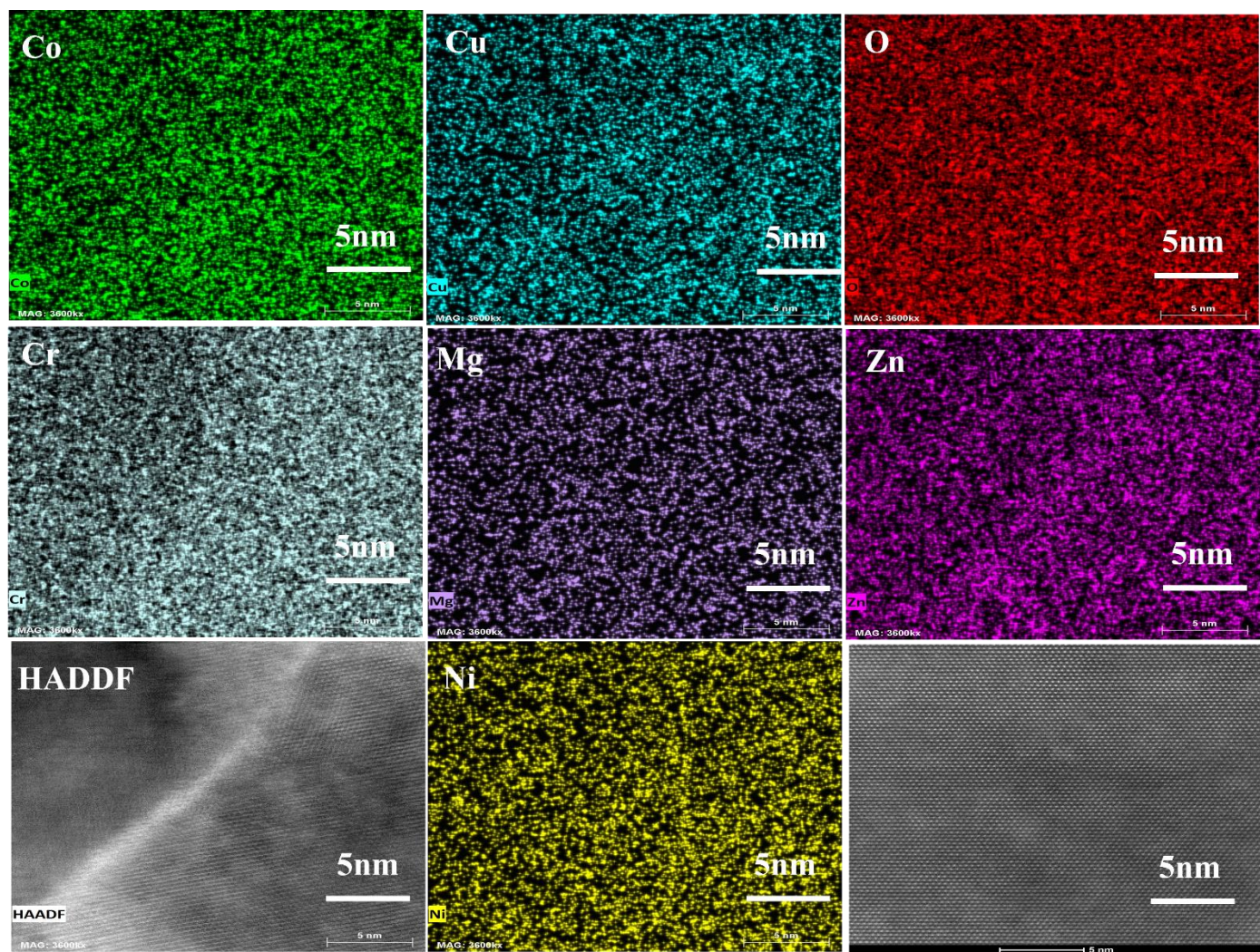


Figure S31. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and energy-dispersive spectroscopy (EDS) elemental mapping images of c-($\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2}$) Cr_2O_4 nanoparticles.

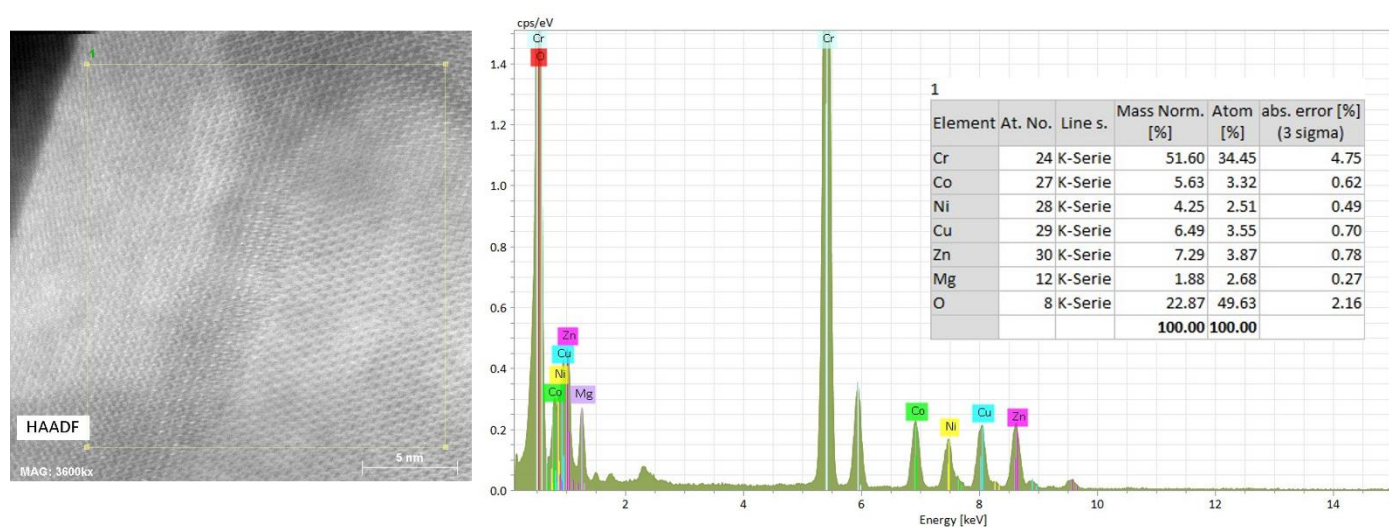


Figure S32. The qualitative analysis with composition of the metals (based on EDS mapping spectral data) of c-($\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2}$) Cr_2O_4 nanoparticles.

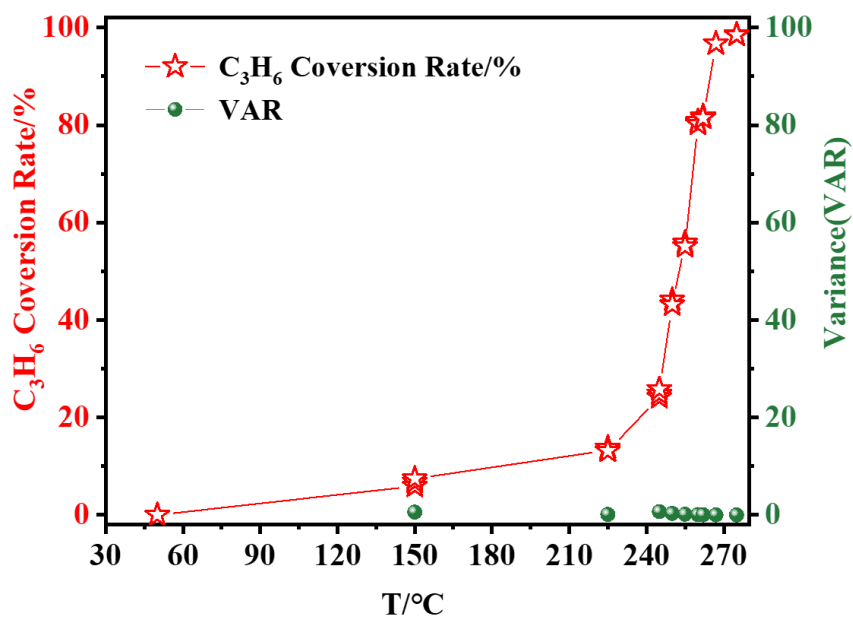


Figure S5a in Supporting Information 2. C₃H₆ light-off curve and variance(VAR) of a-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄, b-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ and c-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ (20000 mL h⁻¹g⁻¹; the feed gases contain 1vol % C₃H₆ and 99vol% air).

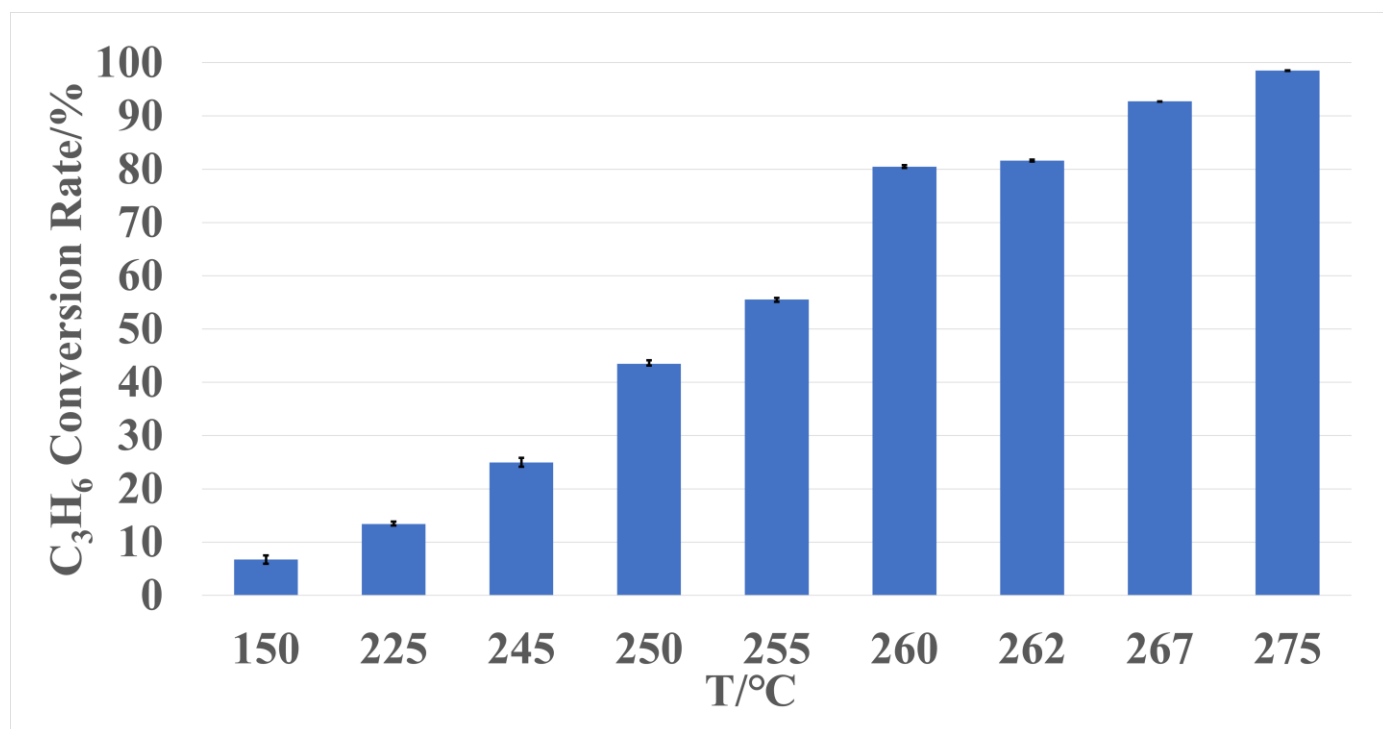


Figure S5b in Supporting Information 2. Histogram of C₃H₆ light-off curve and variance(VAR) in a-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄, b-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ and c-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄(20000 mL h⁻¹g⁻¹; the feed gases contain 1vol % C₃H₆ and 99vol% air)

Table S3 (in Support Information 2) Original data of C₃H₆ light-off curve and variance(VAR) of a-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄, b-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ and c-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄

T/°C	Sample	C ₃ H ₆ Conversion Rate/%	Variance (VAR)
50	a-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄		
	b-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	0.000	0
	c-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄		
150	a-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	5.916	
	b-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	6.784	0.613
	c-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	7.479	
225	a-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	13.269	
	b-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	13.826	0.134
	c-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	13.137	
245	a-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	24.154	
	b-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	24.849	0.710
	c-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	25.831	
250	a-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	43.173	
	b-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	44.138	0.322
	c-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	43.139	
255	a-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	55.810	
	b-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	55.804	0.168
	c-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	55.098	
260	a-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	80.401	
	b-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	80.757	0.074
	c-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	80.223	
262	a-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	81.803	
	b-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	81.693	0.038
	c-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	81.423	
267	a-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	92.697	
	b-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	92.749	0.001
	c-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	92.737	
275	a-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	98.443	
	b-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	98.575	0.004
	c-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	98.524	

5. Figure 6 should include much more details about reaction operating conditions.

Reply: Thanks for the constructive suggestion! We added the schematic details of experimental instruments for C_3H_6 combustion and hydrothermal stability experiment (**Figure S54**). The catalytic activity of C_3H_6 oxidation combustion was evaluated. The catalytic combustion experiments were carried out in a temperature-controlled microreactor (MX-2000, HangZhou MengXiao Instrument Co., Ltd) equipped with an online gas chromatograph (GC2060, Shanghai Ruimin Instrument Co., Ltd). Typically, 30 mg catalyst mixed with 30 mg quartz sand was used for each measurement under a flow rate of 10 mL min^{-1} , which corresponds to a Gas Hourly Space Velocity (GHSV) of $20000\text{ mL h}^{-1}\text{g}^{-1}$. The feed gases contain 1 vol % C_3H_6 and 99 vol % air. The heating rate of the reaction furnace was $5\text{ }^{\circ}\text{C/min}$. The C_3H_6 concentration can be detected in real-time. To evaluate the catalyst's resistance to water vapor, the feeding gas was firstly passed into water bath at $30\text{ }^{\circ}\text{C}$ (Note that the concentration of water vapor was calculated as 4.2% at saturated vapor pressure and $30\text{ }^{\circ}\text{C}$) and then introduced into the catalyst bed. The stability experiments were carried out at a conversion of $\sim 70\%$ in C_3H_6 oxidation combustion under humid conditions (4.2 vol %) for 100 hours.^[1-3]

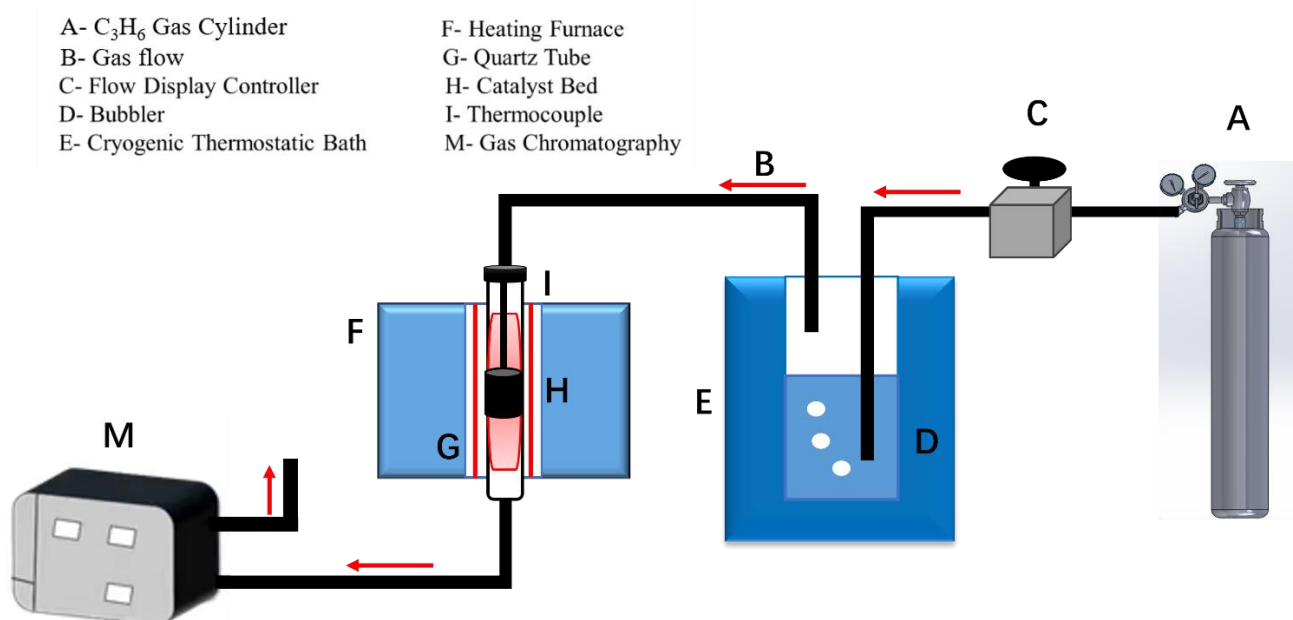


Figure S54. Experimental instruments for C_3H_6 catalytic combustion and hydrothermal stability test.

6. The authors should provide the real/experimental composition of the synthesized catalysts and include it in Table S5. ICP-OES or XRF analyses can be useful.

Reply:

Thanks for the important suggestion! $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$ and their control samples ACr_2O_4 (A=Ni, Mg, Cu, Zn, Co) were prepared three times. Three groups of samples with the same components were subjected to characterization experiments respectively. Three high entropy samples labeled as: a- $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$, b- $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$, c- $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$. The accurate content of each metal ions in a- $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$, b-

(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄, c-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ and their control samples ACr₂O₄(A=Ni, Mg, Cu, Zn, Co) were determined and added through Inductance-coupled plasma (ICP) analysis (ICP-MS) respectively (Table S7, Table S8, Table S9). The accurate content of each sample was obtained through Inductance-coupled plasma (ICP) analysis (ICP-MS), which were close to the thoretical contents.

Original:

In this work, (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ was constructed by a mechanochemistry-mediated method. The essence of this synthetic strategy was the mechanochemical processing of metal precursors, which generated more grain boundaries and interfaces between various metal salts. The description of procedure was shown in Figure 4 and Table S4.

Revised:

In this work, (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ was constructed by a mechanochemistry-mediated method. The essence of this synthetic strategy was the mechanochemical processing of metal precursors, which generated more grain boundaries and interfaces between various metal salts. The description of procedure was shown in Figure 4 and Table S4. In addition, the accurate content of each sample was obtained through Inductance-coupled plasma (ICP) analysis (ICP-MS), which were close to the thoretical contents (Table S7, Table S8, Table S9).

Table S7. The molecular formula of a-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ by Inductance-coupled plasma (ICP) analysis (ICP-MS)

Theoretical Molecular formula	Experimental Molecular formula	Cu	Zn	Co	Ni	Mg	Cr
NiCr ₂ O ₄	NiCr _{2.03} O ₄	0	0	0	20.6 4%	0	41.82 %
MgCr ₂ O ₄	MgCr _{2.15} O ₄	0	0	0	0	18.2 2%	39.13 %
CuCr ₂ O ₄	CuCr _{1.98} O ₄	21.9 3%	0	0	0	0	43.50 %
ZnCr ₂ O ₄	ZnCr _{2.03} O ₄	0	19.0 6%	0	0	0	38.84 %
CoCr ₂ O ₄	CoCr _{1.82} O ₄	0	0	22.85 %	0	0	41.26 %
(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	(Ni _{1.07} MgCu _{1.02} Zn _{1.04} Co _{1.06})Cr _{1.26} O ₄	4.85 %	4.93 %	5.03 %	5.11 %	4.76 %	48.85 %

Table S8. The molecular formula of b-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ by Inductance-coupled plasma (ICP)

analysis (ICP-MS)							
Theoretical Molecular formula	Experimental Molecular formula	Cu	Zn	Co	Ni	Mg	Cr
NiCr ₂ O ₄	NiCr _{2.08} O ₄	0	0	0	19.35%	0	40.25%
MgCr ₂ O ₄	MgCr _{2.00} O ₄	0	0	0	0	20.3%	40.69%
CuCr ₂ O ₄	CuCr _{2.10} O ₄	18.09%	0	0	0	0	37.97%
ZnCr ₂ O ₄	ZnCr _{1.98} O ₄	0	21.68%	0	0	0	42.86%
CoCr ₂ O ₄	CoCr _{1.98} O ₄	0	0	20.77%	0	0	41.08%
(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	(Ni _{1.02} Mg _{1.00} Cu _{1.02} Zn _{1.01} Co) Cr _{10.22} O ₄	4.87%	4.83%	4.79%	4.89%	4.80%	48.96%

Table S9. The molecular formula of c-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ by Inductance-coupled plasma (ICP)

analysis (ICP-MS)							
Theoretical Molecular formula	Experimental Molecular formula	Cu	Zn	Co	Ni	Mg	Cr
NiCr ₂ O ₄	NiCr _{2.01} O ₄	0	0	0	21.03%	0	42.35%
MgCr ₂ O ₄	MgCr _{1.97} O ₄	0	0	0	0	21.81%	43.06%
CuCr ₂ O ₄	CuCr _{2.04} O ₄	20.12%	0	0	0	0	41.09%
ZnCr ₂ O ₄	ZnCr _{2.02} O ₄	0	18.08%	0	0	0	36.48%
CoCr ₂ O ₄	CoCr _{1.96} O ₄	0	0	23.47%	0	0	45.91%
(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	(NiMg _{1.01} Cu _{1.01} Zn _{1.00} Co _{1.01}) Cr _{10.09} O ₄	5.23%	5.20%	5.25%	5.19%	5.26%	52.38%

7. Please provide information in detail about the utilized method for analysis of product mixture on GC.

Reply:

Thanks for the comment! The GC method for the analysis of reactants was added. The concentration of propylene in the inlet and outlet gases was analyzed online using a hydrogen ion flame detector (FID) in gas chromatography (Sharp GC2060). The Porapak Q column was used in this GC. In addition, the gasified temperature in GC was 150°C. The temperature of the Ni-based conversion furnace in gas chromatography was 330°C. The column temperature was 100°C. The temperature of the FID detector was 220 °C.



Figure S60. The picture of Porapak Q column used in the GC.

8. Why were the baselines for Ni2p (Fig9a top) and Co2p (Fig9b bottom) shifted so low?

Reply:

Thanks for the suggestion! We checked the data and re-analysed it again. The baselines for Ni2p (Fig9a top) and Co2p (Fig9b top and bottom) were carefully adjusted. All those results were added into revised version.

Original:

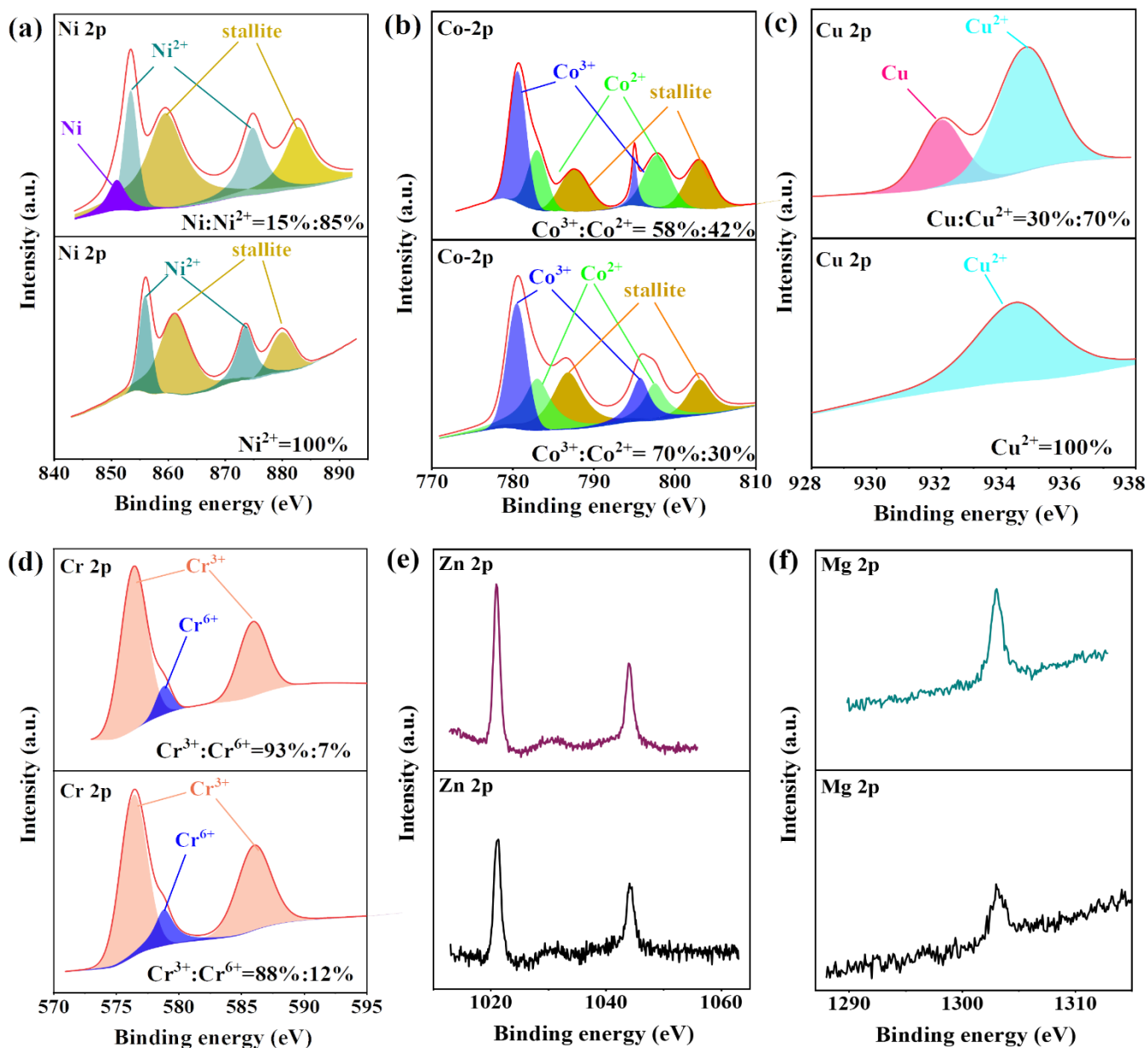


Figure 9 (a) Ni 2p XPS spectra, (b) Co 2p XPS spectra, (c) Cu 2p XPS spectra, (d) Cr 2p XPS spectra, (e) Zn 2p XPS spectra, (f) Mg 2p XPS spectra of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ before and after reduction at 300°C in 5% $\text{H}_2/95\% \text{N}_2$ (The spectra at the bottom is before reduction, while the spectra on the top is after reduction).

Revised:

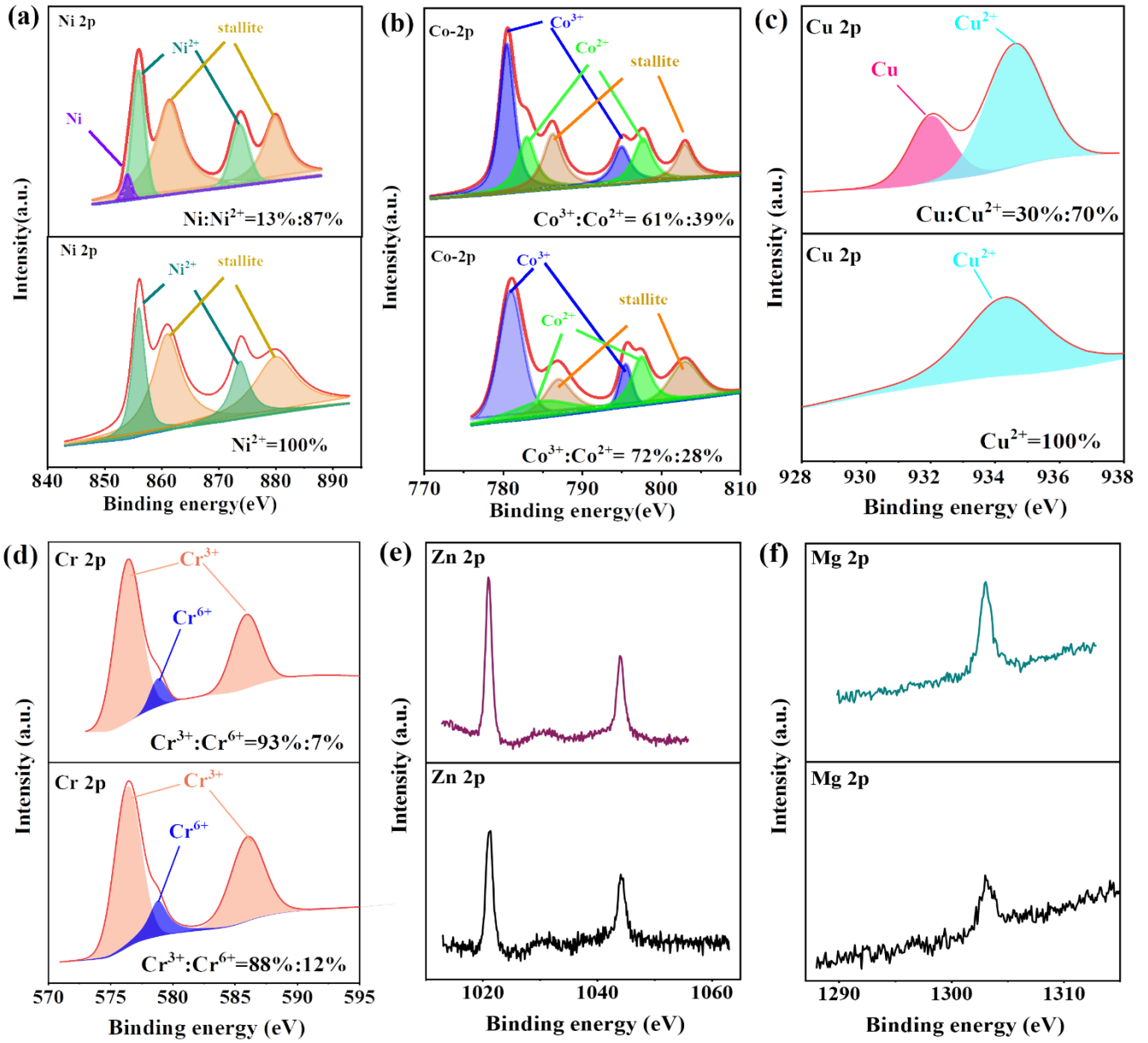


Figure 9 (a) Ni 2p XPS spectra, (b) Co 2p XPS spectra, (c) Cu 2p XPS spectra, (d) Cr 2p XPS spectra, (e) Zn 2p XPS spectra, (f) Mg 2p XPS spectra of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ before reduction and after reduction at 300°C in $5\%\text{H}_2/95\%\text{N}_2$ (The spectra at the bottom belonged to before reduction, while the spectra on the top belonged to after reduction).

9. How were the adsorption energies of C_3H_6 and the dissociation energies of water calculated? Add the equations.

Reply:

Thanks for the key comment! To model the C_3H_6 molecule absorption, the adsorption energy of metal oxide substrate is defined by^[4-6]

$$E[\text{ads}] = E_{\text{total}} - E_{\text{sub}} - E_{\text{mol}} \quad (2)$$

where E_{total} , E_{sub} , E_{mol} is the energy of the metallic oxide structure, metallic oxide substrate, and adsorbed molecule respectively. Meanwhile, to distinguish the effect of H_2O molecules, we have calculated the C_3H_6 absorption energy in dry conditions or containing H_2O molecules, where the H_2O molecule is randomly placed

on the substrates to simulate the real experimental condition.

The dissociation energies of H₂O molecule on these metallic oxide substrates are also calculated under the following formula:



where the dissociated *H and *OH are absorbed on the metallic oxide substrates. Therefore, the dissociation energy is defined by:

$$E[\text{dis}] = E_{\text{dis}} - E_{\text{sub}} - E_{\text{H}_2\text{O}} \quad (4)$$

Where E_{dis} is the energy of the system that H⁺ and OH⁻ have been absorbed on, E_{sub} is the energy of the metallic oxide substrates, and $E_{\text{H}_2\text{O}}$ is the energy of the H₂O molecule. All those calculation details were added into revised manuscript.

The related references were added in the following list:

[9] Tran, R. *et al.* The open catalyst 2022 (OC22) dataset and challenges for oxide electrocatalysts. *ACS Catal.* 13, 3066-3084 (2023).

[10] Chen, D. *et al.* Boosting catalysis of pd nanoparticles in MOFs by pore wall engineering: the roles of electron transfer and adsorption energy. *Adv. Mater.* 32, e2000041 (2020).

[11] Fung, V., Hu, G., Ganesh, P. & Sumpter, B. G. Machine learned features from density of states for accurate adsorption energy prediction. *Nat Commun* 12, 88 (2021).

10. Expand the discussion on how each A = Ni, Mg, Cu, Zn, Co in ACr₂O₄ affects the adsorption of C₃H₆, the dissociation of water and the formation of an oxygen vacancy.

Reply:

Thanks for the comment! We agree with the reviewer. In order to study the effect of single metal species, we have added DFT calculations of the adsorption of C₃H₆, the dissociation of water and the formation of an oxygen vacancy at (111) crystal planes for ACr₂O₄ (single metal at A sites = Ni, Mg, Cu, Zn, Co). Not only that, we also added DFT calculations of the adsorption of C₃H₆, the dissociation of water and the formation of an oxygen vacancy at (111) crystal planes for single metal oxides NiO, MgO, CuO, ZnO, Co₃O₄, Cr₂O₃ (**Figure S33~S35, Table S10~S12**).

For single metal oxides (NiO, MgO, CuO, ZnO, Co₃O₄ and Cr₂O₃), the adsorption energy of C₃H₆ on Co₃O₄ is the highest among them, which is expected to be helpful for propylene oxidation. However, the dissociation energy of water on Co₃O₄ is the lowest among them. Therefore, cobalt oxide is prone to become deactivation in moisture-containing conditions. Moreover, the formation of an oxygen vacancy at (111) crystal planes for ZnO is the lowest among them. This may be related to their metal-oxygen bonding energy and crystal structure.

In addition, D-band center theory is usually employed to describe the adsorption energy of molecules on substrates, here we also introduce the d-band center theory. The density of states (DOS) projected onto the d-states that interact with the adsorbate state can be characterized by the moments of the d DOS. The first

moment is the d-band center:

$$\epsilon_d = \frac{\int_{-\infty}^{\infty} n_d(\epsilon) \epsilon d\epsilon}{\int_{-\infty}^{\infty} n_d(\epsilon) d\epsilon}$$

where ϵ is the energy in the DOS plot and $n_d(\epsilon)$ is the electron density, we find that the d-band center has good linear relationship with the adsorption energy^[1,2]. For the A site = single metal Ni, Mg, Cu, Zn, Co in ACr_2O_4 , we calculate the d-band center of each structure, and also find the good linear relationship with the adsorption energy of C_3H_6 molecules. D-band center tells us if the center value is closer to Fermi level, the adsorption ability would be stronger. Therefore, due to the 3d orbitals of A (single metal at A site= Ni, Mg, Cu, Zn, Co) in ACr_2O_4 and $(\text{NiMgCuZnCo})_{0.2}\text{Cr}_2\text{O}_4$, it is observed that the adsorption energy of C_3H_6 molecules on the surface of $(\text{NiMgCuZnCo})_{0.2}\text{Cr}_2\text{O}_4$ is apparently higher than that of ACr_2O_4 (with single metal on A site) surface.

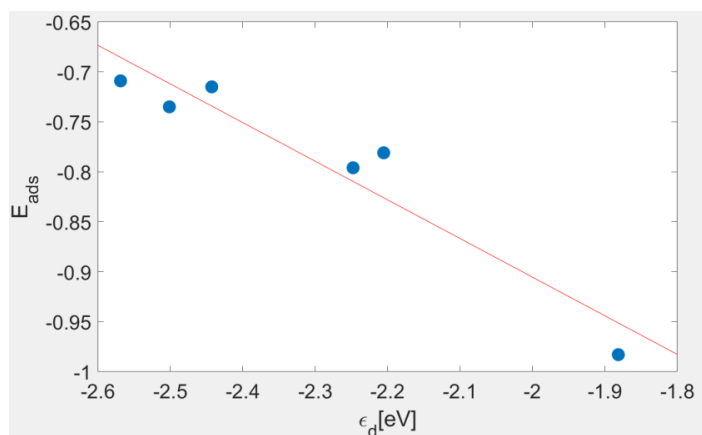


Figure S55. The linear relationship of E_{ads} (the adsorption energy of C_3H_6) and ϵ_d (the value of d-band center).

Then, we wish to discuss the effect of single metal on C_3H_6 adsorption energy in the presence of moisture. Taking CoCr_2O_4 as an example, the D-value ($\Delta E_{\text{ad}} = E_{\text{ad}}(\text{dry conditions}) - E_{\text{ad}}(4.2\text{vol\% water})$) in C_3H_6 adsorption energy with or without water ($\Delta E_{\text{ad}}(311) = -0.381 \text{ eV}$; $\Delta E_{\text{ad}}(220) = -0.397 \text{ eV}$; $\Delta E_{\text{ad}}(111) = -0.33 \text{ eV}$) at (311), (220), (111) crystal planes were all the highest among metal oxides ACr_2O_4 (single metals at A sites = Ni, Mg, Cu, Zn, Co). Moreover, taking Co_3O_4 as an example, the D-value (ΔE_{ad}) in C_3H_6 adsorption energy with or without water ($\Delta E_{\text{ad}}(111) = -0.21 \text{ eV}$) at (111) crystal plane were the highest among single metal oxides (NiO, MgO, CuO, ZnO, Co_3O_4 , Cr_2O_3). Based on those calculations, the type of metal element indeed affected the adsorption behavior of C_3H_6 with 4.2vol% water. Among them, cobalt oxides are the most affected. Molecular H_2O on the Co_3O_4 surface would be decomposed into hydrogen ions and hydroxyl groups and the catalyst would be inactivated via either the hydrogenation of lattice oxygen or the hydroxylation of surface Co^{3+} .^[7]

In addition, the above DFT calculations results were consistent with the results of in situ Raman spectroscopy. In situ Raman spectroscopy was a powerful tool for obtaining insights into the role of water in the Cr–O bond of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, CoCr_2O_4 , and ZnCr_2O_4 catalysts under real reaction conditions. To study the mechanism of water resistance, In situ Raman spectroscopy experiments were carried out with 4.2vol% water. As displayed in **Figure 8(a,d,g)**, the peak between 450 cm^{-1} and 600 cm^{-1} corresponded to Cr–O bonds. The Cr–O bond of CoCr_2O_4 and ZnCr_2O_4 catalysts exhibited a red shift with increased reaction temperature, which can reflect the change in the Cr–O bond force constant calculated by Hooke's law.^[8] In the presence of 4.2vol% H_2O , an increase in reaction temperature could decrease the force constant of the Cr–O bond of CoCr_2O_4 and ZnCr_2O_4 catalysts, thus weakening the Cr–O bonds. This indicated that the crystal structure of CoCr_2O_4 and ZnCr_2O_4 catalysts were unstable with 4.2vol% H_2O . In contrast, an increase in reaction temperature cannot change the force constant of the Cr–O bond in $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ with 4.2vol% H_2O (**Figure 8 c, f, i**). This difference may be due to the lower Gibbs free energy of high entropy $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ structure.^[9] Associated with the results of H_2O -TPD (**Figure 7a**) and DFT calculations(**Figure 1** and **Figure 2**), the chemically adsorbed water on the surface of CoCr_2O_4 and ZnCr_2O_4 catalysts would reduce the adsorption of C_3H_6 at the same time damage their crystal structure, thereby losing the catalytic activity for C_3H_6 oxidation.

Next, the role of different metal elements on the the dissociation energies of H_2O molecule was discussed. The order of H_2O $E_{\text{di}}(111)$ is $\text{CuO} > \text{NiO} > \text{MgO} > \text{Cr}_2\text{O}_3 > \text{ZnO} > \text{Co}_3\text{O}_4$. The dissociation energies of H_2O molecule may be related to the alkalinity of oxides and the metal-oxygen bonding energy.

Moreover, the effect of single metal elements on the formation energy of oxygen vacancy was figured out. According to the different spatial positions, oxygen vacancies can be divided into surface oxygen vacancies and bulk phase oxygen vacancies. If a more detailed classification is made based on the different effects of oxygen vacancies on photocatalytic performance, oxygen vacancies can be divided into two types: subsurface oxygen vacancies and bulk oxygen vacancies. If classified by the number of bound electrons, it can be divided into bound double electron oxygen vacancies, bound single electron oxygen vacancies, and unbound electron oxygen vacancies. Actually, the formation of oxygen defect is related to the metal-oxygen bond energy and the crystal array structure of oxides.

Different metal elements have a significant impact on it. The order of the formation energy of oxygen vacancy at (111) follows $\text{MgO} > \text{Cr}_2\text{O}_3 > \text{Co}_3\text{O}_4 > \text{CuO} > \text{NiO} > \text{ZnO}$. For the dissociation of water on these surfaces, it is found that the dissociation energy by high-entropy oxide $(\text{NiMgCuZnCo})_{0.2}\text{Cr}_2\text{O}_4$ surface is highest, indicating that the H_2O molecules are difficult to dissociate and would not preferentially affect the adsorption of C_3H_6 molecules. However, control samples ACr_2O_4 (single metals at A sites = Ni, Mg, Cu, Zn, Co) showed low dissociation energies of water on their surface. Therefore, from the dissociation of water molecules on these surfaces, we can infer that H_2O molecule will be easier to dissociate on single metal ACr_2O_4 surface and have interactions with the C_3H_6 molecules to hinder their adsorption.

Furthermore, the oxygen vacancy has a positive effect on the catalytic C_3H_6 combustion, and the ratio of oxygen vacancies is proportional to the catalytic ability. From the first-principles calculations, we find that the

oxygen vacancy formation energy of high-entropy oxide surface is lowest compared with other single metal ACr_2O_4 surface. Moreover, oxygen vacancies can activate oxygen molecules, enhance electron transport, and regulate the surface chemical properties of catalysts, which has become one of the most effective means to improve catalytic performance. From the oxygen vacancy energy calculation of these surfaces, it can be concluded that high-entropy oxide surfaces could generate more oxygen vacancies and enhance the catalytic performance.

1. Norskov, J. K. (1990). "Chemisorption on Metal-Surfaces." Reports on Progress in Physics **53**(10): 1253-1295.
2. Norskov, J. K. (1991). "Electronic Factors in Catalysis." Progress in Surface Science **38**(2): 103-144.

Original:

In the presence of 4.2vol% water, the adsorption energy of C_3H_6 on the surfaces of single metal ACr_2O_4 ($\text{A}=\text{Ni}, \text{Mg}, \text{Cu}, \text{Zn}, \text{Co}$) all increased sharply. The presence of H_2O molecules formed competitive adsorption and may reduce the adsorption amount of C_3H_6 on the surface of ACr_2O_4 ($\text{A}=\text{Ni}, \text{Mg}, \text{Cu}, \text{Zn}, \text{Co}$) catalysts, which would affect the C_3H_6 oxidation. In contrast, the presence of H_2O molecules on the surface of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ had little effect on the adsorption energy of C_3H_6 (**Table S1**). For example, the adsorption energies of C_3H_6 on $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ surface were -1.051 eV (crystal plane 311) in dry conditions and -0.96 eV with 4.2vol% water. It seems like high-entropy structure could decrease the competitive adsorption of H_2O with C_3H_6 reactant.

Revised:

In the presence of 4.2vol% water, the adsorption energy of C_3H_6 on the surfaces of single metal ACr_2O_4 ($\text{A}=\text{Ni}, \text{Mg}, \text{Cu}, \text{Zn}, \text{Co}$) all increased sharply. The presence of H_2O molecules formed competitive adsorption and may reduce the adsorption amount of C_3H_6 on the surface of ACr_2O_4 ($\text{A}=\text{Ni}, \text{Mg}, \text{Cu}, \text{Zn}, \text{Co}$) catalysts, which would affect the C_3H_6 oxidation. In contrast, the presence of H_2O molecules on the surface of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ had little effect on the adsorption energy of C_3H_6 (**Table S1**). For example, the adsorption energies of C_3H_6 on $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ surface were -1.051 eV (crystal plane 311) in dry conditions and -0.96 eV with 4.2vol% water. It seems like high-entropy structure could decrease the competitive adsorption of H_2O with C_3H_6 reactant. Then, the effect of single metal on C_3H_6 adsorption energy in the presence of moisture was discussed. Taking CoCr_2O_4 as an example, the D-value ($\Delta E_{\text{ad}} = E_{\text{ad}}(\text{dry conditions}) - E_{\text{ad}}(4.2\text{vol}\% \text{ water})$) in C_3H_6 adsorption energy with or without water ($\Delta E_{\text{ad}}(311) = -0.381 \text{ eV}$; $\Delta E_{\text{ad}}(220) = -0.397 \text{ eV}$; $\Delta E_{\text{ad}}(111) = -0.33 \text{ eV}$) at (311), (220), (111) crystal planes were all the highest among metal oxides ACr_2O_4 (single metals at A sites = Ni, Mg, Cu, Zn, Co). Moreover, taking Co_3O_4 as an example,

the D-value(Δ_{Ead}) in C_3H_6 adsorption energy with or without water ($\Delta_{\text{Ead (111)}} = -0.21\text{eV}$.) at (111) crystal plane were the highest among single metal oxides (NiO, MgO, CuO, ZnO, Co_3O_4 , Cr_2O_3). Based on those calculations, the type of metal element indeed affected the adsorption behavior of C_3H_6 with 4.2vol% water. Among them, cobalt oxides are the most affected. Molecular H_2O on the Co_3O_4 surface would be decomposed into hydrogen ions and hydroxyl groups and the catalyst would be inactivated via either the hydrogenation of lattice oxygen or the hydroxylation of surface Co^{3+} .^[1]

[1] BAE J, SHIN D, JEONG H, et al. Highly Water-Resistant La-Doped Co_3O_4 Catalyst for CO Oxidation [J]. ACS Catalysis, 2019, 9(11): 10093-100.

Original:

Table S1 The adsorption energy of C_3H_6 on the surface of ACr_2O_4 (A=Ni, Mg, Cu, Zn, Co) and $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ in the case of no water and 4.2vol% water respectively by DFT calculation

Sample	Ead (311) /eV	Ead (311) (4.2vol% water) /eV	^a Δ_{Ead} (311) /eV	Ead (220) /eV	Ead (220) (4.2vol% water) /eV	^b Δ_{Ead} (220) /eV
NiCr ₂ O ₄	-0.892	-0.615	0.277	-0.855	-0.571	-0.284
MgCr ₂ O ₄	-0.865	-0.593	0.272	-0.802	-0.537	-0.265
CuCr ₂ O ₄	-0.813	-0.527	0.286	-0.769	-0.491	-0.278
ZnCr ₂ O ₄	-0.744	-0.384	0.36	-0.682	-0.349	-0.333
CoCr ₂ O ₄	-0.852	-0.471	0.381	-0.749	-0.352	-0.397
(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2}) Cr ₂ O ₄	-1.051	-0.963	0.088	-0.974	-0.879	-0.095

a : $\Delta_{\text{Ead (311)}} = \text{Ead (311)} - \text{Ead (311) (4.2vol\% water)}$

b : $\Delta_{\text{Ead (220)}} = \text{Ead (220)} - \text{Ead (220) (4.2vol\% water)}$

Table S2 The dissociation energy of molecular H₂O on the surface of high entropy (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄, and single metal ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co) at crystal plane (220) and (311).

Sample	OH ⁻¹ Ead(311)/eV	OH ⁻¹ Ead(220) /eV
NiCr ₂ O ₄	2.294	2.412
MgCr ₂ O ₄	2.691	2.731
CuCr ₂ O ₄	2.385	2.582
ZnCr ₂ O ₄	2.148	2.379
CoCr ₂ O ₄	2.336	2.532
(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	2.834	2.752

Table S3 Formation energy of oxygen vacancy (Eov) of high entropy (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄, and single metal ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co) at crystal plane (220) and (311).

Sample	Eov (311)/eV	Eov (220) /eV
NiCr ₂ O ₄	4.916	5.637
MgCr ₂ O ₄	4.517	5.639
CuCr ₂ O ₄	4.695	5.748
ZnCr ₂ O ₄	4.773	5.271
CoCr ₂ O ₄	4.843	5.369
(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	4.166	4.562

Revised:

Table S1 The adsorption energy of C₃H₆ on the surface of ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co) and (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ in the case of no water and 4.2vol% water respectively by DFT calculation

Sample	E _{ad} (311) /eV	E _{ad} (311) (4.2vol% water) /eV	^a Δ _{E_{ad}} (311) /eV	E _{ad} (220) /eV	E _{ad} (220) (4.2vol% water) /eV	^b Δ _{E_{ad}} (220) /eV	E _{ad} (111) /eV	E _{ad} (111) (4.2vol% water) /eV	^c Δ _{E_{ad}} (111) /eV
NiCr ₂ O ₄	-0.89	-0.62	0.28	-0.86	-0.57	-0.28	-0.74	-0.57	-0.17
MgCr ₂ O ₄	-0.87	-0.59	0.27	-0.80	-0.54	-0.27	-0.80	-0.49	-0.31
CuCr ₂ O ₄	-0.81	-0.53	0.29	-0.77	-0.49	-0.29	-0.72	-0.49	-0.23
ZnCr ₂ O ₄	-0.74	-0.38	0.36	-0.68	-0.35	-0.33	-0.71	-0.37	-0.34
CoCr ₂ O ₄	-0.85	-0.47	0.38	-0.75	-0.35	-0.40	-0.78	-0.45	-0.33
(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	-1.05	-0.96	0.09	-0.97	-0.88	-0.10	-0.98	-0.87	-0.11

a : Δ_{E_{ad}} (311) =E_{ad} (311) -E_{ad} (311) (4.2vol% water)

b : Δ_{E_{ad}} (220) =E_{ad} (220) -E_{ad} (220) (4.2vol% water)

c : Δ_{E_{ad}} (111) =E_{ad} (111) -E_{ad} (111) (4.2vol% water)

Table S2 The dissociation energy of molecular H₂O on the surface of high entropy (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄, and single metal ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co) at crystal plane (220) , (311) and (111).

Sample	H ₂ O E _{di} (311)/eV	H ₂ O E _{di} (220)/eV	H ₂ O E _{di} (111)/eV
NiCr ₂ O ₄	2.29	2.41	2.62
MgCr ₂ O ₄	2.69	2.73	2.75
CuCr ₂ O ₄	2.39	2.58	2.90
ZnCr ₂ O ₄	2.15	2.38	2.74
CoCr ₂ O ₄	2.34	2.53	2.80
(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	2.83	2.75	2.97

Table S3 Formation energy of oxygen vacancy (Eov) of high entropy (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄, and single metal ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co) at crystal plane (220) , (311) and (111).

Sample	Eov (311)/eV	Eov (220) /eV	Eov (111) /eV
NiCr ₂ O ₄	4.92	5.64	5.96
MgCr ₂ O ₄	4.52	5.64	5.59
CuCr ₂ O ₄	4.70	5.75	5.83
ZnCr ₂ O ₄	4.77	5.27	5.49
CoCr ₂ O ₄	4.84	5.37	5.63
(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	4.17	4.56	4.32

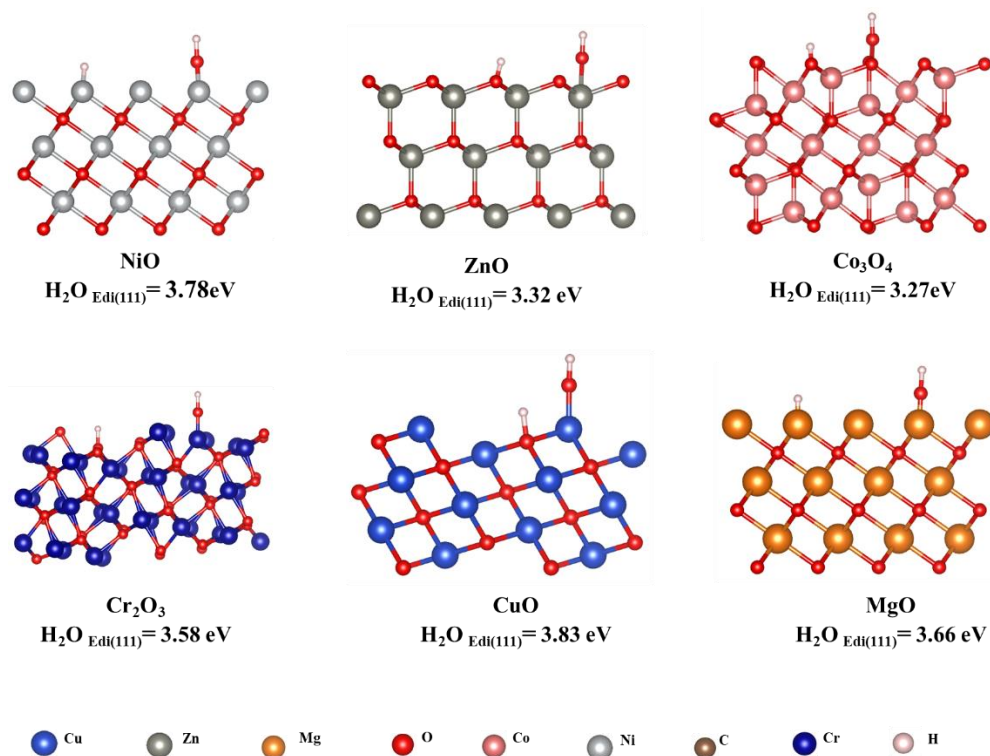


Figure S33. The dissociation energy of molecular H_2O on the surface of NiO, MgO, CuO, ZnO, Co_3O_4 and Cr_2O_3 at crystal plane (111) respectively.

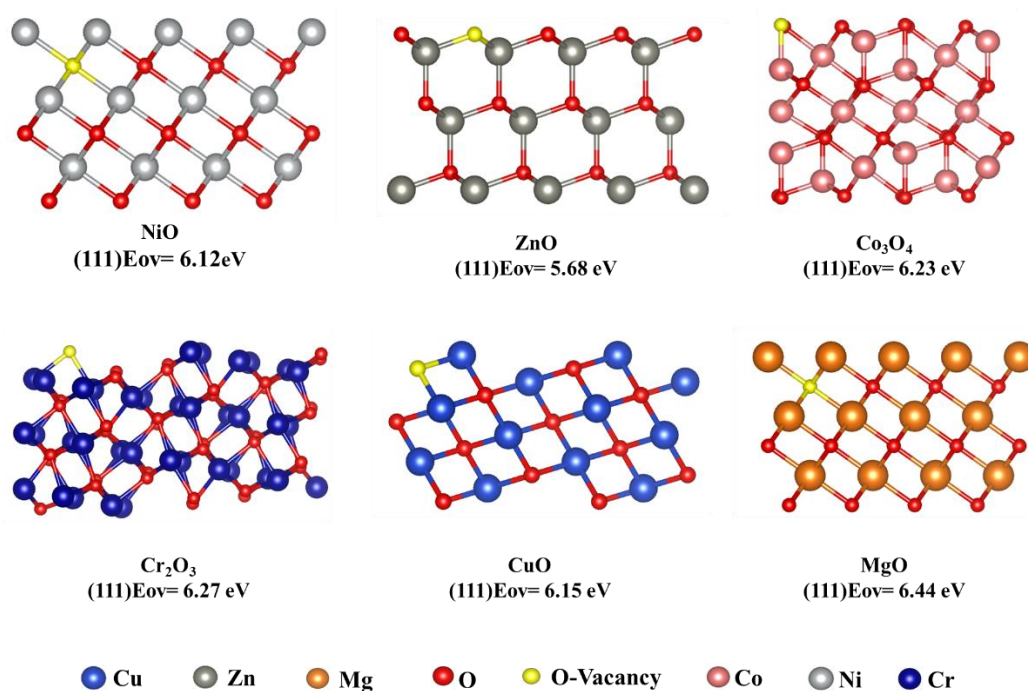


Figure S34. The formation energy of oxygen vacancy (Eov) of NiO, MgO, CuO, ZnO, Co_3O_4 and Cr_2O_3 at crystal plane (111) respectively.

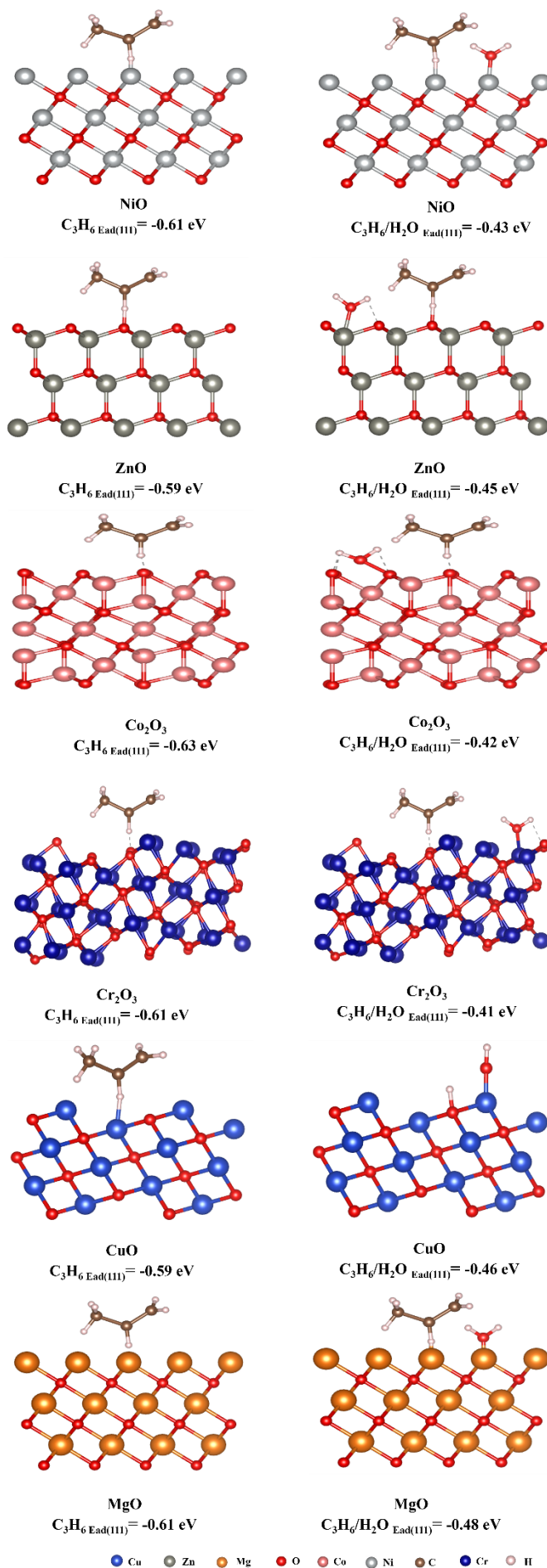


Figure S35. The adsorption energy of C_3H_6 on the surface (111 plane) of NiO, MgO, CuO, ZnO, Co_3O_4 and Cr_2O_3 in the absence and presence of 4.2vol% water vapor.

Table S10 The adsorption energy of C₃H₆ on the surface (111 plane) of NiO, MgO, CuO, ZnO, Co₃O₄, Cr₂O₃ in the absence and presence of 4.2vol% water vapor.

Sample	C ₃ H ₆ E _{ad} (111) /eV	C ₃ H ₆ E _{ad} (111) (4.2vol% water)/eV	^a ΔE _{ad} (111) /eV
NiO	-0.61	-0.43	-0.18
ZnO	-0.59	-0.45	-0.14
Co ₃ O ₄	-0.63	-0.42	-0.21
Cr ₂ O ₃	-0.61	-0.41	-0.20
CuO	-0.59	-0.46	-0.13
MgO	-0.61	-0.48	-0.13

Table S11. The dissociation energy of molecular H₂O on the surface of NiO, MgO, CuO, ZnO, Co₃O₄, Cr₂O₃ at crystal plane (111) respectively.

Sample	H ₂ O E _{di} (111)/eV
NiO	3.78
ZnO	3.32
Co ₃ O ₄	3.27
Cr ₂ O ₃	3.58
CuO	3.83
MgO	3.66

Table S12. The formation energy of oxygen vacancy (Eov) of NiO, MgO, CuO, ZnO, Co₃O₄, Cr₂O₃, at crystal plane (111) respectively.

Sample	Eov (111) /eV
NiO	6.12
ZnO	5.68
Co ₃ O ₄	6.23
Cr ₂ O ₃	6.27
CuO	6.15
MgO	6.44

11. In the description of Figure 2 you state that the dissociation energies of molecular water are calculated and shown in the figure, but in each image you denoted the adsorption energies (Ead) of OH⁻ and not the dissociation energies of molecular water. Which one is correct?

Reply:

Thanks for the careful checking. We sincerely apologize for this mistake when drawing the picture. We changed the adsorption energies (Ead) of OH⁻ into the dissociation energies of molecular water (denoted as H₂O_{Edi(220)} or H₂O_{Edi(311)}) in **Figure 2**. In addition, we have checked the other data carefully.

Original:

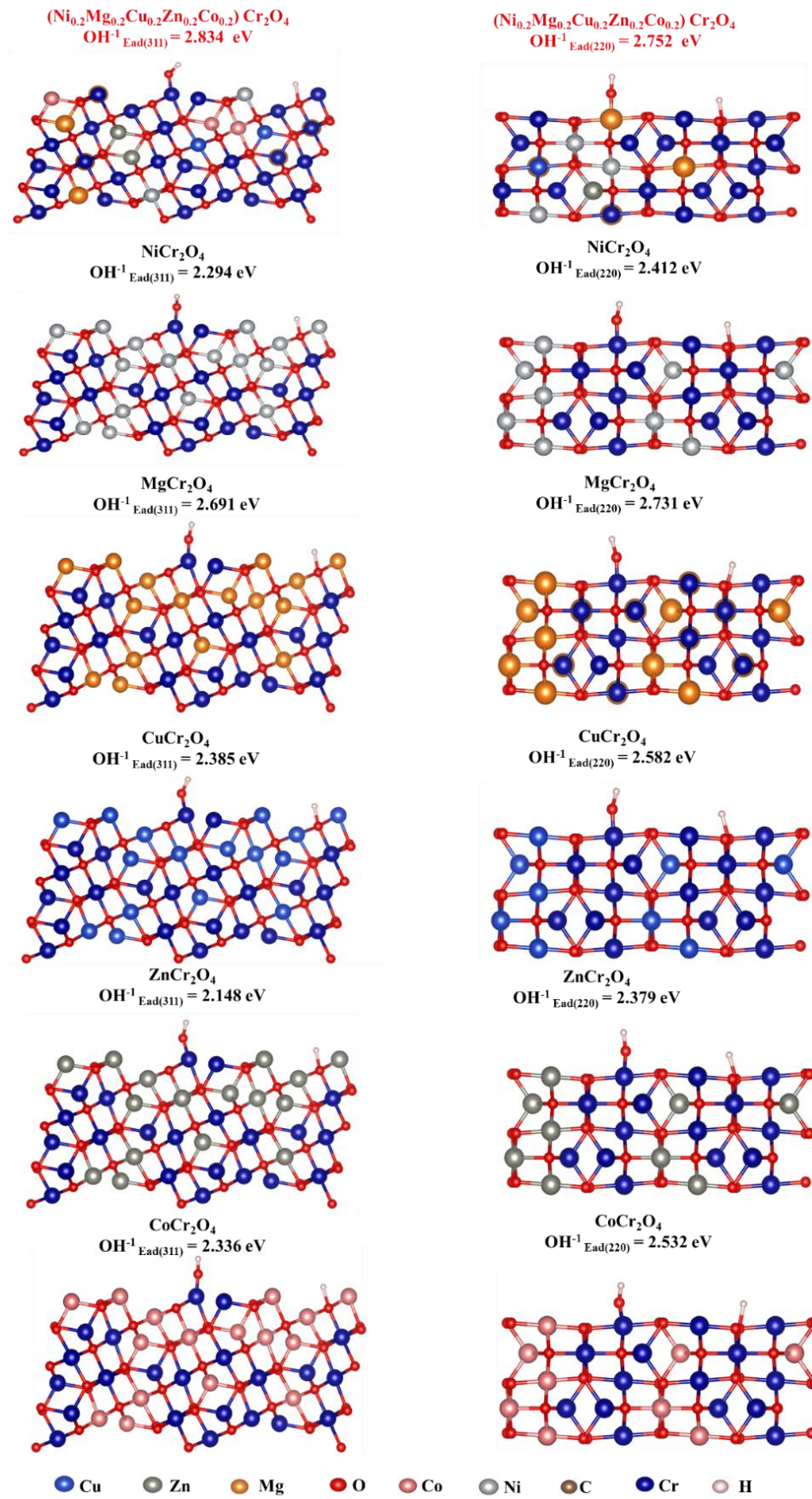


Figure 2. The dissociation energy of molecular H_2O on the surface of high entropy $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, and single metal ACr_2O_4 ($\text{A}=\text{Ni}, \text{Mg}, \text{Cu}, \text{Zn}, \text{Co}$) at crystal plane (220) and (311) respectively.

Revised:

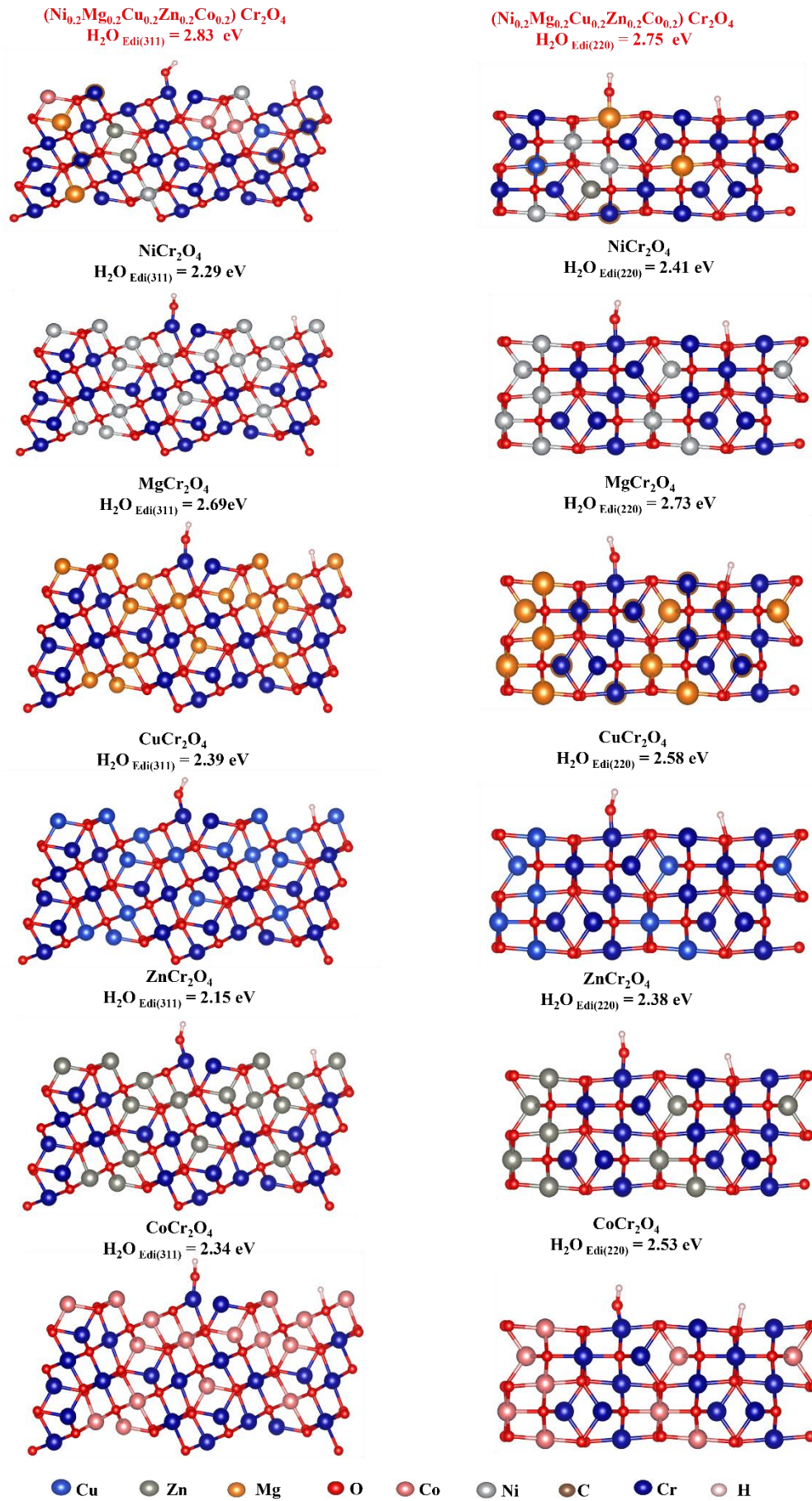


Figure 2. The dissociation energy of molecular H_2O (denoted as $\text{H}_2\text{O}_{\text{Edi}(220)}$ or $\text{H}_2\text{O}_{\text{Edi}(311)}$) on the surface of high entropy $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, and single metal ACr_2O_4 ($\text{A}=\text{Ni}, \text{Mg}, \text{Cu}, \text{Zn}, \text{Co}$) at crystal plane (220) and (311) respectively.

12. Please rotate the images in Figure 3 so that the oxygen vacancy is clearly visible.

Reply:

Thanks for the careful comment! We have rotated the images in **Figure 3** to make the oxygen vacancy clearly visible.

Original:

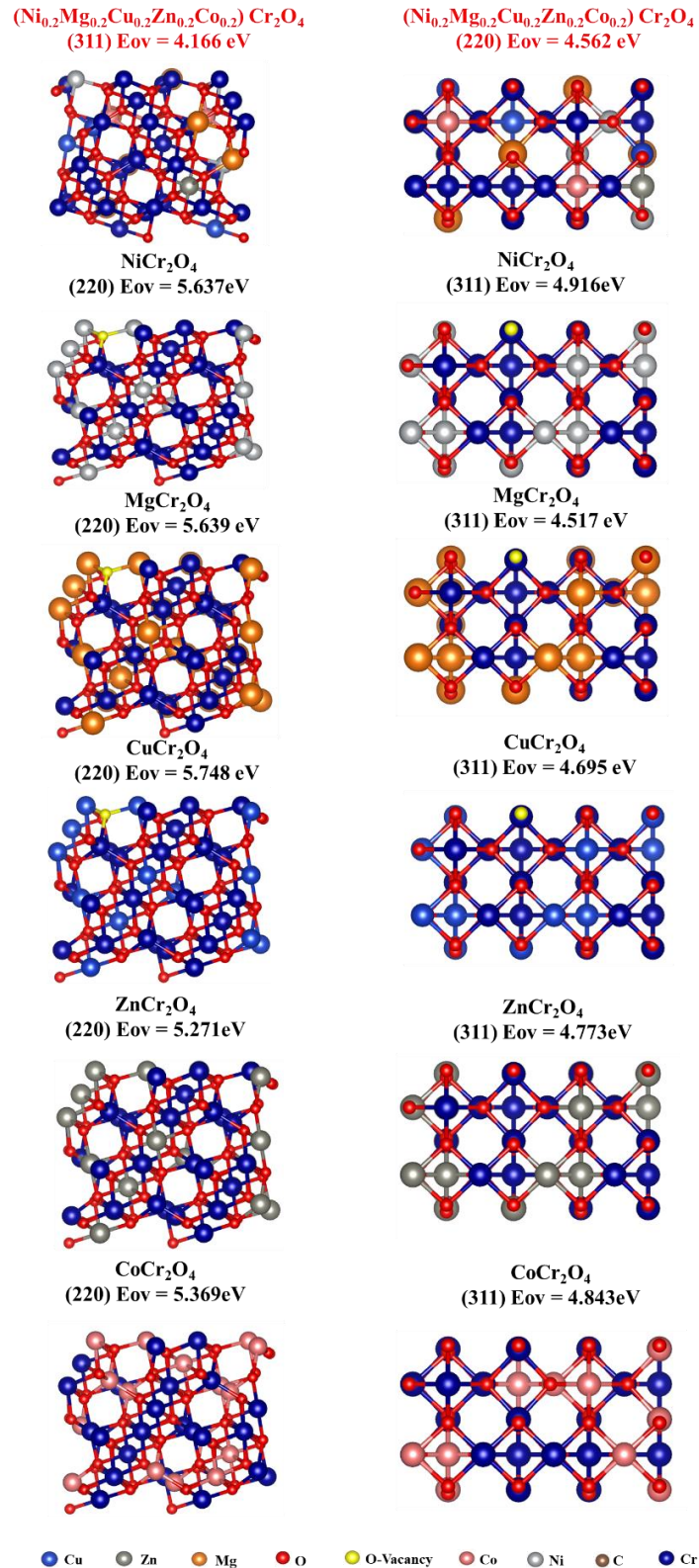
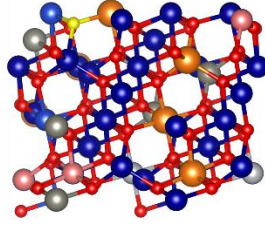
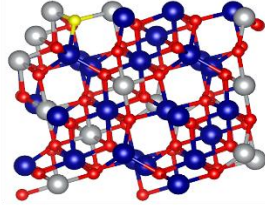


Figure 3. The formation energy of oxygen vacancy (Eov) of high entropy $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, and single metal ACr_2O_4 (A=Ni, Mg, Cu, Zn, Co) at crystal plane (220) and (311) respectively.

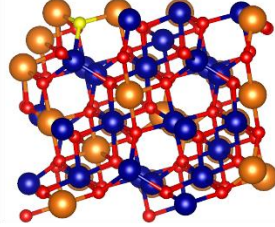
$(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$
(311) Eov = 4.17 eV



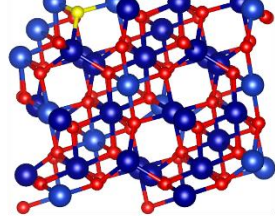
NiCr_2O_4
(311) Eov = 4.92 eV



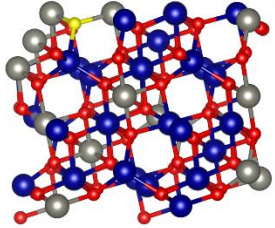
MgCr_2O_4
(311) Eov = 4.52 eV



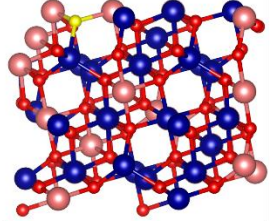
CuCr_2O_4
(311) Eov = 4.70 eV



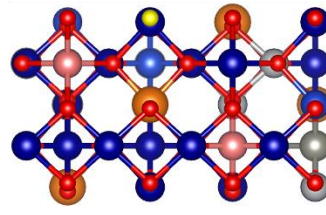
ZnCr_2O_4
(311) Eov = 4.77 eV



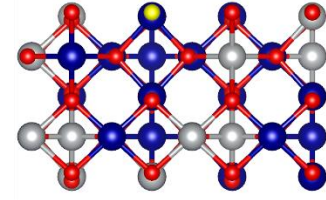
CoCr_2O_4
(311) Eov = 4.84 eV



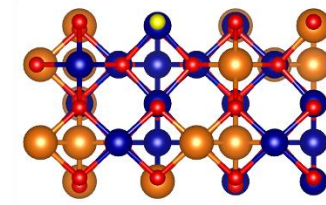
$(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$
(220) Eov = 4.56 eV



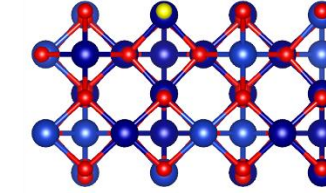
NiCr_2O_4
(220) Eov = 5.64 eV



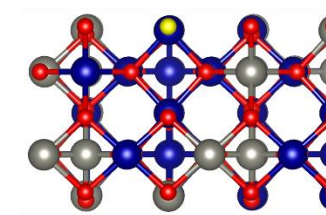
MgCr_2O_4
(220) Eov = 5.64 eV



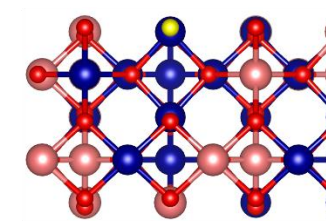
CuCr_2O_4
(220) Eov = 5.75 eV



ZnCr_2O_4
(220) Eov = 5.27 eV



CoCr_2O_4
(220) Eov = 5.37 eV



● Cu ● Zn ● Mg ● O ● O-Vacancy ● Co ● Ni ● Cr

Figure 3. The formation energy of oxygen vacancy (Eov) of high entropy $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, and single metal ACr_2O_4 (A=Ni, Mg, Cu, Zn, Co) at crystal plane (220) and (311) respectively.

13. I suggest that you round the values of the calculated energies to two decimal places.

Reply:

Thanks for the important comment! We have rounded the values of the calculated energies to two decimal places. Please refer to the revised manuscript and supporting materials.

14. I suggest that the authors re-read the manuscript and correct the typos. In several places in the manuscript, spaces before brackets (between a word and a bracket) are missing.

Reply:

Thanks for the suggestion! We have once again organized the logic and made many revisions. Brackets (between a word and a bracket) were added. The paper has been also revised by a native English speaker to improve the grammar and readability. We appreciate for Reviewers' warm work earnestly.

15. There is a discrepancy between the use of DFT calculations and experimental work. On page 9 (and elsewhere) you state that experiments were carried out to validate the DFT results, but in the Methods section you claim that DFT calculations were performed to verify the experimental results. Please correct the discrepancy.

Reply:

Thanks for the careful checking. We sincerely apologize for this mistake in our writing. In this work, theoretical calculations were used as the initial research, and then the theoretical calculations were validated through experiments. Please refer to revised manuscript for accurate expression. In addition, we have checked the manuscript carefully.

Original:

The first-principles calculations were performed under the framework of the density functional theory (DFT) to verify our experimental results, where the codes are implemented in the Vienna *ab initio* simulation package with the projector augmented plane-wave method.

Revised:

The first-principles calculations were performed under the framework of the density functional theory (DFT) before experimental studies, where the codes are implemented in the Vienna *ab initio* simulation package with the projector augmented plane-wave method.

16. Manuscript conclusion section is missing. You can combine Discussion and Conclusion sections or rename the Discussion part to Conclusion portion.

Reply:

Thanks for the careful checking. We renamed the Discussion part to Conclusion portion in revised manuscript.

17. "Meanwhile, Wang et al. ^[3] identified the favorable role of water in the hydrogenation of CO₂ to methanol,

which strongly affected the selectivity and yield of methanol.” – Firstly, this is contrary to what most literature says, while secondly, the review of works here is indeed very poor. The effect of the water during the synthesis of methanol, as well as during the (reverse) water–gas shift reactions is very well documented, which cannot be traced from (authors’) presentation. Some initial points that should be mentioned/ duly referenced:- the mechanisms of the copper-based catalyst deactivation during the CO₂ reduction to methanol- the sulphur poisoning, water vapour and nitrogen dilution effects on the copper-based catalyst dynamics, stability and deactivation during the CO₂ reduction process reactions to methanol - the reaction path analysis of the CO₂ reduction to the methanol through the multisite microkinetic modelling over Cu/ZnO/Al₂O₃ catalysts.

Reply:

Thanks for the careful checking. We have deleted this reference and new references were cited.

Original:

Meanwhile, Wang et al.^[10] identified the favorable role of water in the hydrogenation of CO₂ to methanol, which strongly affected the selectivity and yield of methanol.

Revised:

Fang et al.^[3] shifted the water-sorption equilibrium on the catalyst surface, leading to a greater proportion of free surface that in turn raised the rate of syngas conversion by nearly a factor of 2.

[3] Wei Fang, Cheng tao Wang et al. Physical mixing of a catalyst and a hydrophobic polymer promotes CO hydrogenation through dehydration. Science, 377, 406–410 (2022)

Reviewer: 2

Comments:

Zhang and coworkers investigate the effect of entropic stabilization on the water resistance and catalytic performance of chromate spinels towards the oxidation of propene. Through a combined computational and experimental approach, the authors examine a series of MCr₂O₄ spinel structures, where M is either a single metal (Ni, Co, Zn, Mg, Cu) or a random mixture of all five metals occupying the same crystallographic site (determined to be entropically stabilized). The authors conclude that the entropically-stabilized version of the catalyst shows higher hydrothermal stability than the formal ternary compounds and improved catalytic performance, suggested initially by DFT calculation and corroborated by experiment. On their face, the reported findings seem interesting (and aligned with other reports in the literature). However, the analysis/methodology presented in the current contribution is missing either some key explanatory details or additional, convincing control experiments to back up their claims. My background is not in computation, so I cannot comment on the effectiveness of the calculations or the veracity of the authors’ claims from that angle. I will leave the specifics of those experimental details to reviewers with more relevant expertise. My comments/questions are from an experimental materials perspective, and I think, point to the overall

accessibility of the work for publication in a journal with a broad readership of scientists and engineers.

1. Overall, I think the paper would benefit from some more clear explanations. The chosen materials are highly complex from an experimental and computational perspective. I find that the explanations given for both experimental and computational observations lacking, particularly in light of the complexity or messy-ness of the materials in question. As one example: the authors find that the dissociation energy of water on the surface of the high-entropy oxide is much higher than the single component spinels... why is that? What's the mechanism that's governing this switch? Why is it not just a simple combination of the single component materials?

Reply:

Thanks for the constructive suggestion! We agree with the reviewer that more explanations or comments should be added into this manuscript, in order to make readers better understand the standpoints. All the authors carefully revised the manuscript, and pay more attention to the theoretical explanations for the observed experiment and computational results. For the reviewer's question about the dissociation energy of water, we wish to discuss the result as shown in the following:

First, the structural feature of high entropy oxides (HEOs) is discussed. HEOs are single phase crystalline materials, meaning the different metal ions occupy the same site in a crystal lattice. HEOs should exist as a single-phase material rather than a mixture of phases. In addition, HEOs have significant configurational disorder due to multiple elements inhabiting the same crystallographic site. These elements should be randomly distributed on all scales, all the way down to the atomic scale.^[1~8] One important factor affecting the configurational entropy is the local structure of HEOs, as any type of clustering or segregation of elements will decrease the number of possible microstates, thereby lowering the overall entropy.^[9] For example, the high-resolution transmission electron microscopy (HR-TEM) image along with a selected-area electron diffraction (SAED) pattern of Rock-salt type HEO (R-HEO) was studied.^[19] The well-defined lattice fringes and the SAED results indicated the absence of local clustering (of secondary phases), in agreement with the XRD findings, confirming the phase purity of the material. The corresponding elemental distribution maps obtained by scanning TEM (STEM)–energy-dispersive X-ray spectroscopy (EDX) demonstrated the homogeneity of R-HEO even on the nanometer length scale.^[19] Consistent results were obtained for other HEOs, such as Fluorite type HEO (F-HEO) and Perovskite-based HEO (PE-HEO).^[10~18] Extended X-ray absorption fine structure (EXAFS) studies on R-HEO suggest random distribution of elements in the crystal lattice, owing to the fact that the local chemical environment for all cations was found to be nearly identical.^[20] The combination of these results confirmed the single-phase nature and the statistical distribution of cations in the specific sublattice. Therefore, the high entropy oxide with single-phase XRD was not a simple

combination of the single component materials, not five or more phases.

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Second, from Boltzmann's fundamental entropy formula $S = K_B \ln \Omega$, one can enumerate the number of microstates Ω associated with the configurational entropy of multiple elements occupying the same crystallographic site, S_{conf} . Considering the number of possible distributions of n_i particles of type i over a total number of $N = \sum_i n_i$ states yields the combinatorial factor $\Omega = N! / \prod_i n_i!$, which results in the ideal entropy

$$S_{\text{conf}} = R \ln \left[\frac{N!}{\prod_i n_i!} \right] \approx -R \sum_i x_i \ln x_i \quad (1)$$

where $x_i = n_i / N$ is the fraction of each element and we have used Stirling's approximation. For any number of constituents, this configurational entropy is maximized when the elements are found in equiatomic proportions, as shown for numbers of constituents between 1 and 10. In the case of oxides, this definition can be straightforwardly adapted to include a second sum over sublattices

$$S_{\text{conf}} = -R \sum_s m_s \sum_i x_{i,s} \ln x_{i,s} \quad (2)$$

where m_s is the multiplicity of sublattice s and $x_{i,s}$ is the fraction of element i on sublattice. This modification accounts for potential contributions to the total configurational entropy arising from multiple cation sublattices, oxygen vacancies, or other forms of disorder on the anion sublattice^[5~10]. It can be noted that S_{conf} increased with the addition of more elements to a given system. Furthermore, S_{conf} reached a maximum when all elements were present in equiatomic fractions. In an equiatomic 5-cation system, the maximum S_{conf} value that can be achieved is 1.61 R . The dependency of the free energy of mixing (ΔG_{mix}) on the enthalpy of mixing (ΔH_{mix}) and the entropy of mixing (ΔS_{mix}) is presented in Equation (2).

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}} \quad (2)$$

In many cases, a single phase is achieved if $S_{\text{conf}} \geq 1.5 R$, as then the $T \Delta S_{\text{mix}}$ can be large enough to dominate the free energy landscape and overcome ΔH_{mix} ^[11~18].

High entropy oxides (HEOs) are defined as five or more equimolar metal elements arranged deliberately in a single-phase lattice with even distribution.^[11] The single-phase crystal structure of multicomponent oxides was stabilized via configurational entropy (S_{config}). Toward water-resistance catalysis, the high entropy structure endowed HEOs with two potential features.^[12] First, the lower Gibbs free energy of high entropy catalyst is expected to make it more stable than single metal oxide, even under moisture-containing conditions. Second, various metal components with reactant adsorption sites, reactive sites for activation, and H_2O non-

adsorption sites could be combined into single-phase HEO catalysts. In this regard, the concept of tuning entropy in oxides may contribute to water-resistance catalysis.

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Third, within density functional theory (DFT) calculations, high entropy oxides (HEOs) can be approached using special quasirandom structure (SQS) supercells as specific disorder realizations, from which formation enthalpies can be calculated and information about the local charge states can be obtained. For example, Hu and colleagues^[1] applied DFT calculations to predict the thermodynamic formation barriers of the potential single MEA phase, based on which the dynamic movements of the metal atoms at synthetic (1500 K) and quenched (298 K) temperatures were further simulated using a hybrid Monte Carlo and molecular dynamic approach. Predicted as energetically stable and kinetically favorable using this combination strategy, single-phase Ru-4 MEA ($\text{Ru}_{0.44}\text{Rh}_{0.30}\text{Co}_{0.12}\text{Ni}_{0.14}$) and Ru-5 MEA ($\text{Ru}_{0.25}\text{Rh}_{0.25}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Ir}_{0.1}$) were prepared by the carbothermal shock technique.^[2] For another example, Jia et al.^[3] combined the intrinsic site-isolation effect in inter metalics and strong chemical synergy in HEAs and fabricated a multinary FeCoNiAlTi HEI catalyst. DFT calculations suggest that the Ti atoms with strong adsorption energies facilitate H_2O adsorption, whereas the isolated Al atoms coordinating with Fe, Co, or Ni provide a beneficial GH for efficient adsorption and desorption of H^* . In this way, the conversion of both reactant (H_2O) and intermediate (H^*) are promoted, collectively leading to enhanced HER performances that are superior to those of Pt. In another study, Li et al.^[4] prepared the $\text{Pt}_{18}\text{Ni}_{26}\text{Fe}_{15}\text{Co}_{14}\text{Cu}_{27}$ HEA nanoparticles, which exhibited remarkable methanol oxidation activities and enhanced CO antipoisoning in alkaline solutions. Using DFT calculations, the authors analyzed the partial projected density of states of each element upon methanol adsorption and revealed an efficient site-to-site electron transfer process.

In this work, the water resistance performance of HEOs in catalytic oxidation was initially estimated by theoretical studies. First, with spinel ACr_2O_4 ($\text{A}=\text{Ni, Mg, Cu, Zn, Co}$) as an oxide model and catalytic C_3H_6 oxidation as a typical process, the adsorption behavior of C_3H_6 , dissociation energy of molecular H_2O and the formation energy of oxygen vacancy were estimated by DFT calculation. Compared with single metal oxides ACr_2O_4 ($\text{A}=\text{Ni, Mg, Cu, Zn, Co}$), the competitive adsorption of H_2O with C_3H_6 could be avoided by high entropy $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$. Meanwhile, The $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ offered higher dissociation energy of H_2O than single metal ACr_2O_4 ($\text{A}=\text{Ni, Mg, Cu, Zn, Co}$), suggesting the better hydrothermal stability. Moreover, the formation energy of oxygen vacancies in $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ was much lower than ACr_2O_4 ($\text{A}=\text{Ni, Mg, Cu, Zn, Co}$), which was expected to improve the catalytic oxidation performance.

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In addition , in this work, the dissociation energies of H₂O molecule on these metallic oxide substrates are calculated under the following formula:



where the dissociated *H and *OH are absorbed on the metallic oxide substrates. Therefore, the dissociation energy is defined by:

$$E[\text{dis}] = E_{\text{dis}} - E_{\text{sub}} - E_{\text{H}_2\text{O}} \quad (2)$$

Where E_{dis} is the energy of the system that *H and *OH have been absorbed on, E_{sub} is the energy of the metallic oxide substrates, and $E_{\text{H}_2\text{O}}$ is the energy of the H₂O molecule.

Moreover, we have added DFT calculations of the dissociation energy of molecular H₂O and the formation energy of oxygen vacancy at (111) face of ACr₂O₄ (sing metal at A sites = Ni, Mg, Cu, Zn, Co) as shown in **Figure S16**. The DFT calculation results at (111) face were consistent with crystal faces (311) and (220). Please refer to the supporting information for details.

Original:

1.2 The dissociation energy of molecular H₂O on the surface of ACr₂O₄ by DFT calculation

The dissociation energy of molecular H₂O on the surface of high entropy (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ and single metal ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co) at crystal plane (220) and (311) were calculated by DFT, respectively (**Figure 2 and Table S2**). The dissociation energy of molecular H₂O on the surface of high entropy (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ were 2.834eV (crystal plane 311) and 2.752eV (crystal plane 220). In contrast, the dissociation energy of molecular H₂O on the surface of single metal ACr₂O₄ at crystal plane (311) were 2.148eV~ 2.691eV. The dissociation energy of molecular H₂O on the surface of single metal ACr₂O₄ at the crystal plane (220) were 2.379eV~ 2.731eV.

Revised:

1.2 The dissociation energy of molecular H₂O on the surface of ACr₂O₄ by DFT calculation

The dissociation energy of molecular H₂O on the surface of high entropy (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ and

single metal ACr_2O_4 ($\text{A}=\text{Ni, Mg, Cu, Zn, Co}$) at crystal plane (220), (311) and (111) were calculated by DFT, respectively (Figure 2 and Table S2 and Figure S15). The dissociation energy of molecular H_2O on the surface of high entropy $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ were 2.83eV (crystal plane 311), 2.75eV (crystal plane 220) and 2.97eV (crystal plane 111). In contrast, the dissociation energy of molecular H_2O on the surface of single metal ACr_2O_4 at crystal plane (311) were 2.15eV~ 2.69eV. The dissociation energy of molecular H_2O on the surface of single metal ACr_2O_4 at the crystal plane (220) were 2.38eV~ 2.73eV. The dissociation energy of molecular H_2O on the surface of single metal ACr_2O_4 at the crystal plane (111) were 2.62eV~ 2.90eV. Therefore, the $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ offered higher dissociation energy of H_2O than single metal ACr_2O_4 ($\text{A}=\text{Ni, Mg, Cu, Zn, Co}$), suggesting the better hydrothermal stability.

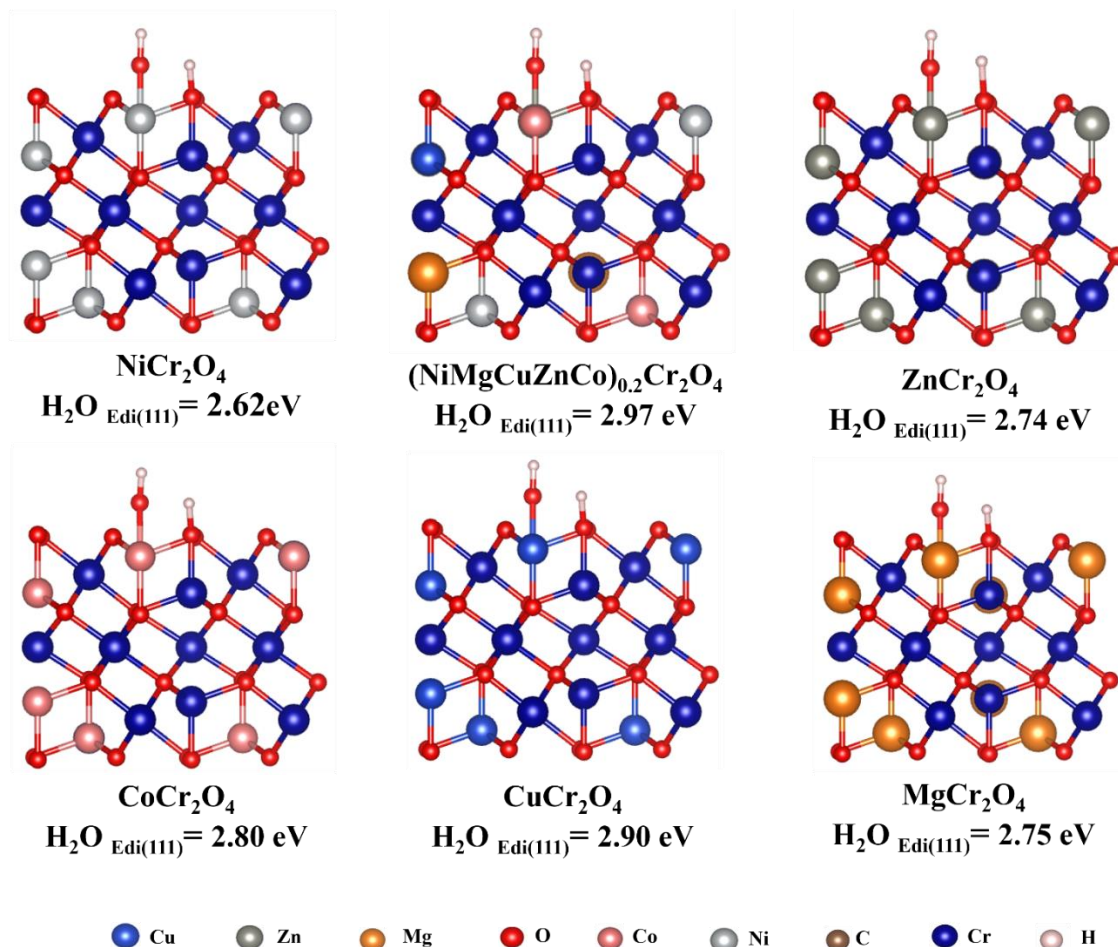


Figure S15. The dissociation energy of molecular H_2O on the surface of high entropy $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, and single metal ACr_2O_4 ($\text{A}=\text{Ni, Mg, Cu, Zn, Co}$) at crystal plane (111).

2. I have some questions about the calculations performed as part of the study: while the formal ternary structures (with a single M occupant on the +2 site in the spinel) have a regular, predictable structure that seems relatively straightforward to model, how is the inherent “randomness” of the M site handled by the computation for the multi-component M site (the entropically stabilized material)?

Reply:

Thanks for the important comment! The “randomness” is not just the atomic random arrangement and we use the precise definition to obtain the “random” structures. According to the special quasirandom structures

(SQS),^[1] SQS cells are the best possible approximations to random alloys or ions in the sense that their cluster vectors closely resemble the cluster vectors of truly random alloys. Here we use ICET package^[2] to generate in icet using a simulated annealing approach. The implementation in icet uses the measure proposed by A. van de Walle^[3]. We need to use Monte Carlo algorithm to generate SQS cell whose correlation function are as close as possible to the target correlation function. We try to approach the target correlation function by swapping two atoms during the simulated annealing process, the structure with the closest correlation function to the target function is the one we choose to proceed the DFT calculations.

For site selectivity, a unique circumstance that can arise when the structure contains more than one crystallographically unique cation site is site selectivity. In certain materials, such as the high entropy perovskite and pyrochlores,^[4,5] almost perfect site selectivity is expected due to the large differences in coordination number and the resulting volume of the cation site, such that there are large energetic penalties to putting, for example, a rare earth ion on the pyrochlore lattice B-site. In these cases, the largest configurational entropy is not achieved, which would occur when there is a perfectly random distribution of all cations across both cation sites. In other structure types, such as the spinel structure, the size of the two cation sites is more comparable and here a higher degree of mixing can be expected. Indeed, even in conventional spinels, such as MgAl_2O_4 , entropy-driven site mixing is observed. In this material, size arguments alone lead to the enthalpically selected ground state with Mg occupying the tetrahedral site and Al preferring the octahedral site. However, quenching from different synthesis temperatures can be used to tune the level of site mixing due to the enhanced configurational entropy.^[6] This picture gets even more complicated once there are more ions involved each with a specific degree of site preference, and especially when d electrons with crystal field effects come into play. For instance, a cation distribution far from the entropic ideal is indeed observed in the case of the spinel $\text{HEO}(\text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni})_3\text{O}_4$, as shown by the cation distribution, which is driven by crystal field effects.^[7,8]

[1] A. Zunger, S.-H. Wei, L. G. Ferreira, and J. E. Bernard. Special quasirandom structures *Physical Review Letters* **65**, 353 (1990)

[2] M. Ångqvist, W. A. Muñoz, J. M. Rahm, E. Fransson, C. Durniak, P. Rozyczko, T. H. Rod, and P. Erhart. ICET—A Python Library for Constructing and Sampling Alloy Cluster Expansions *Advanced Theory and Simulations* **2**, 1900015 (2019)

[3] A. van de Walle, P. Tiwary, M. de Jong, D.L. Olmsted, M. Asta, A. Dick, D. Shin, Y. Wang, L.-Q. Chen, and Z.-K. Liu Efficient stochastic generation of special quasirandom structures *Calphad* **42**, 13 (2013)

[4] Sarkar, Abhishek; Djenadic, Ruzica; Wang, Di; Hein, Christina; Kautenburger, Ralf; Clemens, Oliver; Hahn, Horst Rare earth and transition metal based entropy stabilised perovskite type oxides. *Journal of the European Ceramic Society* 2018, 38, 2318–2327.

[5] Li, Fei; Zhou, Lin; Liu, Ji Xuan; Liang, Yongcheng; Zhang, Guo Jun High-entropy pyrochlores with low thermal conductivity for thermal barrier coating materials. *Journal of Advanced Ceramics* 2019, 8, 576–582.

[6] Schmocker, U.; Waldner, F. The inversion parameter with respect to the space group of MgAl_2O_4 spinels.

Journal of Physics C: Solid State Physics 1976, 9, L235.

[7]Johnstone, Graham HJ; González-Rivas, Mario U; Keith, M Taddei; Sutarto, Ronny; Sawatzky, George A; Green, Robert J;Mohamed, Oudah; Hallas, Alannah M Entropy engineering and tunable magnetic order in the spinel high-entropy oxide. J. Am. Chem. Soc. 2022, 144, 20590–20600

[8] Sarkar, Abhishek; Eggert, Benedikt; Witte, Ralf; Lill, Johanna; Velasco, Leonardo; Wang, Qingsong; Sonar, Janhavika; Ollefs, Katharina; Bhattacharya, Subramshu S; Brand, Richard A; et al. Comprehensive investigation of crystallographic, spin-electronic and magnetic structure of $(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})_3\text{O}_4$: Unraveling the suppression of configuration entropy in high entropy oxides. Acta Mater. 2022, 226, 117581.

3. The DFT-related figures seem to suggest well-defined composition on the surface and bulk sites, but that doesn't seem to be a rigorous model that comports with the reality of the complex sample (which will have, in principle a random occupancy of these sites). If a "randomness" term can't be well handled by the model, did the authors try multiple surface site compositions/permutations? What was the effect of this? Are the only things that matter the surface sites?

Reply:

Thanks for the key suggestion! The entropy increase of mixing is substantially higher when there is a larger number of elements in the mixture, and their proportions are more nearly equal. However, it is not always easy to make models for such structures due to the system sizes that lend themselves to. For example, DFT calculations, are often too small to accommodate a structure that may be regarded as random; the periodicity imposed by boundary conditions introduces correlations that make the modeled structure deviate from the random solid solution. This problem can sometimes be alleviated with the use of so-called special quasirandom structures (SQS) ^[1]. SQS cells are the best possible approximations to random alloys in the sense that their cluster vectors closely resemble the cluster vectors of truly random alloys. Here we use ICET package ^[2] to generate in icet using a simulated annealing approach.

The implementation in icet uses the measure proposed by A. van de Walle ^[3]. We need to use Monte Carlo algorithm to generate SQS cell whose correlation function are as close as possible to the target correlation function. We try to approach the target correlation function by swapping two atoms during the simulated annealing process, the structure with the closest correlation function to the target function is the one we choose to proceed the DFT calculations. In addition, based on the characterization results, such as XRD, TEM, and ICP-MS, our defined model showed that the five metal ions were uniformly distributed on both on the surface and bulk sites.

[1] A. Zunger, S.-H. Wei, L. G. Ferreira, and J. E. Bernard. Special quasirandom structures Physical Review Letters **65**, 353 (1990)

[2] M. Ångqvist, W. A. Muñoz, J. M. Rahm, E. Fransson, C. Durniak, P. Rozyczko, T. H. Rod, and P. Erhart. ICET—A Python Library for Constructing and Sampling Alloy Cluster Expansions Advanced Theory and

[3] A. van de Walle, P. Tiwary, M. de Jong, D.L. Olmsted, M. Asta, A. Dick, D. Shin, Y. Wang, L.-Q. Chen, and Z.-K. Liu Efficient stochastic generation of special quasirandom structures *Calphad* **42**, 13 (2013)

4. The experimental aspects of the paper also raise a series of questions. Perhaps most critically, related to control materials and materials characterization. Some thoughts:

- the characterization of the high-entropy material lacks the kind of spatial resolution and elemental composition data needed to draw sweeping conclusion about surface structure/bulk structure/entropic stabilization. The material seems to be agglomerated nanoscale crystallites and the elemental composition (using EDS mapping) is too low-resolution and low-count to make any assessment of the local composition in any nanoscale domain. EDS mapping is a visual representation of semi-quantitative data, but the composition of the metals (based on spectral data) aren't given. Is there batch-to-batch variability here? How well mixed are these oxides experimentally?

Reply: Thanks for the constructive suggestion! We agree with the reviewer, and more characterizations were added.

To gain a further understanding of the $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ structure at the atomic scale with high-resolution, high resolution STEM-HAADF images were recorded and added. $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ with a clear lattice structure along the [111] zone axis was observed (**Figure 5d**). No foreign metal atoms can be distinguished in the crystal interior. To further confirm this interesting architecture, two other domains with long-range lattice fingers along the [100] zone axis were viewed (**Figure 5e**).

For the issue of repeatability, the optimized high entropy component was prepared three times, and the samples were labeled as a- $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, b- $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, c- $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ respectively. Experiments such as XRD(**Figure S19**), SEM(**Figure S20**), and TEM(**Figure S21~32**) were conducted. High entropy samples a- $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, b- $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, c- $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ all showed characteristic diffraction peaks of cubic phase spinel (JCPDS 80-1668), and no other diffraction peaks were observed. In addition, the accurate content of each metal ions in a- $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, b- $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, c- $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ were determined through Inductance-coupled plasma (ICP) analysis (ICP-MS) respectively (**Table S7, Table S8, Table S9**). The results were close to the theoretical content. We found good repeatability and minimal variability between different batches during material synthesis.

Moreover, EDS mapping is a visual representation of semi-quantitative data, and we determined the composition of the metals (based on spectral data). Finally, we provided elemental composition (using high-resolution STEM-EDS spectra), demonstrating that the elemental distribution is uniform in the nanoscale (**Figure S27~S32**). The proportion of metal Ni, Cu, Zn, Co and Mg was similar on the surface. Meanwhile, reliable ICP-MS data showed that the proportions of five metals Ni, Mg, Cu, Zn, and Co were almost the same, close to the theoretical values.

Finally, we compared the catalytic activity of the three samples. We calculated the variance in the C_3H_6 conversion rate of a- $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$, b- $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$, c- $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$, finding good reproducibility and very low experimental error bars of catalytic activity (Figure S5 and Table S3 in Supporting Information 2.).

Original:

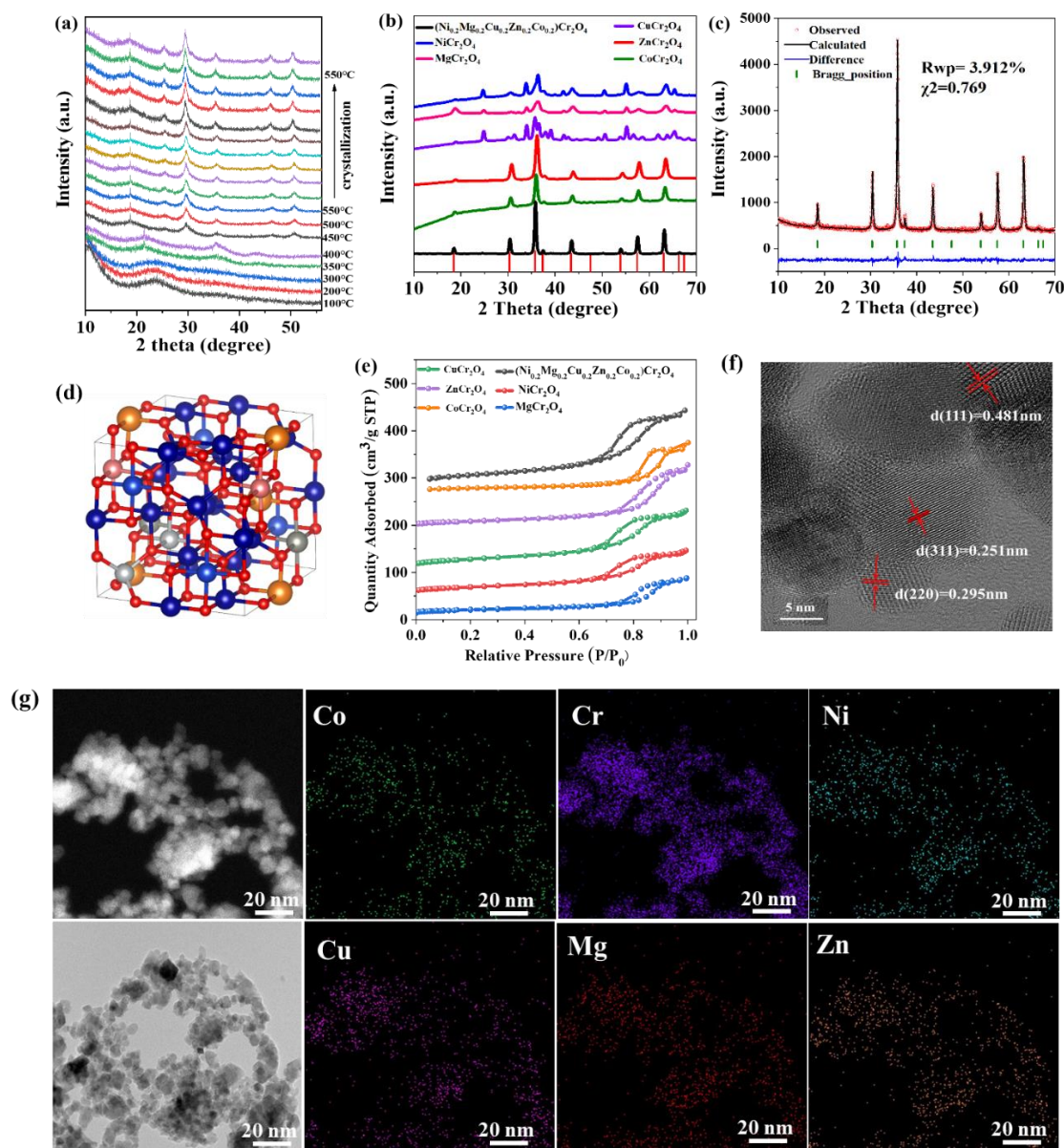


Figure 5. (a) Patterns of in-situ XRD of $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$ catalysts during the programmed heating temperature. (b) X-ray diffraction pattern of $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$ and comparative samples ACr_2O_4 ($A=Ni, Mg, Cu, Zn, Co$). (c) XRD pattern of $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$ with the rietveld refinement result. (d) A structure model of $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$. (e) Nitrogen adsorption–desorption isotherms of ACr_2O_4 ($A=Ni, Mg, Cu, Zn, Co$) and $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$ at 77k. The N_2 uptake of $NiCr_2O_4$, $CuCr_2O_4$, $ZnCr_2O_4$, $CoCr_2O_4$ and $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$ were moved upward by 25, 50, 75, 100, 125 and 150 units respectively. (f) HRTEM image of $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$ nanoparticles. (g) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and energy-dispersive spectroscopy (EDS) elemental mapping images of $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$ nanoparticles.

Original:

The structure model of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ was shown in **Figure 5d**. Then, N_2 sorption measurement at 77 K was carried out (**Figure 5e**). The Brunauer–Emmett–Teller (BET) specific surface areas of ACr_2O_4 ($\text{A}=\text{Ni}, \text{Mg}, \text{Cu}, \text{Zn}, \text{Co}$) were in the range of $68\text{--}75\text{m}^2\text{g}^{-1}$ (**Table S5**), which is comparable to other conventional methods (For example, the specific surface area of ZnCr_2O_4 prepared by the co-precipitation method was $18\text{m}^2\text{g}^{-1}$). The high-resolution TEM (HRTEM) images showed lattice spacings of 0.481, 0.251, and 0.295 nm, which corresponded to the crystal planes (111), (311) and (220) of spinel structure (PDF# 80-1668) respectively (**Figure 5f**). The energy-dispersive spectroscopy (EDS) elemental mapping images demonstrated that Ni, Mg, Cu, Zn, Co, Cr, and O were uniformly distributed within a nanometer domain, suggesting the formation of high-entropy $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ (**Figure 5g**).

Revised:

The structure model of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ was shown in **Figure 5h**. Then, N_2 sorption measurement at 77 K was carried out (**Figure S56**). The Brunauer–Emmett–Teller (BET) specific surface areas of ACr_2O_4 ($\text{A}=\text{Ni}, \text{Mg}, \text{Cu}, \text{Zn}, \text{Co}$) were in the range of $68\text{--}75\text{m}^2\text{g}^{-1}$ (**Table S5**), which is comparable to other conventional methods (For example, the specific surface area of ZnCr_2O_4 prepared by the co-precipitation method was $18\text{m}^2\text{g}^{-1}$). To gain a further understanding of the $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ structure at the atomic scale with high-resolution, high resolution STEM-HAADF images were recorded. $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ with a clear lattice structure along the [111] zone axis was observed (**Figure 5d**). No foreign metal atoms can be distinguished in the crystal interior. To further confirm this interesting architecture, two other domains with long-range lattice fingers along the [100] zone axis were viewed (**Figure 5e**). The high-resolution TEM (HRTEM) images showed lattice spacings of 0.481, 0.251, and 0.295 nm, which corresponded to the crystal planes (111), (311) and (220) of spinel structure (PDF# 80-1668) respectively (**Figure 5f**). The energy-dispersive spectroscopy (EDS) elemental mapping images demonstrated that Ni, Mg, Cu, Zn, Co, Cr, and O were uniformly distributed within a nanometer domain, suggesting the formation of high-entropy $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ (**Figure 5g**).

Revised:

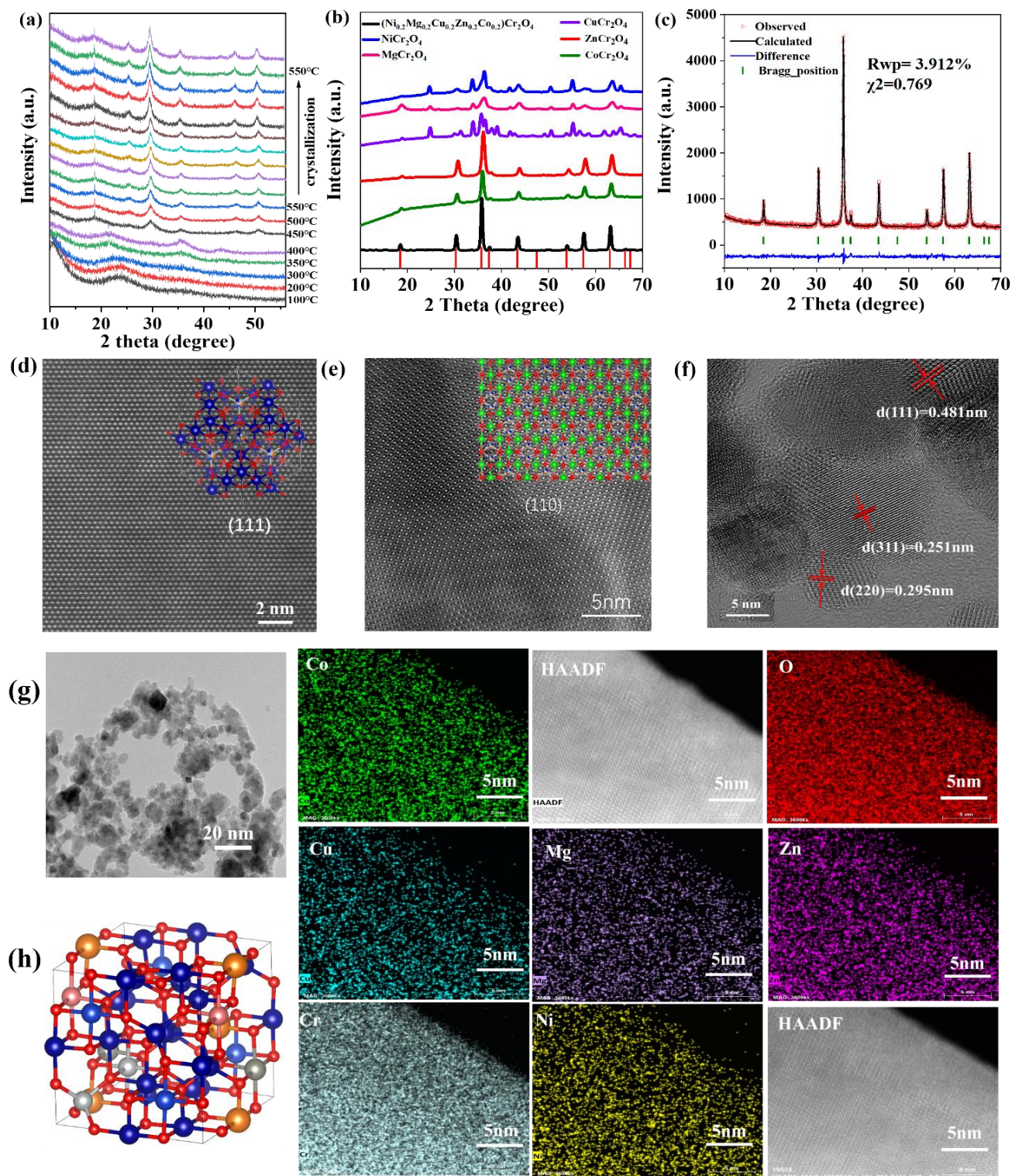


Figure 5. (a) Patterns of in-situ XRD of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ catalysts during the programmed heating temperature. (b) X-ray diffraction pattern of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ and comparative samples ACr_2O_4 ($\text{A}=\text{Ni}, \text{Mg}, \text{Cu}, \text{Zn}, \text{Co}$). (c) XRD pattern of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ with the rietveld refinement result. (d~e) (HAADF-STEM) images of the $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$. (f) HRTEM image of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ nanoparticles. (g) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and energy-dispersive spectroscopy (EDS) elemental mapping images of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ nanoparticles. (h) A structure model of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$.

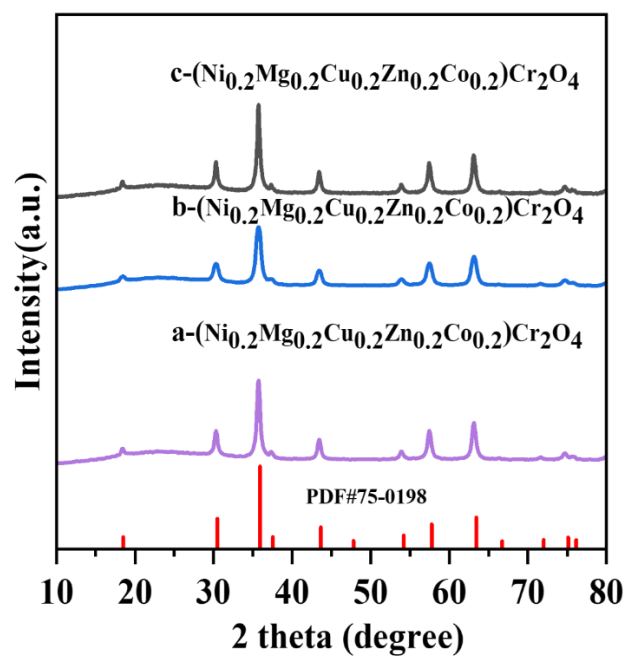


Figure S19. X-ray diffraction patterns of a- $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, b- $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ and c- $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$.

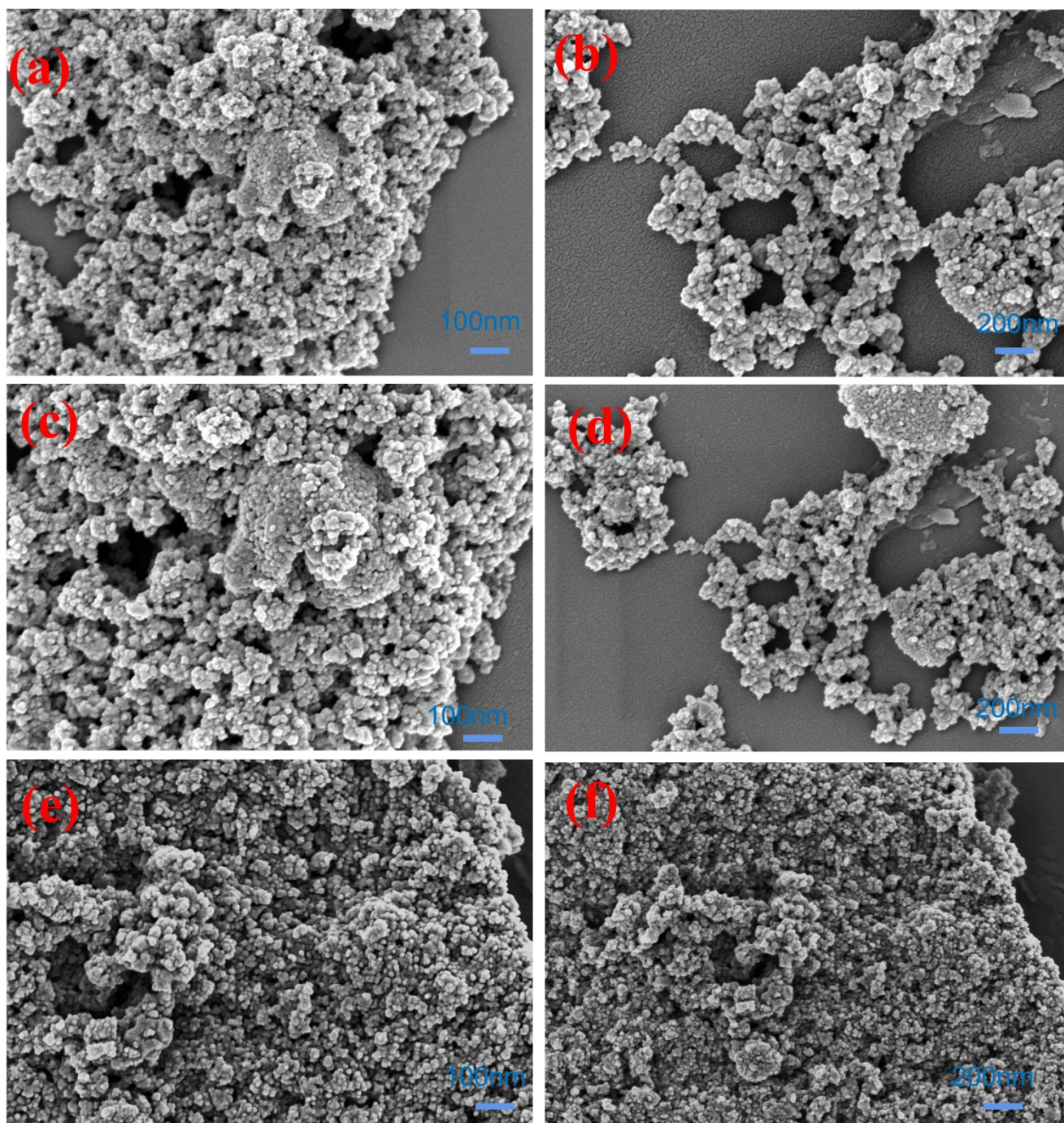
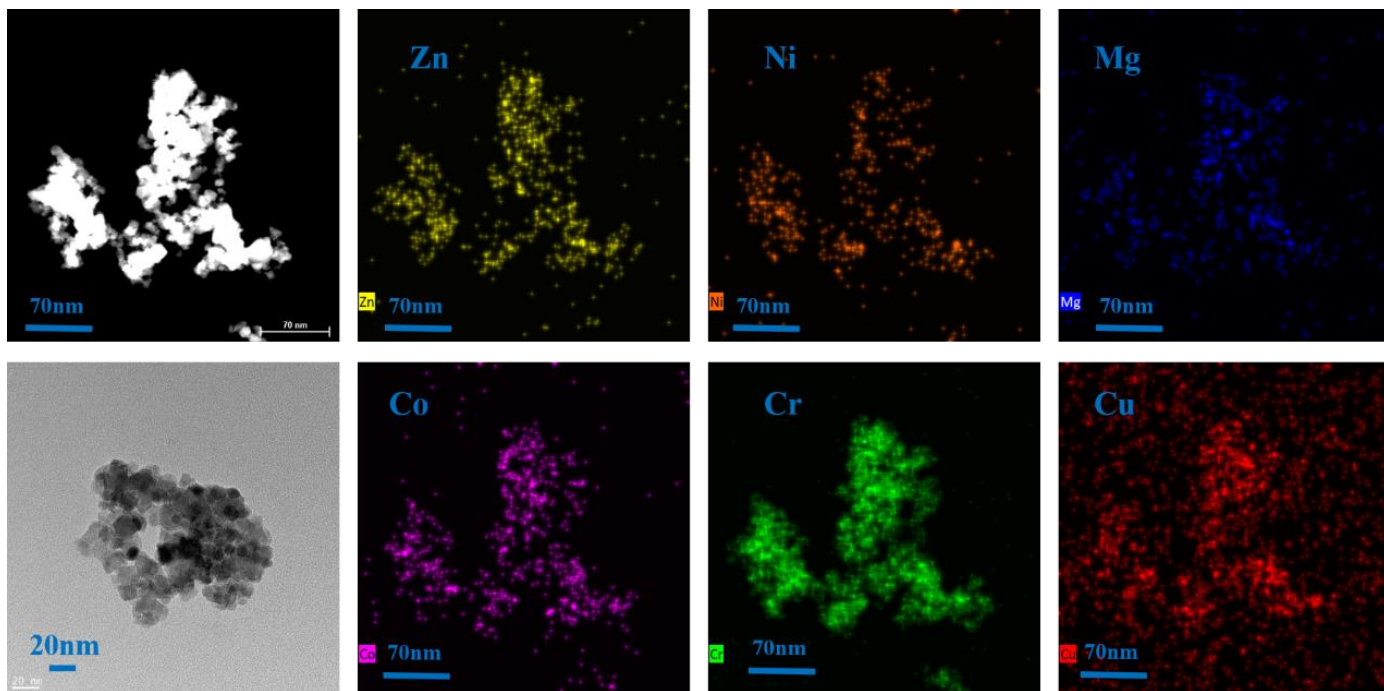
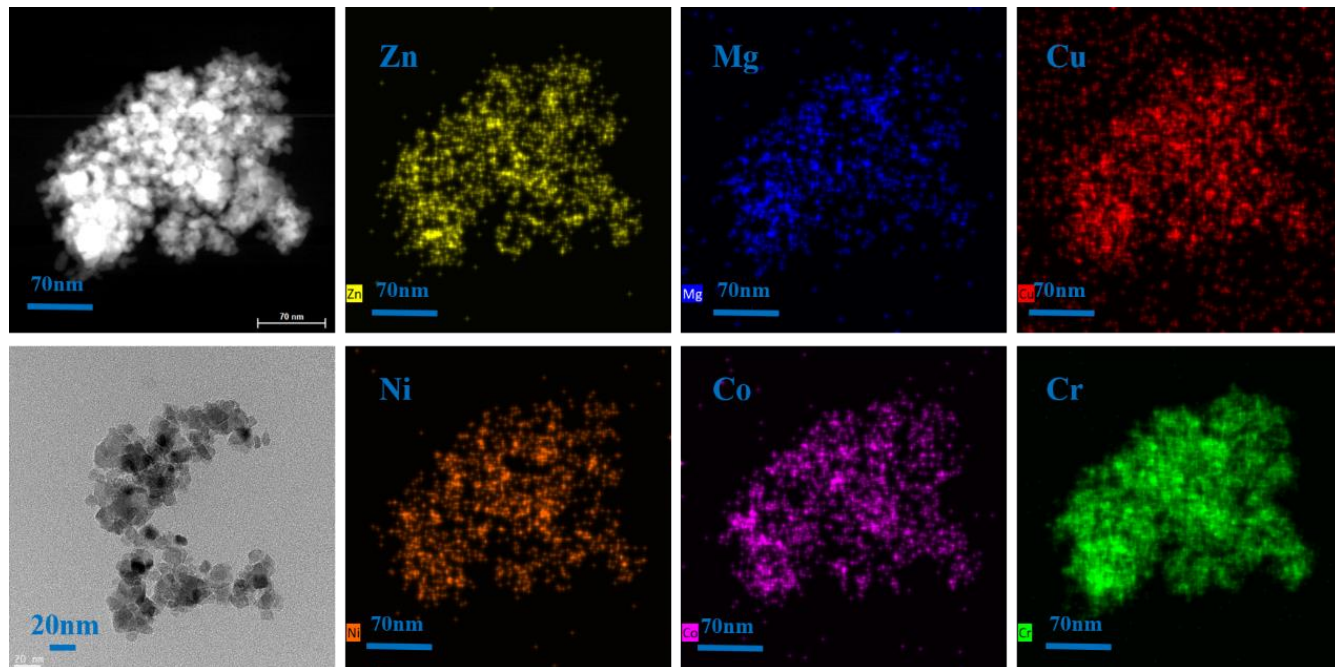


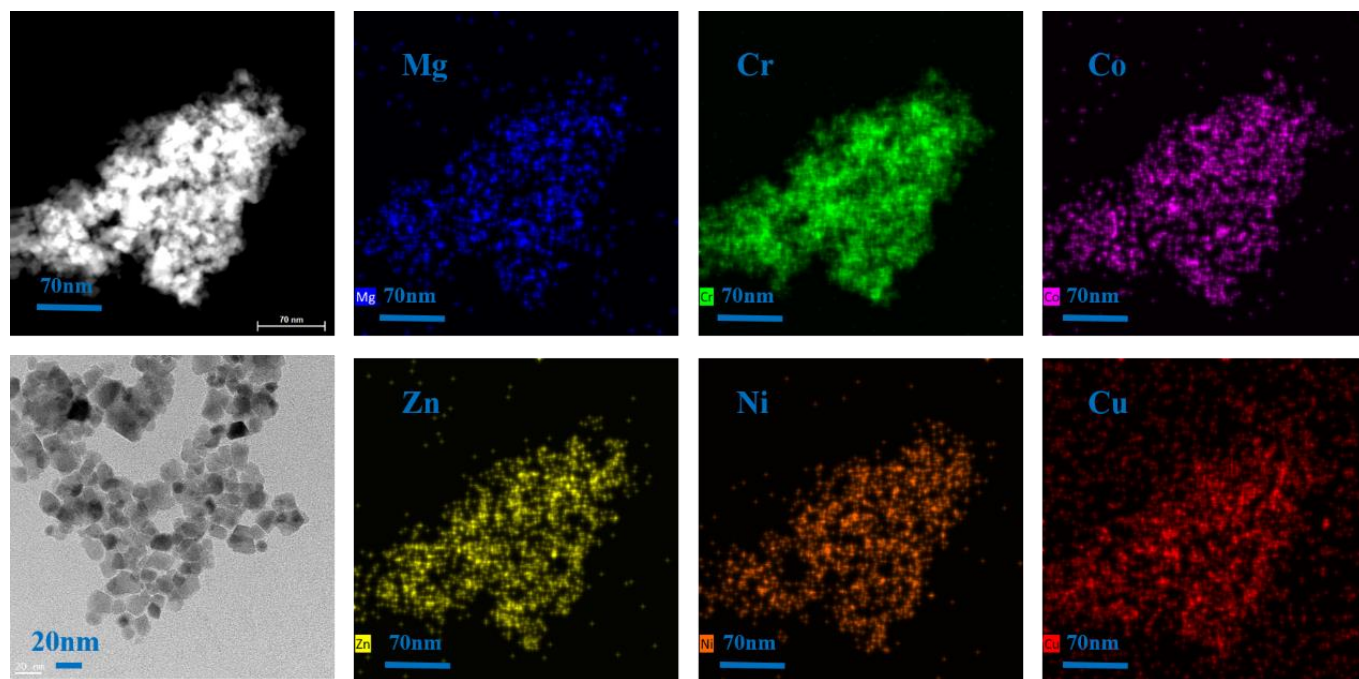
Figure S20. SEM images of (a, b) $a\text{-(Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, (c, d) $b\text{-(Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ and (e, f) $c\text{-(Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$.



FigureS21 High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and energy-dispersive spectroscopy (EDS) elemental mapping images of a-($\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2}$) Cr_2O_4 nanoparticles.



FigureS23 High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and energy-dispersive spectroscopy (EDS) elemental mapping images of b-($\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2}$) Cr_2O_4 nanoparticles.



FigureS25 High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and energy-dispersive spectroscopy (EDS) elemental mapping images of c-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ nanoparticles.

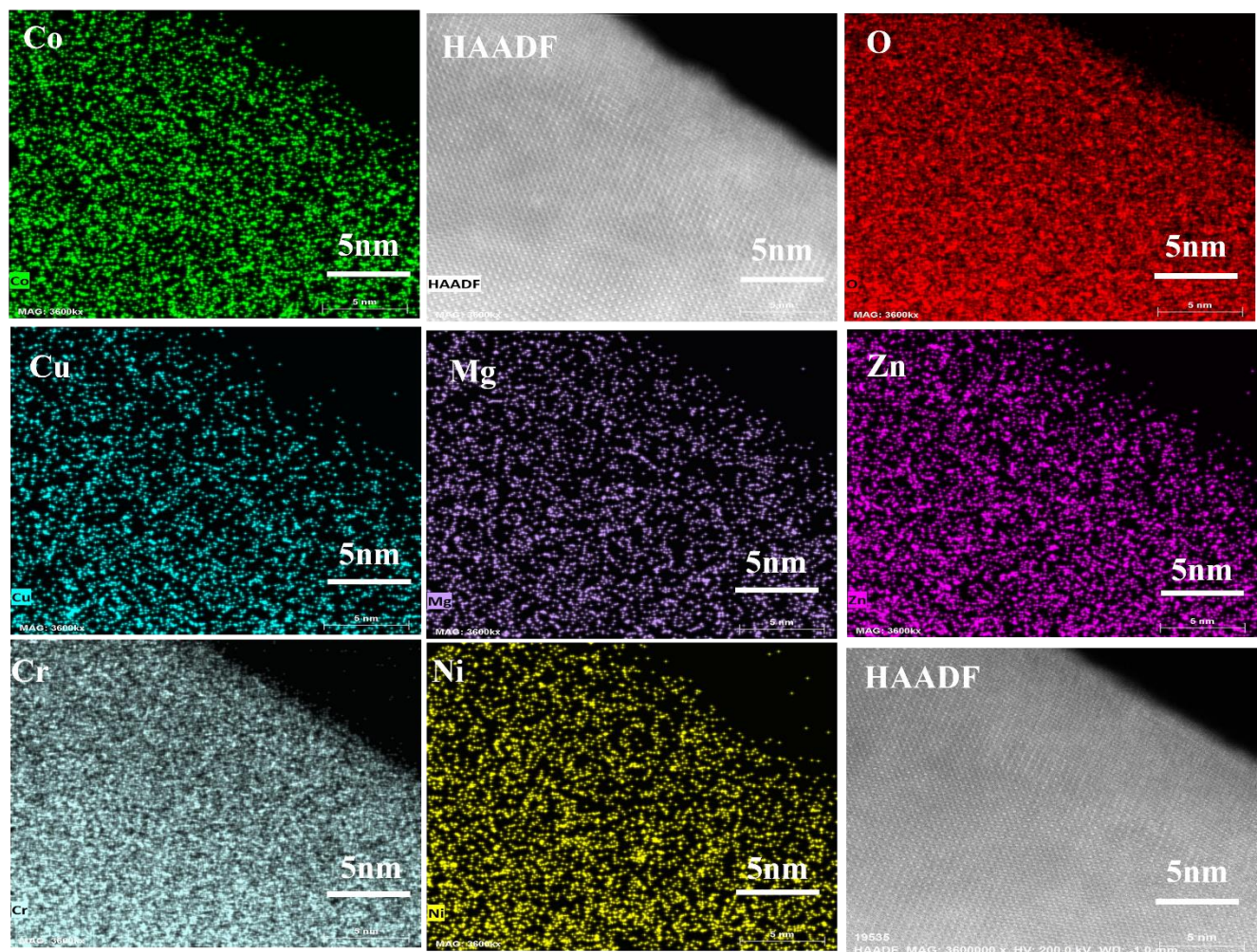


Figure S27.High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and energy-dispersive spectroscopy (EDS) elemental mapping images of a-($\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2}$) Cr_2O_4 nanoparticles.

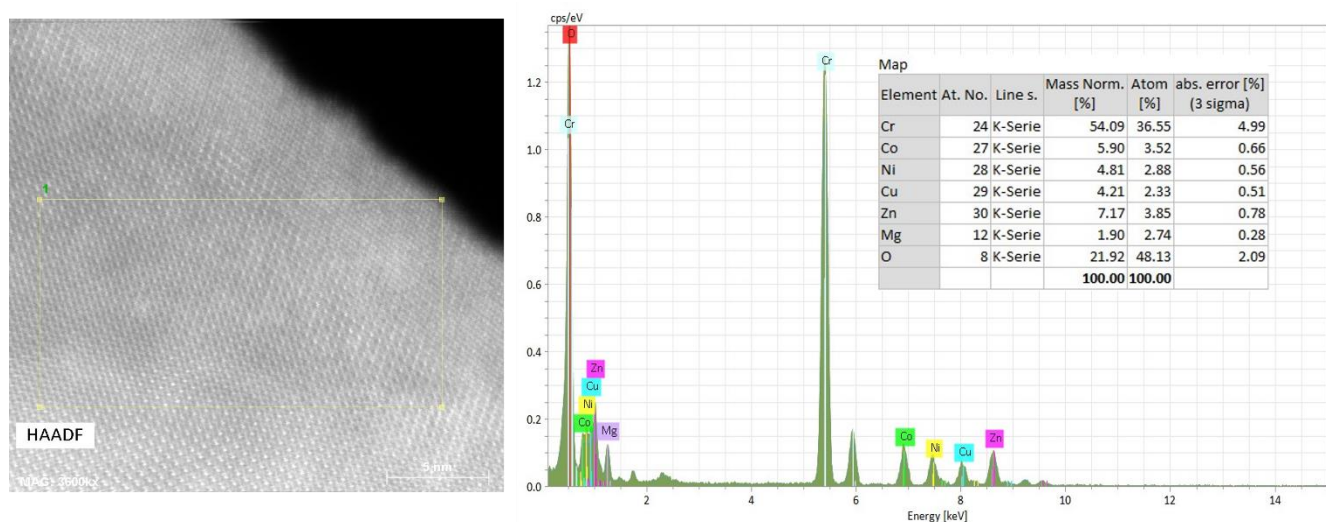


Figure S28.The qualitative analysis with composition of the metals (based on EDS mapping spectral data) of a-($\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2}$) Cr_2O_4 nanoparticles

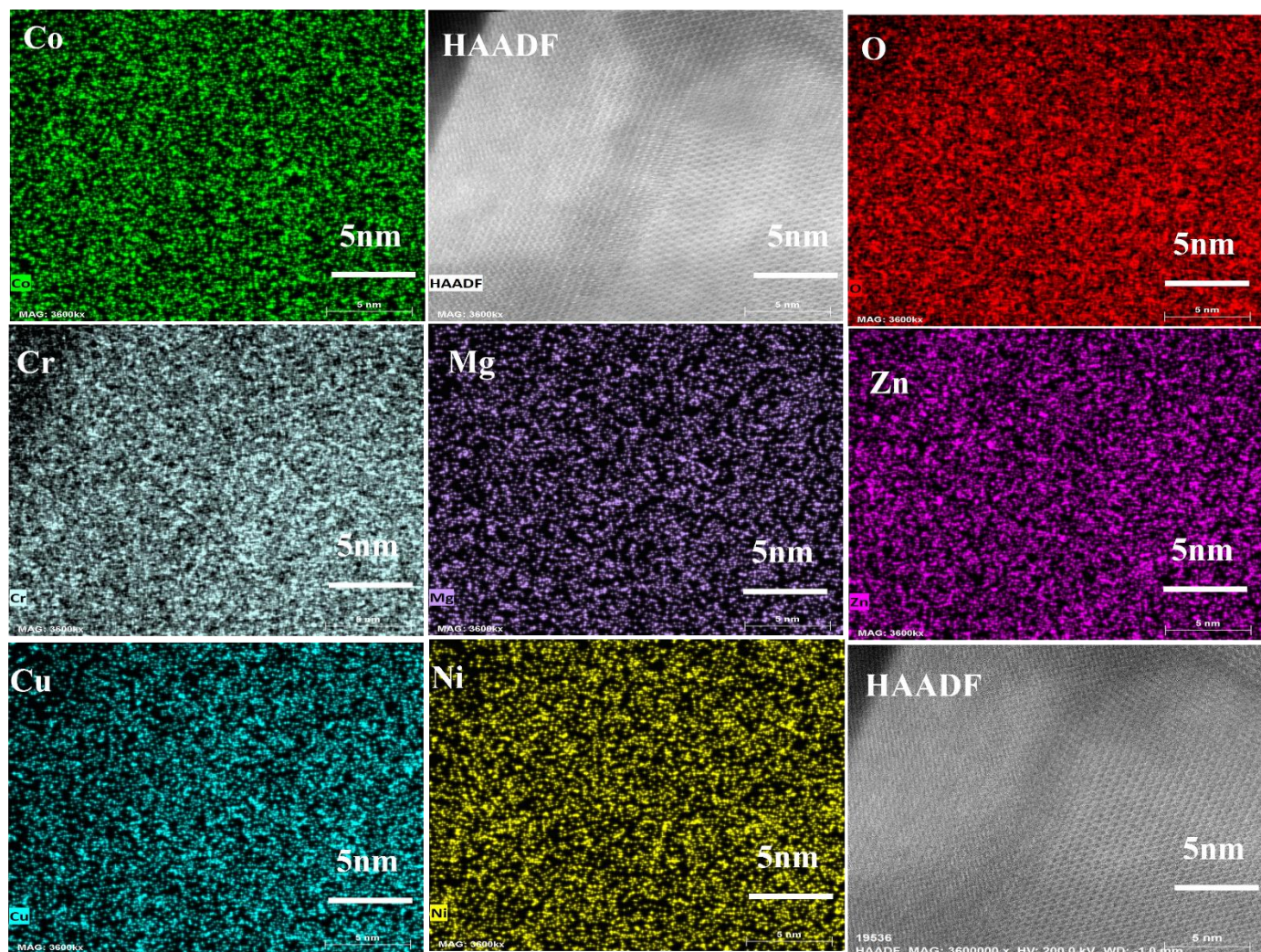


Figure S29. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and energy-dispersive spectroscopy (EDS) elemental mapping images of b-($\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2}$) Cr_2O_4 nanoparticles.

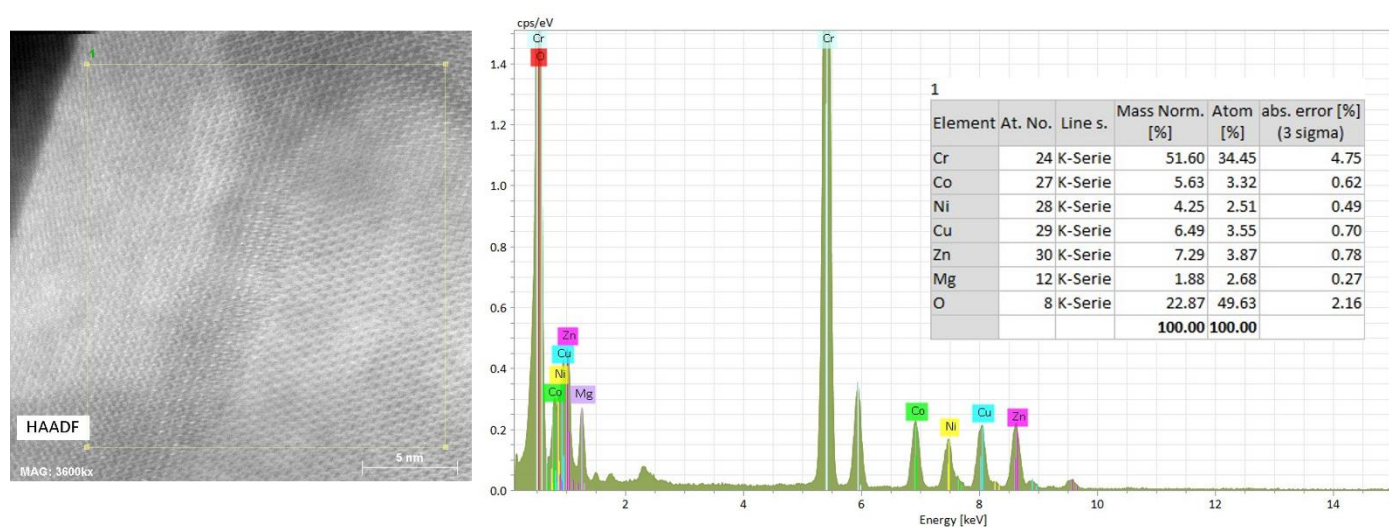


Figure S30. The qualitative analysis with composition of the metals (based on EDS mapping spectral data) of b-($\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2}$) Cr_2O_4 nanoparticles

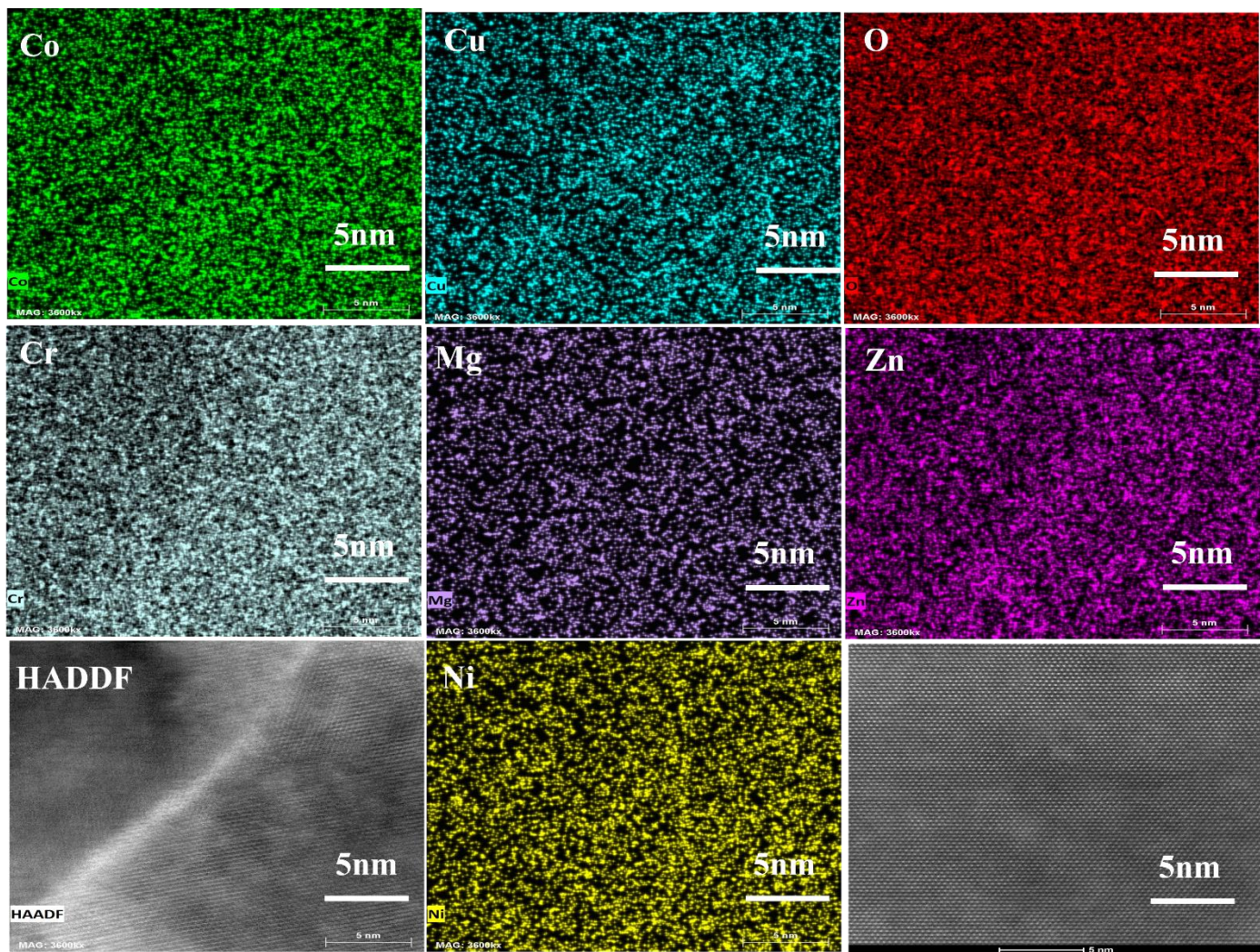


Figure S31. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and energy-dispersive spectroscopy (EDS) elemental mapping images of c-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ nanoparticles.

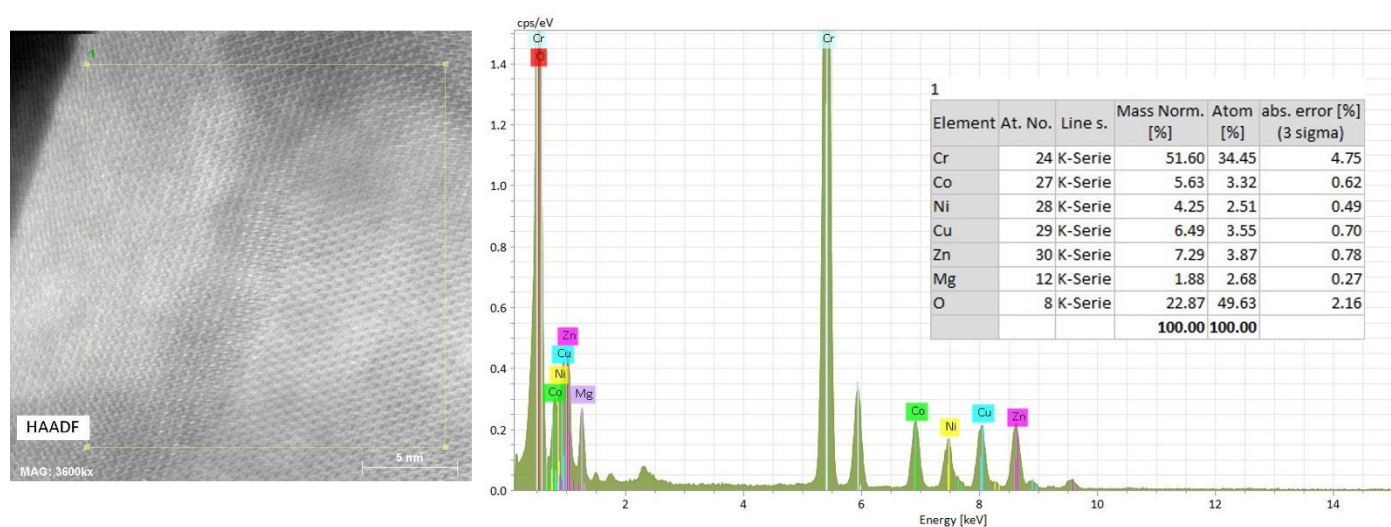


Figure S32. The qualitative analysis with composition of the metals (based on EDS mapping spectral data) of c-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ nanoparticles

Original:

In this work, $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ was constructed by a mechanochemistry-mediated method. The essence of this synthetic strategy was the mechanochemical processing of metal precursors, which generated more grain boundaries and interfaces between various metal salts. The description of procedure was shown in **Figure 4** and **Table S4**.

Revised:

In this work, $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ was constructed by a mechanochemistry-mediated method. The essence of this synthetic strategy was the mechanochemical processing of metal precursors, which generated more grain boundaries and interfaces between various metal salts. The description of procedure was shown in **Figure 4** and **Table S4**. In addition, according to the amount of raw materials added, the accurate content of each sample was obtained through Inductance-coupled plasma (ICP) analysis (ICP-MS) (**Table S7**, **Table S8**, **Table S9**).

Table S7. The molecular formula of a- $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ by Inductance-coupled plasma (ICP) analysis (ICP-MS)

Theoretical Molecular formula	Experimental Molecular formula	Cu	Zn	Co	Ni	Mg	Cr
NiCr_2O_4	$\text{NiCr}_{2.03}\text{O}_4$	0	0	0	20.6 4%	0	41.82 %
MgCr_2O_4	$\text{MgCr}_{2.15}\text{O}_4$	0	0	0	0	18.2 2%	39.13 %
CuCr_2O_4	$\text{CuCr}_{1.98}\text{O}_4$	21.9 3%	0	0	0	0	43.50 %
ZnCr_2O_4	$\text{ZnCr}_{2.03}\text{O}_4$	0	19.0 6%	0	0	0	38.84 %
CoCr_2O_4	$\text{CoCr}_{1.82}\text{O}_4$	0	0	22.85 %	0	0	41.26 %
$(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$	$(\text{Ni}_{1.07}\text{MgCu}_{1.02}\text{Zn}_{1.04}\text{Co}_{1.06})\text{Cr}_{1.26}\text{O}_4$	4.85 %	4.93 %	5.03 %	5.11 %	4.76 %	48.85 %

Table S8. The molecular formula of b-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ by Inductance-coupled plasma (ICP)

analysis (ICP-MS)							
Theoretical Molecular formula	Experimental Molecular formula	Cu	Zn	Co	Ni	Mg	Cr
NiCr ₂ O ₄	NiCr _{2.08} O ₄	0	0	0	19.35%	0	40.25%
MgCr ₂ O ₄	MgCr _{2.00} O ₄	0	0	0	0	20.3%	40.69%
CuCr ₂ O ₄	CuCr _{2.10} O ₄	18.09%	0	0	0	0	37.97%
ZnCr ₂ O ₄	ZnCr _{1.98} O ₄	0	21.68%	0	0	0	42.86%
CoCr ₂ O ₄	CoCr _{1.98} O ₄	0	0	20.77%	0	0	41.08%
(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	(Ni _{1.02} Mg _{1.00} Cu _{1.02} Zn _{1.01} Co) Cr _{10.22} O ₄	4.87%	4.83%	4.79%	4.89%	4.80%	48.96%

Table S9. The molecular formula of c-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ by Inductance-coupled plasma (ICP)

analysis (ICP-MS)							
Theoretical Molecular formula	Experimental Molecular formula	Cu	Zn	Co	Ni	Mg	Cr
NiCr ₂ O ₄	NiCr _{2.01} O ₄	0	0	0	21.03%	0	42.35%
MgCr ₂ O ₄	MgCr _{1.97} O ₄	0	0	0	0	21.81%	43.06%
CuCr ₂ O ₄	CuCr _{2.04} O ₄	20.12%	0	0	0	0	41.09%
ZnCr ₂ O ₄	ZnCr _{2.02} O ₄	0	18.08%	0	0	0	36.48%
CoCr ₂ O ₄	CoCr _{1.96} O ₄	0	0	23.47%	0	0	45.91%
(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	(NiMg _{1.01} Cu _{1.01} Zn _{1.00} Co _{1.01}) Cr _{10.09} O ₄	5.23%	5.20%	5.25%	5.19%	5.26%	52.38%

Revised:

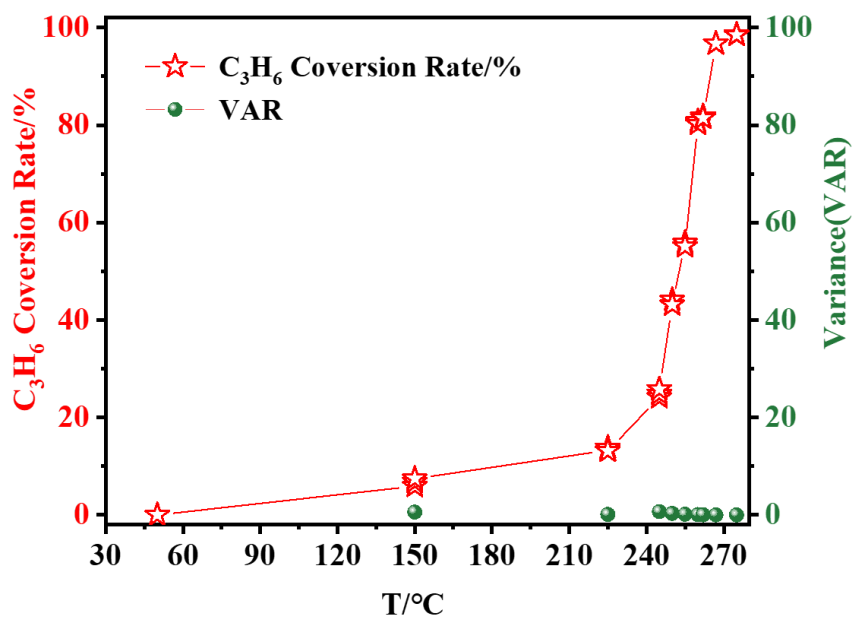


Figure S5a in Supporting Information 2. C₃H₆ light-off curve and variance(VAR) of a- (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄, b-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ and c-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄(20000 mL h⁻¹g⁻¹; the feed gases contain 1vol % C₃H₆ and 99vol% air)

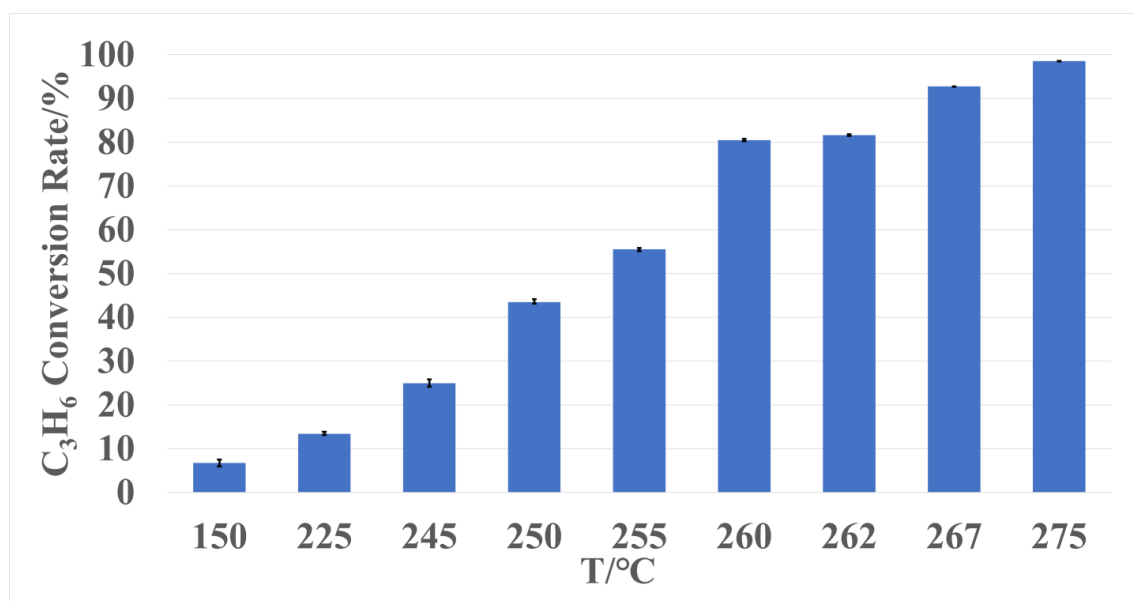


Figure S5b in Supporting Information 2. Histogram of C₃H₆ light-off curve and variance(VAR) in a- (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄, b-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ and c-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄(20000 mL h⁻¹g⁻¹; the feed gases contain 1vol % C₃H₆ and 99vol% air)

Table S3 (in Support Information 2) Original data of C₃H₆ light-off curve and variance(VAR) of a-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄, b-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ and c-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄

T/°C	Sample	C ₃ H ₆ Conversion Rate/%	VAR
50	a-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄		
	b-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	0.000	0
	c-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄		
150	a-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	5.916	
	b-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	6.784	0.613
	c-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	7.479	
225	a-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	13.269	
	b-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	13.826	0.134
	c-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	13.137	
245	a-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	24.154	
	b-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	24.849	0.710
	c-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	25.831	
250	a-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	43.173	
	b-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	44.138	0.322
	c-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	43.139	
255	a-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	55.810	
	b-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	55.804	0.168
	c-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	55.098	
260	a-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	80.401	
	b-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	80.757	0.074
	c-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	80.223	
262	a-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	81.803	
	b-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	81.693	0.038
	c-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	81.423	
267	a-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	92.697	
	b-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	92.749	0.001
	c-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	92.737	
275	a-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	98.443	
	b-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	98.575	0.004
	c-(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	98.524	

5. The main controls use single component oxides (i.e., one M). Do 5 metals really need to be there? What about 3, or 2? Does this impact performance/structure?

Reply:

Thanks for the important comment! As suggested by the reviewer, we prepared ten ternary control samples $(\text{Ni}_{0.5}\text{Mg}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Ni}_{0.5}\text{Cu}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Ni}_{0.5}\text{Zn}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Ni}_{0.5}\text{Co}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Cu}_{0.5}\text{Zn}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Cu}_{0.5}\text{Mg}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Zn}_{0.5}\text{Mg}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Co}_{0.5}\text{Mg}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Co}_{0.5}\text{Cu}_{0.5})\text{Cr}_2\text{O}_4$ and $(\text{Co}_{0.5}\text{Zn}_{0.5})\text{Cr}_2\text{O}_4$.

First, the dissociation energy of molecular H_2O on the surface of 10 ternary control samples at crystal planes (220) and (311) were calculated respectively (**Figure S16~S17 and Table S14**). The dissociation energy of molecular H_2O on the surface of high entropy $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ were 2.83 eV (crystal plane 311) and 2.75 eV (crystal plane 220). In contrast, the dissociation energy of molecular H_2O on the surface of 10 ternary control samples $(\text{Ni}_{0.5}\text{Mg}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Ni}_{0.5}\text{Cu}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Ni}_{0.5}\text{Zn}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Ni}_{0.5}\text{Co}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Cu}_{0.5}\text{Zn}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Cu}_{0.5}\text{Mg}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Zn}_{0.5}\text{Mg}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Co}_{0.5}\text{Mg}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Co}_{0.5}\text{Cu}_{0.5})\text{Cr}_2\text{O}_4$ and $(\text{Co}_{0.5}\text{Zn}_{0.5})\text{Cr}_2\text{O}_4$ at crystal plane (311) were 2.06 eV~2.55 eV. The dissociation energy of molecular H_2O on the surface of 10 ternary control samples $(\text{Ni}_{0.5}\text{Mg}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Ni}_{0.5}\text{Cu}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Ni}_{0.5}\text{Zn}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Ni}_{0.5}\text{Co}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Cu}_{0.5}\text{Zn}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Cu}_{0.5}\text{Mg}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Zn}_{0.5}\text{Mg}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Co}_{0.5}\text{Mg}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Co}_{0.5}\text{Cu}_{0.5})\text{Cr}_2\text{O}_4$ and $(\text{Co}_{0.5}\text{Zn}_{0.5})\text{Cr}_2\text{O}_4$ at the crystal plane (220) were 2.04 eV~2.69 eV. Those results showed that molecular H_2O was easy to dissociate into H^+ and OH^- on the surface of 10 ternary control samples, compared with high entropy $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, then OH^- could react with 10 ternary control samples to form hydroxide. Thus, the structure of 10 ternary control samples was destroyed and the catalytic activity decreased in the C_3H_6 oxidation. This DFT calculation suggested the better hydrothermal stability of high entropy oxide catalysts, which may be induced by their lower Gibbs free energy ($\Delta G = \Delta H - T\Delta S$).

Then, experimental and characterization studies such as XRD (**Figure S36**), SEM (**Figure S37~39**), N_2 isothermal sorption (**Figure S40**) and catalytic performance were conducted and added. Due to the low configuration entropy and high Gibbs free energy for crystalization, many ternary metal oxides cannot form a single phase under the same preparation conditions.

In addition, the $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ catalyst exhibited good catalytic performance for C_3H_6 oxidation with T_{90} (C_3H_6 conversion was 90%) at 265°C, better than that of 10 ternary control samples $(\text{Ni}_{0.5}\text{Mg}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Ni}_{0.5}\text{Cu}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Ni}_{0.5}\text{Zn}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Ni}_{0.5}\text{Co}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Cu}_{0.5}\text{Zn}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Cu}_{0.5}\text{Mg}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Zn}_{0.5}\text{Mg}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Co}_{0.5}\text{Mg}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Co}_{0.5}\text{Cu}_{0.5})\text{Cr}_2\text{O}_4$ and $(\text{Co}_{0.5}\text{Zn}_{0.5})\text{Cr}_2\text{O}_4$ (**Figure S2 in Supporting Information 2**). This result became understandable if the lower formation energy of oxygen vacancies by $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ was considered (Figure 3). Real-world applications (e.g., the treatment of automotive exhaust gas, and volatile organic compound combustion) required solid catalysts to be stable in ubiquitous moisture.^[13-15] Actually, the DFT calculation already suggested better hydrothermal stability of high entropy $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$. To verify the DFT conclusion, the stability experiments were carried out at a C_3H_6 conversion of ~70% with 4.2 vol% water. The C_3H_6 conversion of 10 ternary control samples $(\text{Ni}_{0.5}\text{Mg}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Ni}_{0.5}\text{Cu}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Ni}_{0.5}\text{Zn}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Ni}_{0.5}\text{Co}_{0.5})\text{Cr}_2\text{O}_4$,

$(\text{Cu}_{0.5}\text{Zn}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Cu}_{0.5}\text{Mg}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Zn}_{0.5}\text{Mg}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Co}_{0.5}\text{Mg}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Co}_{0.5}\text{Cu}_{0.5})\text{Cr}_2\text{O}_4$ and $(\text{Co}_{0.5}\text{Zn}_{0.5})\text{Cr}_2\text{O}_4$ continuously decreased in 20h and almost lost their catalytic activity in 50h. In sharp contrast, the activity of high entropy $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ was well retained within 100 hours. All those results have been added into revised manuscript.

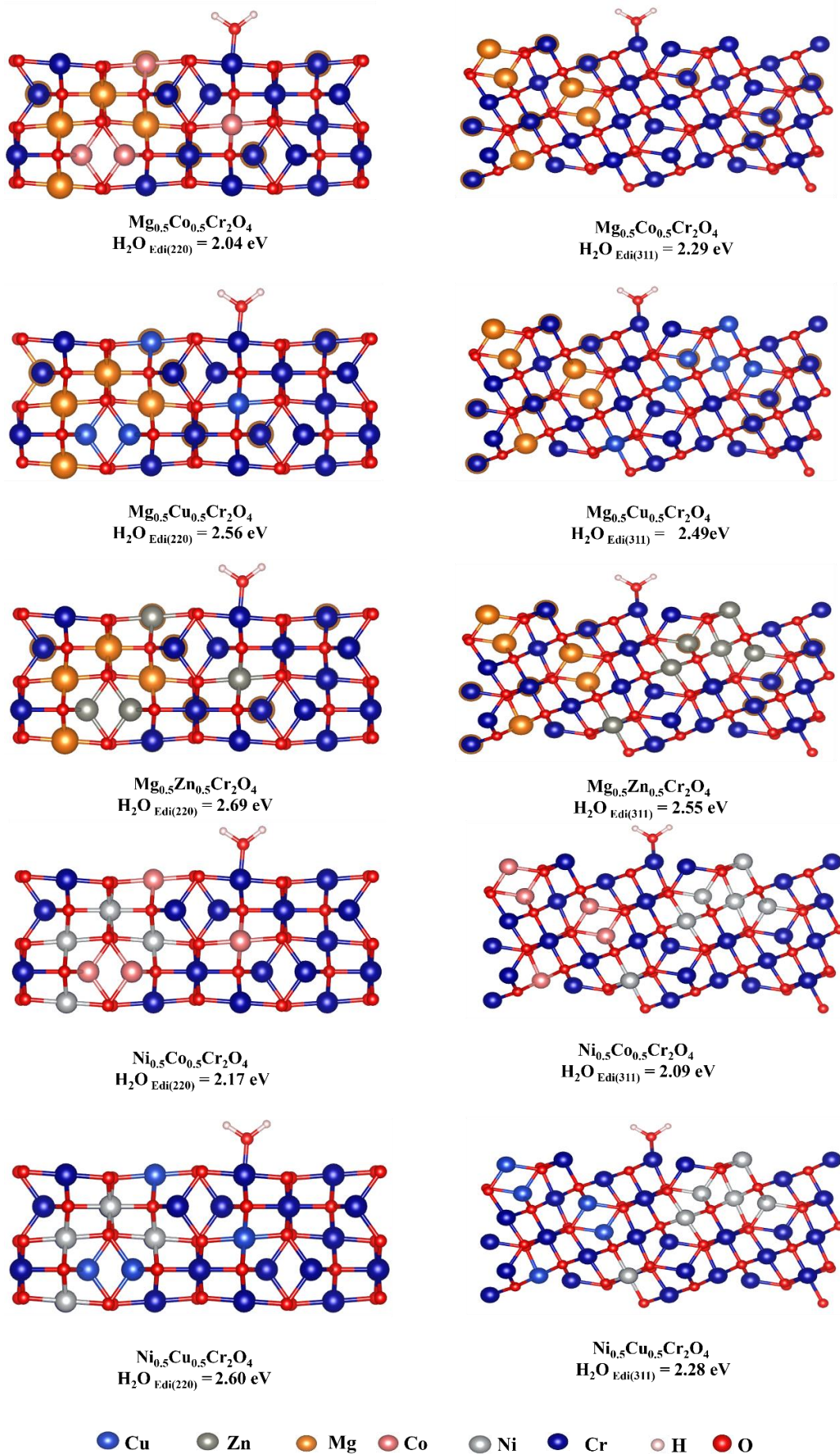


Figure S16. The dissociation energy of molecular H_2O on the surface of control ternary oxide samples $(\text{Cu}_{0.5}\text{Mg}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Zn}_{0.5}\text{Mg}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Co}_{0.5}\text{Mg}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Co}_{0.5}\text{Ni}_{0.5})\text{Cr}_2\text{O}_4$ and $(\text{Ni}_{0.5}\text{Cu}_{0.5})\text{Cr}_2\text{O}_4$ at crystal plane (220) and (311) respectively.

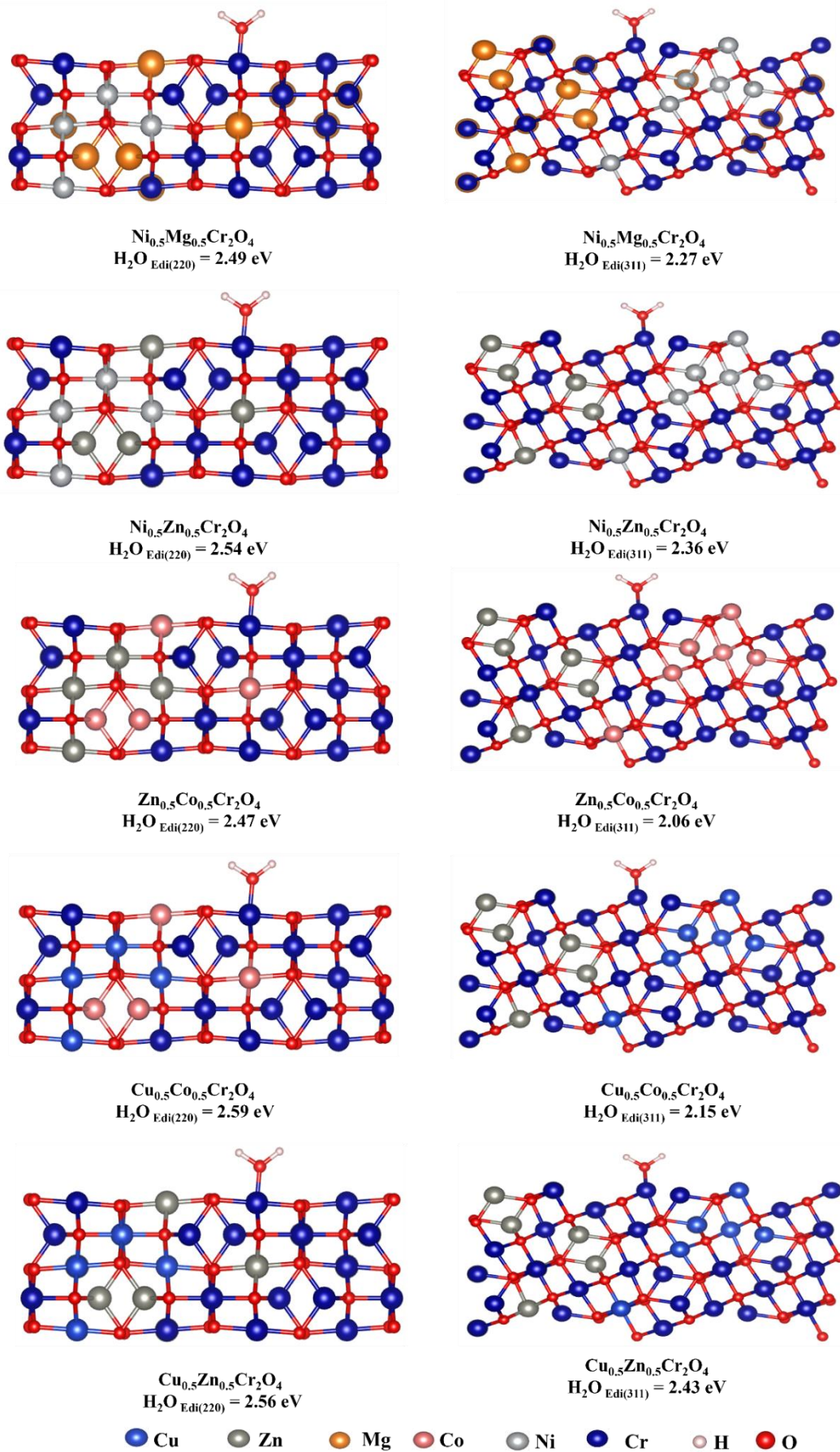


Figure S17. The dissociation energy of molecular H_2O on the surface of ternary control samples ($\text{Ni}_{0.5}\text{Mg}_{0.5}\text{Cr}_2\text{O}_4$, $(\text{Co}_{0.5}\text{Cu}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Ni}_{0.5}\text{Zn}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Zn}_{0.5}\text{Co}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Cu}_{0.5}\text{Zn}_{0.5})\text{Cr}_2\text{O}_4$ at crystal plane (220) and (311) respectively.

Table S13 Molar ratio of ternary control samples prepared by ball milling.

Sample	Ni(OAc) ₂ •4H ₂ O/m mol	Mg(OAc) 2•4H ₂ O/m mol	Cu(OAc) 2/mmol	Zn(OAc) 2/mmol	Co(OAc) ₂ • 4H ₂ O/mm ol	Cr(OAc) 3/mmol
(Ni _{0.5} Mg _{0.5})Cr ₂ O ₄	2	2	-	-	-	8
(Ni _{0.5} Cu _{0.5})Cr ₂ O ₄	2	-	2	-	-	8
(Ni _{0.5} Zn _{0.5})Cr ₂ O ₄	2	-	-	2	-	8
(Ni _{0.5} Co _{0.5})Cr ₂ O ₄	2	-	-	-	2	8
(Cu _{0.5} Zn _{0.5})Cr ₂ O ₄	-	-	2	2	-	8
(Cu _{0.5} Mg _{0.5})Cr ₂ O ₄	-	2	2	-	-	8
(Zn _{0.5} Mg _{0.5})Cr ₂ O ₄	-	2	-	2	-	8
(Co _{0.5} Mg _{0.5})Cr ₂ O ₄	-	2	-	-	2	8
(Co _{0.5} Cu _{0.5})Cr ₂ O ₄	-	-	2	-	2	8
(Co _{0.5} Zn _{0.5})Cr ₂ O ₄	-	-	-	2	2	8

Table S14 The dissociation energy of molecular H₂O on the surface of high entropy 10 ternary control samples (Ni_{0.5}Mg_{0.5})Cr₂O₄, (Ni_{0.5}Cu_{0.5})Cr₂O₄, (Ni_{0.5}Zn_{0.5})Cr₂O₄, (Ni_{0.5}Co_{0.5})Cr₂O₄, (Cu_{0.5}Zn_{0.5})Cr₂O₄, (Cu_{0.5}Mg_{0.5})Cr₂O₄, (Zn_{0.5}Mg_{0.5})Cr₂O₄, (Co_{0.5}Mg_{0.5})Cr₂O₄, (Co_{0.5}Cu_{0.5})Cr₂O₄ and (Co_{0.5}Zn_{0.5})Cr₂O₄ at crystal plane (220) and (311).

Sample	H ₂ O Edi (311)/eV	H ₂ O Edi (220)/eV
(Ni _{0.5} Mg _{0.5})Cr ₂ O ₄	2.27	2.49
(Ni _{0.5} Cu _{0.5})Cr ₂ O ₄	2.28	2.60
(Ni _{0.5} Zn _{0.5})Cr ₂ O ₄	2.36	2.54
(Ni _{0.5} Co _{0.5})Cr ₂ O ₄	2.09	2.17
(Cu _{0.5} Zn _{0.5})Cr ₂ O ₄	2.43	2.56
(Cu _{0.5} Mg _{0.5})Cr ₂ O ₄	2.49	2.56
(Zn _{0.5} Mg _{0.5})Cr ₂ O ₄	2.55	2.69
(Co _{0.5} Mg _{0.5})Cr ₂ O ₄	2.29	2.04
(Co _{0.5} Cu _{0.5})Cr ₂ O ₄	2.15	2.59
(Co _{0.5} Zn _{0.5})Cr ₂ O ₄	2.06	2.47

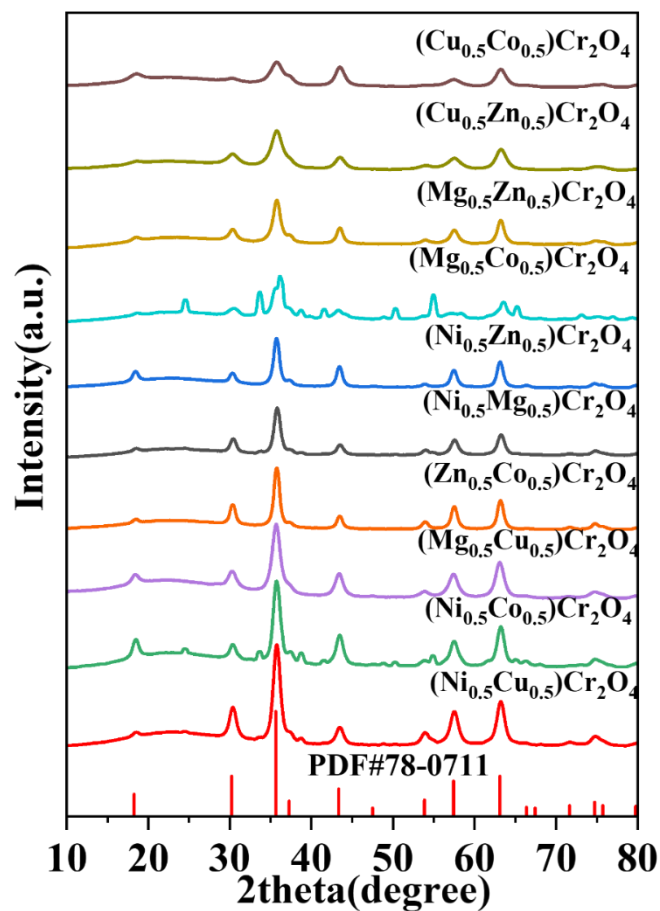


Figure S36. XRD patterns of 10 ternary control samples $(\text{Ni}_{0.5}\text{Mg}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Ni}_{0.5}\text{Cu}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Ni}_{0.5}\text{Zn}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Ni}_{0.5}\text{Co}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Cu}_{0.5}\text{Zn}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Cu}_{0.5}\text{Mg}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Zn}_{0.5}\text{Mg}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Co}_{0.5}\text{Mg}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Co}_{0.5}\text{Cu}_{0.5})\text{Cr}_2\text{O}_4$ and $(\text{Co}_{0.5}\text{Zn}_{0.5})\text{Cr}_2\text{O}_4$

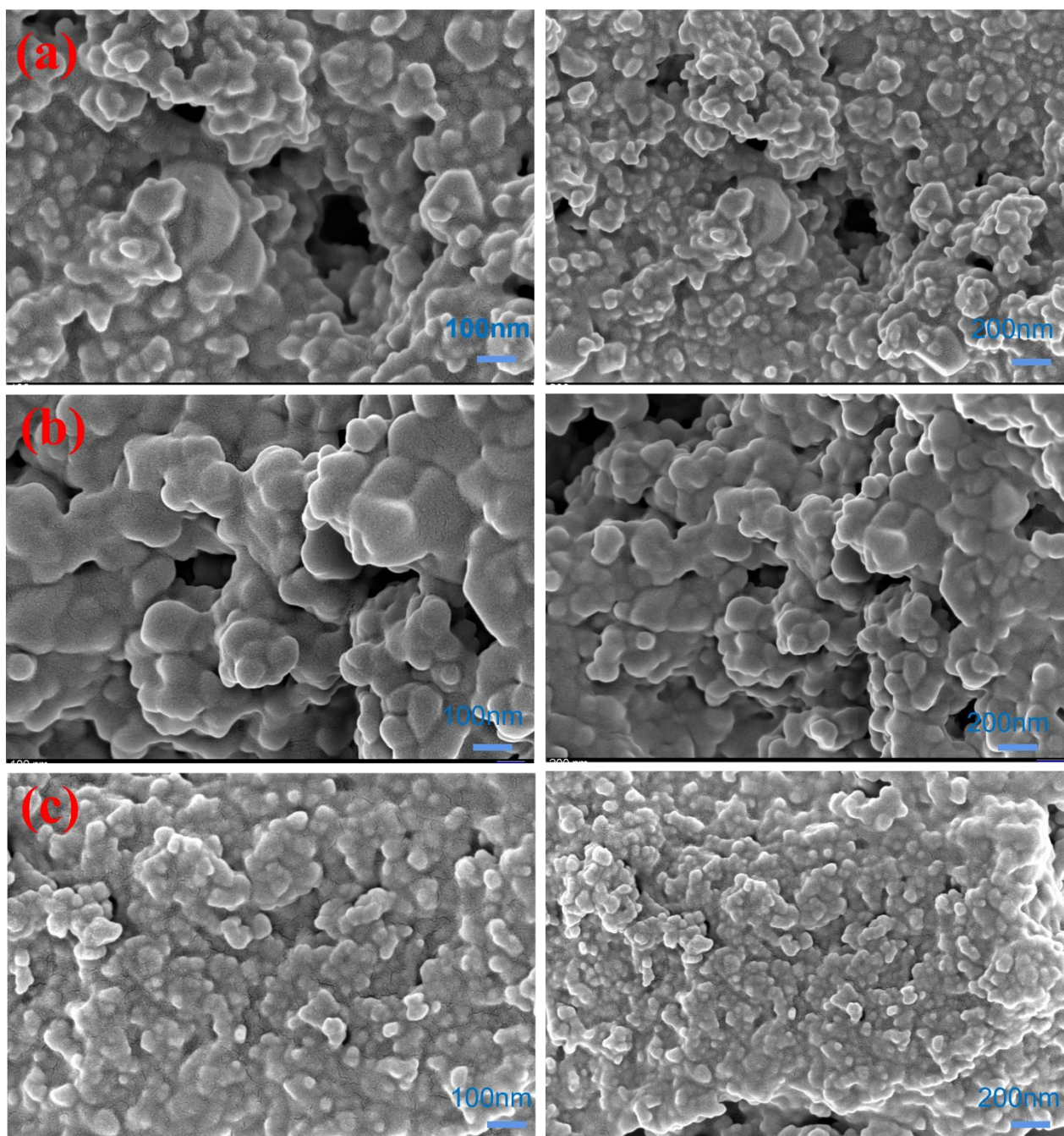


Figure S37. SEM images of ternary control samples $(\text{Ni}_{0.5}\text{Mg}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Ni}_{0.5}\text{Cu}_{0.5})\text{Cr}_2\text{O}_4$ and $(\text{Ni}_{0.5}\text{Zn}_{0.5})\text{Cr}_2\text{O}_4$

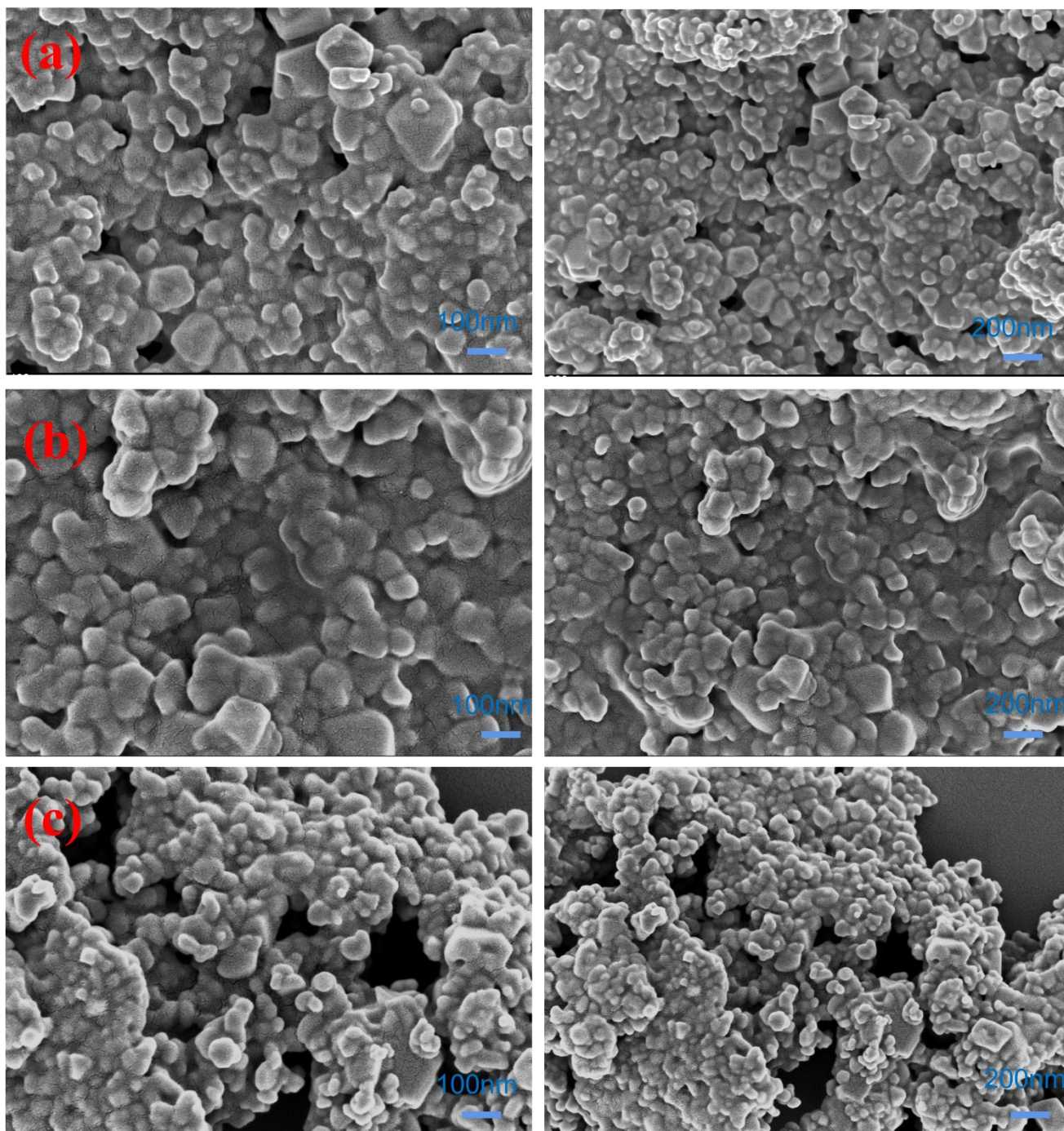


Figure S38. SEM images of ternary control samples $(\text{Ni}_{0.5}\text{Co}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Cu}_{0.5}\text{Zn}_{0.5})\text{Cr}_2\text{O}_4$ and $(\text{Cu}_{0.5}\text{Mg}_{0.5})\text{Cr}_2\text{O}_4$

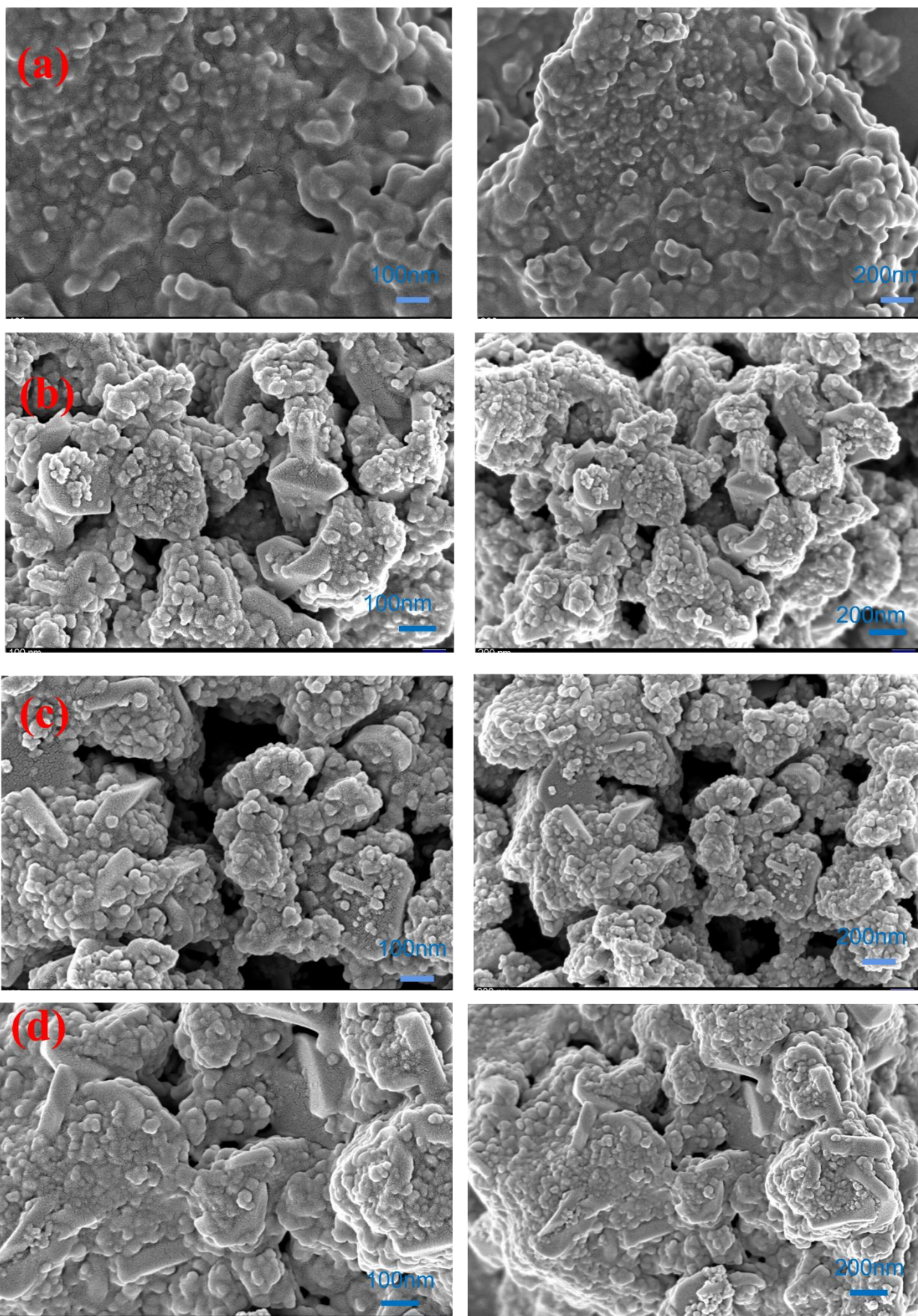


Figure S39. SEM images of ternary control samples $(\text{Zn}_{0.5}\text{Mg}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Co}_{0.5}\text{Mg}_{0.5})\text{Cr}_2\text{O}_4$, $(\text{Co}_{0.5}\text{Cu}_{0.5})\text{Cr}_2\text{O}_4$ and $(\text{Co}_{0.5}\text{Zn}_{0.5})\text{Cr}_2\text{O}_4$

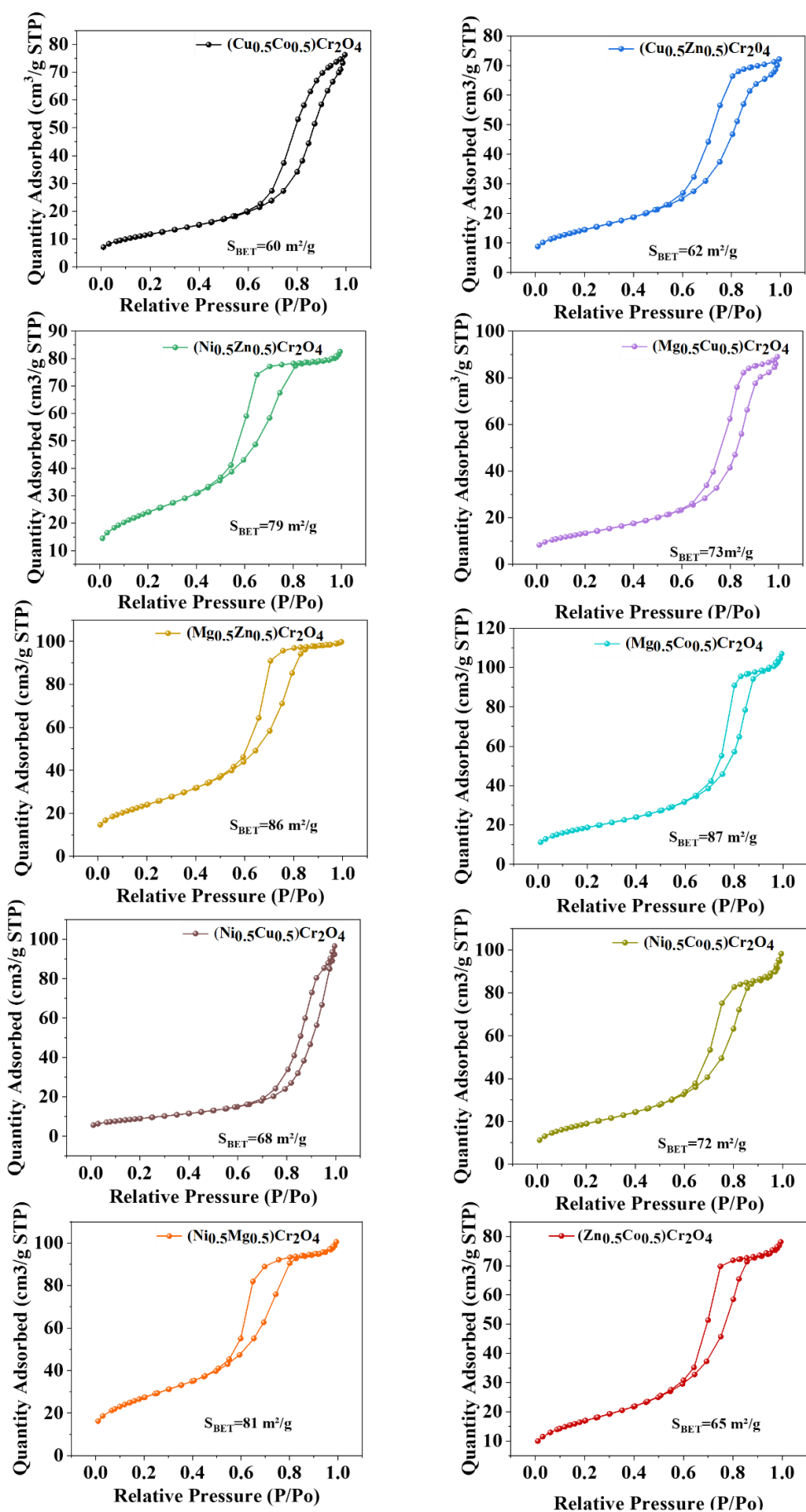


Figure S40. N₂ adsorption isothermal curves (77K) of 10 ternary oxide control samples (Ni_{0.5}Mg_{0.5})Cr₂O₄, (Ni_{0.5}Cu_{0.5})Cr₂O₄, (Ni_{0.5}Zn_{0.5})Cr₂O₄, (Ni_{0.5}Co_{0.5})Cr₂O₄, (Cu_{0.5}Zn_{0.5})Cr₂O₄, (Cu_{0.5}Mg_{0.5})Cr₂O₄, (Zn_{0.5}Mg_{0.5})Cr₂O₄, (Co_{0.5}Mg_{0.5})Cr₂O₄, (Co_{0.5}Cu_{0.5})Cr₂O₄ and (Co_{0.5}Zn_{0.5})Cr₂O₄.

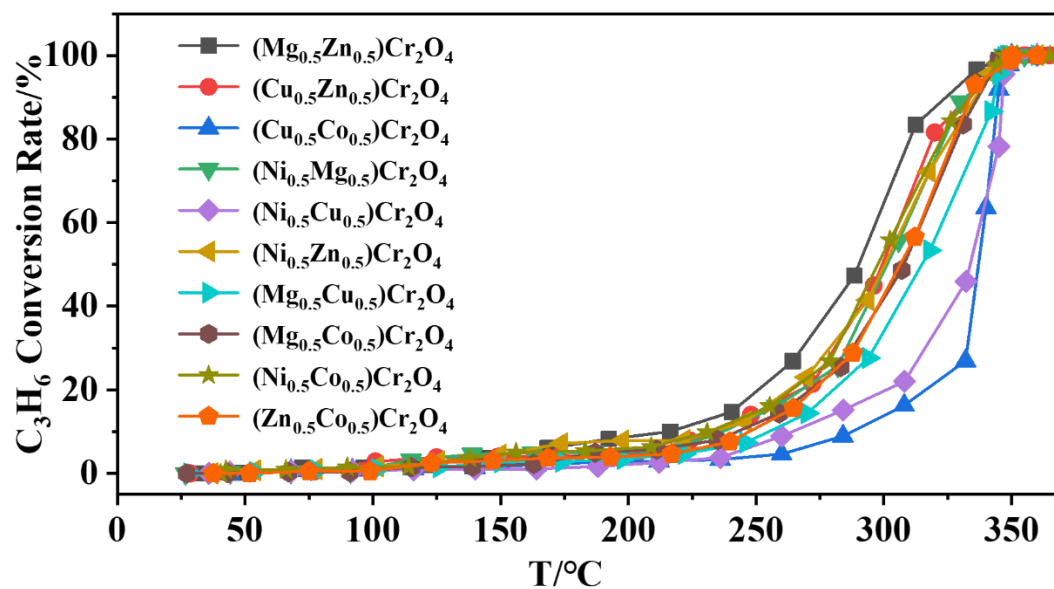


Figure S2 in Supporting Information 2. C_3H_6 light-off curve of 10 ternary oxide control samples (20000 $mL\ h^{-1}g^{-1}$; the feed gases contain 1vol % C_3H_6 and 99vol% air)

6. To make an appropriate/rigorous comparison, the materials and the control materials should be the same phase (minimally) and ideally, the same grain size/morphology/loading, etc. To wit, several of the “control” single metal spinels are not the correct phase by XRD (either a mixture of phases or unidentified other oxides. No TEM or other characterization is given for these samples. Are these the samples being used for catalytic testing? It is unclear that the catalytic samples were held at the very same testing conditions. Overall, it is difficult to assess the appropriateness of the comparisons between the high entropy material and the control materials without these details.

Reply:

Thanks for the useful suggestion! We agree with the reviewer's viewpoint. For the supported catalysts by the impregnation synthesis process, unifying the loading amount, size, and morphology of surface metals is required before the comparison of catalyst activity.^[1-4] Impregnation and drying is a frequently used preparation method among others due to its simple execution. The first step is contacting a metal precursor solution with porous support. Common precursors include inorganic metal salts, such as metal sulfates, carbonates, chlorides, nitrates, or acetates, and organic metal complexes, such as metal acetylacetonates. The most commonly used solvent for inorganic salts is water because of the high solubility of many precursors, whereas organic solvents are mainly used for organometallic precursors.^[5,6] To prevent premature deposition of the metal precursor in bulk solution, concentrations below (super)saturation are required. Common support materials consist of refractory oxides such as SiO₂, Al₂O₃, or TiO₂. These materials exhibit high specific surface areas, high porosities, and high thermal and mechanical stability and come in a variety of pore sizes, while they are mostly chemically inert.^[7-10] However, above common method seems difficult in the system of high entropy oxides and control oxides, which would be discussed in the following.

[1] Torres Galvis, H. M.; Bitter, J. H.; Khare, C. B.; Ruiten beek, M.; Dugulan, A. I.; de Jong, K. P. *Science*, **2012**,335, 835.

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For high entropy metal oxides (HEOs), such as HEOs with AB_2O_4 structure, there was a significant difference in configuration entropy compared to single metal oxides. Therefore, at the same calcination temperature, HEOs samples were more likely to become single-phase. However, some single metal oxides can only form multi phases. The crystal structures of HEOs and comparison samples such as single metal oxides were examined by XRD (**Figure 5b**). $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$, $ZnCr_2O_4$ and $CoCr_2O_4$ all showed characteristic diffraction peaks of cubic phase spinel (JCPDS 80-1668), and no other diffraction peaks were observed. However, pure $NiCr_2O_4$, $MgCr_2O_4$ and $CuCr_2O_4$ spinel could not be obtained under the same preparation conditions of 550°C calcination in air. This result can be explained by the effect of configurational entropy. Based on the quantitative relationship between randomness (ω) and entropy through the Boltzmann equation ($S = k \ln(\omega)$), the enhanced permutation number of atoms would contribute significant configurational entropy (S_{config}).^[9, 16-21] Actually, the configurational entropy of transition metal oxide systems can be calculated according to the following equation: ^[22-27]

$$\Delta S_{config} = -R * \left(\sum_{i=1}^n x_i \ln x_i \right)_{M-site} \quad (2)$$

where M refers to the cationic element, R is the gas content, x_i represents the mole fractions of the metal cations, and n is the total number of cation species. By calculation, ΔS_{config} value of $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$ is -9.752, while ΔS_{config} value of single metal ACr_2O_4 (A=Ni, Mg, Cu, Zn, Co) is -5.287. This difference would contribute to lower Gibbs free energy ($\Delta G = \Delta H - T\Delta S$) of $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$ for crystallization at 550°C by at least 4.12 kJ/mol.

The different temperatures required for the crystallization of HEOs samples and comparison samples such as single metal oxides would lead to the different growth degree of particles during the calcination process. It seems impossible to control the particle size of HEOs samples and comparison samples to be the same. In this work, the structural formula of AB_2O_4 was maintained at the same calcination temperature, only changing the number of species in the A site. Then, the effects of changes in configuration entropy and microstate number on crystallization and catalytic activity were investigated.

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- 14 Hu, R., Jin, S. & Sha, G. Application of atom probe tomography in understanding high entropy alloys: 3D local chemical compositions in atomic scale analysis. *Prog. Mater. Sci.* **117**, 100740 (2021).
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- 28 Yao, Y. *et al.* Carbothermal shock synthesis of high-entropy-alloy nanoparticles. *Science* **359**, 1489–1494 (2018).

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- 30 Feng, D. *et al.* Holey lamellar high-entropy oxide as an ultra-high-activity heterogeneous catalyst for solvent-free aerobic oxidation of benzyl alcohol. *Angew. Chemie* **59**, 19503–19509 (2020).
- 31 Gu, K. *et al.* Defect-rich high-entropy oxide nanosheets for efficient 5-hydroxymethylfurfural electrooxidation. *Angew. Chemie* **60**, 20253–20258 (2021).
- 32 Witte, R. *et al.* High-entropy oxides: An emerging prospect for magnetic rare-earth transition metal perovskites. *Phys. Rev. Lett.* **3**, 034406 (2019).
- 33 Tang, L. *et al.* High configuration entropy activated lattice oxygen for O₂ formation on perovskite electrocatalyst. *Adv. Funct. Mater.* **32**, 2112157 (2022).
- 34 Zhang, J. *et al.* Long-range antiferromagnetic order in a rocksalt high entropy oxide. *Chem. Mater.* **31**, 3705–3711 (2019).
- 35 Sarkar, A. *et al.* High entropy oxides for reversible energy storage. *Nat. Commun.* **9**, 3400 (2018).
- 36 Zhao, J. *et al.* Exsolution-dissolution of supported metals on high-entropy Co₃MnNiCuZnO_x: Toward sintering-resistant catalysis. *ACS Catal.* **11**, 12247–12257 (2021).

In addition, to study repeatability, the control samples NiCr₂O₄, MgCr₂O₄, CuCr₂O₄, ZnCr₂O₄, and CoCr₂O₄ were prepared three times respectively. The accurate content of each metal ions in NiCr₂O₄, MgCr₂O₄, CuCr₂O₄, ZnCr₂O₄, and CoCr₂O₄ were determined through Inductance-coupled plasma (ICP) analysis (ICP-MS) respectively (**Table S7, Table S8, Table S9**). Moreover, as suggested by the reviewer, we have added SEM (**Figure S41**), TEM (**Figure S42~51**), H₂O-TPD, and O₂-TPD experiments (**Figure 7**) for the control samples NiCr₂O₄, MgCr₂O₄, CuCr₂O₄, ZnCr₂O₄, CoCr₂O₄.

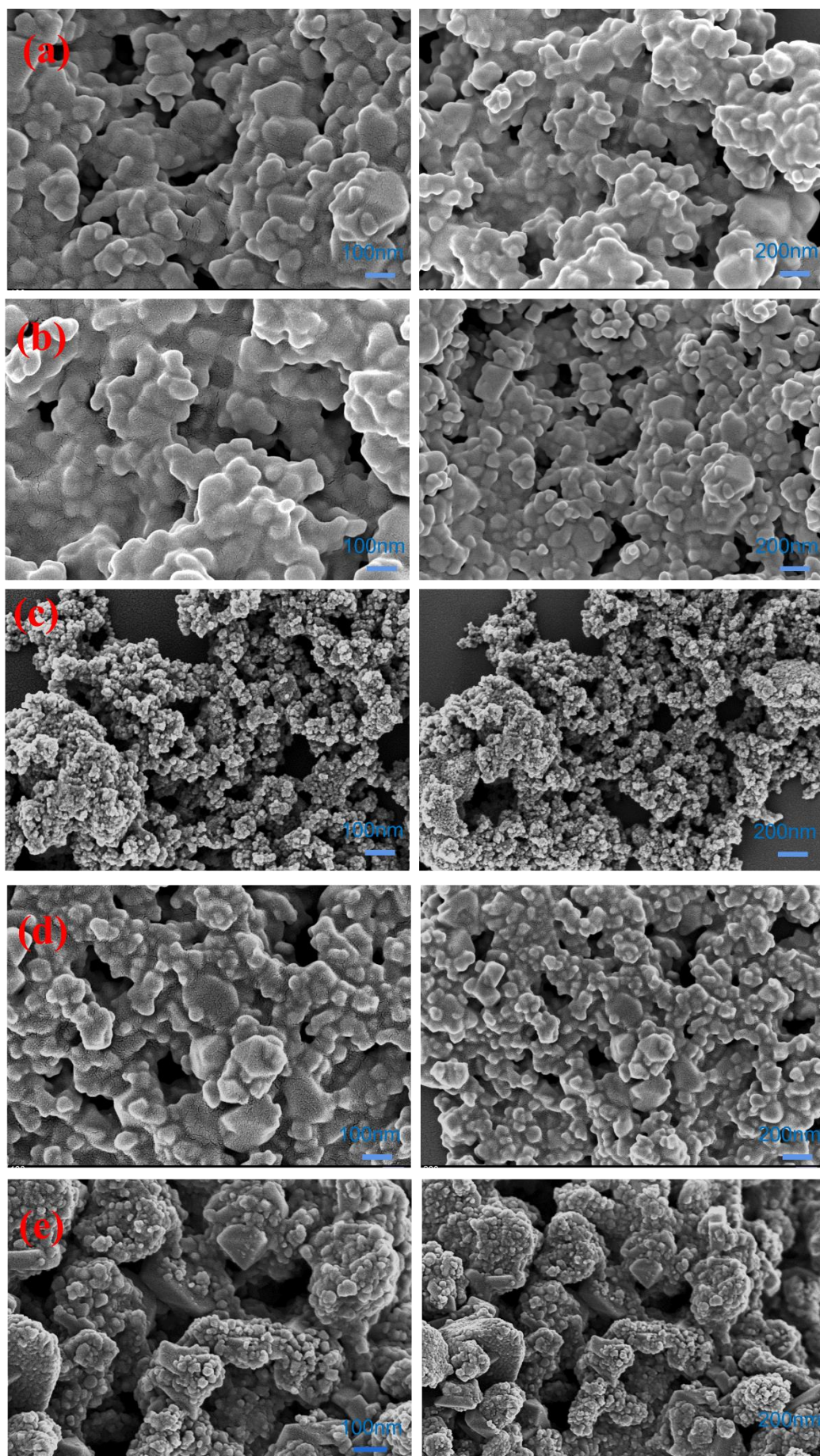
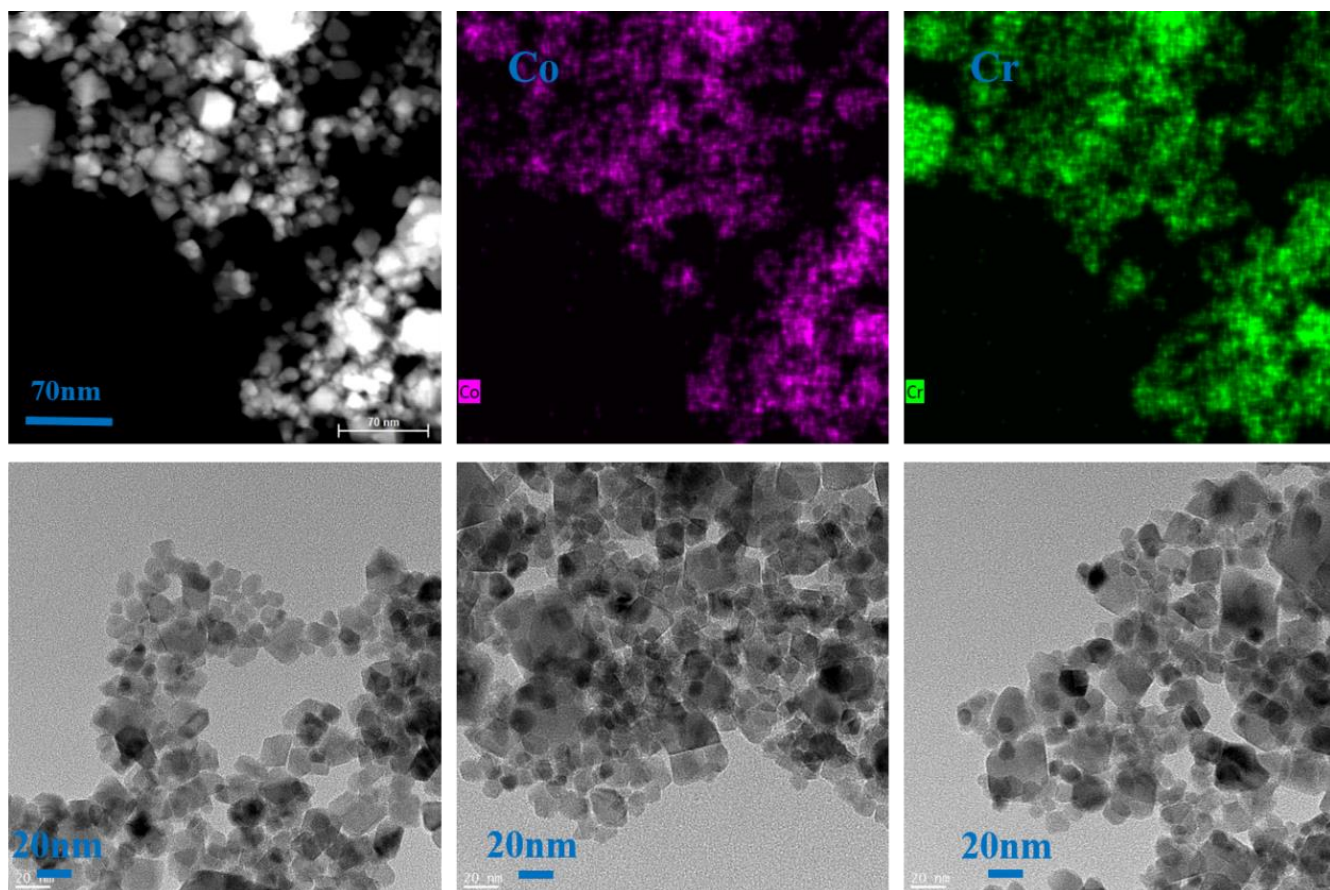
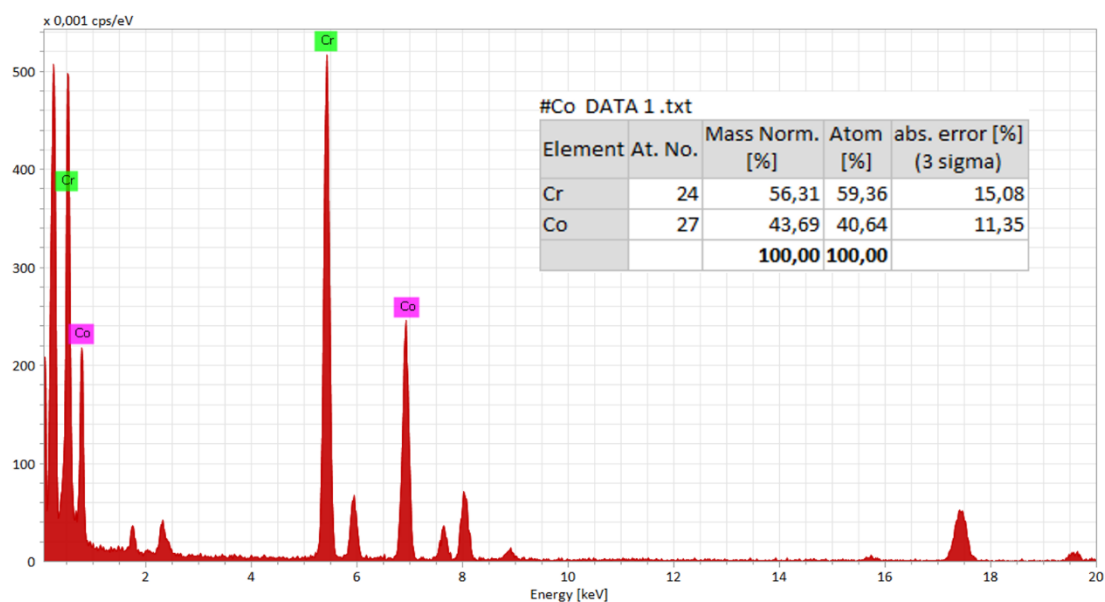


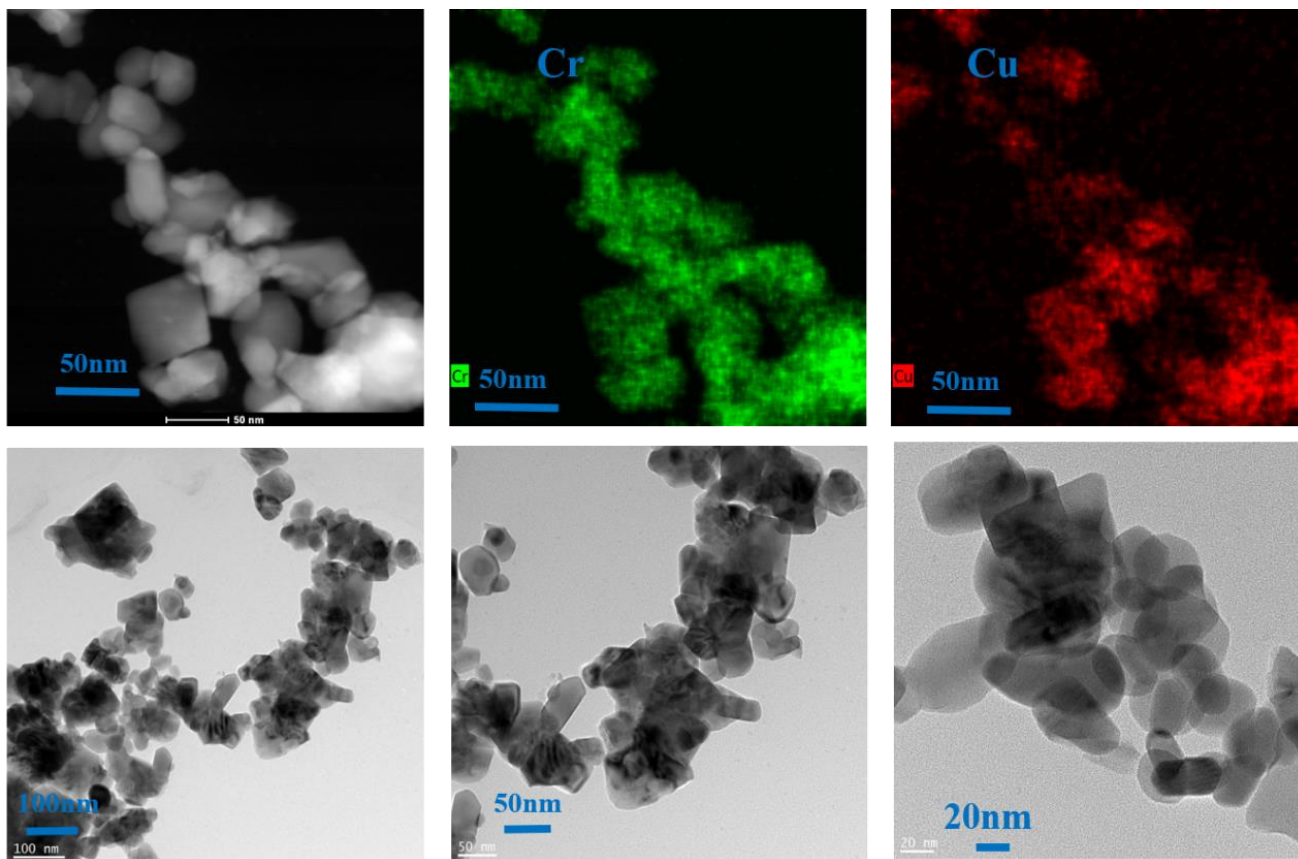
Figure S41. SEM of control samples NiCr_2O_4 , MgCr_2O_4 , CuCr_2O_4 , ZnCr_2O_4 and CoCr_2O_4



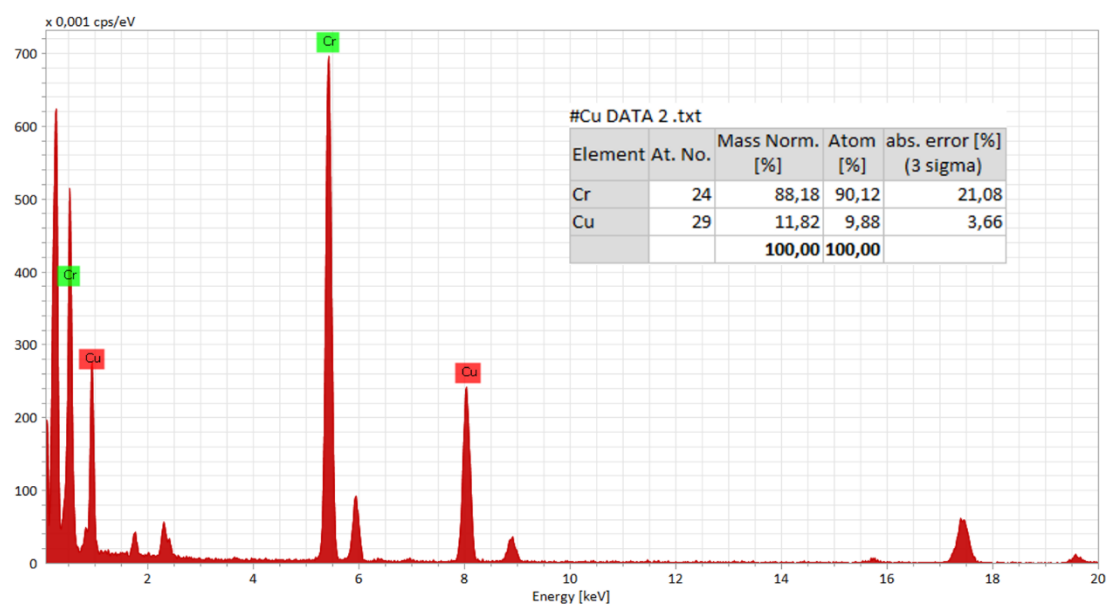
FigureS42 High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and energy-dispersive spectroscopy (EDS) elemental mapping images of CoCr_2O_4 nanoparticles.



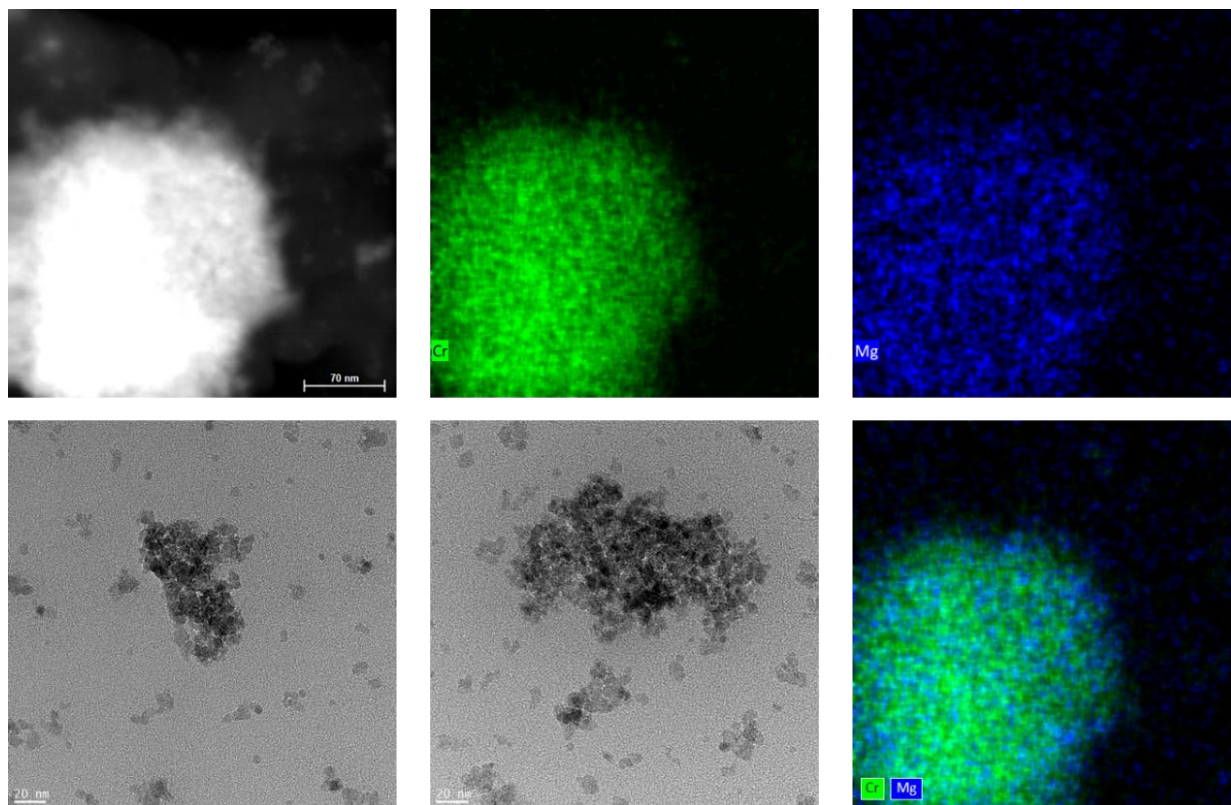
FigureS43 The qualitative analysis with composition of the metals (based on EDS mapping spectral data) of CoCr_2O_4 nanoparticles.



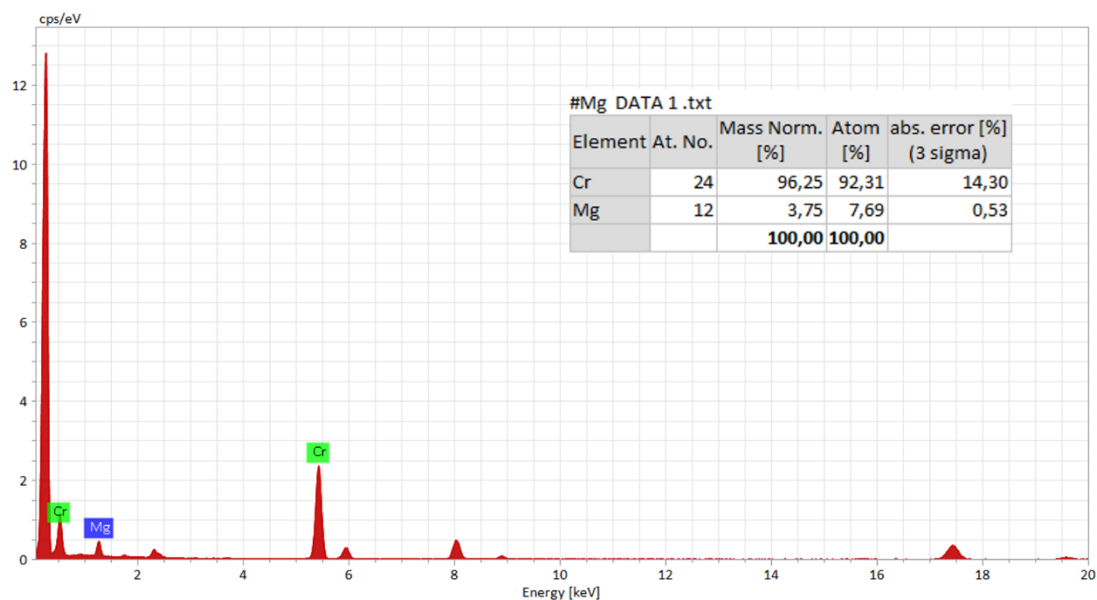
FigureS44 High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and energy-dispersive spectroscopy (EDS) elemental mapping images of CuCr_2O_4 nanoparticles.



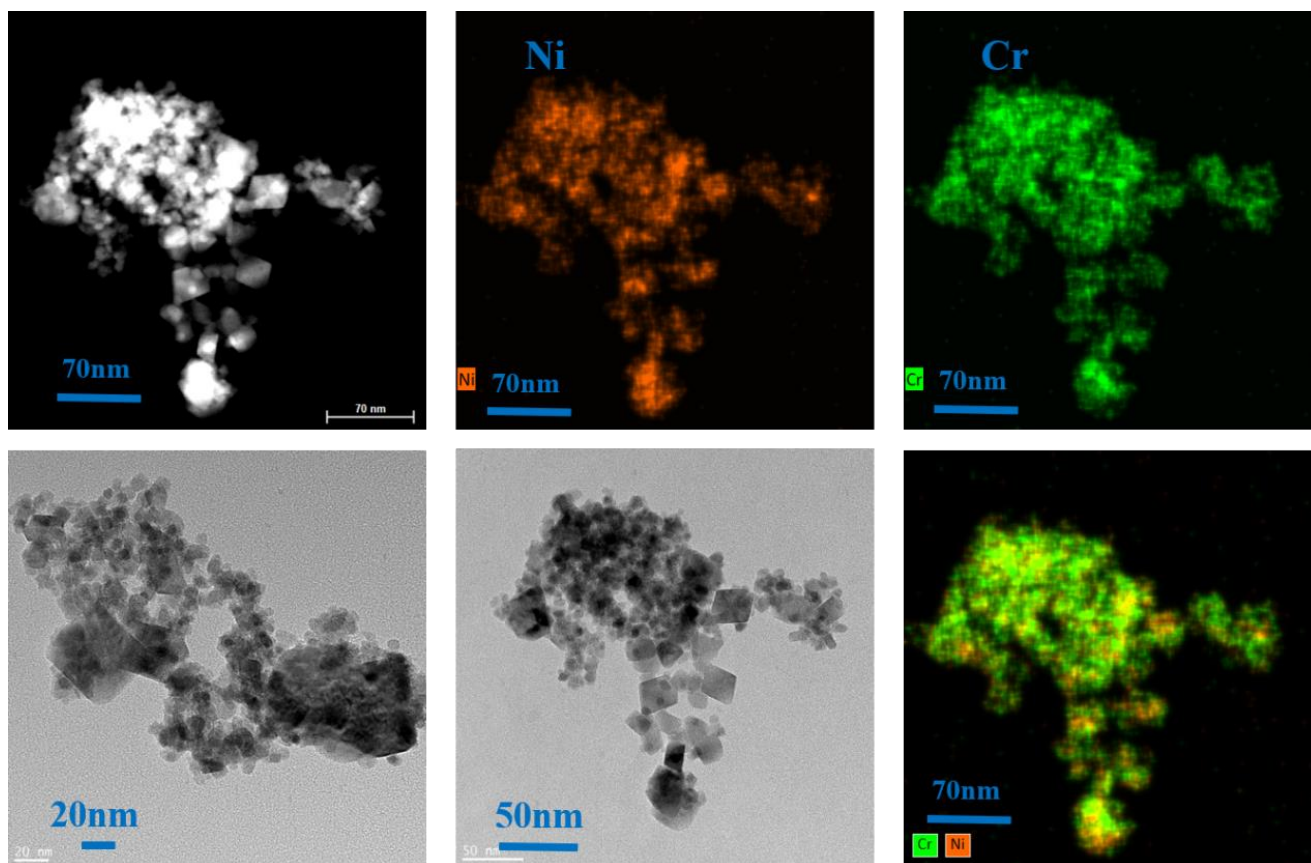
FigureS45 The qualitative analysis with composition of the metals (based on EDS mapping spectral data) of CuCr_2O_4 nanoparticles



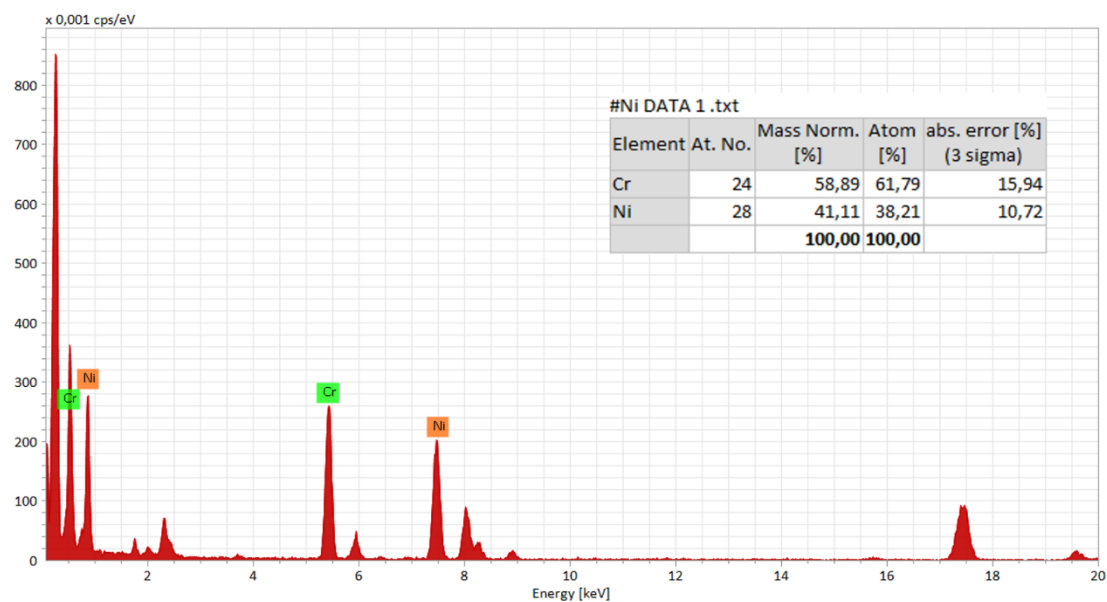
FigureS46 High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and energy-dispersive spectroscopy (EDS) elemental mapping images of MgCr_2O_4 nanoparticles.



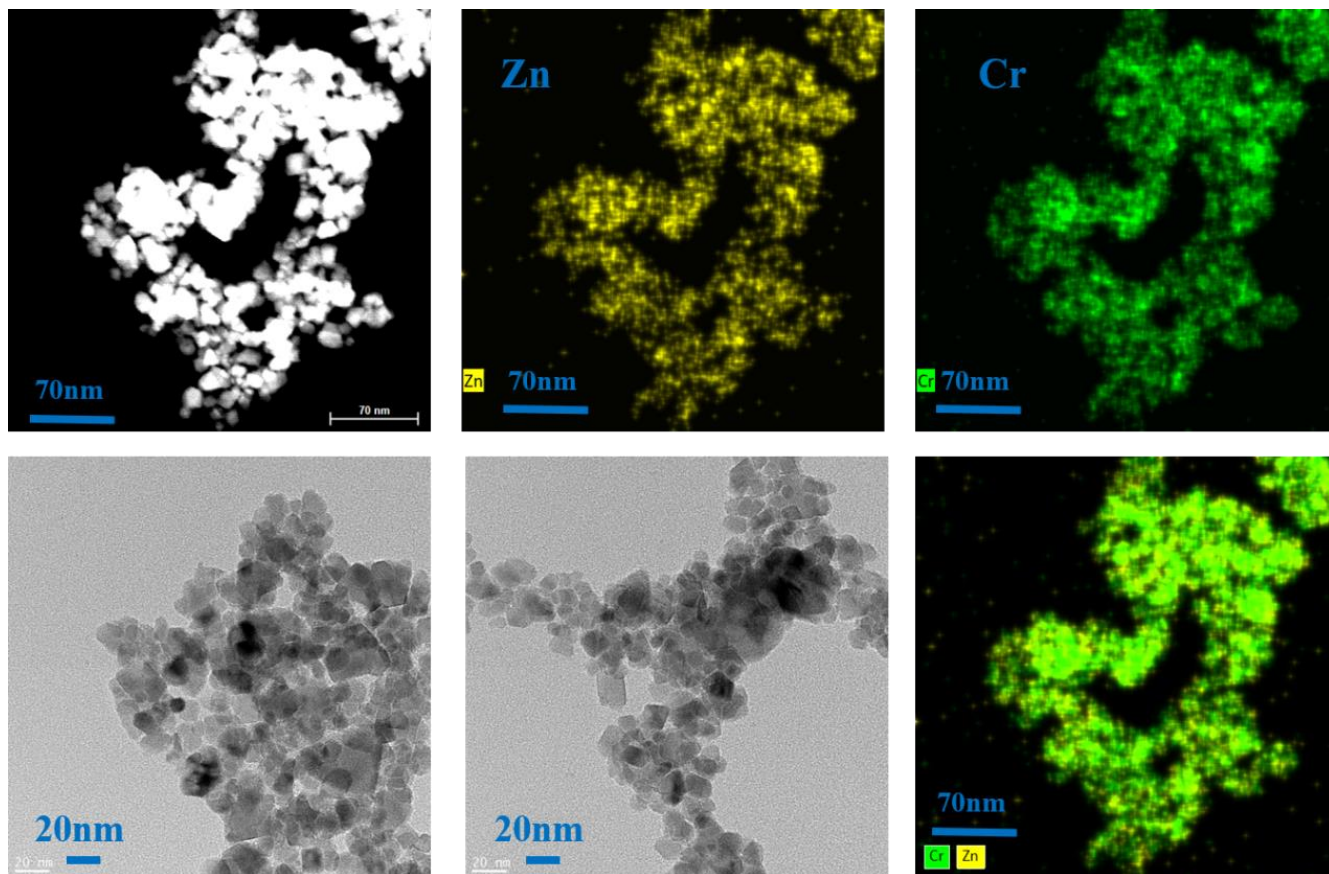
FigureS47 The qualitative analysis with composition of the metals (based on EDS mapping spectral data) of MgCr_2O_4 nanoparticles



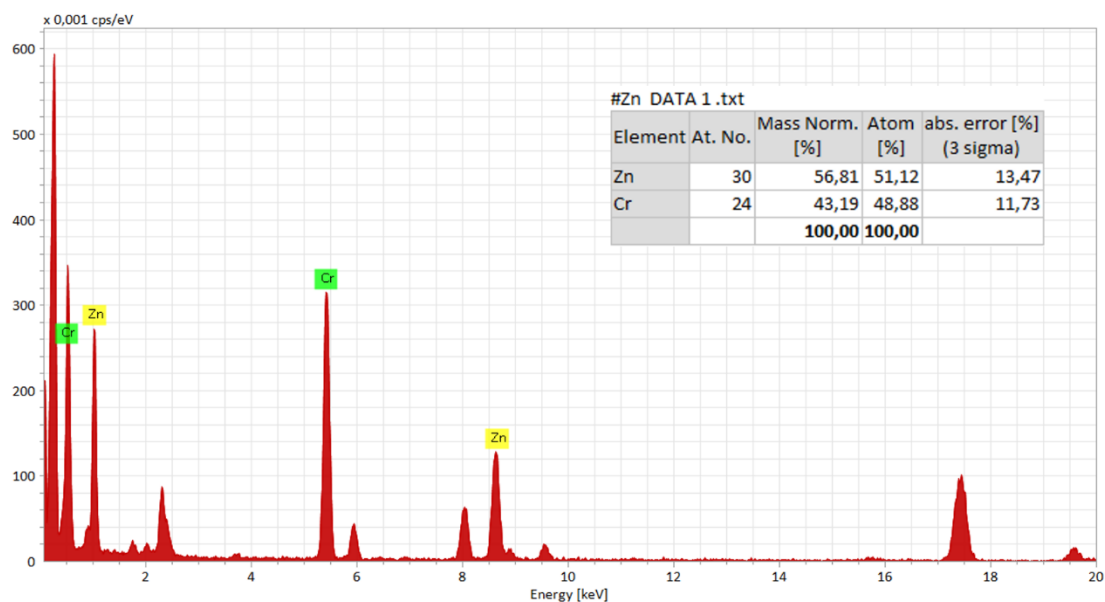
FigureS48 High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and energy-dispersive spectroscopy (EDS) elemental mapping images of NiCr_2O_4 nanoparticles.



FigureS49 The qualitative analysis with composition of the metals (based on EDS mapping spectral data) of NiCr_2O_4 nanoparticles



FigureS50 High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and energy-dispersive spectroscopy (EDS) elemental mapping images of ZnCr_2O_4 nanoparticles.



FigureS51 The qualitative analysis with composition of the metals (based on EDS mapping spectral data) of ZnCr_2O_4 nanoparticles

Original:

In this work, $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ was constructed by a mechanochemistry-mediated method. The essence of this synthetic strategy was the mechanochemical processing of metal precursors, which generated more grain boundaries and interfaces between various metal salts. The description of procedure was shown in **Figure 4** and **Table S4**.

Revised:

In this work, $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ was constructed by a mechanochemistry-mediated method. The essence of this synthetic strategy was the mechanochemical processing of metal precursors, which generated more grain boundaries and interfaces between various metal salts. The description of procedure was shown in **Figure 4** and **Table S4**. In addition, according to the amount of raw materials added, the accurate content of each sample was obtained through Inductance-coupled plasma (ICP) analysis (ICP-MS) (**Table S7**, **Table S8**, **Table S9**).

Table S7. The molecular formula of a- $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ by Inductance-coupled plasma (ICP) analysis (ICP-MS)

Theoretical Molecular formula	Experimental Molecular formula	Cu	Zn	Co	Ni	Mg	Cr
NiCr_2O_4	$\text{NiCr}_{2.03}\text{O}_4$	0	0	0	20.6 4%	0	41.82 %
MgCr_2O_4	$\text{MgCr}_{2.15}\text{O}_4$	0	0	0	0	18.2 2%	39.13 %
CuCr_2O_4	$\text{CuCr}_{1.98}\text{O}_4$	21.9 3%	0	0	0	0	43.50 %
ZnCr_2O_4	$\text{ZnCr}_{2.03}\text{O}_4$	0	19.0 6%	0	0	0	38.84 %
CoCr_2O_4	$\text{CoCr}_{1.82}\text{O}_4$	0	0	22.85 %	0	0	41.26 %
$(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$	$(\text{Ni}_{1.07}\text{MgCu}_{1.02}\text{Zn}_{1.04}\text{Co}_{1.06})\text{Cr}_{1.26}\text{O}_4$	4.85 %	4.93 %	5.03 %	5.11 %	4.76 %	48.85 %

Table S8. The molecular formula of b-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ by Inductance-coupled plasma (ICP)

analysis (ICP-MS)							
Theoretical Molecular formula	Experimental Molecular formula	Cu	Zn	Co	Ni	Mg	Cr
NiCr ₂ O ₄	NiCr _{2.08} O ₄	0	0	0	19.35%	0	40.25%
MgCr ₂ O ₄	MgCr _{2.00} O ₄	0	0	0	0	20.3%	40.69%
CuCr ₂ O ₄	CuCr _{2.10} O ₄	18.09%	0	0	0	0	37.97%
ZnCr ₂ O ₄	ZnCr _{1.98} O ₄	0	21.68%	0	0	0	42.86%
CoCr ₂ O ₄	CoCr _{1.98} O ₄	0	0	20.77%	0	0	41.08%
(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	(Ni _{1.02} Mg _{1.00} Cu _{1.02} Zn _{1.01} Co) Cr _{10.22} O ₄	4.87%	4.83%	4.79%	4.89%	4.80%	48.96%

Table S9. The molecular formula of c-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ by Inductance-coupled plasma (ICP)

analysis (ICP-MS)							
Theoretical Molecular formula	Experimental Molecular formula	Cu	Zn	Co	Ni	Mg	Cr
NiCr ₂ O ₄	NiCr _{2.01} O ₄	0	0	0	21.03%	0	42.35%
MgCr ₂ O ₄	MgCr _{1.97} O ₄	0	0	0	0	21.81%	43.06%
CuCr ₂ O ₄	CuCr _{2.04} O ₄	20.12%	0	0	0	0	41.09%
ZnCr ₂ O ₄	ZnCr _{2.02} O ₄	0	18.08%	0	0	0	36.48%
CoCr ₂ O ₄	CoCr _{1.96} O ₄	0	0	23.47%	0	0	45.91%
(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	(NiMg _{1.01} Cu _{1.01} Zn _{1.00} Co _{1.01}) Cr _{10.09} O ₄	5.23%	5.20%	5.25%	5.19%	5.26%	52.38%

Original:

To study the water resistance mechanism of (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄, H₂O-TPD experiments were conducted (**Figure 7a**). The peak of (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ appeared at a low temperature (80°C)

compared with ZnCr_2O_4 and CoCr_2O_4 . It revealed that the H_2O adsorption ability of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ was weaker, matching well with the DFT calculation results (Figures 1-2). Furthermore, the H_2O desorption peak of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ was smaller. This result indicated that there were fewer adsorption sites for water on $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, compared to ZnCr_2O_4 and CoCr_2O_4 . Hence, the amount of water molecules adsorbed by $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ was smaller compared to ZnCr_2O_4 and CoCr_2O_4 .

The oxygen species of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, ZnCr_2O_4 , and CoCr_2O_4 were closely related to their C_3H_6 oxidation performance, so O_2 -TPD experiments were conducted (**Figure 7b**). Two desorption peaks of oxygen species appeared at around 350 and 720°C for ZnCr_2O_4 . The O_2 peak desorbed at below 400°C was usually considered as the reactive oxygen species (ROS) of oxide catalysts. [17,46,51-53] Notably, $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ desorbed surface lattice oxygen at a lower temperature (220°C) than ZnCr_2O_4 (320°C) and CoCr_2O_4 (315°C). This feature suggested the lower formation energy of oxygen vacancy in $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, matching well with the DFT calculation (Figure 3). The ROS were weaker bonded with adjacent atoms and easier to escape from the catalyst surface, crucially leading to the enhanced catalytic performance of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ in C_3H_6 oxidation (Figure 6a).

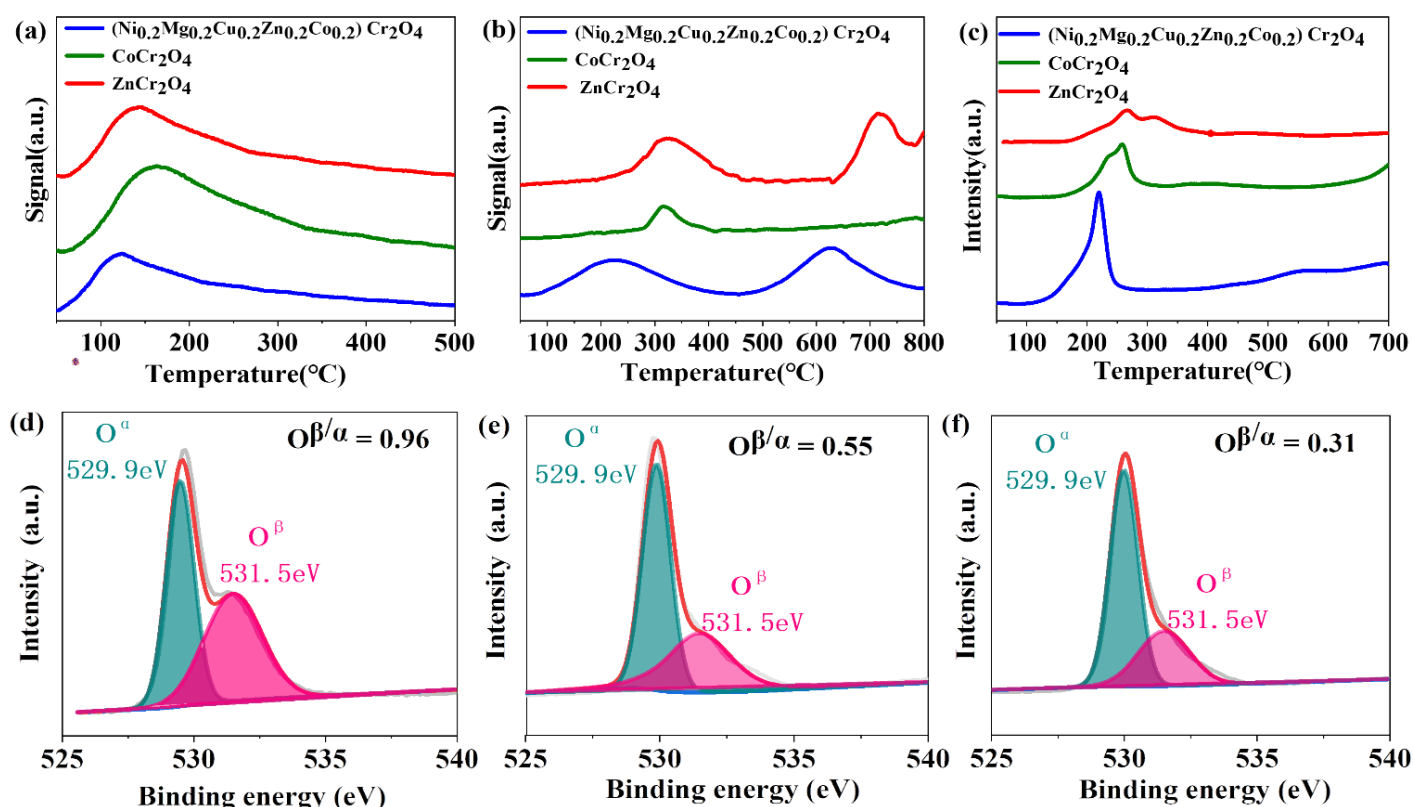


Figure 7 (a) H_2O -TPD profiles, (b) O_2 -TPD profiles (c) H_2 -TPR profiles of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, ZnCr_2O_4 and CoCr_2O_4 . (d) O^{1s} XPS spectra of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$. (e) O^{1s} XPS spectra of ZnCr_2O_4 . (f) O^{1s} XPS spectra of CoCr_2O_4 .

Revised:

To study the water resistance mechanism of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, H_2O -TPD experiments were conducted (**Figure 7a**). The peak of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ appeared at a low temperature (80°C) compared with NiCr_2O_4 , MgCr_2O_4 , CuCr_2O_4 , CoCr_2O_4 and ZnCr_2O_4 . It revealed that the H_2O adsorption ability of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ was weaker, matching well with the DFT calculation results (Figures 1-2). Furthermore, the H_2O desorption peak of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ was smaller. This result indicated that there were fewer adsorption sites for water on $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ and the amount of water molecules adsorbed by $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ was lower compared to NiCr_2O_4 , MgCr_2O_4 , CuCr_2O_4 , CoCr_2O_4 and ZnCr_2O_4 .

The oxygen species were closely related to their C_3H_6 oxidation performance, so O_2 -TPD experiments were conducted (**Figure 7b**). The O_2 peak desorbed at below 400°C was usually considered as the reactive oxygen species (ROS) of oxide catalysts.^[17,46,51-53] Notably, $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ desorbed surface active oxygen at a lower temperature (220°C) than NiCr_2O_4 (532°C), MgCr_2O_4 (420°C), CuCr_2O_4 (485°C), ZnCr_2O_4 (320°C) and CoCr_2O_4 (315°C). This feature suggested the lower formation energy of oxygen vacancy in $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, matching well with the DFT calculation (Figure 3). The ROS were weaker bonded with adjacent atoms and easier to escape from the catalyst surface, crucially leading to the enhanced catalytic performance of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ in C_3H_6 oxidation (Figure 6a).

- 17 Muller, D. A., Nakagawa, N., Ohtomo, A., Grazul, J. L. & Hwang, H. Y. Atomic-scale imaging of nanoengineered oxygen vacancy profiles in SrTiO_3 . *Nature* **430**, 657–661 (2004).
- 46 Zheng, Y. *et al.* Oxygen vacancies in a catalyst for VOCs oxidation: Synthesis, characterization, and catalytic effects. *J. Mater. Chem. A* **10**, 14171–14186 (2022).
- 51 Yu, K., Lou, L. L., Liu, S. & Zhou, W. Asymmetric oxygen vacancies: the intrinsic redox active sites in metal oxide catalysts. *Adv. Sci.* **7**, 1901970 (2020).
- 52 Fang, Y. *et al.* Oxygen vacancy-governed opposite catalytic performance for C_3H_6 and C_3H_8 combustion: The effect of the Pt electronic structure and chemisorbed oxygen species. *Environ. Sci. Technol.* **56**, 3245–3257 (2022).
- 53 Lin, J. *et al.* Activation of an Ir-in- CeO_2 catalyst by pulses of CO: The role of oxygen vacancy and carbonates in CO oxidation. *Catal. Today* **180**, 155–160 (2012).

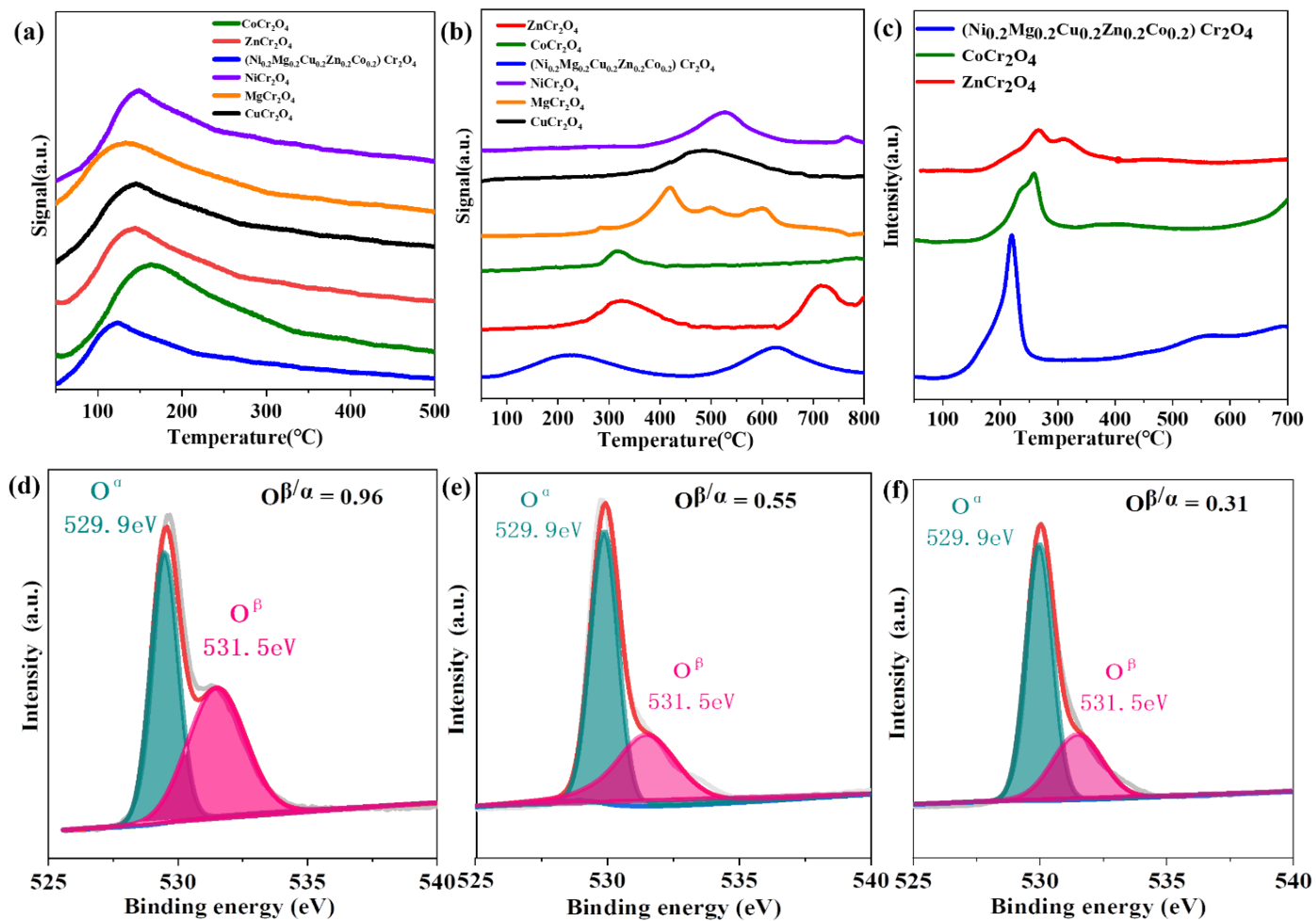


Figure 7 (a) H₂O -TPD profiles, (b) O₂ -TPD profiles of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, ZnCr_2O_4 , CoCr_2O_4 , NiCr_2O_4 , CuCr_2O_4 and MgCr_2O_4 . (c) H₂-TPR profiles of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, ZnCr_2O_4 and CoCr_2O_4 . (d) O 1s XPS spectra of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$. (e) O 1s XPS spectra of ZnCr_2O_4 . (f) O 1s XPS spectra of CoCr_2O_4 .

Reviewer: 3

Comments:

The high-entropy oxide presented herein displays more efficient catalytic activity and higher resiliency to water degradation than current catalysts. Density functional theory, H₂O-temperature programmed desorption, raman spectroscopy, x-ray photoelectron spectroscopy, and x-ray diffraction were all used to characterize the water resistance and catalytic activity. The manuscript is well written, dense with experimental findings, and timely: high-entropy oxides for robust catalysis is an exciting topic. There is also strong theory to support the conclusions. This work can be published in its current state but would be stronger with some revisions.

Recommendations:

1. It appears that the propylene molecules modeled in figure 1 are not consistently positioned between the models with and without water. It is unclear whether they migrated during relaxations or were placed intentionally.

Reply:

Thanks for the suggestion! There are some interactions between the propylene molecules and water molecules. Therefore, the positions of propylene molecules would have deviations with and without water. Here we use the first-principles calculations software (VASP) to fully relax the atomic positions of these models until all the forces are less than 0.03 eV/Å. Therefore, the models migrate during relaxations with and without water molecules.

2. It was mentioned that the lattice spacings found in the experimental results corresponded to the following crystal faces: (111), (311), and (220). However, it appears that the (111) face was not investigated with DFT. It is unclear why.

Reply:

Thanks for the careful comment! We have added DFT calculations of the adsorption energy of C₃H₆, the dissociation energy of molecular H₂O and the formation energy of oxygen vacancy at (111) face respectively. The DFT calculation results at (111) face were consistent with crystal faces (311) and (220). Please refer to the supporting information for details.

Original:

1.1 The adsorption energy of C₃H₆ on the surface of ACr₂O₄ by DFT calculation

Spinel oxides, mostly with the composition AB₂O₄ (where A and B are metal ions), are a class of common catalysts.^[28] In this study, C₃H₆ catalytic oxidation by ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co) was selected as a model. A sites (A=Ni, Mg, Cu, Zn, Co) in ACr₂O₄ were tuned from single to five metal ions. The adsorption energy of C₃H₆ on the surface of single metal ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co) and (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄

in the dry or 4.2vol% water conditions were calculated respectively(**Figure 1, Figure S1**). In the presence of 4.2vol% water, the adsorption energy of C₃H₆ on the surfaces of single metal ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co) all increased sharply. The presence of H₂O molecules formed competitive adsorption and may reduce the adsorption amount of C₃H₆ on the surface of ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co) catalysts, which would affect the C₃H₆ oxidation. In contrast, the presence of H₂O molecules on the surface of (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ had little effect on the adsorption energy of C₃H₆ (**Table S1**). For example, the adsorption energies of C₃H₆ on (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ surface were -1.051eV (crystal plane 311) in dry conditions and -0.963eV with 4.2vol% water. It seems like high-entropy structure could decrease the competitive adsorption of H₂O with C₃H₆ reactant.

Revised:

1.1 The adsorption energy of C₃H₆ on the surface of ACr₂O₄ by DFT calculation

Spinel oxides, mostly with the composition AB₂O₄ (where A and B are metal ions), are a class of common catalysts.^[28]In this study, C₃H₆ catalytic oxidation by ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co) was selected as a model. A sites (A=Ni, Mg, Cu, Zn, Co) in ACr₂O₄ were tuned from single to five metal ions. **The adsorption energy of C₃H₆ on the surface of single metal ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co) and (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ in the dry or 4.2vol% water conditions were calculated respectively(Figure 1, Figure S1, Figure S52).** In the presence of 4.2vol% water, the adsorption energy of C₃H₆ on the surfaces of single metal ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co) all increased sharply. The presence of H₂O molecules formed competitive adsorption and may reduce the adsorption amount of C₃H₆ on the surface of ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co) catalysts, which would affect the C₃H₆ oxidation. In contrast, the presence of H₂O molecules on the surface of (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ had little effect on the adsorption energy of C₃H₆ (**Table S1**). For example, the adsorption energies of C₃H₆ on (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ surface were -1.051eV (crystal plane 311) in dry conditions and -0.963eV with 4.2vol% water. It seems like high-entropy structure could decrease the competitive adsorption of H₂O with C₃H₆ reactant.

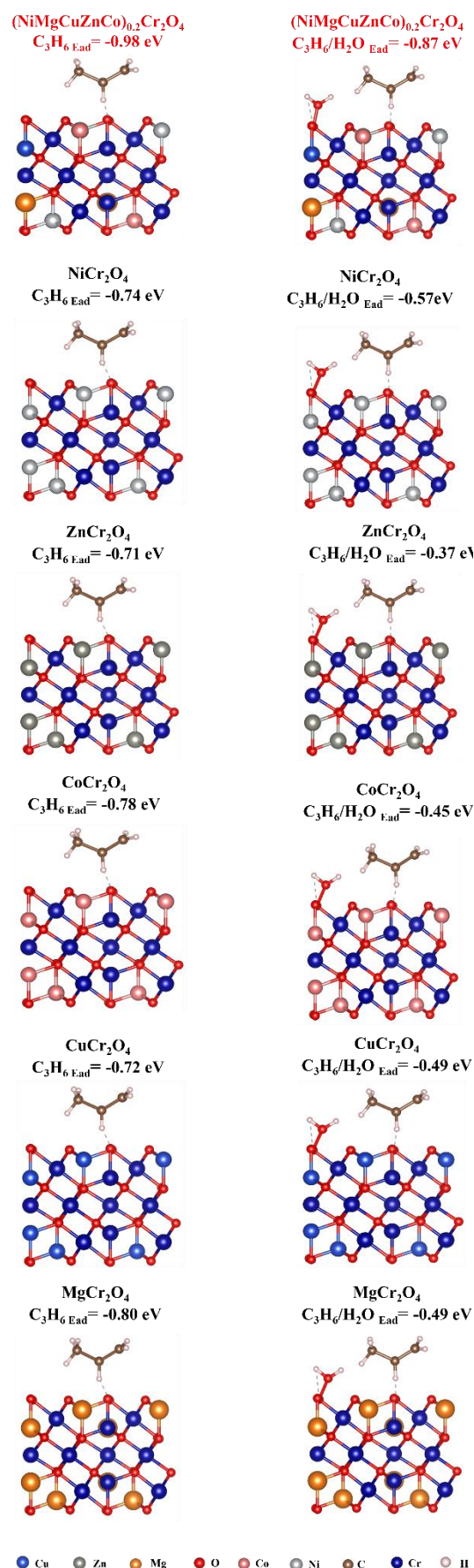


Figure S52. The adsorption energy of C_3H_6 on the surface (111 crystal plane) of high entropy $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ and single metal ACr_2O_4 (A=Ni, Mg, Cu, Zn, Co) in the absence and presence of 4.2vol% water vapor.

Original:

1.2 The dissociation energy of molecular H₂O on the surface of ACr₂O₄ by DFT calculation

The dissociation energy of molecular H₂O on the surface of high entropy (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ and single metal ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co) at crystal plane (220) and (311) were calculated by DFT, respectively (Figure 2 and Table S2). The dissociation energy of molecular H₂O on the surface of high entropy (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ were 2.834eV (crystal plane 311) and 2.752eV (crystal plane 220). In contrast, the dissociation energy of molecular H₂O on the surface of single metal ACr₂O₄ at crystal plane (311) were 2.148eV~ 2.691eV. The dissociation energy of molecular H₂O on the surface of single metal ACr₂O₄ at the crystal plane (220) were 2.379eV~ 2.731eV.

Revised:

1.2 The dissociation energy of molecular H₂O on the surface of ACr₂O₄ by DFT calculation

The dissociation energy of molecular H₂O on the surface of high entropy (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ and single metal ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co) at crystal plane (220), (311) and (111) were calculated by DFT, respectively (Figure 2 and Table S2 and Figure S15). The dissociation energy of molecular H₂O on the surface of high entropy (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ were 2.83eV (crystal plane 311), 2.75eV (crystal plane 220) and 2.97eV (crystal plane 111). In contrast, the dissociation energy of molecular H₂O on the surface of single metal ACr₂O₄ at crystal plane (311) were 2.15eV~ 2.69eV. The dissociation energy of molecular H₂O on the surface of single metal ACr₂O₄ at the crystal plane (220) were 2.38eV~ 2.73eV. The dissociation energy of molecular H₂O on the surface of single metal ACr₂O₄ at the crystal plane (111) were 2.62eV~ 2.90eV. Those results showed that molecular H₂O was easy to dissociate into H⁺ and OH⁻ on the surface of single metal ACr₂O₄ compared with (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄, then OH⁻ could react with single metal ACr₂O₄ to form hydroxide. Thus, the structure of single metal ACr₂O₄ was destroyed and the catalytic activity decreased in the C₃H₆ oxidation. This DFT calculation suggested the better hydrothermal stability of high entropy oxide catalysts, which may be induced by their lower Gibbs free energy ($\Delta G = \Delta H - T\Delta S$).

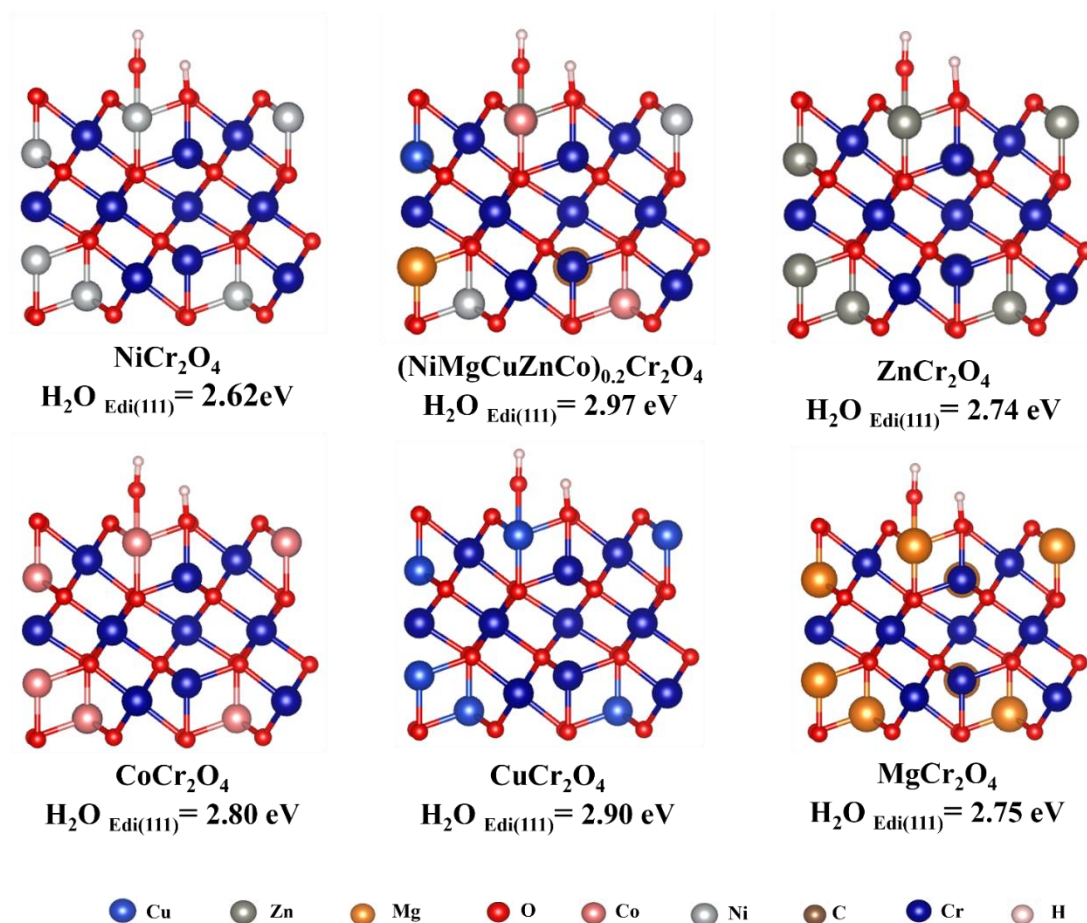


Figure S15. The dissociation energy of molecular H_2O on the surface of high entropy $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, and single metal ACr_2O_4 ($\text{A}=\text{Ni}, \text{Mg}, \text{Cu}, \text{Zn}, \text{Co}$) at crystal plane (111).

Original:

1.3 The formation energy of oxygen vacancy in oxides by DFT calculation

The oxygen vacancy of oxide catalysts were considered decisive to their catalytic performance.^[29] For example, Ma et al.^[30] found that the activity and selectivity of the ZnCrOx catalyst in the transformation of syngas (CO/H₂) strongly depended on the concentration of oxygen vacancy. Chen et al.^[31] directly identified oxygen vacancy sites participated in the dissociative activation of the water molecule, which was the rate-determining step for the low-temperature WGS reaction. Meanwhile, Wang et al.^[32] found the generation of high concentrations of surface oxygen vacancies in GaZrOx would promote the selective hydrogenation of CO₂ to propane. To evaluate how high entropy structure affected surface oxygen, the formation energy of oxygen vacancy in binary and high entropy oxides were calculated by DFT calculation in **Figure 3**. The formation energy of oxygen vacancy (E_{OV}) was calculated by

$$E_{OV} = E_{slab, OV} - E_{slab} + 1/2E_{O_2} \quad (1)$$

where $E_{slab, OV}$ is the energy of the defective oxide slab surface, E_{slab} is the energy of the perfect slab surface, and E_{O_2} is the energy of the gaseous oxygen molecule. The formation energy of oxygen vacancy in (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ was lower than single metal ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co) in the crystal plane (220) and (311) respectively(**Figure 3 and Table S3**). Generally, the local configuration of multi-metal species with different atomic radius in HEOs would lead to structural distortions, and this feature was expected to promote the oxygen vacancy formation in HEOs.

Revised:

1.3 The formation energy of oxygen vacancy in oxides by DFT calculation

The oxygen vacancy of oxide catalysts were considered decisive to their catalytic performance.^[29] For example, Ma et al.^[30] found that the activity and selectivity of the ZnCrOx catalyst in the transformation of syngas (CO/H₂) strongly depended on the concentration of oxygen vacancy. Chen et al.^[31] directly identified oxygen vacancy sites participated in the dissociative activation of the water molecule, which was the rate-determining step for the low-temperature WGS reaction. Meanwhile, Wang et al.^[32] found the generation of high concentrations of surface oxygen vacancies in GaZrOx would promote the selective hydrogenation of CO₂ to propane. To evaluate how high entropy structure affected surface oxygen, the formation energy of oxygen vacancy in binary and high entropy oxides were calculated by DFT calculation in **Figure 3**. The formation energy of oxygen vacancy (E_{OV}) was calculated by

$$E_{OV} = E_{slab, OV} - E_{slab} + 1/2E_{O_2} \quad (1)$$

where $E_{slab, OV}$ is the energy of the defective oxide slab surface, E_{slab} is the energy of the perfect slab surface, and E_{O_2} is the energy of the gaseous oxygen molecule. The formation energy of oxygen vacancy in (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ was lower than single metal ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co) in the crystal plane (220), (311) and (111) respectively(**Figure 3 , Table S3 and Figure S53**). Generally, the local configuration of multi-metal species with different atomic radius in HEOs would lead to structural distortions, and this feature was expected to promote the oxygen vacancy formation in HEOs.

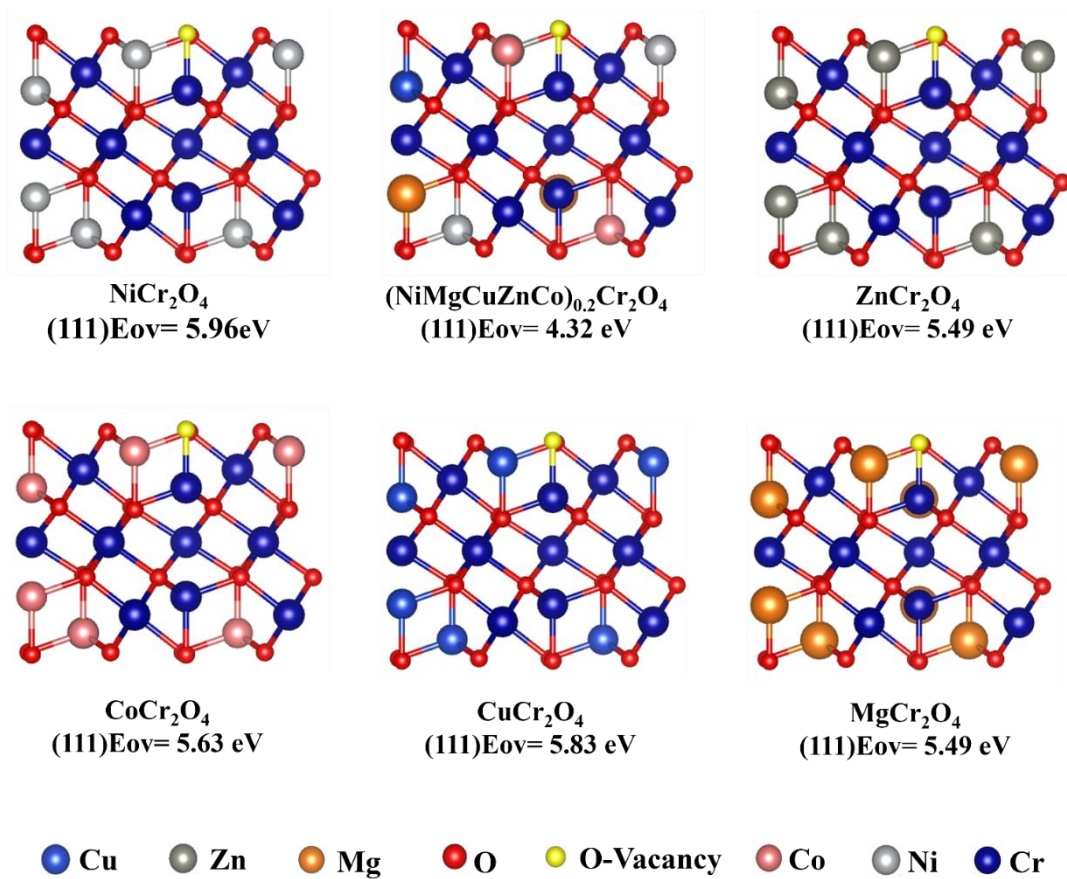


Figure S53. The formation energy of oxygen vacancy (Eov) of high entropy $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, and single metal ACr_2O_4 (A=Ni, Mg, Cu, Zn, Co) at crystal plane (111).

Original:

Table S1 The adsorption energy of C₃H₆ on the surface of ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co) and (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ in the case of no water and 4.2vol% water respectively by DFT calculation

Sample	E _{ad} (311) /eV	E _{ad} (311) (4.2vol% water) /eV	^a Δ _{E_{ad}} (311) /eV	E _{ad} (220) /eV	E _{ad} (220) (4.2vol% water) /eV	^b Δ _{E_{ad}} (220) /eV
NiCr ₂ O ₄	-0.892	-0.615	0.277	-0.855	-0.571	-0.284
MgCr ₂ O ₄	-0.865	-0.593	0.272	-0.802	-0.537	-0.265
CuCr ₂ O ₄	-0.813	-0.527	0.286	-0.769	-0.491	-0.278
ZnCr ₂ O ₄	-0.744	-0.384	0.36	-0.682	-0.349	-0.333
CoCr ₂ O ₄	-0.852	-0.471	0.381	-0.749	-0.352	-0.397
(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	-1.051	-0.963	0.088	-0.974	-0.879	-0.095

a : Δ_{E_{ad}} (311) =E_{ad} (311) -E_{ad} (311) (4.2vol% water)

b : Δ_{E_{ad}} (220) =E_{ad} (220) -E_{ad} (220) (4.2vol% water)

Table S2 The dissociation energy of molecular H₂O on the surface of high entropy (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄, and single metal ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co) at crystal plane (220) and (311).

Sample	OH ⁻¹ E _{ad} (311)/eV	OH ⁻¹ E _{ad} (220) /eV
NiCr ₂ O ₄	2.294	2.412
MgCr ₂ O ₄	2.691	2.731
CuCr ₂ O ₄	2.385	2.582
ZnCr ₂ O ₄	2.148	2.379
CoCr ₂ O ₄	2.336	2.532
(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	2.834	2.752

Table S3 Formation energy of oxygen vacancy (Eov) of high entropy (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄, and single metal ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co) at crystal plane (220) and (311).

Sample	Eov (311)/eV	Eov (220) /eV
NiCr ₂ O ₄	4.916	5.637
MgCr ₂ O ₄	4.517	5.639
CuCr ₂ O ₄	4.695	5.748
ZnCr ₂ O ₄	4.773	5.271
CoCr ₂ O ₄	4.843	5.369
(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	4.166	4.562

Revised:

Table S1 The adsorption energy of C₃H₆ on the surface of ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co) and (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ in the case of no water and 4.2vol% water respectively by DFT calculation

Sample	E _{ad} (311) (4.2vol% water) /eV	E _{ad} (311) (4.2vol% water) /eV	^a Δ _{E_{ad}} (311) /eV	E _{ad} (220) (4.2vol% water) /eV	E _{ad} (220) (4.2vol% water) /eV	^b Δ _{E_{ad}} (220) /eV	E _{ad} (111) (4.2vol% water) /eV	E _{ad} (111) (4.2vol% water) /eV	^c Δ _{E_{ad}} (111) /eV
NiCr ₂ O ₄	-0.89	-0.62	0.28	-0.86	-0.57	-0.28	-0.74	-0.57	-0.17
MgCr ₂ O ₄	-0.87	-0.59	0.27	-0.80	-0.54	-0.27	-0.80	-0.49	-0.31
CuCr ₂ O ₄	-0.81	-0.53	0.29	-0.77	-0.49	-0.29	-0.72	-0.49	-0.23
ZnCr ₂ O ₄	-0.74	-0.38	0.36	-0.68	-0.35	-0.33	-0.71	-0.37	-0.34
CoCr ₂ O ₄	-0.85	-0.47	0.38	-0.75	-0.35	-0.40	-0.78	-0.45	-0.33
(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	-1.05	-0.96	0.09	-0.97	-0.88	-0.10	-0.98	-0.87	-0.11

a : Δ_{E_{ad}} (311) =E_{ad} (311) -E_{ad} (311) (4.2vol% water)

b : Δ_{E_{ad}} (220) =E_{ad} (220) -E_{ad} (220) (4.2vol% water)

c : Δ_{E_{ad}} (111) =E_{ad} (111) -E_{ad} (111) (4.2vol% water)

Table S2 The dissociation energy of molecular H₂O on the surface of high entropy (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄, and single metal ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co) at crystal plane (220) , (311) and (111).

Sample	H ₂ O E _{di} (311)/eV	H ₂ O E _{di} (220)/eV	H ₂ O E _{di} (111)/eV
NiCr ₂ O ₄	2.29	2.41	2.62
MgCr ₂ O ₄	2.69	2.73	2.75
CuCr ₂ O ₄	2.39	2.58	2.90
ZnCr ₂ O ₄	2.15	2.38	2.74
CoCr ₂ O ₄	2.34	2.53	2.80
(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	2.83	2.75	2.97

Table S3 Formation energy of oxygen vacancy (Eov) of high entropy (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄, and single metal ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co) at crystal plane (220) , (311) and (111).

Sample	Eov (311)/eV	Eov (220) /eV	Eov (111) /eV
NiCr ₂ O ₄	4.92	5.64	5.96
MgCr ₂ O ₄	4.52	5.64	5.59
CuCr ₂ O ₄	4.70	5.75	5.83
ZnCr ₂ O ₄	4.77	5.27	5.49
CoCr ₂ O ₄	4.84	5.37	5.63
(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	4.17	4.56	4.32

3. It is unclear which sites were used to model the oxygen vacancy in the high-entropy oxide, zinc, and cobalt structures. It would be helpful if they were highlighted with the yellow atom (O-vacancy) as was done for the other structures in figure 3.

Reply:

Thanks for the careful comment! We have rotated the images in Figure 3 to make the oxygen vacancy clearly visible. In addition, the oxygen vacancy in the high-entropy oxide, zinc, and cobalt structures were highlighted with the yellow atom (O-vacancy) in Figure 3.

Original:

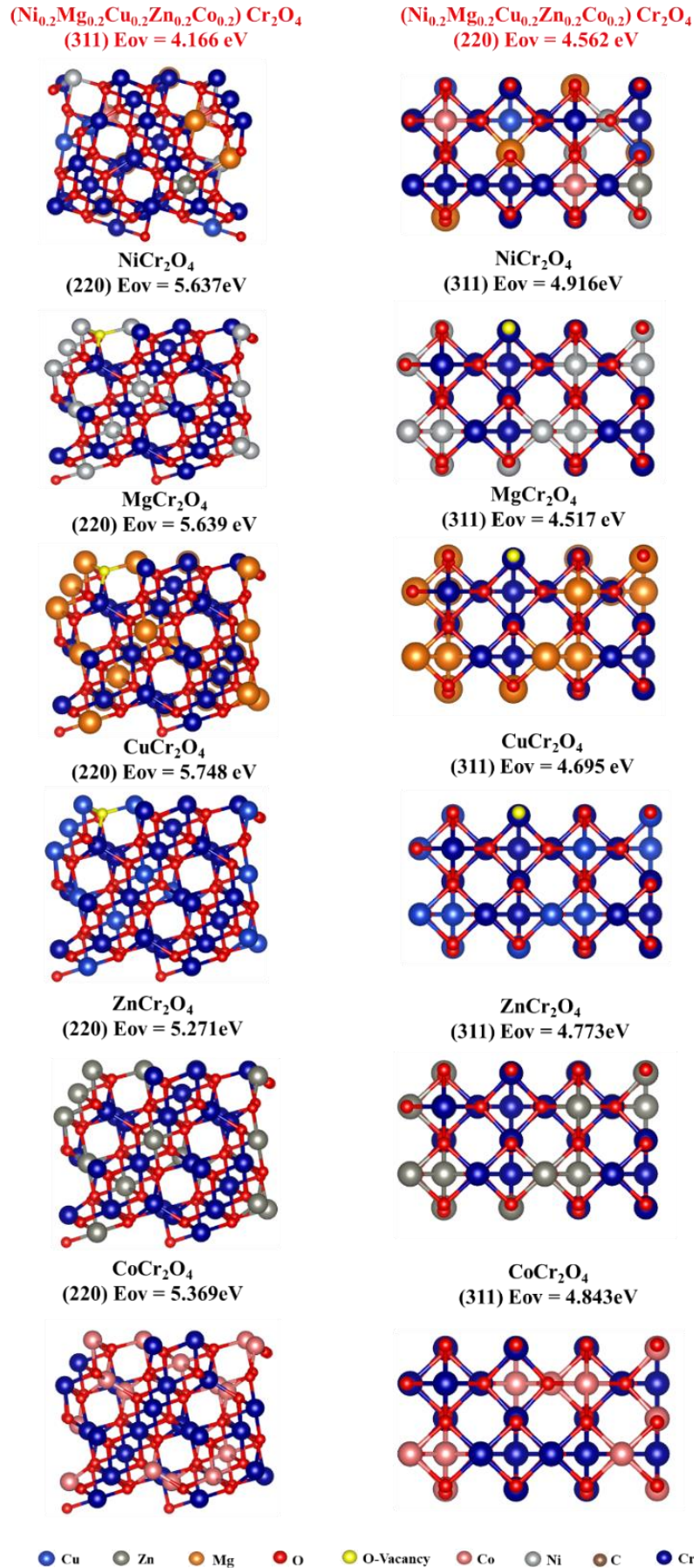


Figure 3. The formation energy of oxygen vacancy (Eov) of high entropy $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, and single metal ACr_2O_4 (A=Ni, Mg, Cu, Zn, Co) at crystal plane (220) and (311) respectively.

Revised:

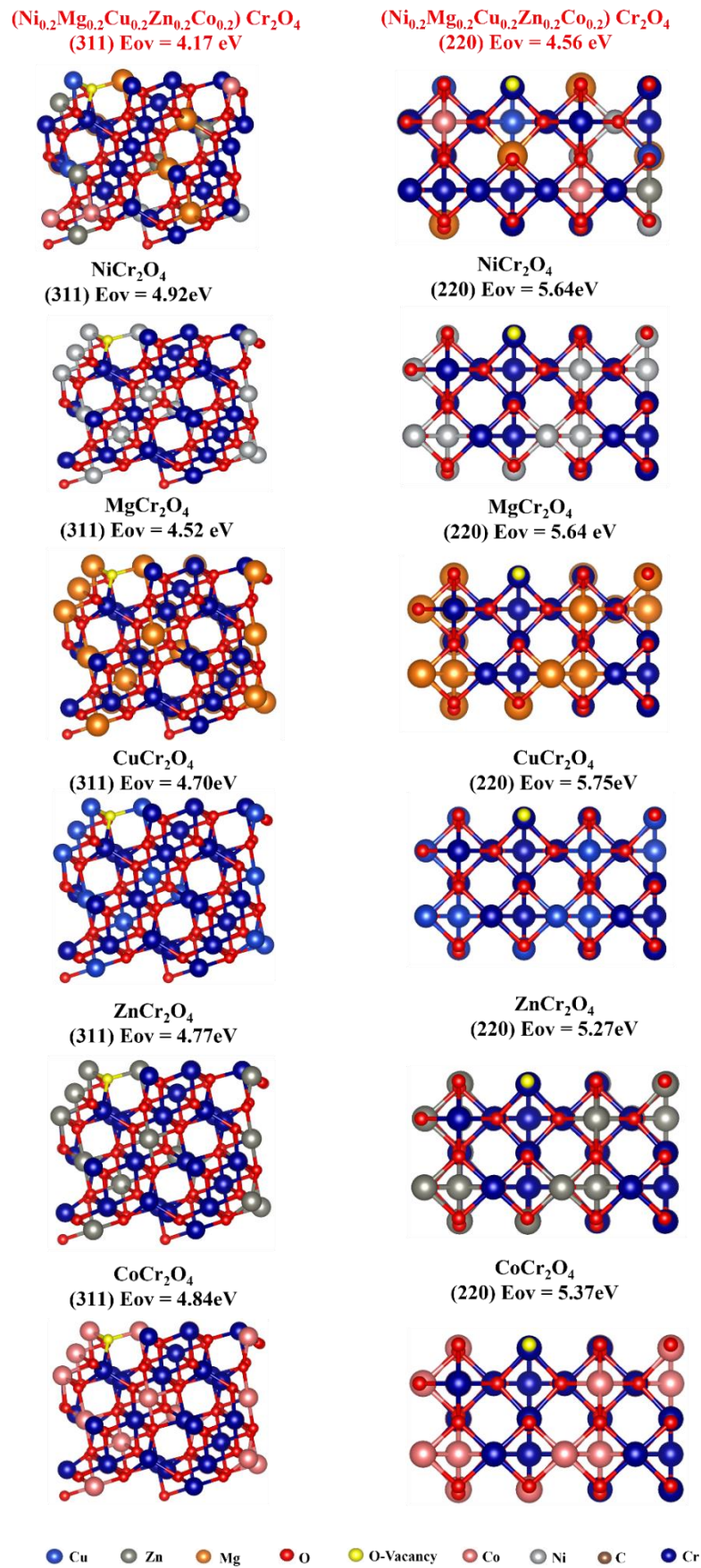


Figure 3. The formation energy of oxygen vacancy (Eov) of high entropy $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, and single metal ACr_2O_4 (A=Ni, Mg, Cu, Zn, Co) at crystal plane (220) and (311) respectively.

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

While extensive in replying, some critical comments, for example about balance (2) or literature (12) were not really addressed, which can also be extended to some other - it's not about volume, but rather required correction content.

Reviewer #2 (Remarks to the Author):

The authors constructively addressed comments from three detailed reviews, adding control experiments and additional explanation to bolster their manuscript. The revised manuscript is appropriate for publication.

Reviewer #3 (Remarks to the Author):

The authors have addressed my concerns. I recommend publishing the manuscript.

Response to the reviewers' comments

Dear Reviewers,

We are very grateful for your professional review work on our article. These comments are valuable and very helpful in revising and improving our paper. According to your nice suggestions, we have made extensive corrections to our previous manuscript, a point-by-point response to the reviewers' comments is listed below. In this revised version, all changes to our manuscript are all highlighted in yellow color.

Reviewer: 1

Comments:

While extensive in replying, some critical comments, for example about balance (2) or literature (12) were not really addressed, which can also be extended to some other - it's not about volume, but rather required correction content.

Reply:

Thanks for the constructive suggestion! We are very sorry about literature 12, which is an error in our manuscript writing. We have deleted reference 12 and replaced it with a new relevant reference.

Original:

As another example, palladium-based materials were efficient catalysts for methane combustion, while the H₂O-poisoning issue appeared at <450°C, due to the hydroxylation of the PdO phase.^[12]

Revised: As another example, the NH₃ selective catalytic reduction (NH₃-SCR) catalyst is exposed to temperature of above 650°C, at which the zeolite framework of SCR catalysts would be damaged due to the simultaneous presence of moisture. That is, the SCR catalyst encounters harsh hydrothermal aging environment during use, which would deactivate the catalyst.^[12]

12 Joshi, S.Y., Kumar, A. et al. New insights into the mechanism of NH₃-SCR over Cu- and Fe-zeolite catalyst: apparent negative activation energy at high temperature and catalyst unit design consequences. *Appl. Catal. B* **226**, 565–574(2017).

To answer the reviewer's question about carbon balance, we have added **supporting information 3 file**. In order to calculate carbon balance, it is necessary to measure the precise concentration of CO₂. To observe CO₂ product, the chromatography in this work contained a conversion furnace with a Ni-based catalyst. Low-concentration CO₂ was converted into CH_x, which then entered the FID detector, and finally a signal would appear. But now there are two thorny practical problems that cannot be solved. **First**, to figure out the liner relationship between CO₂ concentration and GC peak area, we conducted the standard curves of four concentration ranges for CO₂, 0.02~0.08% (**Figure S1~S20, Figure S3-1 and Table S1 in supporting information 3**), 0.1~0.2% (**Figure S21~S35, Figure S3-2 and Table S2 in supporting information 3**), 0.5~1.5% (**Figure S36~S59, Figure S3-3 and Table S3 in supporting information 3**) and 2.5~5% (**Figure S60~S77, Figure S3-4 and Table S4 in supporting information 3**). We found that there was a difference in the fitted formula between changed concentration CO₂ standard curve (please refer to the original GC spectrum in Support Information 3 for details). This indicated that the conversion furnace cannot achieve complete conversion of low concentration CO₂ in time.

Table S1 (in Support Information 3) Original data of CO₂ internal standard curve of 0.02%~0.08% range

CO ₂ Concentration (%)	Peak area					Average
0.02	0	0	0	0	0	0
0.04	28.2511	26.1812	28.2508	27.3211	29.9618	27.9932
0.06	37.5088	37.8132	36.2076	38.4856	37.8392	37.5708
0.08	35.2377	34.1741	35.4906	35.9345	36.0265	35.3726

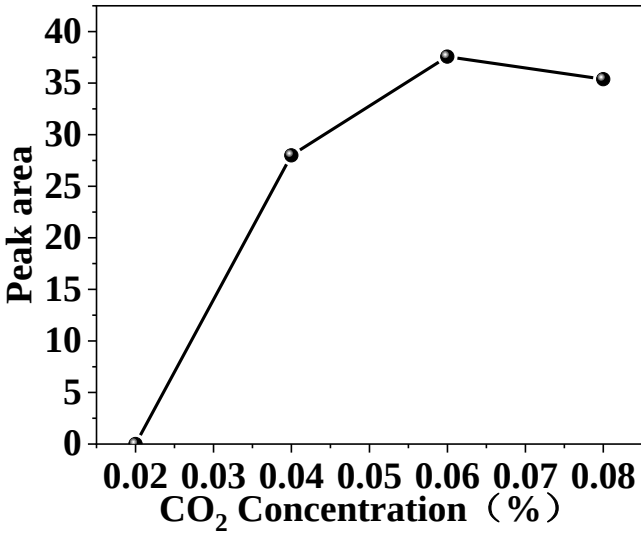


Figure S3-1 (in Support Information 3) CO₂ Standard curve (positive linear relationship between peak area and concentration) of 0.02%~0.08% CO₂.

Table S2 (in Support Information 3) Original data of CO₂ internal standard curve of 0.1%~0.2% range

CO ₂ Concentration (%)	Peak area					Average
0.1	6945.9	6922.8	6952.4	6905.6	6949.6	6935.2
0.15	1906.2	1905.6	1905.7	1899.7	1899.7	1903.3
0.2	2818.8	2856.2	2810.5	2853.5	2854.9	2838.7

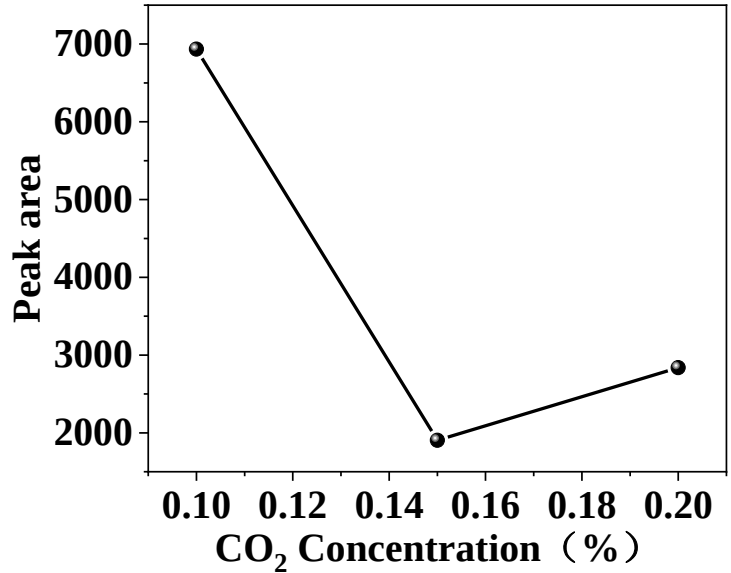


Figure S3-2 (in Support Information 3) CO₂ Standard curve (positive linear relationship between peak area and concentration) of 0.1%~0.2% CO₂.

Table S3 (in Support Information 3) Original data of CO₂ internal standard curve of 0.5%~1.5% range

CO ₂ Concentration (%)	Peak area					Average
0.5%	284.1	284.5	284.2	285.1	284.9	284.4
1.17%	3465.7	3465.4	3465.8	3466.5	3465.5	3465.6
1.5%	5347.5	5344.5	5344.3	5342.7	5351.9	5352.6

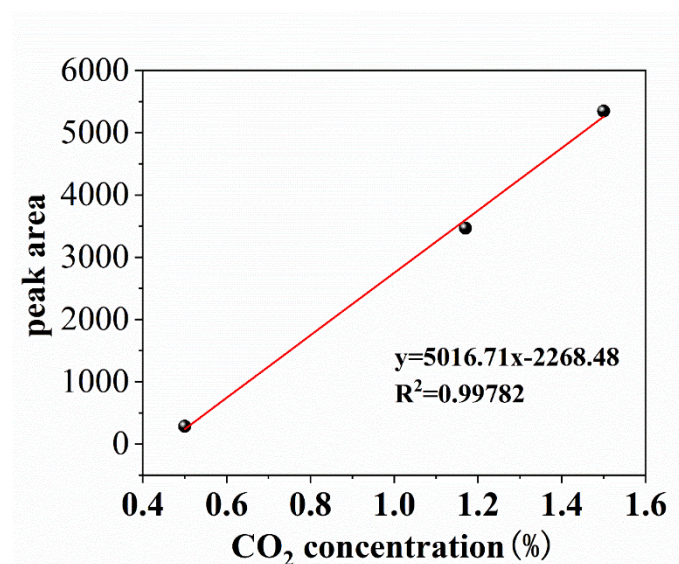


Figure S3-3 (in Support Information 3) CO₂ Standard curve (positive linear relationship between peak area and concentration) of 0.5%~1.5% CO₂.

Table S4 (in Support Information 3) Original data of CO₂ internal standard curve of 2.5%~5% range.

CO ₂ Concentration (%)		Peak area				Average
2.5%	10237	10542	10108	10266	10423	9778
3.5%	14304	13973	14255	14577	14304	14420
5%	21144	19813	19548	21522	21169	19485

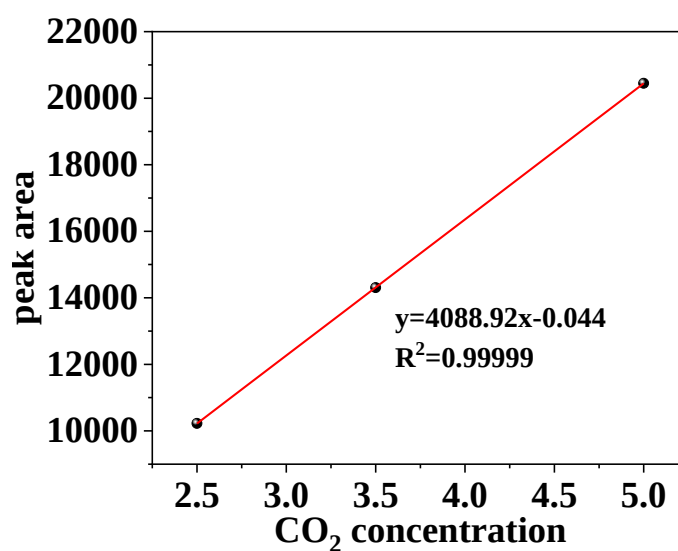


Figure S3-4 (in Support Information 3) CO₂ Standard curve (positive linear relationship between peak area and concentration) of 2.5%~5% CO₂.

Second, 1% of CO₂ in N₂ was passed through reaction furnaces without catalysts at 30 °C, 100 °C, 200 °C, and 300 °C, and we found that different reactor temperatures had a significant impact on the area of CO₂ (**Figure S110~S129, Figure S3-5 and Table S5 in supporting information 3**). This is because the efficiency of real-time conversion of carbon dioxide to CH_x varies at different temperatures in the conversion furnace; High temperature facilitates the conversion of low concentration carbon dioxide. So, the precise concentration of CO₂ cannot be accurately detected.

Table S5 (in Support Information 3) Original data of CO₂ peak area at different temperatures(10 mL/min , Feed gas ratio: 1vol % CO₂ and 99vol% N₂).

Temperature (°C)		Peak area				Average
30	38.6	39.0	37.3	39.4	38.4	34.5
100	67.5	68.3	68.8	65.8	70.2	68.12
200	107.0	100.0	96.9	95.3	91.5	98.14
300	351.8	296.2	341.4	293.4	309.9	318.54

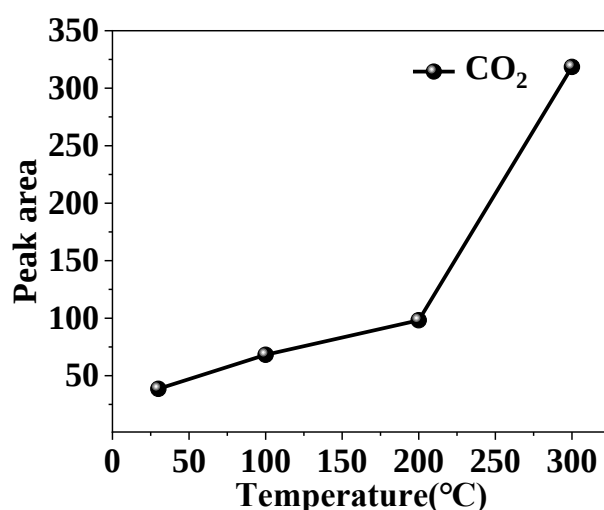


Figure S3-5 (in Support Information 3) CO₂ of peak area with temperature (10 mL/min , Feed gas ratio: 1vol % CO₂ and 99vol% N₂).

At the same time, 1% of C₃H₆ in N₂ was subjected to reaction furnaces at 30 °C, 100 °C, 200 °C, and 300 °C, and we found that different temperatures had almost no effect on the area of C₃H₆ (Figure S78~S109, Figure S3-6 and Table S6 in supporting information 3). So, the precise concentration of C₃H₆ can be accurately detected.

Table S6 (in Support Information 3) Original data of C₃H₆ peak area at different temperatures (10 mL/min , Feed gas ratio: 1vol % C₃H₆ and 99vol% air).

Temperature (°C)	Peak area									Average
30	2485	2156	1963	2600	2242	2761	2362	2022		2324
100	2626	2323	2085	2773	2455	2207	2201	2473		2393
200	2448	2273	2571	2313	2509	2206	2207	2355		2360
300	2561	2233	2734	2389	2202	2202	2398	2198		2365

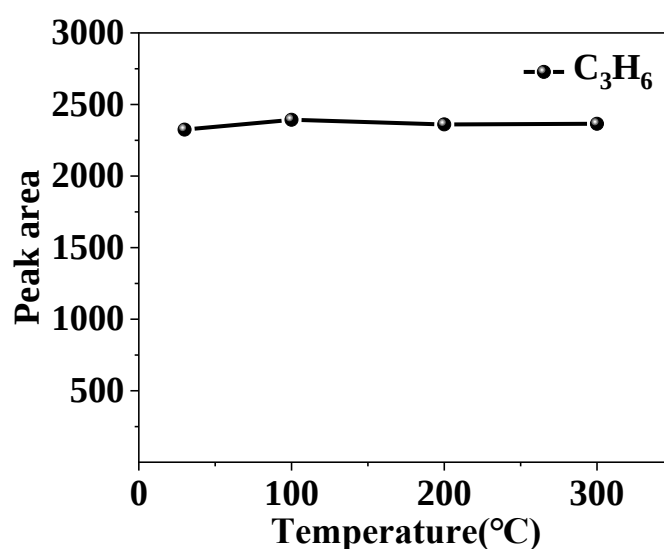


Figure S3-6 (in Support Information 3) C₃H₆ of peak areas with temperature (10 mL/min , Feed gas ratio: 1vol % C₃H₆ and 99vol% air).

Therefore, we concluded that Ni-based conversion furnace cannot transform all CO₂ in time, and FID detectors cannot detect the true concentration of CO₂ generated. In addition, 1% CO₂ and 5% CO₂ were passed through the TCD detector respectively, but the signal of CO₂ cannot be detected, while the TCD detector can only detect N₂ (**Figure S130~S141 in supporting information 3**). This indicated that carbon balance also cannot be calculated using a TCD detector. Due to CO₂ concentration cannot be precisely determined, the calculation of carbon balance seems difficult in current system.

Therefore, in this work, the ratio of the remaining area of C₃H₆ and the initial area was used to calculate the C₃H₆ conversion rate, which was consistent with the calculation methods in many literatures. C₃H₆ is a common type of volatile organic compounds (VOC). Therefore, we have investigated many relevant literatures about how to calculate the VOC conversion rate in the VOC combustion reaction.^[1~6] For example, a denary multi-element oxide catalyst showed high performance and superior stability for catalytic methane combustion over 100 hours (Nature Catalysis, **2021**, 4(1): 62-70.). The measurement of catalytic performance was as follows: Catalytic methane combustion was conducted in a fixed-bed flow reactor at atmospheric pressure. To determine the conversions of the reactants and the formation of products, a gas chromatograph (GC-2010 plus, Shimadzu) was employed, equipped with a silica capillary column (SH-Rt-Q-BOND) and a barrier ionization discharge detector. All of the lines between the reactor outlet and GC sampling loop inlet were heat-traced to 423K to prevent product condensation. Methane conversion was calculated as follows:

$$\text{CH}_4 \text{ conversion} = ([\text{CH}_4]_{\text{in}} - [\text{CH}_4]_{\text{out}}) / [\text{CH}_4]_{\text{in}} \times 100.$$

[CH₄]_{in} and [CH₄]_{out} represent the inlet and outlet amount of CH₄.

For another example, a defective Pt/TiO_{2-x} catalyst was proposed to uncover the different catalytic mechanisms of C₃H₆ combustion (*Environ. Sci. Technol.* **2022**, 56, 5, 3245–3257). The reactant C₃H₆ in the outlet streams was analyzed using an online gas chromatograph (GC 2030). The C₃H₆ was detected using a flame ionization detector (FID) equipped with a FFAP capillary column. The conversion of C₃H₆ was calculated by the following equation:

$$\text{C}_3\text{H}_6 \text{ conversion} = (\text{C}_3\text{H}_6_{\text{in}} - \text{C}_3\text{H}_6_{\text{out}}) / \text{C}_3\text{H}_6_{\text{in}} \times 100\%.$$

[C₃H₆]_{in} and [C₃H₆]_{out} represent the inlet and outlet amount of C₃H₆.

[1] FANG Y, LI H, ZHANG Q, et al. Oxygen Vacancy-Governed Opposite Catalytic

Performance for C₃H₆ and C₃H₈ Combustion: The Effect of the Pt Electronic Structure and Chemisorbed Oxygen Species [J]. Environmental Science & Technology, **2022**, 56(5): 3245-57

[2] FANG Y, LI L, YANG J, et al. Engineering the Nucleophilic Active Oxygen Species in CuTiO_x for Efficient Low-Temperature Propene Combustion [J]. Environmental Science & Technology, **2020**, 54(23): 15476-88.

[3] NIE L, MEI D, XIONG H, et al. Activation of surface lattice oxygen in single-atom Pt/CeO₂ for low-temperature CO oxidation [J]. Nature, **2017**, 358(6369): 1419-23.

[4] LI T, YAO Y, HUANG Z, et al. Denary oxide nanoparticles as highly stable catalysts for methane combustion [J]. Nature Catalysis, **2021**, 4(1): 62-70.

[5] NIE L, MEI D, XIONG H, et al. Activation of surface lattice oxygen in single-atom Pt/CeO₂ for low-temperature CO oxidation [J]. Science, **2017**, 358(6369): 1419-23.

[6] HAO H, JIN B, LIU W, et al. Robust Pt@TiO_x/TiO₂ Catalysts for Hydrocarbon Combustion: Effects of Pt-TiO_x Interaction and Sulfates [J]. ACS Catalysis, **2020**, 10(22): 13543-8.

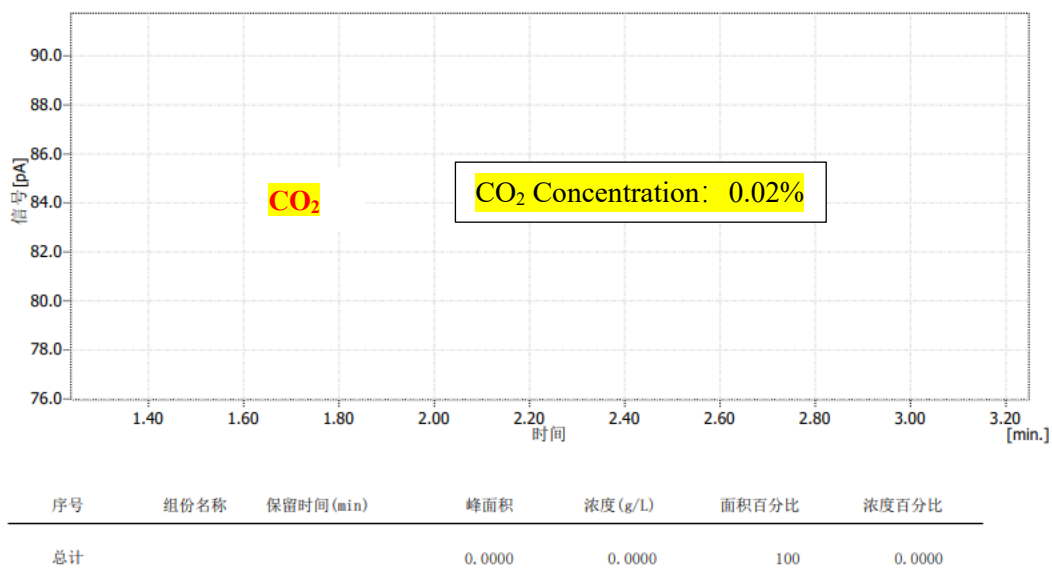


Figure S1 Original GC spectra at 30°C (10 mL/min , 0.02vol % CO₂, 19.9vol% O₂ and 80.08vol% N₂)

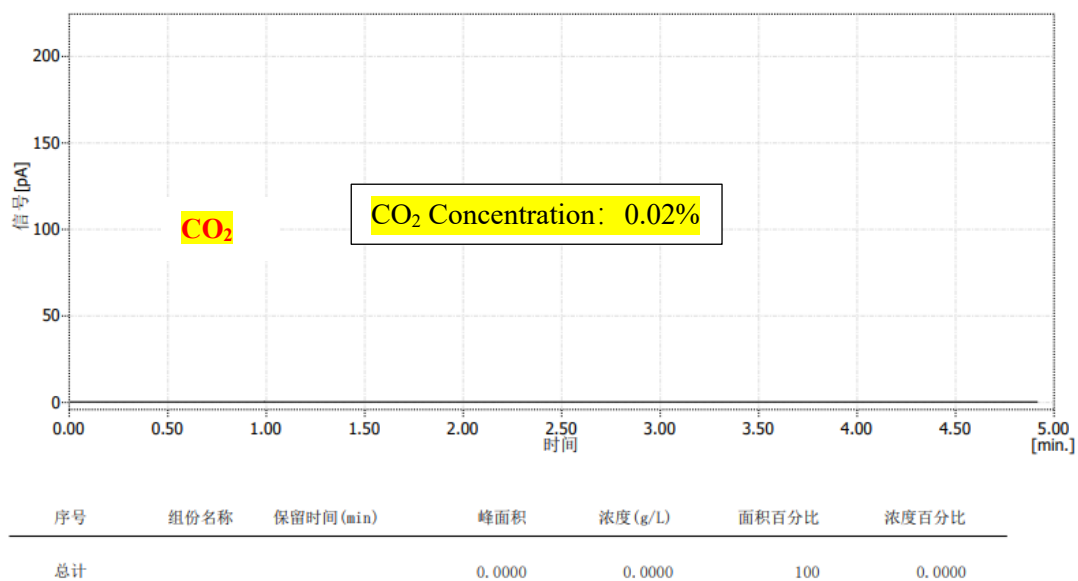


Figure S2 Original GC spectra at 30°C(10 mL/min , 0.02vol % CO₂, 19.9vol% O₂ and 80.08vol% N₂)

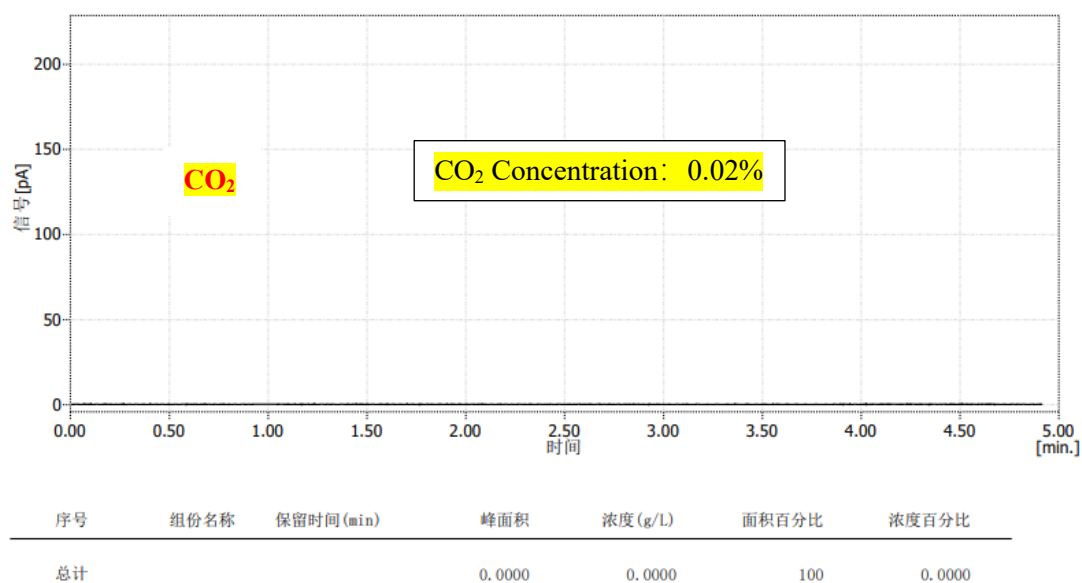


Figure S3 Original GC spectra at 30°C (10 mL/min , 0.02vol % CO₂, 19.9vol% O₂ and 80.08vol% N₂)

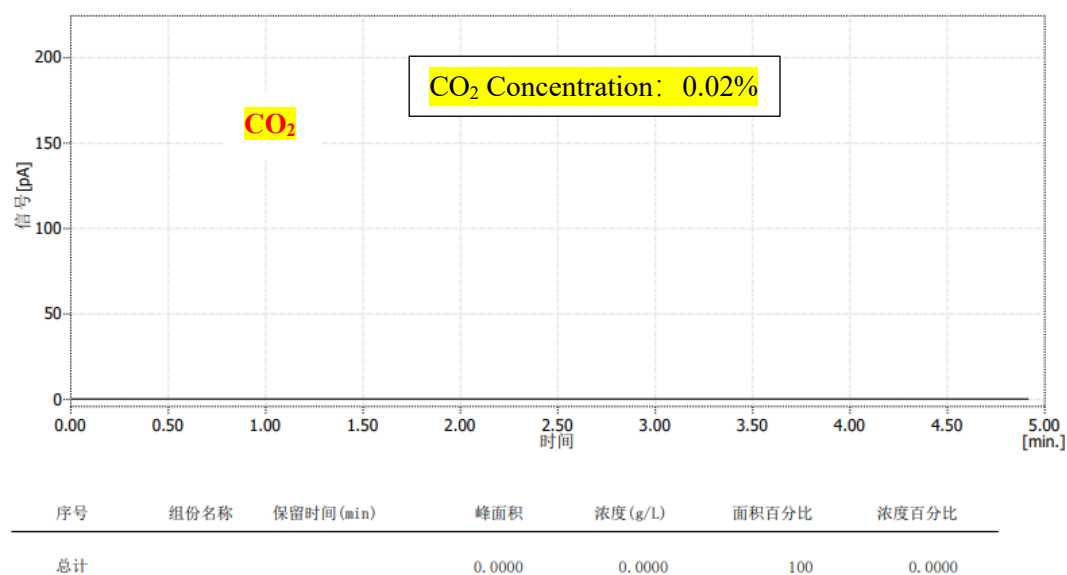


Figure S4 Original GC spectra at 30°C (10 mL/min , 0.02vol % CO₂, 19.9vol% O₂ and 80.08vol% N₂)

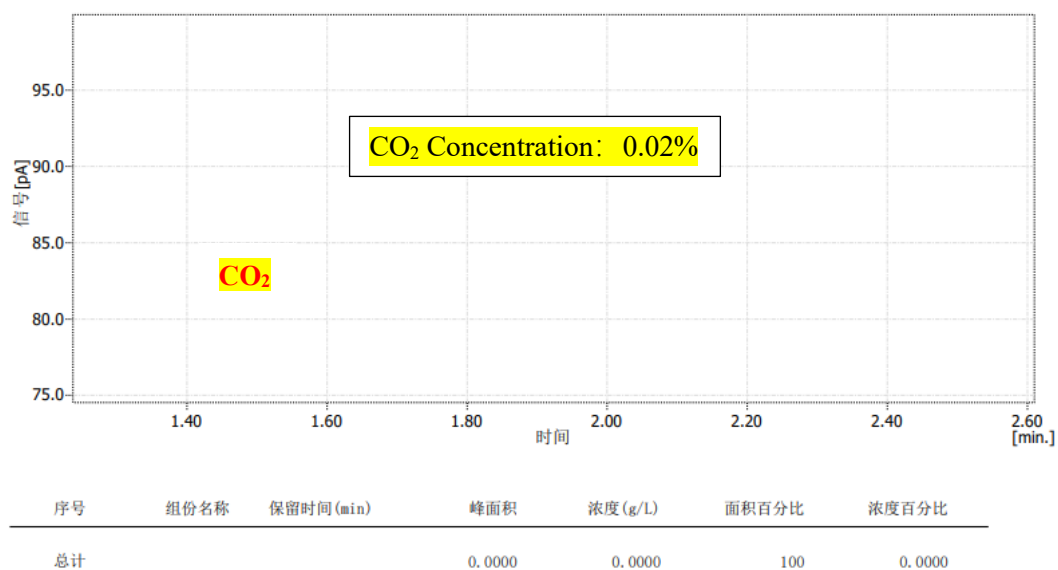


Figure S5 Original GC spectra at 30°C (10 mL/min , 0.02vol % CO₂, 19.9vol% O₂ and 80.08vol% N₂)

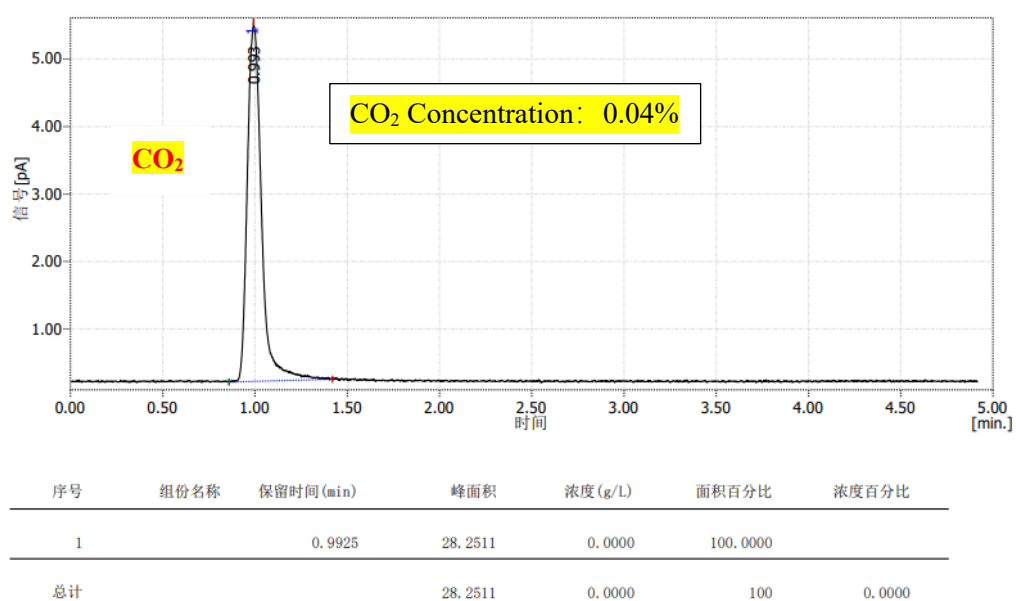
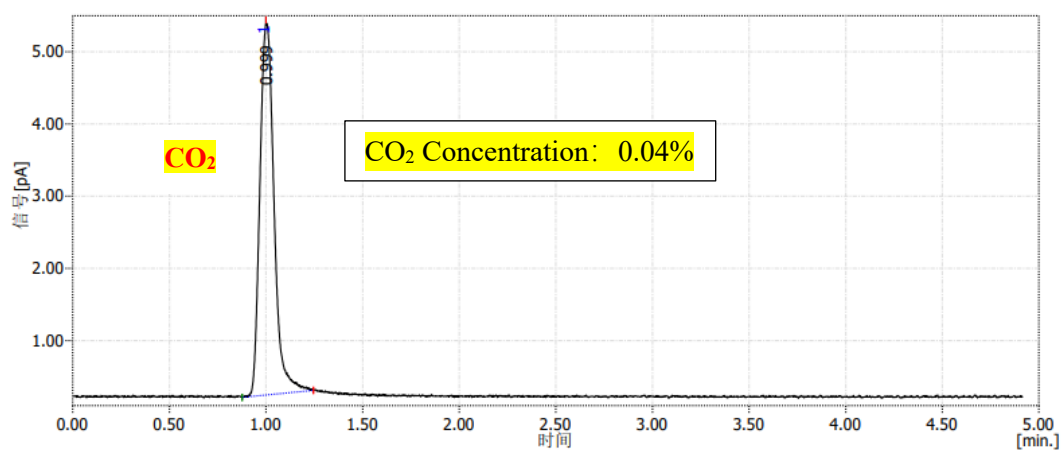
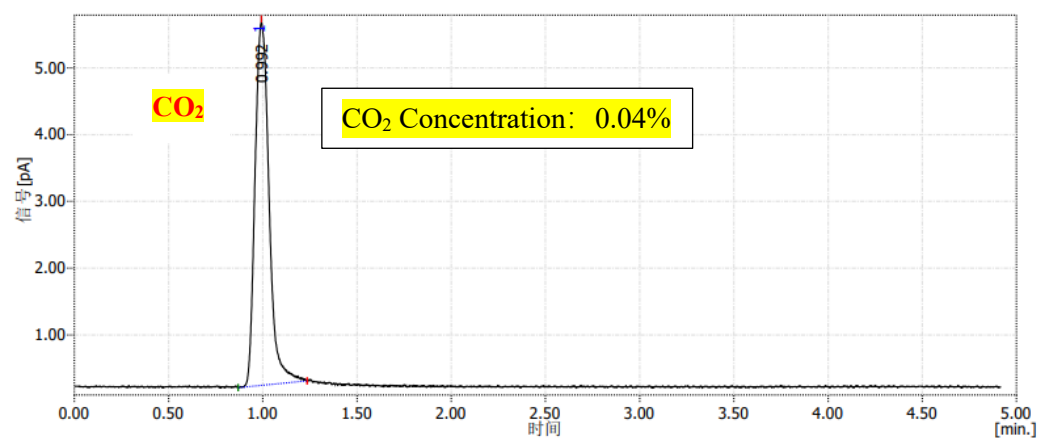


Figure S6 Original GC spectra at 30°C (10 mL/min , 0.04vol % CO₂, 19.9vol% O₂ and 80.06vol% N₂)



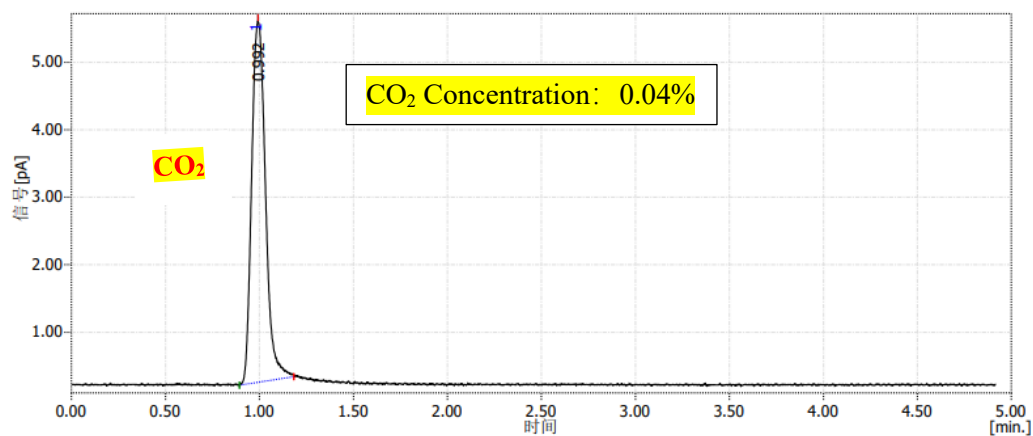
序号	组份名称	保留时间(min)	峰面积	浓度(g/L)	面积百分比	浓度百分比
1		0.9992	26.2812	0.0000	100.0000	
总计			26.2812	0.0000	100	0.0000

Figure S7 Original GC spectra at 30°C(10 mL/min , 0.04vol % CO₂, 19.9vol% O₂ and 80.06vol% N₂)



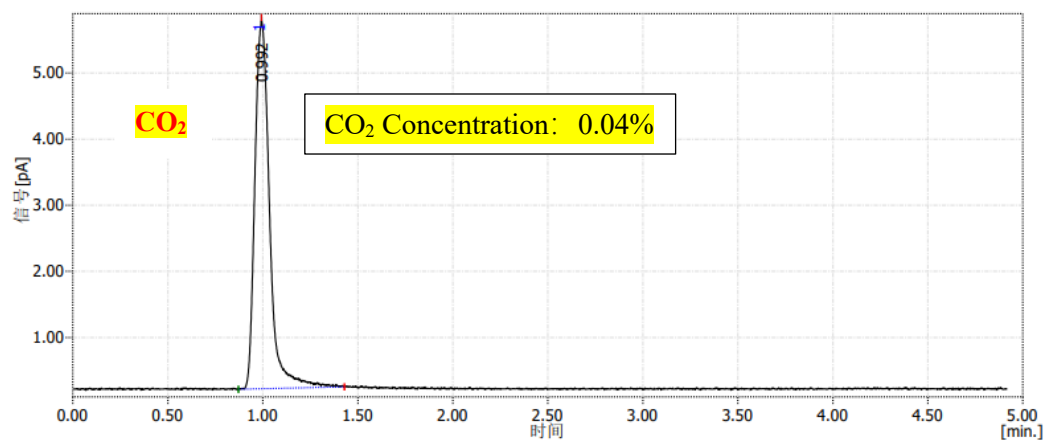
序号	组份名称	保留时间(min)	峰面积	浓度(g/L)	面积百分比	浓度百分比
1		0.9917	28.2508	0.0000	100.0000	
总计			28.2508	0.0000	100	0.0000

Figure S8 Original GC spectra at 30°C(10 mL/min , 0.04vol % CO₂, 19.9vol% O₂ and 80.06vol% N₂)



序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		0.9917	27.3211	0.0000	100.0000	
总计			27.3211	0.0000	100	0.0000

Figure S9 Original GC spectra at 30°C (10 mL/min, 0.04vol % CO₂, 19.9vol% O₂ and 80.06vol% N₂)



序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		0.9917	29.9618	0.0000	100.0000	
总计			29.9618	0.0000	100	0.0000

Figure S10 Original GC spectra at 30°C (10 mL/min, 0.04vol % CO₂, 19.9vol% O₂ and 80.06vol% N₂)

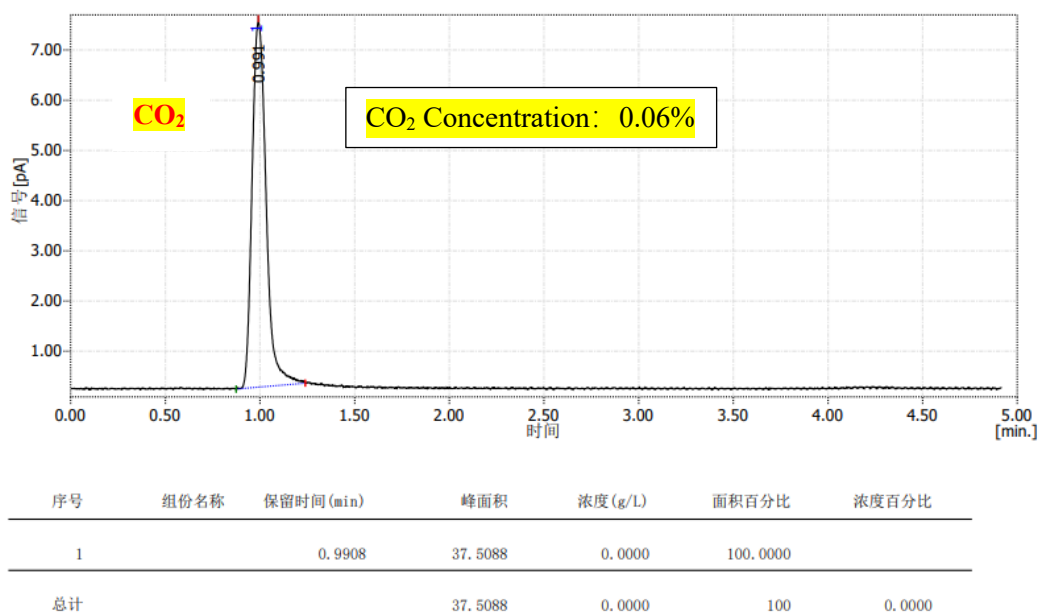


Figure S11 Original GC spectra at 30°C (10 mL/min , 0.06vol % CO₂, 19.9vol% O₂ and 80.04vol% N₂)

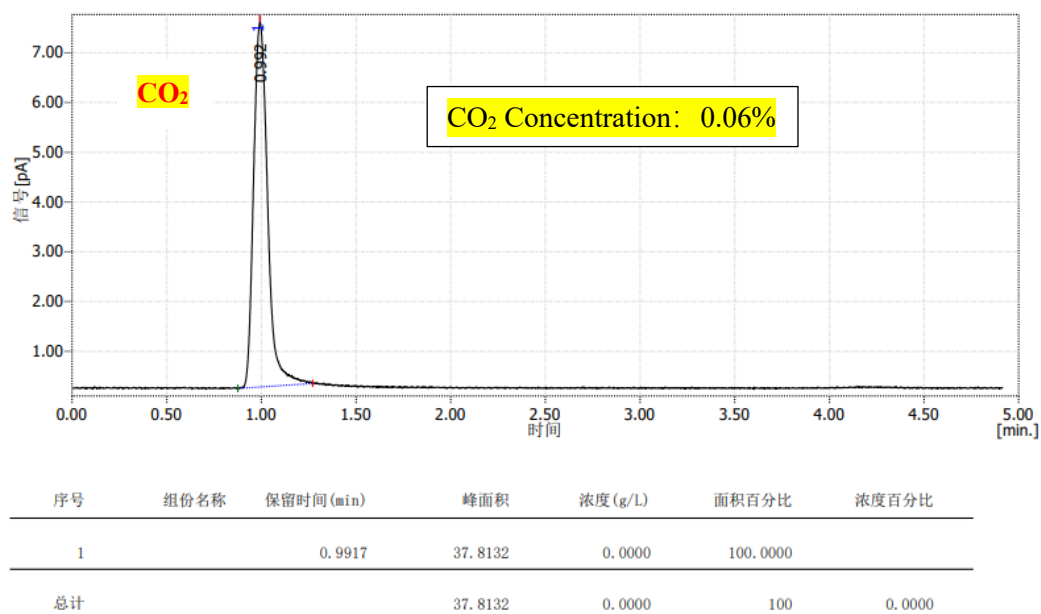
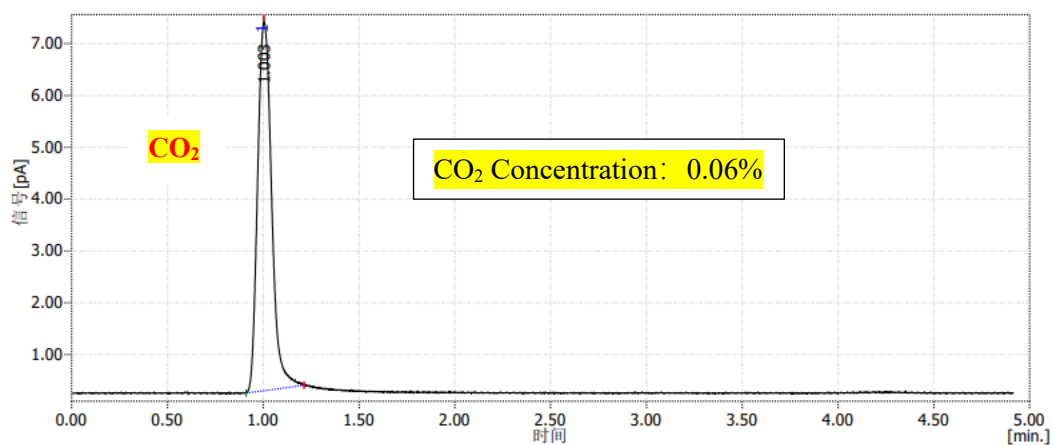
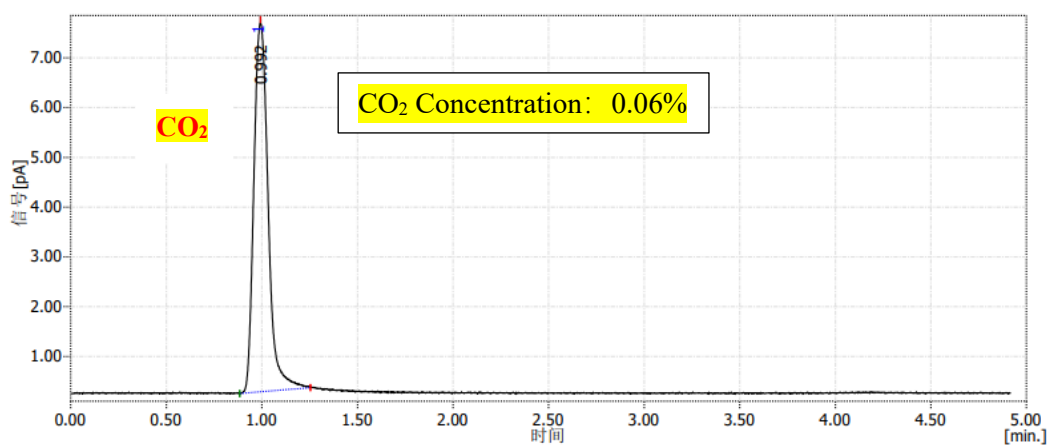


Figure S12 Original GC spectra at 30°C (10 mL/min , 0.06vol % CO₂, 19.9vol% O₂ and 80.04vol% N₂)



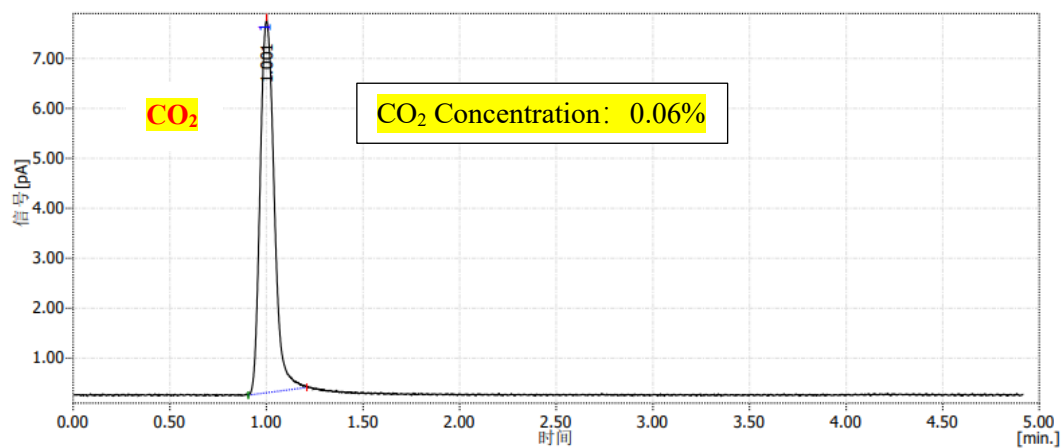
序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		1.0033	36.2076	0.0000	100.0000	
总计			36.2076	0.0000	100	0.0000

Figure S13 Original GC spectra at 30°C (10 mL/min , 0.06vol % CO₂, 19.9vol% O₂ and 80.04vol% N₂)



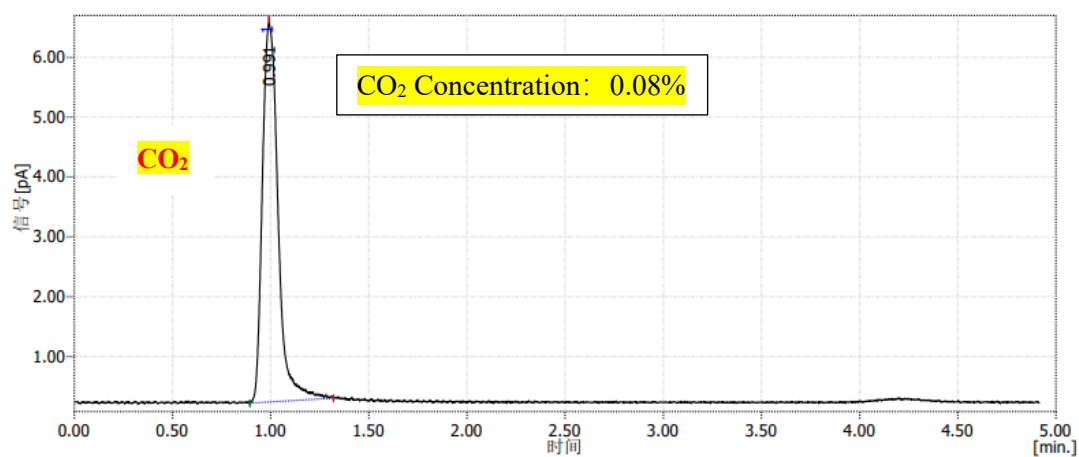
序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		0.9917	38.4856	0.0000	100.0000	
总计			38.4856	0.0000	100	0.0000

Figure S14 Original GC spectra at 30°C (10 mL/min , 0.06vol % CO₂, 19.9vol% O₂ and 80.04vol% N₂)



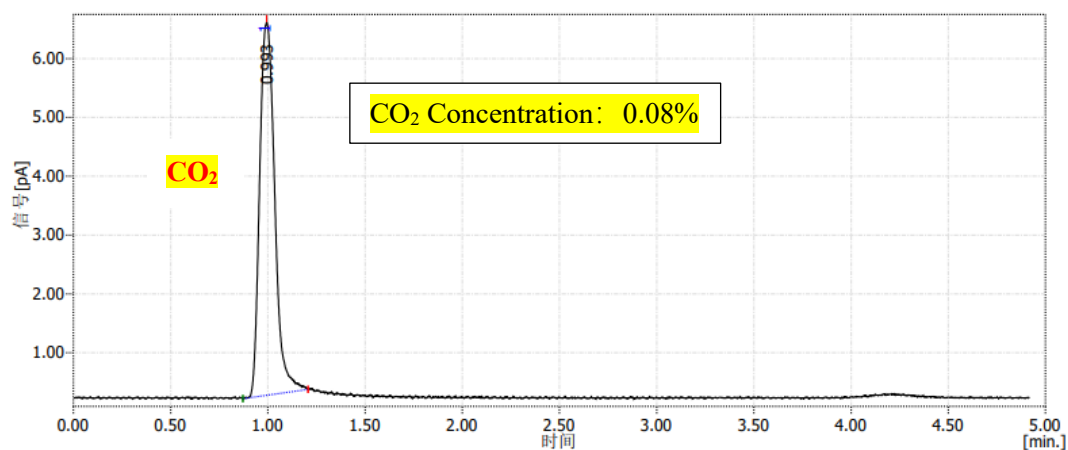
序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		1.0008	37.8392	0.0000	100.0000	
总计			37.8392	0.0000	100	0.0000

Figure S15 Original GC spectra at 30°C (10 mL/min , 0.06vol % CO₂, 19.9vol% O₂ and 80.04vol% N₂)



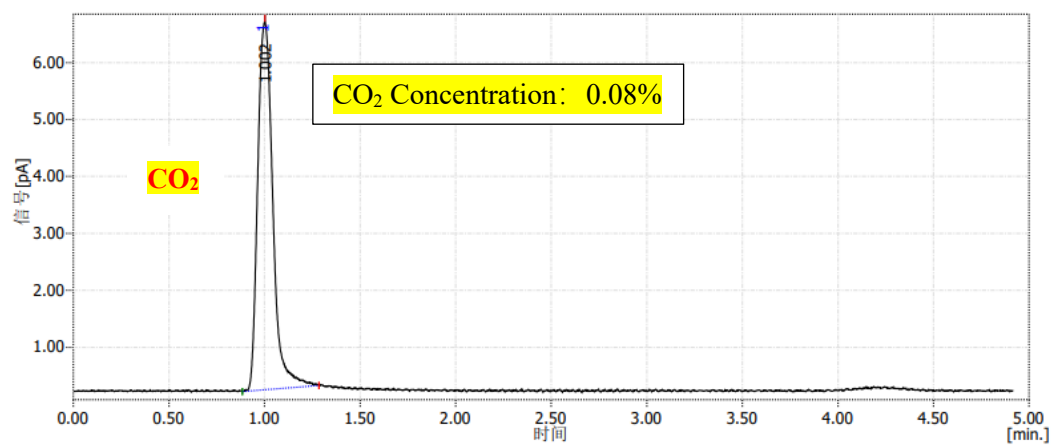
序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		0.9908	35.2377	0.0000	100.0000	
总计			35.2377	0.0000	100	0.0000

Figure S16 Original GC spectra at 30°C (10 mL/min , 0.08vol % CO₂, 19.9vol% O₂ and 80.02vol% N₂)



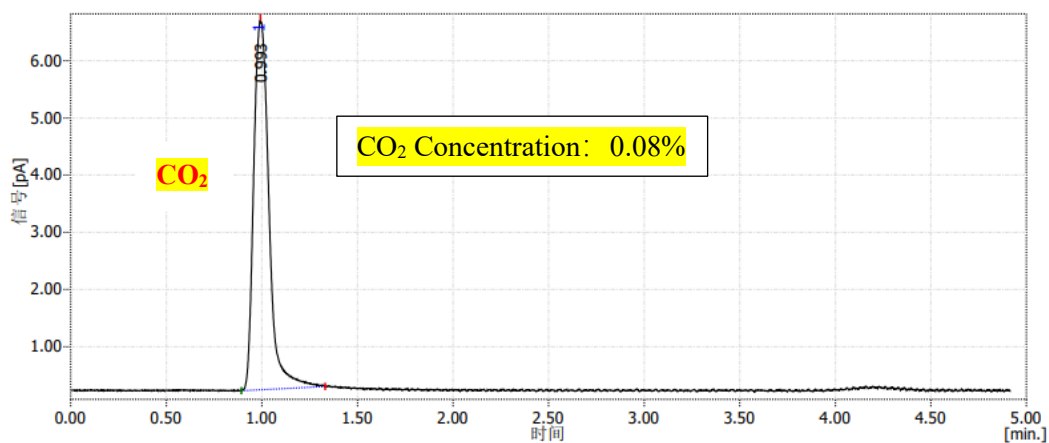
序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		0.9933	34.1741	0.0000	100.0000	
总计			34.1741	0.0000	100	0.0000

Figure S17 Original GC spectra at 30°C(10 mL/min , 0.08vol % CO₂, 19.9vol% O₂ and 80.02vol% N₂)



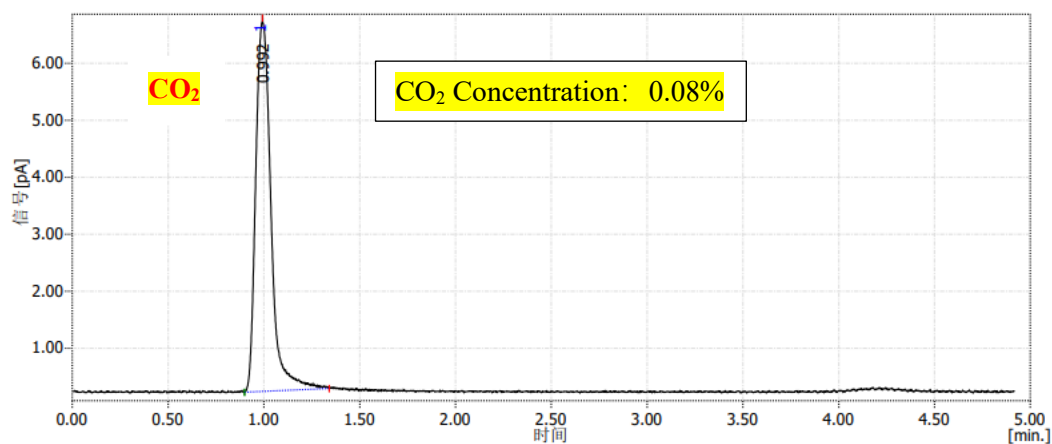
序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		1.0017	35.4906	0.0000	100.0000	
总计			35.4906	0.0000	100	0.0000

Figure S18 Original GC spectra at 30°C(10 mL/min , 0.08vol % CO₂, 19.9vol% O₂ and 80.02vol% N₂)



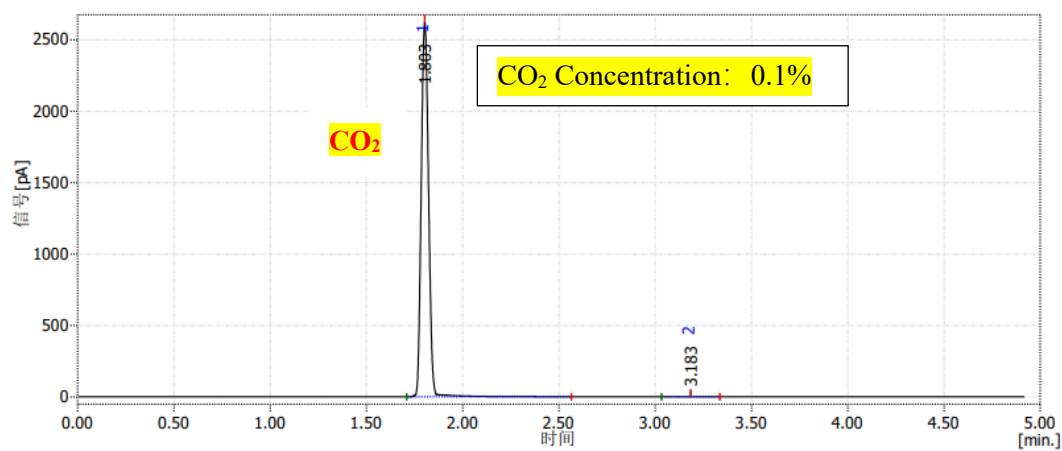
序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		0.9925	35.9354	0.0000	100.0000	
总计			35.9354	0.0000	100	0.0000

Figure S19 Original GC spectra at 30°C(10 mL/min , 0.08vol % CO₂, 19.9vol% O₂ and 80.02vol% N₂)



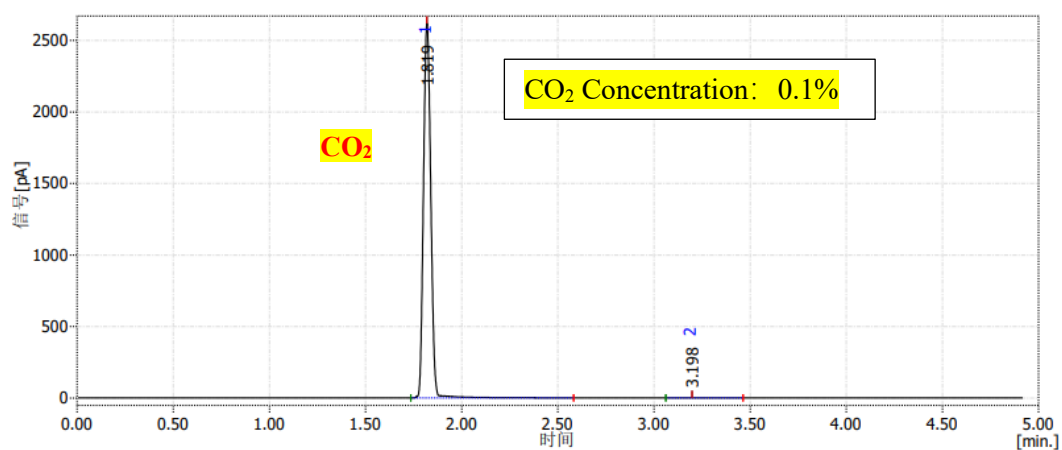
序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		0.9917	36.0265	0.0000	100.0000	
总计			36.0265	0.0000	100	0.0000

Figure S20 Original GC spectra at 30°C(10 mL/min , 0.08vol % CO₂, 19.9vol% O₂ and 80.02vol% N₂)



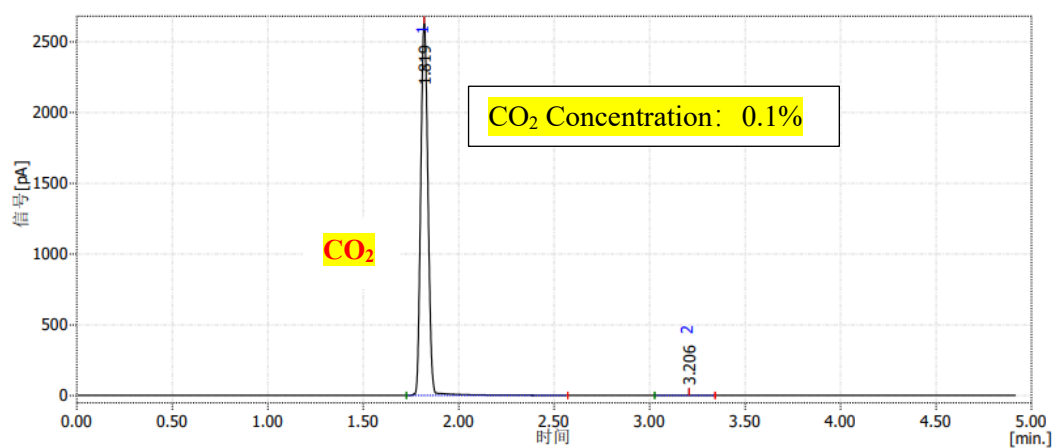
序号	组份名称	保留时间(min)	峰面积	浓度()	面积百分比	浓度百分比
1		1.8026	6945.9350		99.9519	
2		3.1833	3.3403		0.0481	
总计			6949.2750	0.0000	100	0.0000

Figure S21 Original GC spectra at 30°C(10 mL/min , 0.1vol % CO₂, 19.9vol% O₂ and 80.00vol% N₂)



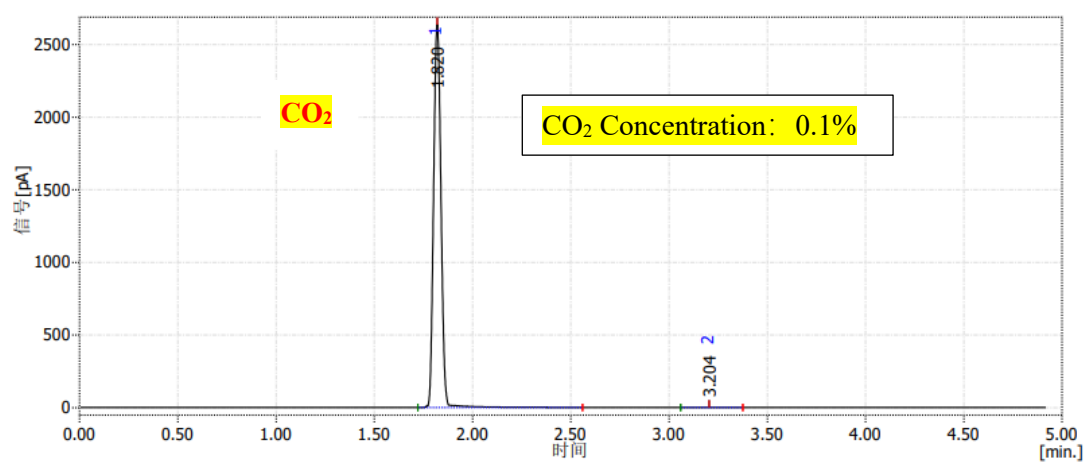
序号	组份名称	保留时间(min)	峰面积	浓度()	面积百分比	浓度百分比
1		1.8192	6922.8940		99.9501	
2		3.1975	3.4579		0.0499	
总计			6926.3520	0.0000	100	0.0000

Figure S22 Original GC spectra at 30°C (10 mL/min , 0.1vol % CO₂, 19.9vol% O₂ and 80.00vol% N₂)



序号	组份名称	保留时间 (min)	峰面积	浓度 ()	面积百分比	浓度百分比
1		1.8192	6952.4200		99.9503	
2		3.2058	3.4570		0.0497	
总计			6955.8770	0.0000	100	0.0000

Figure S23 Original GC spectra at 30°C (10 mL/min , 0.1vol % CO₂, 19.9vol% O₂ and 80.00vol% N₂)



序号	组份名称	保留时间 (min)	峰面积	浓度 ()	面积百分比	浓度百分比
1		1.8201	6905.6050		99.9446	
2		3.2042	3.8304		0.0554	
总计			6909.4360	0.0000	100	0.0000

Figure S24 Original GC spectra at 30°C (10 mL/min , 0.1vol % CO₂, 19.9vol% O₂ and 80.00vol% N₂)

80.00vol% N₂)

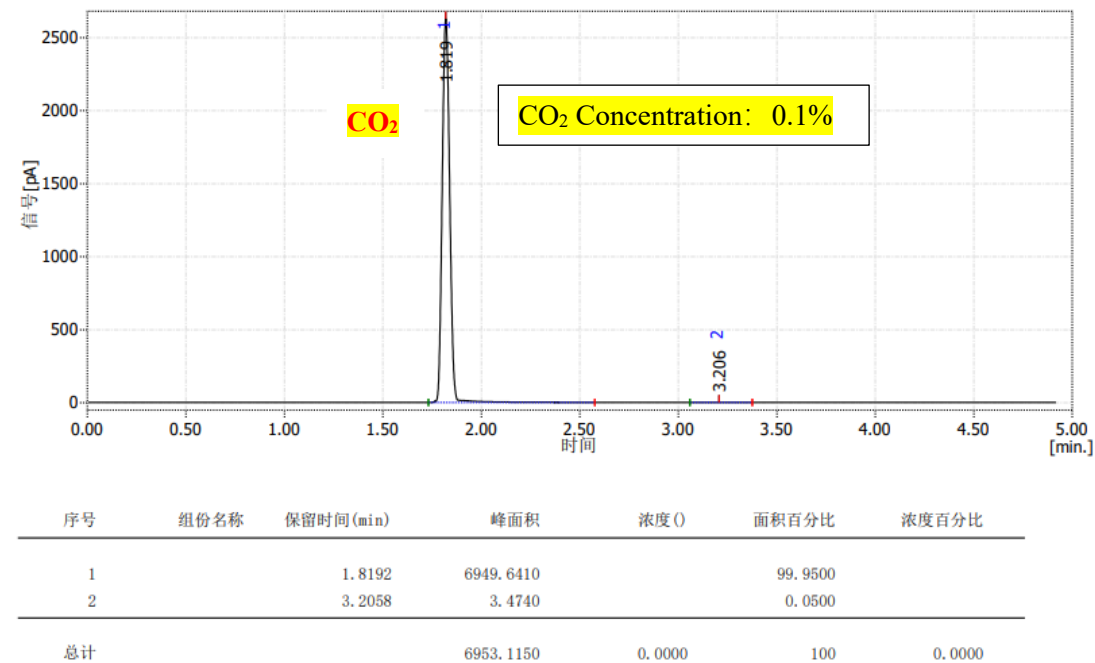


Figure S25 Original GC spectra at 30°C (10 mL/min , 0.1vol % CO₂, 19.9vol% O₂ and 80.00vol% N₂)

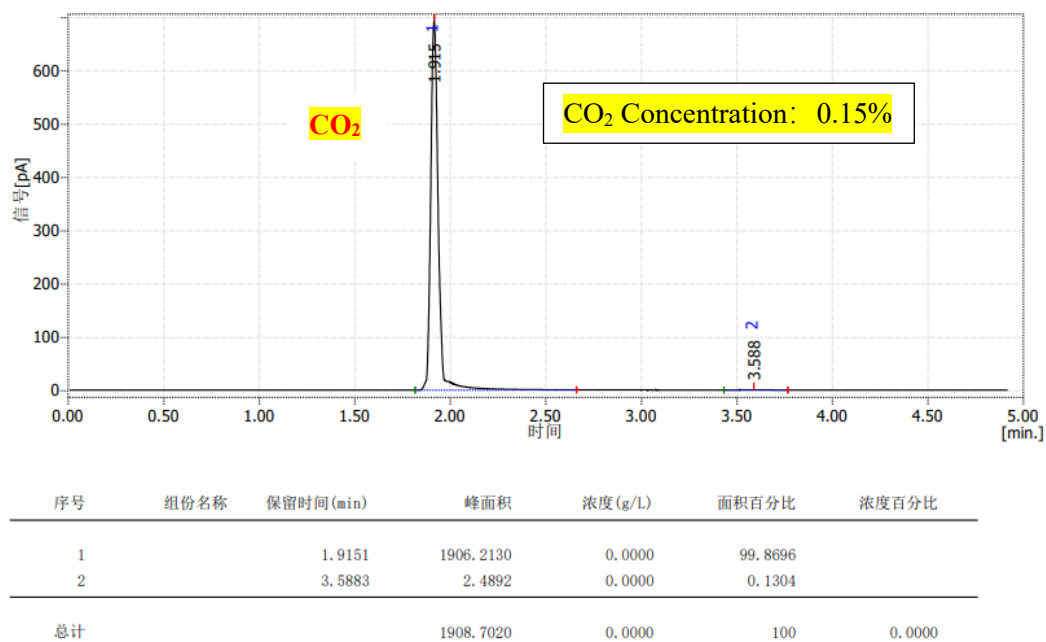


Figure S26 Original GC spectra at 30°C (10 mL/min , 0.15vol % CO₂, 19.9vol% O₂ and

79.95vol% N₂)

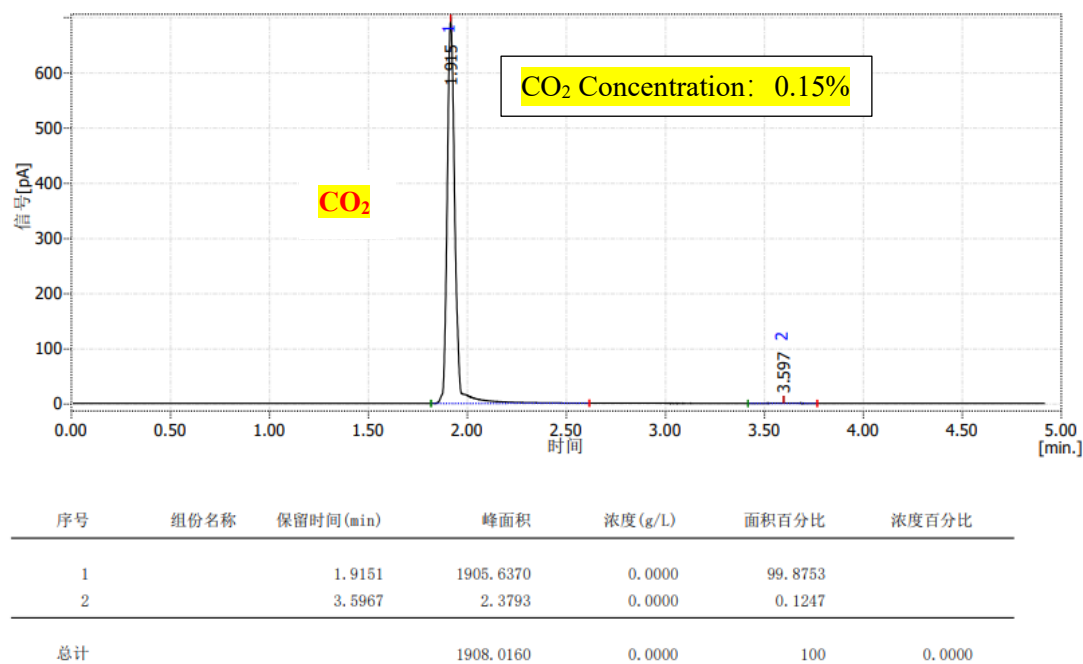


Figure S27 Original GC spectra at 30°C(10 mL/min , 0.15vol % CO₂, 19.9vol% O₂ and 79.95vol% N₂)

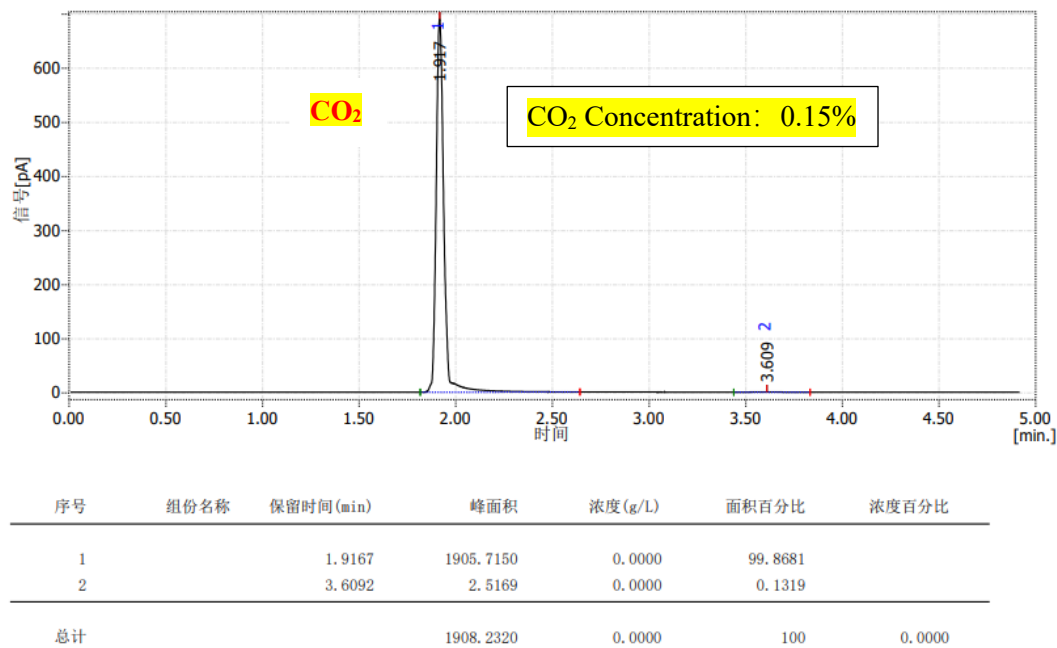
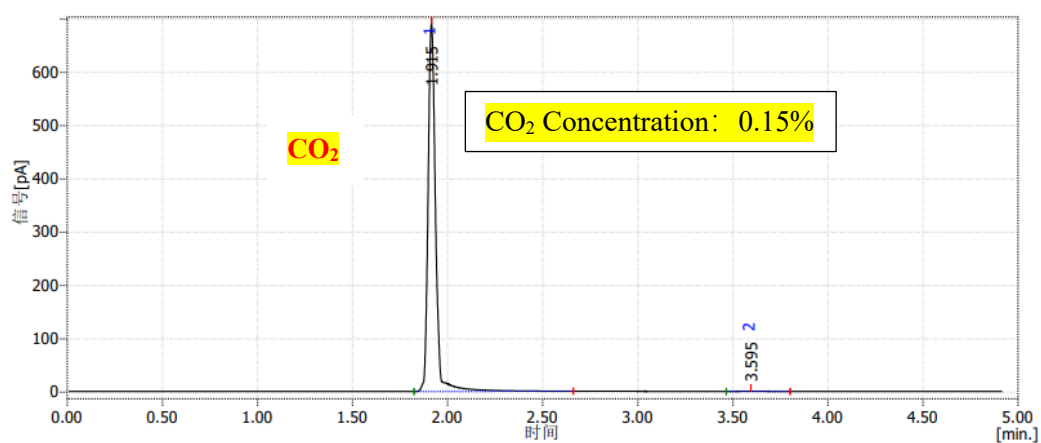
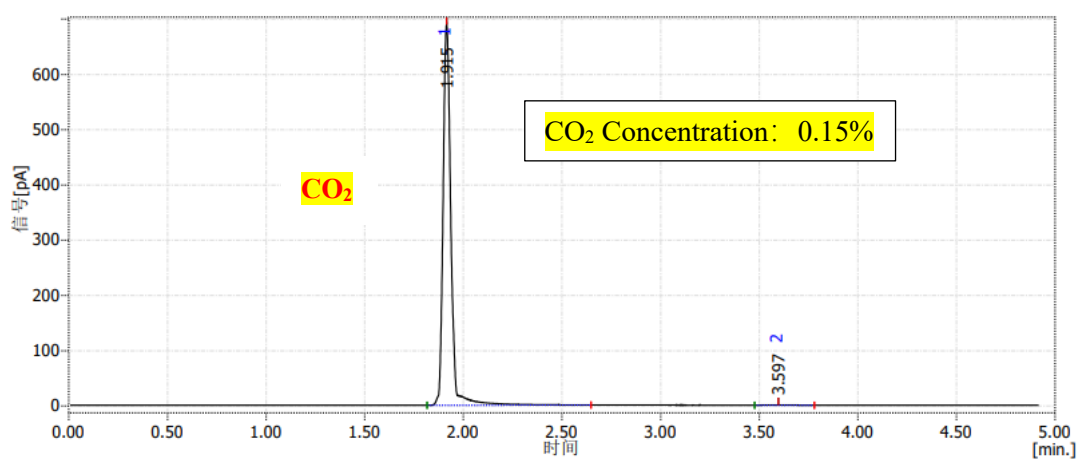


Figure 28 Original GC spectra at 30°C (10 mL/min , 0.15vol % CO₂, 19.9vol% O₂ and 79.95vol% N₂)



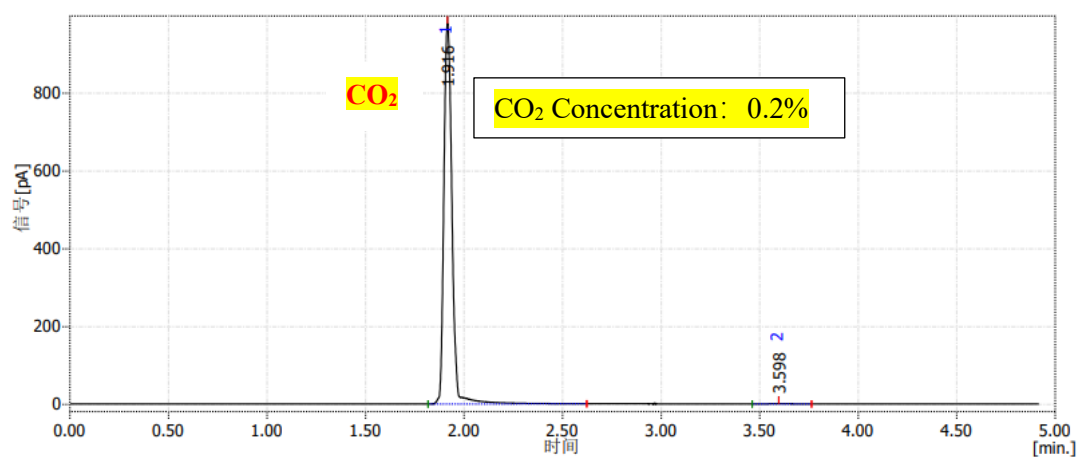
序号	组份名称	保留时间(min)	峰面积	浓度(g/L)	面积百分比	浓度百分比
1		1.9151	1899.7520	0.0000	99.8770	
2		3.5950	2.3402	0.0000	0.1230	
总计			1902.0920	0.0000	100	0.0000

Figure S29 Original GC spectra at 30°C(10 mL/min , 0.15vol % CO₂, 19.9vol% O₂ and 79.95vol% N₂)



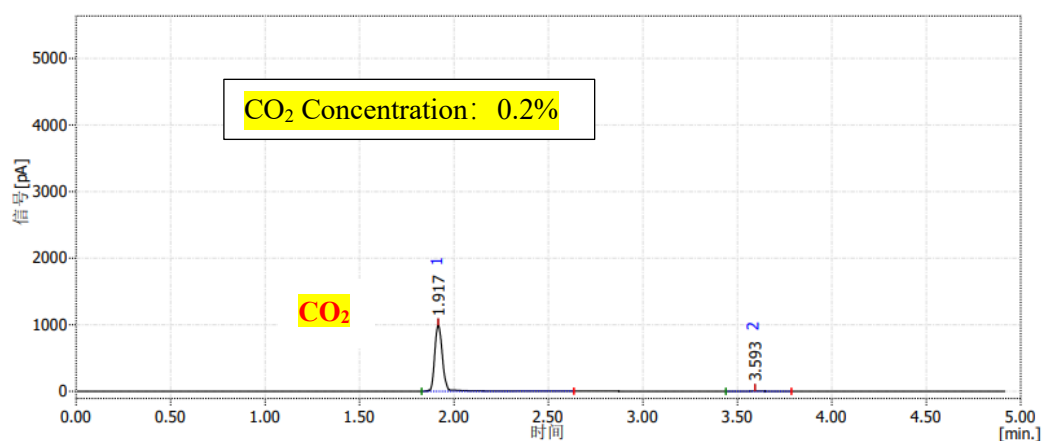
序号	组份名称	保留时间(min)	峰面积	浓度(g/L)	面积百分比	浓度百分比
1		1.9151	1899.7840	0.0000	99.8791	
2		3.5967	2.2987	0.0000	0.1209	
总计			1902.0830	0.0000	100	0.0000

Figure S30 Original GC spectra at 30°C(10 mL/min , 0.15vol % CO₂, 19.9vol% O₂ and 79.95vol% N₂)



序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		1.9159	2818.8100	0.0000	99.9201	
2		3.5975	2.2542	0.0000	0.0799	
总计			2821.0640	0.0000	100	0.0000

Figure S31 Original GC spectra at 30°C (10 mL/min , 0.2vol % CO₂, 19.9vol% O₂ and 79.90vol% N₂)



序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		1.9167	2856.2010	0.0000	99.9171	
2		3.5925	2.3706	0.0000	0.0829	
总计			2858.5720	0.0000	100	0.0000

Figure S32 Original GC spectra at 30°C (10 mL/min , 0.2vol % CO₂, 19.9vol% O₂ and 79.90vol% N₂)

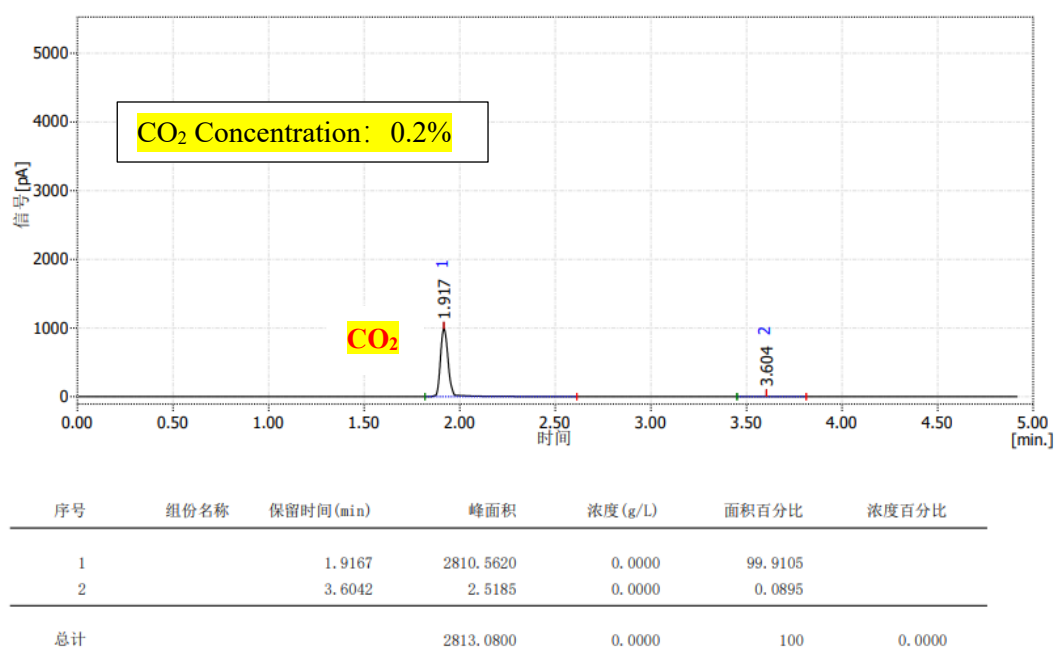


Figure S33 Original GC spectra at 30°C(10 mL/min , 0.2vol % CO₂, 19.9vol% O₂ and 79.90vol% N₂)

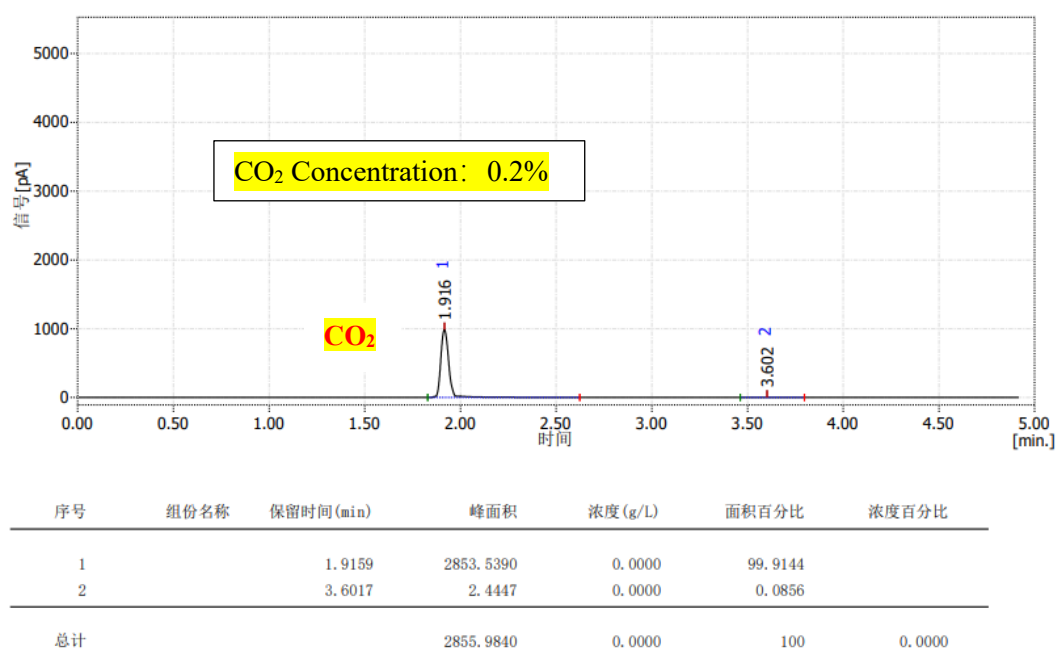
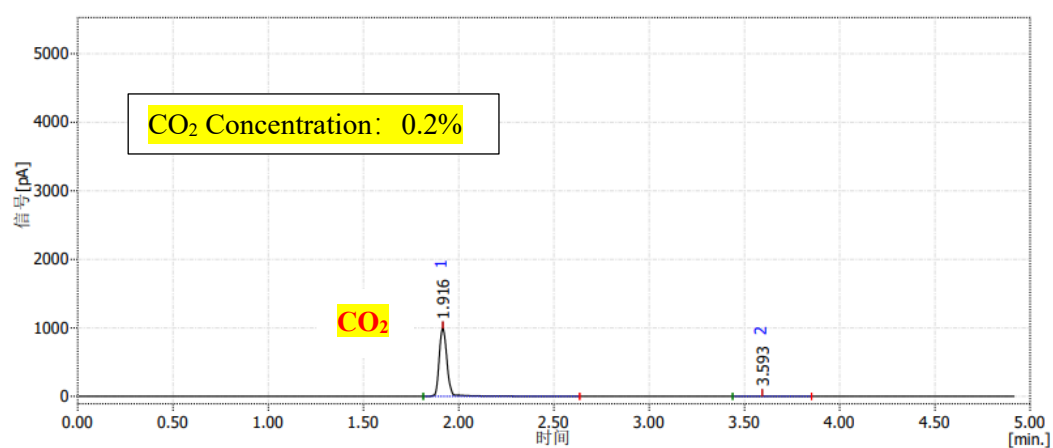
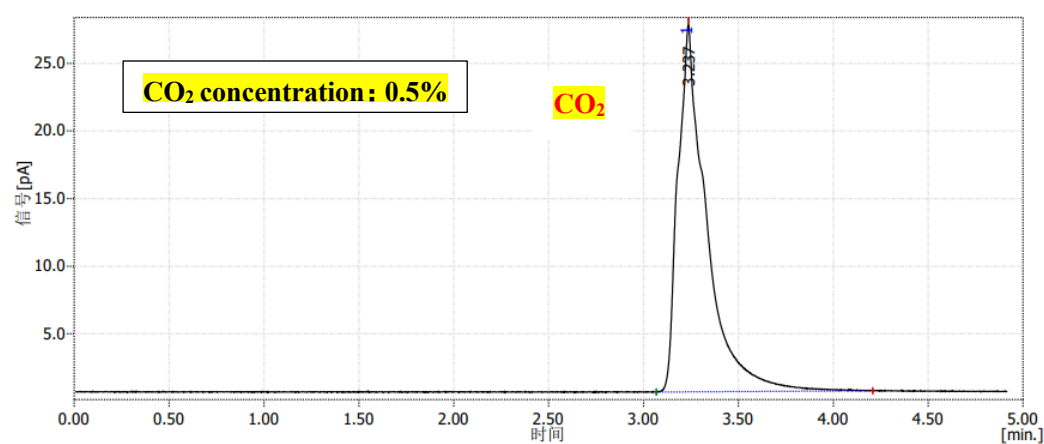


Figure S34 Original GC spectra at 30°C(10 mL/min , 0.2vol % CO₂, 19.9vol% O₂ and 79.90vol% N₂)



序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		1.9159	2854.9060	0.0000	99.9054	
2		3.5933	2.7039	0.0000	0.0946	
总计			2857.6100	0.0000	100	0.0000

Figure S35 Original GC spectra at 30°C(10 mL/min , 0.2vol % CO₂, 19.9vol% O₂ and 79.90vol% N₂)



序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		3.2367	284.1229	0.0000	100.0000	
总计			284.1229	0.0000	100	0.0000

Figure S36 Original GC spectra (10 mL/min , 0.5vol % CO₂, 19.9vol% O₂ and 79.6 vol% N₂)

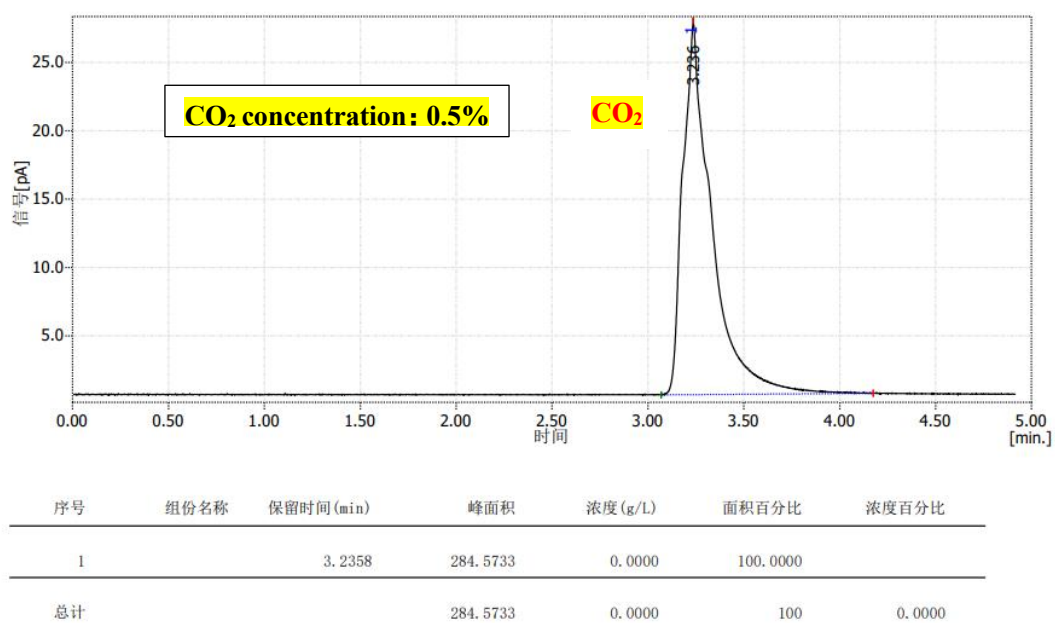


Figure S37 Original GC spectra (10 mL/min , 0.5vol % CO₂, 19.9vol% O₂ and 79.6 vol% N₂)

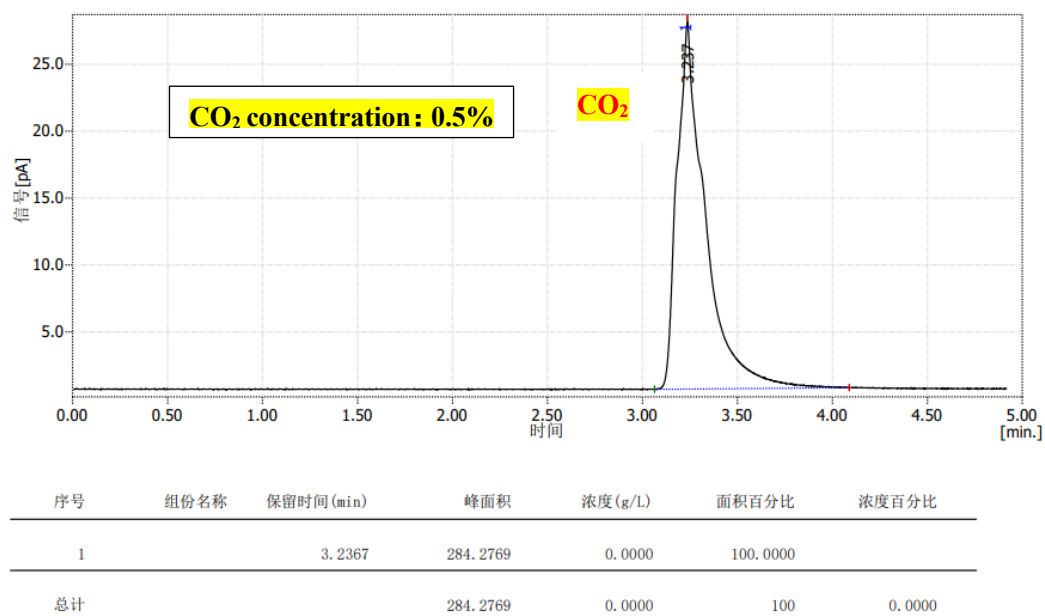
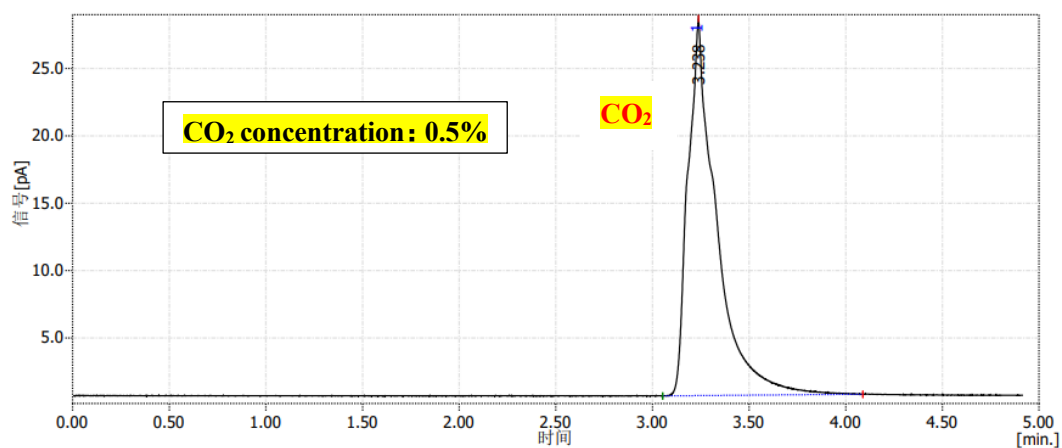
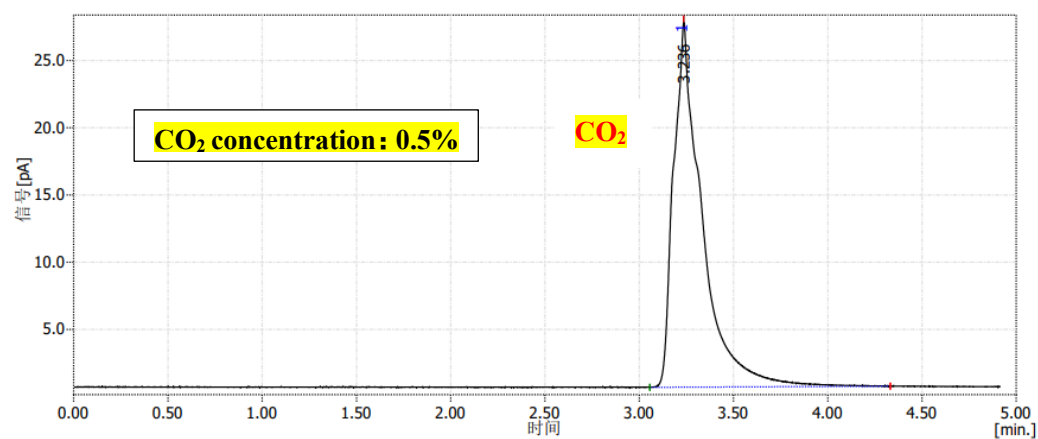


Figure S38 Original GC spectra (10 mL/min , 0.5vol % CO₂, 19.9vol% O₂ and 79.6 vol% N₂)



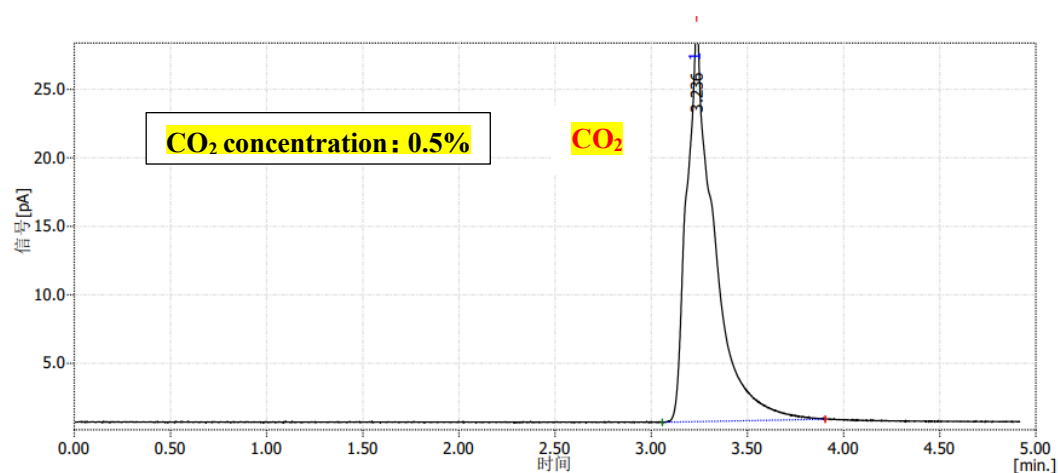
序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		3.2383	285.1243	0.0000	100.0000	
总计			285.1243	0.0000	100	0.0000

Figure S39 Original GC spectra (10 mL/min , 0.5vol % CO₂, 19.9vol% O₂ and 79.6 vol% N₂)



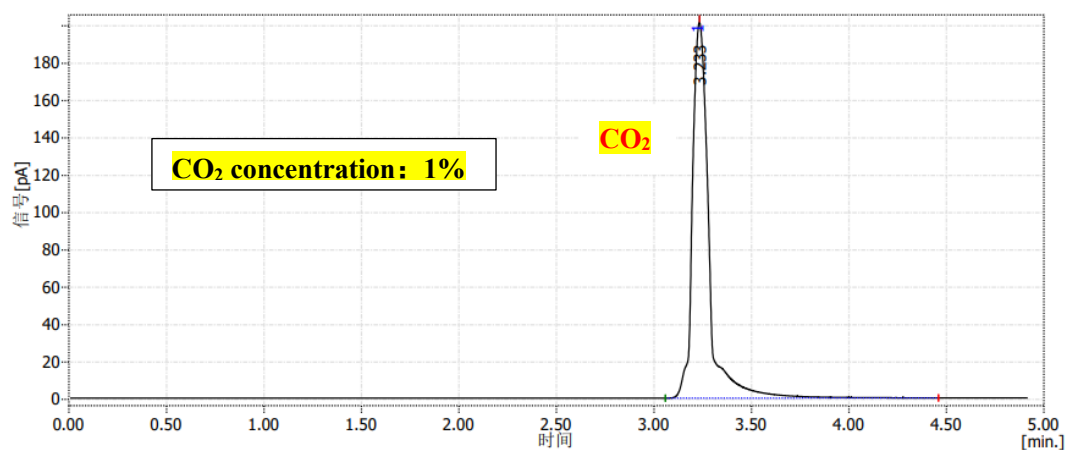
序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		3.2358	284.9263	0.0000	100.0000	
总计			284.9263	0.0000	100	0.0000

Figure S40 Original GC spectra (10 mL/min , 0.5vol % CO₂, 19.9vol% O₂ and 79.6 vol% N₂)



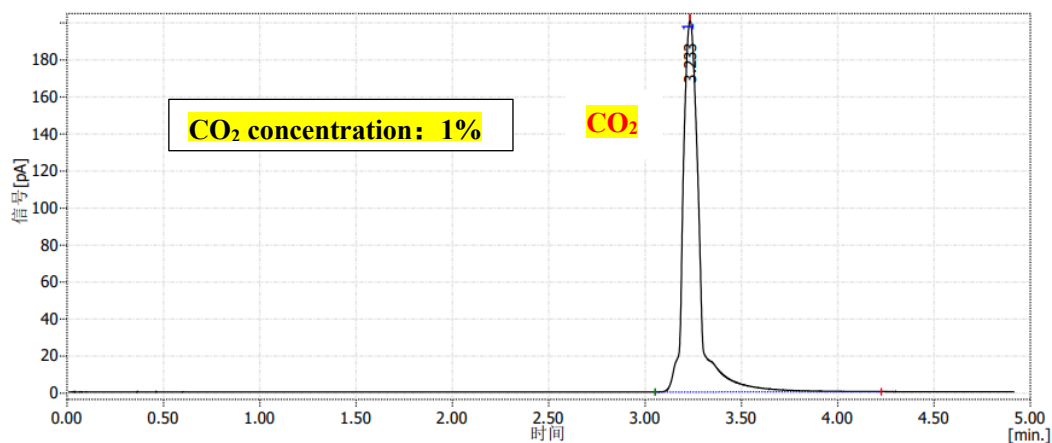
序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		3.2358	284.4328	0.0000	100.0000	
总计			284.4328	0.0000	100	0.0000

Figure S41 Original GC spectra (10 mL/min , 0.5vol % CO₂, 19.9vol% O₂ and 79.6 vol% N₂)



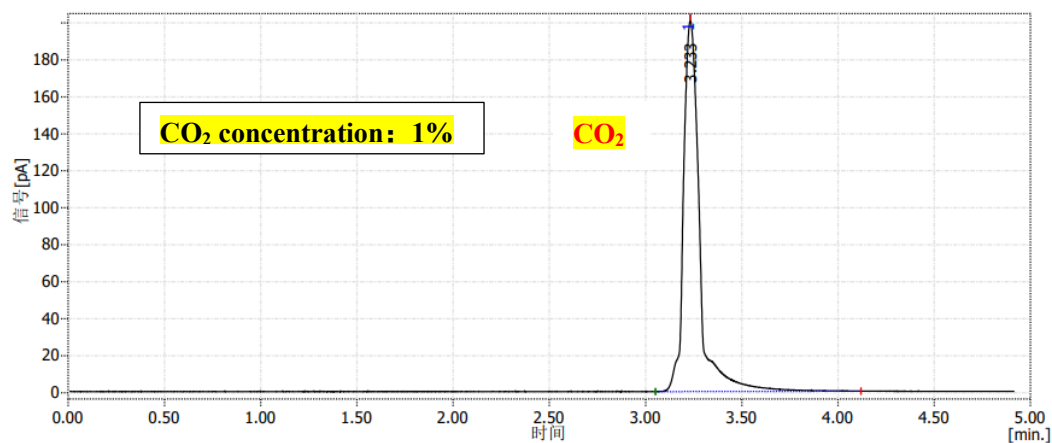
序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		3.2333	1177.2000	0.0000	100.0000	
总计			1177.2000	0.0000	100	0.0000

Figure S42 Original GC spectra (10 mL/min , 1vol % CO₂, 19.9vol% O₂ and 79.1 vol% N₂)



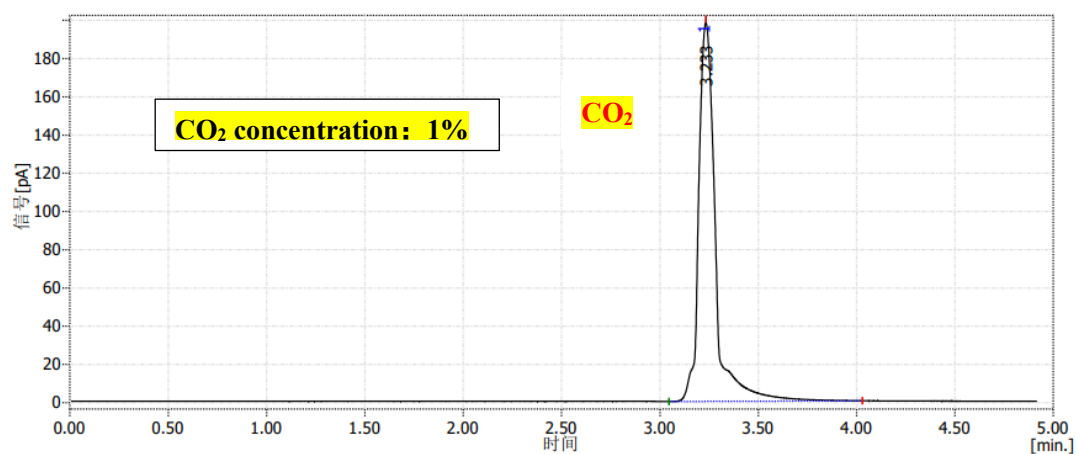
序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		3.2325	1166.0830	0.0000	100.0000	
总计			1166.0830	0.0000	100	0.0000

Figure S43 Original GC spectra (10 mL/min , 1vol % CO₂, 19.9vol% O₂ and 79.1 vol% N₂)



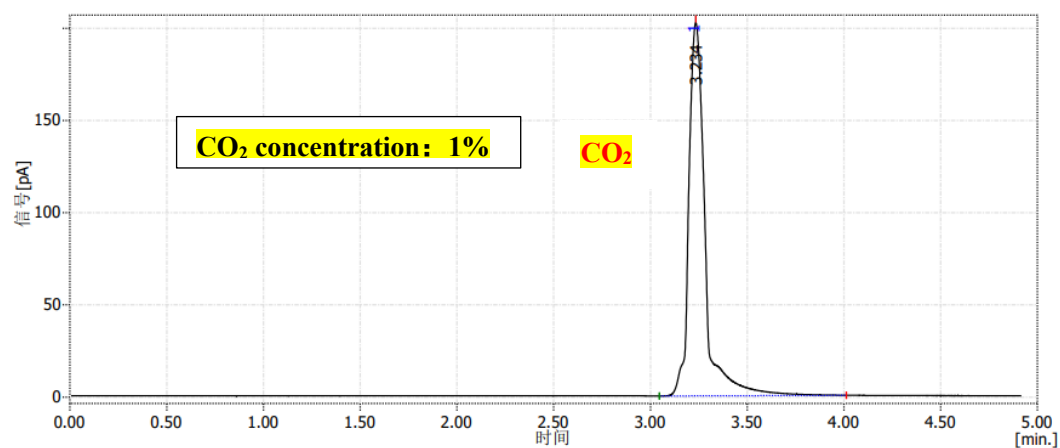
序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		3.2325	1162.0830	0.0000	100.0000	
总计			1162.0830	0.0000	100	0.0000

Figure S44 Original GC spectra (10 mL/min , 1vol % CO₂, 19.9vol% O₂ and 79.1 vol% N₂)



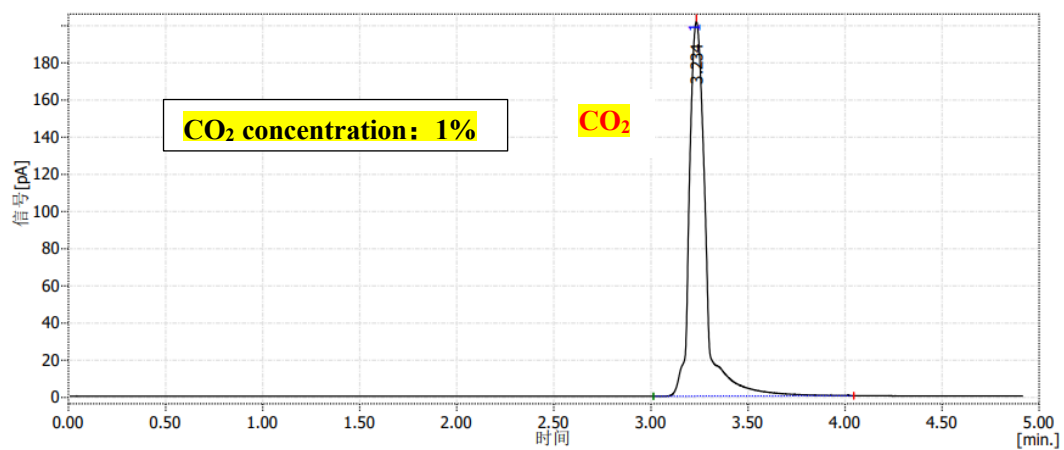
序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		3.2333	1161.8170	0.0000	100.0000	
总计			1161.8170	0.0000	100	0.0000

Figure S45 Original GC spectra (10 mL/min , 1vol % CO₂, 19.9vol% O₂ and 79.1 vol% N₂)



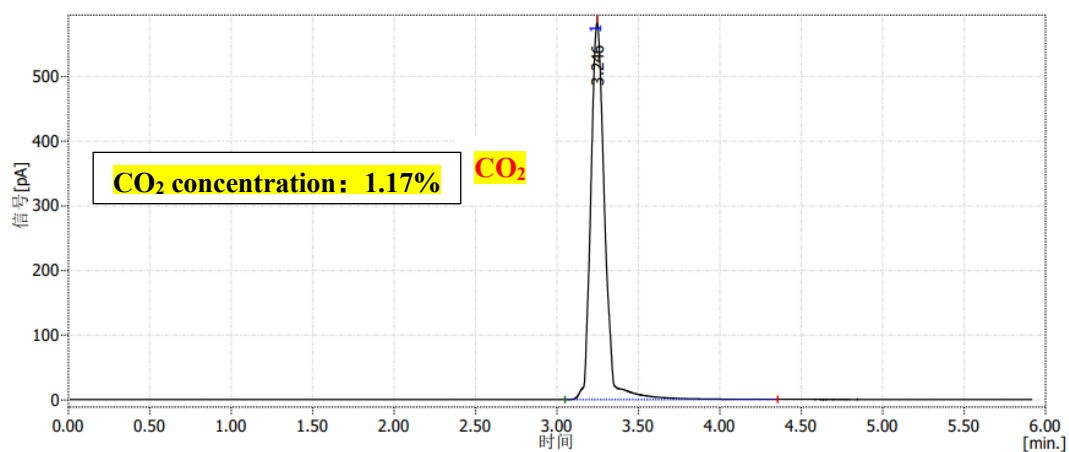
序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		3.2342	1177.2290	0.0000	100.0000	
总计			1177.2290	0.0000	100	0.0000

Figure S46 Original GC spectra (10 mL/min , 1vol % CO₂, 19.9vol% O₂ and 79.1 vol% N₂)



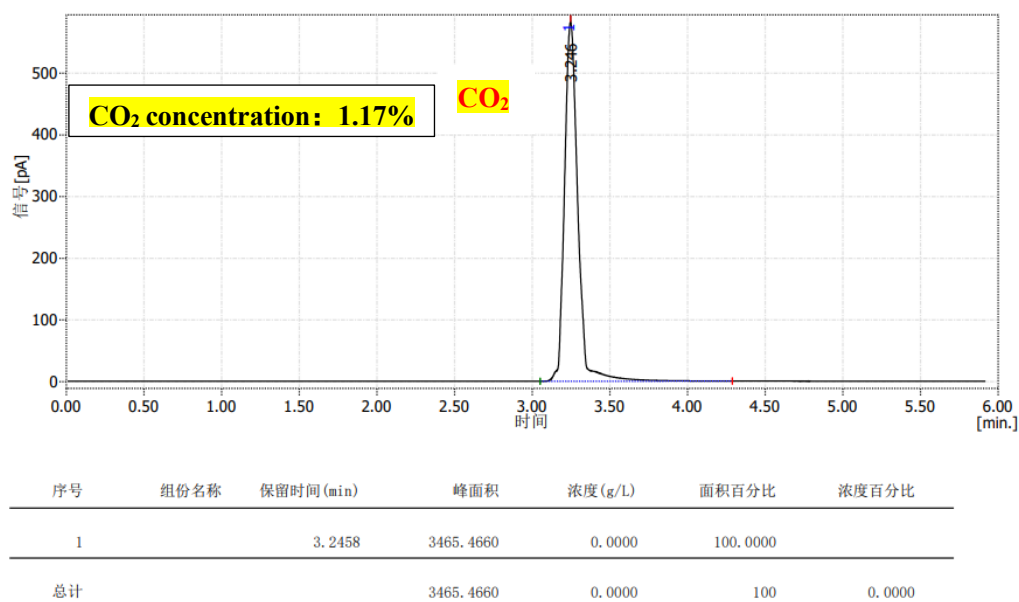
序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		3.2342	1180.8170	0.0000	100.0000	
总计			1180.8170	0.0000	100	0.0000

Figure S47 Original GC spectra (10 mL/min , 1vol % CO₂, 19.9vol% O₂ and 79.1 vol% N₂)



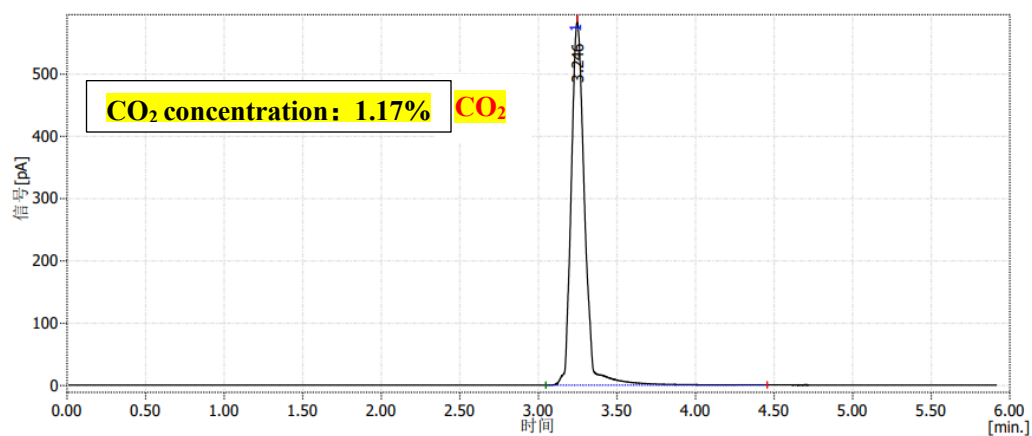
序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		3.2458	3465.7030	0.0000	100.0000	
总计			3465.7030	0.0000	100	0.0000

Figure S48 Original GC spectra (10 mL/min , 1.17vol % CO₂, 19.9vol% O₂ and 78.93 vol% N₂)



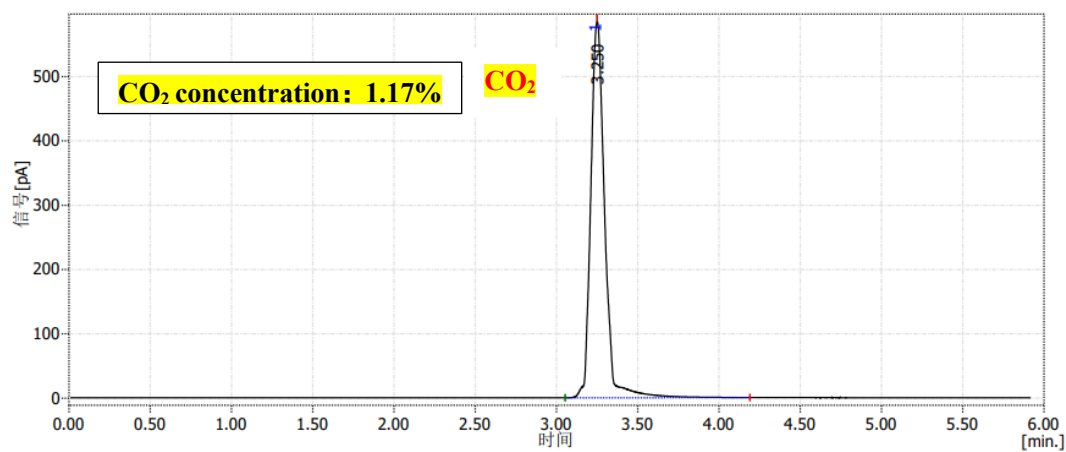
序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		3.2458	3465.4660	0.0000	100.0000	
总计			3465.4660	0.0000	100	0.0000

Figure S49 Original GC spectra (10 mL/min , 1.17vol % CO₂, 19.9vol% O₂ and 78.93 vol% N₂)



序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		3.2458	3465.8100	0.0000	100.0000	
总计			3465.8100	0.0000	100	0.0000

Figure S50 Original GC spectra (10 mL/min , 1.17vol % CO₂, 19.9vol% O₂ and 78.93 vol% N₂)



序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		3.2500	3466.5600	0.0000	100.0000	
总计			3466.5600	0.0000	100	0.0000

Figure S51 Original GC spectra (10 mL/min , 1.17vol % CO₂, 19.9vol% O₂ and 78.93 vol% N₂)

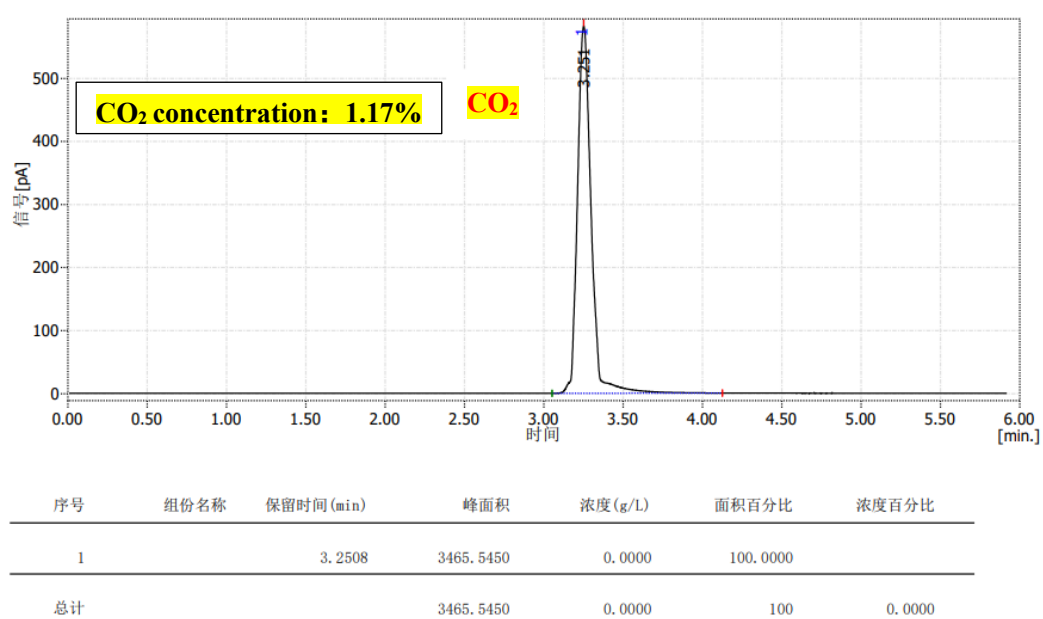


Figure S52 Original GC spectra (10 mL/min , 1.17vol % CO₂, 19.9vol% O₂ and 78.93 vol% N₂)

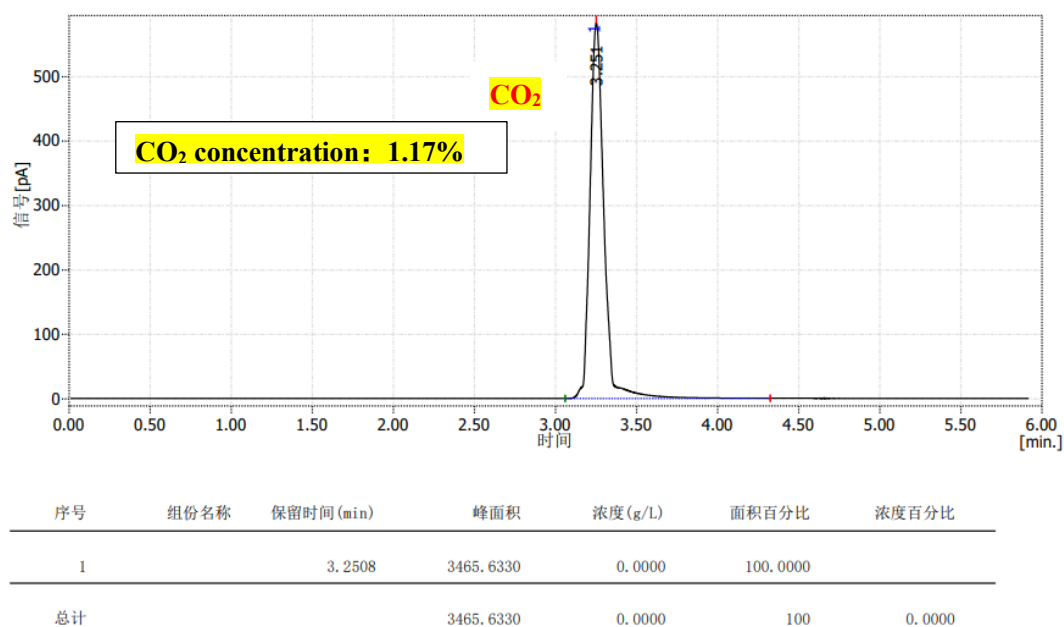
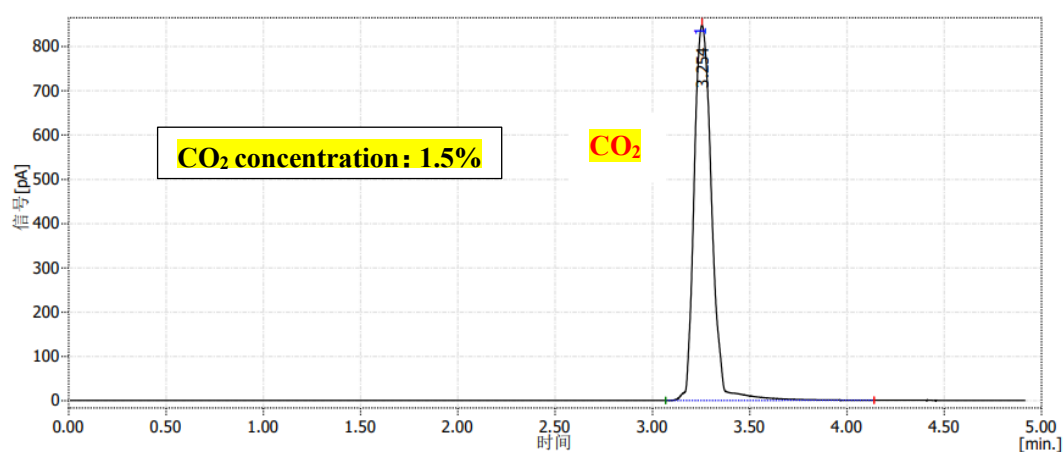
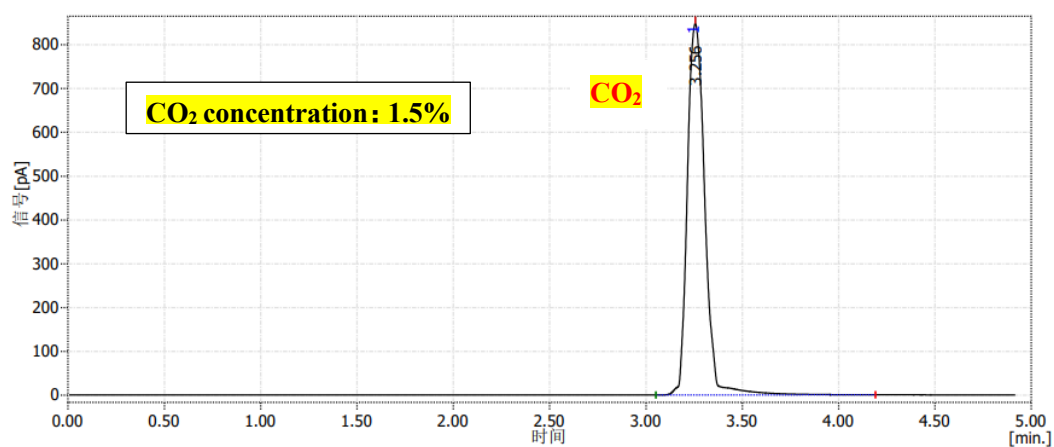


Figure S53 Original GC spectra (10 mL/min , 1.17vol % CO₂, 19.9vol% O₂ and 78.93 vol% N₂)



序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		3.2542	5347.5420	0.0000	100.0000	
总计			5347.5420	0.0000	100	0.0000

Figure S54 Original GC spectra (10 mL/min , 1.5vol % CO₂, 19.9vol% O₂ and 78.6 vol% N₂)



序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		3.2558	5344.5800	0.0000	100.0000	
总计			5344.5800	0.0000	100	0.0000

Figure S55 Original GC spectra (10 mL/min , 1.5vol % CO₂, 19.9vol% O₂ and 78.6 vol% N₂)

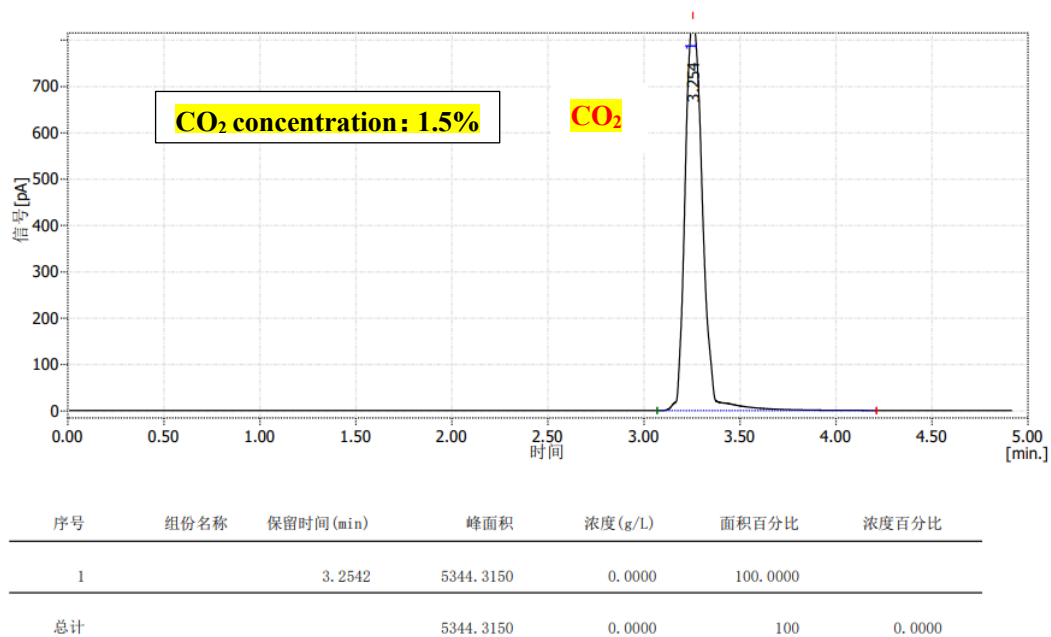


Figure S56 Original GC spectra (10 mL/min , 1.5vol % CO₂, 19.9vol% O₂ and 78.6 vol% N₂)

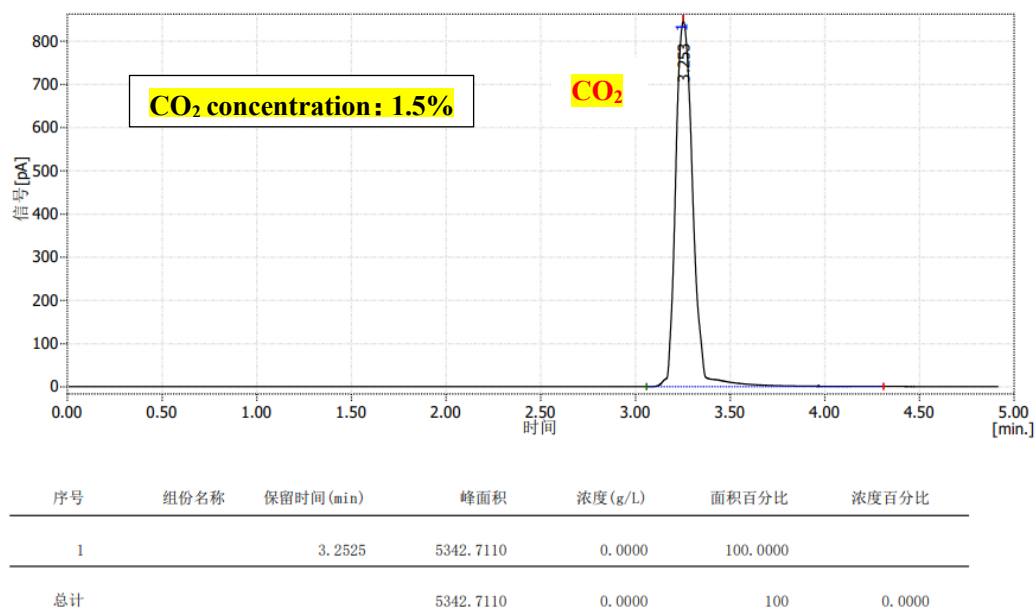


Figure S57 Original GC spectra (10 mL/min , 1.5vol % CO₂, 19.9vol% O₂ and 78.6 vol% N₂)

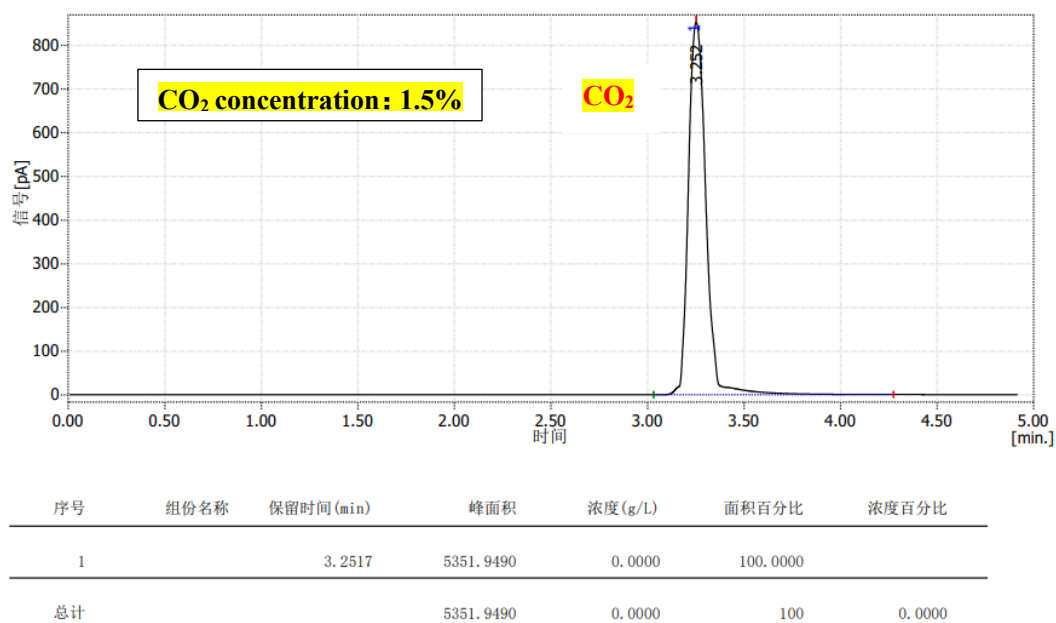


Figure S58 Original GC spectra (10 mL/min , 1.5vol % CO₂, 19.9vol% O₂ and 78.6 vol% N₂)

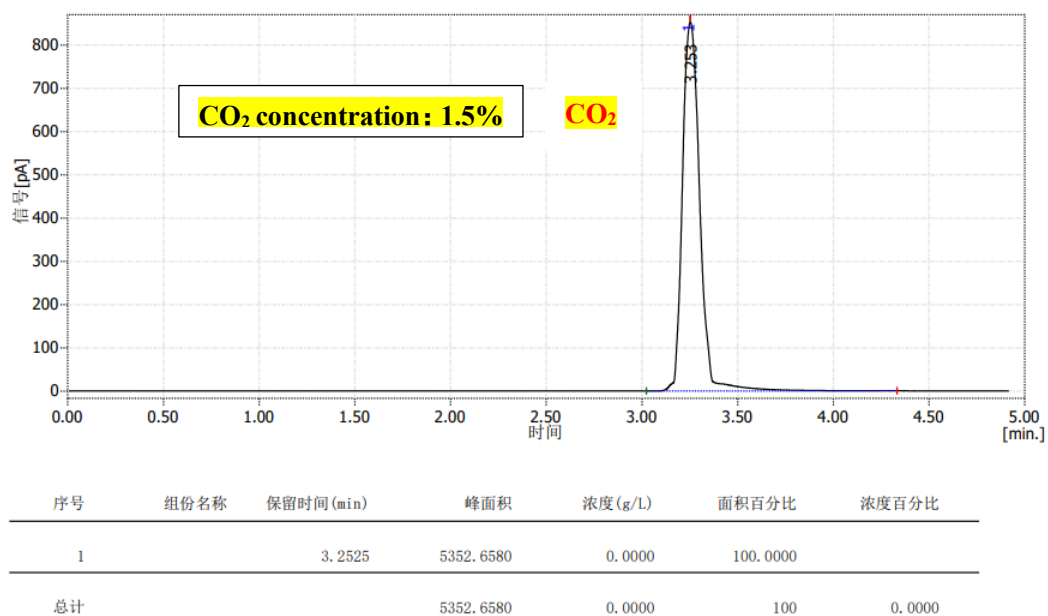
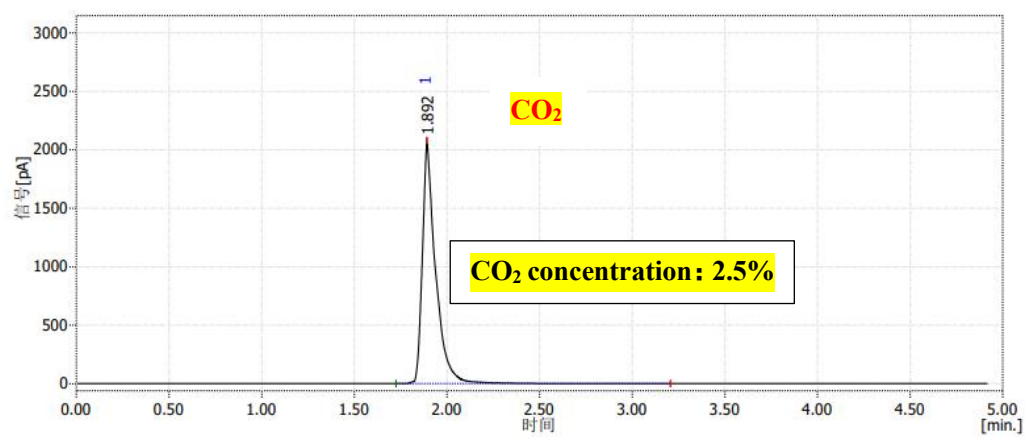
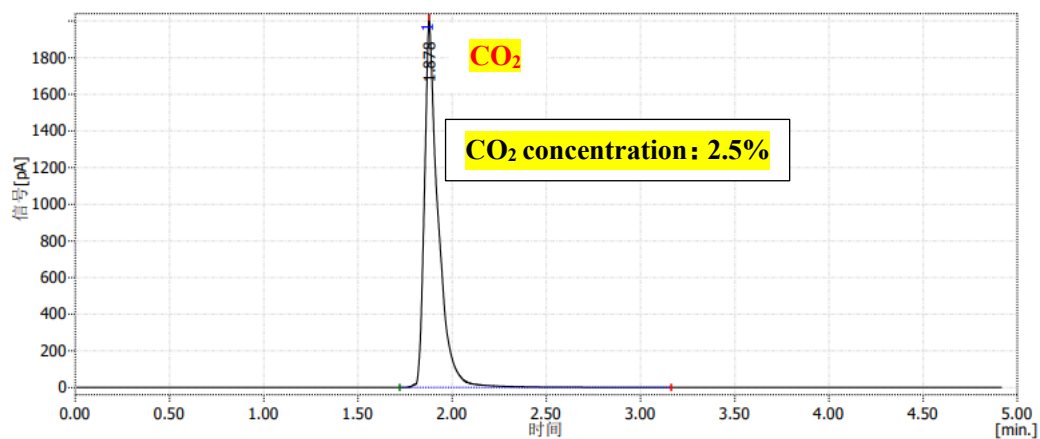


Figure S59 Original GC spectra (10 mL/min , 1.5vol % CO₂, 19.9vol% O₂ and 78.6 vol% N₂)



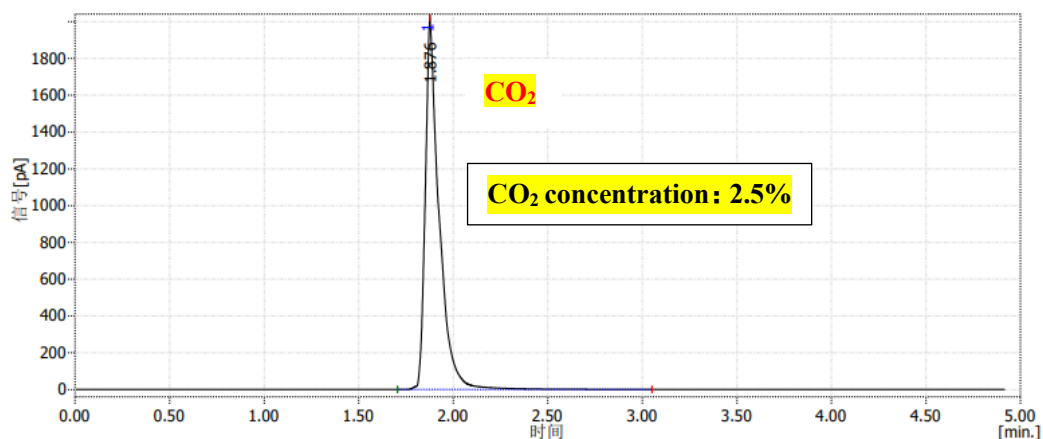
序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		1.8917	10266.8200	0.0000	100.0000	
总计			10266.8200	0.0000	100	0.0000

Figure S60 Original GC spectra (10 mL/min , 2.5vol % CO₂, 19.9vol% O₂ and 77.6 vol% N₂)



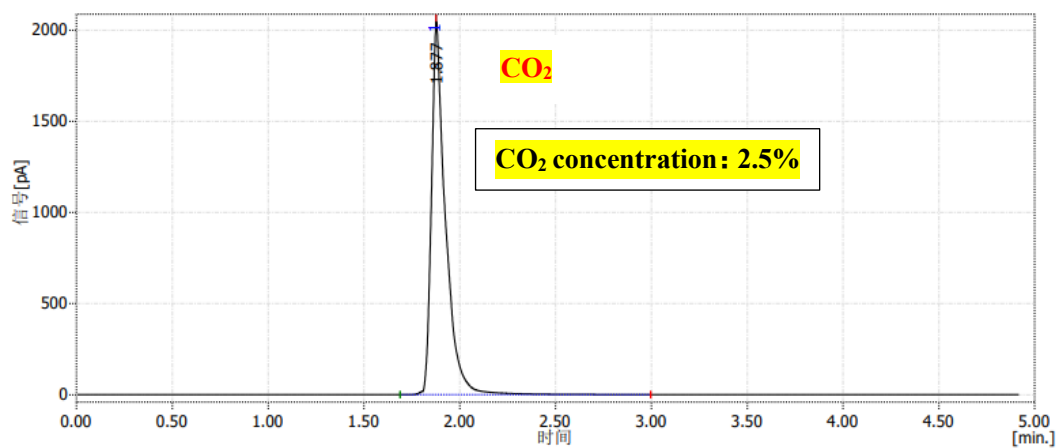
序号	组份名称	保留时间(min)	峰面积	浓度(g/L)	面积百分比	浓度百分比
1		1.8776	10108.0100	0.0000	100.0000	
总计			10108.0100	0.0000	100	0.0000

Figure S61 Original GC spectra (10 mL/min , 2.5vol % CO₂, 19.9vol% O₂ and 77.6 vol% N₂)



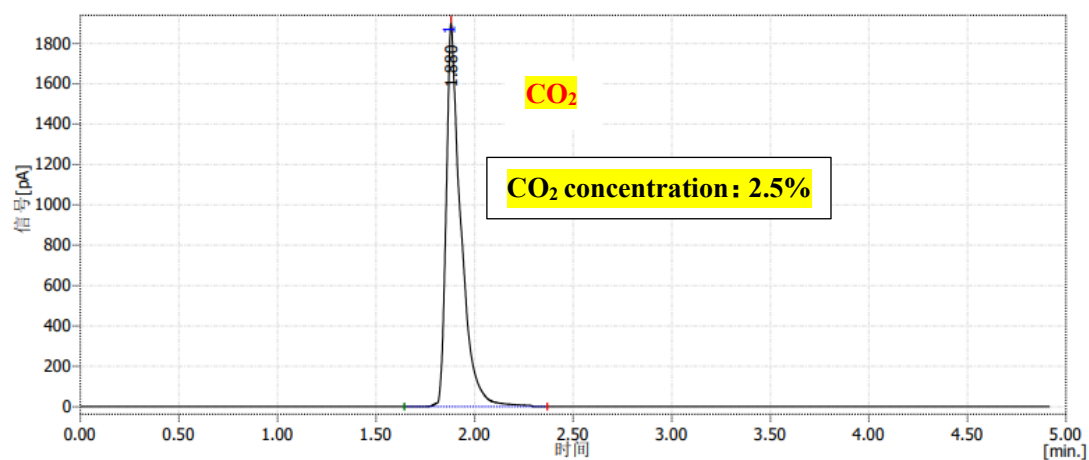
序号	组份名称	保留时间(min)	峰面积	浓度(g/L)	面积百分比	浓度百分比
1		1.8759	10237.8100	0.0000	100.0000	
总计			10237.8100	0.0000	100	0.0000

Figure S62 Original GC spectra (10 mL/min , 2.5vol % CO₂, 19.9vol% O₂ and 77.6 vol% N₂)



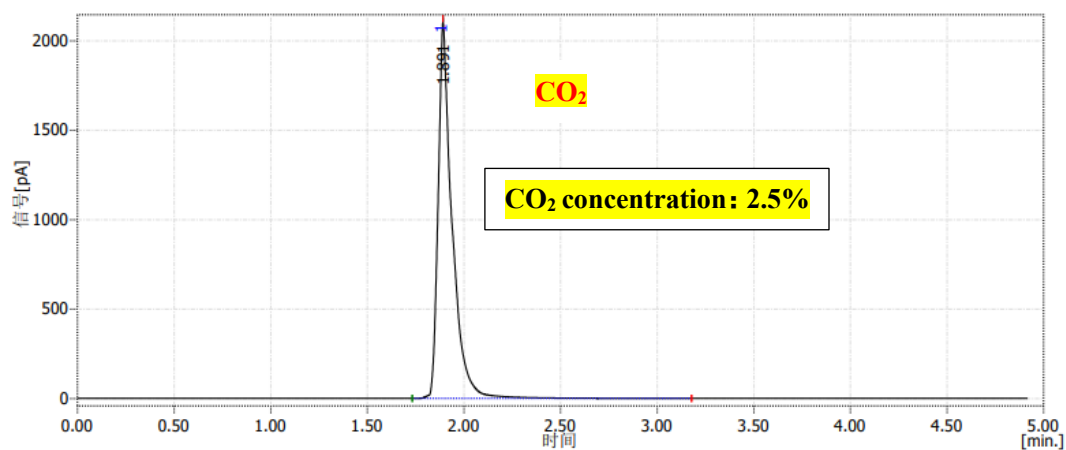
序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		1.8767	10433.2400	0.0000	100.0000	
总计			10433.2400	0.0000	100	0.0000

Figure S63 Original GC spectra (10 mL/min , 2.5vol % CO_2 , 19.9vol% O_2 and 77.6 vol% N_2)



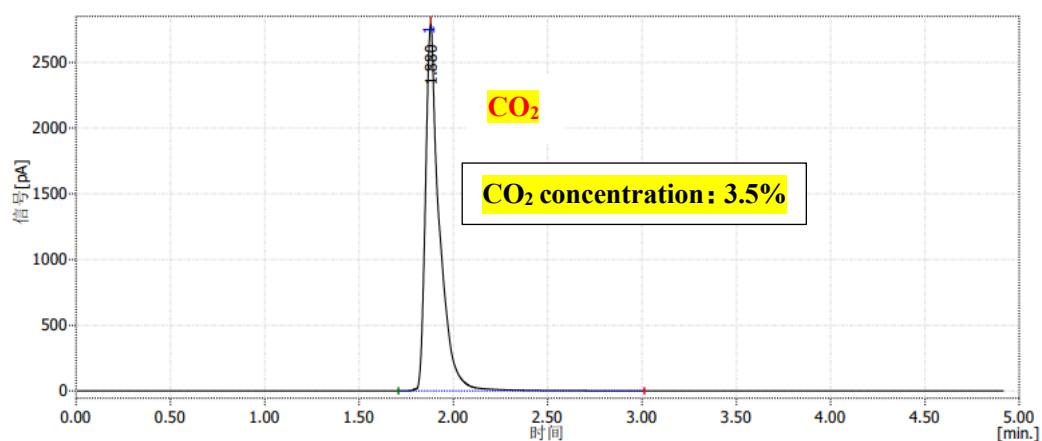
序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		1.8801	9778.7370	0.0000	100.0000	
总计			9778.7370	0.0000	100	0.0000

Figure S64 Original GC spectra (10 mL/min , 2.5vol % CO_2 , 19.9vol% O_2 and 77.6 vol% N_2)



序号	组份名称	保留时间(min)	峰面积	浓度(g/L)	面积百分比	浓度百分比
1		1.8909	10542.2200	0.0000	100.0000	
总计			10542.2200	0.0000	100	0.0000

Figure S65 Original GC spectra (10 mL/min , 2.5vol % CO₂, 19.9vol% O₂ and 77.6 vol% N₂)



序号	组份名称	保留时间(min)	峰面积	浓度(g/L)	面积百分比	浓度百分比
1		1.8801	14304.2000	0.0000	100.0000	
总计			14304.2000	0.0000	100	0.0000

Figure S66 Original GC spectra (10 mL/min , 3.5vol % CO₂, 19.9vol% O₂ and 76.6 vol% N₂)

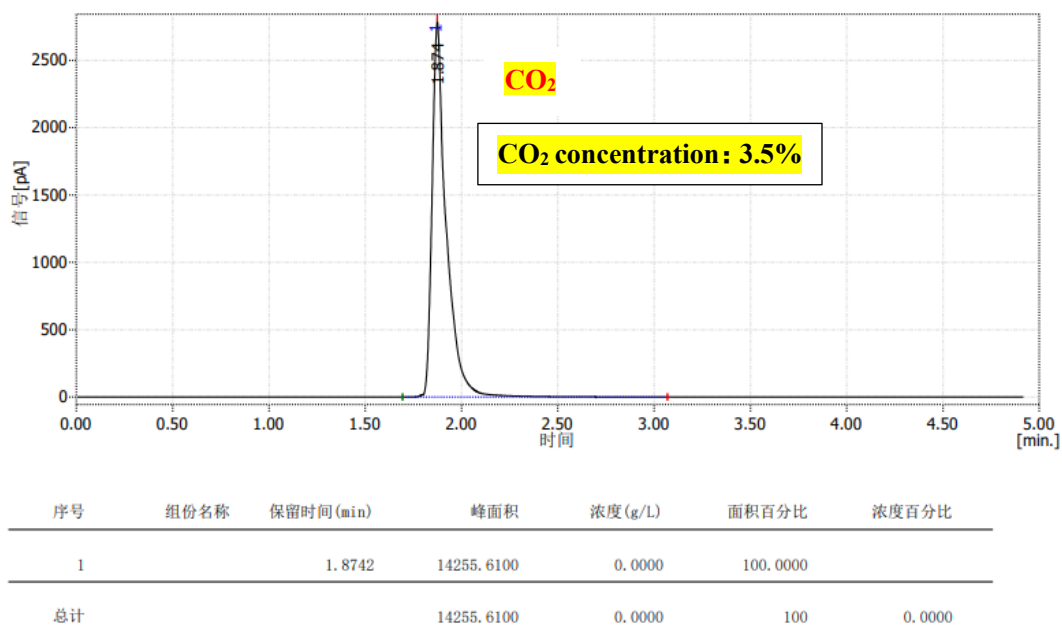


Figure S67 Original GC spectra (10 mL/min , 3.5vol % CO₂, 19.9vol% O₂ and 76.6 vol% N₂)

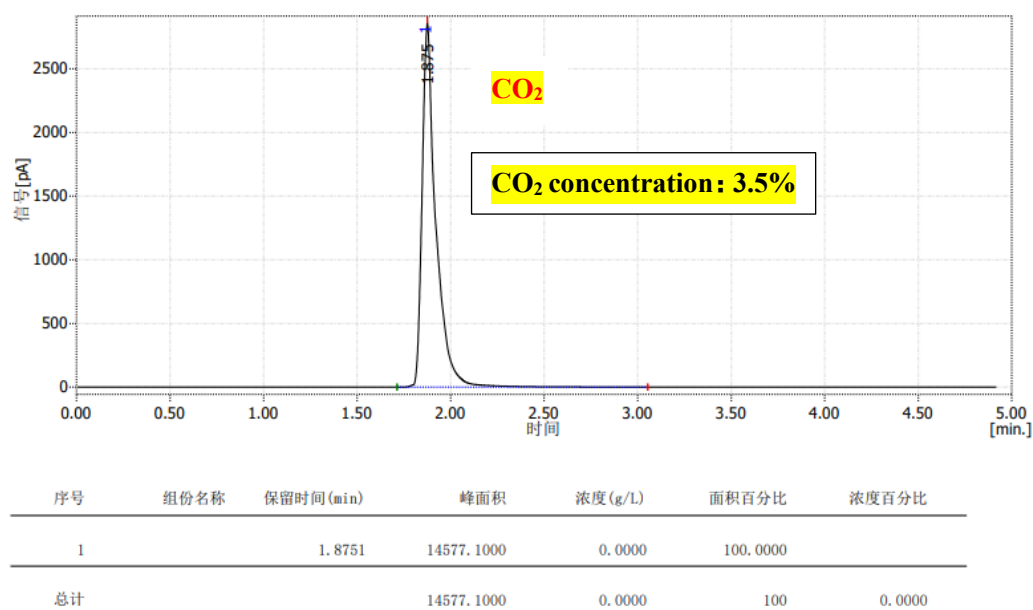


Figure S68 Original GC spectra (10 mL/min , 3.5vol % CO₂, 19.9vol% O₂ and 76.6 vol% N₂)

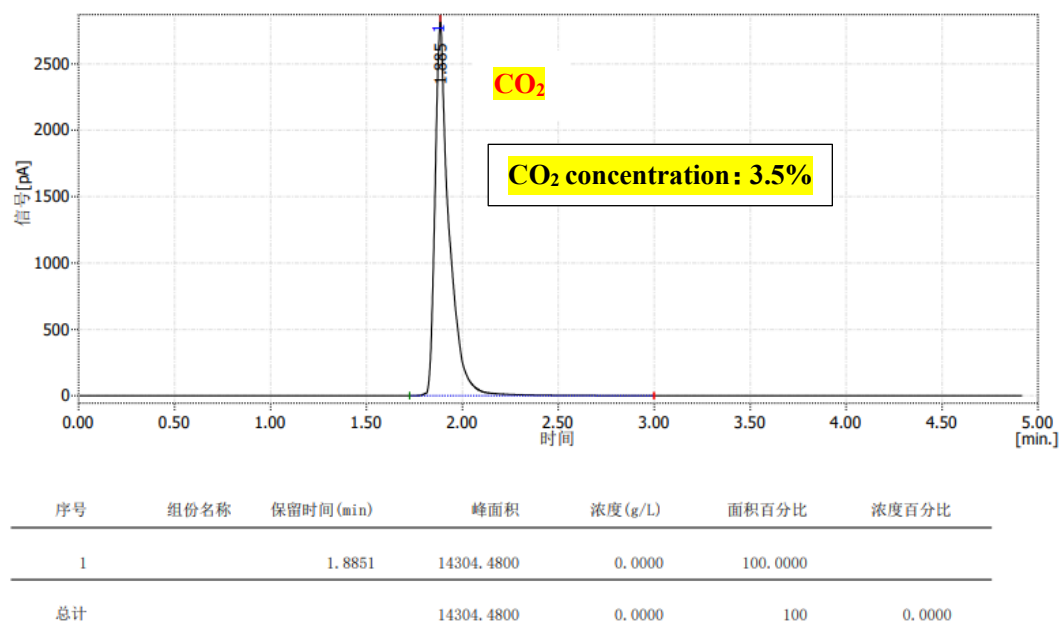


Figure S69 Original GC spectra (10 mL/min , 3.5vol % CO₂, 19.9vol% O₂ and 76.6 vol% N₂)

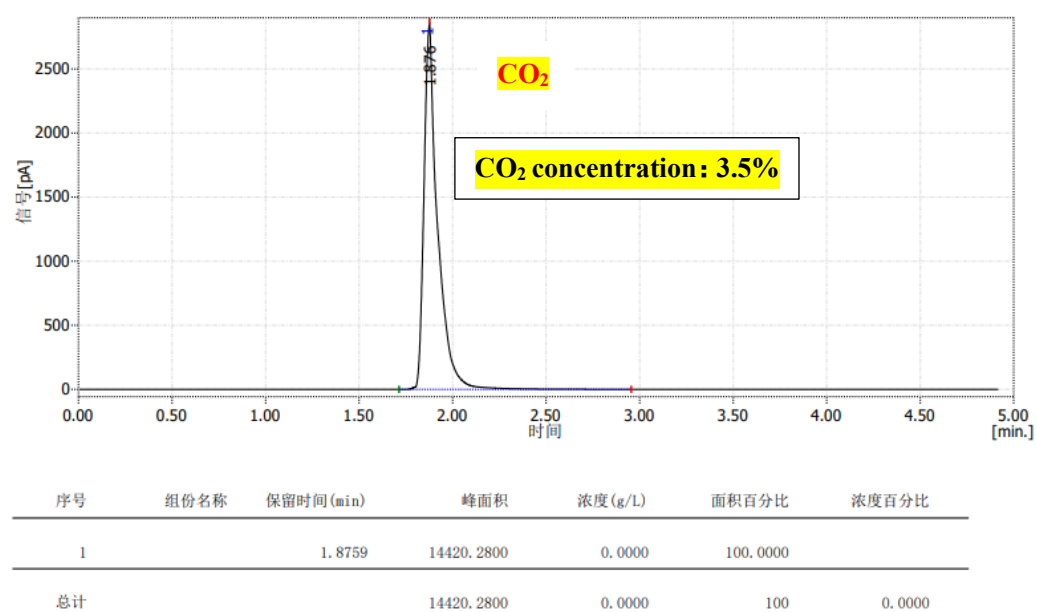


Figure S70 Original GC spectra (10 mL/min , 3.5vol % CO₂, 19.9vol% O₂ and 76.6 vol% N₂)

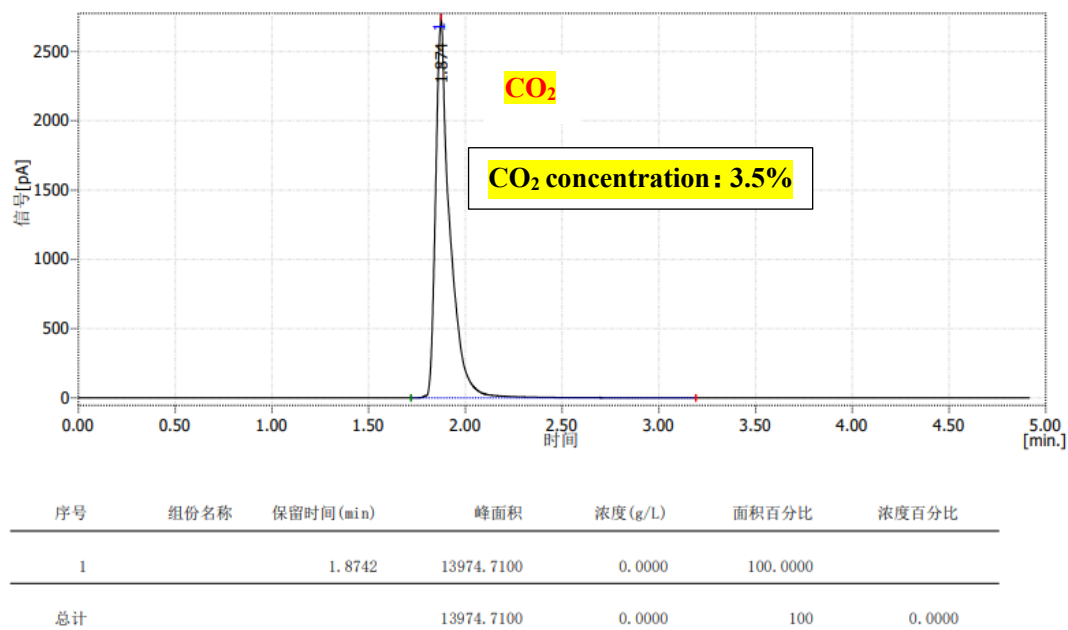


Figure S71 Original GC spectra (10 mL/min , 3.5vol % CO₂, 19.9vol% O₂ and 76.6 vol% N₂)

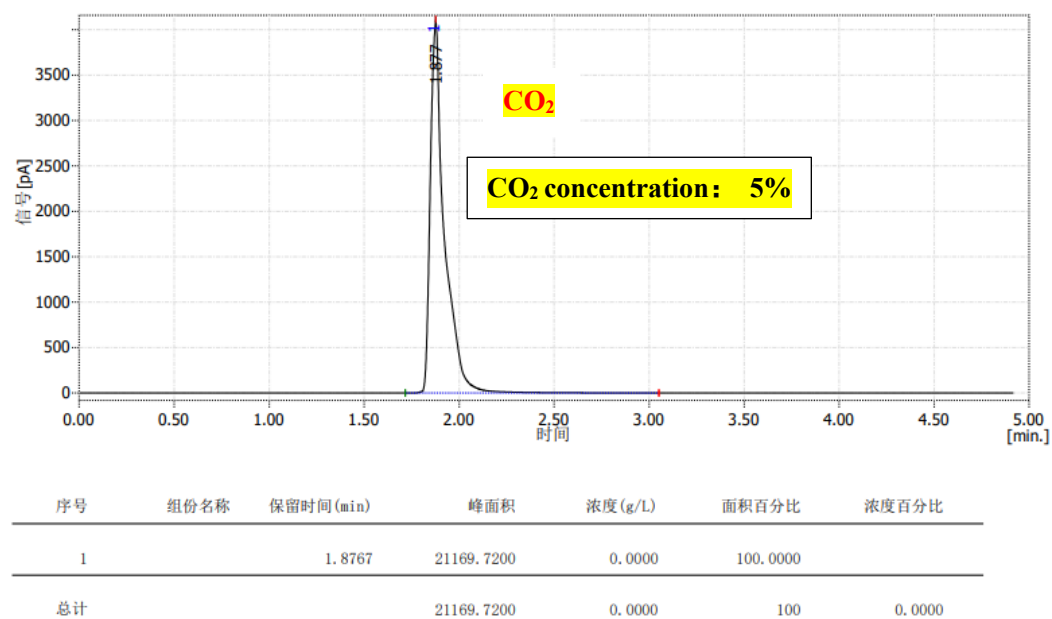


Figure S72 Original GC spectra (10 mL/min , 5vol % CO₂, 19.9vol% O₂ and 75.1 vol% N₂)

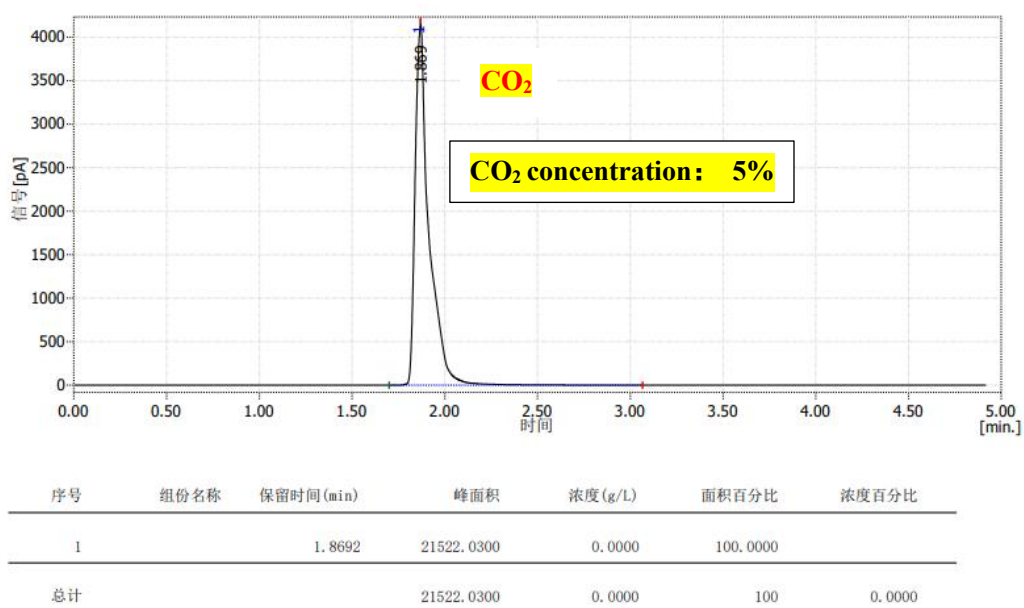


Figure S73 Original GC spectra (10 mL/min , 5vol % CO₂, 19.9vol% O₂ and 75.1 vol% N₂)

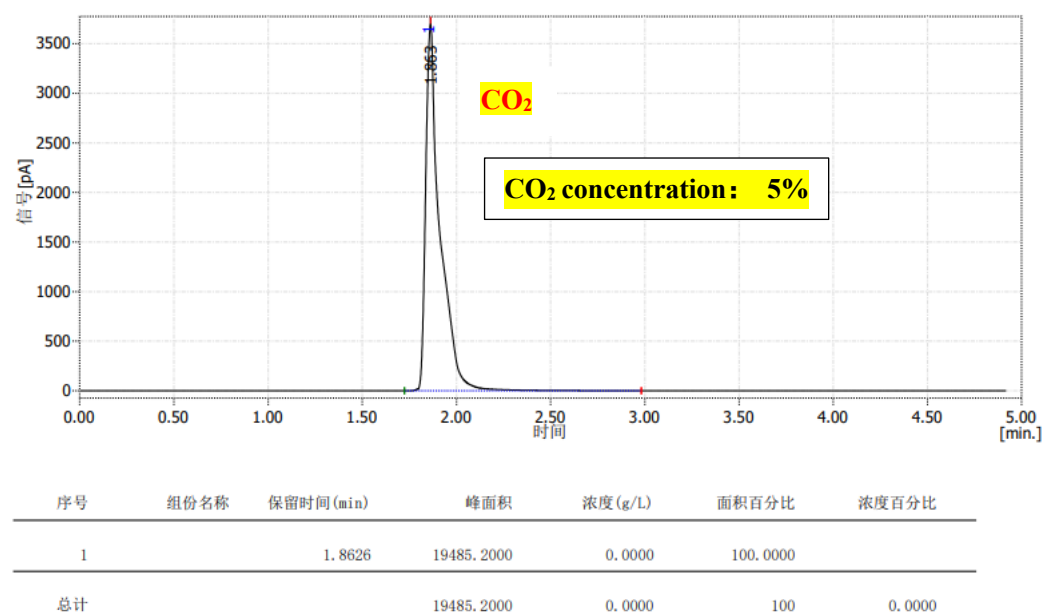


Figure S74 Original GC spectra (10 mL/min , 5vol % CO₂, 19.9vol% O₂ and 75.1 vol% N₂)

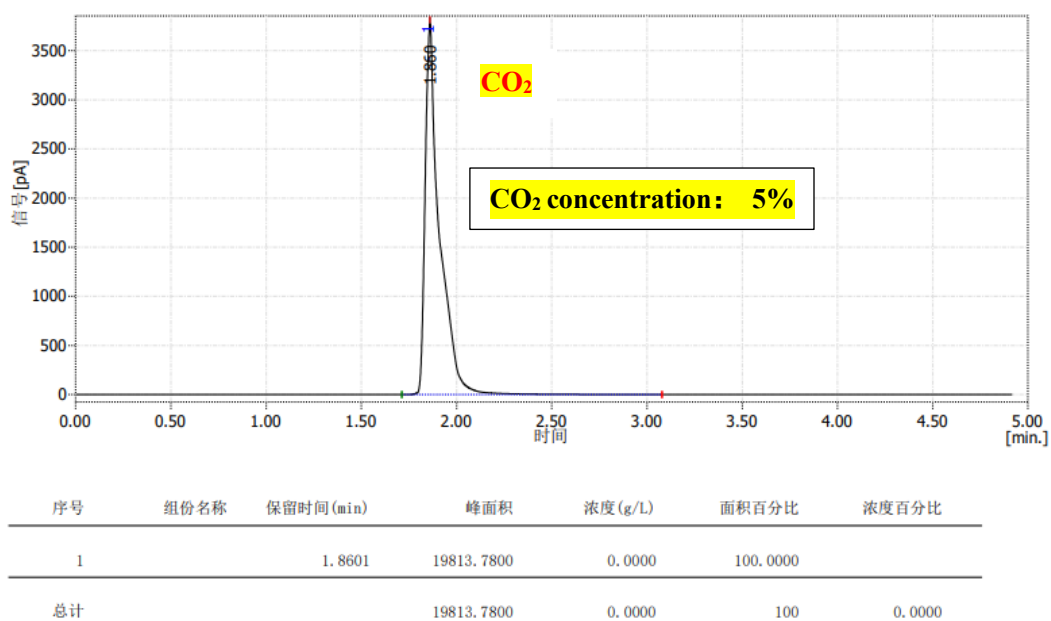


Figure S75 Original GC spectra (10 mL/min , 5vol % CO₂, 19.9vol% O₂ and 75.1 vol% N₂)

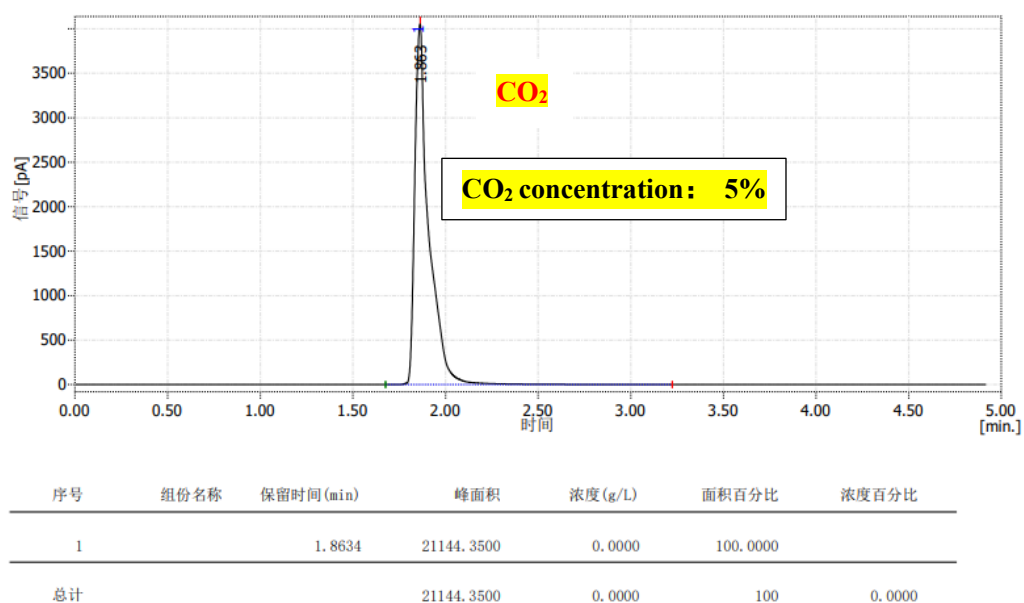
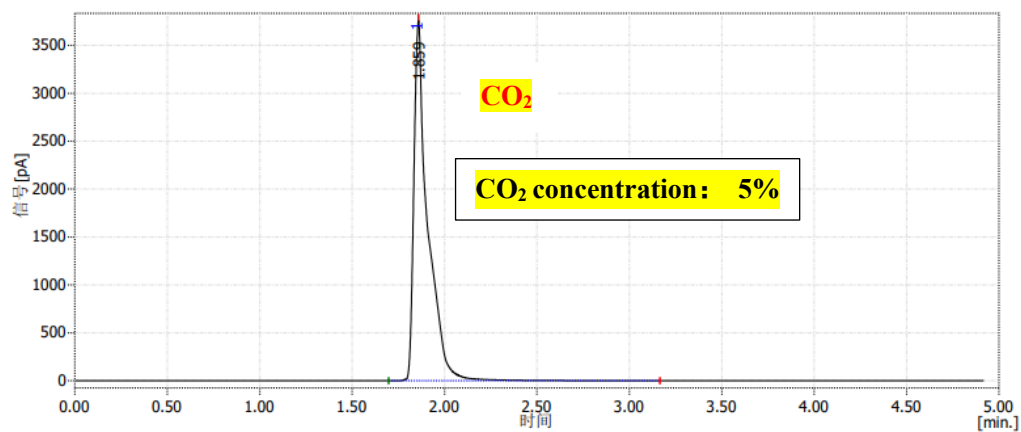
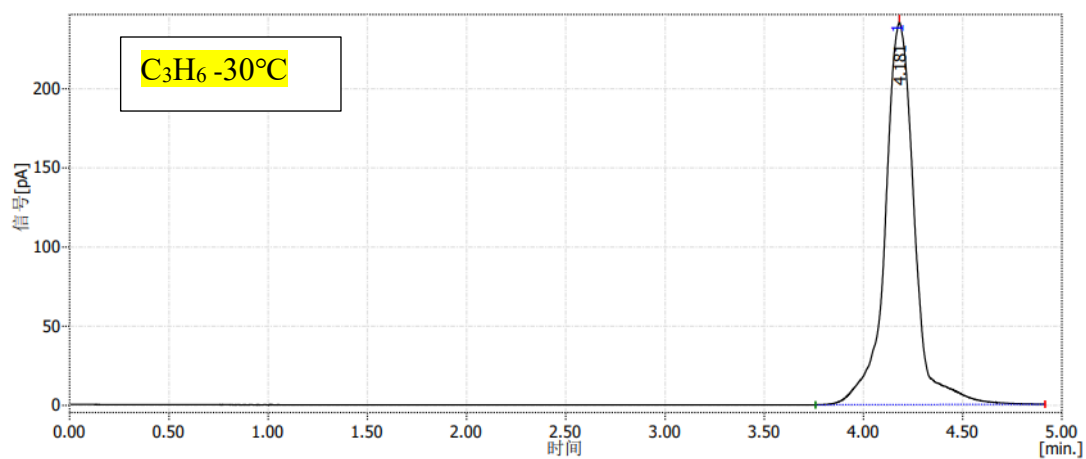


Figure S76 Original GC spectra (10 mL/min , 5vol % CO₂, 19.9vol% O₂ and 75.1 vol% N₂)



序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		1.8592	19548.3900	0.0000	100.0000	
总计			19548.3900	0.0000	100	0.0000

Figure S77 Original GC spectra (10 mL/min , 5vol % CO₂, 19.9vol% O₂ and 75.1 vol% N₂)



序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		4.1809	2485.1190	0.0000	100.0000	
总计			2485.1190	0.0000	100	0.0000

Figure S78 Original GC spectra at 30°C (10 mL/min , Feed gas ratio: 1vol % C₃H₆ and 99vol% air).

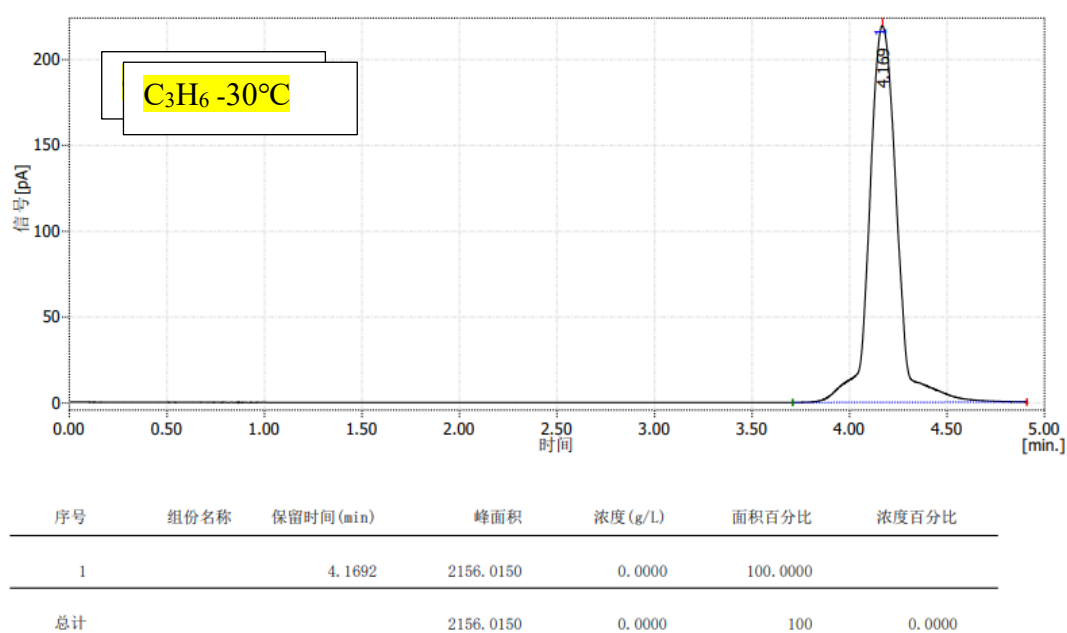


Figure S79 Original GC spectra at 30°C (10 mL/min , Feed gas ratio: 1vol % C₃H₆ and 99vol% air)

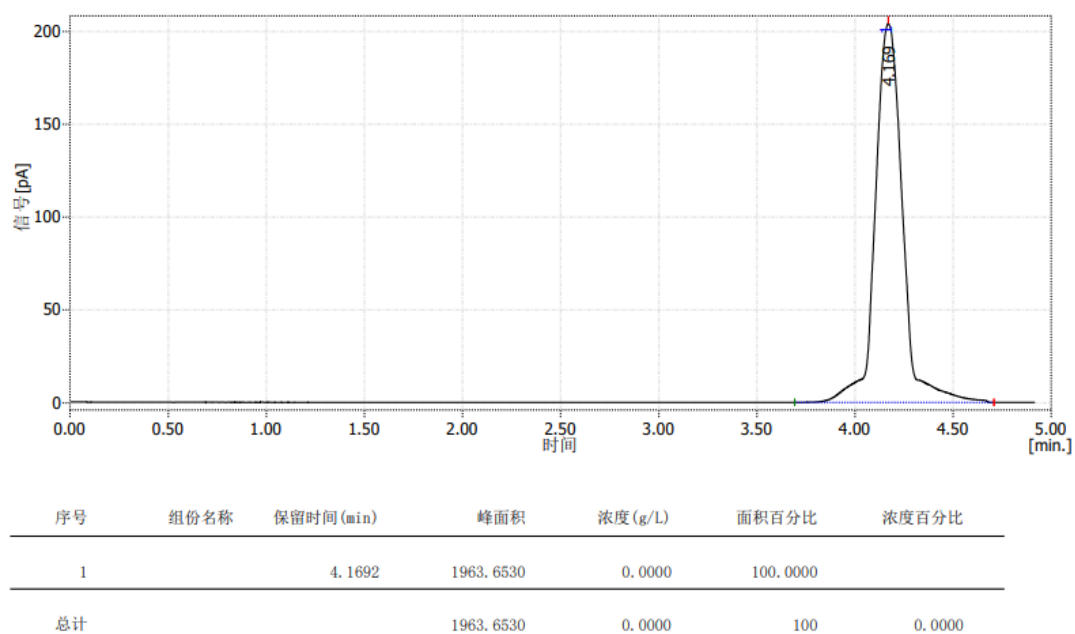
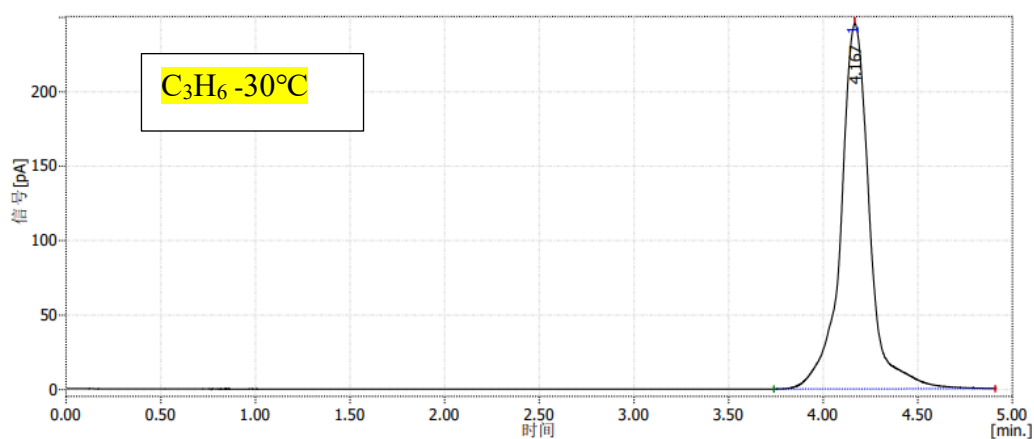
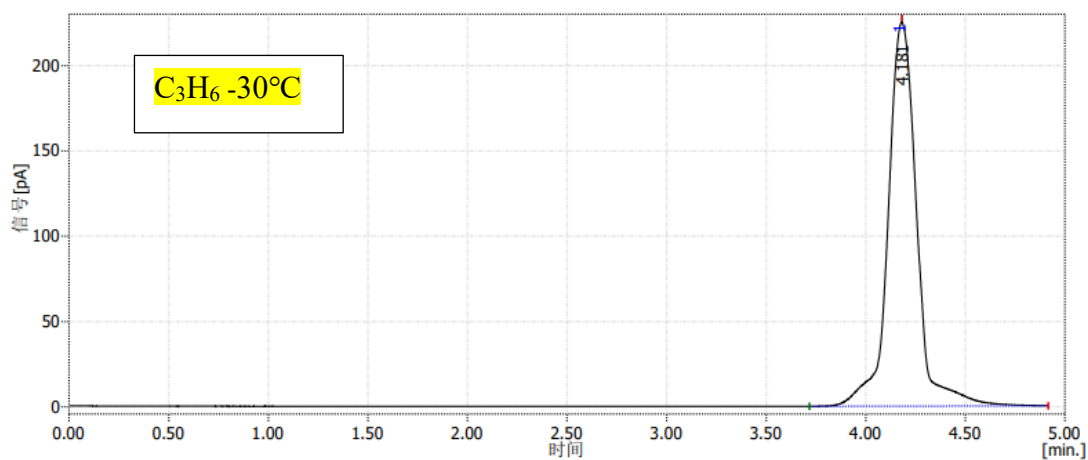


Figure S80 Original GC spectra at 30°C (10 mL/min , Feed gas ratio: 1vol % C₃H₆ and 99vol% air)



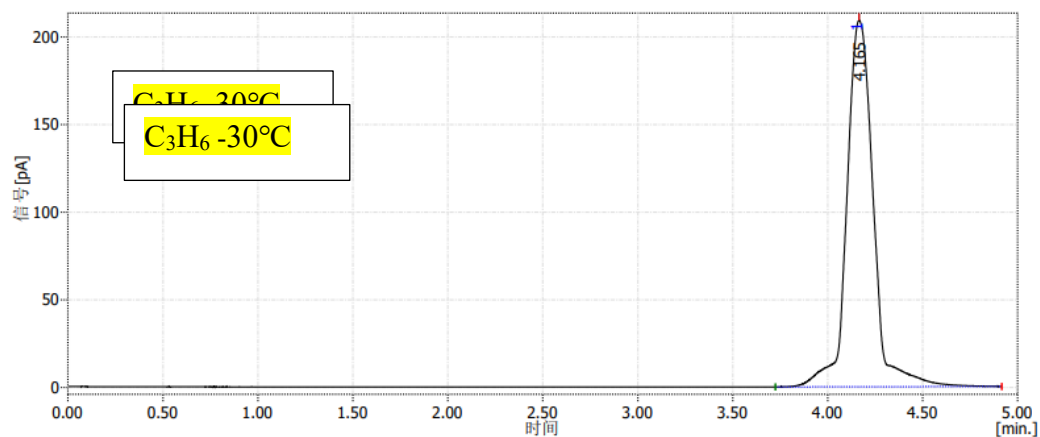
序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		4.1667	2600.9520	0.0000	100.0000	
总计			2600.9520	0.0000	100	0.0000

Figure S81 Original GC spectra at 30°C (10 mL/min , Feed gas ratio: 1vol % C₃H₆ and 99vol% air)



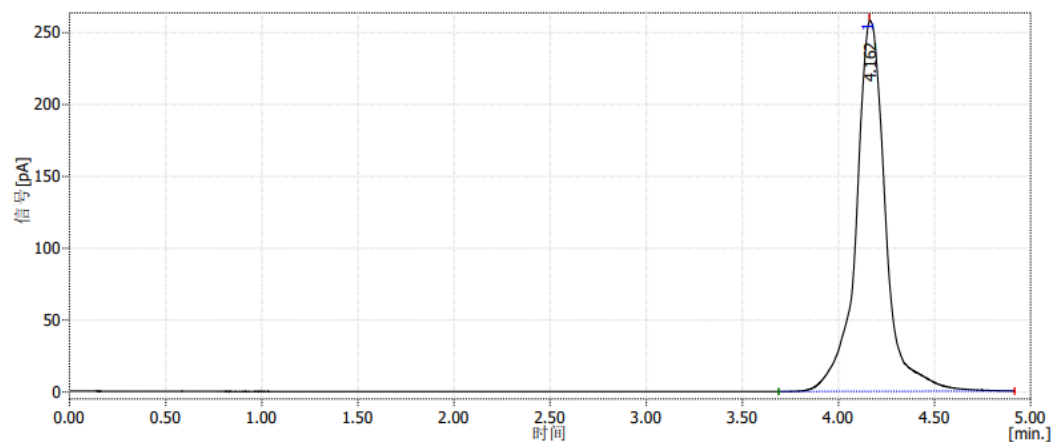
序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		4.1809	2242.4360	0.0000	100.0000	
总计			2242.4360	0.0000	100	0.0000

Figure S82 Original GC spectra at 30°C (10 mL/min , Feed gas ratio: 1vol % C₃H₆ and 99vol% air)



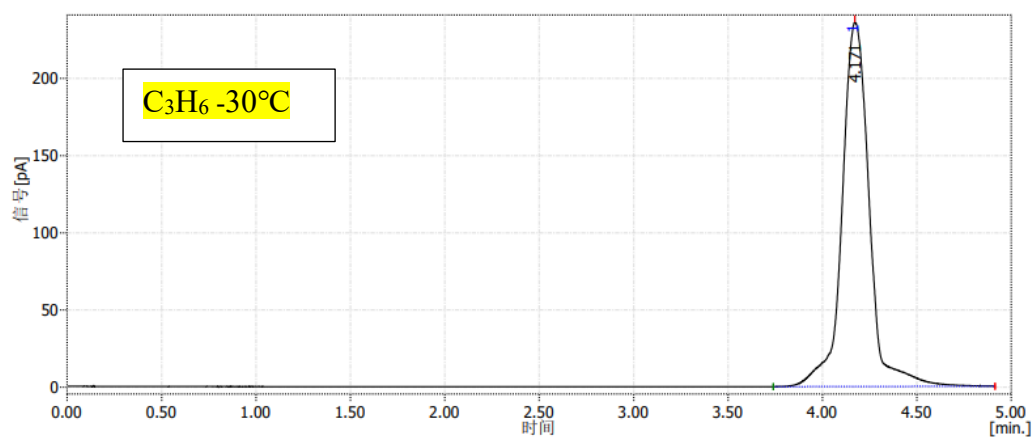
序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		4.1650	2022.6510	0.0000	100.0000	
总计			2022.6510	0.0000	100	0.0000

Figure S83 Original GC spectra at 30°C (10 mL/min , Feed gas ratio: 1vol % C₃H₆ and 99vol% air)



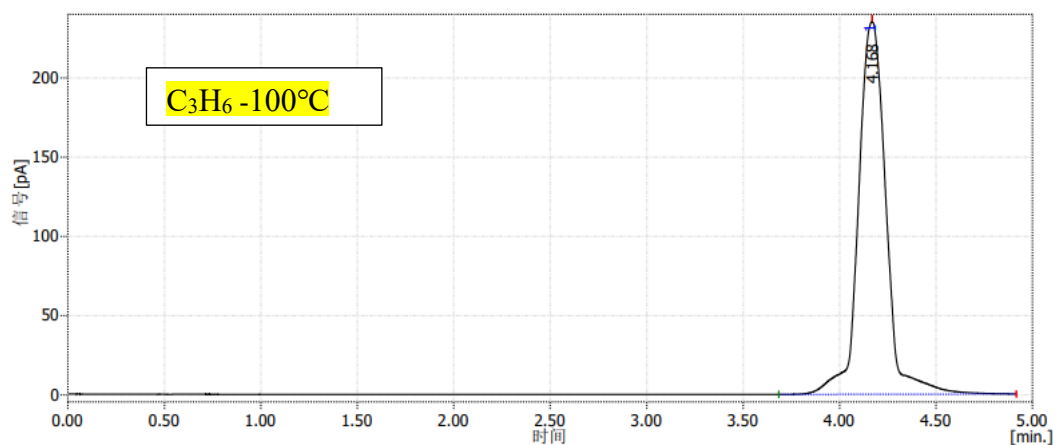
序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		4.1617	2761.2760	0.0000	100.0000	
总计			2761.2760	0.0000	100	0.0000

Figure S84 Original GC spectra at 30°C (10 mL/min , Feed gas ratio: 1vol % C₃H₆ and 99vol% air)



序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		4.1709	2362.8190	0.0000	100.0000	
总计			2362.8190	0.0000	100	0.0000

Figure S85 Original GC spectra at $30^\circ C$ (10 mL/min , Feed gas ratio: 1vol % C_3H_6 and 99vol% air)



序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		4.1684	2323.6380	0.0000	100.0000	
总计			2323.6380	0.0000	100	0.0000

Figure S86 Original GC spectra at $100^\circ C$ (10 mL/min , Feed gas ratio: 1vol % C_3H_6 and 99vol% air)

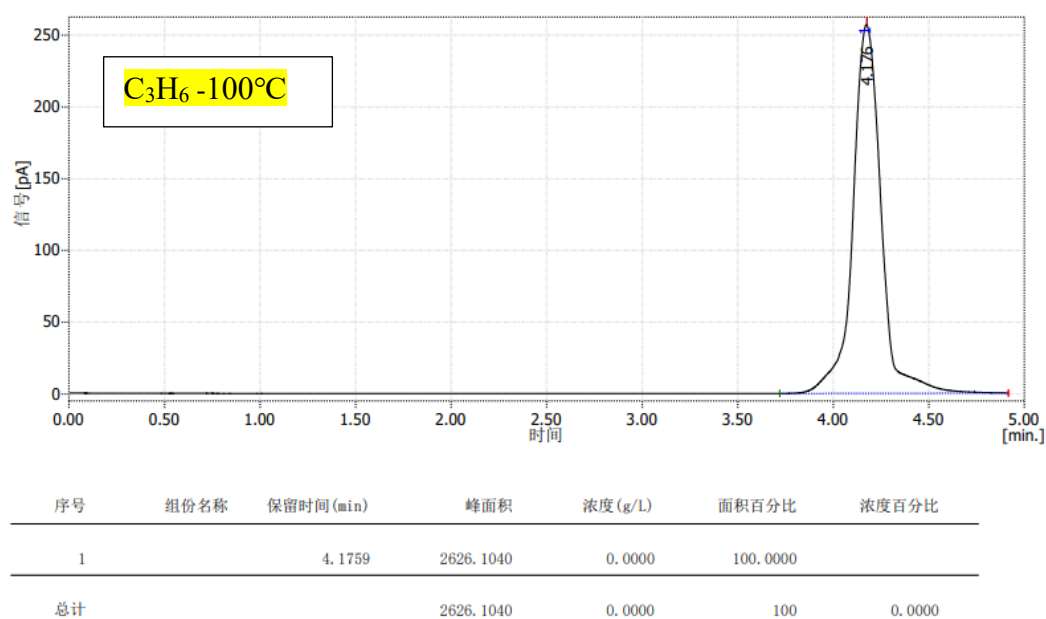


Figure S87 Original GC spectra at 100°C (10 mL/min , Feed gas ratio: 1vol % C₃H₆ and 99vol% air)

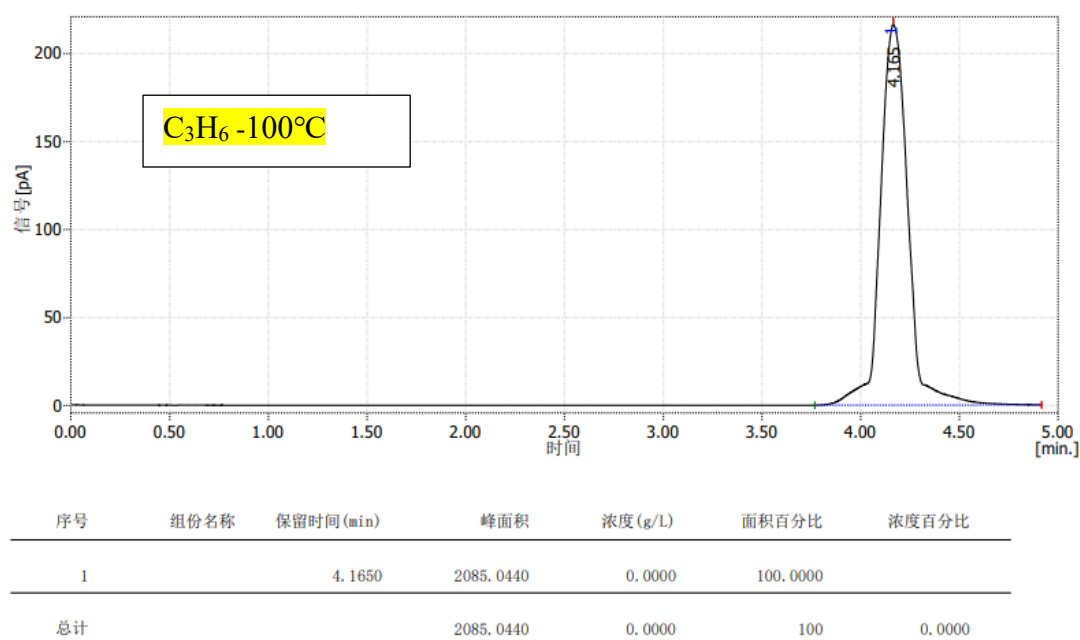


Figure S88 Original GC spectra at 100°C (10 mL/min , Feed gas ratio: 1vol % C₃H₆ and 99vol% air)

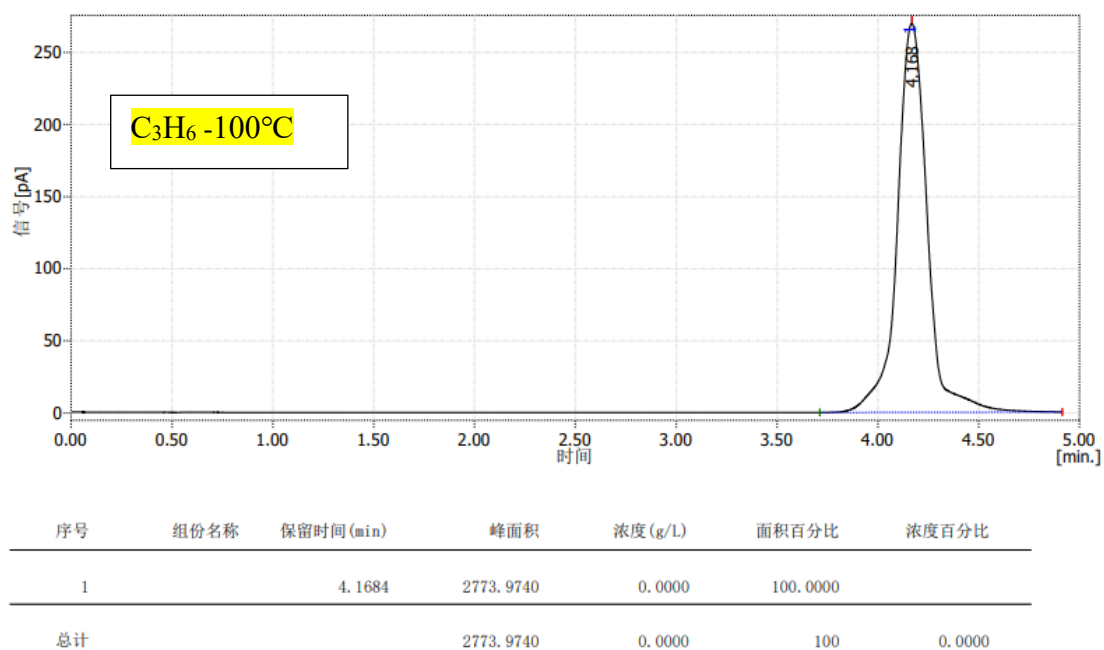


Figure S89 Original GC spectra at 100°C (10 mL/min , Feed gas ratio: 1vol % C₃H₆ and 99vol% air)

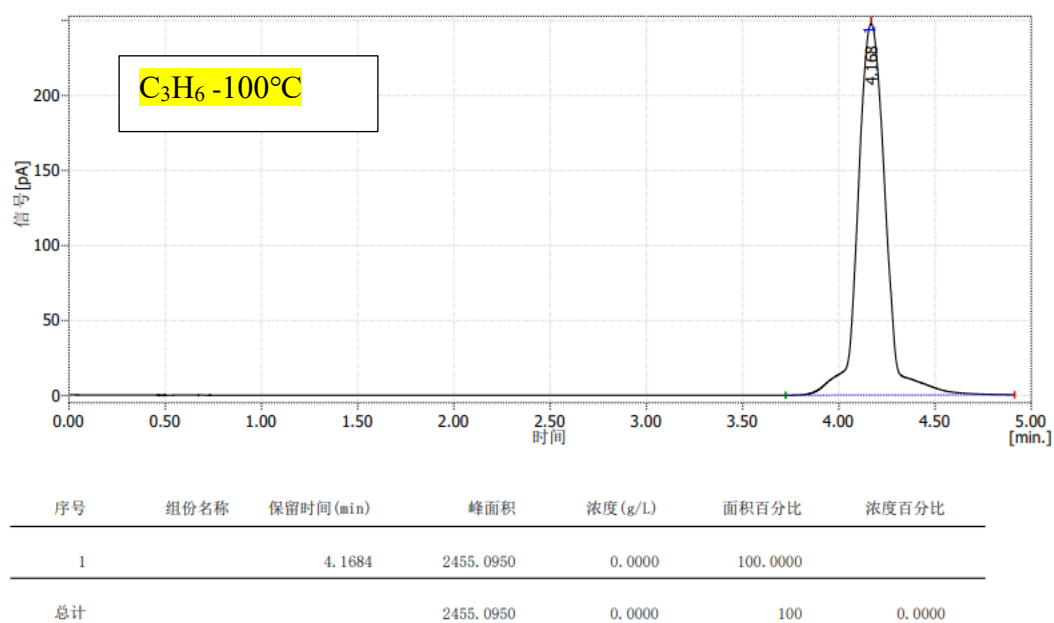
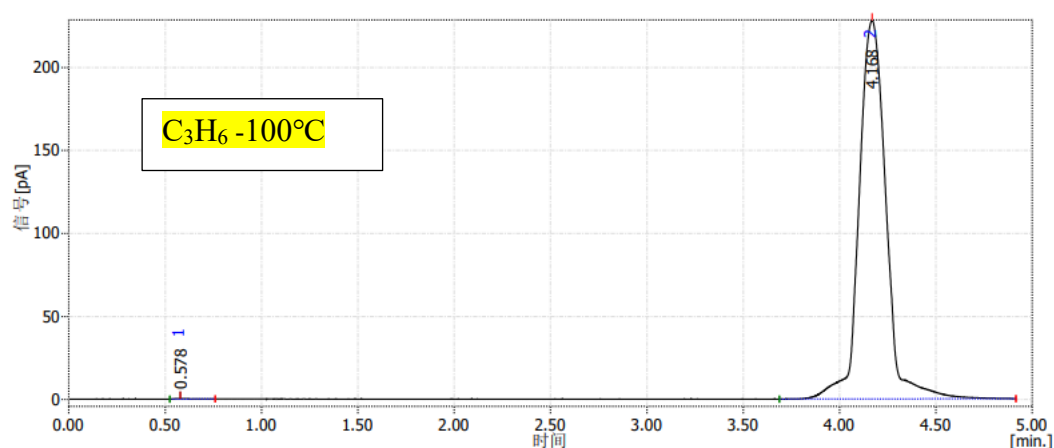
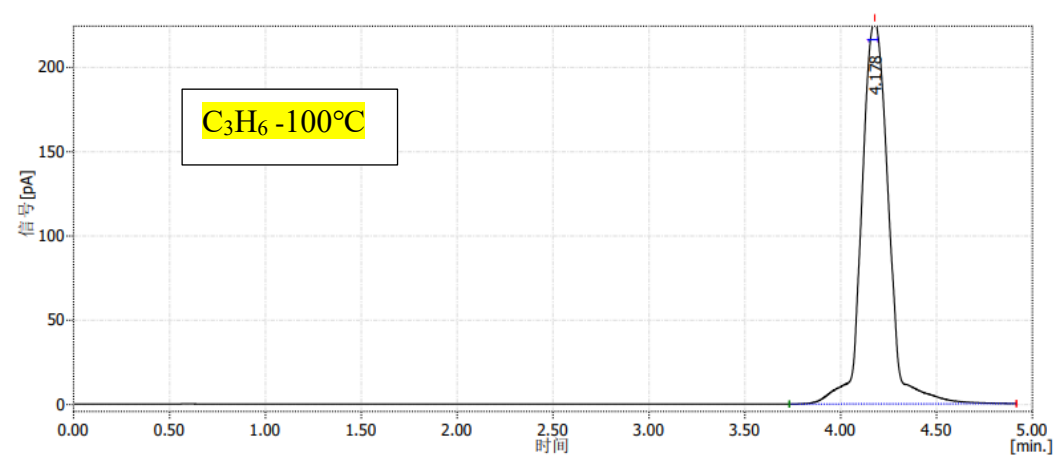


Figure S90 Original GC spectra at 100°C (10 mL/min , Feed gas ratio: 1vol % C₃H₆ and 99vol% air)



序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		0.5783	1.4409	0.0000	0.0652	
2		4.1684	2207.2600	0.0000	99.9348	
总计			2208.7010	0.0000	100	0.0000

Figure S91 Original GC spectra at $100^\circ C$ (10 mL/min , Feed gas ratio: 1vol % C_3H_6 and 99vol% air)



序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		4.1775	2201.5910	0.0000	100.0000	
总计			2201.5910	0.0000	100	0.0000

Figure S92 Original GC spectra at $100^\circ C$ (10 mL/min , Feed gas ratio: 1vol % C_3H_6 and 99vol% air)

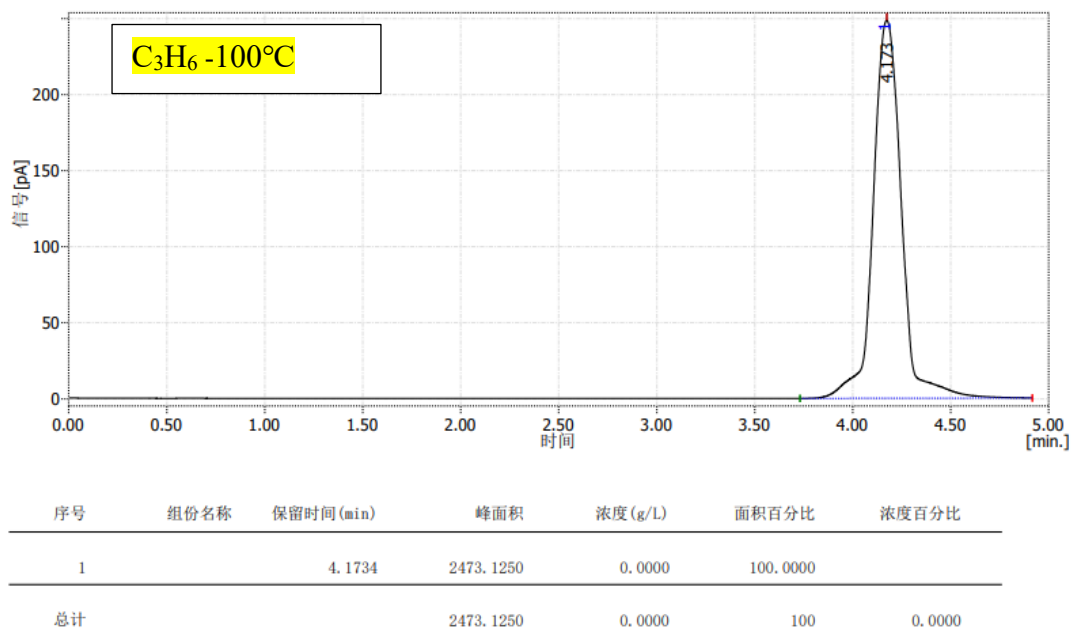


Figure S93 Original GC spectra at 100°C (10 mL/min , Feed gas ratio: 1vol % C₃H₆ and 99vol% air)

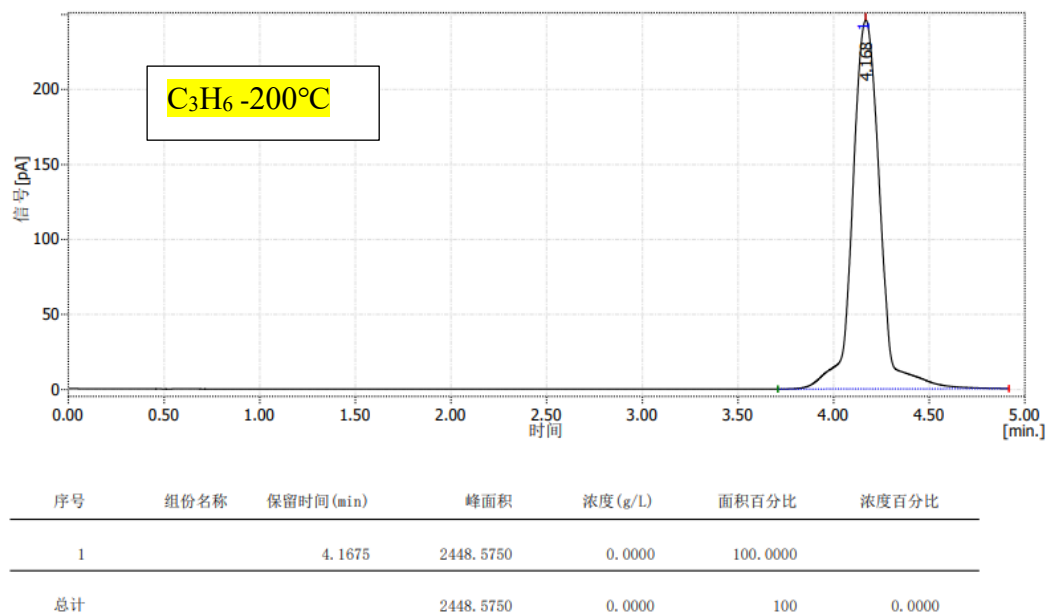
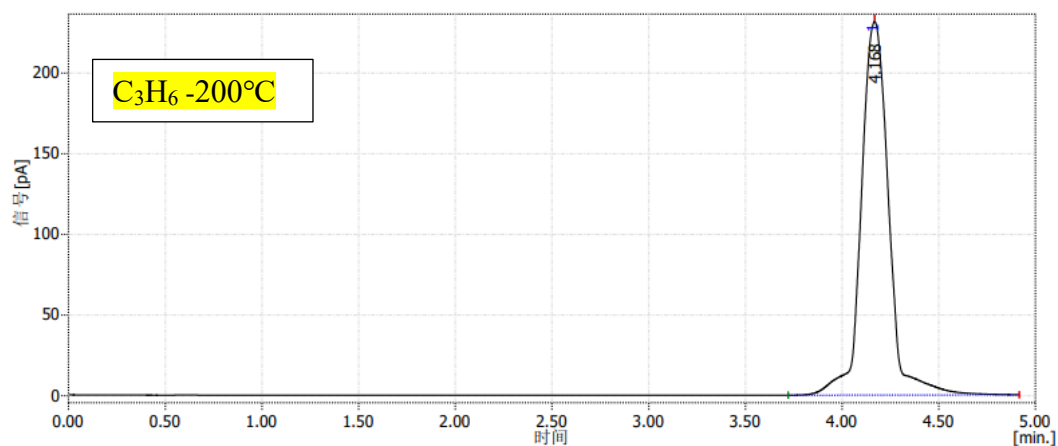
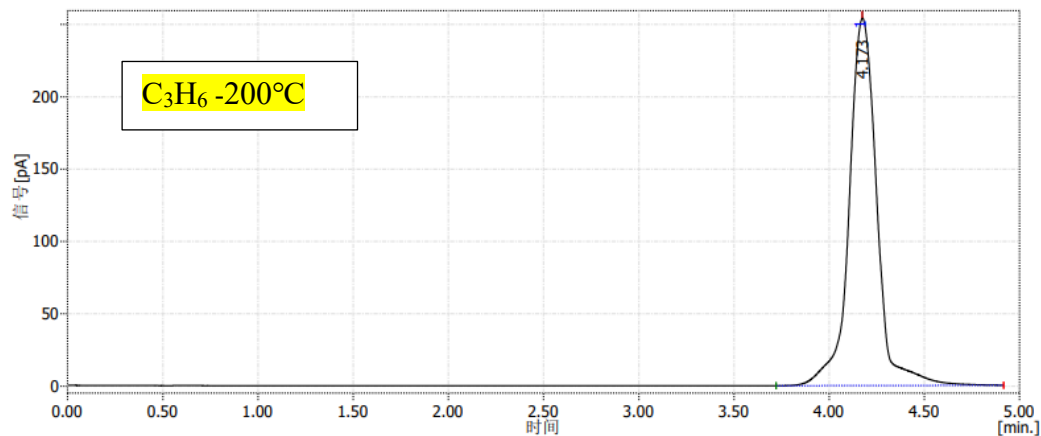


Figure S94 Original GC spectra at 200°C (10 mL/min , Feed gas ratio: 1vol % C₃H₆ and 99vol% air)



序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		4.1684	2273.3590	0.0000	100.0000	
总计			2273.3590	0.0000	100	0.0000

Figure S95 Original GC spectra at $200^\circ C$ (10 mL/min , Feed gas ratio: 1vol % C_3H_6 and 99vol% air)



序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		4.1734	2571.9280	0.0000	100.0000	
总计			2571.9280	0.0000	100	0.0000

Figure S96 Original GC spectra at $200^\circ C$ (10 mL/min , Feed gas ratio: 1vol % C_3H_6 and 99vol% air)

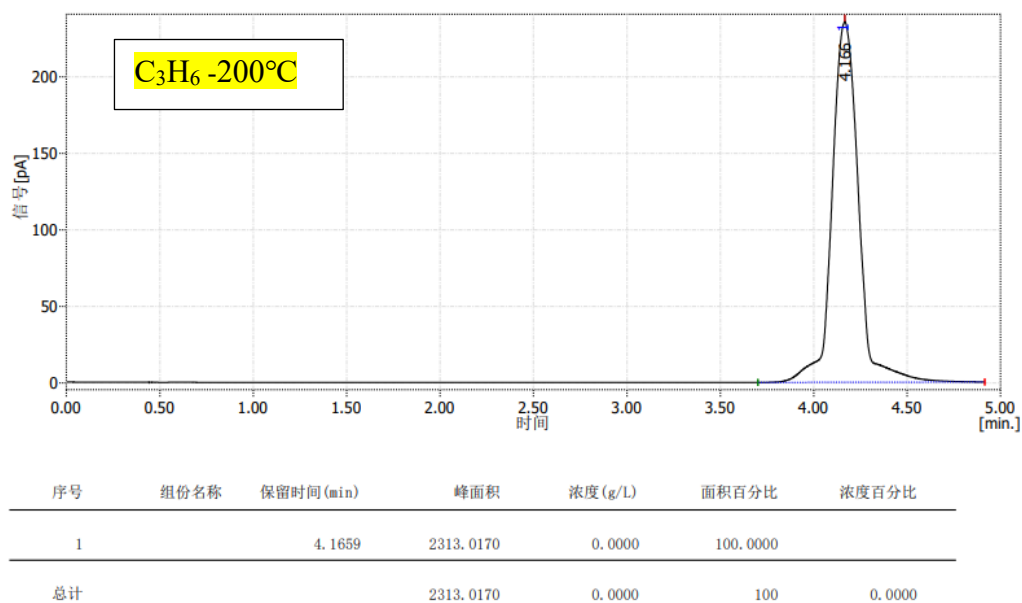


Figure S97 Original GC spectra at $200^\circ C$ (10 mL/min , Feed gas ratio: 1vol % C_3H_6 and 99vol% air)

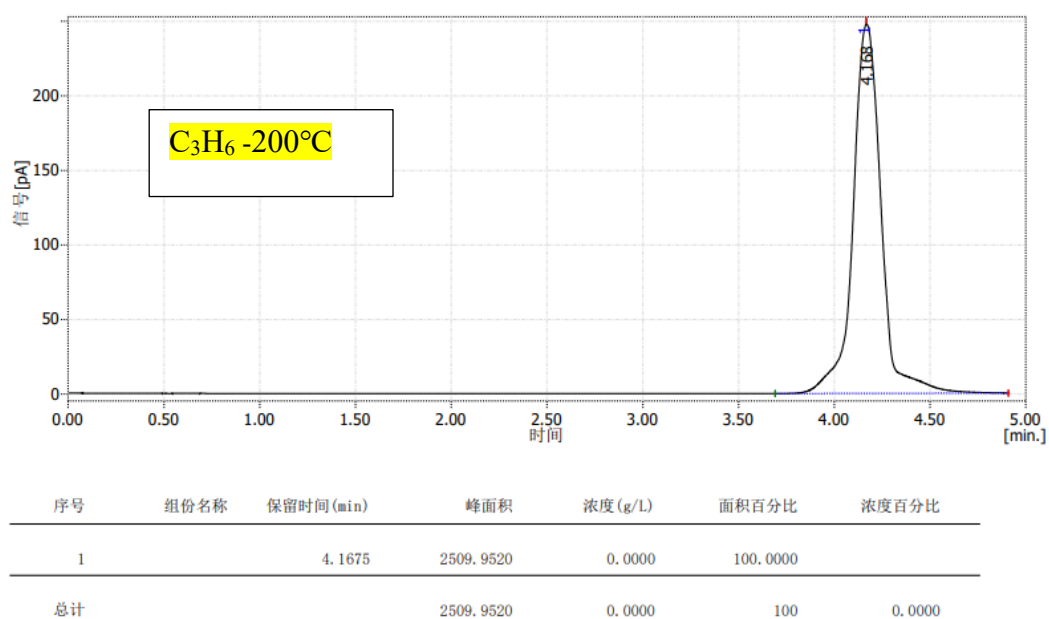


Figure S98 Original GC spectra at $200^\circ C$ (10 mL/min , Feed gas ratio: 1vol % C_3H_6 and 99vol% air)

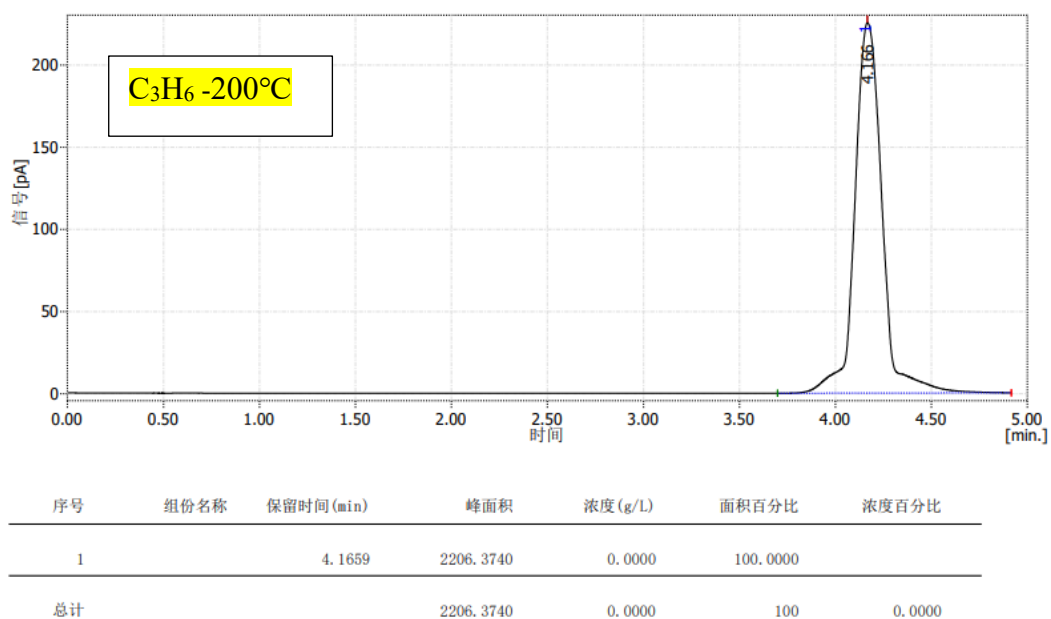


Figure S99 Original GC spectra at 200°C (10 mL/min , Feed gas ratio: 1vol % C₃H₆ and 99vol% air)

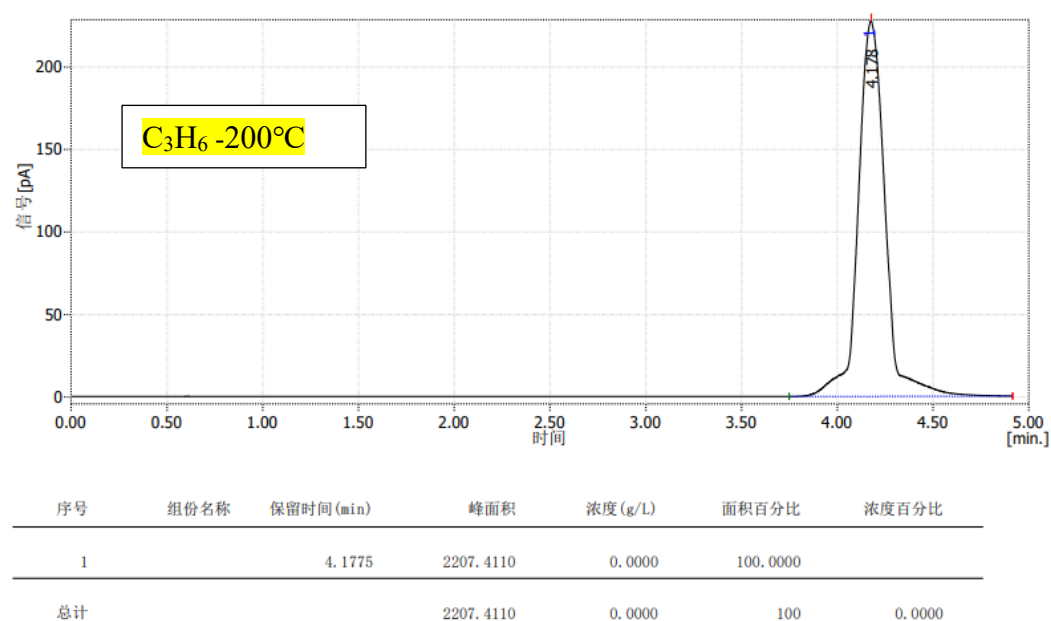


Figure S100 Original GC spectra at 200°C (10 mL/min , Feed gas ratio: 1vol % C₃H₆ and 99vol% air)

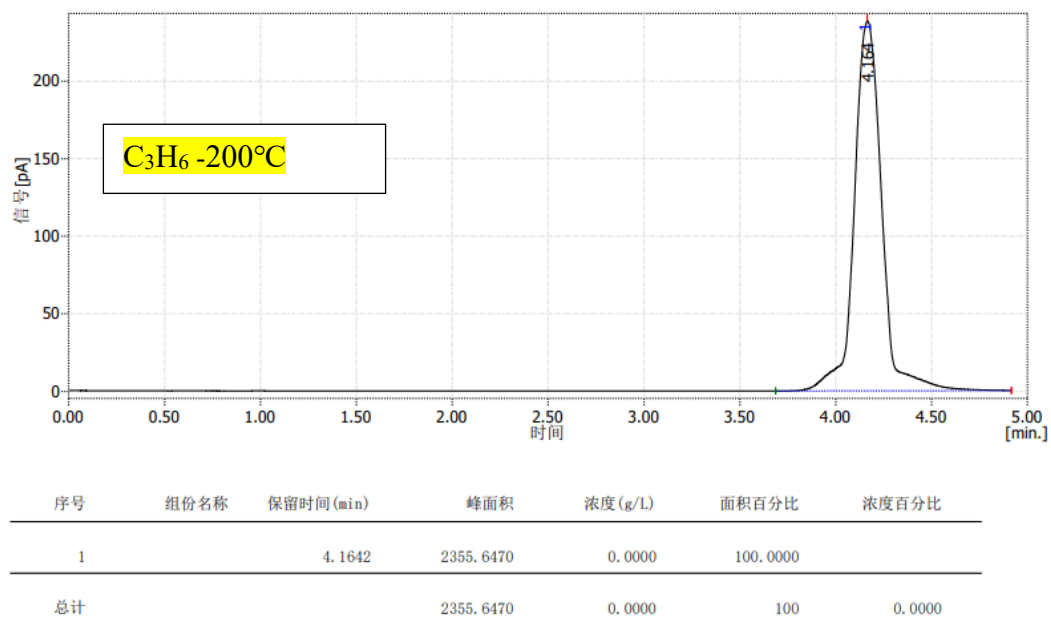


Figure S901 Original GC spectra at 200°C (10 mL/min , Feed gas ratio: 1vol % C₃H₆ and 99vol% air)

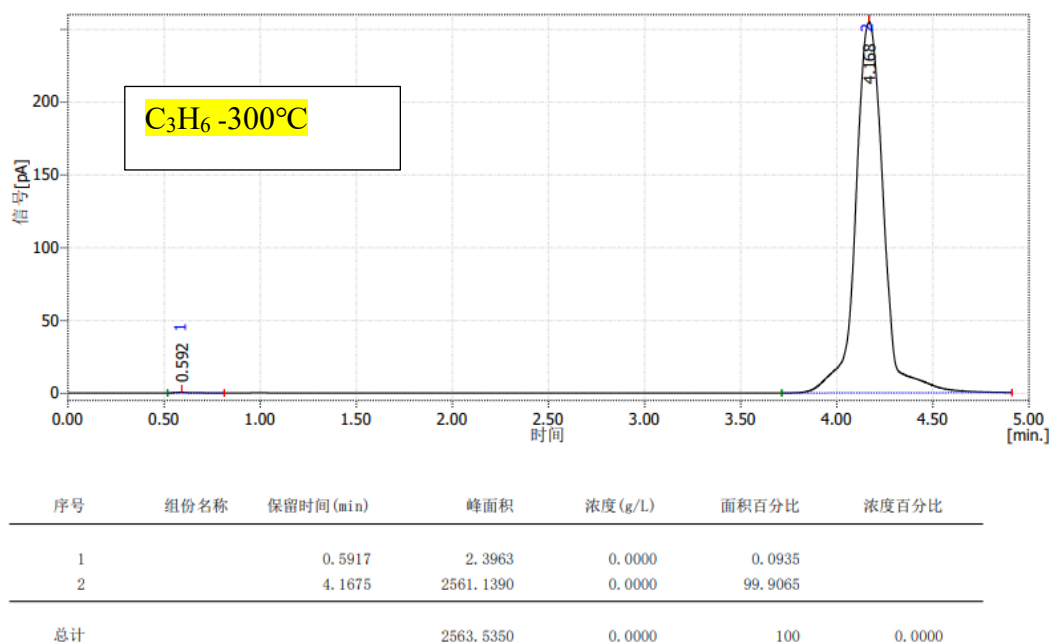


Figure S102 Original GC spectra at 300°C (10 mL/min , Feed gas ratio: 1vol % C₃H₆ and 99vol% air)

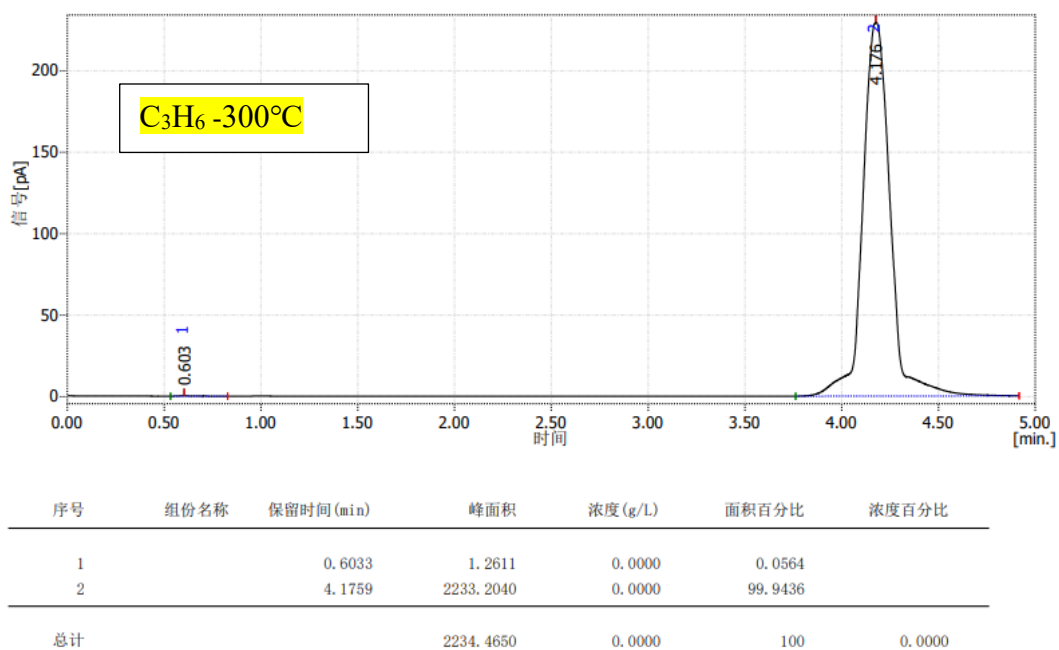


Figure S103 Original GC spectra at 300°C (10 mL/min , Feed gas ratio: 1vol % C_3H_6 and 99vol% air)

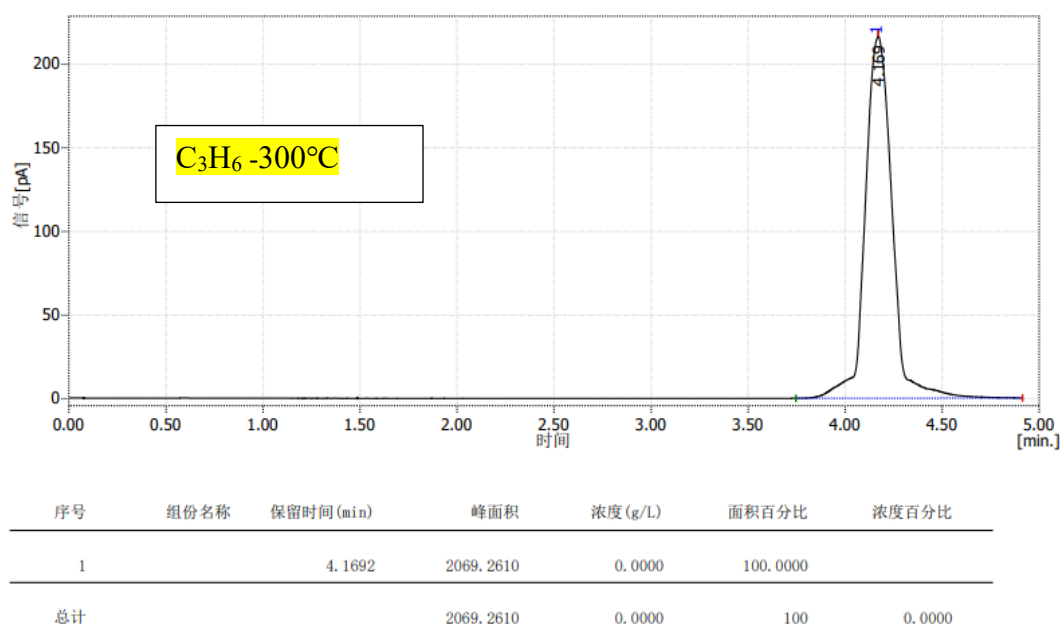


Figure S104 Original GC spectra at 300°C (10 mL/min , Feed gas ratio: 1vol % C_3H_6 and 99vol% air)

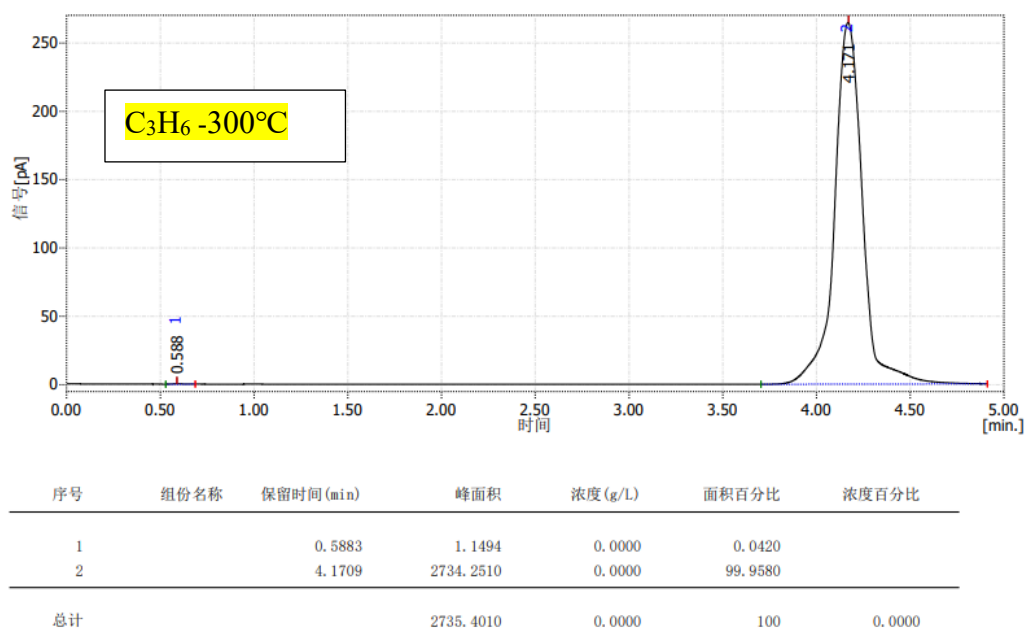


Figure S105 Original GC spectra at 300°C (10 mL/min , Feed gas ratio: 1vol % C₃H₆ and 99vol% air)

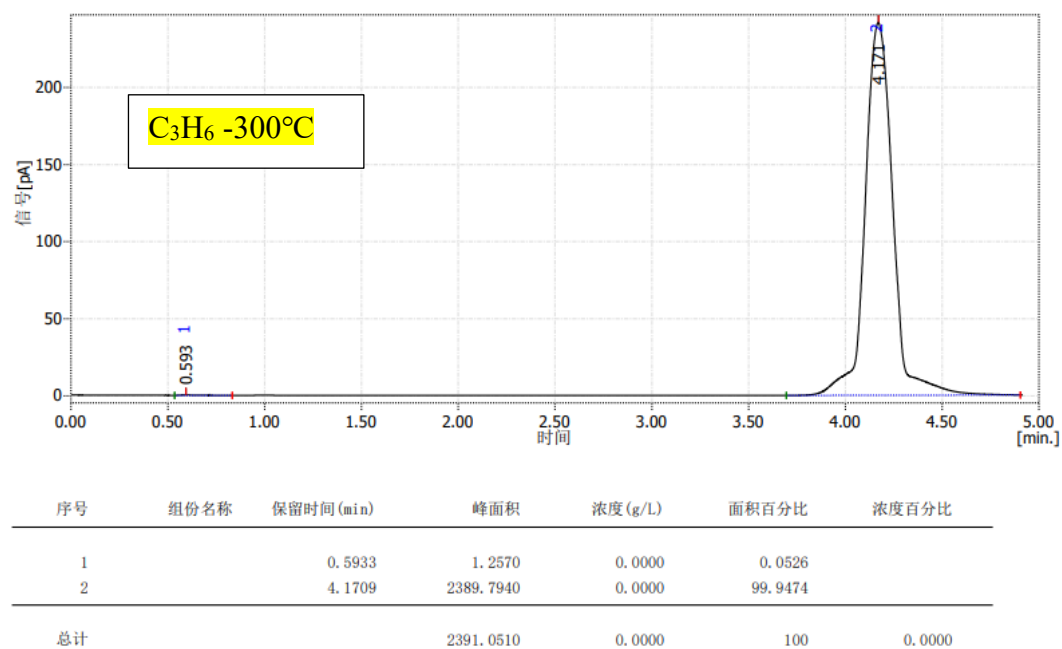
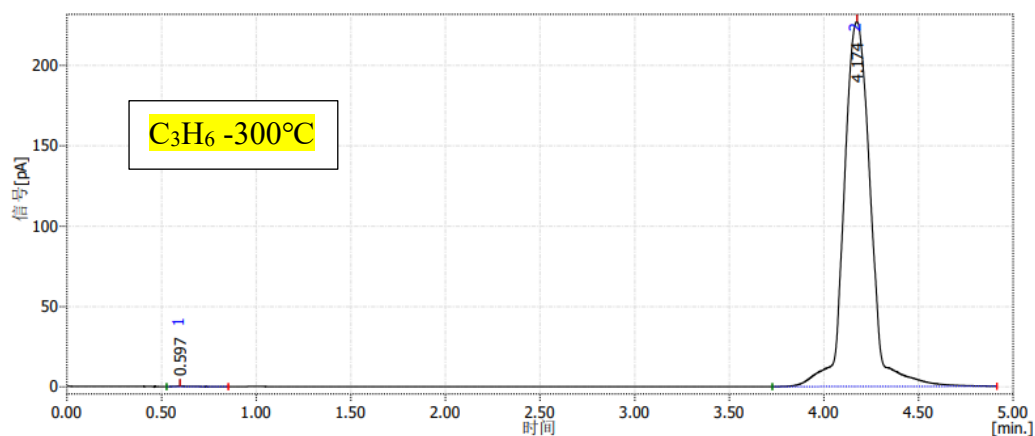
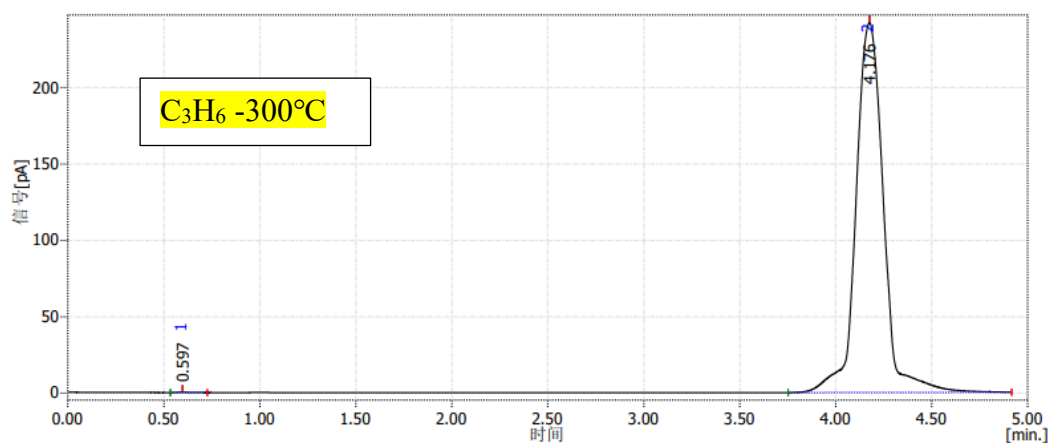


Figure S106 Original GC spectra at 300°C (10 mL/min , Feed gas ratio: 1vol % C₃H₆ and 99vol% air)



序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		0.5967	1.1059	0.0000	0.0502	
2		4.1742	2201.6100	0.0000	99.9498	
总计			2202.7160	0.0000	100	0.0000

Figure S107 Original GC spectra at $300^\circ C$ (10 mL/min , Feed gas ratio: 1vol % C_3H_6 and 99vol% air)



序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		0.5967	1.1515	0.0000	0.0480	
2		4.1759	2398.3680	0.0000	99.9520	
总计			2399.5190	0.0000	100	0.0000

Figure S108 Original GC spectra at $300^\circ C$ (10 mL/min , Feed gas ratio: 1vol % C_3H_6 and 99vol% air)

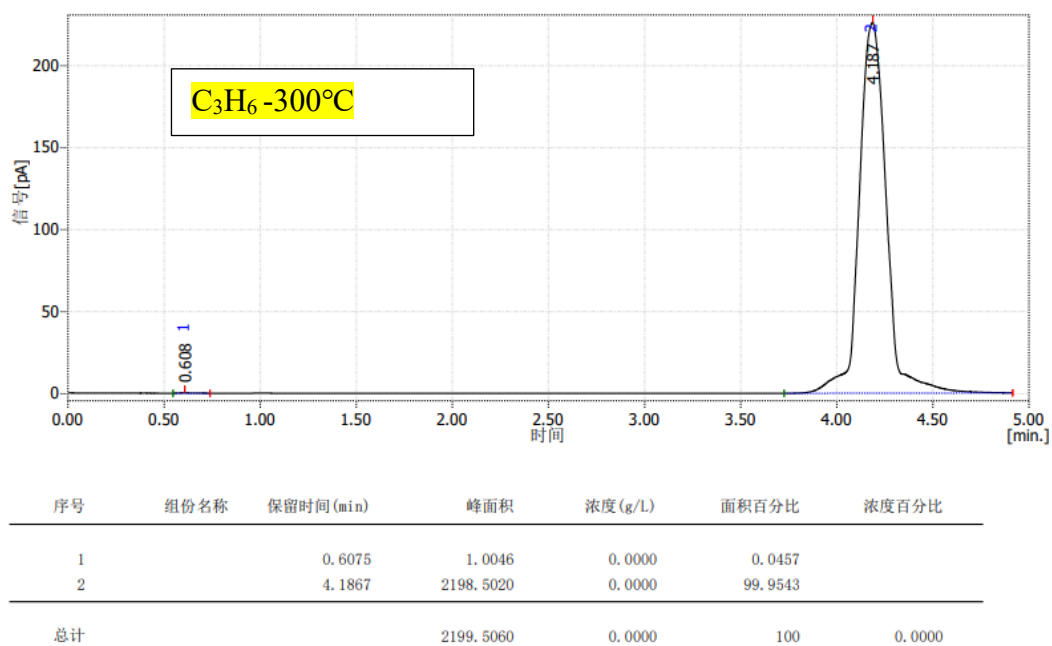


Figure S109 Original GC spectra at 300°C (10 mL/min , Feed gas ratio: 1vol % C₃H₆ and 99vol% air)

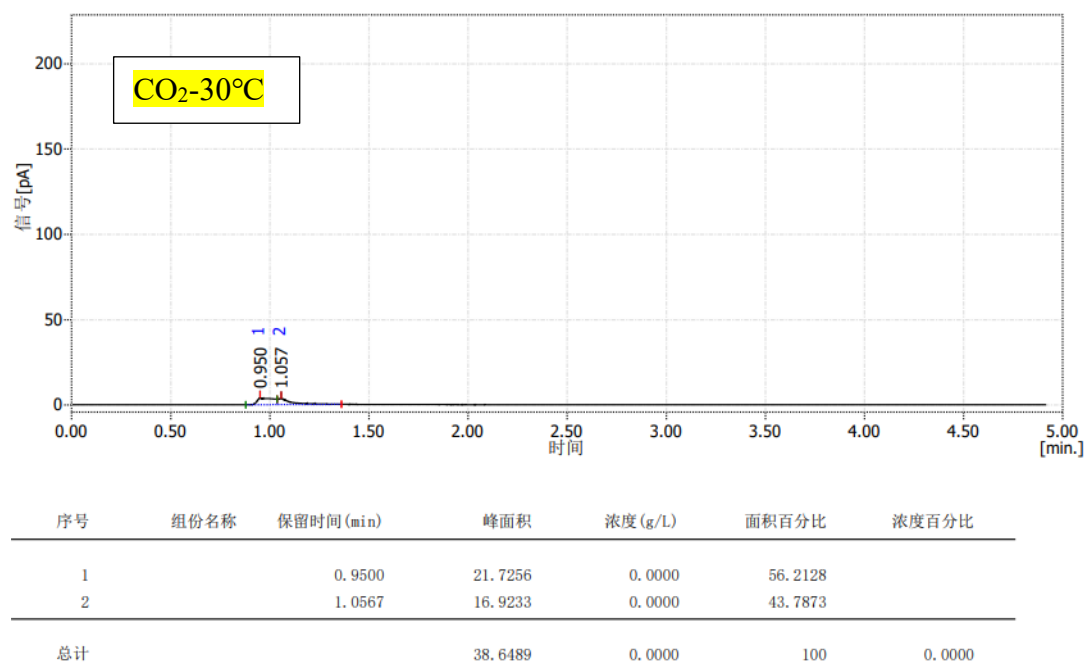


Figure S110 Original GC spectra at 30°C (10 mL/min , Feed gas ratio: 1vol % CO₂ and 99vol% N₂).

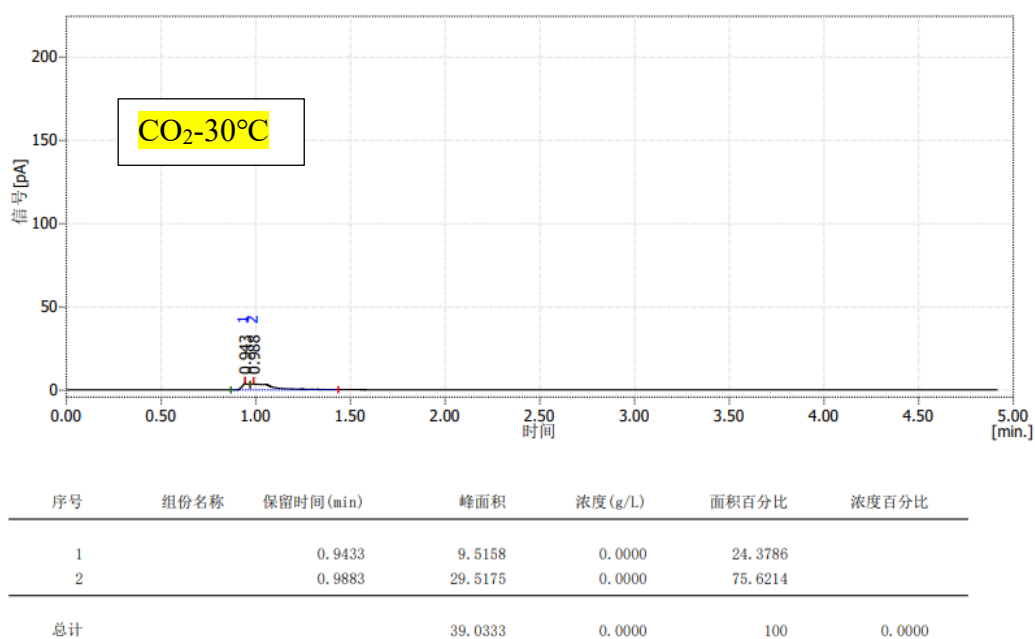


Figure S111 Original GC spectra at 30°C (10 mL/min , Feed gas ratio: 1vol % CO₂ and 99vol% N₂).

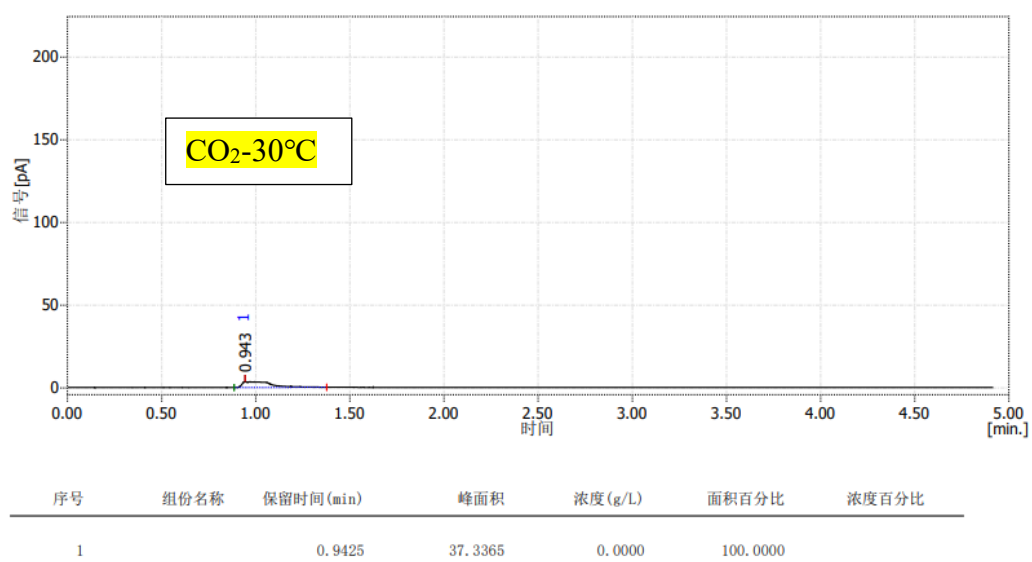


Figure S112 Original GC spectra at 30°C (10 mL/min , Feed gas ratio: 1vol % CO₂ and 99vol% N₂).

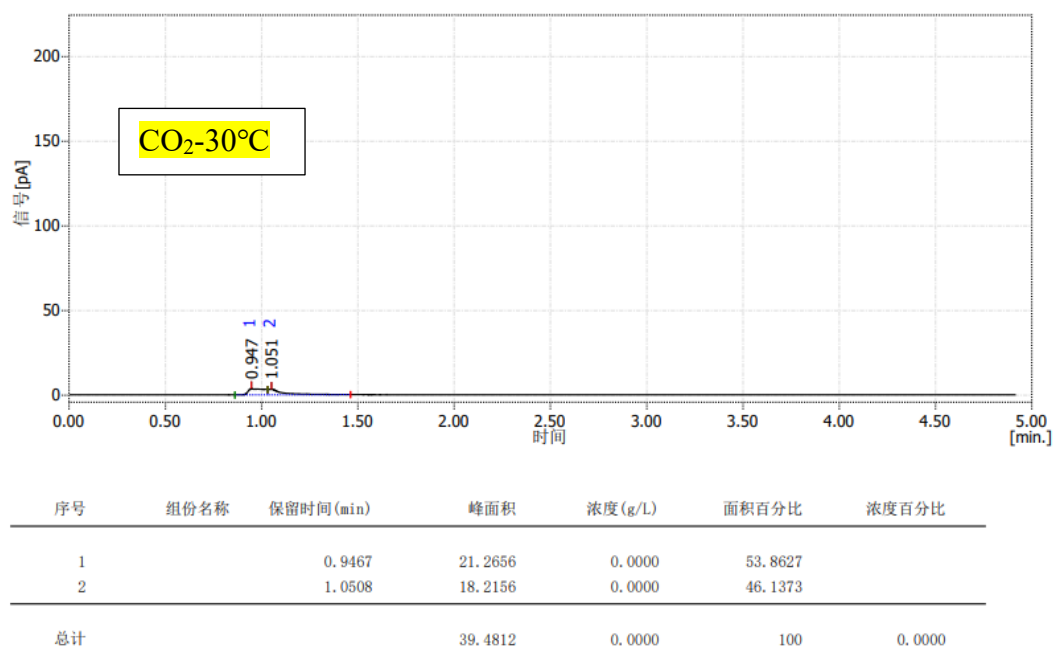


Figure S113 Original GC spectra at 30°C (10 mL/min , Feed gas ratio: 1vol % CO₂ and 99vol% N₂).

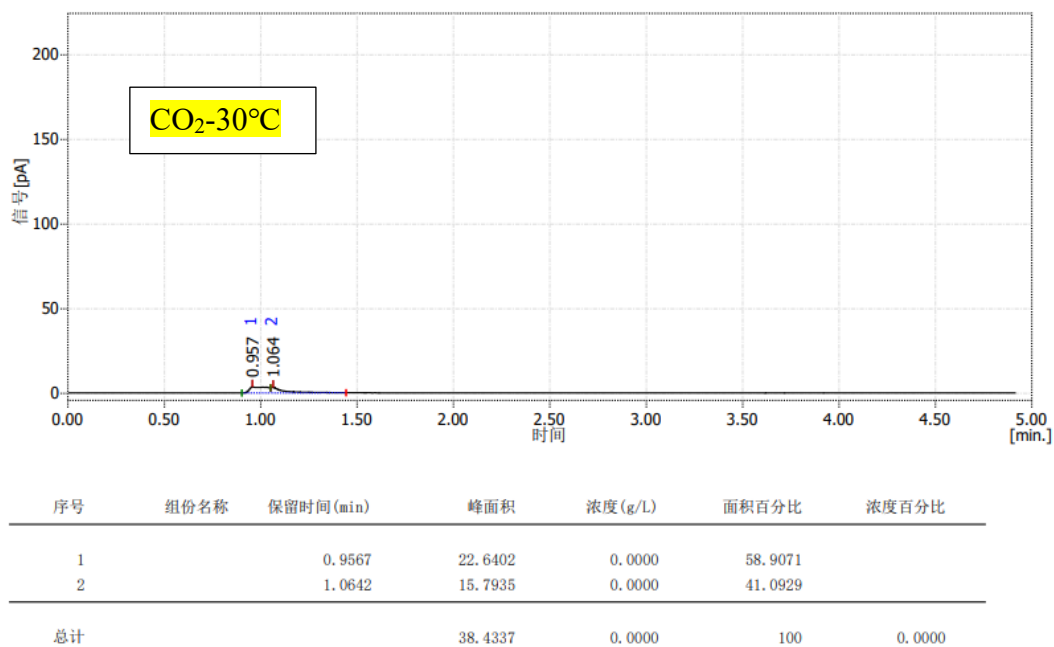


Figure S114 Original GC spectra at 30°C (10 mL/min , Feed gas ratio: 1vol % CO₂ and 99vol% N₂).

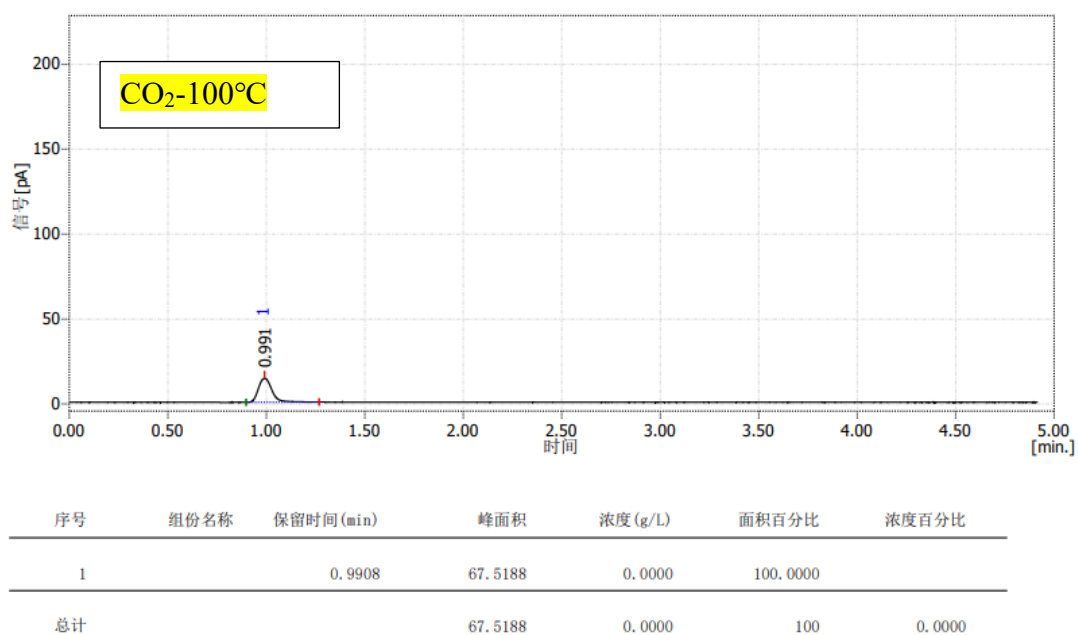


Figure S115 Original GC spectra at 100°C (10 mL/min , Feed gas ratio: 1vol % CO₂ and 99vol% N₂).

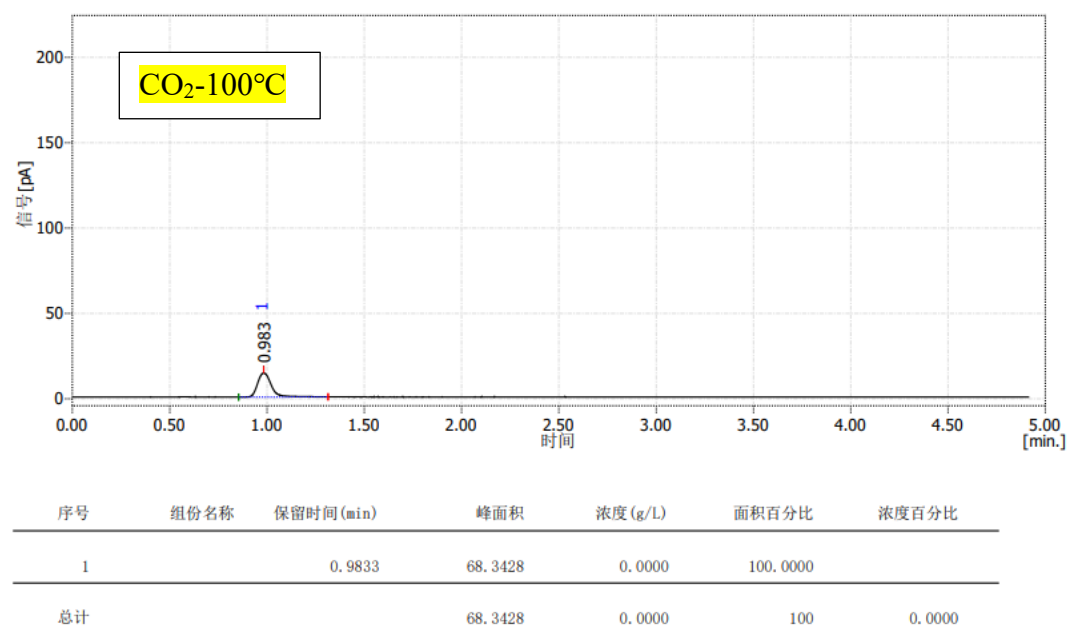
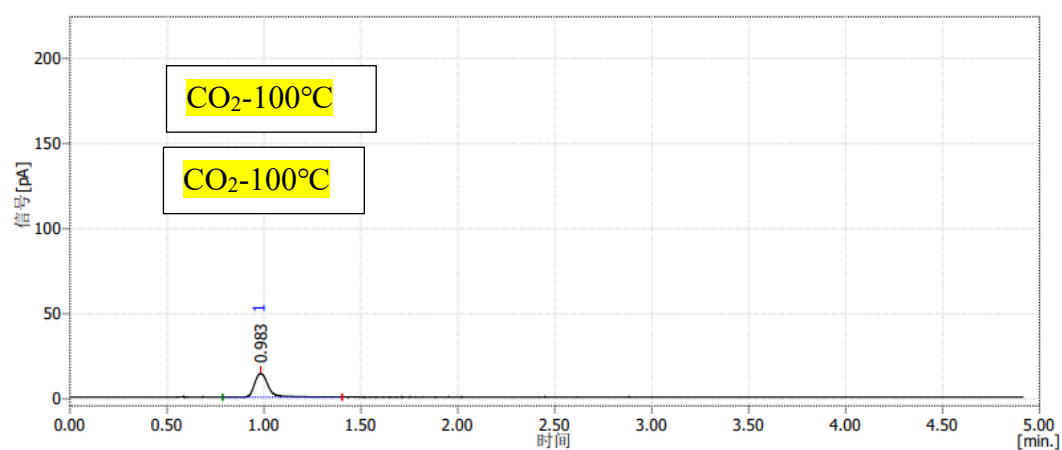
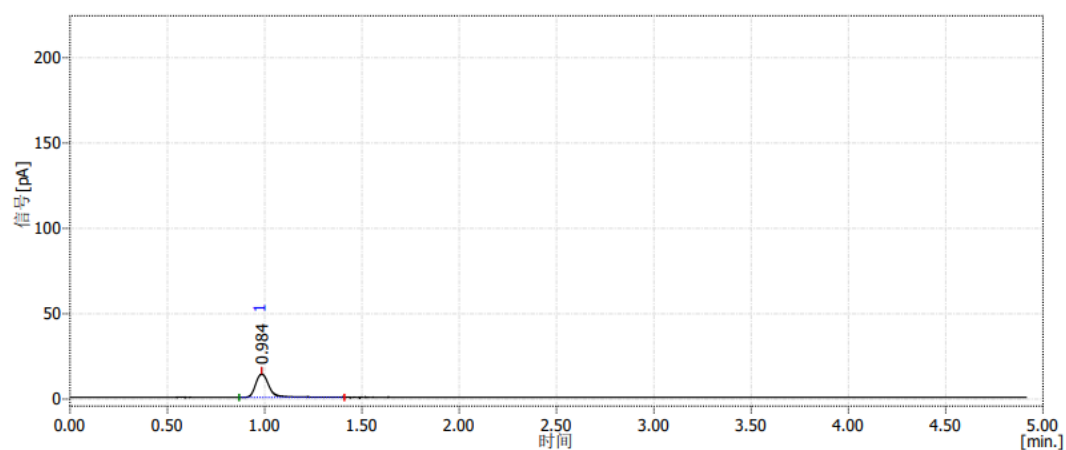


Figure S116 Original GC spectra at 100°C (10 mL/min , Feed gas ratio: 1vol % CO₂ and 99vol% N₂).



序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		0.9825	68.8857	0.0000	100.0000	
总计			68.8857	0.0000	100	0.0000

Figure S117 Original GC spectra at 100°C (10 mL/min , Feed gas ratio: 1vol % CO₂ and 99vol% N₂).



序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		0.9842	65.8524	0.0000	100.0000	
总计			65.8524	0.0000	100	0.0000

Figure S118 Original GC spectra at 100°C (10 mL/min , Feed gas ratio: 1vol % CO₂ and 99vol% N₂).

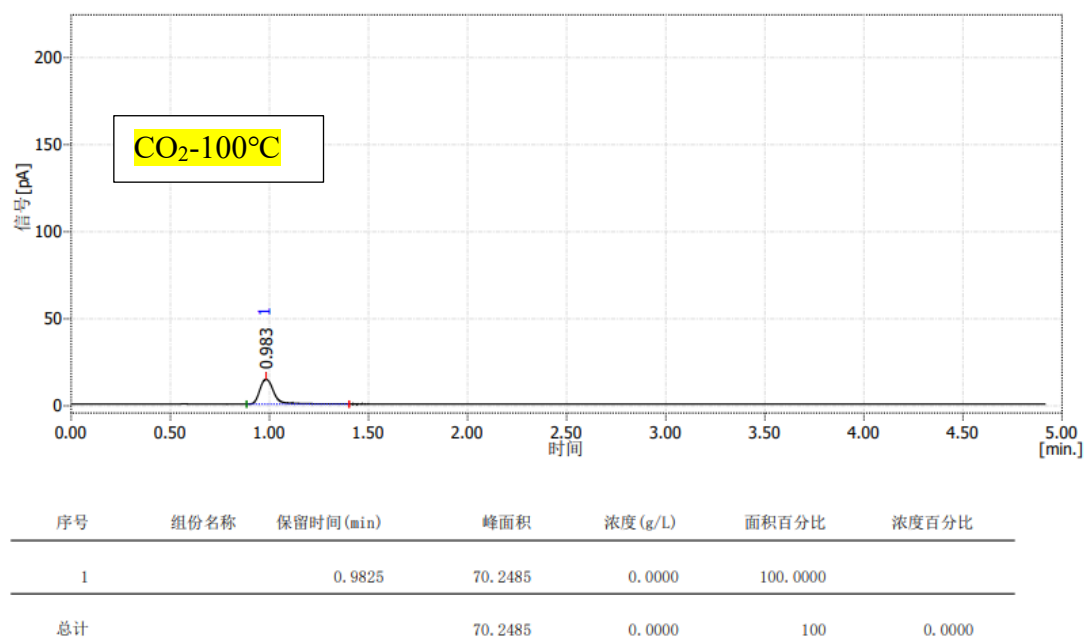


Figure S119 Original GC spectra at 100°C (10 mL/min , Feed gas ratio: 1vol % CO₂ and 99vol% N₂).

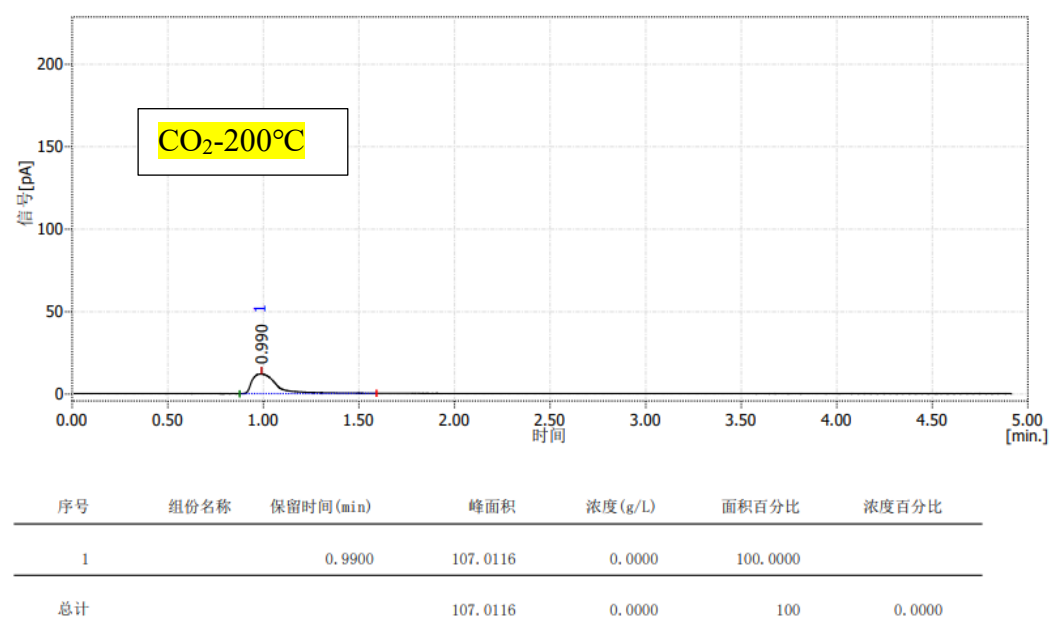


Figure S120 Original GC spectra at 200°C (10 mL/min , Feed gas ratio: 1vol % CO₂ and 99vol% N₂).

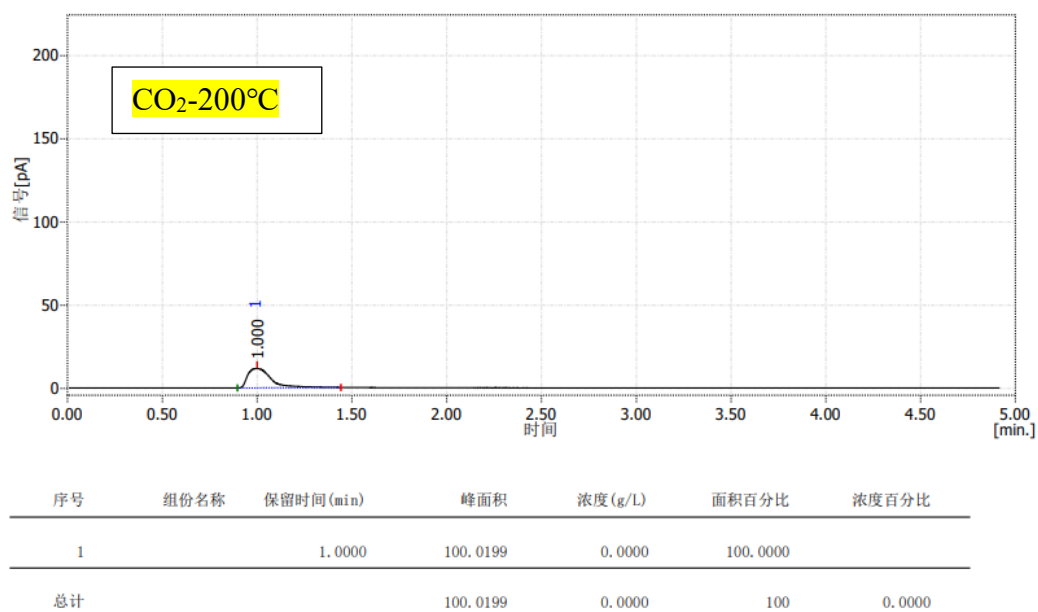


Figure S121 Original GC spectra at 200°C (10 mL/min , Feed gas ratio: 1vol % CO₂ and 99vol% N₂).

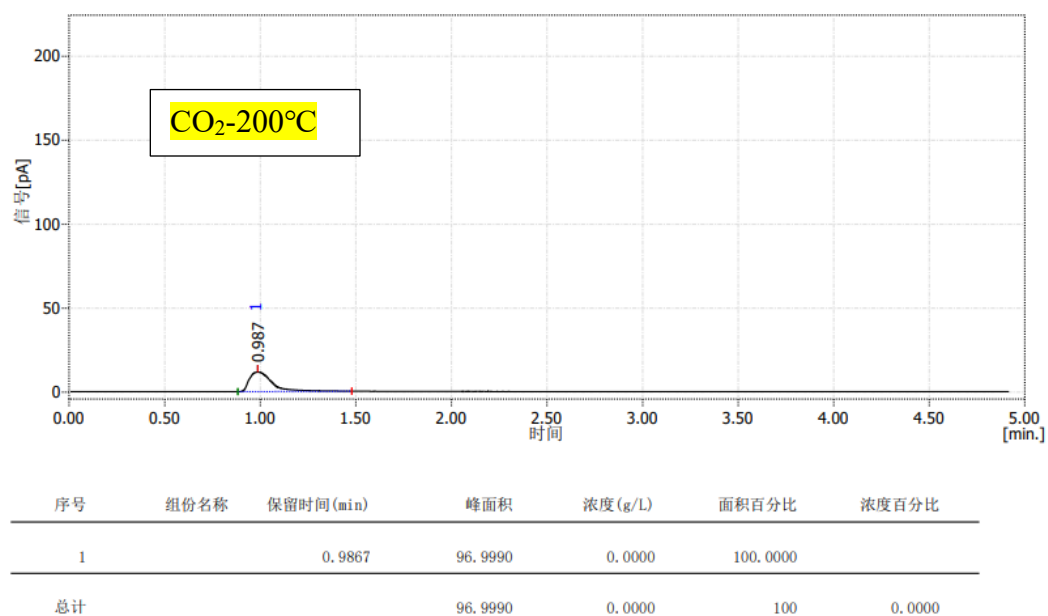
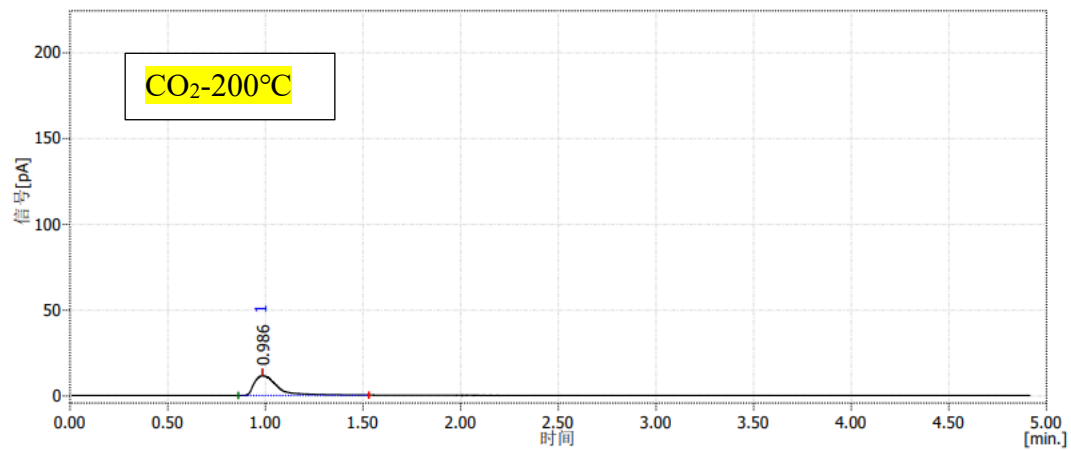
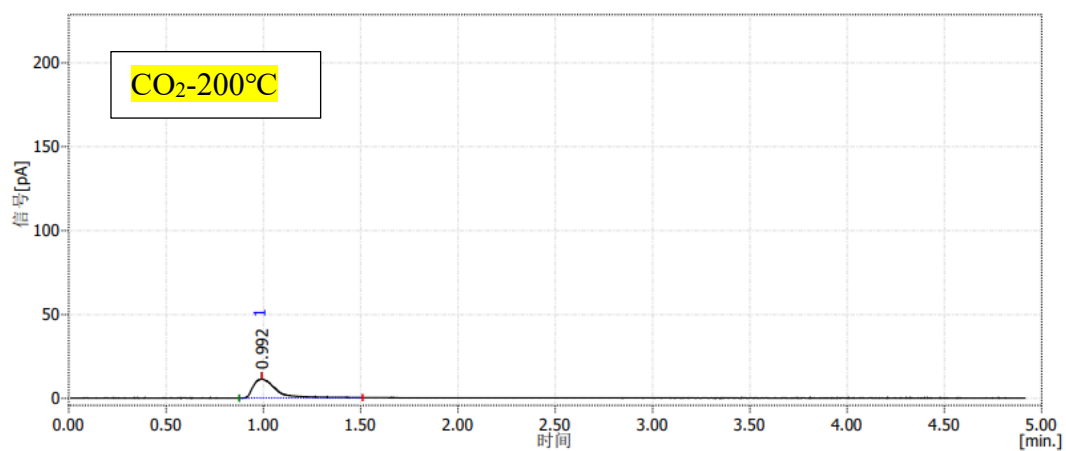


Figure S122 Original GC spectra at 200°C (10 mL/min , Feed gas ratio: 1vol % CO₂ and 99vol% N₂).



序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		0.9858	95.3822	0.0000	100.0000	
总计			95.3822	0.0000	100	0.0000

Figure S123 Original GC spectra at 200°C (10 mL/min , Feed gas ratio: 1vol % CO₂ and 99vol% N₂).



序号	组份名称	保留时间 (min)	峰面积	浓度 (g/L)	面积百分比	浓度百分比
1		0.9917	91.5865	0.0000	100.0000	
总计			91.5865	0.0000	100	0.0000

Figure S124 Original GC spectra at 200°C (10 mL/min , Feed gas ratio: 1vol % CO₂ and 99vol% N₂).

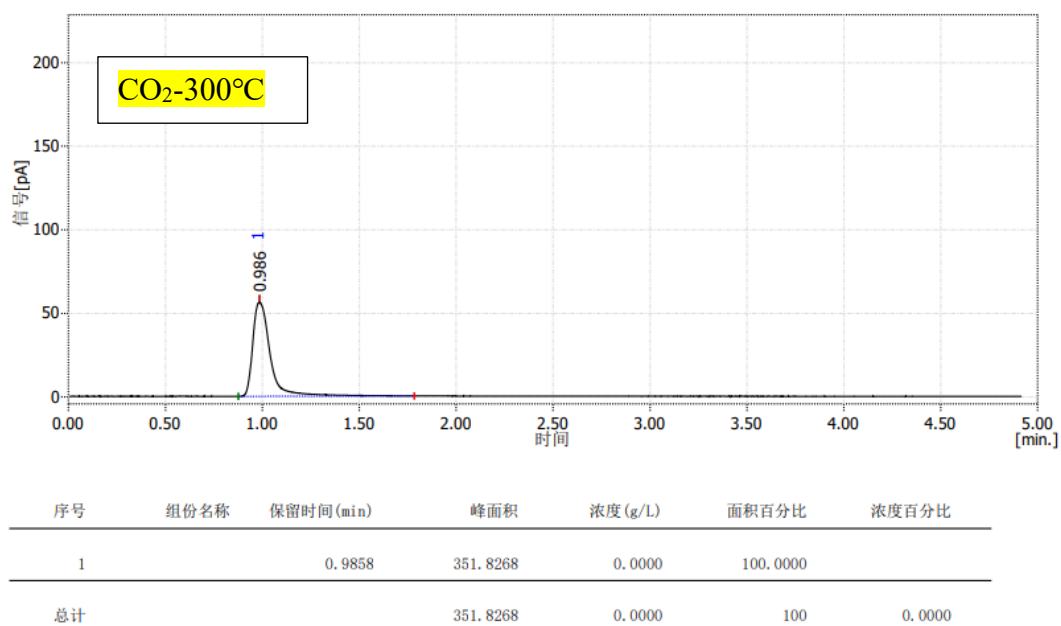


Figure S125 Original GC spectra at 300°C (10 mL/min , Feed gas ratio: 1 vol % CO₂ and 99vol% N₂).

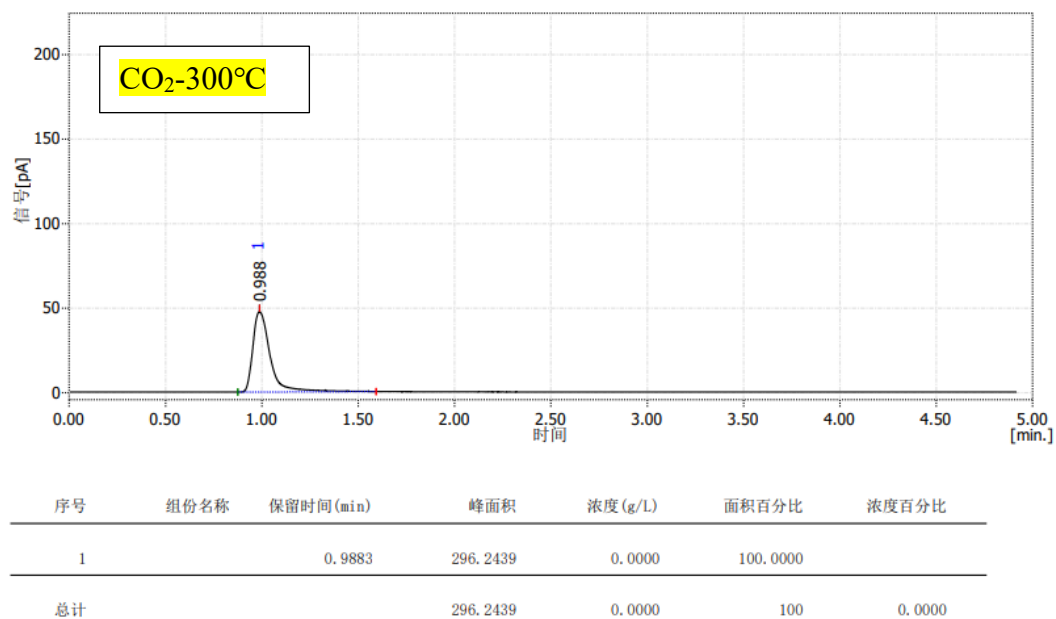


Figure S126 Original GC spectra at 300°C (10 mL/min , Feed gas ratio: 1 vol % CO₂ and 99vol% N₂).

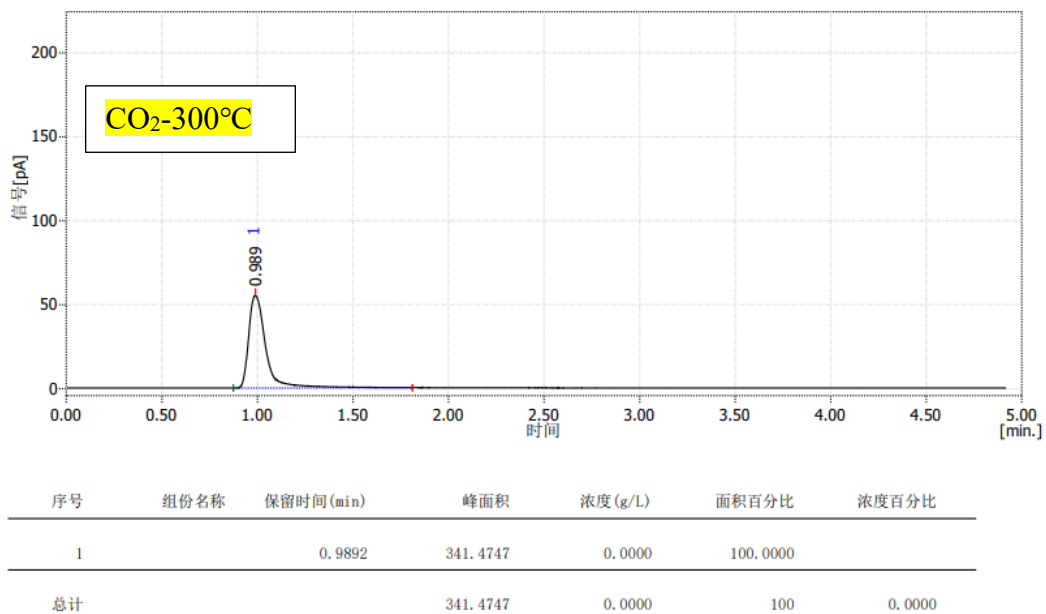


Figure S127 Original GC spectra at 300°C (10 mL/min , Feed gas ratio: 1vol % CO₂ and 99vol% N₂).

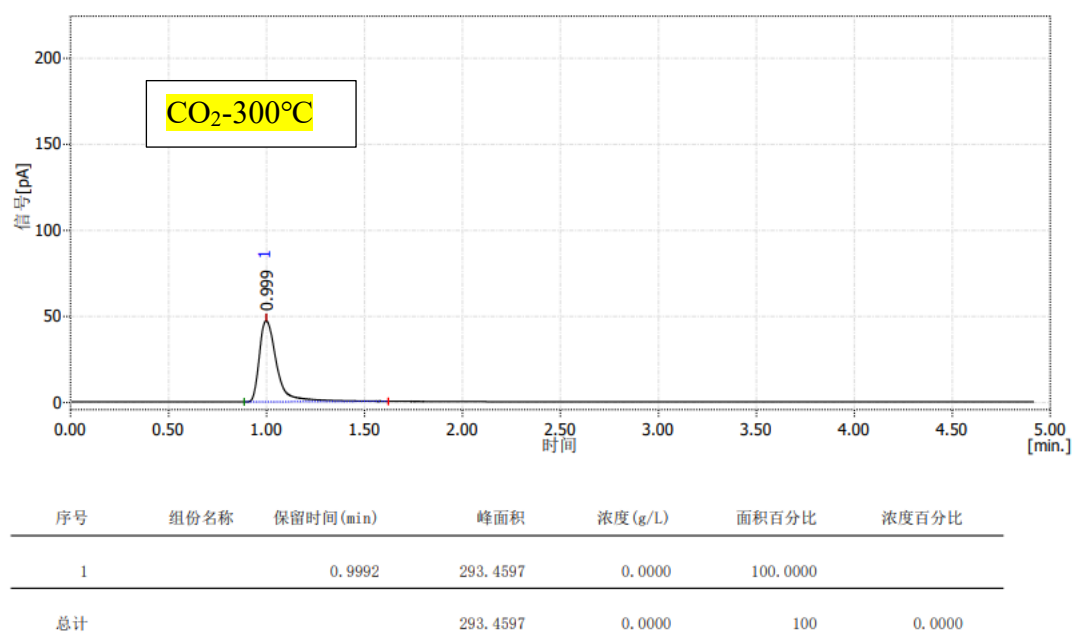


Figure S128 Original GC spectra at 300°C (10 mL/min , Feed gas ratio: 1vol % CO₂ and 99vol% N₂).

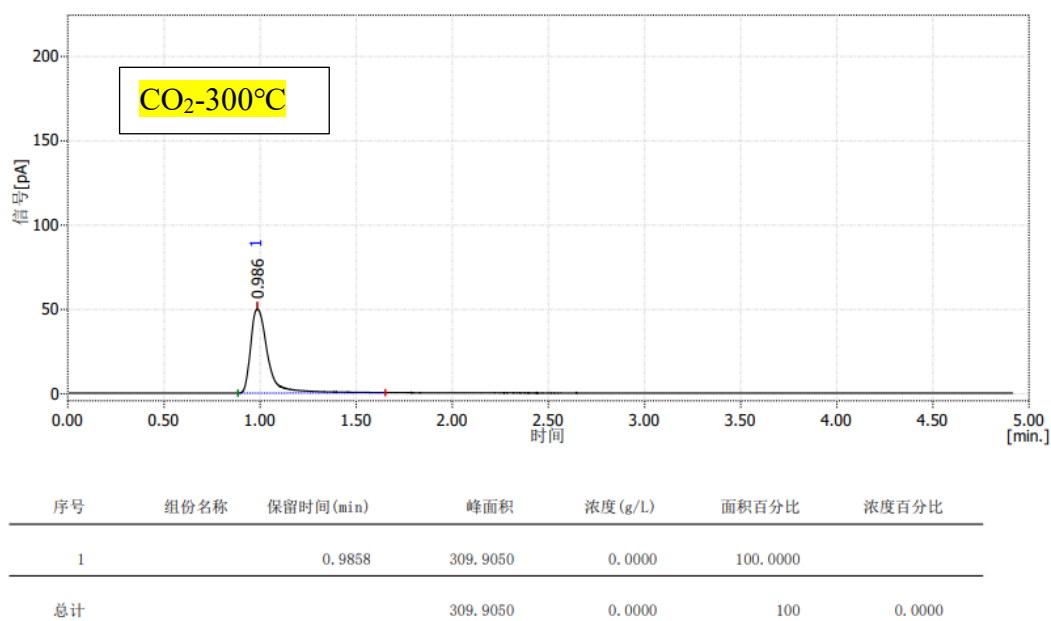


Figure S129 Original GC spectra at 300°C (10 mL/min , Feed gas ratio: 1 vol % CO₂ and 99vol% N₂).

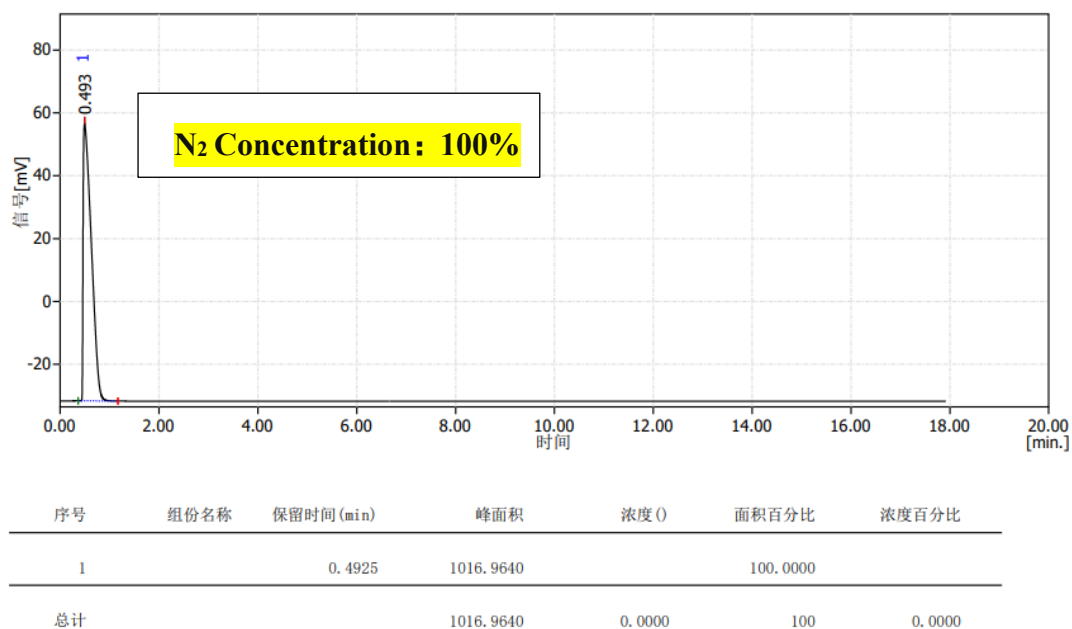
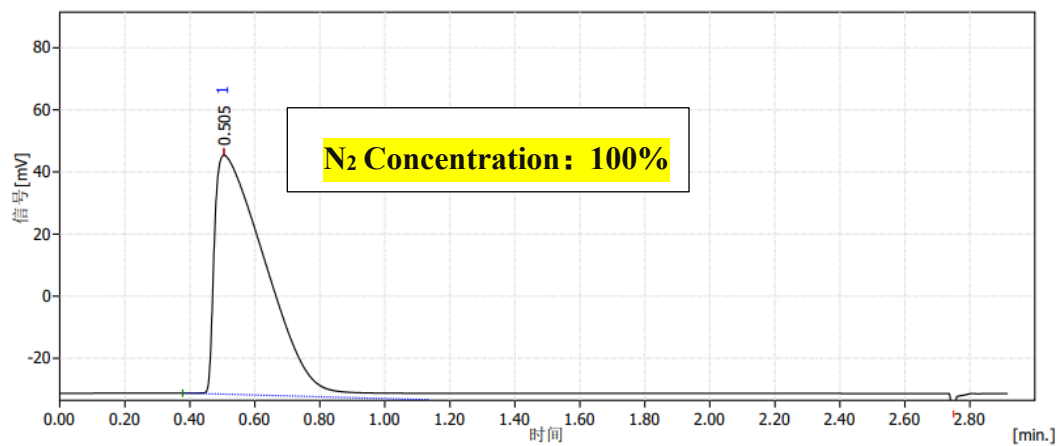
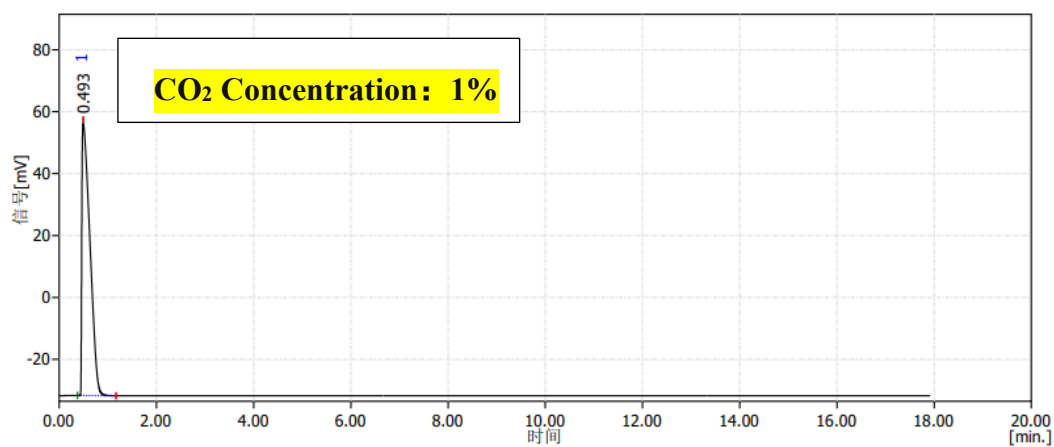


Figure S130. Original GC spectra at 30°C (10 mL/min , Feed gas ratio: 100vol% N₂) by TCD detector.



序号	组份名称	保留时间(min)	峰面积	浓度()	面积百分比	浓度百分比
1		0.5050	1274.3280		100.0000	
总计			1274.3280	0.0000	100	0.0000

Figure S131 Original GC spectra at 30°C (10 mL/min , Feed gas ratio: 100vol% N₂) by TCD detector.



序号	组份名称	保留时间(min)	峰面积	浓度()	面积百分比	浓度百分比
1		0.4925	1012.7510		100.0000	
总计			1012.7510	0.0000	100	0.0000

Figure S132 Original GC spectra at 30°C (10 mL/min , Feed gas ratio: 1vol % CO₂ and 99vol% N₂) by TCD detector.

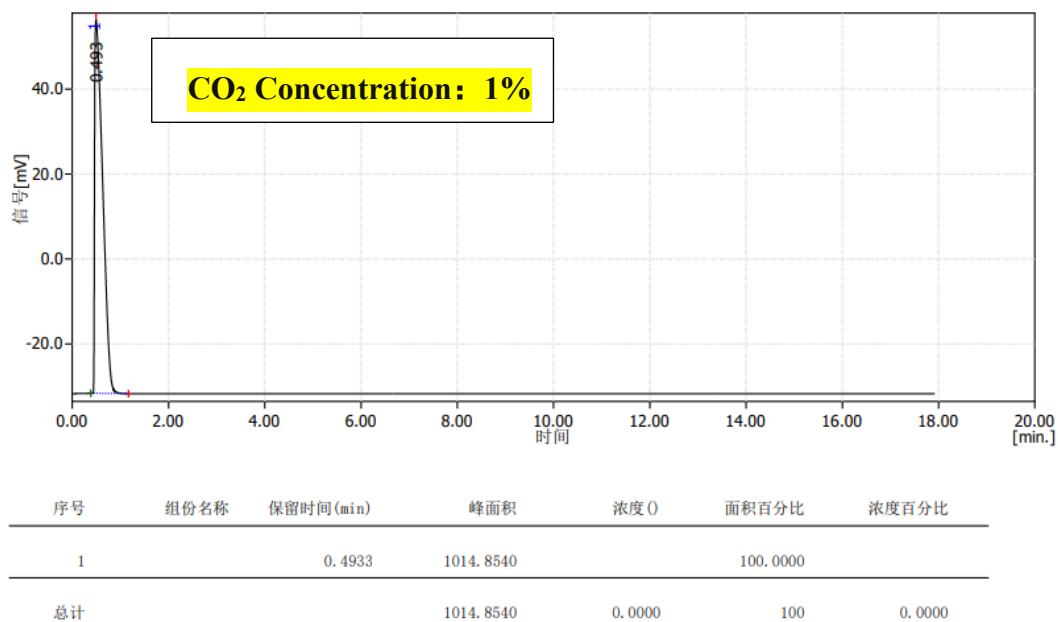


Figure S133 Original GC spectra at 30°C (10 mL/min , Feed gas ratio: 1vol % CO₂ and 99vol% N₂) by TCD detector.

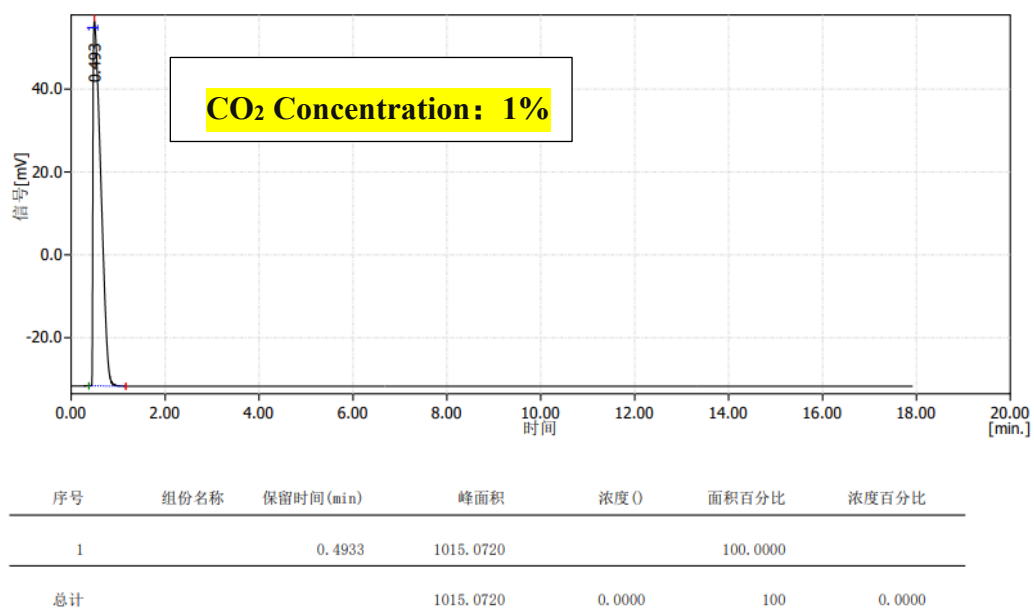
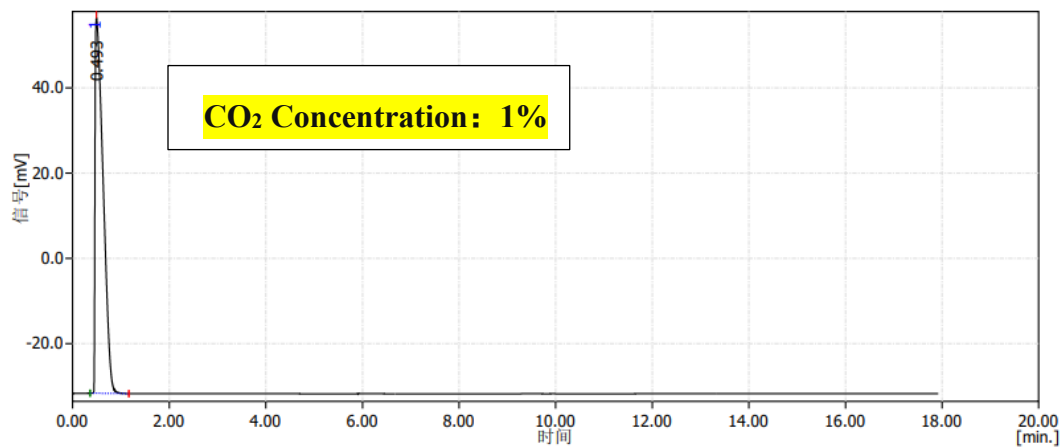
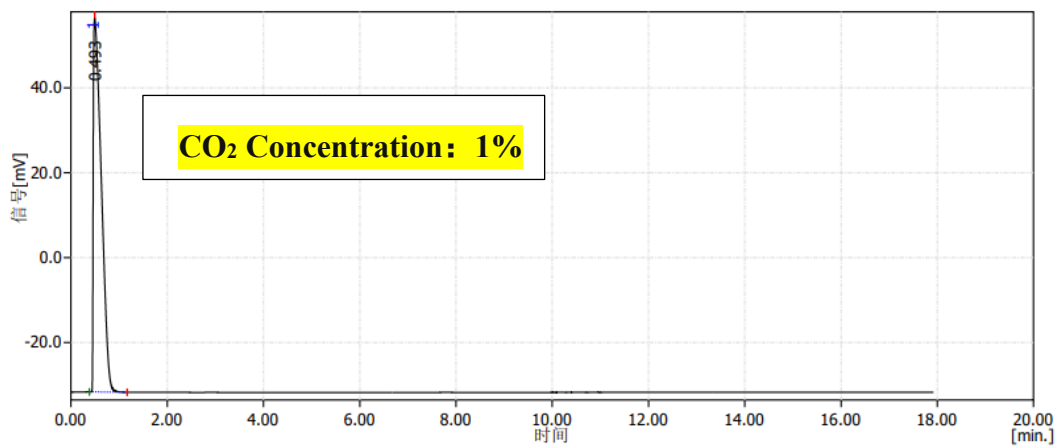


Figure S134 Original GC spectra at 30°C (10 mL/min , Feed gas ratio: 1vol % CO₂ and 99vol% N₂) by TCD detector.



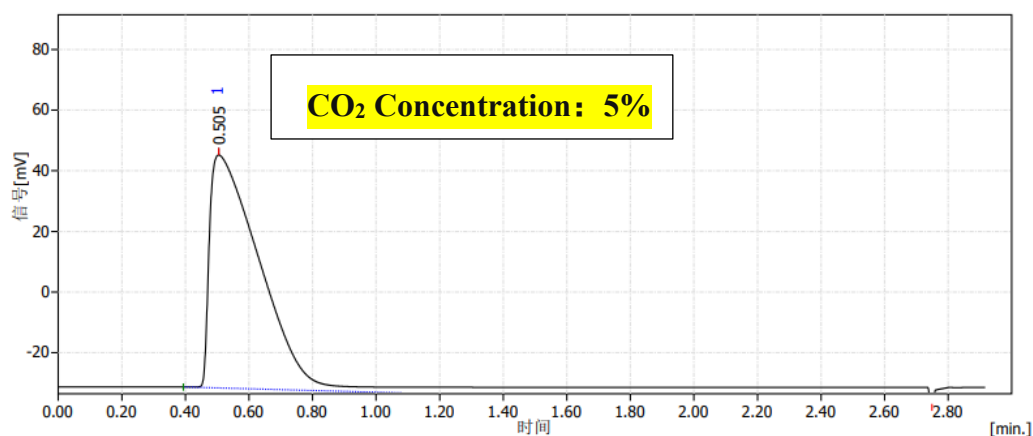
序号	组份名称	保留时间(min)	峰面积	浓度()	面积百分比	浓度百分比
1		0.4925	1015.7330		100.0000	
总计			1015.7330	0.0000	100	0.0000

Figure S135 Original GC spectra at 30°C (10 mL/min , Feed gas ratio: 1vol % CO₂ and 99vol% N₂) by TCD detector.



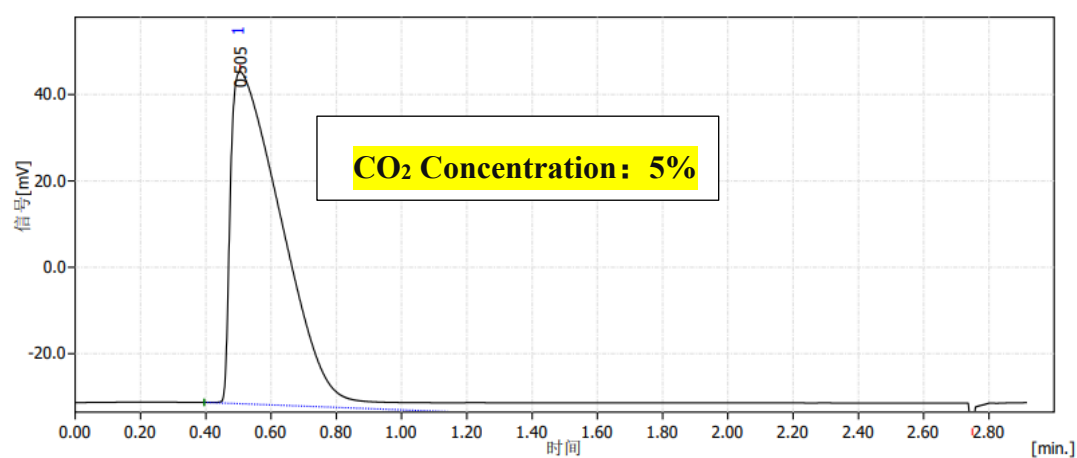
序号	组份名称	保留时间(min)	峰面积	浓度()	面积百分比	浓度百分比
1		0.4925	1015.8790		100.0000	
总计			1015.8790	0.0000	100	0.0000

Figure S136 Original GC spectra at 30°C (10 mL/min , Feed gas ratio: 1vol % CO₂ and 99vol% N₂) by TCD detector.



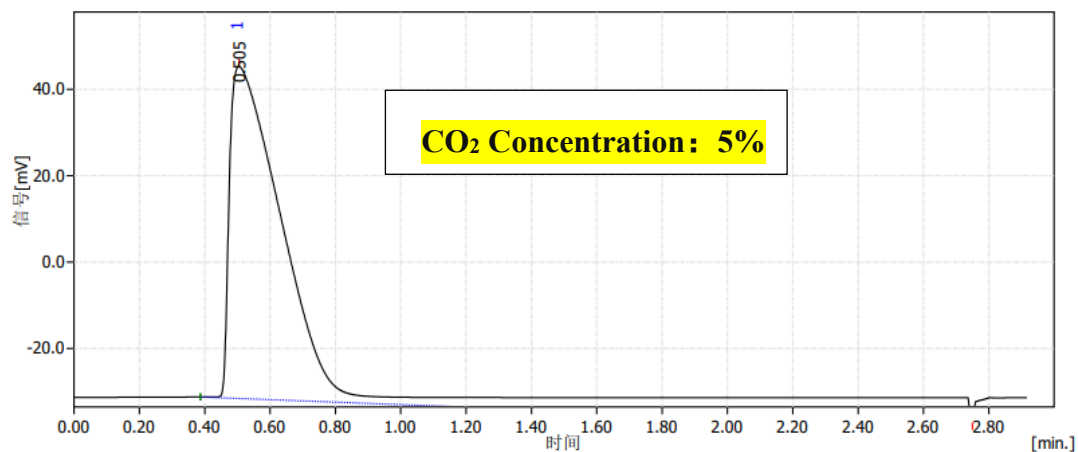
序号	组份名称	保留时间(min)	峰面积	浓度()	面积百分比	浓度百分比
1		0.5050	1268.4300		100.0000	
总计			1268.4300	0.0000	100	0.0000

Figure S1377 Original GC spectra at 30°C (10 mL/min , Feed gas ratio: 5vol % CO₂ and 95vol% N₂) by TCD detector.



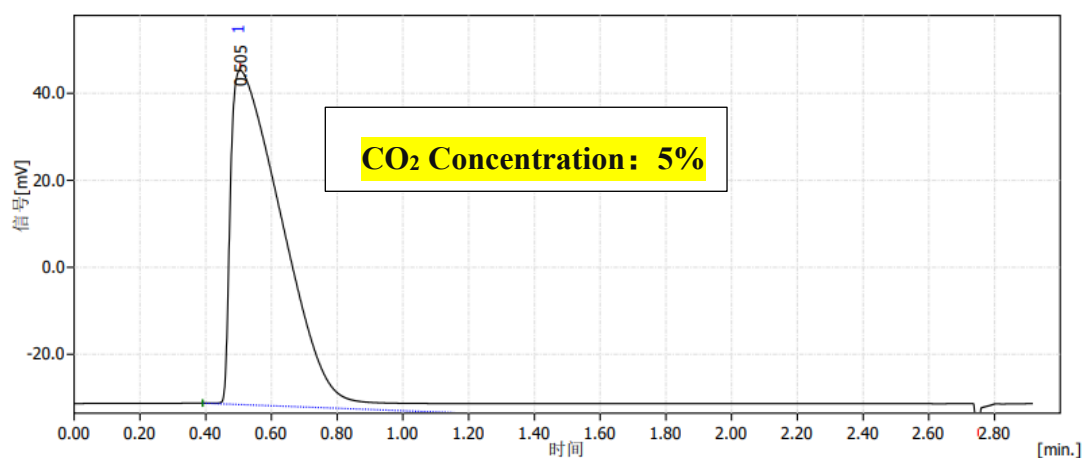
序号	组份名称	保留时间(min)	峰面积	浓度()	面积百分比	浓度百分比
1		0.5050	1269.4660		100.0000	
总计			1269.4660	0.0000	100	0.0000

Figure S138 Original GC spectra at 30°C (10 mL/min , Feed gas ratio: 5vol % CO₂ and 95vol% N₂) by TCD detector.



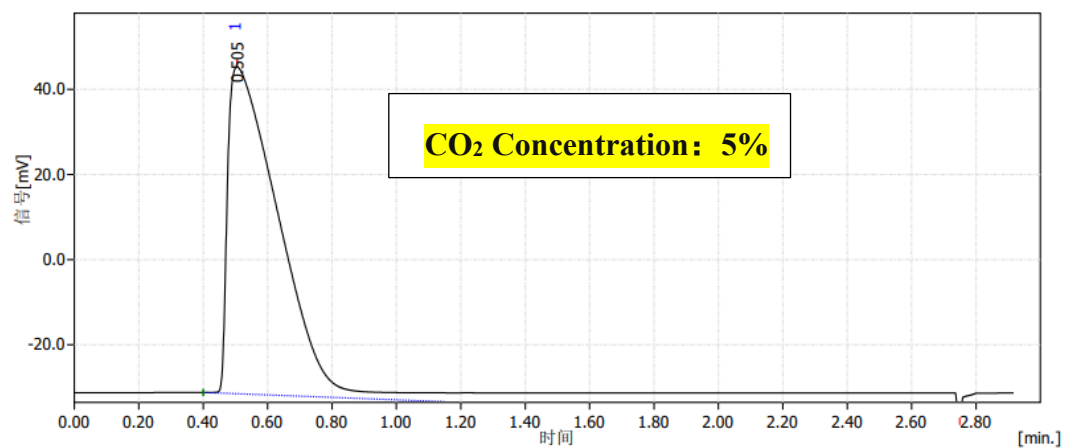
序号	组份名称	保留时间(min)	峰面积	浓度()	面积百分比	浓度百分比
1		0.5050	1269.3190		100.0000	
总计			1269.3190	0.0000	100	0.0000

Figure S139 Original GC spectra at 30°C (10 mL/min , Feed gas ratio: 5vol % CO₂ and 95vol% N₂) by TCD detector.



序号	组份名称	保留时间(min)	峰面积	浓度()	面积百分比	浓度百分比
1		0.5050	1269.5390		100.0000	
总计			1269.5390	0.0000	100	0.0000

Figure S140 Original GC spectra at 30°C (10 mL/min , Feed gas ratio: 5vol % CO₂ and 95vol% N₂) by TCD detector.



序号	组份名称	保留时间(min)	峰面积	浓度()	面积百分比	浓度百分比
1		0.5050	1269.3930		100.0000	
总计			1269.3930	0.0000	100	0.0000

Figure S141 Original GC spectra at 30°C (10 mL/min , Feed gas ratio: 5vol % CO₂ and 95vol% N₂) by TCD detector.

REVIEWER COMMENTS

Reviewer #4 (Remarks to the Author):

This study develops a high water-resistant metal oxide catalyst for propylene catalytic oxidation using a high-entropy approach. While the authors have performed comprehensive DFT calculations and characterizations to investigate the catalyst's water resistance, the water-resistance efficacy of the HEO catalyst remains insufficiently substantiated. Moreover, the water stability mechanism is ambiguous, and the DFT calculations appear to be unsubstantiated. Consequently, I contend that this manuscript may not meet the publication standards of Nature Communications. I offer the following detailed suggestions for the authors' consideration.

1. Regarding the issue of carbon balance, we consider it might be related to the instrumentation used by the authors. It is suggested that the authors characterize the samples after reaction to observe whether carbon deposition has occurred on the surface of the catalyst.
2. why the author chose these elements (Ni, Mg, Cu, Zn, Co, Cr) to construct a moisture resistant high entropy oxide catalyst?
3. the authors need to characterize the samples after the reaction to further demonstrate the water resistance of the catalyst.
4. The authors tested the water resistance of the catalyst at a humidity of 4.2 vol%. What is the reason for choosing this humidity? It is suggested to supplement tests of water resistance at humidity levels of 10 vol% to better study the tolerance of the catalyst under different humidity conditions.
5. I recommend that the authors conduct activity tests and characterizations on the catalyst after hydrothermal aging at 800 oC to better study the catalyst's hydrothermal stability. The current activity tests do not demonstrate that the HEO catalyst possesses good hydrothermal stability.
6. High-entropy catalysts have a complex structure with many types of active sites. When calculating the adsorption and dissociation energies of C₃H₆ and H₂O using DFT, how did the authors consider the position of adsorption?
7. Has the adsorption energy of H₂O been calculated through DFT? What are the results?

Response to the reviewers' comments

Dear Reviewers,

We are very grateful for your professional review work on our article. These comments are valuable and very helpful in revising and improving our paper. According to your nice suggestions, we have made extensive corrections to our previous manuscript, a point-by-point response to the reviewers' comments is listed below. In this revised version, all changes to our manuscript are all highlighted in yellow color.

Reviewer: 4

Comments:

This study develops a high water-resistant metal oxide catalyst for propylene catalytic oxidation using a high-entropy approach. While the authors have performed comprehensive DFT calculations and characterizations to investigate the catalyst's water resistance, the water-resistance efficacy of the HEO catalyst remains insufficiently substantiated. Moreover, the water stability mechanism is ambiguous, and the DFT calculations appear to be unsubstantiated. Consequently, I contend that this manuscript may not meet the publication standards of Nature Communications. I offer the following detailed suggestions for the authors' consideration.

1. Regarding the issue of carbon balance, we consider it might be related to the instrumentation used by the authors. It is suggested that the authors characterize the samples after reaction to observe whether carbon deposition has occurred on the surface of the catalyst.

Reply:

Thanks for the important suggestion! We sincerely apologize for the issue of carbon balance has not been properly addressed. The previous instrument used for chromatography was GC-2060. To observe CO₂ product, the GC-2060 chromatography contained a conversion furnace with a Ni-based catalyst. Low-concentration CO₂ was converted into CH_x, which then entered the FID detector, and finally a signal would appear. The conversion furnace cannot achieve complete conversion of low concentration CO₂ to CH_x in time. Therefore, the carbon balance value cannot be accurately calculated by GC-2060.

According to your constructive suggestion, we have replaced the instrument with a new manufacturer (Shimadzu GC-2014C) (**Figure S59**). We found that there was no significant difference in the catalytic performance of the catalyst when tested on chromatography produced by different manufacturers GC-2060 and GC-2014C (Detecting only C₃H₆ concentration). In this work, the ratio of the remaining area of C₃H₆ and the initial area was used to calculate the C₃H₆ conversion rate, which was consistent with the calculation methods in many literatures^[1~6]. The conversion of C₃H₆ was calculated by the following equation:

$$\text{C}_3\text{H}_6 \text{ conversion} = (\text{C}_3\text{H}_6 \text{ in} - \text{C}_3\text{H}_6 \text{ out}) / \text{C}_3\text{H}_6 \text{ in} \times 100\%.$$

[C₃H₆]_{in} and [C₃H₆]_{out} represent the inlet and outlet amount of C₃H₆.

However, the Shimadzu GC-2014C chromatography can accurately calculate the carbon balance value. We would like to express sincere thanks to your sincere suggestion, which enabled us to solve this difficult

problem that had troubled us before. Strictly, to ensure the authenticity of the data, we have provided images of the original data in the chromatography (**Figure S61~ Figure S75**). According to the CO₂ internal standard curve (**Figure S60**), the area of CO₂ for different samples at different temperatures can be input into the CO₂ standard curve formula to obtain the generated CO₂ concentration (**Table S16~S17**).

$$\text{Remaining C}_3\text{H}_6 \text{ concentration (\%)} = (\text{Remaining C}_3\text{H}_6 \text{ area/initial C}_3\text{H}_6 \text{ area}) \times 100\%$$

$$\text{Value of carbon balance} = [(\text{generated CO}_2 \text{ concentration}/3) + (\text{Remaining C}_3\text{H}_6 \text{ concentration})]/1\%$$

(The initial concentration of C₃H₆ is 1%).

- [1] FANG Y, LI H, ZHANG Q, et al. Oxygen Vacancy-Governed Opposite Catalytic Performance for C₃H₆ and C₃H₈ Combustion: The Effect of the Pt Electronic Structure and Chemisorbed Oxygen Species [J]. Environmental Science & Technology, **2022**, 56(5): 3245-57
- [2] FANG Y, LI L, YANG J, et al. Engineering the Nucleophilic Active Oxygen Species in CuTiO_x for Efficient Low-Temperature Propene Combustion [J]. Environmental Science & Technology, **2020**, 54(23): 15476-88.
- [3] NIE L, MEI D, XIONG H, et al. Activation of surface lattice oxygen in single-atom Pt/CeO₂ for low-temperature CO oxidation [J]. Nature, **2017**, 358(6369): 1419-23.
- [4] LI T, YAO Y, HUANG Z, et al. Denary oxide nanoparticles as highly stable catalysts for methane combustion [J]. Nature Catalysis, **2021**, 4(1): 62-70.
- [5] NIE L, MEI D, XIONG H, et al. Activation of surface lattice oxygen in single-atom Pt/CeO₂ for low-temperature CO oxidation [J]. Science, **2017**, 358(6369): 1419-23.
- [6] HAO H, JIN B, LIU W, et al. Robust Pt@TiO_x/TiO₂ Catalysts for Hydrocarbon Combustion: Effects of Pt-TiO_x Interaction and Sulfates [J]. ACS Catalysis, **2020**, 10(22): 13543-8.

Original:

C₃H₆ oxidation reaction experiment

Typically, 30 mg catalyst mixed with 100 mg quartz sand was used under 10 mL min⁻¹, which corresponds to a Gas Hourly Space Velocity (GHSV) of 20000 mL h⁻¹g⁻¹. The feed gases contained 1vol % C₃H₆, 19.9vol% O₂ and 79.1vol% N₂. The stability experiments were carried out at a conversion of 70% in C₃H₆ oxidation combustion under humid conditions (4.2vol% H₂O) for 100 hours.

Revised:

C₃H₆ oxidation reaction experiment and calculation of Carbon Balance Values

Typically, 30 mg catalyst mixed with 100 mg quartz sand was used under 10 mL min⁻¹, which corresponds to a Gas Hourly Space Velocity (GHSV) of 20000 mL h⁻¹g⁻¹. The feed gases contained 1vol % C₃H₆, 19.9vol% O₂ and 79.1vol% N₂. The stability experiments were carried out at a conversion of 70% in C₃H₆ oxidation combustion under humid conditions (4.2vol% H₂O) for 100 hours. **The images of the original data**

by (Shimadzu GC-2014C) (**Figure S59**) were shown in **Figure S61~ Figure S75**. According to the CO₂ internal standard curve (**Figure S60**), values of carbon balance were obtained (**Table S16~S17**).

$$\text{Remaining C}_3\text{H}_6 \text{ concentration}(\%) = (\text{Remaining C}_3\text{H}_6 \text{ area}/\text{initial C}_3\text{H}_6 \text{ area}) \times 100\%$$

$$\text{Value of carbon balance} = [(\text{generated CO}_2 \text{ concentration}/3) + (\text{Remaining C}_3\text{H}_6 \text{ concentration})]/1\%$$

(The initial concentration of C₃H₆ is 1%).

Table S16 Calculation of Carbon Balance Values for Different Samples.

Sample	Initial C ₃ H ₆ area	Temperature	Generated CO ₂ concentration /3(%)	Remaining C ₃ H ₆ concentration ^a (%)	Value of carbon balance ^b
CoCr ₂ O ₄	16167.33	300.7°C	0.19	0.77	96
MgCr ₂ O ₄	16989.80	280.5°C	0.16	0.77	93
(Ni _{0.5} Mg _{0.5})Cr ₂ O ₄	17165.15	282.3°C	0.39	0.74	113
(Mg _{0.5} Zn _{0.5})Cr ₂ O ₄	16484.24	264.4°C	0.23	0.73	97
(Cu _{0.5} Zn _{0.5})Cr ₂ O ₄	17280.15	272.0°C	0.28	0.79	107
(Ni _{0.5} Cu _{0.5})Cr ₂ O ₄	16908.79	308.1°C	0.28	0.78	106
(Ni _{0.5} Zn _{0.5})Cr ₂ O ₄	11488.75	293.7°C	0.44	0.58	102
(Mg _{0.5} Cu _{0.5})Cr ₂ O ₄	11691.93	294.0°C	0.23	0.72	95
(Mg _{0.5} Co _{0.5})Cr ₂ O ₄	17224.38	283.0°C	0.21	0.75	96
(Ni _{0.5} Co _{0.5})Cr ₂ O ₄	16662.64	278.7°C	0.28	0.73	101
(Zn _{0.5} Co _{0.5})Cr ₂ O ₄	11338.6	287.8°C	0.19	0.71	90

a: Remaining C₃H₆ concentration (%) = Remaining C₃H₆ area/initial C₃H₆ area

b: Value of carbon balance = [(generated CO₂ concentration/3) + (Remaining C₃H₆ concentration)]/1% (The initial concentration of propylene is 1%. The CO₂ concentration generated of samples were calculated based on a standard curve with a CO₂ concentration of 0.5% -1%.

Table S17 The area of CO₂ in chromatography, within the concentration range of 0.5% to 1% at room

temperature.

CO ₂ concentration	peak area						average
0.5%	2684.3	2650.1	2656.3	2672.3	2659.9	2665.6	2664.75
0.75%	4224.7	3856	3976.8	4000.3	3976.8	3917.7	3992.05
1%	5326.9	5398.4	5314.5	5260.4	5332.8	5331.6	5327.43



Figure S59 Photos of the new chromatography(GC-2014C) used for calculating value of carbon balance.

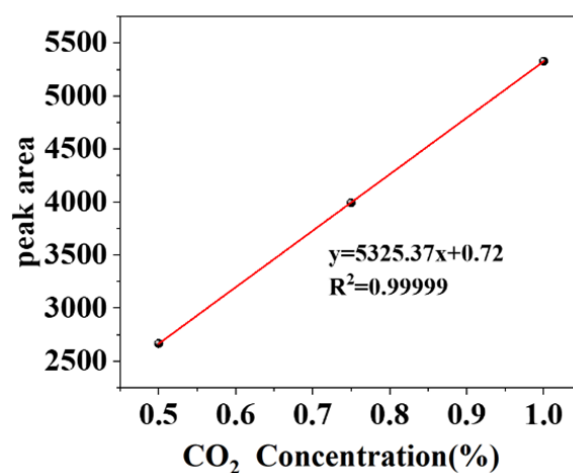
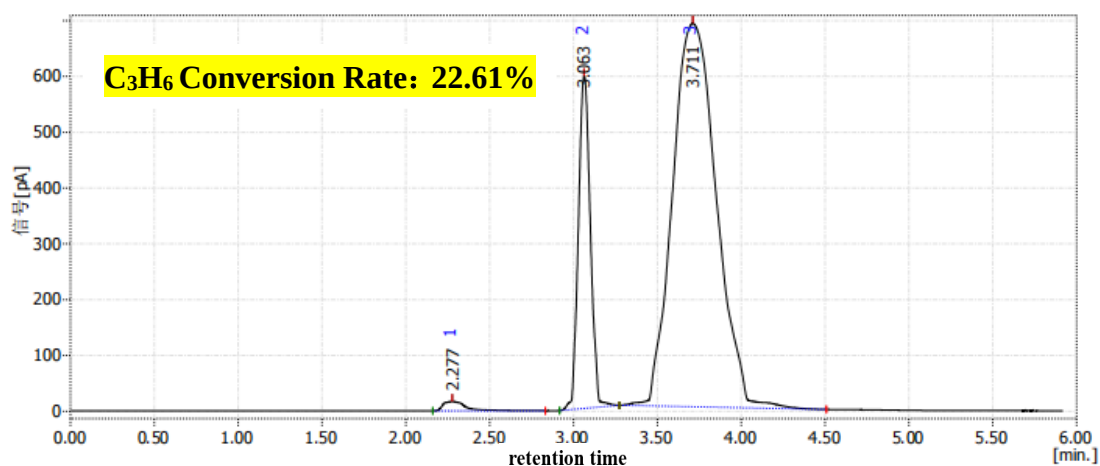
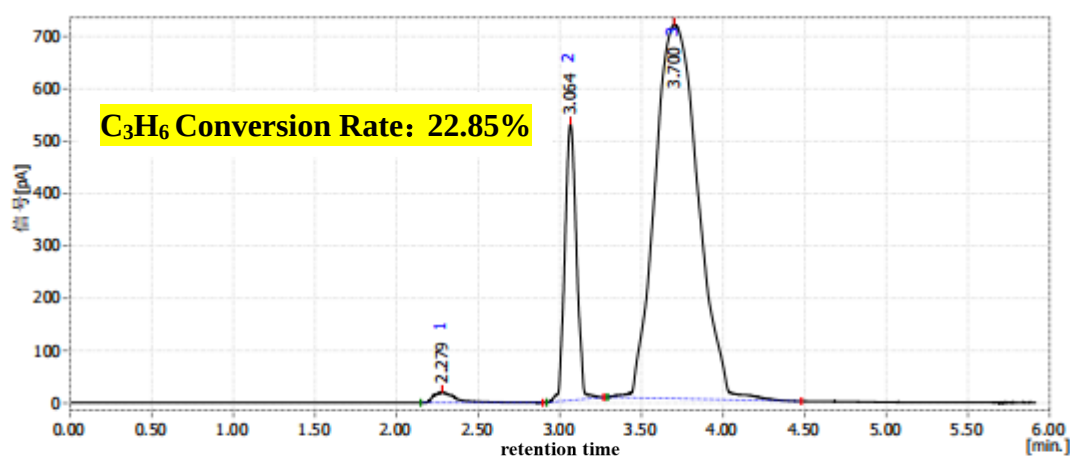


Figure S60 The standard curve of CO₂ within the concentration range of 0.5%~1% at room temperature.



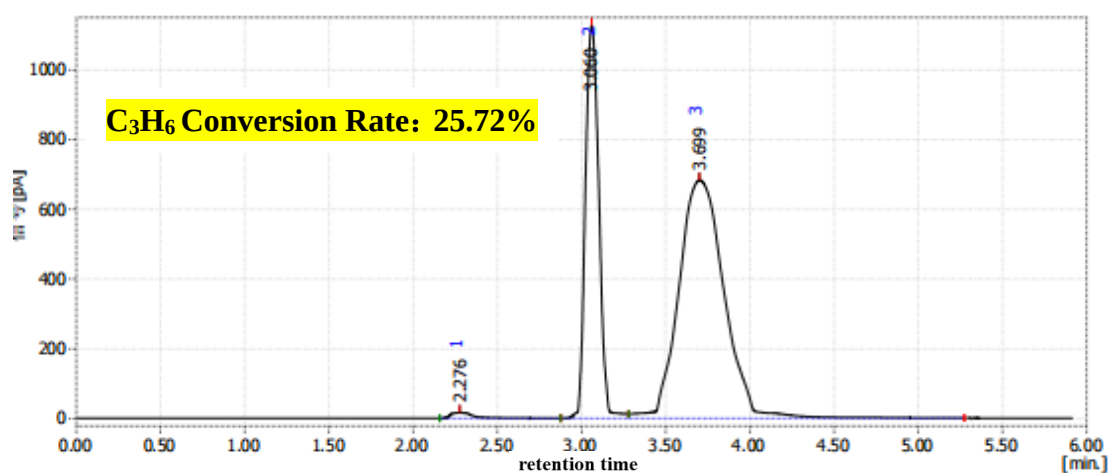
	retention time	peak area	concentration	Area percentage
1	2.2767	158.1006		1.0115
2	3.0625	2960.2470		18.9392
3	3.7108	12511.9300		80.0493

Figure S61 Original GC spectra of CoCr₂O₄ at 300.7°C (10 mL/min , Feed gas ratio: 1vol % C₃H₆ and 99vol% air)



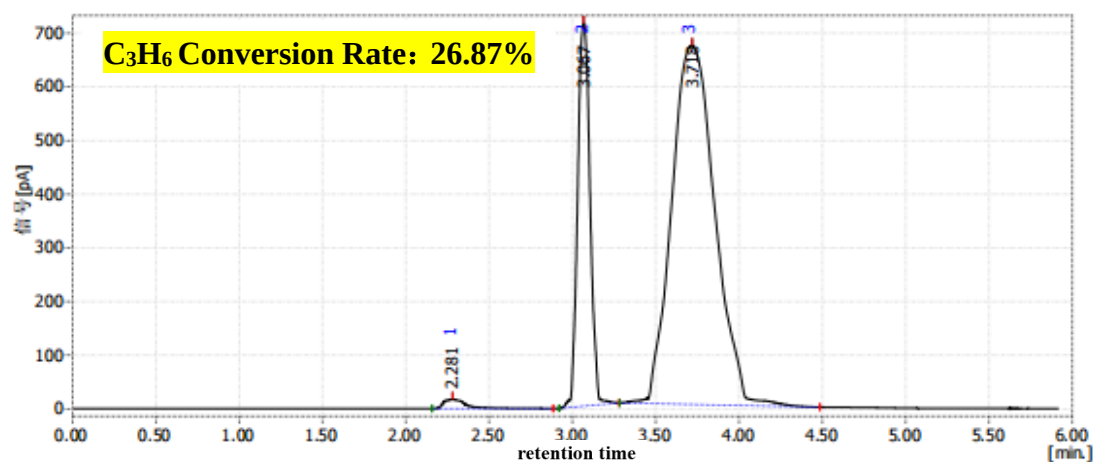
	retention time	peak area	concentration	Area percentage
1	2.2792	184.0992		1.1585
2	3.0642	2599.5460		16.3582
3	3.7000	13107.7100		82.4833

Figure S62 Original GC spectra of MgCr₂O₄ at 280°C (10 mL/min , Feed gas ratio: 1vol % C₃H₆ and 99vol% air)



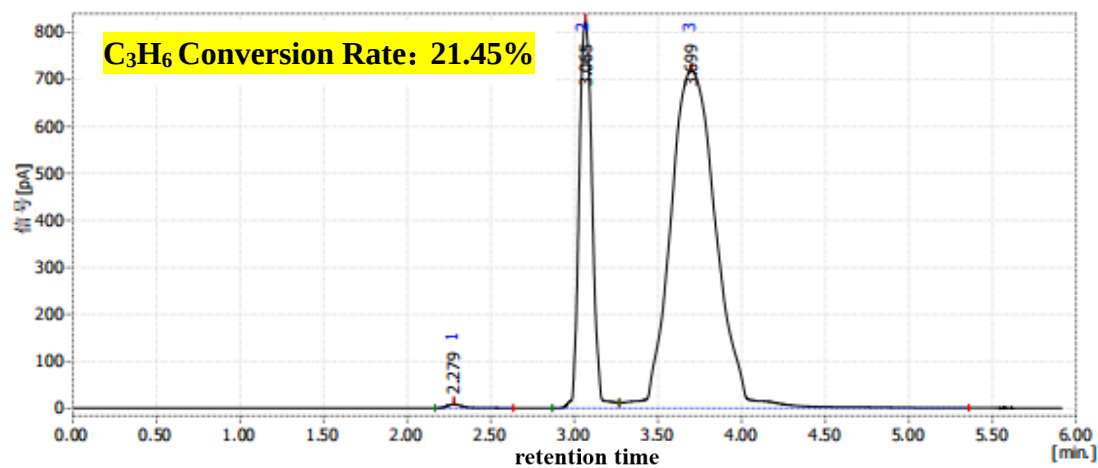
	retention time	peak area	concentration	Area percentage
1	2.2759	147.1126		0.7670
2	3.0600	6281.9720		32.7519
3	3.6992	12751.3900		66.4811

Figure S63 Original GC spectra of (Ni_{0.5}Mg_{0.5})Cr₂O₄ at 282°C (10 mL/min , Feed gas ratio: 1vol % C₃H₆ and 99vol% air)



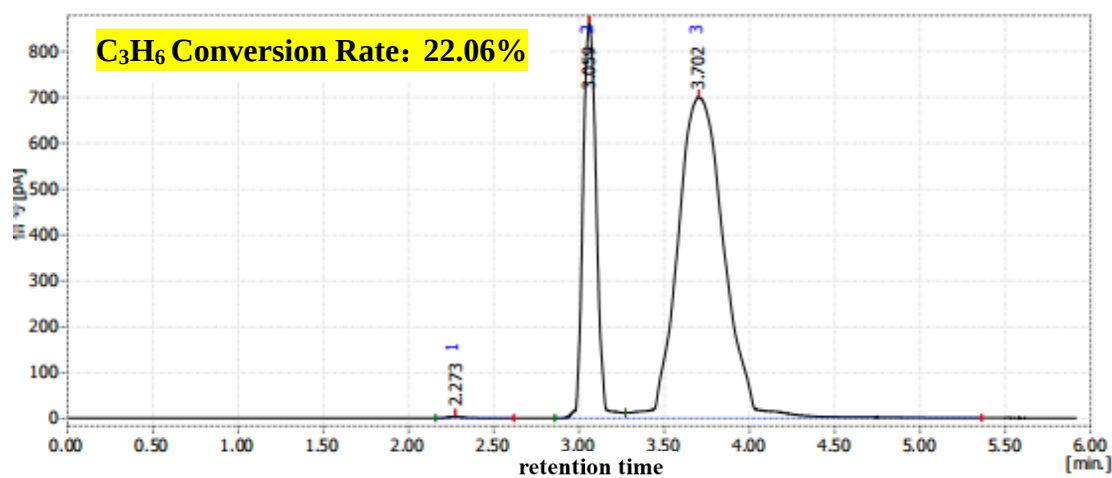
	retention time	peak area	concentration	Area percentage
1	2.2809	159.3673		1.0018
2	3.0667	3692.8800		23.2139
3	3.7175	12055.8300		75.7843
总计		15908.0800	0.0000	100

Figure S64 Original GC spectra of (Mg_{0.5}Zn_{0.5})Cr₂O₄ at 264.4°C (10 mL/min , Feed gas ratio: 1vol % C₃H₆ and 99vol% air)



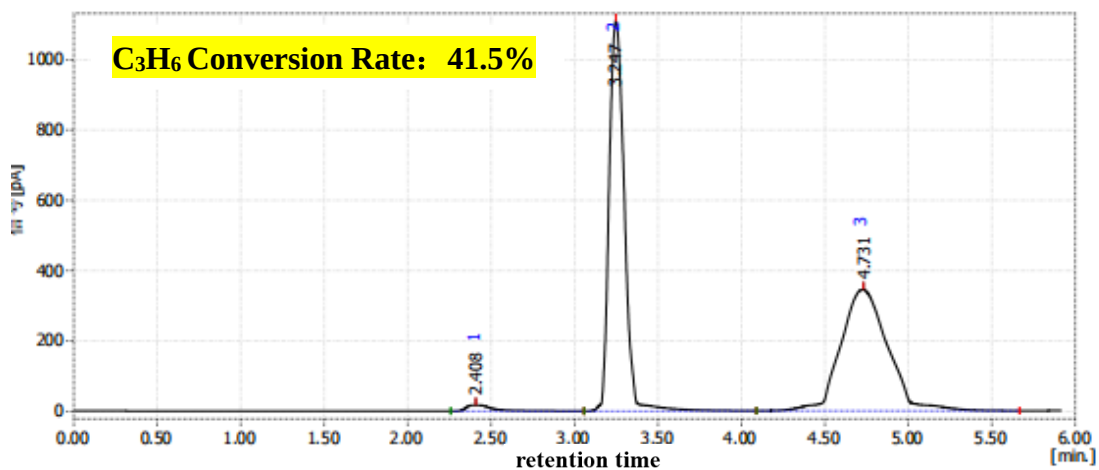
	retention time	peak area	concentration	Area percentage
1	2.2792	50.9346		0.2814
2	3.0650	4478.7630		24.7410
3	3.6992	13572.9100		74.9777
总计		18102.6000	0.0000	100
				0.0000

Figure S65 Original GC spectra of (Cu_{0.5}Zn_{0.5})Cr₂O₄ at 272°C (10 mL/min , Feed gas ratio: 1vol % C₃H₆ and 99vol% air)



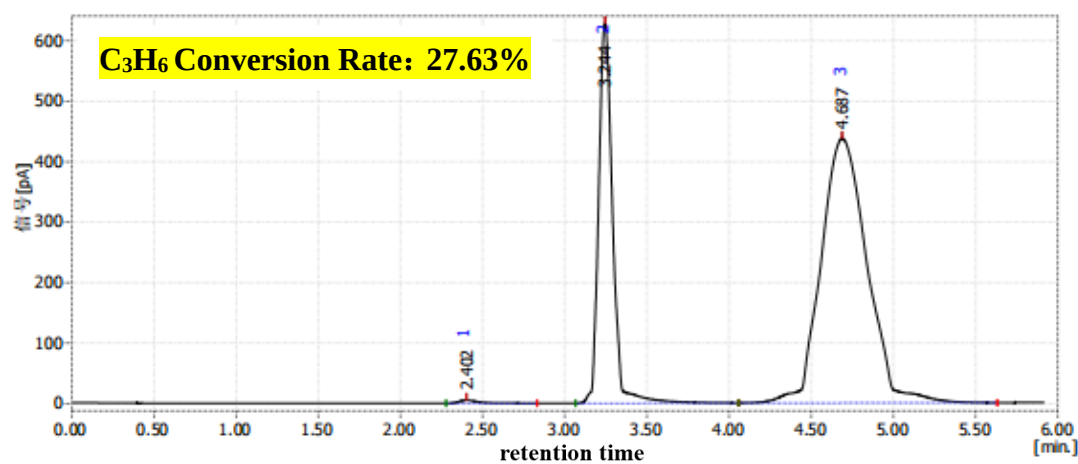
	retention time	peak area	concentration	Area percentage
1	2.2734	19.6187		0.1097
2	3.0592	4682.0840		26.1862
3	3.7017	13178.2800		73.7041
总计		17879.9800	0.0000	100
				0.0000

Figure S66 Original GC spectra of (Ni_{0.5}Cu_{0.5})Cr₂O₄ at 308.1°C (10 mL/min , Feed gas ratio: 1vol % C₃H₆ and 99vol% air)



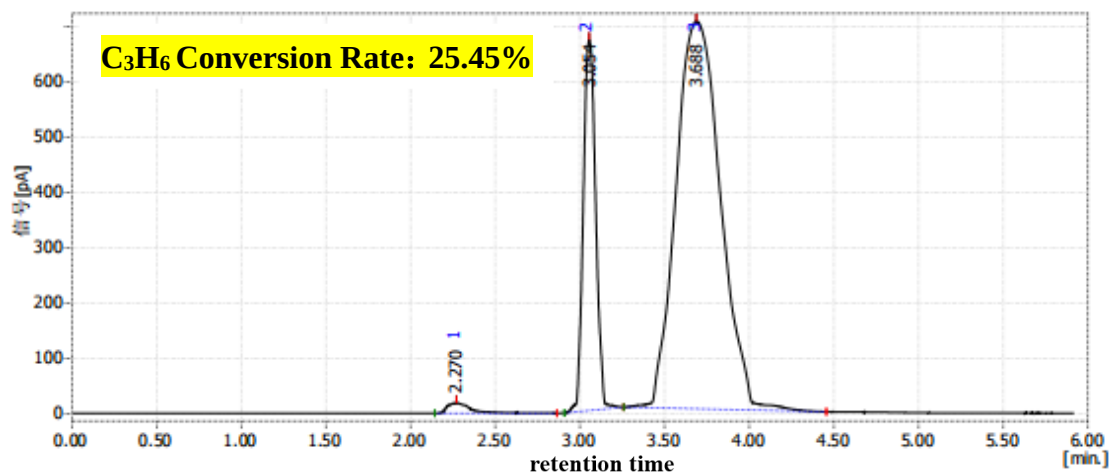
	retention time	peak area	concentration	Area percentage
1	2.4084	177.2897	0.0000	1.2729
2	3.2467	7030.2690	0.0000	50.4771
3	4.7310	6720.0930	0.0000	48.2500
总计		13927.6500	0.0000	100
				0.0000

Figure S67 Original GC spectra of (Ni_{0.5}Zn_{0.5})Cr₂O₄ at 293.7°C (10 mL/min , Feed gas ratio: 1vol % C₃H₆ and 99vol% air)



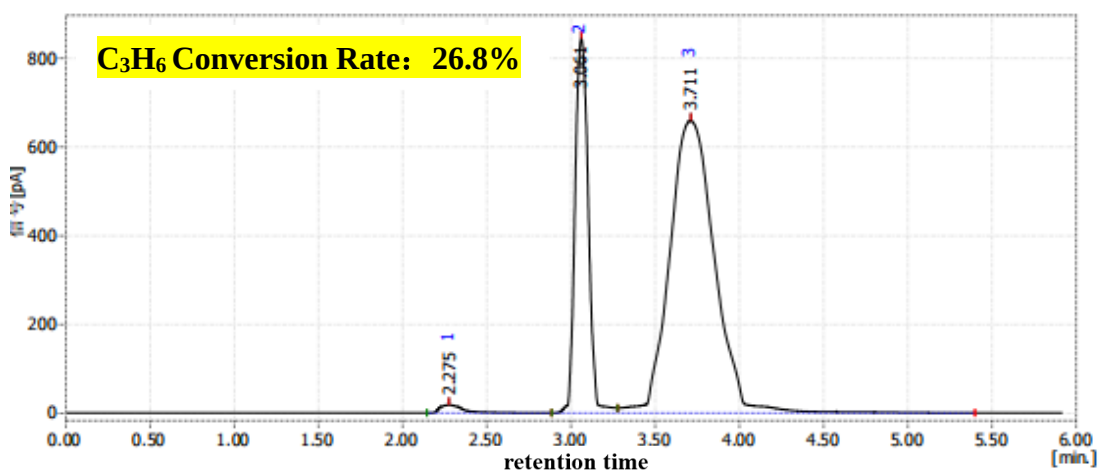
	retention time	peak area	concentration	Area percentage
1	2.4017	39.3101	0.0000	0.3221
2	3.2442	3704.2210	0.0000	30.3486
3	4.6868	8462.0510	0.0000	69.3294

Figure S68 Original GC spectra of (Mg_{0.5}Cu_{0.5})Cr₂O₄ at 294°C (10 mL/min , Feed gas ratio:1vol % C₃H₆ and 99vol% air)



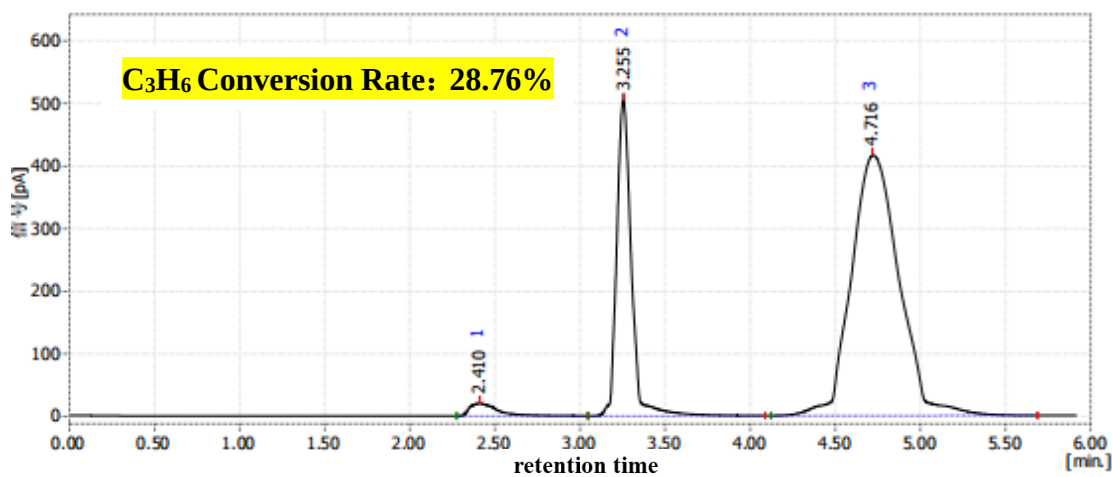
	retention time	peak area	concentration	Area percentage
1	2.2701	175.6855		1.0692
2	3.0542	3415.8770		20.7890
3	3.6875	12839.6400		78.1418
总计		16431.2000	0.0000	100

Figure S69 Original GC spectra of (Mg_{0.5}Co_{0.5})Cr₂O₄ at 283°C (10 mL/min , Feed gas ratio: 1vol % C₃H₆ and 99vol% air)



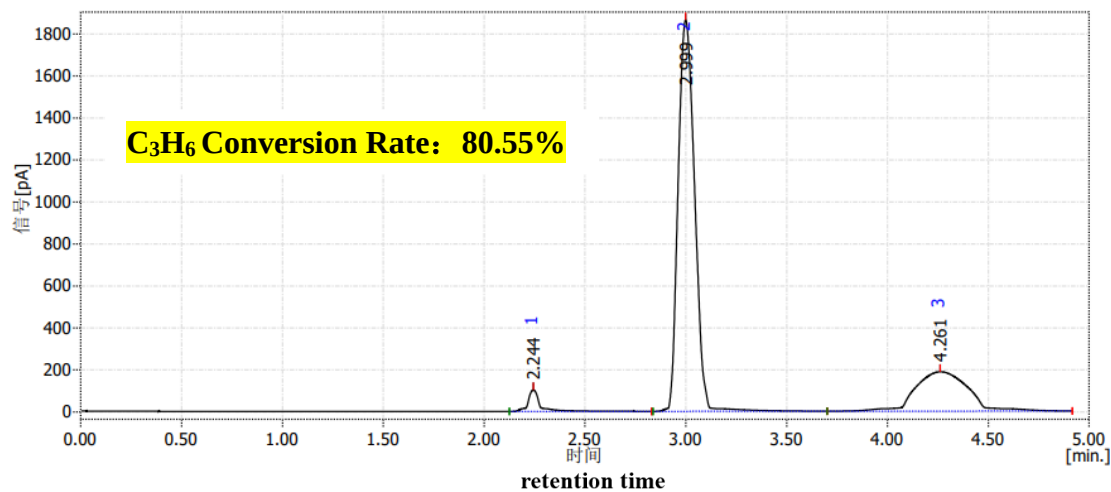
	retention time	peak area	concentration	Area percentage
1	2.2751	176.7150		1.0398
2	3.0608	4622.9270		27.2006
3	3.7108	12196.0700		71.7597
总计		16995.7100	0.0000	100

Figure S70 Original GC spectra of (Ni_{0.5}Co_{0.5})Cr₂O₄ at 278.7°C (10 mL/min , Feed gas ratio: 1vol % C₃H₆ and 99vol% air)



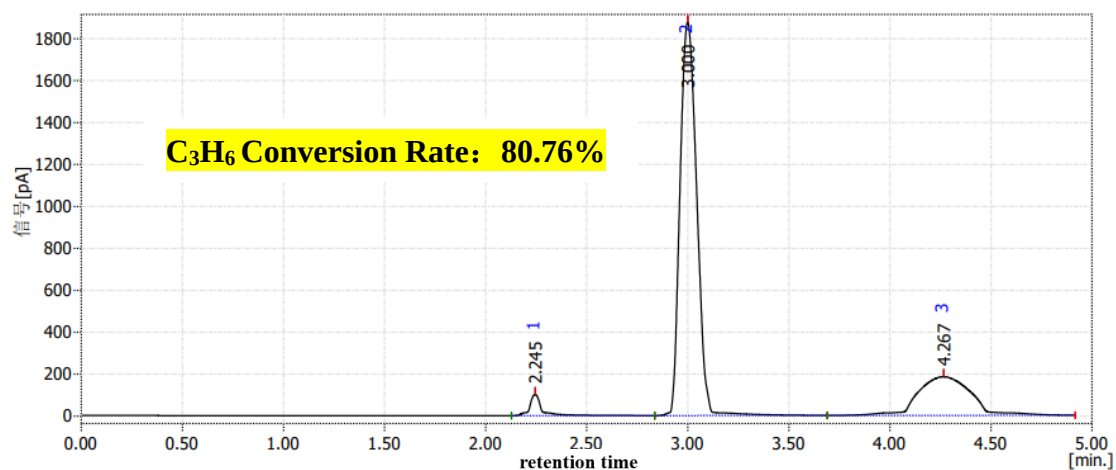
	retention time	peak area	concentration	Area percentage	
1	2.4100	230.8507	0.0000	2.0432	
2	3.2550	2990.6590	0.0000	26.4699	
3	4.7160	8076.8390	0.0000	71.4869	
总计		11298.3500	0.0000	100	0.0000

Figure S71 Original GC spectra of (Zn_{0.5}Co_{0.5})Cr₂O₄ at 287.8°C (10 mL/min , Feed gas ratio: 1vol % C₃H₆ and 99vol% air)



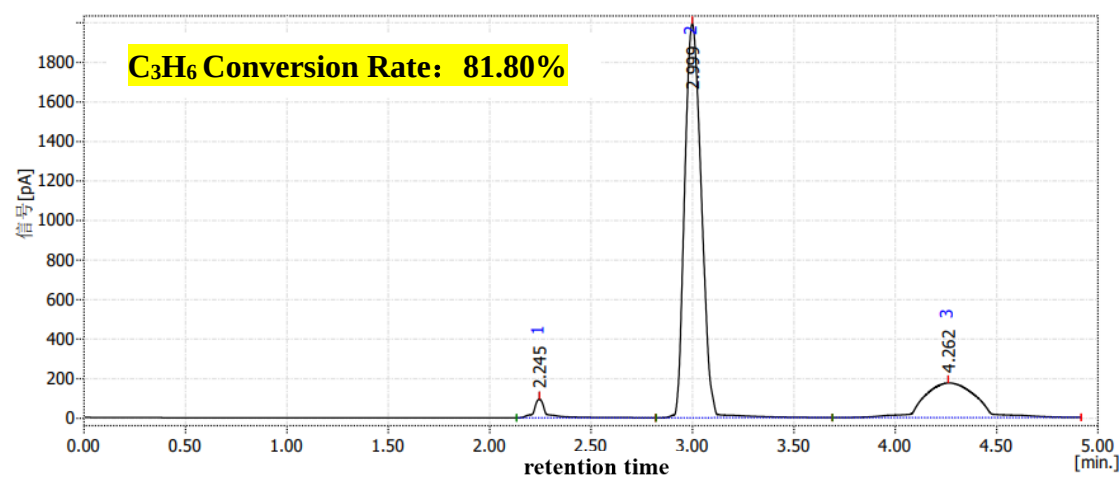
	retention time	peak area	concentration	Area percentage	
1	2.2442	420.1075		2.9087	
2	2.9992	10610.4400		73.4624	
3	4.2609	3412.8180		23.6290	
总计		14443.3600	0.0000	100	0.0000

Figure S72 Original GC spectra of a-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ at 258°C (10 mL/min , Feed gas ratio:1vol % C₃H₆ and 99vol% air)



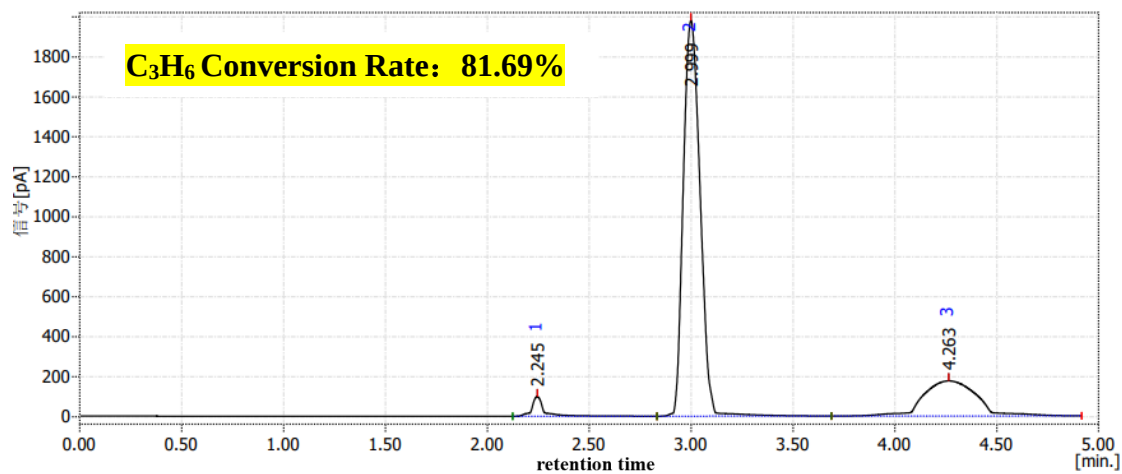
	retention time	peak area	concentration	Area percentage
1	2.2451	412.6517		2.8396
2	3.0000	10768.5300		74.1026
3	4.2667	3350.7290		23.0577

Figure S73 Original GC spectra of b-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ at 258 °C (10 mL/min , Feed gas ratio:1vol % C₃H₆ and 99vol% air)



	retention time	peak area	concentration	Area percentage
1	2.2451	381.9244		2.5461
2	2.9992	11450.0900		76.3317
3	4.2617	3168.4330		21.1223
总计		15000.4500	0.0000	100

Figure S74 Original GC spectra of a-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ at 262 °C (10 mL/min , Feed gas ratio:1vol % C₃H₆ and 99vol% air)



	retention time	peak area	concentration	Area percentage
1	2.2451	399.0277		2.6666
2	2.9992	11377.3700		76.0321
3	4.2634	3187.5130		21.3013

Figure S75 Original GC spectra of b-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ at 262 °C (10 mL/min , Feed gas ratio:1vol % C₃H₆ and 99vol% air)

In the C₃H₆ combustion reaction, C₃H₆ reacted with oxygen to produce carbon dioxide and water. However, carbon deposition may occur on the surface of the catalyst, which may be due to incomplete combustion of C₃H₆ with side reactions. Carbon deposition would affect the activity and stability of catalysts, so it was necessary to analyze and evaluate them, as suggested by the reviewer.

First, TGA analysis was conducted on the spent Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2}Cr₂O₄ catalyst after 100 hours of C₃H₆ combustion stability experiments at T₇₀ (temperatures that C₃H₆ conversion was 70%) in the presence of 4.2 vol% moisture. The mass loss at 100-600 °C corresponded to the desorption of moisture or impurity on the catalyst. If coke were present in the sample, they would decompose into gaseous products during the further heating process (600-800°C).^[1] This mass change was manifested on the thermogravimetric curve as the mass gradually decreases with increasing temperature, forming a peak of mass loss. However, no significant mass loss was observed in the **Figure S76**, indicating that the catalyst produced little coke (~0.73wt%) during the 100h reaction process.

Then, Raman spectrum of the spent Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2}Cr₂O₄ catalyst after 100 hours of C₃H₆ combustion stability experiments at T₇₀ (temperatures that C₃H₆ conversion was 70%) in the presence of 4.2 vol% moisture was shown in **Figure S77**. There were two distinct characteristic peaks attributed to carbon at 1348 cm⁻¹ and 1580 cm⁻¹, corresponding to the D band (structural defects or disordered carbon) and the G band (graphite structured carbon), respectively. The ratio I_D/I_G (integral ratio of D-band to G-band) represented the graphitization degree of coke deposits.^[2] The I_D/I_G ratio of spent Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2}Cr₂O₄ catalyst was 2.31, indicating that the graphitization degree of formed coke was medium after 100 hours in C₃H₆ combustion reaction.

In addition, the C₃H₆ temperature programmed surface reaction (C₃H₆-TPSR) analysis was conducted using the chemisorption analyzer. The catalyst (50 mg) underwent pre-reduction in a 10% H₂/Ar mixture (40 mL/min) at 800 °C for 2 hours, followed by purification in He (40 mL/min) for 1 hour and subsequent cooling to 50 °C. The C₃H₆-TPSR test involved exposing the catalyst to a mixture of 1% C₃H₆/He at a flow rate of 50 mL/min. The temperature was then raised from 50 to 800 °C at a heating rate of 10 °C/min. The procedures for carbon dioxide temperature programmed surface reaction (CO₂-TPSR) experiments were similar to those of C₃H₆-TPSR, with the exception of employing a different feed gas mixture consisting of 1% CO₂/He.

The peaks of CO and CO₂ were almost invisible in the C₃H₆-TPSR curve, which was understandable considering the absence of oxygen in this process (**Figure S78a**). It has been reported in the literature ^[3] that at high temperatures, carbon dioxide (CO₂) reacted with carbon on the sample surface to produce CO, an important chemical reaction often referred to as carbon oxidation. However, in the CO₂-TPSR curve, the CO peak was almost invisible (**Figure S78b**). This showed that there was not so much carbon deposition produced during the C₃H₆ combustion at 800 °C, in agreement with TGA and Raman results.

- [1] .Koeken, A. C. J.; Torres Galvis, H. M.; Davidian, T.; Ruitenbeek, M.; de Jong, K. P., Suppression of Carbon Deposition in the Iron-Catalyzed Production of Lower Olefins from Synthesis Gas. *Angewandte Chemie International Edition* ,**2012**, 51 (29), 7190-7193.
- [2]. Hikima, S.; Keller, M.; Matsuo, H.; Matsuzaki, Y.; Otomo, J., Carbon-dioxide activation by methane with iron-doped barium zirconate in chemical looping cracking system. *Chemical Engineering Journal* ,**2021**, 417, 128012.
- [3] Zhang, S.; Ying, M.; Yu, J.; Zhan, W.; Wang, L.; Guo, Y.; Guo, Y., NixAl₁₀O₂- δ mesoporous catalysts for dry reforming of methane: The special role of NiAl₂O₄ spinel phase and its reaction mechanism. *Applied Catalysis B: Environmental* **2021**, 291, 120074.

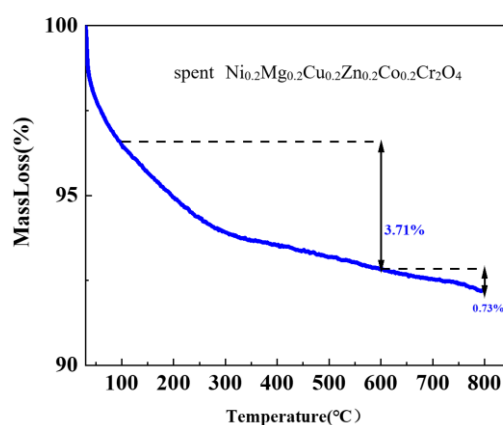


Figure S76 TGA spectra of spent Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2}Cr₂O₄ catalysts after 100 hours of C₃H₆ combustion stability experiments at T₇₀ (temperatures that C₃H₆ conversion was 70%) in the presence of 4.2 vol% moisture.

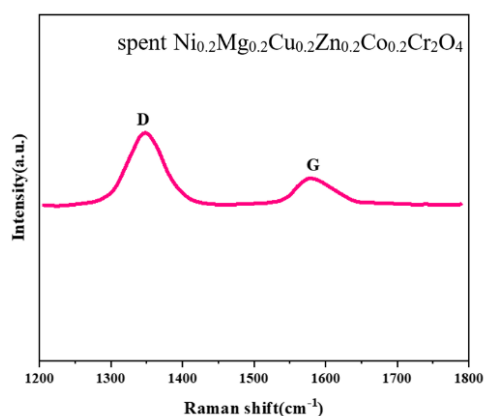


Figure S77 Raman spectra of spent Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2}Cr₂O₄ catalysts after 100 hours of C₃H₆ combustion stability experiments at T₇₀ (temperatures that C₃H₆ conversion was 70%) in the presence of 4.2 vol% moisture.

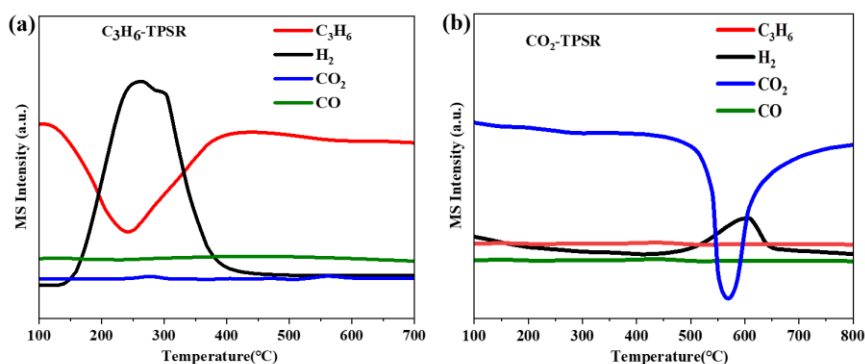


Figure S78. TPSR profiles of $\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2}\text{Cr}_2\text{O}_4$ catalyst from 100 to 800 °C and maintained at 800 °C for 60 min: (a) C_3H_6 -TPSR profiles of the reduced $\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2}\text{Cr}_2\text{O}_4$ catalyst with 1 % C_3H_6 /He, (b) CO_2 -TPSR profiles of the coked $\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2}\text{Cr}_2\text{O}_4$ catalyst (coking by C_3H_6 at 800 °C for 60 min) with 1 % CO_2 /He.

2. why the author chose these elements (Ni, Mg, Cu, Zn, Co, Cr) to construct a moisture resistant high entropy oxide catalyst?

Reply:

Thanks for the key comment! We sincerely apologize for not providing a detailed explanation of this important issue in the original manuscript. We have added explanations in the revised manuscript. In the C_3H_6 combustion reaction, the selection of elements such as Ni, Mg, Cu, Zn, Co, and Cr to construct high entropy oxides (HEOs) catalysts with water resistance capability was based on the structure and property of high-entropy structure. The combination of these elements in HEOs can bring several features.

HEOs are oxides composed of five or more different elements with higher chemical complexity and diversity. According to the Gibbs free energy equation, the free energy tends to minimize under higher configurational entropy, rendering HEOs more stable under moisture-containing conditions. Additionally, the structure of HEOs allows for rapid structural adjustments and element rearrangements when subjected to aggressive ions such as OH^- or H^+ at high temperatures, mitigating damage from these ions.^[1] In contrast, single oxides are more susceptible to be damaged by OH^- or H^+ . Moreover, HEOs exhibit significant disorder and local short-range order within their structures.^[2] This high degree of complexity makes HEOs difficult for water vapor molecules to find specific adsorption sites on their surfaces. Thus, compared to the single metal oxide, the adsorption energy of water molecules on the catalyst surface decreased. The dissociation energy of water molecules on the catalyst surface increased (**Figure 2**).

In high-entropy oxide AB_2O_4 , the selection range of the A-site element is typically based on atomic radius and coordination chemistry principles. This is due to that the A-site element needs to coordinate with oxygen atoms and other elements, achieving a coordination that must adhere to certain geometric and

electronic structure requirements. First, the selection of the A-site element is influenced by the atomic radius. Within the crystal structure, coordination bonds between the A-site element and oxygen atoms are contingent upon the atomic radius of the A-site element. If the atomic radius of the A-site element is either too large or too small, lattice distortion or an unstable crystal structure may ensue.^[3] Therefore, pivotal in ensuring the stability of the crystal structure is the selection of an appropriately sized A-site element. Second, the selection of A-site element is constrained by coordination chemistry principles. Within the crystal structure, the A-site element must satisfy specific coordination numbers and geometric configurations to uphold the crystal's stability. Typically, the A-site element will coordinate with a certain number of oxygen atoms (such as octahedral or tetrahedral coordination), thereby forming a stable coordination environment. Additionally, in high-entropy oxide AB_2O_4 , the B-site element frequently assumes the role of providing stability to the crystal structure, while its oxidation activity also influences the chemical properties.^[4~5] In this work, opting for the Cr element as the B-site element serves to enhance the stability of the HEOs under conditions of water vapor.

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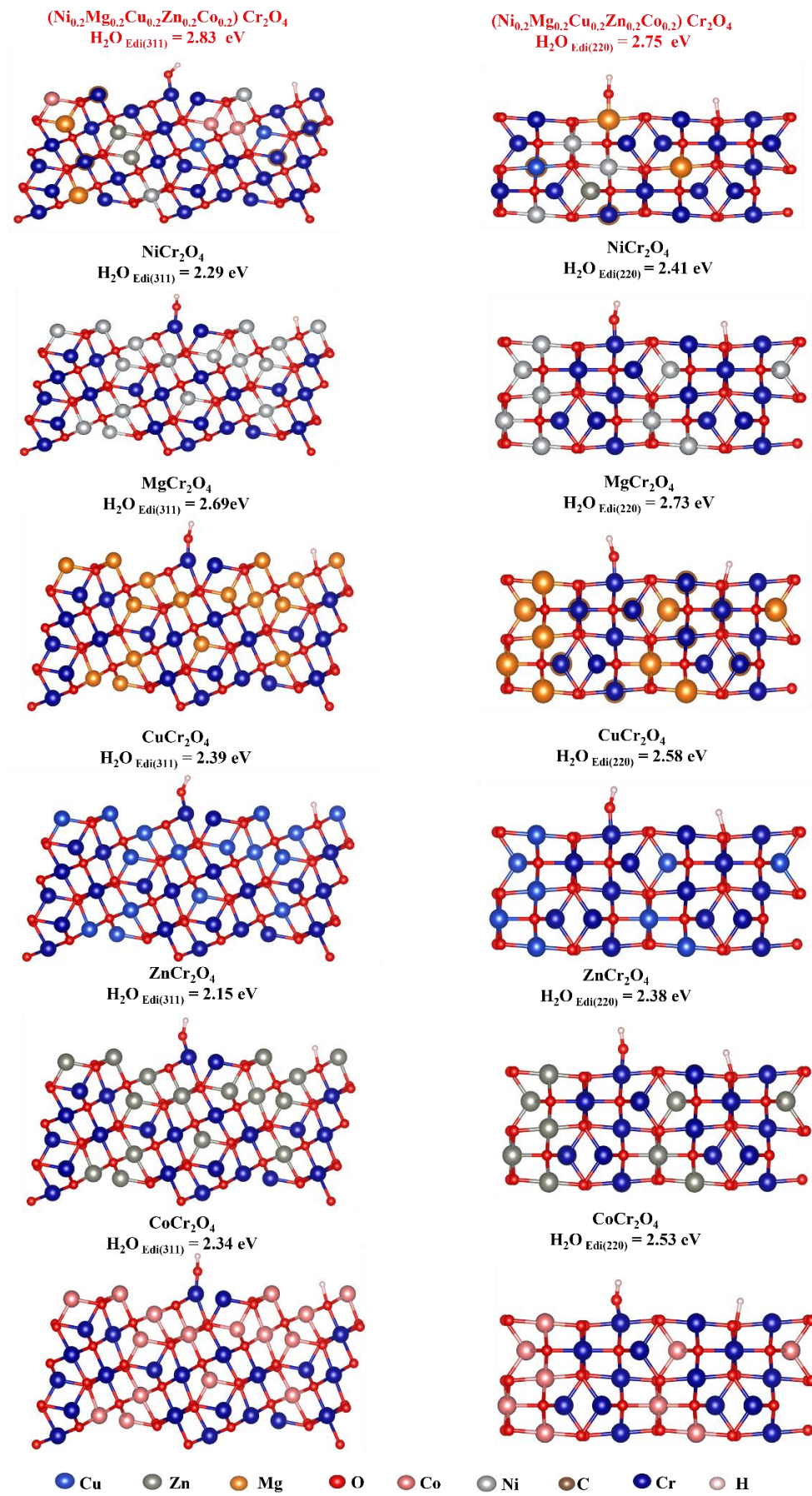


Figure 2. The dissociation energy of molecular H_2O on the surface of high entropy $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, and single metal ACr_2O_4 ($\text{A}=\text{Ni}, \text{Mg}, \text{Cu}, \text{Zn}, \text{Co}$) at crystal plane (220) and (311) respectively.

Original:

1.1 The adsorption energy of C₃H₆ on the surface of ACr₂O₄ by DFT calculation

Spinel oxides, especially AB₂O₄ (where A and B are metal ions), are a class of common catalysts.^[15] In this study, C₃H₆ catalytic oxidation by ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co) was selected as a model. A sites (A=Ni, Mg, Cu, Zn, Co) in ACr₂O₄ were tuned from single to five metal ions. The adsorption energy of C₃H₆ on the surface of single metal ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co) and (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ in the dry or 4.2vol% water conditions were calculated respectively (Figure 1, Figure S1, and Figure S2).

Revised:

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3. the authors need to characterize the samples after the reaction to further demonstrate the water resistance of the catalyst.

Reply:

Thanks for the helpful suggestion! We sincerely apologize for not fully characterizing the sample after the reaction. The stability experiments were carried out at a C₃H₆ conversion of ~70% with 4.2vol% water (Figure 6b). The C₃H₆ conversion of single metal ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co) continuously decreased in 20h and almost lost their catalytic activity in 50h. In sharp contrast, the activity of high entropy (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ was well retained within 100 hours. As suggested by the reviewer, to figure out the water resistance results, XRD, BET, and TGA characterization of the spent (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ catalyst were conducted and added.

The XRD pattern of the spent (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ catalyst after 100 hours of high-temperature steam exposure was unchanged (Figure S79). Composed of oxides of multiple metallic elements, the high-entropy oxide catalyst forms a highly complex lattice network. This complexity imparts excellent structural stability, allowing the catalyst to retain its original crystalline structure even under extreme conditions.^[1] Additionally, while the high-temperature steam environment may induce hydration or redox reactions on the catalyst surface, the high-entropy oxide catalyst likely exhibits outstanding chemical

stability, effectively resisting the impacts of such reactions.^[2] Thus, even after prolonged experimentation, the crystalline structure of the catalyst remains unchanged.

Furthermore, the spent (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ catalyst showed almost no change in its surface area after 100 hours of high-temperature steam exposure(**Figure S80**). The specific surface area of the fresh catalyst was 75 m²/g and that of the spent catalyst was 72.8 m²/g. This may be related to Gibbs free energy. High-entropy oxides typically exhibited higher entropy and lower Gibbs free energy, indicating greater disorder and randomness. This structural characteristic made them less susceptible to significant structural rearrangement or grain growth in high-temperature water vapor environments, thus maintaining a relatively stable specific surface area.^[4]

TGA analysis was conducted on the spent Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2}Cr₂O₄ catalyst after 100 hours of C₃H₆ combustion stability experiments at T₇₀ (temperatures that C₃H₆ conversion was 70%) in the presence of 4.2 vol% moisture. The mass reduction at 100-600 °C corresponded to the desorption of impurities or H₂O on the catalyst. If carbon or carbon compounds were present in the sample, they would decompose into gaseous products during the heating process at 600-800 °C.^[5~6] Due to the escape of gaseous products from the sample container, the quality of the sample decreased. This mass loss was manifested on the thermogravimetric curve as the mass gradually decreases with increasing temperature, forming a peak of mass loss.^[7~8] However, no significant quality decrease was observed in the **Figure S76**, indicating that the catalyst produced little coke during the reaction process. This indicated that the catalyst had strong resistance to carbon deposition, especially considering its high catalytic activity.

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Original:

To verify DFT calculations (Figures 1-3), C₃H₆ oxidation by as-made oxide samples was carried out (**Figure 6a**). There was no the influence of internal and external diffusion for C₃H₆ oxidation (**Figure S32~S33**). The (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ catalyst exhibited good catalytic performance for C₃H₆ oxidation with T₉₀ (C₃H₆ conversion was 90%) at 265°C, better than that of single metal ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co) (318°C~350°C) (**Table S7**). This result became understandable if the lower formation energy of oxygen vacancies by (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ was considered (Figure 3). Real-world applications required catalysts to be stable in ubiquitous moisture.^[42-44] Actually, the DFT calculation already suggested better hydrothermal stability of high entropy (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄. To verify the DFT conclusion, the stability experiments were carried out at a C₃H₆ conversion of ~70% with 4.2vol% water (**Figure 6b**). The C₃H₆ conversion of single metal ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co) continuously decreased in 20h and almost lost their catalytic activity in 50h. In sharp contrast, the activity of high entropy (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ was well retained within 100 hours. This huge difference encouraged us to conduct more characterization for water resistance mechanism exploration.

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demonstrate the water resistance of the catalyst, XRD, BET, and TGA characterization of the spent $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ catalyst were conducted. The XRD pattern of the spent $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ catalyst after reaction was unchanged(**Figure S79**). Furthermore, the spent $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ catalyst showed almost no change in its surface area after reaction (**Figure S80**). No significant mass loss was observed in the TGA analysis of spent catalyst (**Figure S76**), indicating that the catalyst produced little coke (0.73wt%) during the reaction process. This indicated that the catalyst had strong resistance to carbon deposition, especially considering its high catalytic activity.

Moreover, tests of water resistance at humidity levels of 10 vol% was conducted to further demonstrate the water resistance (**Figure S81**). In addition, the $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ catalyst was aged at 800 °C in the presence of 4.2vol% moisture for 30 hours. Then, the aged catalyst was subjected to XRD, BET and stability experiments of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ at T_{70} in 4.2vol% moisture within 100h. The crystal structure and specific surface area are almost unchanged (**Figure S82~s83**).After being aged at 800 °C in the presence of 4.2vol% moisture for 30 hours, the activity of spent $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ was still well maintained in stability experiments at T_{70} in 4.2vol% moisture within 100h(**Figure S84**). TGA test results indicated that no carbon deposition has occurred during the aging process of 800 °C(**Figure S85**).

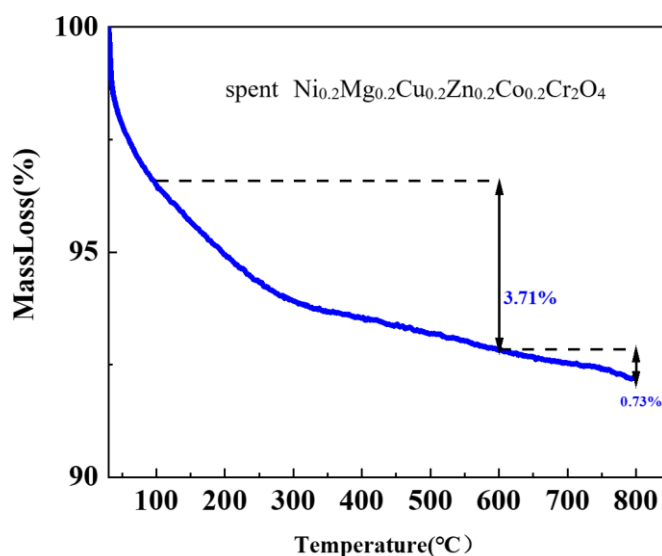


Figure S76 TGA spectra of spent $\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2}\text{Cr}_2\text{O}_4$ catalysts after 100 hours of C_3H_6 combustion stability experiments at T_{70} (temperatures that C_3H_6 conversion was 70%) in the presence of 4.2 vol% moisture.

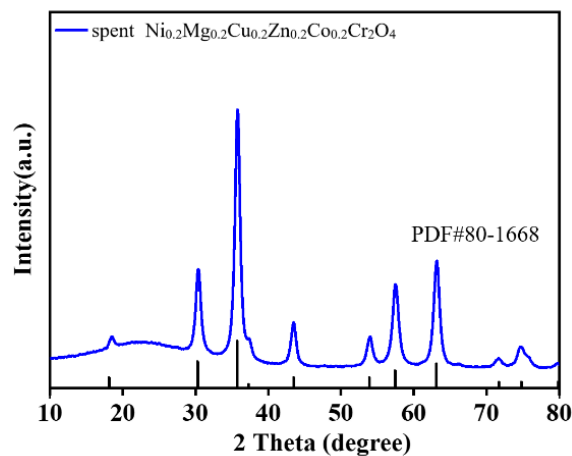


Figure S79 XRD spectra of spent $\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2}\text{Cr}_2\text{O}_4$ catalysts after 100 hours of C_3H_6 combustion stability experiments at T_{70} (temperatures that C_3H_6 conversion was 70%) in the presence of 4.2 vol% moisture.

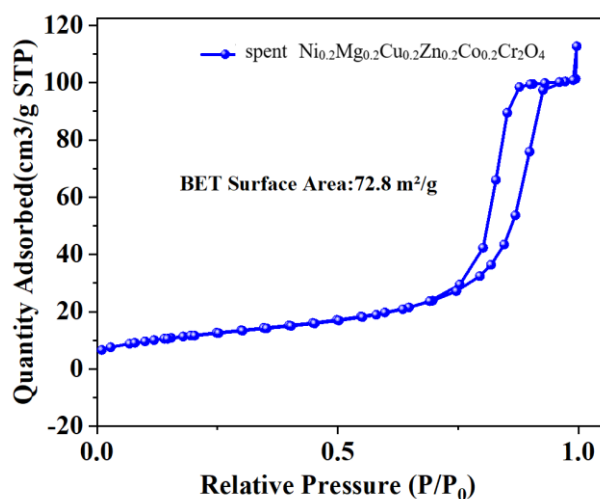


Figure S80. Nitrogen adsorption-desorption isotherms of spent $\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2}\text{Cr}_2\text{O}_4$ catalysts after 100 hours of C_3H_6 combustion stability experiments at T_{70} (temperatures that C_3H_6 conversion was 70%) in the presence of 4.2 vol% moisture.

4. The authors tested the water resistance of the catalyst at a humidity of 4.2 vol%. What is the reason for choosing this humidity? It is suggested to supplement tests of water resistance at humidity levels of 10 vol% to better study the tolerance of the catalyst under different humidity conditions.

Reply:

Thanks for the constructive suggestion! We sincerely apologize for not clearly explaining the reason for choosing 4.2% water vapor in the text. Catalytic combustion is an important industrial process that often being conducted at atmospheric pressure. In actual industrial production and laboratory conditions, there is often a certain level of humidity in the air, i.e. water vapor. At a certain temperature, when the equilibrium state is reached, the rate of water molecules in the liquid and gas phases reaches dynamic equilibrium, and the concentration of water vapor in the gas phase is called the saturated vapor pressure of water. 4.2% water vapor is the saturated vapor pressure of water vapor in the air at 30 °C. ^[1~3] The 4.2% water vapor is closest to the actual working conditions, ^[4~7] which more realistically simulates the conditions in the actual operating environment to ensure the reliability and repeatability of the experimental results.

In addition, tests of water resistance at humidity levels of 10 vol% was added. The bubbler bubbled in a water bath at 30°C to simulate 4.2vol% water vapor, while bubbling in a water bath at 70°C can simulate 10vol% water vapor . After 100 hours of propylene combustion experiments with 10 vol% water vapor, the high-entropy oxide catalyst exhibited persistent catalytic activity without any signs of inactivation, although slight fluctuations in conversion rates were observed (**Figure S81**). The results confirmed the stability and activity maintenance ability of the high-entropy oxide catalyst under the condition of 10vol% water vapor. The result was in good agreement with the results of the DFT calculations.

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Revised:

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hydrothermal stability of high entropy $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$. To verify the DFT conclusion, the stability experiments were carried out at a C_3H_6 conversion of $\sim 70\%$ with 4.2vol% water (**Figure 6b**). 4.2% water vapor was the saturated vapor pressure of water vapor in the air at 30°C .^[42-44] The 4.2% water vapor was closest to the actual working conditions. The C_3H_6 conversion of single metal ACr_2O_4 ($\text{A}=\text{Ni}, \text{Mg}, \text{Cu}, \text{Zn}, \text{Co}$) continuously decreased in 20h and almost lost their catalytic activity in 50h. In sharp contrast, the activity of high entropy $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ was well retained within 100 hours. To further demonstrate the water resistance of the catalyst, XRD, BET, and TGA characterization of the spent $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ catalyst were conducted. The XRD pattern of the spent $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ catalyst after reaction was unchanged (**Figure S79**). Furthermore, the spent $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ catalyst showed almost no change in its surface area after reaction (**Figure S80**). No significant quality decrease was observed in the TGA analysis (**Figure S76**), indicating that the catalyst produced little coke (0.73wt%) during the reaction process. This indicated that the catalyst had strong resistance to carbon deposition, especially considering its high catalytic activity.

Moreover, tests of water resistance at humidity levels of 10 vol% was conducted to further demonstrate the water resistance (**Figure S81**). In addition, the $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ catalyst was aged at 800°C in the presence of 4.2vol% moisture for 30 hours. Then, the aged catalyst was subjected to XRD, BET and stability experiments of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ at T_{70} in 4.2vol% moisture within 100h. The crystal structure and specific surface area are almost unchanged (**Figure S82~s83**). After being aged at 800°C in the presence of 4.2vol% moisture for 30 hours, the activity of spent $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ was still well maintained in stability experiments at T_{70} in 4.2vol% moisture within 100h (**Figure S84**). TGA test results indicated that no carbon deposition has occurred during the aging process of 800°C (**Figure S85**).

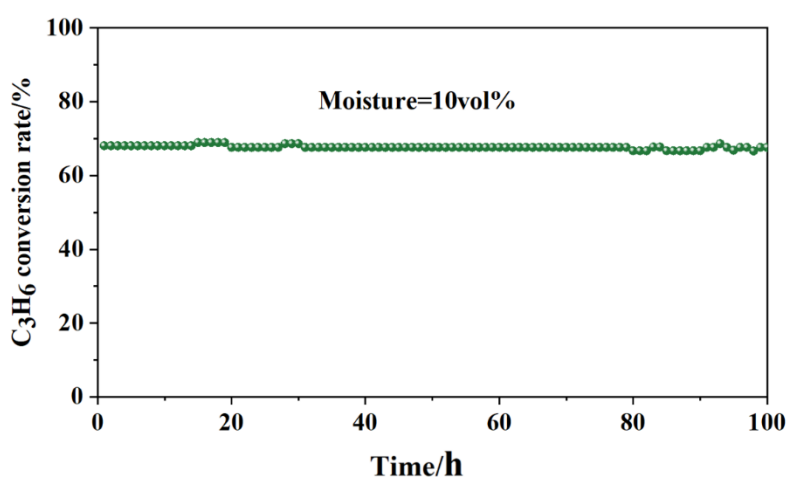


Figure S81. Stability experiments of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ at T_{70} (temperatures that C_3H_6 conversion was 70%) in the presence of 10vol% moisture.

5. I recommend that the authors conduct activity tests and characterizations on the catalyst after

hydrothermal aging at 800°C to better study the catalyst's hydrothermal stability. The current activity tests do not demonstrate that the HEO catalyst possesses good hydrothermal stability.

Reply:

Thanks for the important suggestion! We strongly agree with the reviewer. The current activity indeed did not demonstrate that the HEO catalyst possessed good hydrothermal stability. According to your useful recommendations, the $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ catalyst was aged at 800 °C in the presence of 4.2vol% moisture for 30 hours. Then, the aged catalyst was subjected to XRD, BET and stability experiments of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ at T_{70} (temperatures that C_3H_6 conversion was 70%) in the presence of 4.2vol% moisture within 100h.

The spent $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ showed characteristic diffraction peaks of cubic phase spinel (JCPDS 80-1668), and no other diffraction peaks were observed(**Figure S82**). This indicated that the action of water vapor was not enough to destroy this complex lattice structure at 800°C, and the crystal structure of the catalyst can remain stable, thus maintaining the catalytic activity.^[1~2] In addition, the specific surface area of the catalyst was also one of the important factors affecting the catalytic activity. The active site of a catalyst was usually located on its surface, so the maintenance of specific surface area was critical to the activity of the catalyst.^[3~6] The results showed that the specific surface area of the spent $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ catalyst was 75.2 m²/g after aged at 800 °C in the presence of 4.2vol% moisture for 30 hours, which was not significantly affected, which mean that the exposure of the active site was not seriously affected, and the catalytic activity was maintained (**Figure S83**).

In addition, after being aged at 800 °C in the presence of 4.2vol% moisture for 30 hours, the activity of spent $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ was still well maintained in stability experiments at T_{70} (temperatures that C_3H_6 conversion was 70%) in the presence of 4.2vol% moisture within 100h(**Figure S84**). The conversion rate fluctuated slightly, but it was not inactivated. TGA test results indicated that no carbon deposition has occurred during the aging process of 800 °C(**Figure S85**).

[1] Zhang, J.; Yan, J.; Calder, S.; Zheng, Q.; McGuire, M. A.; Abernathy, D. L.; Ren, Y.; Lapidus, S. H.; Page, K.; Zheng, H.; Freeland, J. W.; Budai, J. D.; Hermann, R. P., Long-Range Antiferromagnetic Order in a Rocksalt High Entropy Oxide. *Chemistry of Materials* **2019**, 31 (10), 3705-3711.

[2] Sun, Y.; Dai, S., High-entropy materials for catalysis: A new frontier. *Science Advances* **2021**, 7 (20), eabg1600.

- [3] Chen, H.; Jie, K.; Jafta, C. J.; Yang, Z.; Yao, S.; Liu, M.; Zhang, Z.; Liu, J.; Chi, M.; Fu, J.; Dai, S., An ultrastable heterostructured oxide catalyst based on high-entropy materials: A new strategy toward catalyst stabilization via synergistic interfacial interaction. *Applied Catalysis B: Environmental* **2020**, 276, 119155.
- [4] Chen, H.; Fu, J.; Zhang, P.; Peng, H.; Abney, C. W.; Jie, K.; Liu, X.; Chi, M.; Dai, S., Entropy-stabilized metal oxide solid solutions as CO oxidation catalysts with high-temperature stability. *Journal of Materials Chemistry A* **2018**, 6 (24), 11129-11133.
- [5] Sarkar, A.; Velasco, L.; Wang, D.; Wang, Q.; Talasila, G.; de Biasi, L.; Kubel, C.; Brezesinski, T.; Bhattacharya, S. S.; Hahn, H.; Breitung, B., High entropy oxides for reversible energy storage. *Nat Commun* **2018**, 9 (1), 3400.
- [6] Oses, C.; Toher, C.; Curtarolo, S., High-entropy ceramics. *Nature Reviews Materials* **2020**, 5 (4), 295-309.

Original:

To verify DFT calculations (Figures 1-3), C₃H₆ oxidation by as-made oxide samples was carried out (**Figure 6a**). There was no the influence of internal and external diffusion for C₃H₆ oxidation (**Figure S32~S33**). The (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ catalyst exhibited good catalytic performance for C₃H₆ oxidation with T₉₀ (C₃H₆ conversion was 90%) at 265°C, better than that of single metal ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co) (318°C~350°C) (**Table S7**). This result became understandable if the lower formation energy of oxygen vacancies by (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ was considered (Figure 3). Real-world applications required catalysts to be stable in ubiquitous moisture.^[42-44] Actually, the DFT calculation already suggested better hydrothermal stability of high entropy (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄. To verify the DFT conclusion, the stability experiments were carried out at a C₃H₆ conversion of ~70% with 4.2vol% water (**Figure 6b**). The C₃H₆ conversion of single metal ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co) continuously decreased in 20h and almost lost their catalytic activity in 50h. In sharp contrast, the activity of high entropy (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ was well retained within 100 hours. This huge difference encouraged us to conduct more characterization for water resistance mechanism exploration.

Revised:

To verify DFT calculations (Figures 1-3), C₃H₆ oxidation by as-made oxide samples was carried out (**Figure 6a**). There was no the influence of internal and external diffusion for C₃H₆ oxidation (**Figure S32~S33**). The (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ catalyst exhibited good catalytic performance for C₃H₆ oxidation with T₉₀ (C₃H₆ conversion was 90%) at 265°C, better than that of single metal ACr₂O₄ (A=Ni, Mg,

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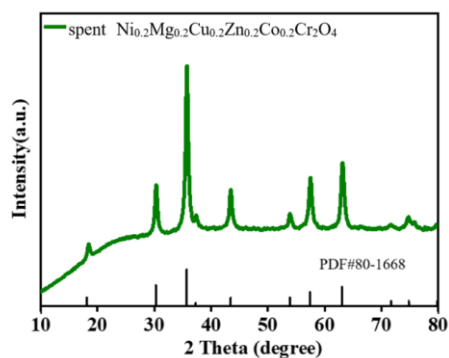


Figure S82. XRD spectra of spent $\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2}\text{Cr}_2\text{O}_4$ catalyst after hydrothermal aging at 800°C for 30h in the presence of 4.2 vol% moisture.

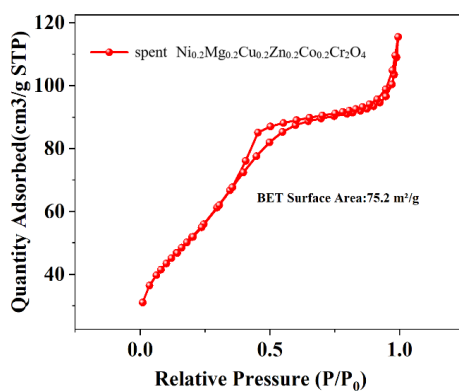


Figure S83. Nitrogen adsorption–desorption isotherms of spent $\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2}\text{Cr}_2\text{O}_4$ catalyst after hydrothermal aging at 800°C for 30h in the presence of 4.2 vol% moisture.

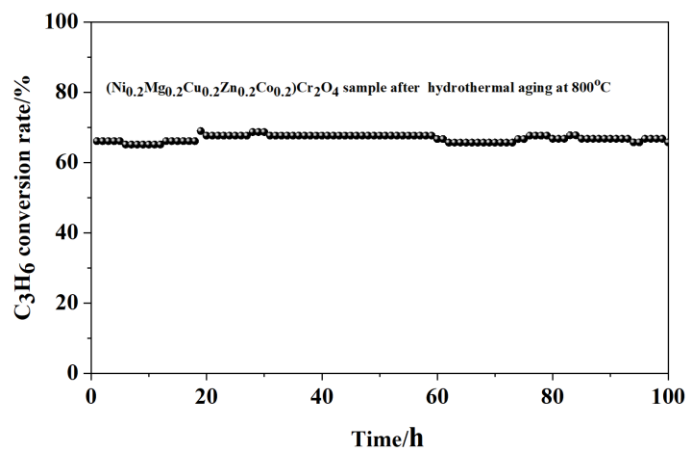


Figure S84. After hydrothermal aging at 800°C for 30h and then stability experiments of (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ was conducted in the presence of 4.2vol% moisture.

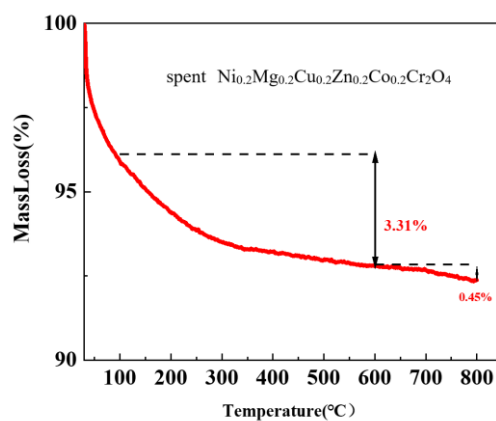


Figure S85. TGA isotherms of spent Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2}Cr₂O₄ catalyst after hydrothermal aging at 800°C for 30h in the presence of 4.2 vol% moisture.

6. High-entropy catalysts have a complex structure with many types of active sites. When calculating the adsorption and dissociation energies of C₃H₆ and H₂O using DFT, how did the authors consider the position of adsorption?

Reply:

Thanks for the constructive question! That is really a key issue affecting the energy calculation. We sincerely apologize for not making it clear. Therefore, we have added it in the revised Supporting information.

Original:

To deal with the C₃H₆ molecule absorption, the adsorption energy in metallic oxide substrate is defined by [9-11]

$$E[\text{ads}] = E_{\text{total}} - E_{\text{sub}} - E_{\text{mol}} \quad (2)$$

where E_{total} , E_{sub} , E_{mol} is the energy of the alloy structure, metallic oxide substrate, and adsorbed molecule, respectively. Here, to distinguish the system with and without H₂O molecules, we have calculated the absorption energy containing H₂O molecules and not containing the H₂O molecules, where the H₂O molecule is randomly placed on the substrates to simulate the real experimental condition.

Revised:

A series of typical active sites on these complex structures, such as the top site, hollow site, bridge site and so on were considered. Moreover, we have calculated these typical sites on different transition metal elements to serve as possible positions for determining the optimum active sites for the adsorption and dissociation energies of C₃H₆ and H₂O using DFT (**Figure 1**). Due to that DFT can only determine the local minimum for an initial structure, we have considered the different orientation for the C₃H₆ and H₂O molecules to obtain the optimum position of the adsorption. To deal with the C₃H₆ molecule absorption, the adsorption energy in metallic oxide substrate is defined by [9-11]

$$E[\text{ads}] = E_{\text{total}} - E_{\text{sub}} - E_{\text{mol}} \quad (2)$$

where E_{total} , E_{sub} , E_{mol} is the energy of the alloy structure, metallic oxide substrate, and adsorbed molecule, respectively. Here, to distinguish the system with and without H₂O molecules, we have calculated the absorption energy containing H₂O molecules and not containing the H₂O molecules, where the H₂O molecule is randomly placed on the substrates to simulate the real experimental condition.

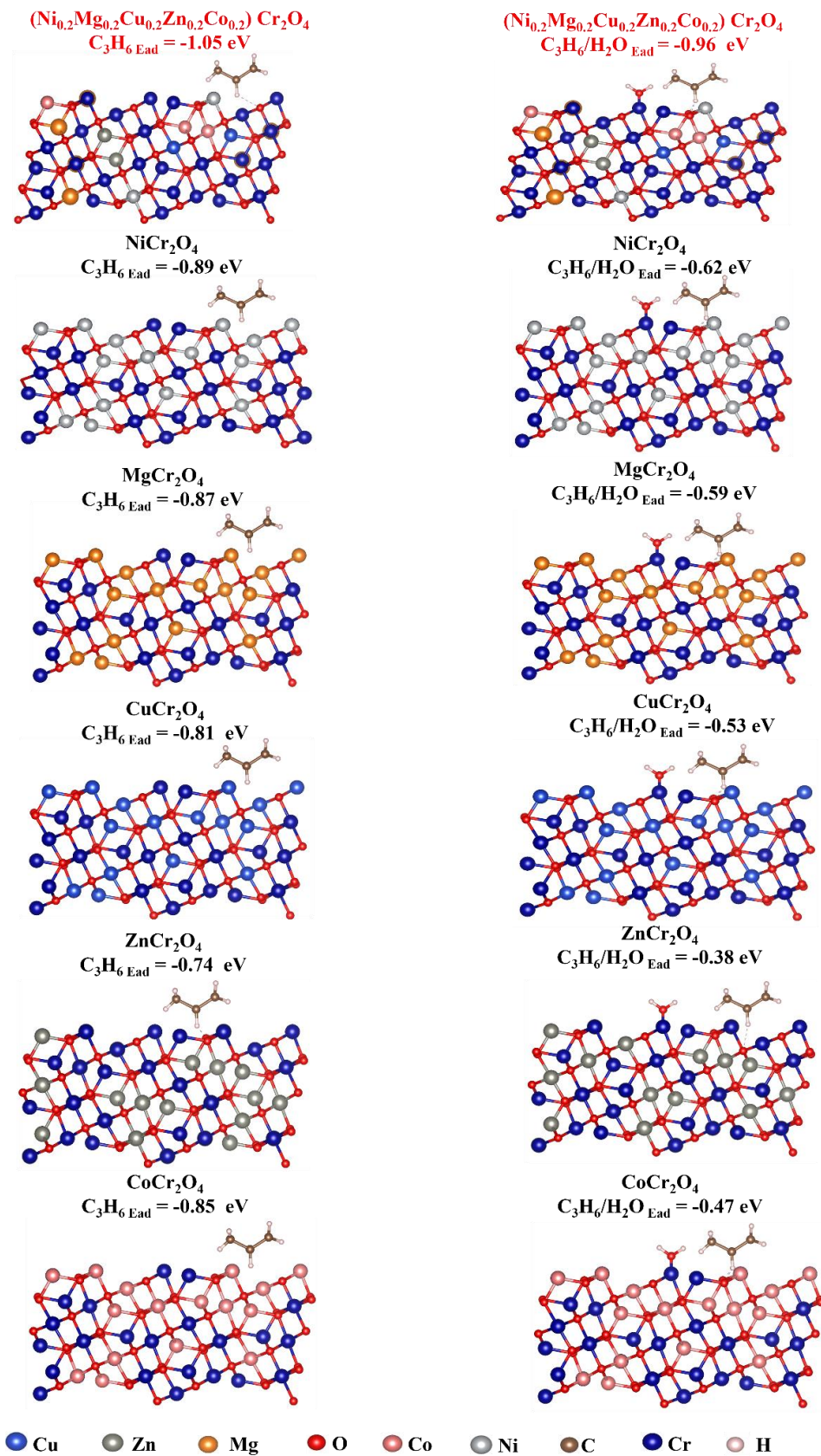


Figure 1. The adsorption energy of C_3H_6 on the surface (311 plane) of high entropy $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ and single metal ACr_2O_4 ($\text{A}=\text{Ni}, \text{Mg}, \text{Cu}, \text{Zn}, \text{Co}$) in the absence and presence of 4.2vol% water vapor.

7. Has the adsorption energy of H₂O been calculated through DFT? What are the results?

Reply:

Thanks for the constructive comment! We sincerely apologize for ignoring this important calculation. Based on your useful suggestion, we have added this calculation. The adsorption energy of H₂O on the surface of high entropy (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ and single metal ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co) at crystal plane (220), (311) and (111) were calculated by DFT, respectively (**Figure S86~S88**). The results showed that the water adsorption energy of high-entropy (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ was the lowest of them. This may be due to that the lower Gibbs free energy of (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ to make it more stable than single metal oxide, even under moisture-containing conditions.^[1] Moreover, various metal components with reactant adsorption sites, reactive sites for activation, and H₂O non-adsorption sites could be combined into single-phase high-entropy (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ catalysts.^[2]

[1] Aamlid, S. S.; Oudah, M.; Rottler, J.; Hallas, A. M., Understanding the Role of Entropy in High Entropy Oxides. *Journal of the American Chemical Society* **2023**, 145 (11), 5991-6006.

[2] Sun, Y.; Dai, S., High-entropy materials for catalysis: A new frontier. *Science Advances* **2021**, 7 (20), eabg1600.

Original:

1.2 The dissociation energy of molecular H₂O on the surface of ACr₂O₄ by DFT calculation

The dissociation energy of molecular H₂O on the surface of high entropy (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ and single metal ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co) at crystal plane (220), (311) and (111) were calculated by DFT, respectively (**Figure 2, Table S2 and Figure S3**). The dissociation energy of molecular H₂O on the surface of high entropy (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ were 2.83eV (311), 2.75eV (220) and 2.97eV (111). In contrast, the dissociation energy of molecular H₂O on the surface of single metal ACr₂O₄ at (311) were 2.15eV~ 2.69eV, at (220) were 2.38eV~ 2.73eV and at (111) were 2.62eV~ 2.90eV. The dissociation energy of molecular H₂O on the surface of ternary control samples at crystal plane (220) and (311) respectively were shown in **Figure S4~S5 and Table S3**. Those results showed that molecular H₂O was easy to dissociate into H⁺ and OH⁻ on the surface of single metal ACr₂O₄ compared with (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄, then OH⁻ could react with single metal ACr₂O₄ to form hydroxide. Thus, the structure of single metal ACr₂O₄ was destroyed and the catalytic activity decreased in the C₃H₆ oxidation. This DFT calculation suggested the better hydrothermal stability of high entropy oxide catalysts, which may be induced by their lower Gibbs free energy ($\Delta G = \Delta H - T\Delta S$).

Revised:

1.2 The dissociation energy and adsorption energy of molecular H₂O on the surface of ACr₂O₄ by DFT calculation

The dissociation energy of molecular H₂O on the surface of high entropy (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ and single metal ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co) at crystal plane (220), (311) and (111) were calculated by DFT, respectively (Figure 2, Table S2 and Figure S3). The dissociation energy of molecular H₂O on the surface of high entropy (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ were 2.83eV (311), 2.75eV (220) and 2.97eV (111). In contrast, the dissociation energy of molecular H₂O on the surface of single metal ACr₂O₄ at (311) were 2.15eV~ 2.69eV, at (220) were 2.38eV~ 2.73eV and at (111) were 2.62eV~ 2.90eV. The dissociation energy of molecular H₂O on the surface of ternary control samples at crystal plane (220) and (311) respectively were shown in Figure S4~S5 and Table S3. Those results showed that molecular H₂O was easy to dissociate into H⁺ and OH⁻ on the surface of single metal ACr₂O₄ compared with (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄, then OH⁻ could react with single metal ACr₂O₄ to form hydroxide. Thus, the structure of single metal ACr₂O₄ was destroyed and the catalytic activity decreased in the C₃H₆ oxidation. In addition, the adsorption energy of H₂O on the surface of high entropy (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ and single metal ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co) at crystal plane (220), (311) and (111) were calculated by DFT, respectively (Figure S86~S88). The results showed that the water adsorption energy of high-entropy (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ was the lowest of them. This DFT calculation suggested the better hydrothermal stability of high entropy oxide catalysts, which may be induced by their lower Gibbs free energy ($\Delta G = \Delta H - T\Delta S$).

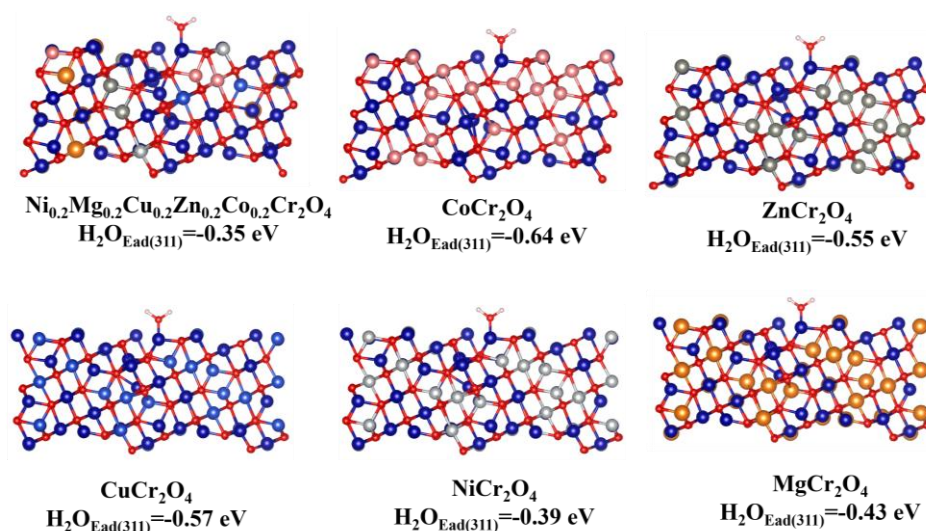


Figure S86. The adsorption energy of H₂O on the surface (311 plane) of high entropy (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ and single metal ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co).

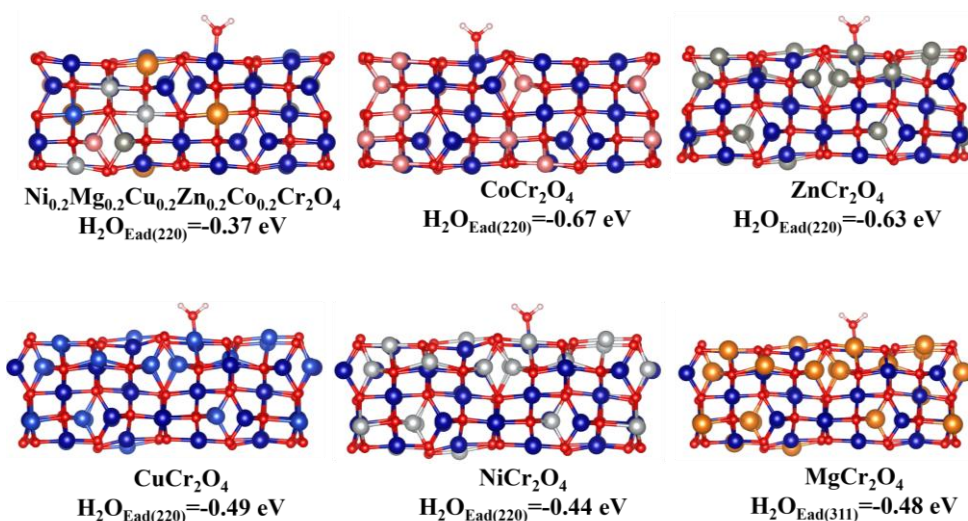


Figure S87. The adsorption energy of H_2O on the surface (220 plane) of high entropy $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ and single metal ACr_2O_4 ($\text{A}=\text{Ni}, \text{Mg}, \text{Cu}, \text{Zn}, \text{Co}$).

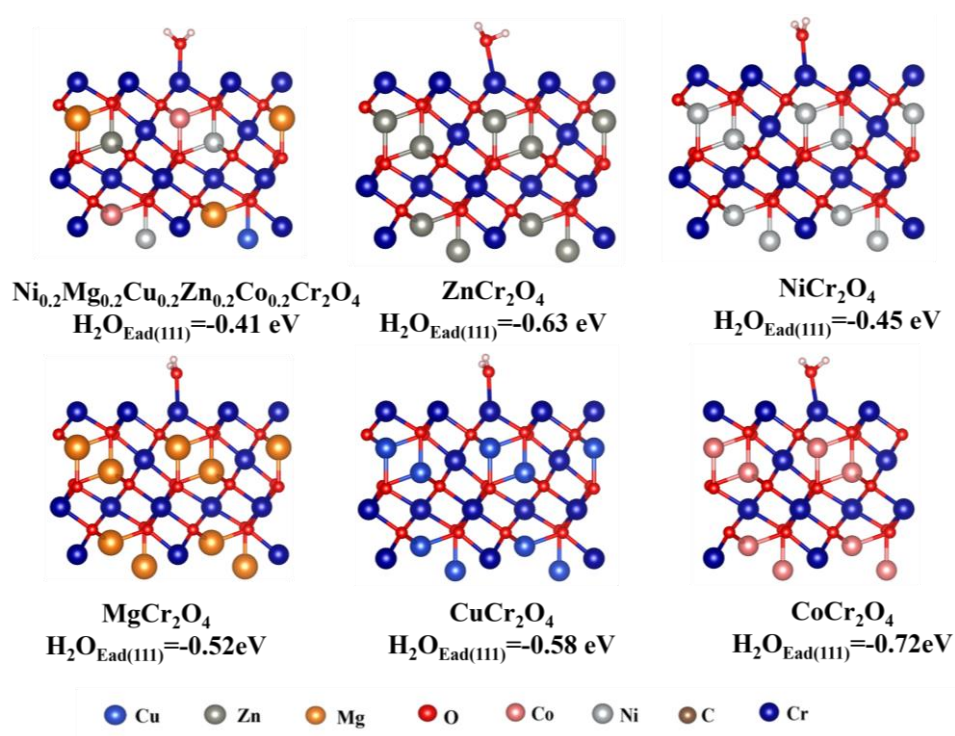


Figure S88. The adsorption energy of H_2O on the surface (111 plane) of high entropy $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ and single metal ACr_2O_4 ($\text{A}=\text{Ni}, \text{Mg}, \text{Cu}, \text{Zn}, \text{Co}$).

REVIEWER COMMENTS

Reviewer #4 (Remarks to the Author):

For the revision of this manuscript, the authors have added, hydrothermal stability test, 10vol% humidity resistance test, and characterizations before and after reaction, aiming at addressing the reviewers' comments. Meanwhile, the carbon balance was tested using updated GC with Ni catalyst FID. In my opinion, this manuscript has been improved significantly and most of the reviewers' comments have been resolved. However, the DFT part and mechanism discussion still have some issues which need to be addressed before publication.

Comment 1: For DFT model, and the author seems to have not systematically considered the substitution of A-site atoms in the spinel structure. The placement of atoms is relatively arbitrary and has not been compared using Gibbs free energy of the system. How did the author build the DFT model, how the set the position of the atoms in the model?

Comment 2: Many literature reports that the oxidation of propylene not only involves lattice oxygen vacancies, but also is related to surface adsorbed oxygen. In theory, the author also provides data on the adsorption of O₂ on the catalyst surface, including adsorption energy and charge transfer.

Comment 3: The format of the manuscript needs to be revised deeply. Line 91 At, Line 90 space, Line 170 S86-S88 (S5-S85 are missing). Figure 1-Figure 3 should be re-organized. Format errors also exist in Supporting Information

Response to the reviewers' comments

Dear Reviewers,

We would like to express sincere thanks to the reviewer for the useful suggestions, which enabled us to solve this difficult problem that had troubled us before. These comments are valuable and very helpful in revising and improving our paper. According to your nice suggestions, we have made extensive corrections to our previous manuscript, a point-by-point response to the reviewers' comments is listed below. In this revised version, all changes to our manuscript are all highlighted in yellow color.

Reviewer #4

Comments:

For the revision of this manuscript, the authors have added, hydrothermal stability test, 10vol% humidity resistance test, and characterizations before and after reaction, aiming at addressing the reviewers' comments. Meanwhile, the carbon balance was tested using updated GC with Ni catalyst FID. In my opinion, this manuscript has been improved significantly and most of the reviewers' comments have been resolved. However, the DFT part and mechanism discussion still have some issues which need to be addressed before publication.

Comment 1: For DFT model, and the author seems to have not systematically considered the substitution of A-site atoms in the spine structure. The placement of atoms is relatively arbitrary and has not been compared using Gibbs free energy of the system. How did the author build the DFT model, how the set the position of the atoms in the model?

Reply:

Thanks for the constructive suggestion!

Initially, we carefully investigated the literatures, according to the design of high entropy oxide model. For example, Vladislav A. Mints and co-workers^[4] made the high-entropy oxide model randomly occupied by each of the elements with equal probability. In addition, Svane, K. L. and their co-workers^[5] also constructed random element occupation model for the electrocatalysis investigation, which inspired the

model in this work. They built the high-entropy metal oxide structures by random occupation, where all elements with equal probability. The lattice constant was chosen as the average of that calculated for the six single oxide. This method lacked of accurate model construction, so we used a more quantitative approach by defining the correlation function to measure the random order of metal oxide structure. When the correlation functions were zero, we can assert that the high-entropy metal oxide was perfectly random.

As we focused on the high-entropy metal oxide, the substituted metallic atoms would randomly occupy A-site positions. We used Special Quasi-random Structures (SQS) to find a supercell whose cluster correlation functions as best as possible match those of the random structures,^[1] to approximate random (disordered) solid solution structures for high-entropy metal oxide. We employed ICET package to generate possible SQS for randomly occupation of A-site atoms.^[2] Therefore, the A-site atoms were relatively random in order to construct the high-entropy metal oxide.

Meanwhile, S.-H. Wei *et al* has shown that it was possible to design "special quasirandom structures" (SQS's) that mimicked for small N (even $N=8$) the first few, physically most relevant radial correlation functions of an infinite, perfectly random structure far better than the standard technique did. These SQS's were shown to be short-period superlattices of 4-16 atoms/cell whose layers were stacked in rather nonstandard orientations. Since these SQS's mimicked well the local atomic structure of the random alloy, their electronic properties, calculable via first-principles techniques, providing a representation of the electronic structure of the alloy. They demonstrated the usefulness of these SQS's by applying them to semiconductor alloys.^[3] To verify this point, we chose $(\text{NiMgCuZnCo})_{0.2}\text{Cr}_2\text{O}_4$ as the example to show that the energy-independent for different occupation of A-site atoms. We generated 20 SQS to calculate the energy as shown in **Figure S89**, and the relative energy were almost less than 0.2 eV, indicating that the energy was converged. Therefore, one of them could be selected for modeling and would not significantly affect the final results of DFT calculation.

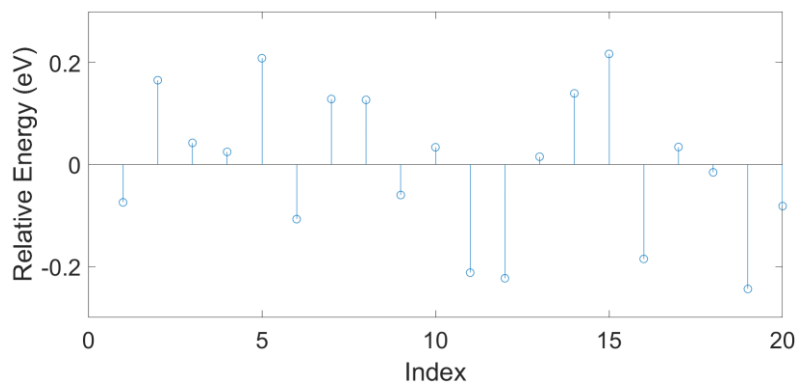


Figure S89. Relative energy of 20 SQS, where the mean energy is set to zero.

- [1] Alex Zunger, S.-H. Wei, L. G. Ferreira, and James E. Bernard Special quasirandom structures. *Phys. Rev. Lett.* 65, 353 (1990)
- [2] Ångqvist, M. et al. ICET – A Python Library for constructing and sampling alloy cluster expansions. *Adv. Theory Simulations* 2, 1900015 (2019).
- [3] S.-H. Wei, L. G. Ferreira, James E. Bernard, and Alex Zunger Electronic properties of random alloys: Special quasirandom structures. *Phys. Rev. B* 42, 9622 (1990)
- [4] Vladislav A. Mints, Katrine L. Svane, Jan Rossmeisl, and Matthias Arenz Exploring the High-Entropy Oxide Composition Space: Insights through Comparing Experimental with Theoretical Models for the Oxygen Evolution Reaction. *ACS Catal.* 2024, 14, 9, 6936–6944
- [5] Svane, K. L.; Rossmeisl, J. Theoretical Optimization of Compositions of High-Entropy Oxides for the Oxygen Evolution Reaction. *Angew. Chem.* 2022, 134 (19), e202201146

Revised:

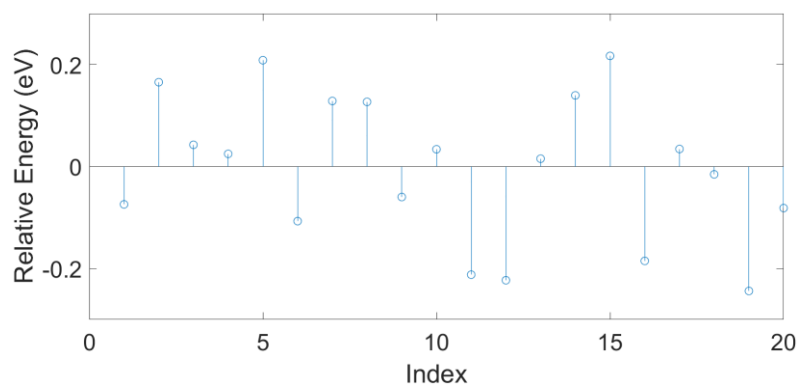


Figure S89. Relative energy of 20 SQS, where the mean energy is set to zero.

Comment 2: Many literature reports that the oxidation of propylene not only involves lattice oxygen vacancies, but also is related to surface adsorbed oxygen. In theory, the author also provides data on the adsorption of O₂ on the catalyst surface, including adsorption energy and charge transfer.

Reply:

Thanks for the useful suggestion!

We have added DFT calculations on oxygen adsorption energy and charge transfer (**Figure S90~92**). For three different crystal planes (220), (311) and (111), the charge transfer of (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ was higher than those of ACr₂O₄ (A=single metal Ni, Mg, Cu, Zn, Co) respectively. On the (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ catalyst, more transfer of electrons from the metal surface to the anti-bonding orbitals of oxygen molecules would activate oxygen molecules, thereby promoting catalytic activity in some degree.^[1] Compared to single metal oxides, (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ had higher oxygen adsorption energy, and oxygen molecules can likely adsorb on the active sites on the catalyst surface. These active sites would activate oxygen by interacting with oxygen molecules, being expected to promoting subsequent catalytic reactions.^[2]

[1] Shi, J.; Qi, T.; Sun, B.-C.; Chu, G.-W.; Chen, J.-F., Catalytic oxidation of benzyl alcohol over MnO₂: Structure-activity description and reaction mechanism. *Chemical Engineering Journal* **2022**, *440*, 135802.

[2] Jian, Y.; Tian, M.; He, C.; Xiong, J.; Jiang, Z.; Jin, H.; Zheng, L.; Albilali, R.; Shi,

J.-W., Efficient propane low-temperature destruction by Co_3O_4 crystal facets engineering: Unveiling the decisive role of lattice and oxygen defects and surface acid-base pairs. *Applied Catalysis B: Environmental* **2021**, 283, 119657.

Original:

The oxygen species of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, ZnCr_2O_4 , and CoCr_2O_4 were closely related to their C_3H_6 oxidation performance, so O_2 -TPD experiments were conducted (**Figure 7b**). Two desorption peaks of oxygen species appeared at around 350 and 720°C for ZnCr_2O_4 .^[46-48] The O_2 peak desorbed at below 400°C was usually considered as the reactive oxygen species (ROS) of oxide catalysts.^[16, 44, 49-51] Notably, $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ desorbed surface lattice oxygen at a lower temperature (220°C) than ZnCr_2O_4 (320°C) and CoCr_2O_4 (315°C). This feature suggested the lower formation energy of oxygen vacancy in $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, matching well with the DFT calculation (Figure 3). The weak binding between ROS and adjacent atoms made it easier to escape from the catalyst surface, which was crucial for enhancing the catalytic performance of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ in C_3H_6 oxidation (Figure 6a).^[43, 50]

Revised:

The oxygen species of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, ZnCr_2O_4 , and CoCr_2O_4 were closely related to their C_3H_6 oxidation performance, so O_2 -TPD experiments were conducted (**Figure 7b**). Two desorption peaks of oxygen species appeared at around 350 and 720°C for ZnCr_2O_4 .^[46-48] The O_2 peak desorbed at below 400°C was usually considered as the reactive oxygen species (ROS) of oxide catalysts.^[16, 44, 49-51] Notably, $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ desorbed surface lattice oxygen at a lower temperature (220°C) than ZnCr_2O_4 (320°C) and CoCr_2O_4 (315°C). This feature suggested the lower formation energy of oxygen vacancy in $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, matching well with the DFT calculation (Figure 3). The weak binding between ROS and adjacent atoms made it easier to escape from the catalyst surface, which was crucial for enhancing the catalytic performance of

($\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2}$) Cr_2O_4 in C_3H_6 oxidation (Figure 6a).^[43, 50] In addition, Oxygen adsorption energy and charge transfer were shown in **Figure S90~92**. For three different crystal planes (220), (311) and (111), the charge transfer of ($\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2}$) Cr_2O_4 was higher than those of single metal ACr_2O_4 (A=Ni, Mg, Cu, Zn or Co) respectively, facilitating the activation of oxygen molecules. Compared to single metal oxides, ($\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2}$) Cr_2O_4 had higher oxygen adsorption energy, and oxygen molecules can stably adsorb on the active sites on the catalyst surface. These active sites would activate oxygen by interacting with oxygen molecules, being expected to promoting subsequent catalytic reactions.

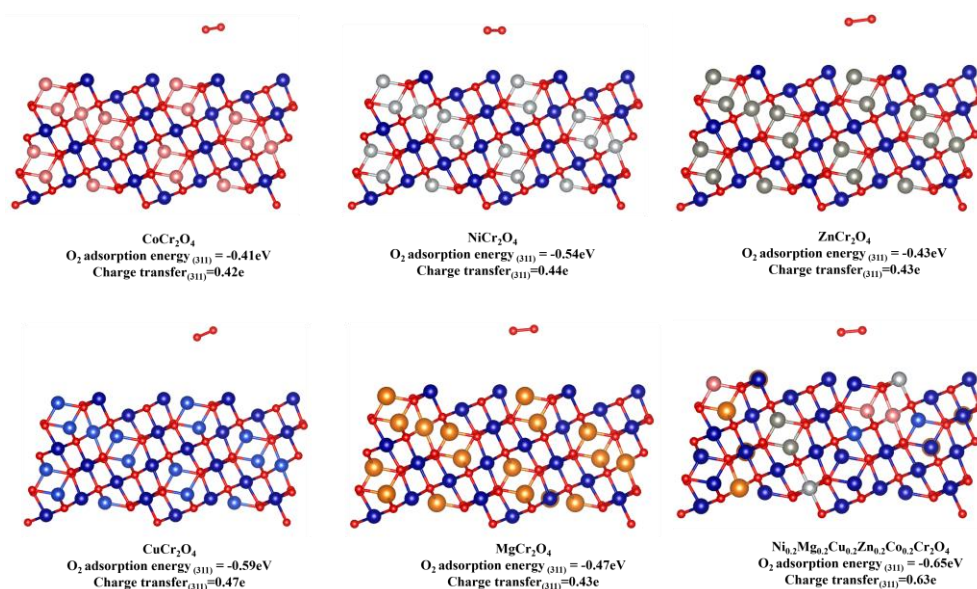


Figure S90 O_2 adsorption energy and charge transfer on the surface (311 plane) of high entropy ($\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2}$) Cr_2O_4 and single metal ACr_2O_4 (A=Ni, Mg, Cu, Zn, Co).

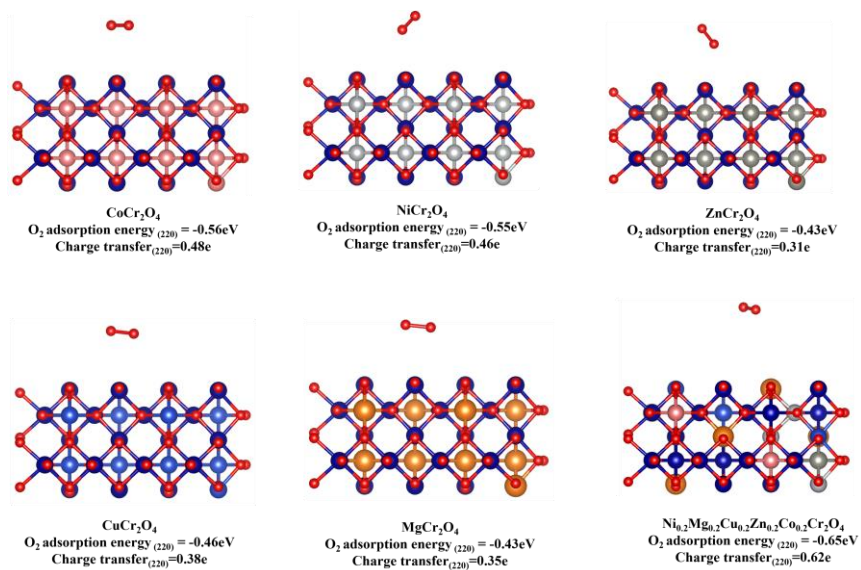


Figure S91 O₂ adsorption energy and charge transfer on the surface (220 plane) of high entropy (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ and single metal ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co).

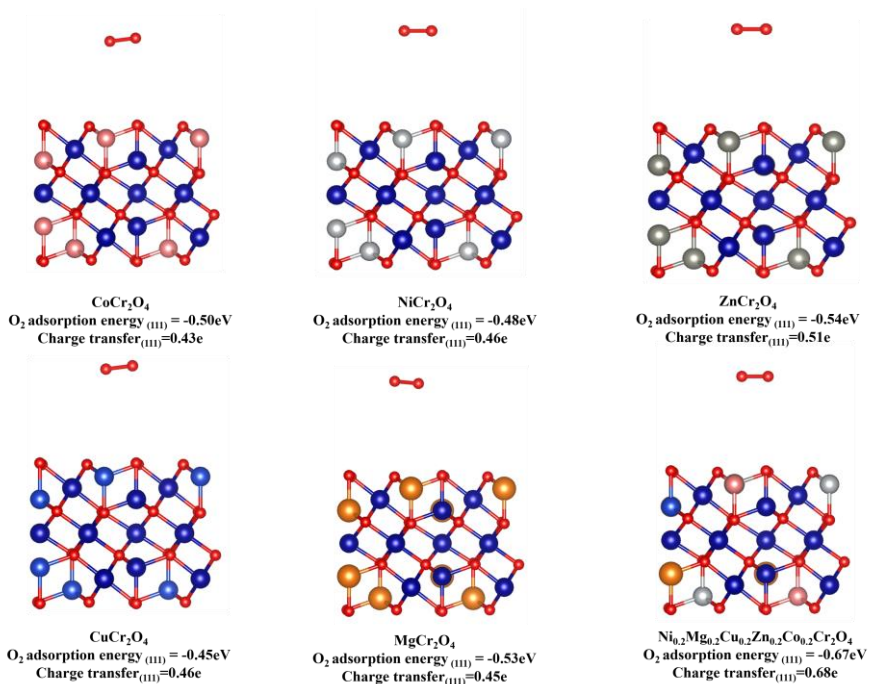


Figure S92 O₂ adsorption energy and charge transfer on the surface (111 plane) of high entropy (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ and single metal ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co).

Comment 3: The format of the manuscript needs to be revised deeply. Line 91 At, Line 90 space, Line 170 S86-S88 (S5-S85 are missing). Figure 1-Figure 3 should be re-organized. Format errors also exist in Supporting Information.

Reply:

Thanks for the useful suggestion!

We sincerely apologize for this mistake. We have revised the formatting errors in the original manuscript and supporting information. The position of Line 170 S86-S88 has been readjusted. Figures 1 ~ 3 have been reorganized. Meanwhile, all the authors have carefully checked the manuscript and made several modifications.

Original:

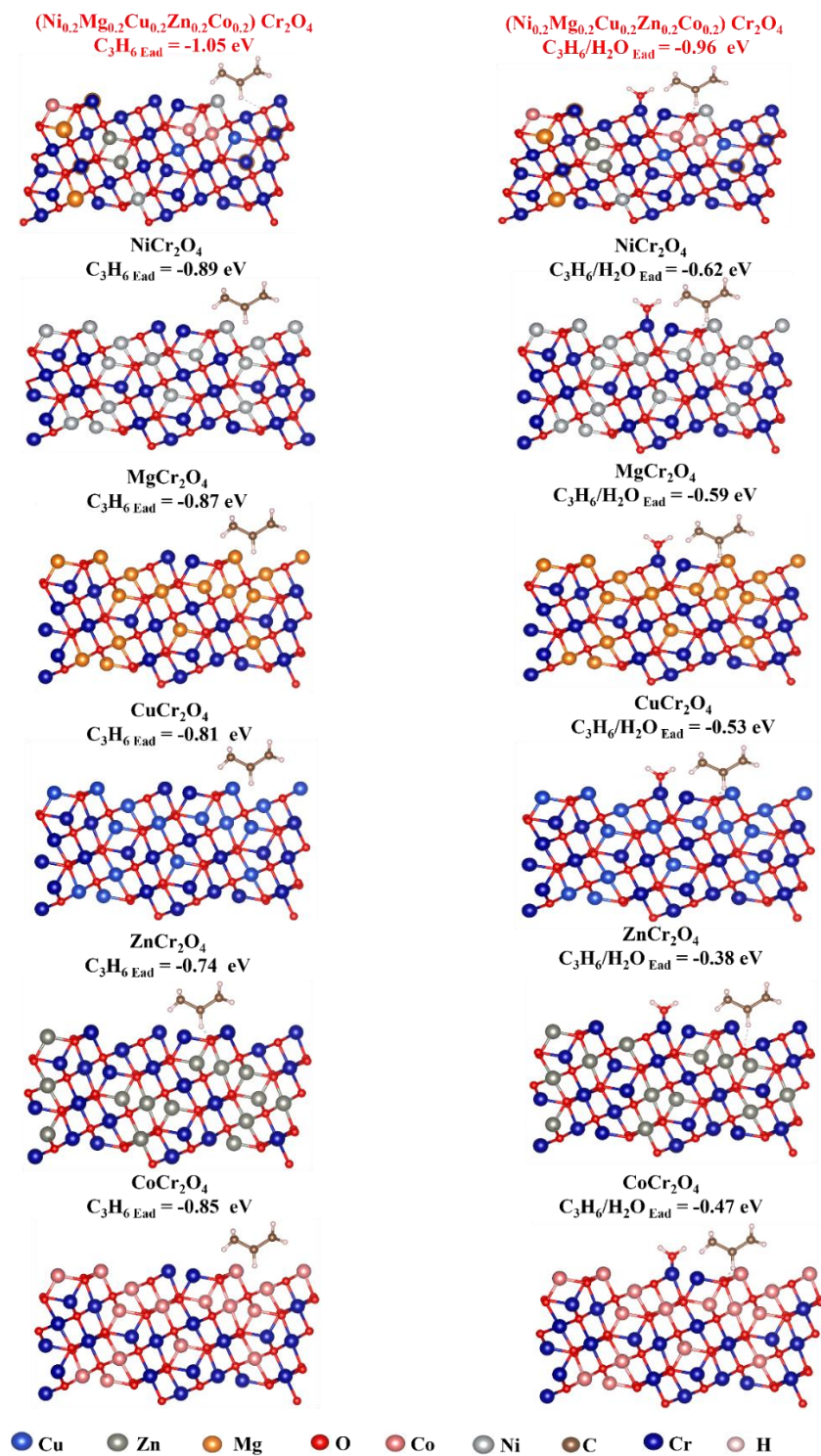


Figure 1. The adsorption energy of C_3H_6 on the surface (311 plane) of high entropy $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ and single metal ACr_2O_4 ($\text{A}=\text{Ni}, \text{Mg}, \text{Cu}, \text{Zn}, \text{Co}$) in the absence and presence of 4.2vol% water vapor.

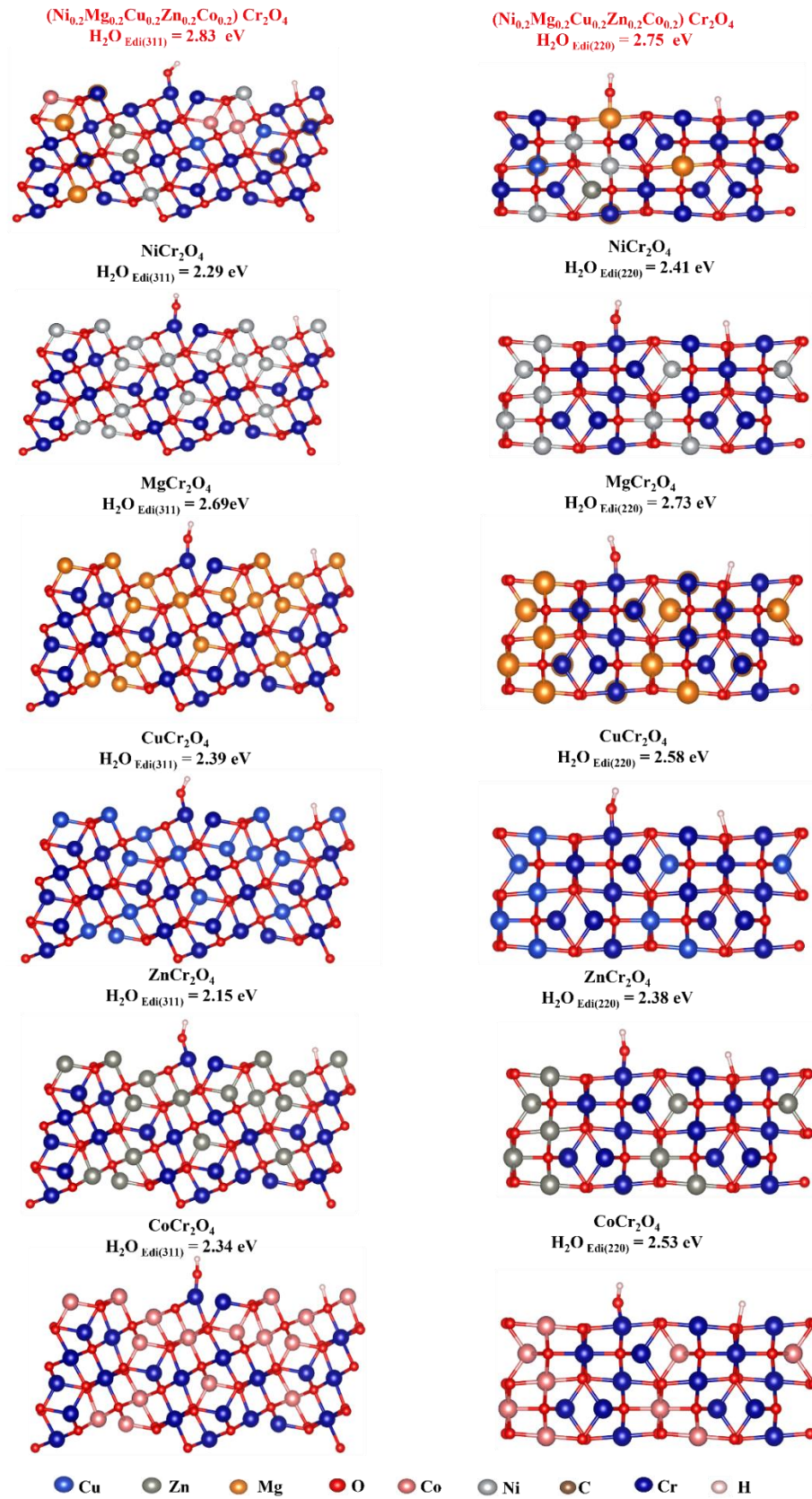


Figure 2. The dissociation energy of molecular H_2O on the surface of high entropy $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, and single metal ACr_2O_4 ($\text{A}=\text{Ni}, \text{Mg}, \text{Cu}, \text{Zn}, \text{Co}$) at crystal plane (220) and (311) respectively.

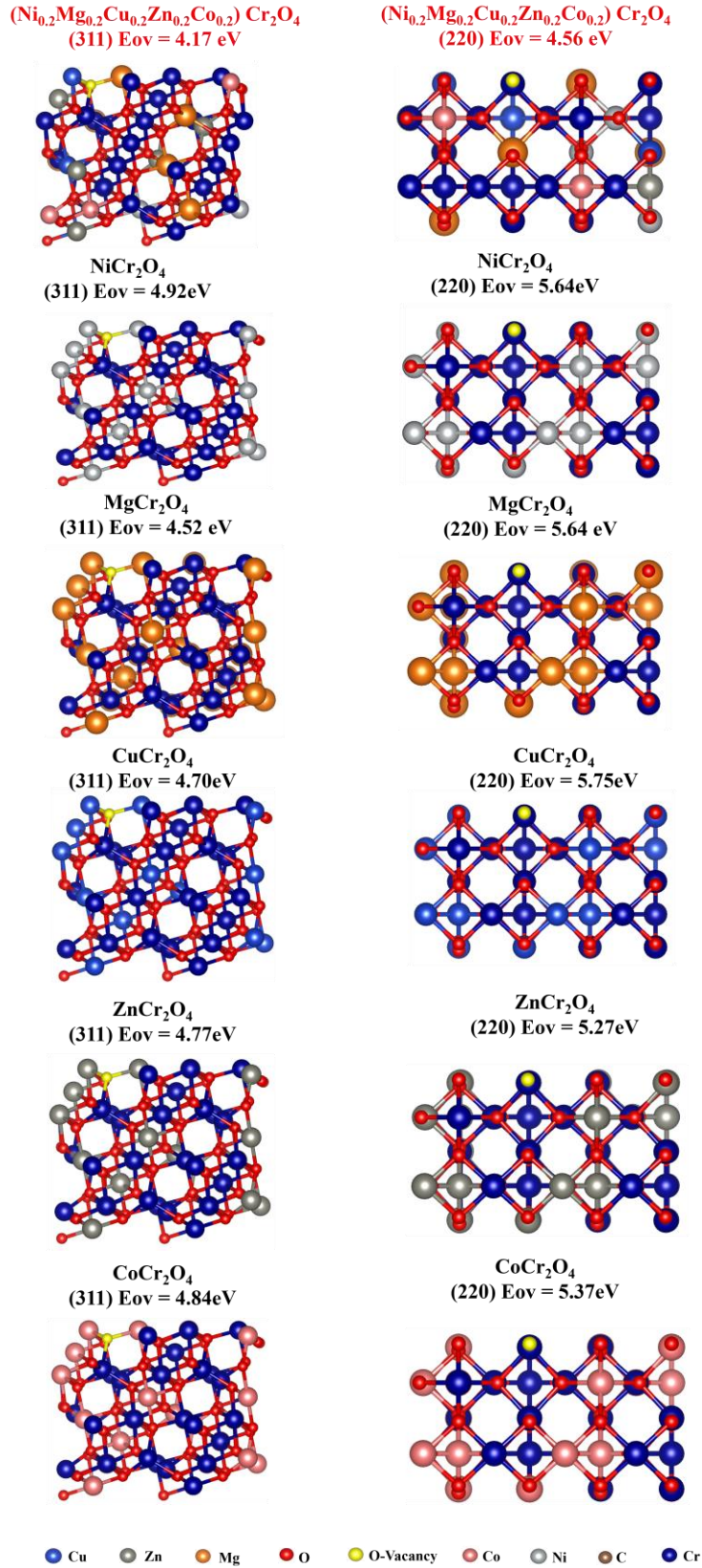


Figure 3. The formation energy of oxygen vacancy (Eov) of high entropy $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, and single metal ACr_2O_4 ($A=\text{Ni}, \text{Mg}, \text{Cu}, \text{Zn}, \text{Co}$) at crystal plane (220) and (311) respectively.

Revised:

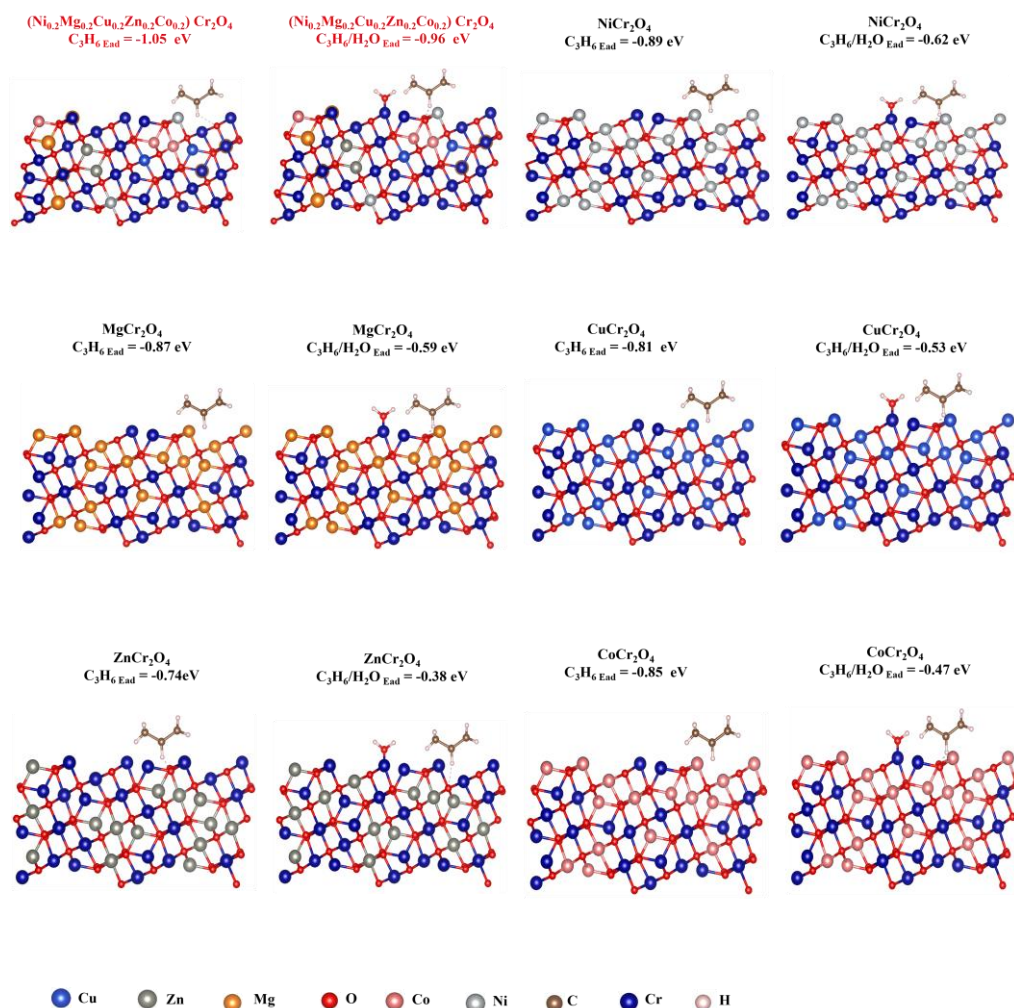


Figure 1. The adsorption energy of C_3H_6 on the surface (311 plane) of high entropy $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ and single metal ACr_2O_4 ($\text{A}=\text{Ni}, \text{Mg}, \text{Cu}, \text{Zn}, \text{Co}$) in the absence and presence of 4.2vol% water vapor.

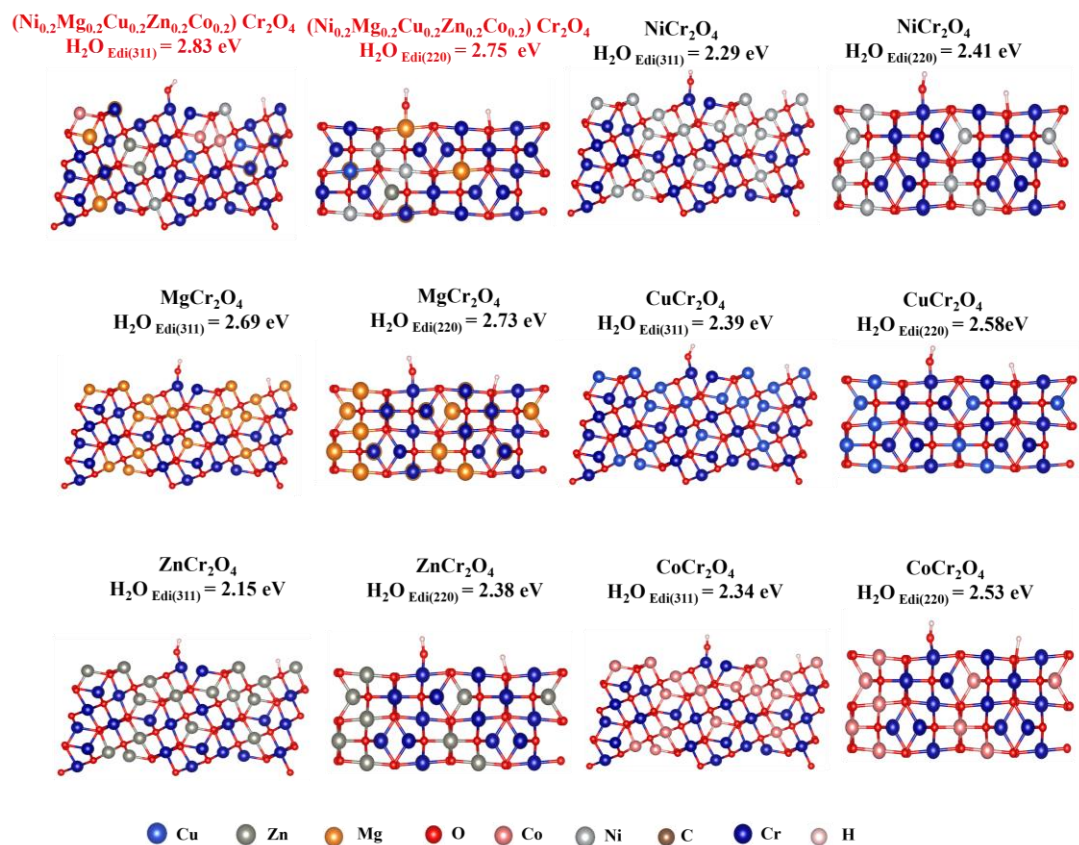


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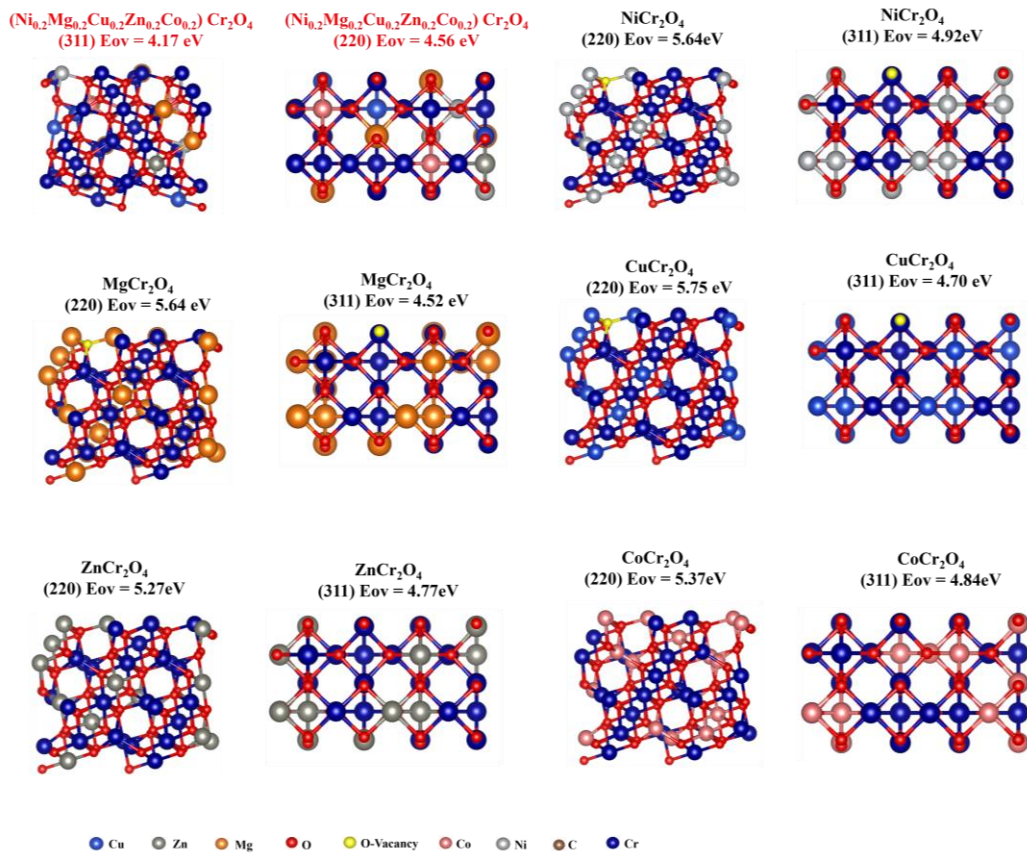


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REVIEWERS' COMMENTS

Reviewer #4 (Remarks to the Author):

Issues have been well addressed in this revised manuscript, this work is publishable under current state.