

Supporting Information for Designing Water Resistant High Entropy Oxide Materials

Supplementary Information includes:

Supplementary Methods

Supplementary Figures

Supplementary Tables

Supplementary Methods:

DFT calculation method:

All the first-principles calculations are performed under the framework of the density functional theory (DFT), where the codes are implemented in the Vienna *ab initio* simulation package with the projector augmented plane-wave method.^[1, 2] The generalized gradient approximation (GGA) proposed by the Perdew-Burke-Ernzerhof (PBE) functional is selected to treat the exchange-correlation potential.^[3, 4] The long-range van der Waals interaction is described by the DFT-D3 approach.^[5] The cut-off energy for the plane wave is set to 520 eV and the energy criterion is set to 10^{-5} eV in the iterative solution of the Kohn-Sham equation. A vacuum layer of 12 Å is added perpendicular to avoid the interactions between periodic adjacent images. The Brillouin zone was sampled with allowed spacing between k points in 0.2 Å^{-1} , with a Γ -centered Monkhorst-Pack k-point grid. All the structures are relaxed until the residual forces on the atoms have declined to less than 0.01 eV/Å. The 3D charge density plot is employed by VESTA software.^[6] The high-entropy oxide structure models are constructed by random atom replacements to achieve the so-called special quasi-random structures (SQS),^[7] where the cluster vectors are close to the target cluster vector. For the $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Zn}_{0.2}\text{Cu}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ structure, random atoms (Ni, Mg, Zn, Cu, Co) need to occupy the Mg atomic positions of MgCr_2O_4 structure according to their ratios, and the cluster vectors must be as close as possible to the target vectors. Here we use the ICET package to construct the high-entropy oxide structures,^[8] where the (220) and (311) planes are employed to proceed to the following calculations. For the metal oxide substrate, we first calculate the formation energy of oxygen vacancy $E[\text{Vac}]$, which is defined by:

$$E[\text{Vac}] = E_{\text{vac}} + \frac{1}{2}E_{\text{O}_2} - E_{\text{host}} \quad (1)$$

Where E_{vac} is the total energy of the structures removing one oxygen atom, E_{O_2} is the energy of one molecular oxygen, and E_{host} is the total energy of a metal oxide structure.

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 C_3H_6 and H_2O 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.

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.

Materials:

Chemicals involved in the manuscript are used directly without purification. Cu(OAc)₂ (CAS: 142-71-2) (>99.9%, Aladdin), Zn(OAc)₂ (CAS: 557-34-6) (>99.9%, Aladdin), Ni(OAc)₂•4H₂O (CAS: 6018-89-9) (>99.9%, Aladdin), Co(OAc)₂•4H₂O (CAS: 6147-53-1) (>99.9%, Aladdin), Mg(OAc)₂•4H₂O (CAS: 142-72-3) (>99%, Adamas) and Cr(OAc)₃ (CAS: 1066-30-4) (>96%, Greagent).

Sample synthesis:

(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄: 1 mmol Cu(OAc)₂, 1 mmol Zn(OAc)₂, 1 mmol Ni(OAc)₂•4H₂O, 1 mmol Co(OAc)₂•4H₂O, 1 mmol Mg(OAc)₂•4H₂O, and 10 mmol Cr(OAc)₃ were added together to a stainless steel reactor (80 ml) along with 10 stainless steel balls (4 × diameter 1.2 cm; 6 × diameter 0.5 cm). The reactor was then put on a high-speed vibrating ball miller (MSK-SFM-3,

Hefei MTICo., Ltd.), and ground for 0.5h. Finally, the intermediate product was calcined at 550°C for 2h in air. The description of this ball milling procedure was shown in Figure 4. The obtained samples were referred to as $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$.

NiCr_2O_4 : 5 mmol $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ and 10 mmol $\text{Cr}(\text{OAc})_3$ were added together to a stainless steel reactor (80 ml) along with 10 stainless steel balls ($4 \times$ diameter 1.2 cm; $6 \times$ diameter 0.5 cm). The reactor was then put on a high-speed vibrating ball miller (MSK-SFM-3, Hefei MTICo., Ltd.), and ground for 0.5h. Finally, the intermediate product was calcined at 550°C for 2h in air. The obtained samples were referred to as NiCr_2O_4 .

MgCr_2O_4 : 5 mmol $\text{Mg}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ and 10 mmol $\text{Cr}(\text{OAc})_3$ were added together to a stainless steel reactor (80 ml) along with 10 stainless steel balls ($4 \times$ diameter 1.2 cm; $6 \times$ diameter 0.5 cm). The reactor was then put on a high-speed vibrating ball miller (MSK-SFM-3, Hefei MTICo., Ltd.), and ground for 0.5h. Finally, the intermediate product was calcined at 550°C for 2h in air. The obtained samples were referred to as MgCr_2O_4 .

CuCr_2O_4 : 5 mmol $\text{Cu}(\text{OAc})_2$ and 10 mmol $\text{Cr}(\text{OAc})_3$ were added together to a stainless steel reactor (80 ml) along with 10 stainless steel balls ($4 \times$ diameter 1.2 cm; $6 \times$ diameter 0.5 cm). The reactor was then put on a high-speed vibrating ball miller (MSK-SFM-3, Hefei MTICo., Ltd.), and ground for 0.5h. Finally, the intermediate product was calcined at 550°C for 2h in air. The obtained samples were referred to as CuCr_2O_4 .

ZnCr_2O_4 : 5 mmol $\text{Zn}(\text{OAc})_2$ and 10 mmol $\text{Cr}(\text{OAc})_3$ were added together to a stainless steel reactor (80 ml) along with 10 stainless steel balls ($4 \times$ diameter 1.2 cm; $6 \times$ diameter 0.5 cm). The reactor was then put on a high-speed vibrating ball miller (MSK-SFM-3, Hefei MTICo., Ltd.), and ground for 0.5h. Finally, the intermediate product was calcined at 550°C for 2h in air. The obtained samples were referred to as ZnCr_2O_4 .

CoCr_2O_4 : 5 mmol $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ and 10 mmol $\text{Cr}(\text{OAc})_3$ were added together to a stainless steel reactor (80 ml) along with 10 stainless steel balls ($4 \times$ diameter 1.2 cm; $6 \times$ diameter 0.5 cm). The reactor was then put on a high-speed vibrating ball miller (MSK-SFM-3, Hefei MTICo., Ltd.), and ground for 0.5h. Finally, the intermediate product was calcined at 550°C for 2h in air. The obtained samples were referred to as CoCr_2O_4 .

Sample characterization:

The powder X-ray diffraction (XRD) data of samples were collected by PAN analytical X'Pert Pro

MPD diffractometer using an X'Celerator RTMS detector. **N₂adsorption–desorption** isotherms and specific surface areas were determined by using a TriStar II 3020 volumetric adsorption analyzer. Before measurement, the samples were degassed at 150°C for at least 6 hr. Characterization of the morphology and size of the catalyst using scanning electron microscopy (**SEM**, Hitachi SU8010).

High-angle annular dark-field scanning transmission electron microscopy (**HAADF–STEM**) images were obtained using a Nion Ultra STEM 100 with a probe aberration correction. Before the test, a lacey carbon film on copper grids was chosen to disperse (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ powder. In addition, to avoid the interference of Cu from the copper grids, the mapping signals were collected far away from the border of the copper grids. X-ray photoelectron spectroscopy (**XPS**) tests were undertaken by AXIS Ultra DLD instrument using a monochromatic Al K α X-ray source. The contaminated carbon C 1 s at 284.6 eV was chosen as a reference to calibrate BE values. **HARKE-SPCA contact angle** measuring instrument was used to characterize the wettability of the catalyst surface, with water droplets of 5 μ l. The average of six randomly selected measurements was used as the final result. Temperature-programmed O₂ desorption (**O₂-TPD**) was carried out on a fixed bed microreactor. Before the test, 100 mg of samples were pretreated under 30.0 Vol% O₂/Ar atmosphere at 300°C for 1 h. After cooling to room temperature, the temperature programming was started at a rate of 10 °C/min from 30 to 900 °C under Ar flow. The effluent gases were determined by an online mass spectrometer (MS, SOPTOP, Shanghai). The signals at mass-to-charge (m/z) ratios of 32 (O₂). Temperature-programmed H₂O desorption (**H₂O-TPD**) was carried out on a fixed bed microreactor. Typically, 50 mg of the catalysts were placed in a U-type quartz tube. Temperature programming was started at a rate of 10 °C/min from 30 to 600 °C under Ar flow. The effluent gases were determined by an online mass spectrometer (MS, SOPTOP, Shanghai). The signals at mass-to-charge (m/z) ratios of 18 (H₂O) were detected. **C₃H₆-TPD** was conducted on the Micromeritics Autochem 2920 Chemisorption Analyzer equipped with a Mass spectrometer (Hiden Analytical). 50 mg of the sample was treated in the air at 500°C for 1 h, purged with Ar for 30 min, and cooled to 50°C. The sample was then exposed to a flow of C₃H₆ (5 vol% C₃H₆ in Ar) for 1 h before being purged with Ar flow for 1 h. Finally, the sample was heated up to 400°C with a heating rate of 10°C min⁻¹ in Ar flow. Mass spectrometer signals at m/z of 41, 18, and 44 was monitored. **H₂-TPR** was conducted by using a TP-5079 instrument (supplied by Tianjin Xianquan Industry and Trade

Development Co.). A powder sample (0.05 g) with 40–60 mesh was loaded into a quartz fixed-bed reactor and pretreated under an O₂/He (5% O₂, 30 mL/min) flow at a temperature of 350 °C for 1 h. After that, the sample was introduced a purge of 6 vol% H₂/N₂ at a flow rate of 30 mL min⁻¹. When the condition was stable, the temperature was elevated to 800 °C at a rate of 10 °C min⁻¹ and the variation in the H₂ concentration was recorded using a TCD detector. The static water contact angle (θ_w) was measured using a VCA Optima surface analysis/goniometry system using a water droplet size of 30 μ L. At least five measurements for each sample were averaged.

In-situ Raman

The Raman scattering measurements were performed with multichannel modular triple Raman systems (Jobin-Yvon LABRAM HR800) with confocal microscopy. The solid-state diode laser (532 nm) as an excited source and a 50LWD object lens was used to focus the depolarized laser beam on a spot of about 1 μ m in diameter. The Raman scattering was collected with a CCD array detector and in the range of 100-1200 cm⁻¹ with a resolution of 2 cm⁻¹. Each reported spectrum is the average of two scans with an exposure time each of 100s. ex-situ Raman spectrums were measured at room temperature. To evaluate the catalyst's resistance to water vapor, the feed gas was first passed into constant-temperature water at 30°C and then introduced into an in-situ cell. During the C₃H₆ oxidation test, the catalyst sample was treated by the gas flow with a temperature rise from 30°C to 300°C. In-situ Raman spectrums were measured with the desired temperature in an in-situ cell. The reagent gas during in situ Raman experiment was the same as the gas of activity measurement, under a flow rate of 10 mL min⁻¹(1vol % C₃H₆, 19.9vol% O₂, and 79.1vol% N₂).

In-situ DRIFTS

The in situ diffuse reflectance infrared Fourier transform spectra (in-situ DRIFTS) were recorded using a Thermo IS50 spectrometer, equipped with an MCT detector and a high-temperature reaction sample chamber (Praying Mantis, Harrick). Prior to the analysis, the catalyst sample was pretreated under N₂ flow at 300 °C for 1 h. The spectrum at the desired temperature was considered as the relative background, and the sample was subsequently cooled to room temperature. The reaction gas mixture (10 mL/min, 1vol % C₃H₆, 19.9vol% O₂, and 79.1vol% N₂) without or with 4.2vol% water was introduced into the reaction cell under the temperature-programmed process. The catalyst sample was treated by the gas flow with a temperature rise from 50°C to 320°C. The sampling interval was 5 min.

In-situ XRD

In situ XRD experiments were performed through a Bruker (Germany) model D8 Advance powder diffractometer, featuring an Anton Paar (Austria) XRK900 reaction temperature chamber. The diffractometer is equipped with a high-resolution VÅNTEC-1 position-sensitive detector complemented by a radial Soller slits system. To avoid possible misalignments in the position or deformation of the sample due to the use of the temperature chamber, the diffractometer uses a parallel incident beam through large-size sealed Gobel " mirrors (60 mm) for CuK α radiation ($\lambda = 0.15405$ nm). Temperature control is accurately achieved using thermocouples placed very close to the sample holder inside the temperature chamber. The powder diffractometer was calibrated according to the manufacturer's specifications. Corundum, LaB6, and silicon standards were tested at a wide range of 2θ angles to verify resolution and compute the instrumental contribution for structural adjustments. In situ XRD experiments were performed after 0.5 h of ball milling of the acetate salt. During the tests, The heating rate is 5 °C/min with raise the temperature from 100 degrees to 550 degrees and then maintain for 2 h at 550°C. XRD 5 min scans were continuously performed in a 10°-80° 2θ range with a step of 0.03° and 0.2 s step time. X-ray tube characteristics were 40 kV and 40 mA.

In Situ XPS

The in Situ XPS experiments were carried out in a SPECS instrument equipped with a PHOIBOS 150 MCD 9 analyzer operated in the FAT mode at pass energy of 20 eV. Non-monochromatic Al K α radiation(1486.6 eV) was used to provoke electron emission from the samples and the X-ray source worked at 210 W and 14 kV. Three or five scans were summed to get a single spectrum. The pressure during the measurements was kept in the 10⁻⁹ mbar range. The (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ samples were previously reduced under pure 5%H₂/95%N₂ (30 mL/min) at 300°C for 1 h and cooled to 30°C. The elemental valence and composition of catalysts were measured using X-ray photoelectron spectroscopy (XPS).

Catalytic performance test:

The catalytic activity of C₃H₆ 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 100 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 mL h⁻¹g⁻¹. The feed gases contain 1vol % C₃H₆ and 99vol% air. The feed gas C₃H₆ and product CO₂ can be detected in real-time. To evaluate the catalyst's resistance to water vapor, the feed gas was firstly passed into constant temperature water at 30°C and then introduced into the catalyst bed. The stability experiments were carried out at a conversion of 70% in C₃H₆ oxidation combustion under humid conditions(4.2vol%) for 100 hours.^[12-14]

C₃H₆ conversion was calculated using the following expression:

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

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

Supplementary Figures:

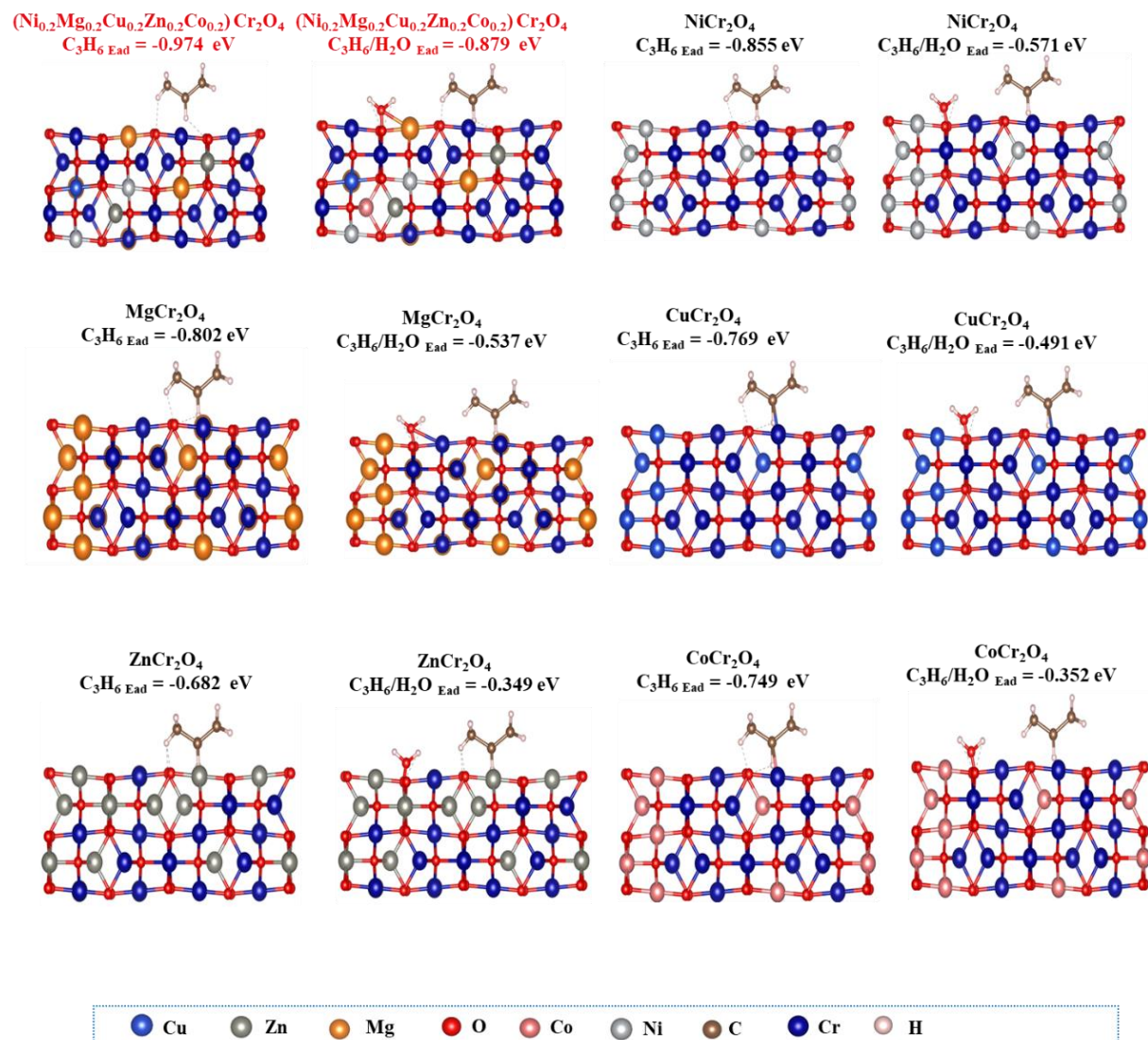


Figure S1. The adsorption energy of C_3H_6 on the surface (220 plane) by DFT calculation. The adsorption energy of C_3H_6 on the surface (220 plane) of high entropy $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$ and single metal ACr_2O_4 (A=Ni, Mg, Cu, Zn, Co) in the absence and presence of 4.2vol% water vapor.

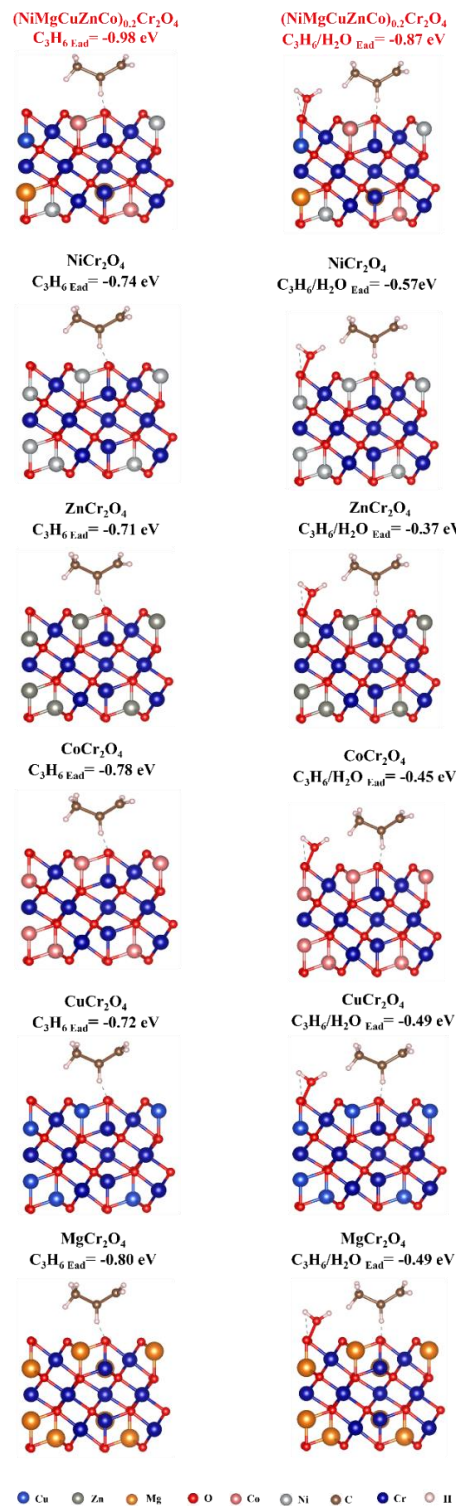


Figure S2. The adsorption energy of C_3H_6 on the surface (111 plane) by DFT calculation. The adsorption energy of C_3H_6 on the surface (111 plane) of high entropy $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ and single metal ACr_2O_4 ($\text{A}=\text{Ni}, \text{Mg}, \text{Cu}, \text{Zn}, \text{Co}$) in the absence and presence of 4.2vol% water vapor.

The adsorption energy of C_3H_6 on the surface (220 plane) of ACr_2O_4 ($A=Ni, Mg, Cu, Zn, Co$) and $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$ in the drying conditions and 4.2vol% water were calculated respectively (Figure S1). In the presence of 4.2vol% water, the adsorption energy of C_3H_6 on the surfaces of ACr_2O_4 ($A=Ni, Mg, Cu, Zn, Co$) 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 ($A=Ni, Mg, Cu, Zn, Co$) catalysts, which would affect the C_3H_6 oxidation. In contrast, the adsorption energy of C_3H_6 on $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$ surface was -0.974eV (crystal plane 220) in the drying conditions. The adsorption energy of C_3H_6 on the whole structure of $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$ and a water molecule was -0.879 eV (crystal plane 220) with 4.2vol% water. Interestingly, the presence of H_2O molecules on the surface of $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$ had little effect on the adsorption energy of C_3H_6 .

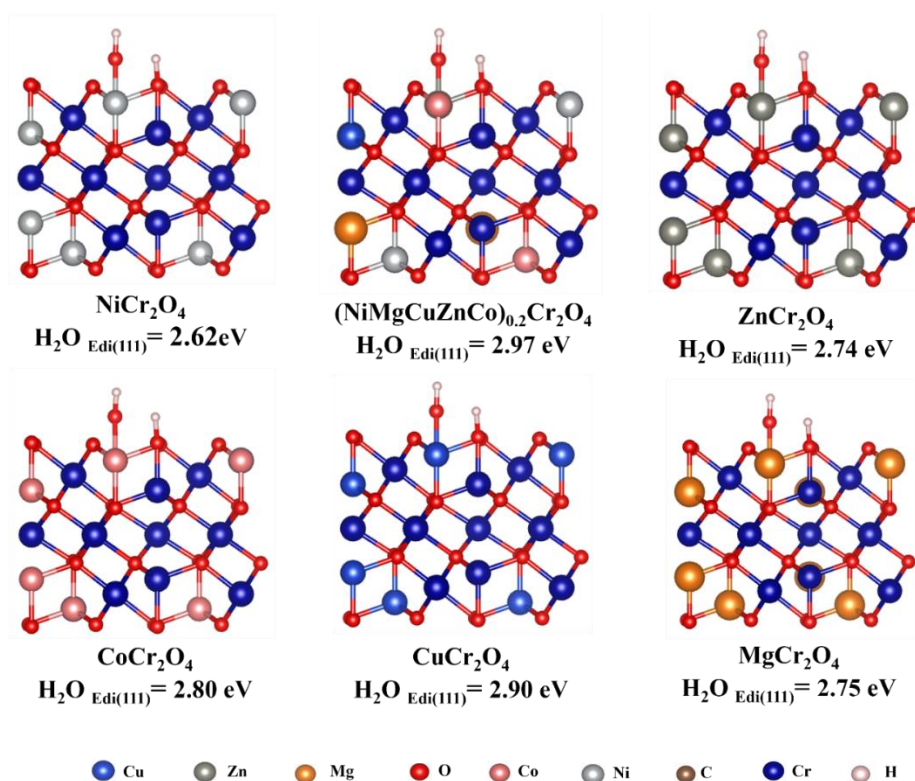


Figure S3. The dissociation energy of molecular H_2O by DFT calculation. The dissociation energy of molecular H_2O on the surface of high entropy $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, and single metal ACr_2O_4 ($\text{A}=\text{Ni}, \text{Mg}, \text{Cu}, \text{Zn}, \text{Co}$) at crystal plane (111).

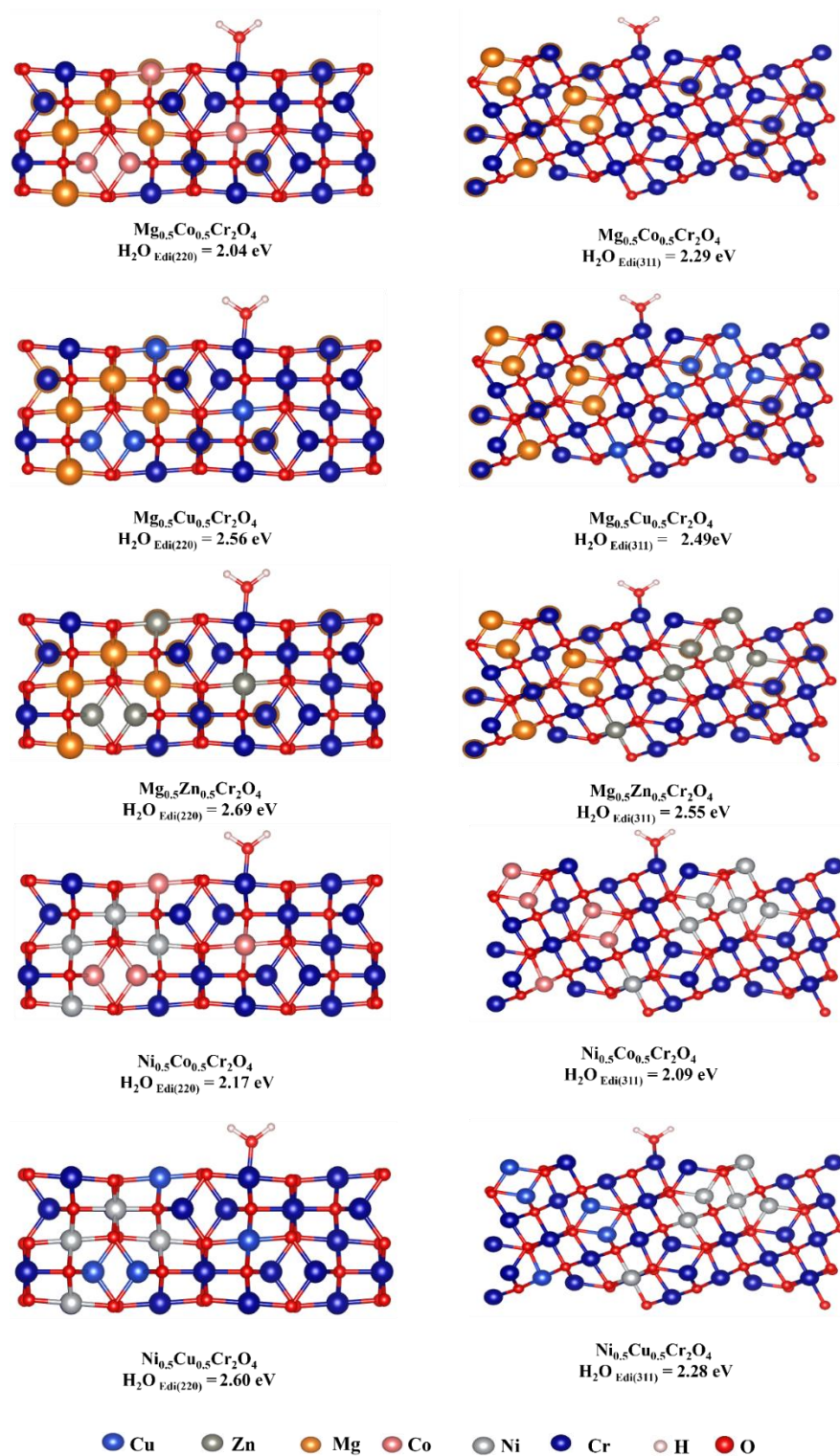


Figure S4. The dissociation energy of molecular H_2O by DFT calculation. The dissociation energy of molecular H_2O on the surface of ternary control samples at crystal plane (220) and (311) respectively.

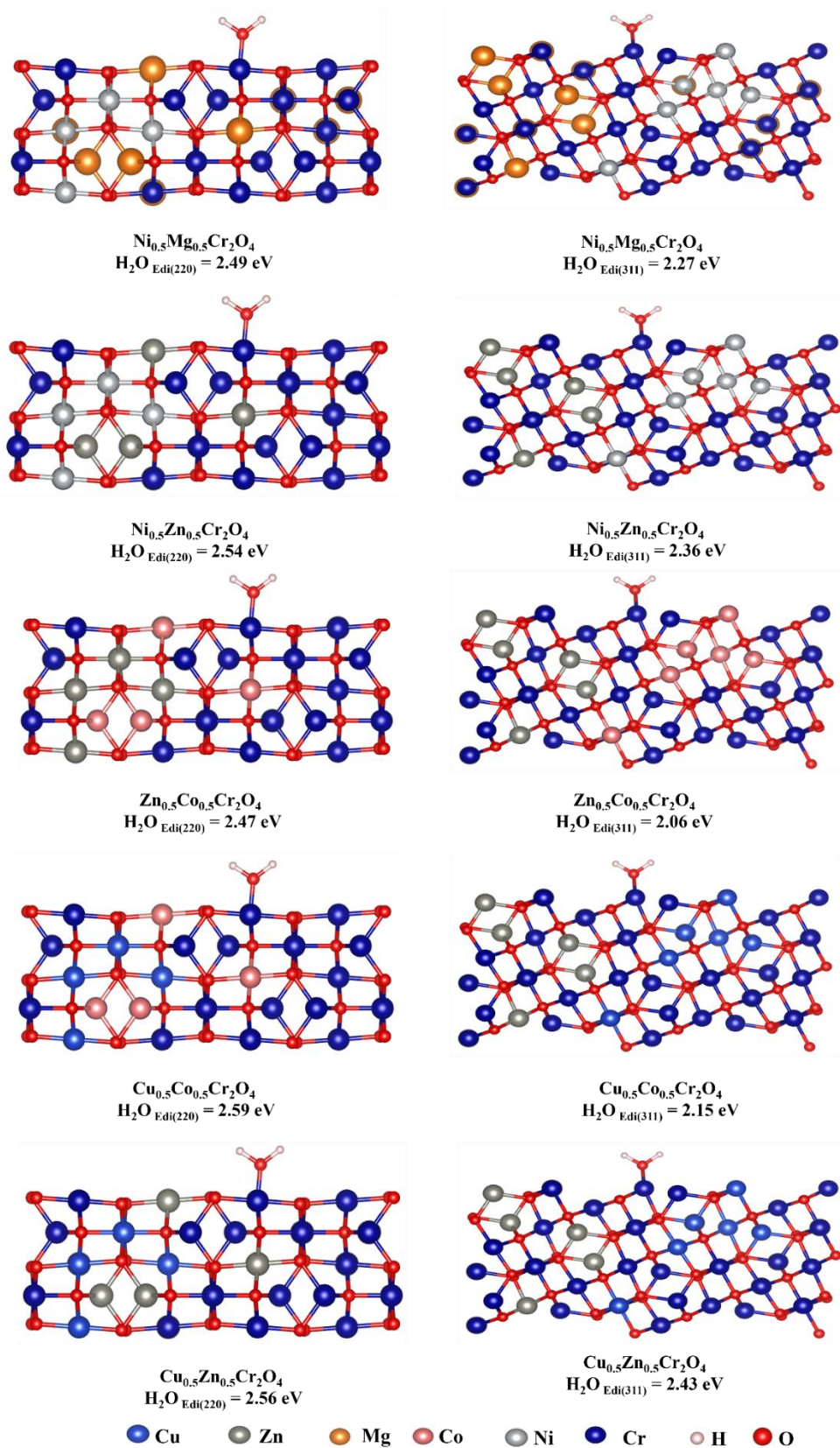


Figure S5. The dissociation energy of molecular H_2O by DFT calculation. The dissociation energy of molecular H_2O on the surface of ternary control samples at crystal plane (220) and (311) respectively.

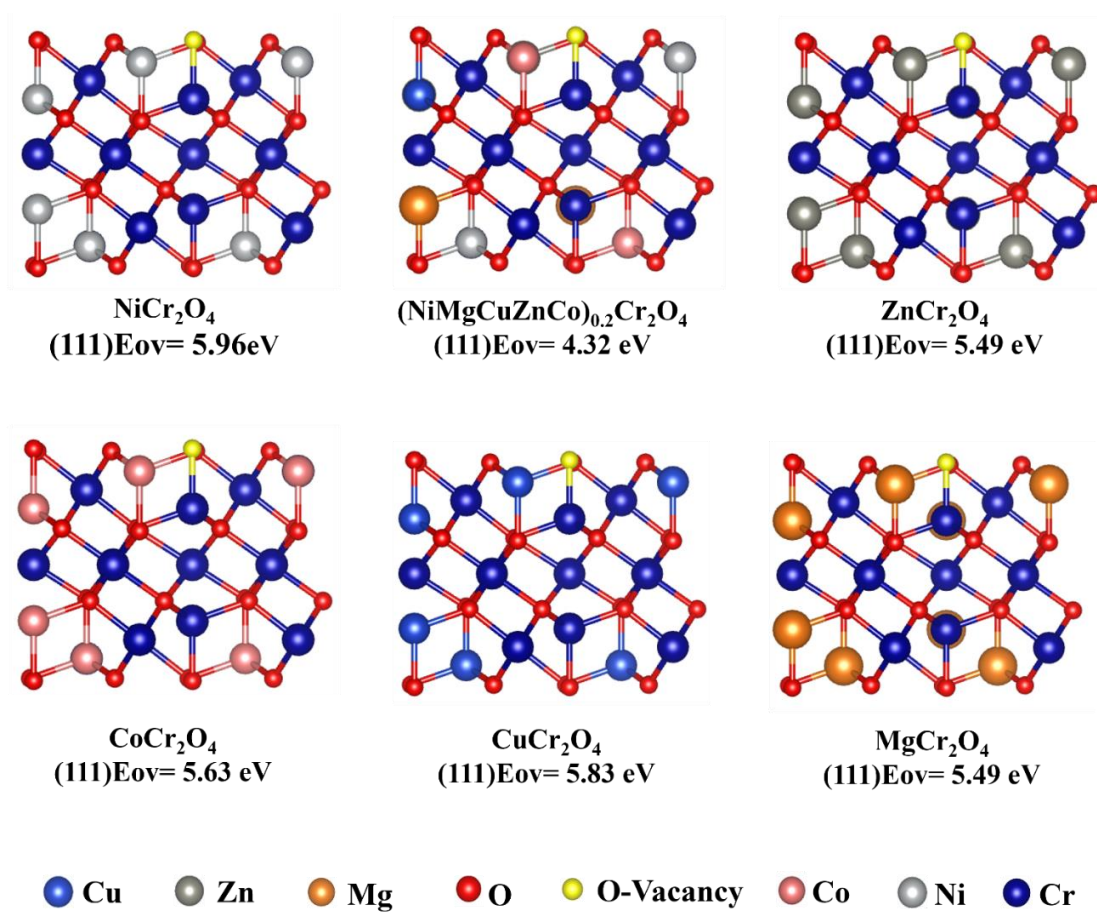


Figure S6. The formation energy of oxygen vacancy by DFT calculation. The formation energy of oxygen vacancy (Eov) of high entropy $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, and single metal ACr_2O_4 (A=Ni, Mg, Cu, Zn, Co) at crystal plane (111).

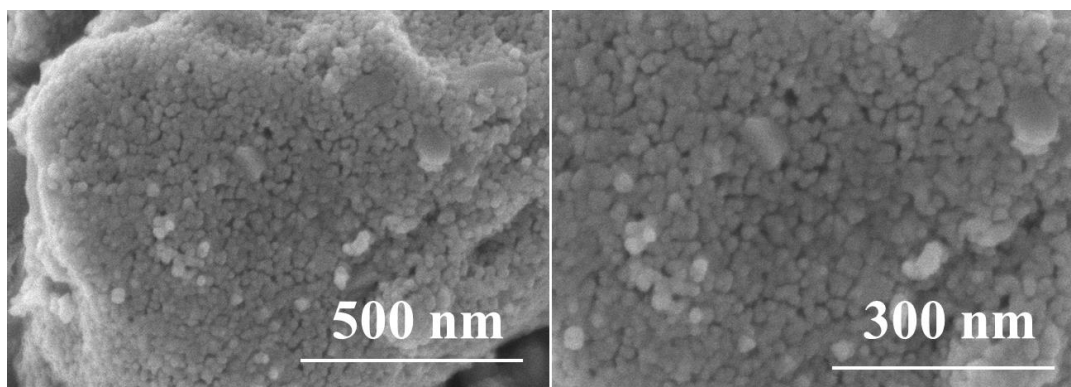


Figure S7. The SEM characterization. The SEM images of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ prepared by using the ball milling method.

As shown in **Figure S7**, the catalyst $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ was composed of many small particles, and there were many pores from the surface to the interior. This was due to the constant shearing and collision during the mechanical ball milling process. **Figure 5g** showed the TEM image of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, presenting the morphology of nanoparticles with a size of 2–30 nm, which matched well with the SEM result (Figure S7) and XRD result (**Figure 5b**). The crystallite size 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 determined from the XRD peak broadening employing Scherrer's formula^[15], given by:

$$D = K\lambda / \beta_{hkl} \cos \theta \quad (5)$$

where D is the crystallite size, K is shaped depending parameter and is taken here as 1 considering the particles to be spherical in shape, λ is the X-ray wavelength (1.5405 Å), β is the angular line width at half maximum intensity, and θ is the Bragg angle in degree. The value of the crystallite size D was 7.67 nm evaluated from the slope of the Scherrer's plot $\frac{\cos \theta}{\lambda}$ versus $\frac{1}{\beta_{hkl}}$

for $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ using the crystal plane (311). N_2 sorption 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 a typical type IV isotherm with an H_3 -type hysteresis loop between $P/P_0 = \sim 0.6$ –0.9. Moreover, the pore size distribution of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ by using the Barrett–Joyner–Halenda (BJH) model located within ~2–30 nm, indicating the formation of mesoporous structure (**Figure S9**).

According to Hooke's law,^[16] the Cr–O bond force constant (k) was calculated, which represented the Cr–O bond strength. The bond force constant (k) was calculated using equation (6)–(7).

$$\omega = \frac{1}{2\pi c} \sqrt{k/\mu} \quad (6)$$

$$\mu = (M_{Cr} \times M_O) / (M_{Cr} + M_O) \quad (7)$$

where w = Raman shift (cm^{-1}), c = speed of light (cm s^{-1}), μ = effective mass of chromium and oxygen, M_{Cr} = atomic mass of chromium (kg), and M_O = atomic mass of oxygen (kg).

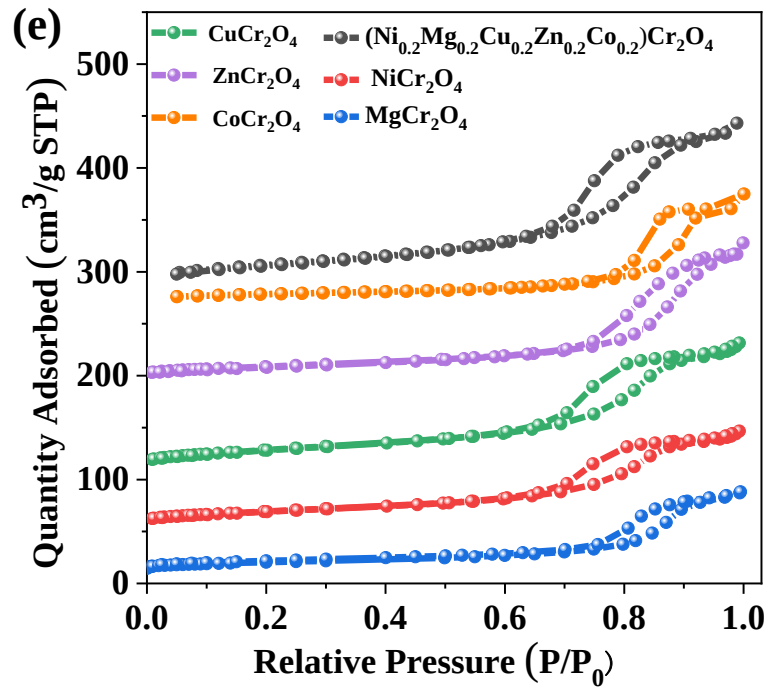


Figure S8. The nitrogen adsorption–desorption characterization. Nitrogen adsorption–desorption isotherms of ACr_2O_4 ($A=\text{Ni, Mg, Cu, Zn, Co}$) and $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ at 77K. The N_2 uptake of NiCr_2O_4 , CuCr_2O_4 , ZnCr_2O_4 , CoCr_2O_4 and $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ were moved upward by 25, 50, 75, 100, 125 and 150 units respectively.

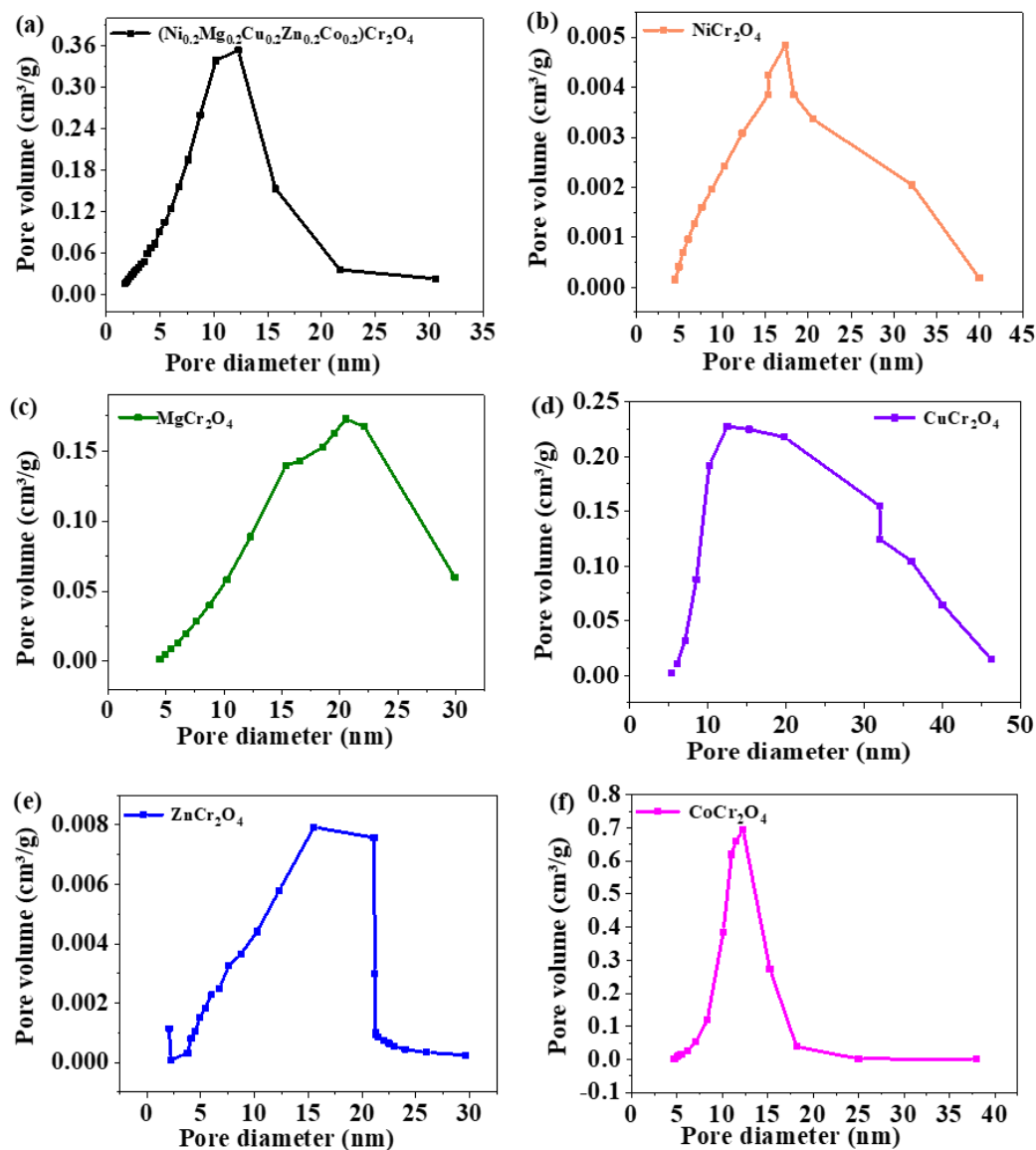


Figure S9. Pore-size distribution. (a) $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, (b ~ f) ACr_2O_4 (A=Ni, Mg, Cu, Zn, Co) catalysts.

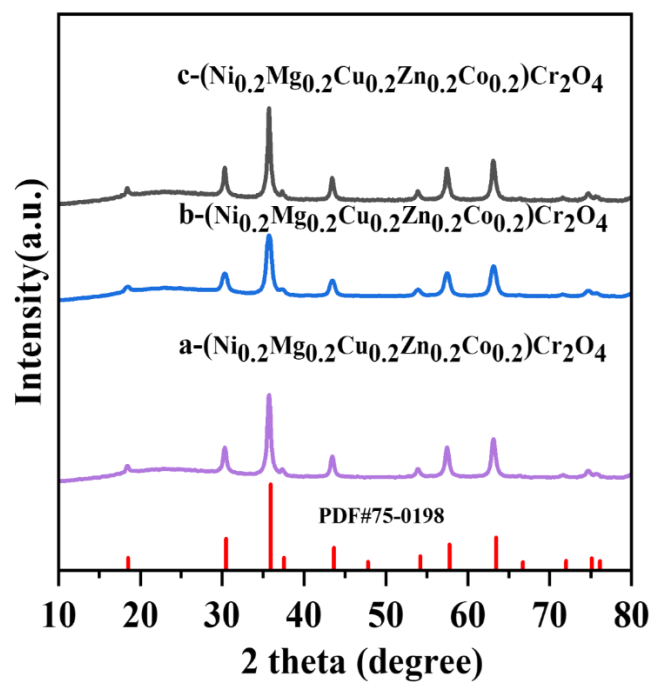


Figure S10. X-ray diffraction pattern characterization. a-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄, b-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄, c-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄.

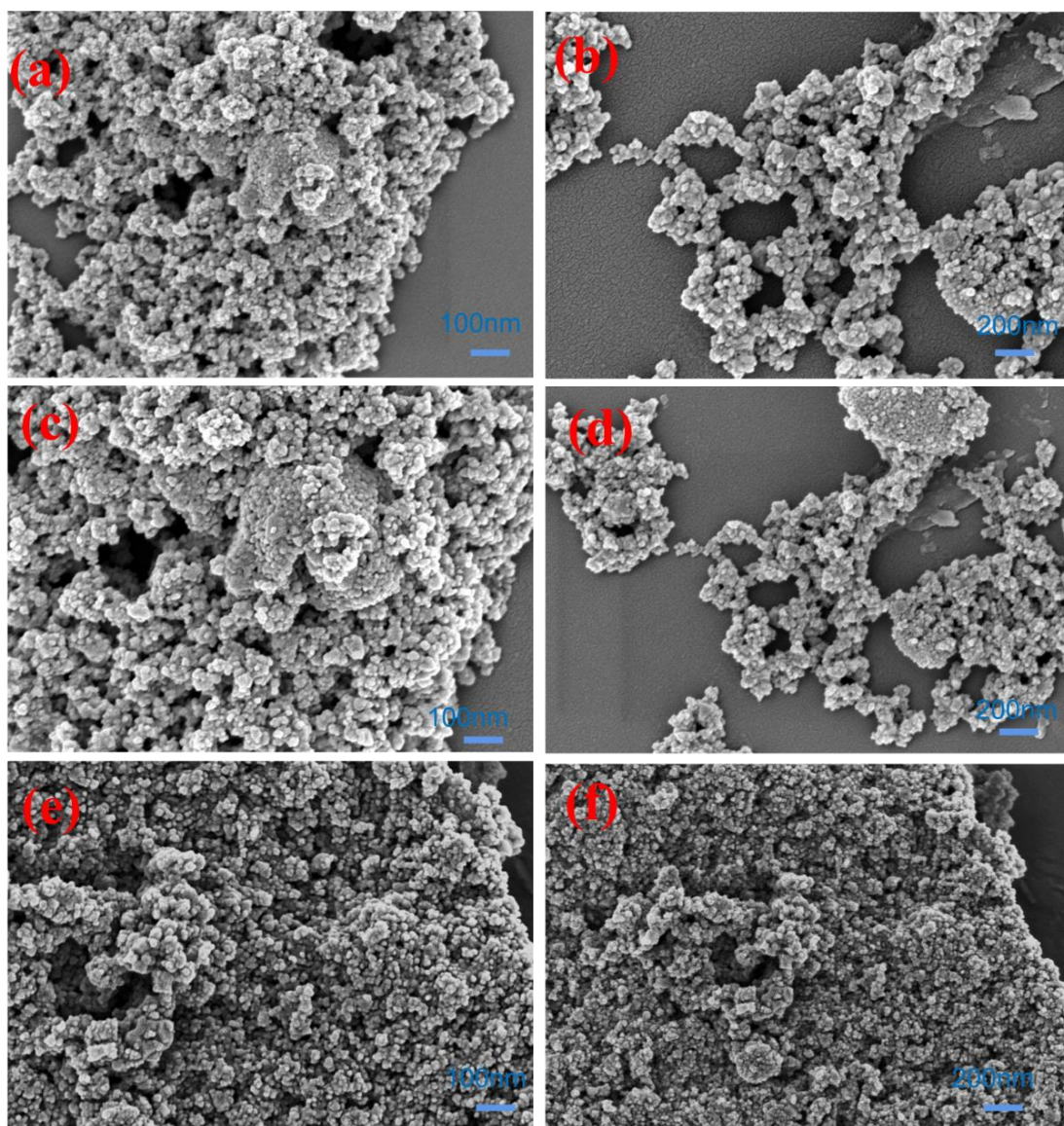
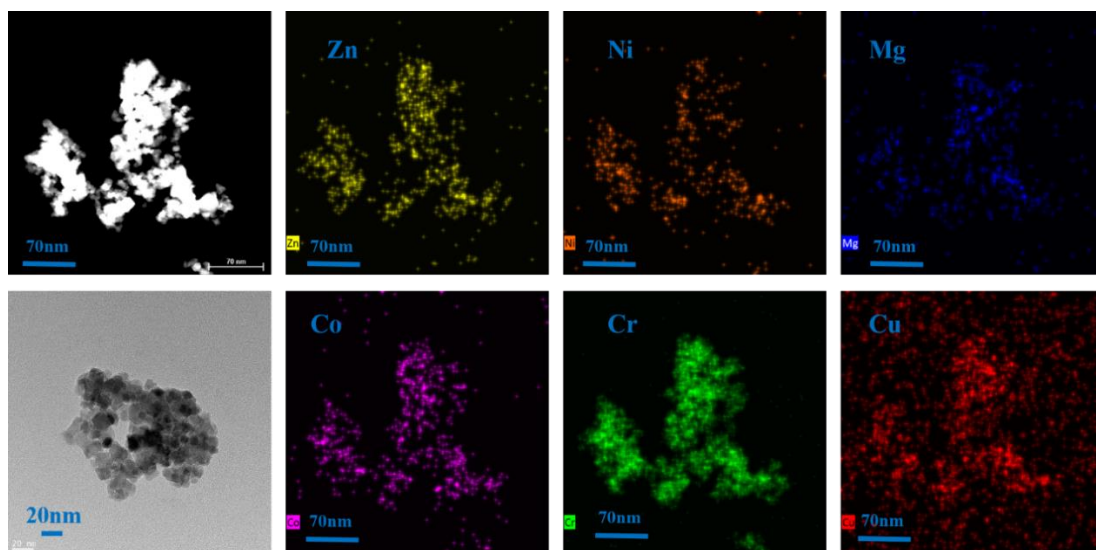
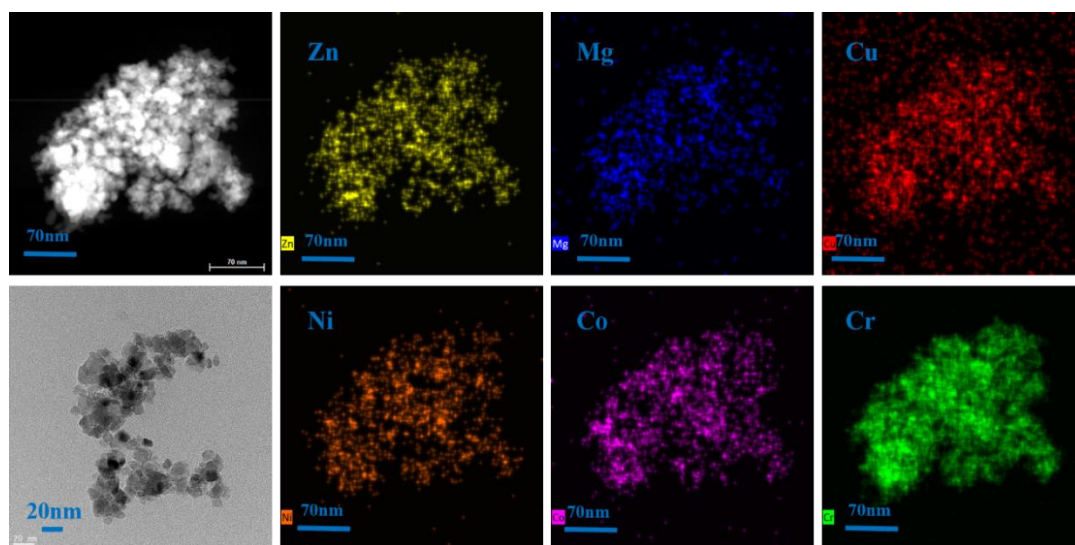


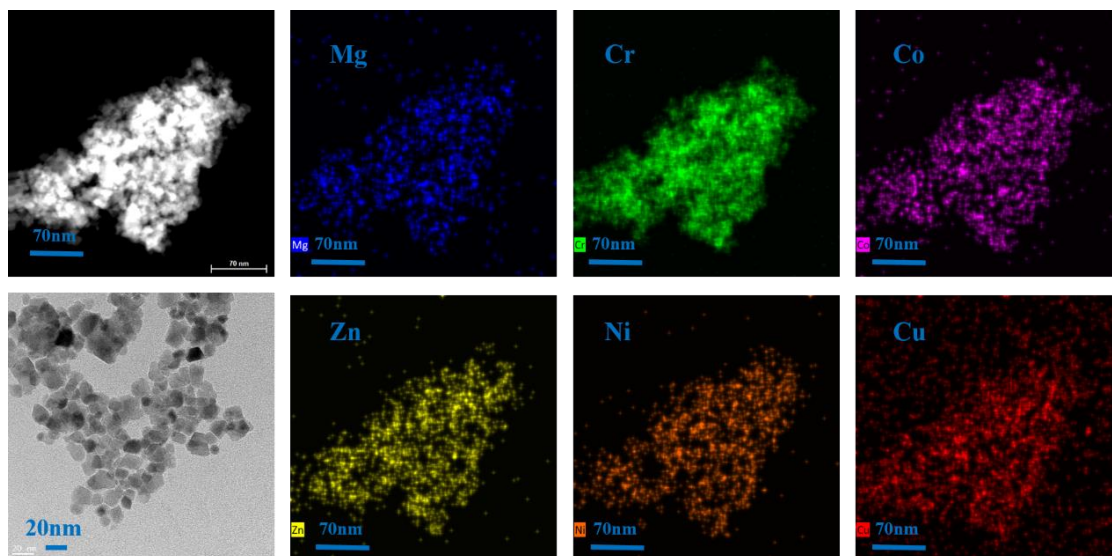
Figure S11. SEM characterization. (a, b) a- $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$, (c, d) b- $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ and (e, f) c- $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$.



FigureS12 TEM characterization. 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.



FigureS13 TEM characterization. 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.



FigureS14 TEM characterization. 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.

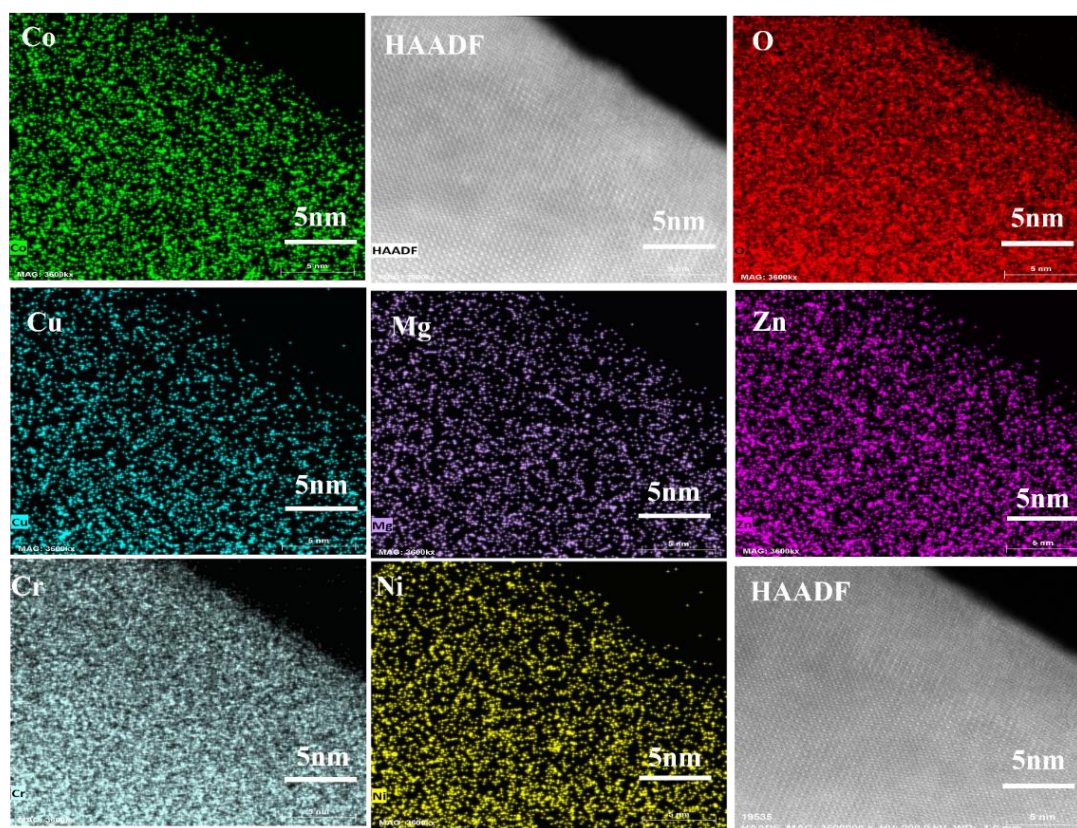


Figure S15. TEM characterization. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and energy-dispersive spectroscopy (EDS) elemental mapping images of a-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ nanoparticles.

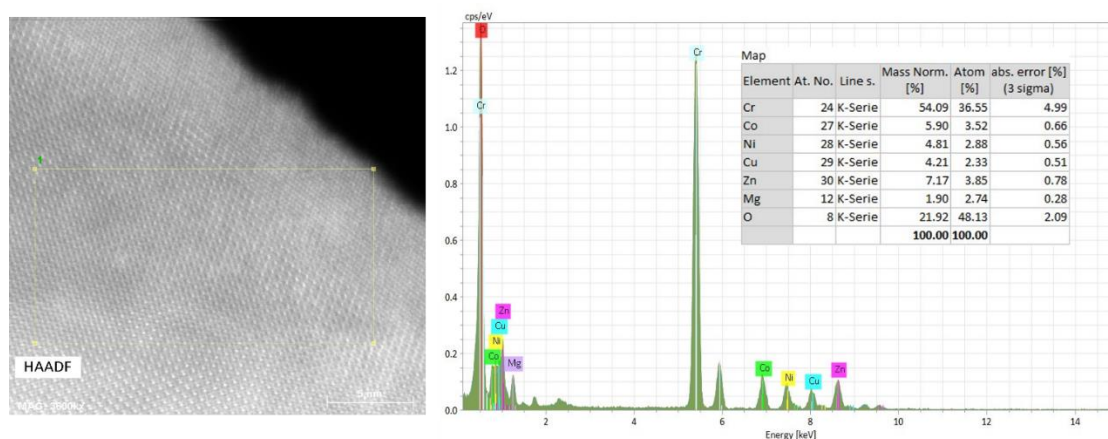


Figure S16 The qualitative analysis. Composition of the metals (based on EDS mapping spectral data) for a-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ nanoparticles

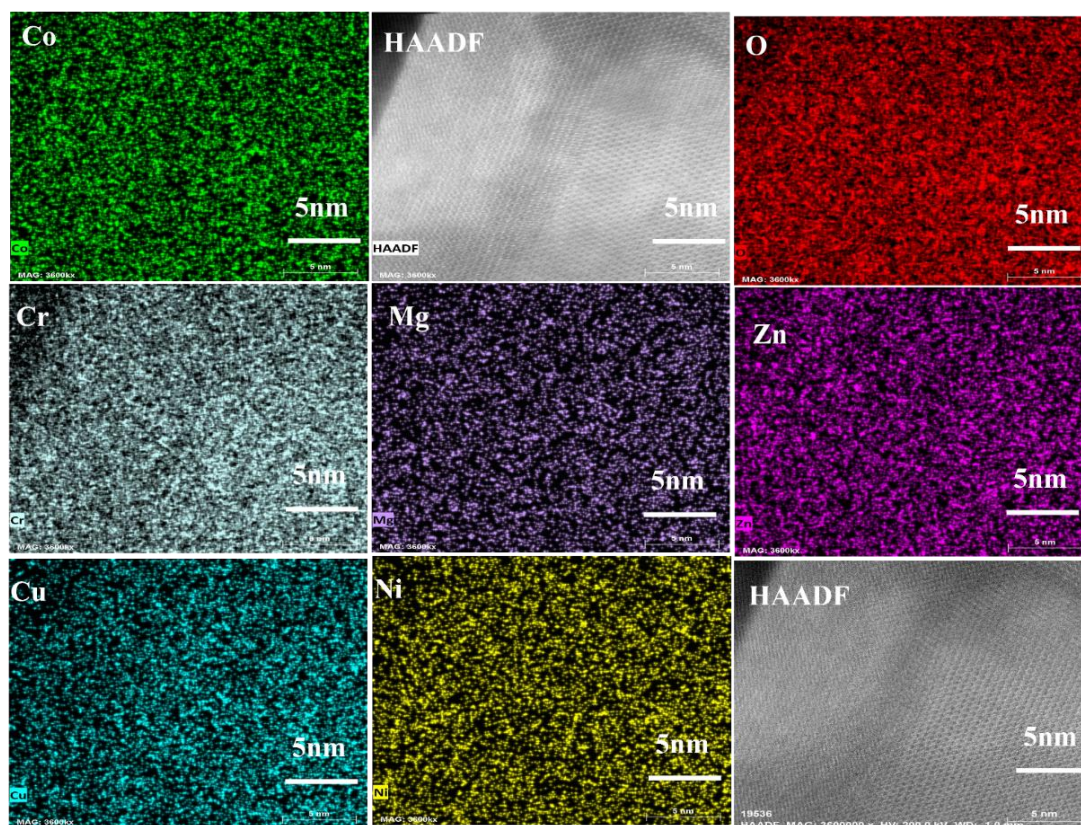


Figure S17. TEM characterization. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and energy-dispersive spectroscopy (EDS) elemental mapping images of b-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ nanoparticles.

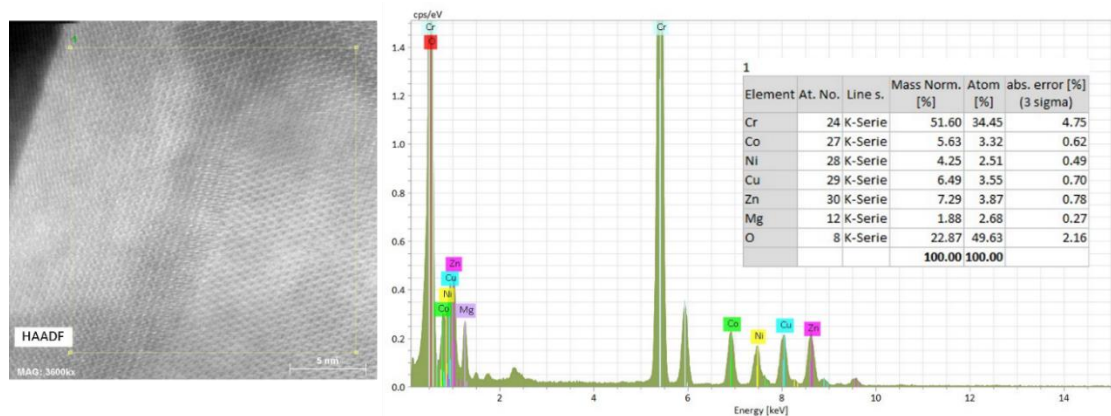


Figure S18. The quality analysis. The qualitative analysis with composition of the metals (based on EDS mapping spectral data) of b-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ nanoparticles

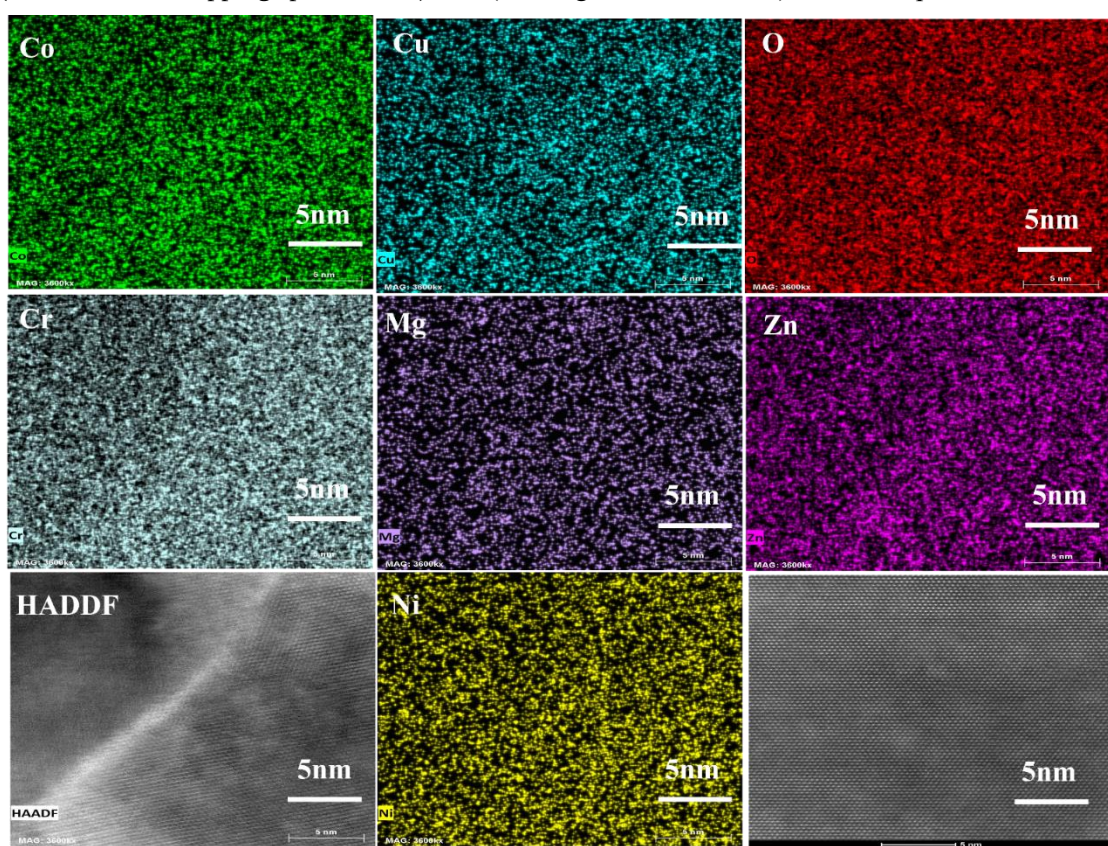


Figure S19. TEM characterization. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and energy-dispersive spectroscopy (EDS) elemental mapping images of c-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ nanoparticles.

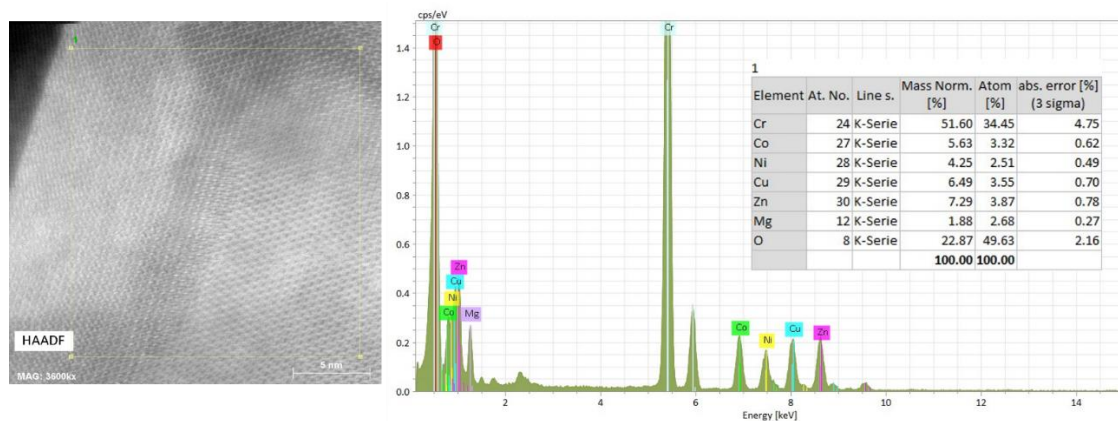


Figure S20. The qualitative analysis. Composition of the metals (based on EDS mapping spectral data) of $c\text{-(Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ nanoparticles

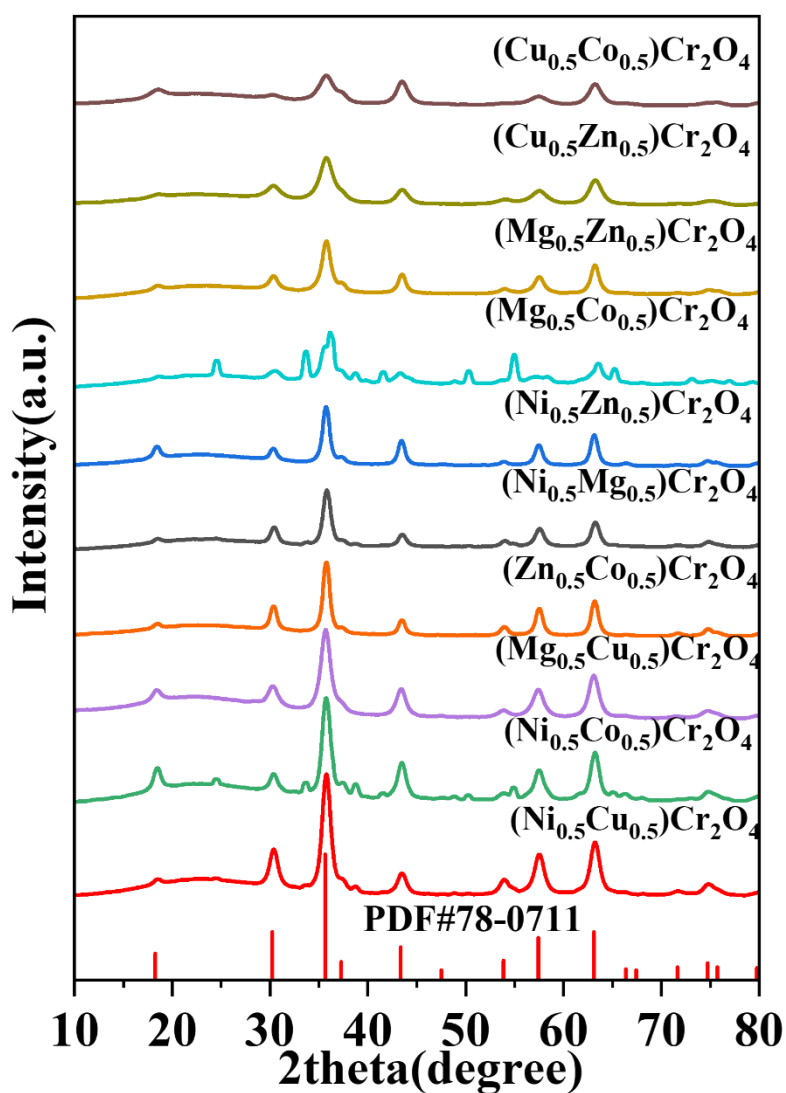


Figure S21. XRD characterization. XRD images of 10 ternary control samples

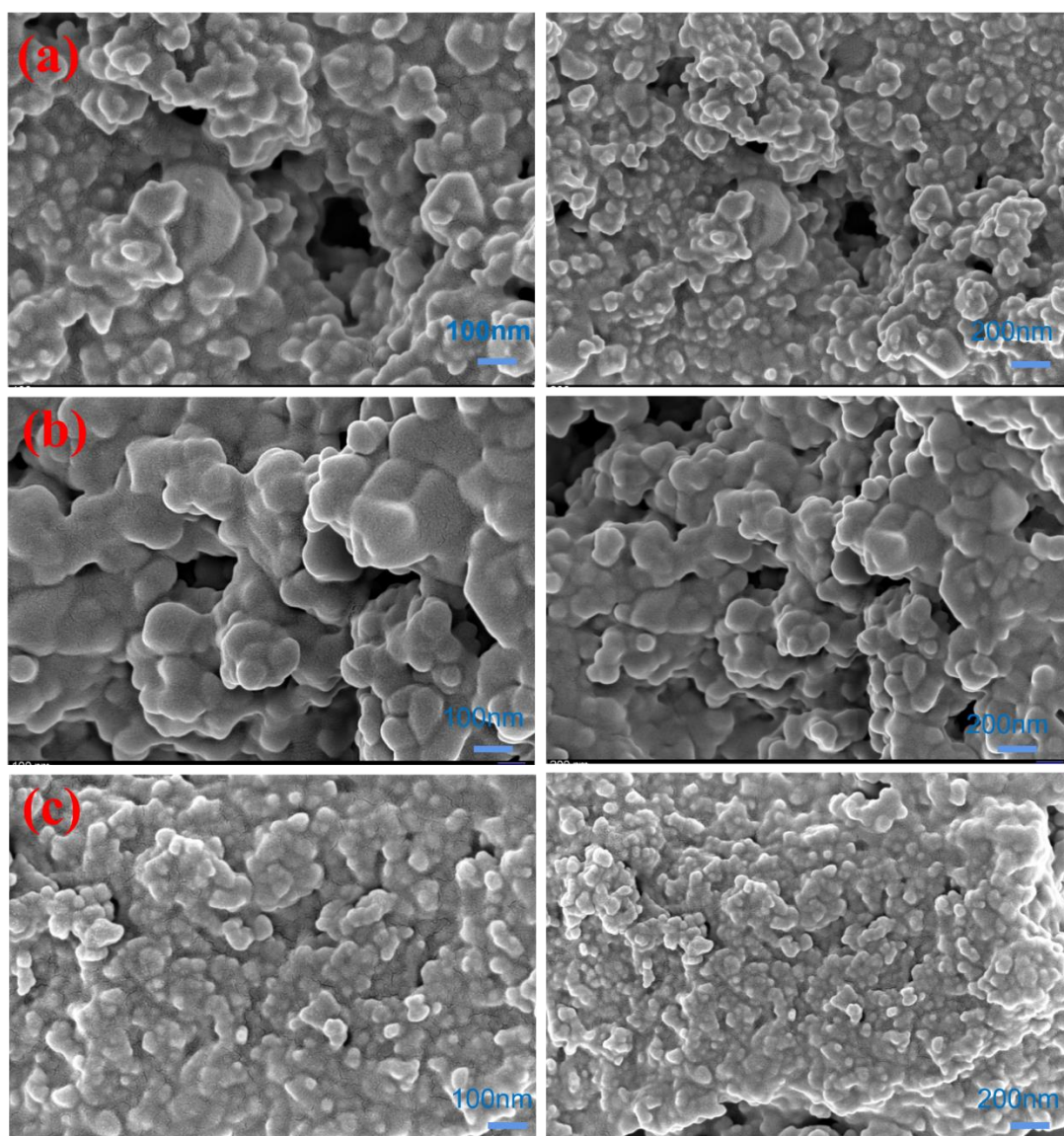


Figure S22. SEM images of ternary control samples. (a) $(\text{Ni}_{0.5}\text{Mg}_{0.5})\text{Cr}_2\text{O}_4$, (b) $(\text{Ni}_{0.5}\text{Cu}_{0.5})\text{Cr}_2\text{O}_4$, (c) $(\text{Ni}_{0.5}\text{Zn}_{0.5})\text{Cr}_2\text{O}_4$

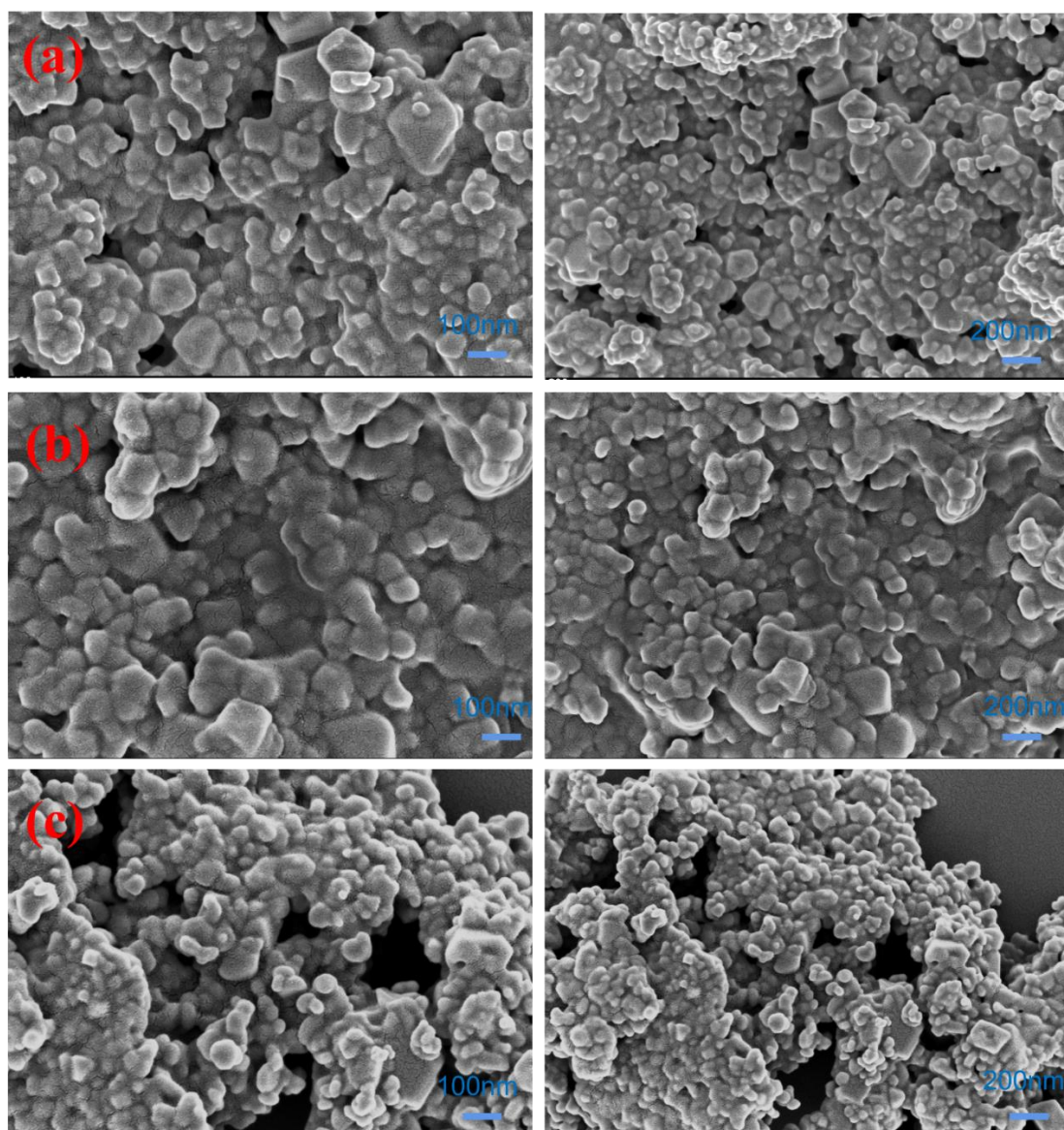


Figure S23 SEM images of ternary control samples. (a) $(\text{Ni}_{0.5}\text{Co}_{0.5})\text{Cr}_2\text{O}_4$, (b) $(\text{Cu}_{0.5}\text{Zn}_{0.5})\text{Cr}_2\text{O}_4$, (c) $(\text{Cu}_{0.5}\text{Mg}_{0.5})\text{Cr}_2\text{O}_4$

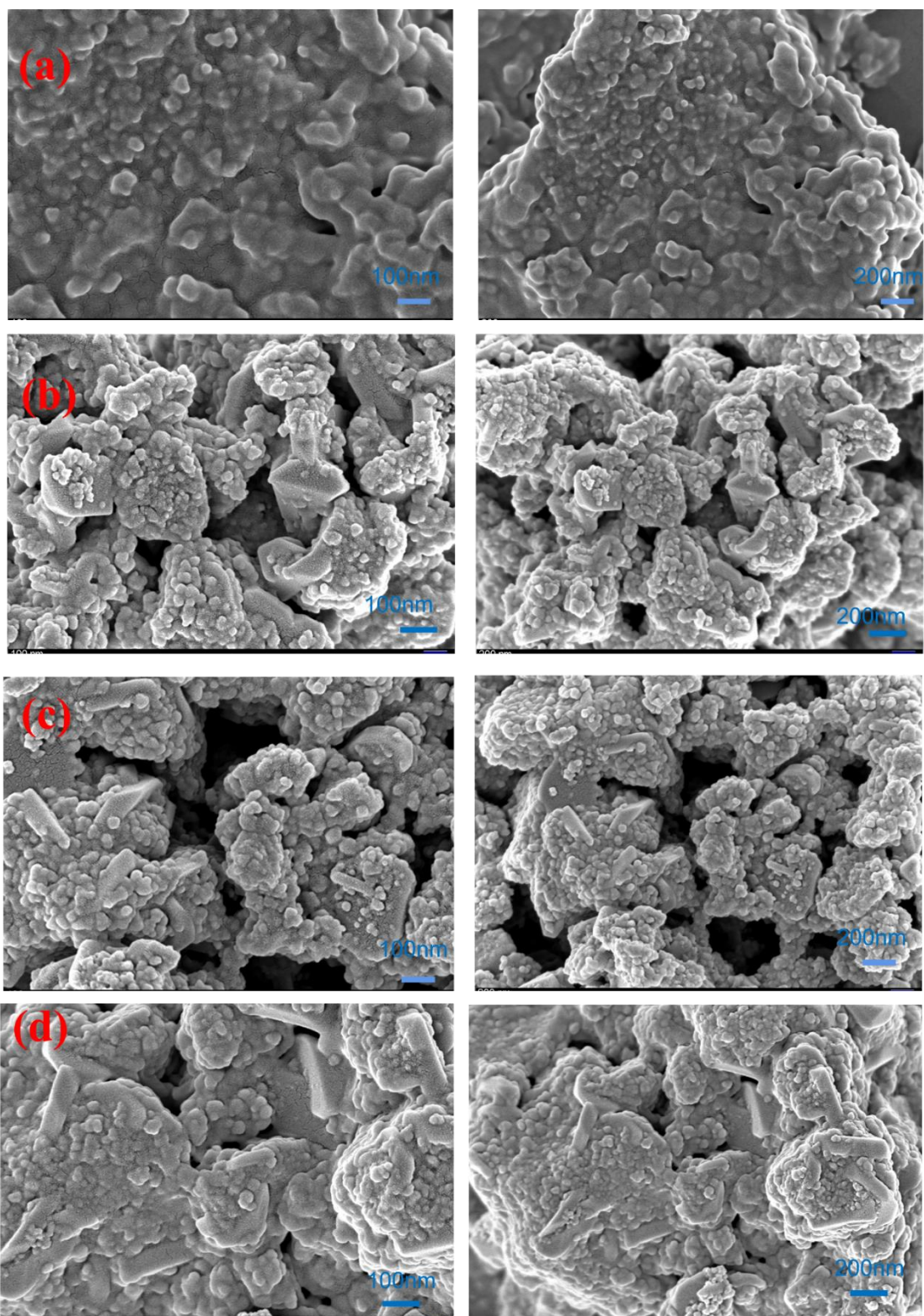


Figure S24. SEM images of ternary control samples. (a) $(\text{Zn}_{0.5}\text{Mg}_{0.5})\text{Cr}_2\text{O}_4$, (b) $(\text{Co}_{0.5}\text{Mg}_{0.5})\text{Cr}_2\text{O}_4$, (c) $(\text{Co}_{0.5}\text{Cu}_{0.5})\text{Cr}_2\text{O}_4$ and (d) $(\text{Co}_{0.5}\text{Zn}_{0.5})\text{Cr}_2\text{O}_4$.

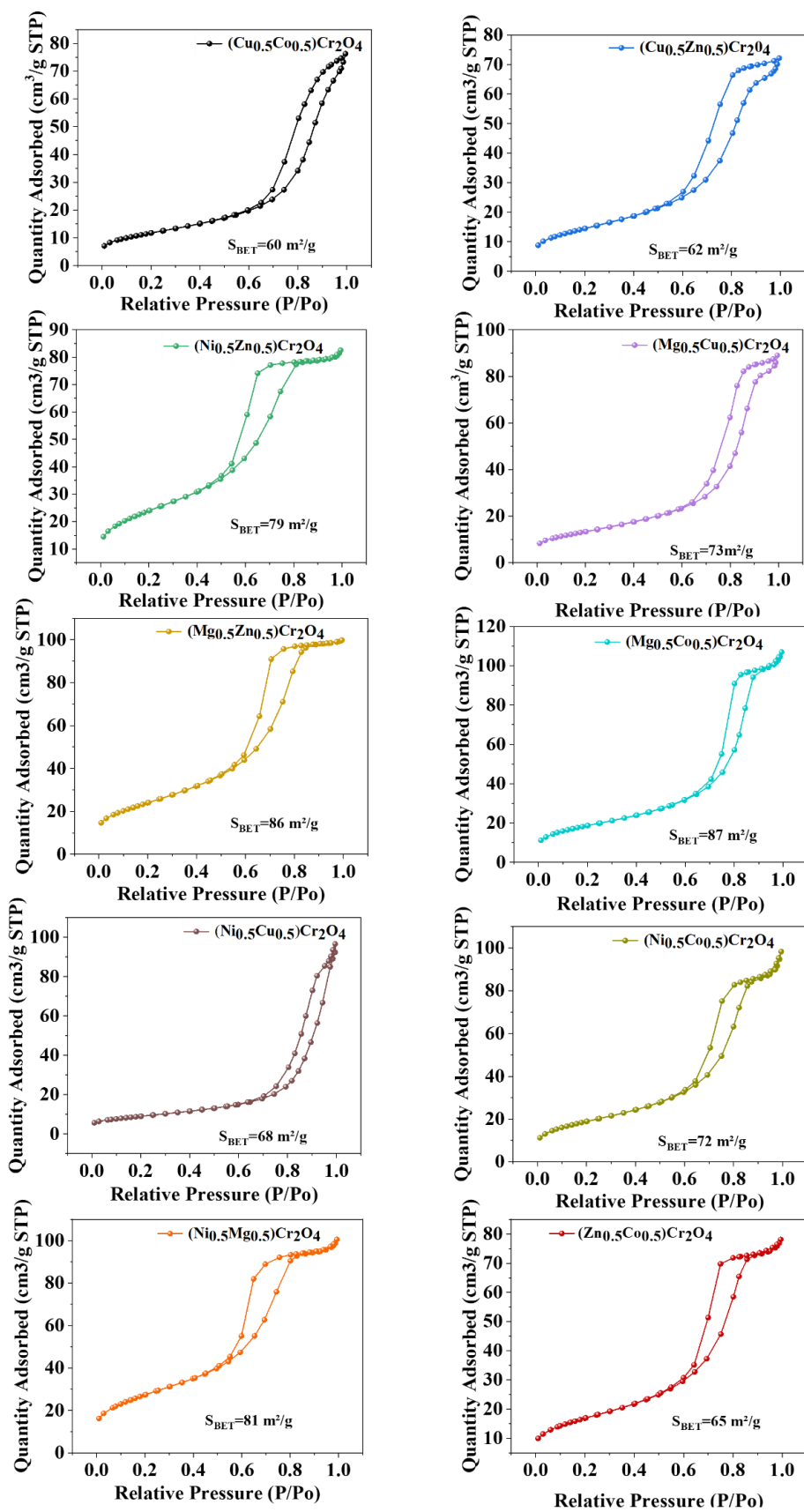


Figure S25. Pore size distribution experiment. N₂ adsorption curve of 10 ternary control samples.

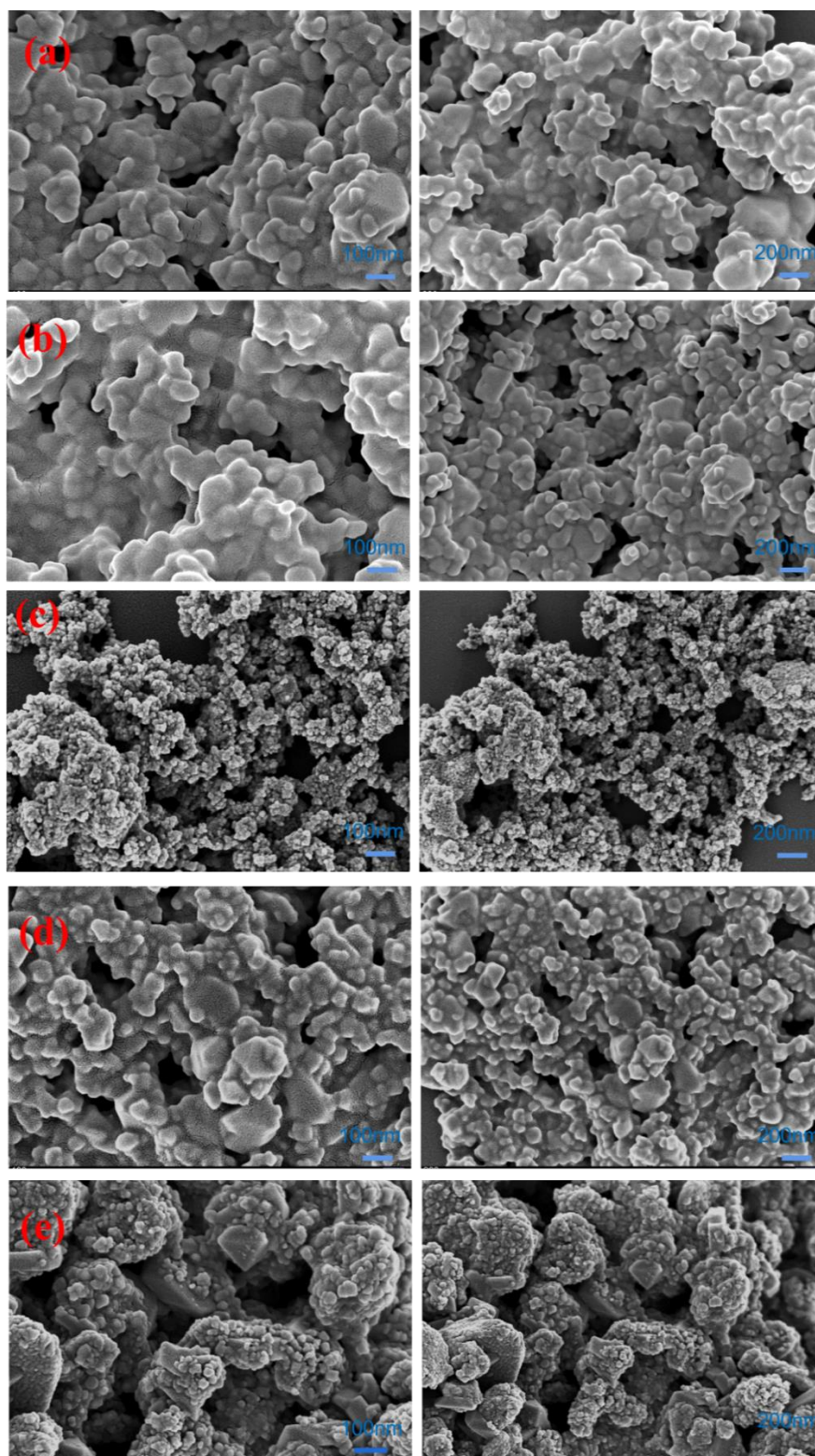
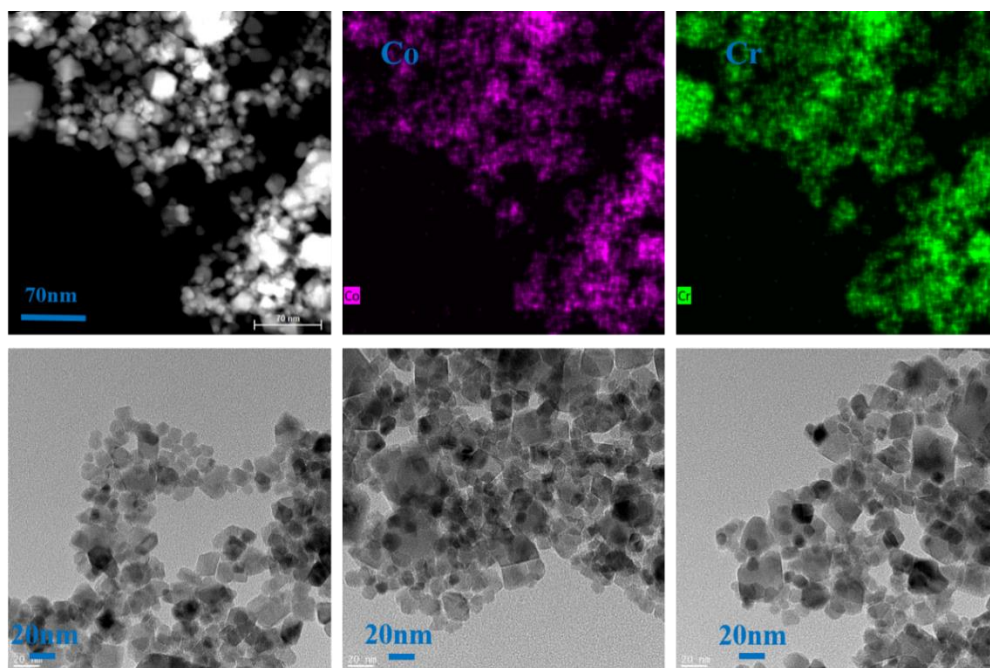
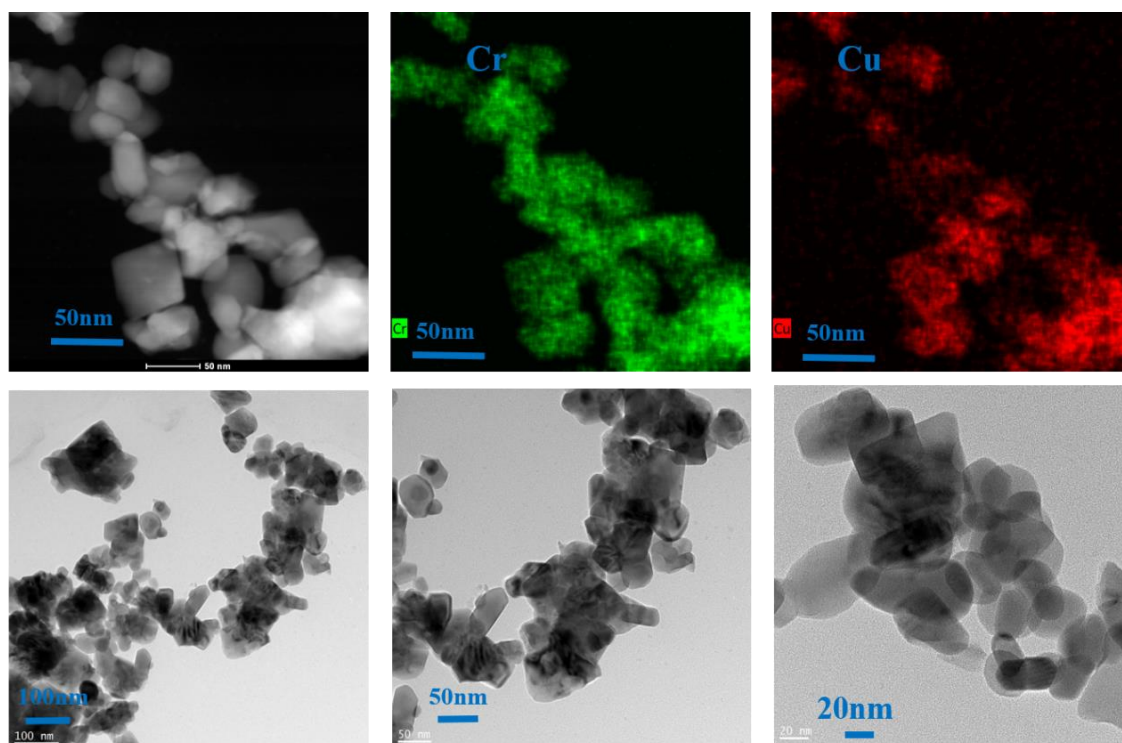


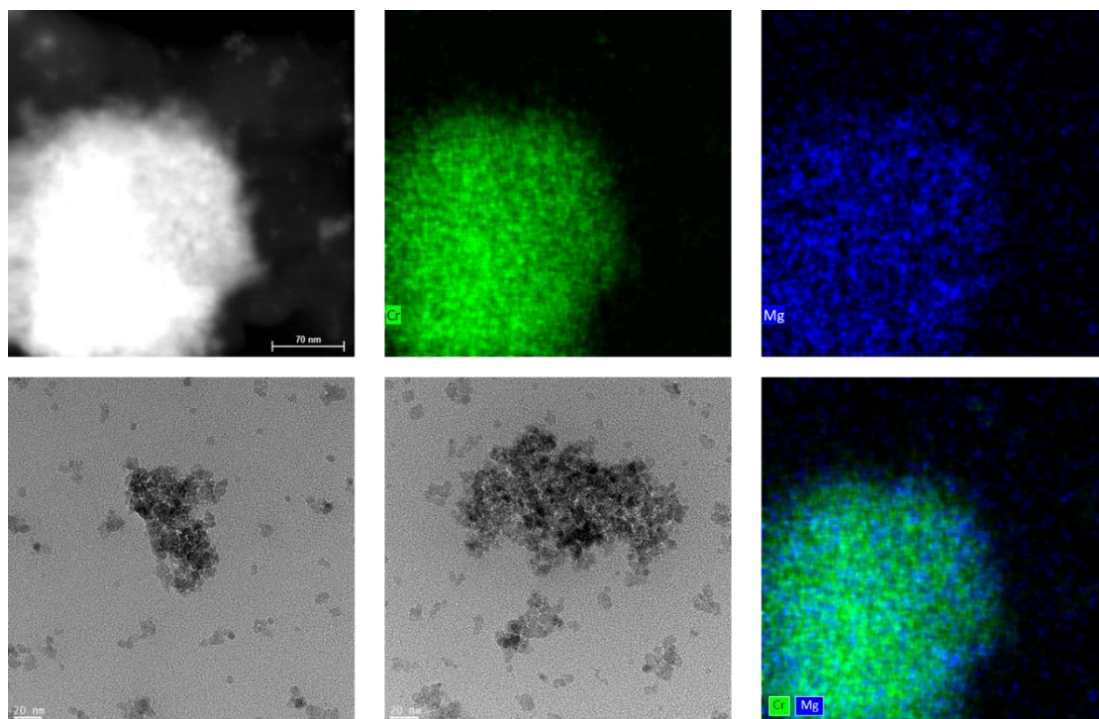
Figure S26. SEM characterization of control samples. (a) NiCr_2O_4 , (b) MgCr_2O_4 , (c) CuCr_2O_4 , (d) ZnCr_2O_4 , (e) CoCr_2O_4



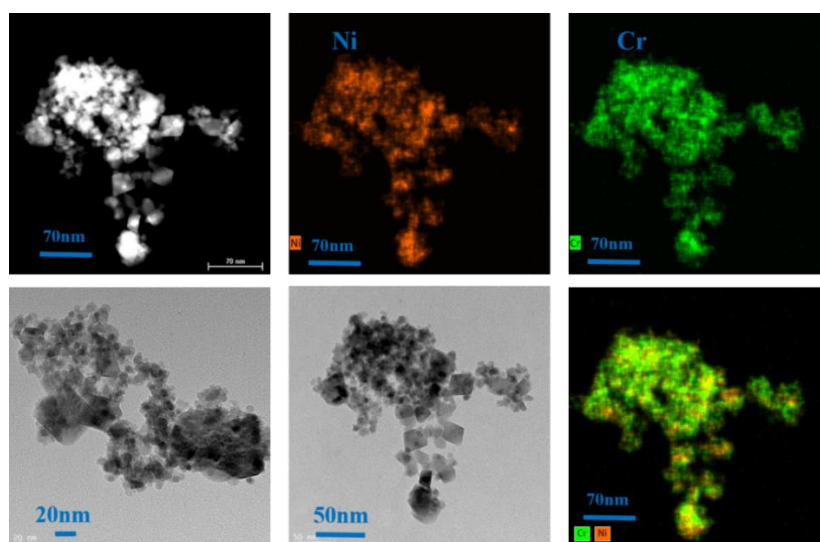
FigureS27 TEM characterization. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and energy-dispersive spectroscopy (EDS) elemental mapping images of CoCr_2O_4 nanoparticles.



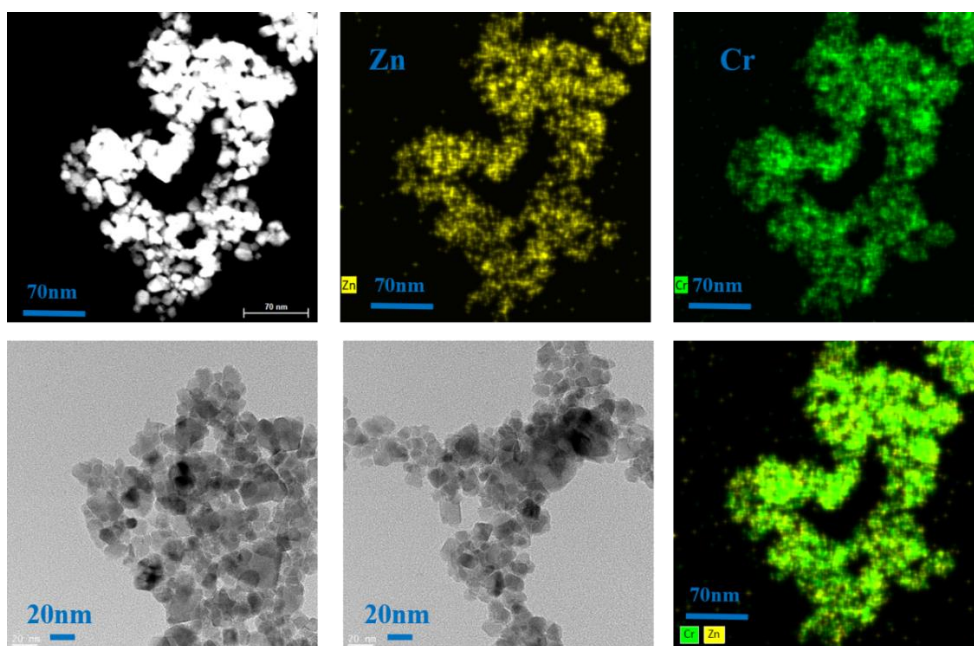
FigureS28 TEM characterization. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and energy-dispersive spectroscopy (EDS) elemental mapping images of CuCr_2O_4 nanoparticles.



FigureS29 TEM characterization. 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.



FigureS30 TEM characterization. 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.



FigureS31 TEM characterization. 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.

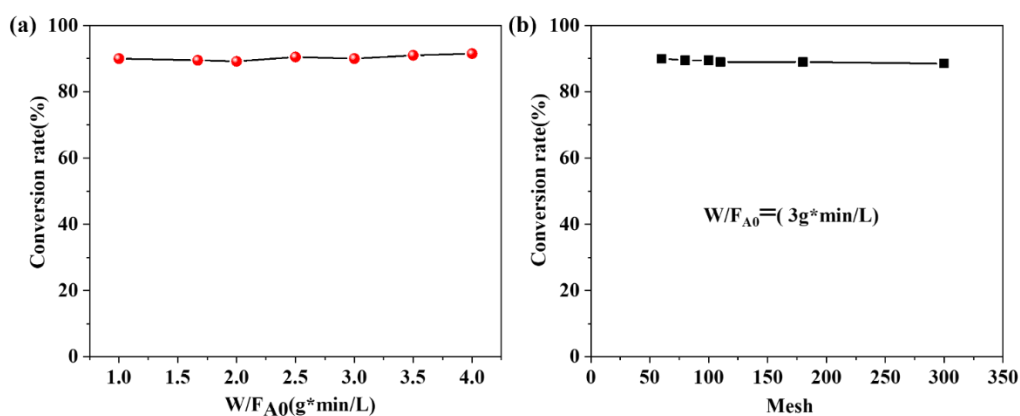


Figure S32 Internal diffusion and external diffusion. (a)The influence of internal diffusion for C_3H_6 oxidation. (b) The influence of external diffusion C_3H_6 oxidation.

In addition, to study 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 combustion, it was necessary to study the influence of internal and external diffusion. First, whether the existence of internal 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 internal 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 almost unchanged by changing the mesh size of the (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ catalyst. These results suggested that there was no effect of external diffusion(**Figure S18b**).

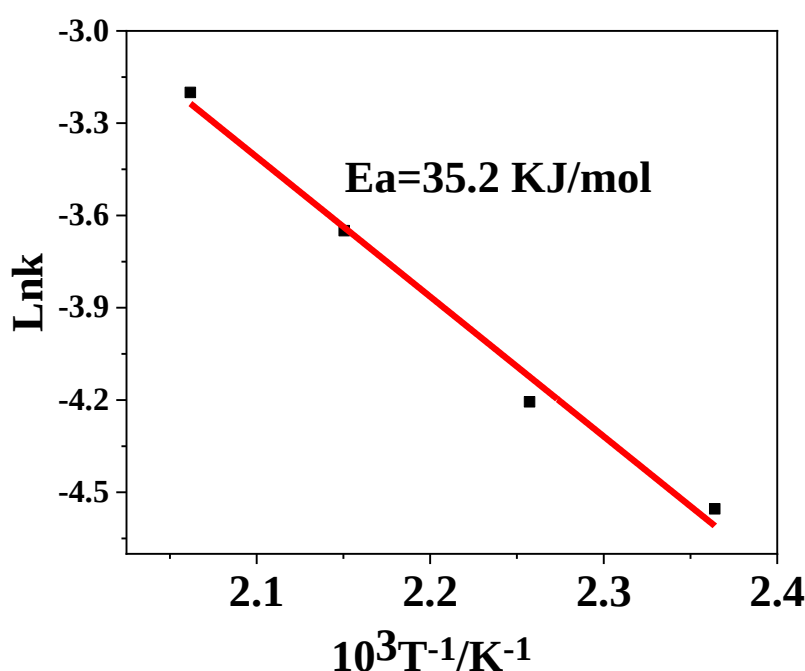


Figure S33 Reaction kinetics. Reaction kinetics of C₃H₆ oxidation of (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ catalyst from Arrhenius plots.

To further investigate the reaction behavior of (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄, the apparent activation energy (E_a) was calculated. Avoiding the impact of mass and heat transfer, the E_a was calculated at a C₃H₆ conversion below 15% respectively. ^[17] The E_a calculated by the Arrhenius diagram was 35.2 kJmol⁻¹(**Figure S33**). The stronger reducibility and rich oxygen vacancies of (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ were crucial for the continuous formation of active oxygen. Moreover, the high specific surface area, small particle size, and well-dispersed species made (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ easier to expose more active sites, which were beneficial for the

adsorption of C_3H_6 molecules. Therefore, all the features of $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$ illustrated that the reaction may proceed through the M–K mechanism with lower activation energy. This fully proved that the existence of abundant oxygen vacancies in $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$ lead to a lower activation energy and showed good catalytic performance in C_3H_6 catalytic oxidation.

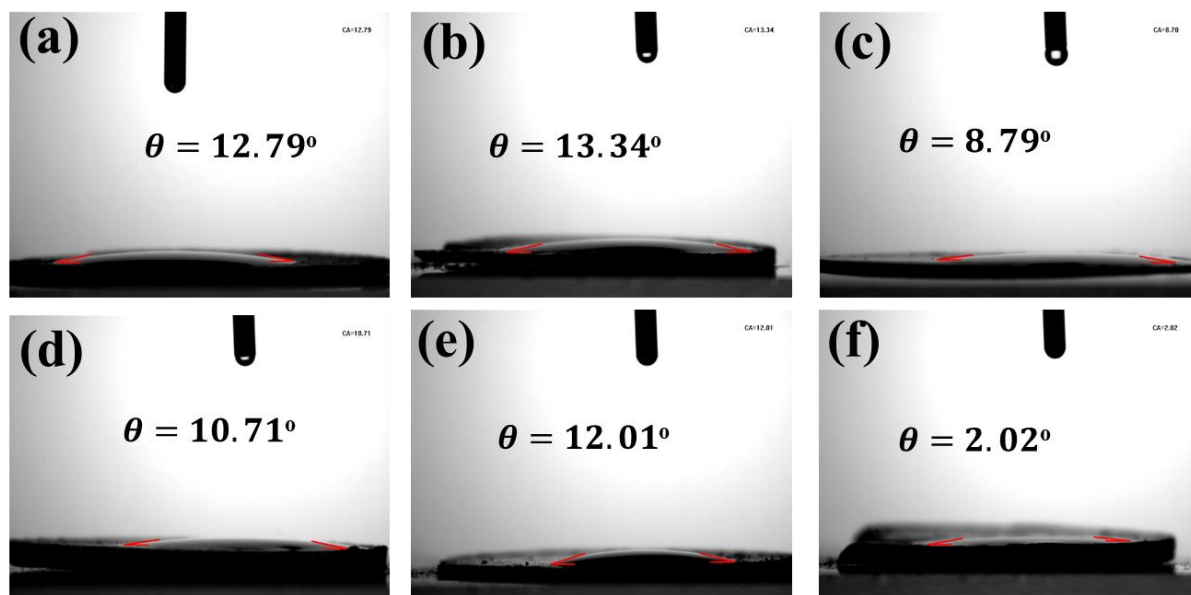


Figure S34. Comparison of contact angles. Sample CA Diagram of (a) $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$ (b) $NiCr_2O_4$ (c) $MgCr_2O_4$ (d) $CuCr_2O_4$ (e) $ZnCr_2O_4$ (f) $CoCr_2O_4$.

In order to study the water resistance mechanism of $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$, the contact angle test was also conducted (**Figure S34**). However, experiments showed that the surfaces of $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$ and ACr_2O_4 ($A=Ni, Mg, Cu, Zn, Co$) were hydrophilic. Interestingly, DFT calculation showed that the water molecules on the surface of $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$ would not affect the adsorption of C_3H_6 , but the water molecules on the surface of ACr_2O_4 ($A=Ni, Mg, Cu, Zn, Co$) would prevent the adsorption of C_3H_6 (Figure 1). In conclusion, although the surface of $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$ was hydrophilic, the binding energy of water and $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$ was weak, and water molecules were easy to be desorbed. Moreover, the water molecules on the surface of $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$ would not affect the adsorption of C_3H_6 to ensure the good catalytic performance of C_3H_6 oxidation.

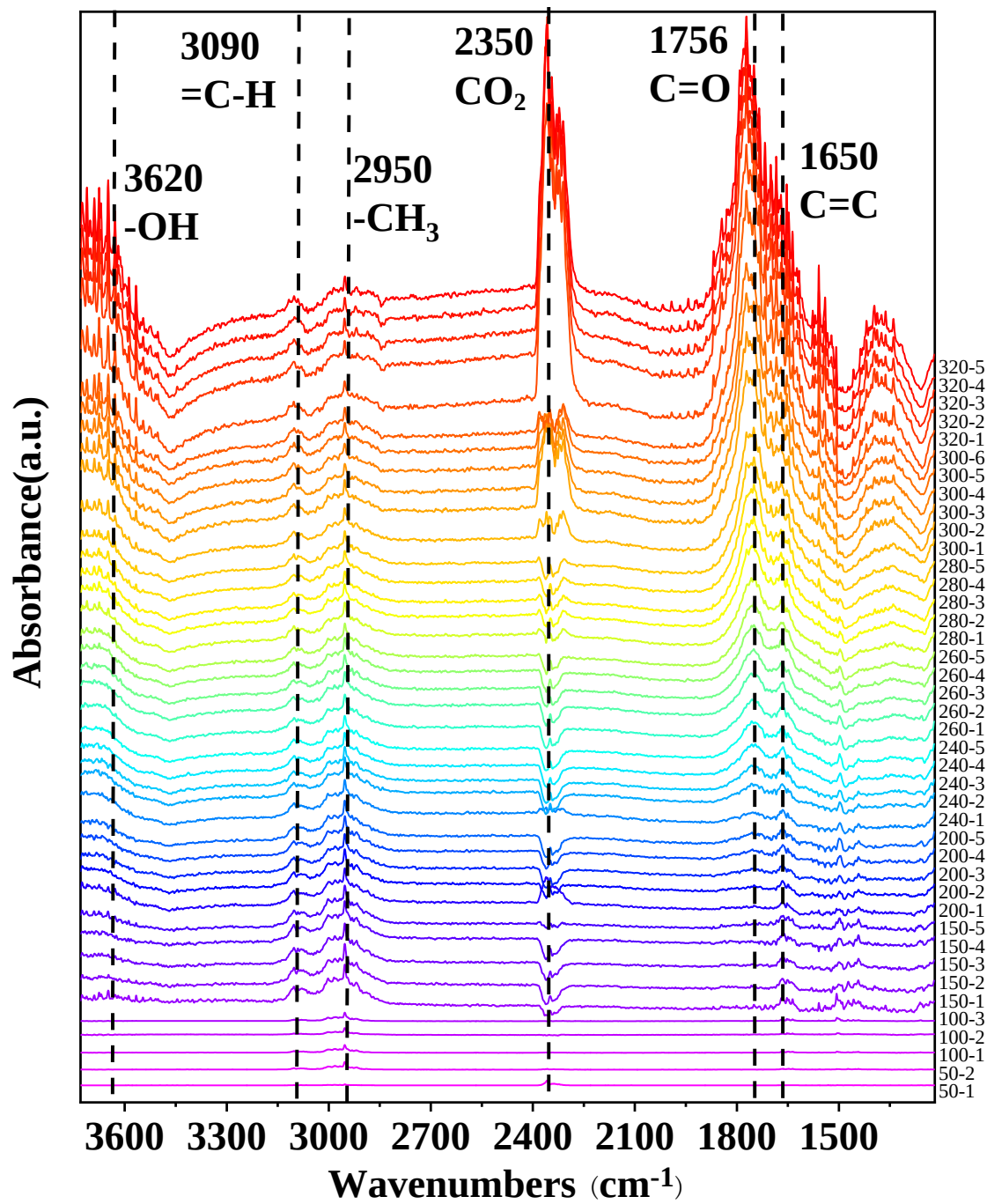


Figure S35. In situ DRIFT spectra. C₃H₆ catalytic oxidation for (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ catalyst at different temperatures without water. (10 mL/min, 1 vol % C₃H₆ and 99 vol% air; sampling interval was 5 min).

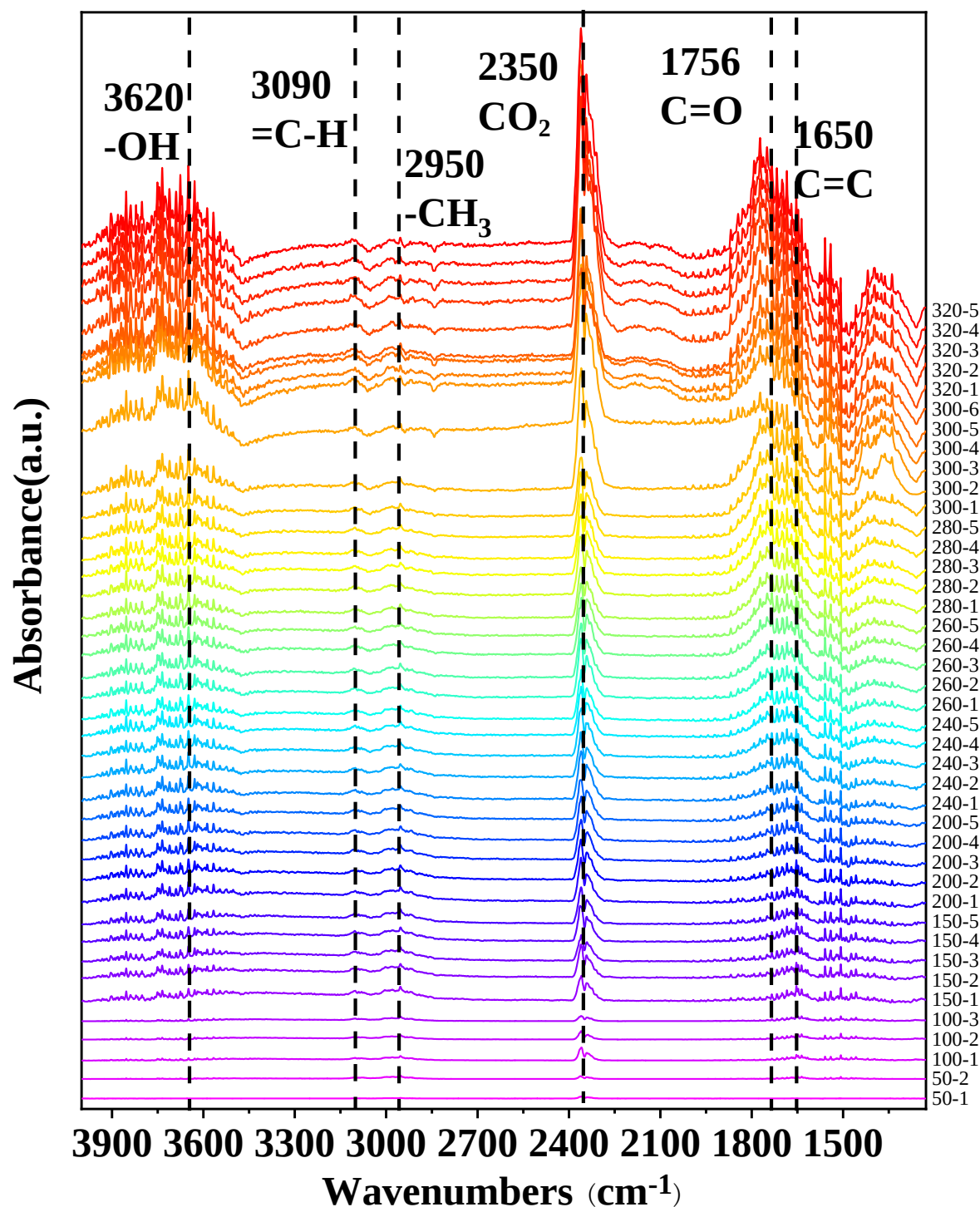


Figure S36. In situ DRIFT spectra. C₃H₆ catalytic oxidation for (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ catalyst at different temperatures with 4.2vol% water. (10 mL/min, 1vol % C₃H₆ and 99vol% air ; sampling interval was 5 min).

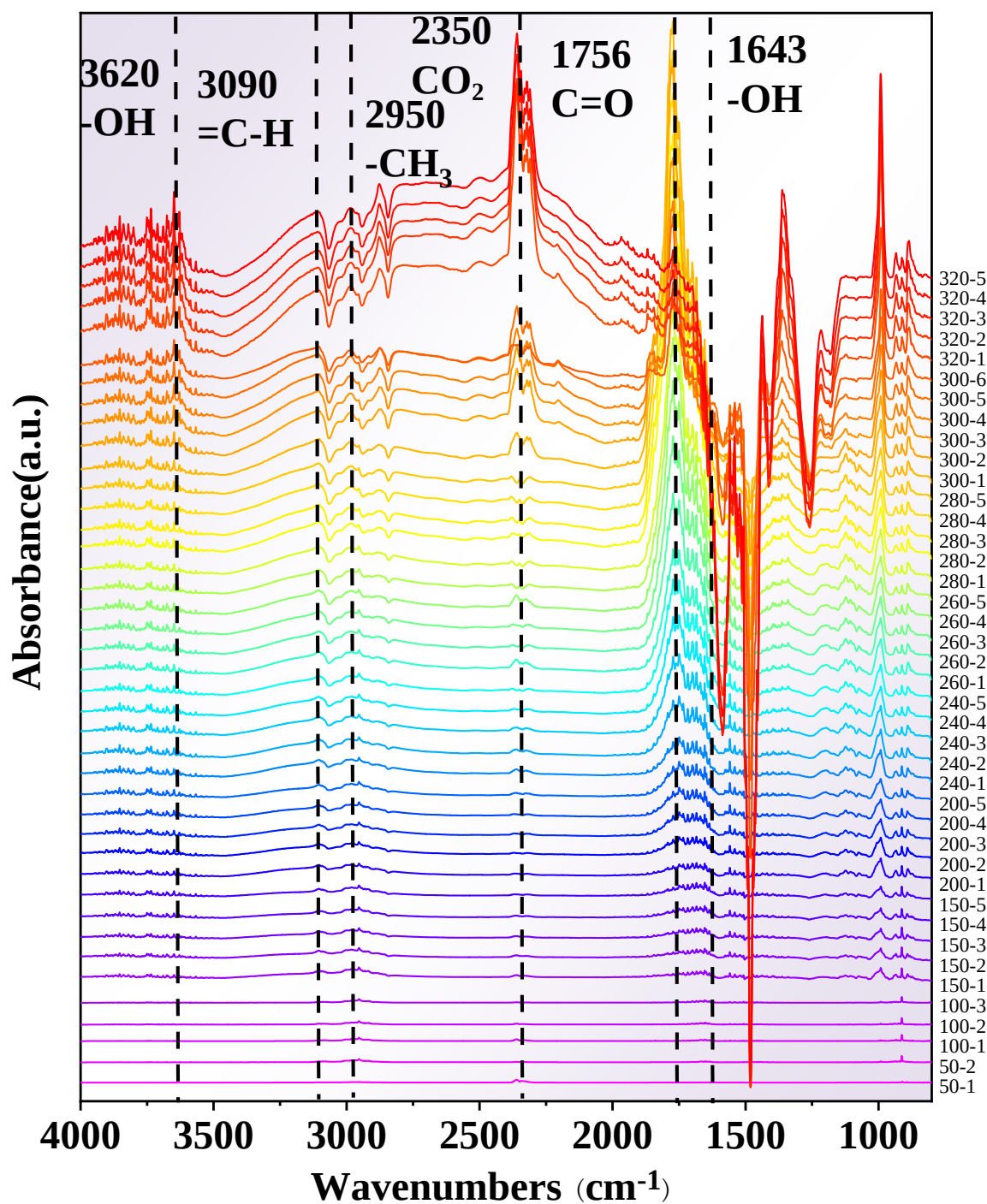


Figure S37. In situ DRIFT spectra. C_3H_6 catalytic oxidation for $CoCr_2O_4$ catalyst at different temperatures without water. (10 mL/min, 1vol % C_3H_6 and 99vol% air ; sampling interval was 5 min).

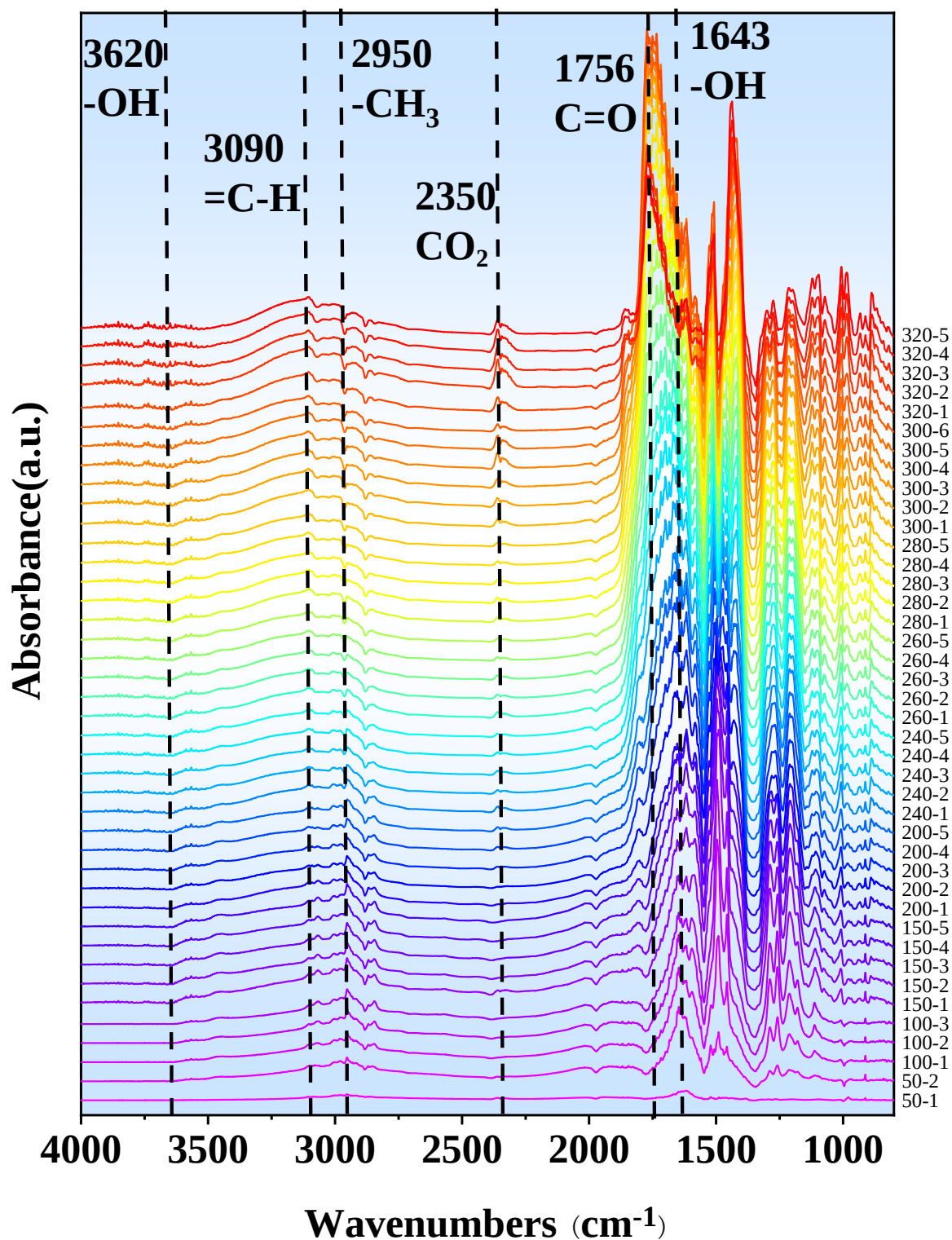


Figure S38. In situ DRIFT spectra. In situ DRIFT spectra of C_3H_6 catalytic oxidation for $CoCr_2O_4$ catalyst at different temperatures with 4.2vol% water. (10 mL/min, 1vol % C_3H_6 and 99vol% air; sampling interval was 5 min).

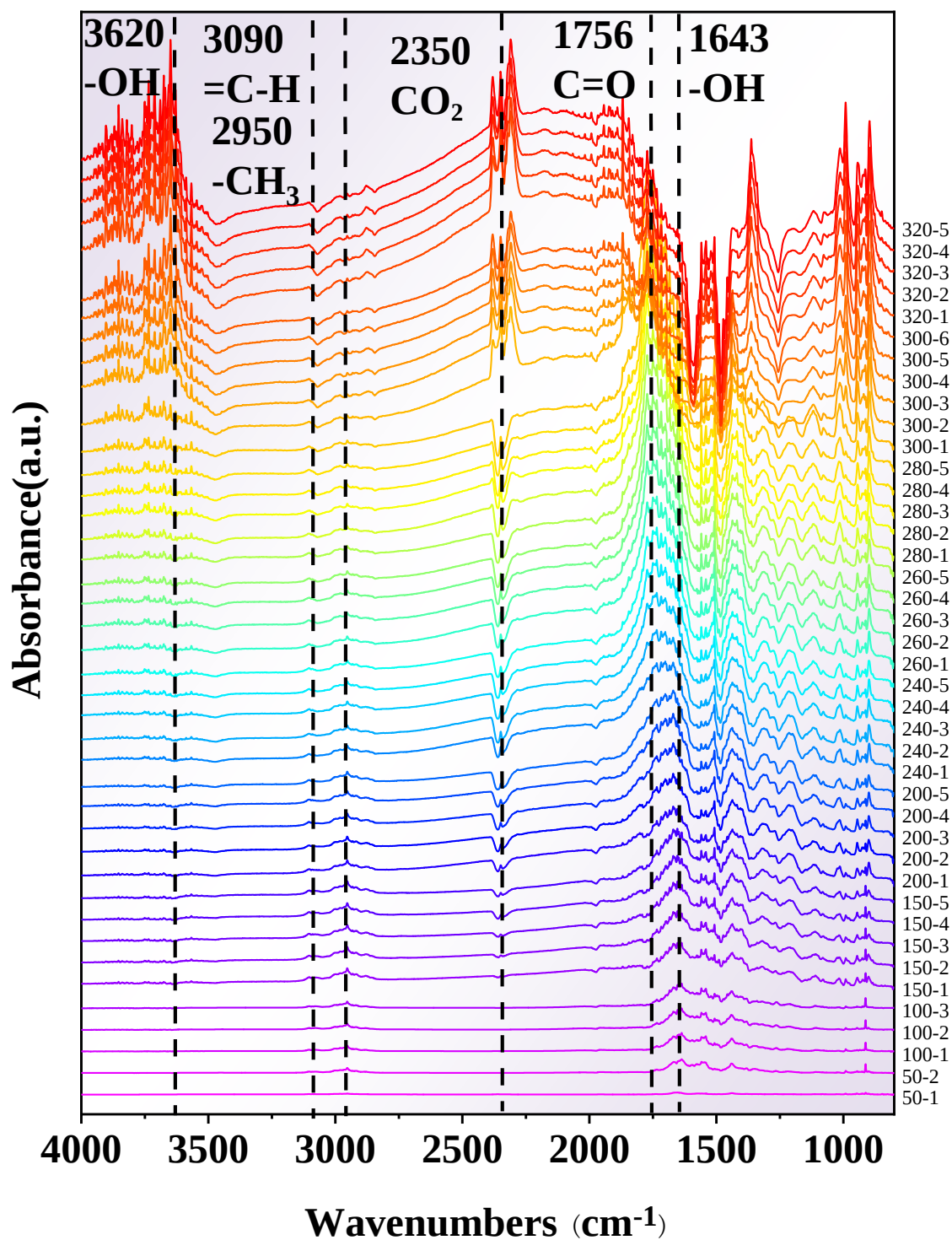


Figure S39. In situ DRIFT spectra. C_3H_6 catalytic oxidation for $ZnCr_2O_4$ catalyst at different temperatures without water. (10 mL/min, 1vol % C_3H_6 and 99vol% air ; sampling interval was 5 min).

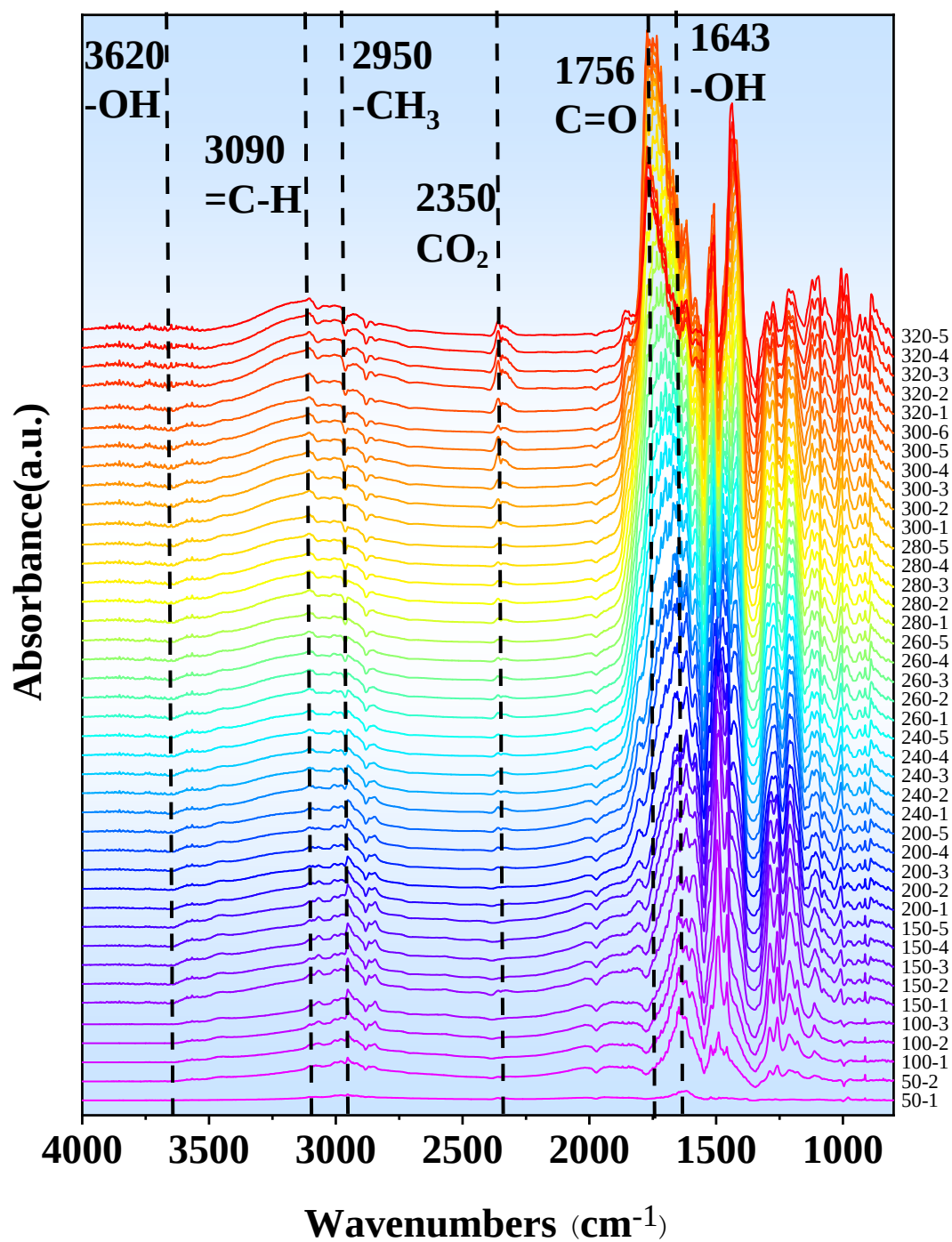


Figure S40. In situ DRIFT spectra. C₃H₆ catalytic oxidation for ZnCr₂O₄ catalyst at different temperatures with 4.2vol% water. (10 mL/min, 1vol % C₃H₆ and 99vol% air ; sampling interval was 5 min).

In order to study the mechanism of water resistance, in-situ infrared experiments were carried out with 4.2vol% water and without water respectively. The in-situ infrared spectrum of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ without water was shown in **Figure S35**. Only 1650cm^{-1} , 2950cm^{-1} , and 3090cm^{-1} appeared peaks in the background spectrogram at 100°C . The band at 1650cm^{-1} , 2950cm^{-1} , and 3090cm^{-1} corresponded to C=C species, $-\text{CH}_3$ species, and $=\text{C}-\text{H}$ species respectively. These were characteristic peaks of C_3H_6 . From 100°C to 320°C , the peaks at 2350cm^{-1} , 1756cm^{-1} , and 3620cm^{-1} corresponded to C=O species, CO_2 species, and $-\text{OH}$ species respectively. These peaks became large during the heating process due to the formation of CO_2 and H_2O in C_3H_6 catalytic oxidation. The in-situ infrared spectrum 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 the presence of 4.2vol% water was shown in **Figure S36**. In the background spectrum at 100°C , there was only a characteristic peak of C_3H_6 . From 150°C to 320°C , the peak at 3620cm^{-1} was always present due to 4.2vol% water existing. During the heating process from 100°C to 320°C , the peaks at 2350cm^{-1} , 1756cm^{-1} , and 3620cm^{-1} became large respectively. However, the increased amplitude of these peaks was smaller than that in Figure S9, which indicated that the generation of CO_2 and H_2O was slightly smaller than that in Figure S9. This slight inhibition can be explained by the blocking of some active sites by H_2O or the competitive adsorption of water and oxygen.

The in-situ infrared spectrum of CoCr_2O_4 without water was shown in **Figure S37**. No characteristic peak of C_3H_6 can be seen at 150°C . Since the adsorption energy of C_3H_6 on CoCr_2O_4 was relatively large and the surface was difficult to adsorb C_3H_6 compared to $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$. This result was consistent with the DFT calculation (**Figure 1**). From 100°C to 320°C , the peaks at 1756cm^{-1} , 2350cm^{-1} , and 3620cm^{-1} became large, corresponding to C=O species, CO_2 species, and $-\text{OH}$ species respectively. This proved the formation of CO_2 and H_2O in C_3H_6 catalytic oxidation. The in-situ infrared spectrum of CoCr_2O_4 in the presence of 4.2vol% water was shown in **Figure S38**. From 150°C to 320°C , the peak at 3620cm^{-1} had been very weak. This showed that the amount of H_2O generated in C_3H_6 catalytic oxidation was very small. There was no characteristic peak of C_3H_6 in the spectrogram at 150°C , but the peak at 1643cm^{-1} was very large. Interestingly, the peak at 1643cm^{-1} was getting bigger during the heating process from 100°C to 320°C . The band at 1643cm^{-1} was attributed to the water vapor species (Figure S10). These results showed that water can be adsorbed on the surface of CoCr_2O_4 and reacted with surface active oxygen substances to form

active hydroxyl groups, thus hindering the adsorption of C_3H_6 , which was not conducive to the C_3H_6 catalytic oxidation. This result was consistent with DFT calculation (**Figure 1** and **Figure 2**) and catalytic performance in C_3H_6 oxidation (**Figure 6**). The in situ infrared spectrum of $ZnCr_2O_4$ without water was shown in **Figure S39**. The in-situ infrared spectrum of $ZnCr_2O_4$ in the presence of 4.2vol% water was shown in **Figure S40**. The peak at 1643cm^{-1} was getting larger from 100°C to 320°C . The band at 1643 cm^{-1} was attributed to water-absorbing species. These results showed that water can be adsorbed on the surface of $ZnCr_2O_4$, which hindered the adsorption of C_3H_6 and was unfavorable to the C_3H_6 catalytic oxidation, matching the results of DFT calculation (**Figure 1**) and catalytic performance (**Figure 6**) well. This showed that $ZnCr_2O_4$ and $CoCr_2O_4$ had no water resistance, while $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$ had the advantage of good water resistance under humid conditions.

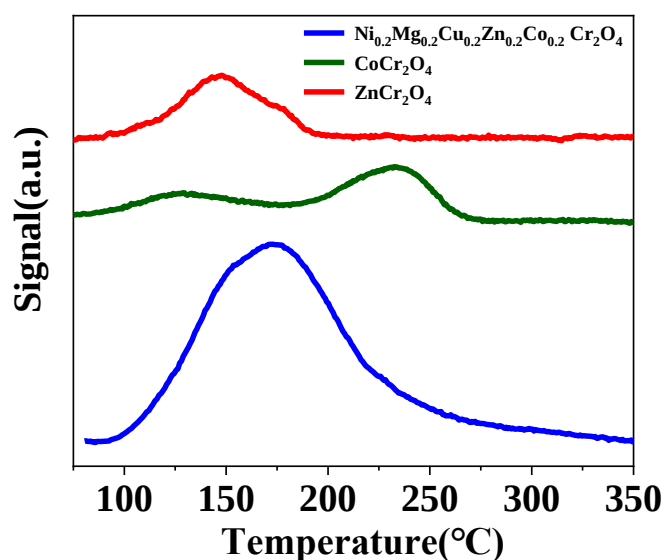


Figure S41. Adsorption capacity of propylene. C_3H_6 -TPD profiles of $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$, $ZnCr_2O_4$ and $CoCr_2O_4$.

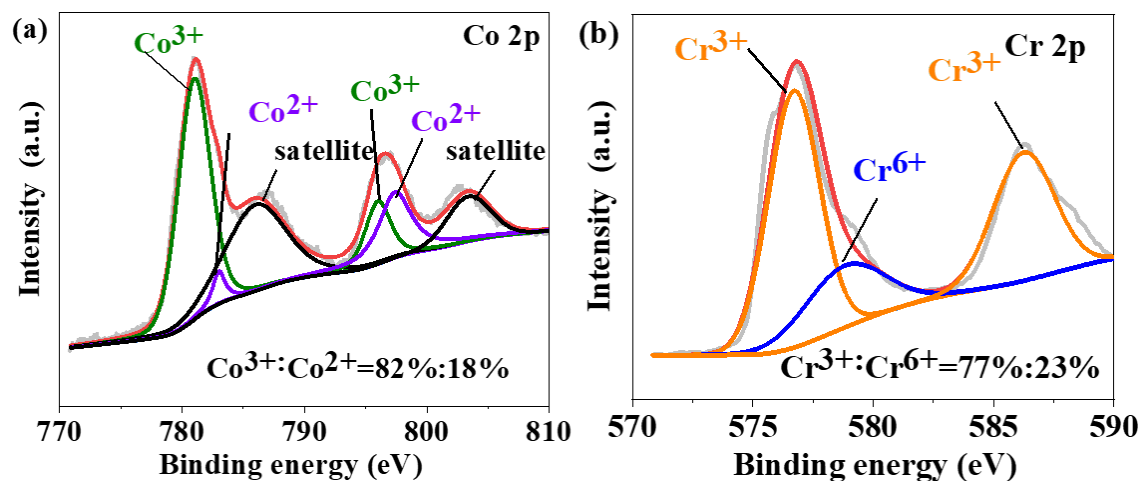


Figure S42. XPS characterization. (a) Co 2p XPS spectra, (b) Cr 2p XPS spectra of CoCr_2O_4 catalyst.

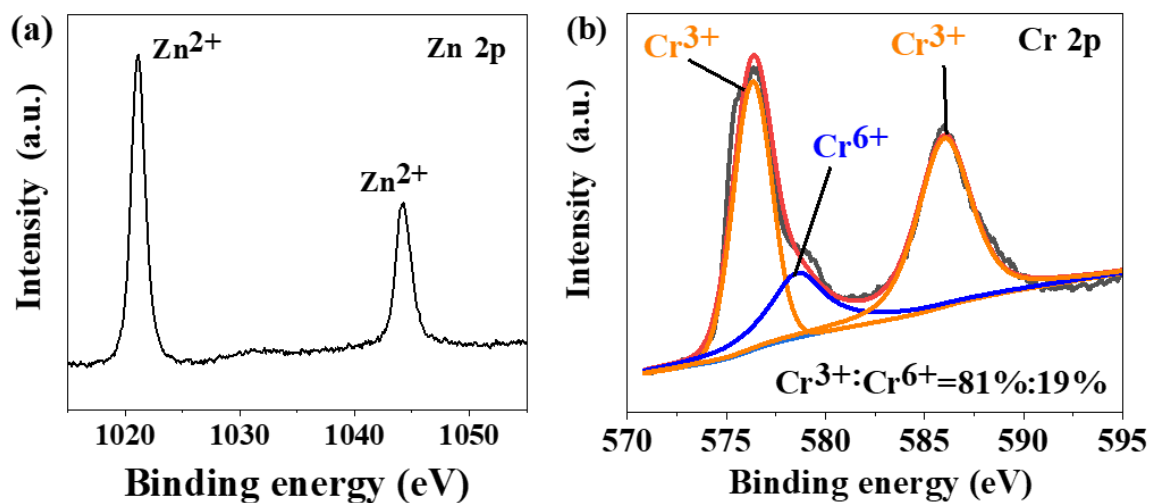


Figure S43. XPS characterization. (a) Zn 2p XPS spectra, (b) Cr 2p XPS spectra of ZnCr_2O_4 catalyst.

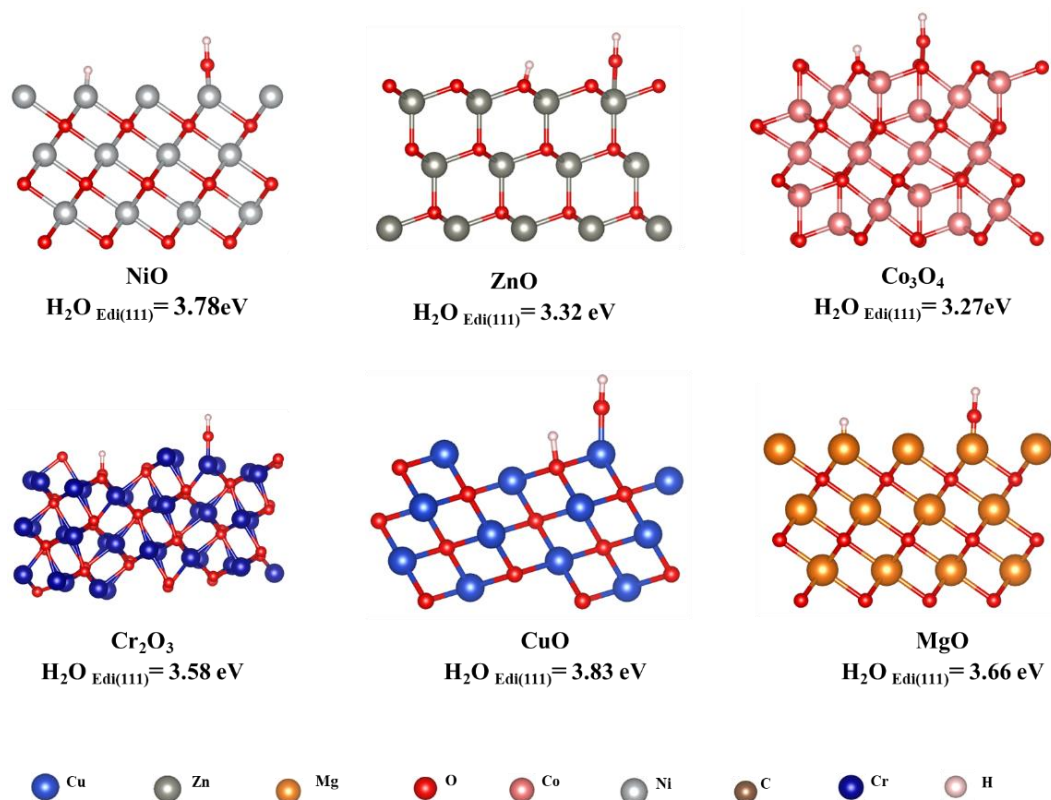


Figure S44. The dissociation energy of molecular H₂O by DFT calculation. The dissociation energy of molecular H₂O on the surface of NiO, MgO, CuO, ZnO, Co₃O₄, Cr₂O₃ at crystal plane (111) respectively.

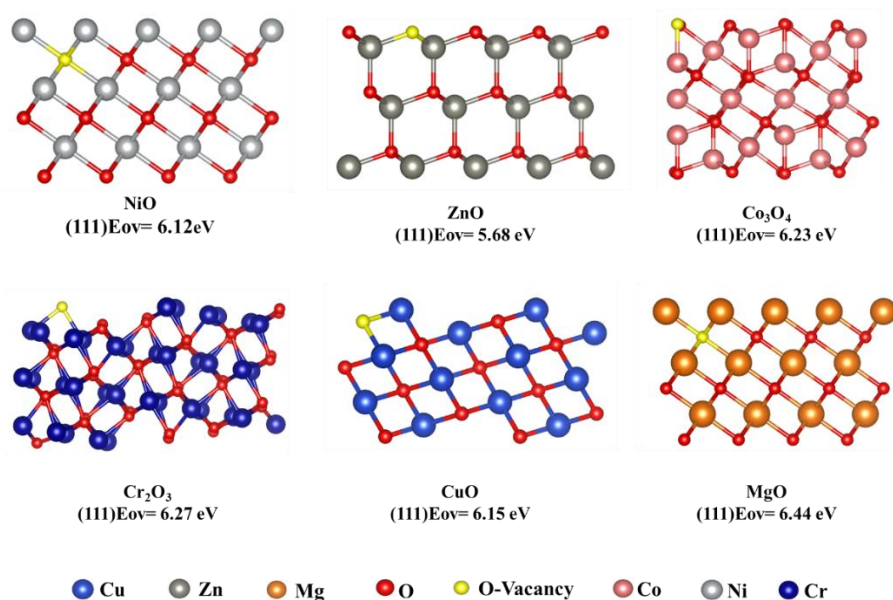


Figure S45. The formation energy of oxygen vacancy by DFT calculation. The formation energy of oxygen vacancy (Eov) of NiO, MgO, CuO, ZnO, Co₃O₄, Cr₂O₃ at crystal plane (111) respectively.

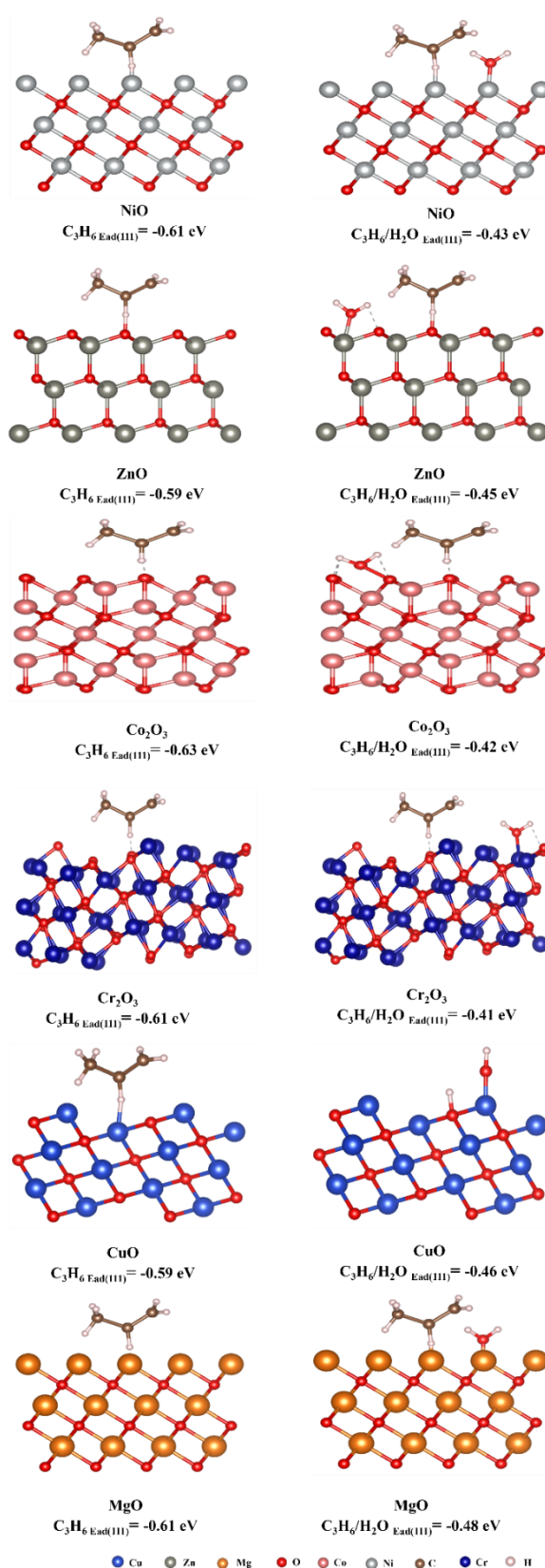


Figure S46. The adsorption energy of C_3H_6 by DFT calculation. The adsorption energy of C_3H_6 on the surface (111 plane) of NiO, MgO, CuO, ZnO, Co_3O_4 , Cr_2O_3 in the absence and presence of 4.2vol% water vapor.

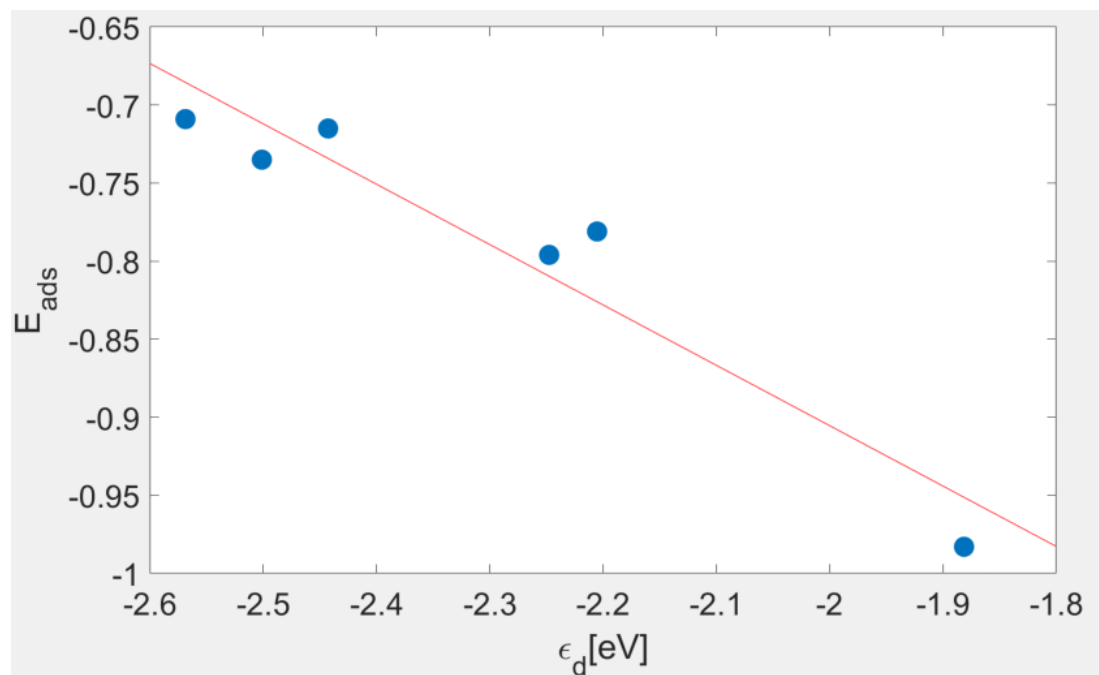


Figure S47. Parameters used in DFT calculation process. The linear relationship of E_{ads} and ϵ_d .

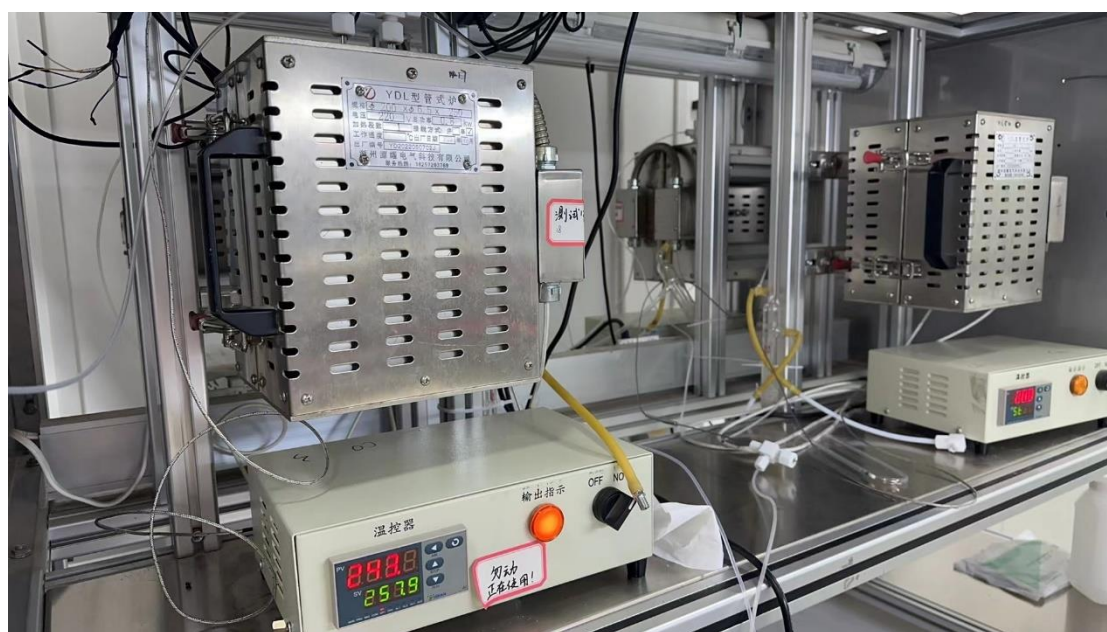


Figure S48. Photos about experimental equipment. Experimental instruments for C_3H_6 combustion and hydrothermal stability test.

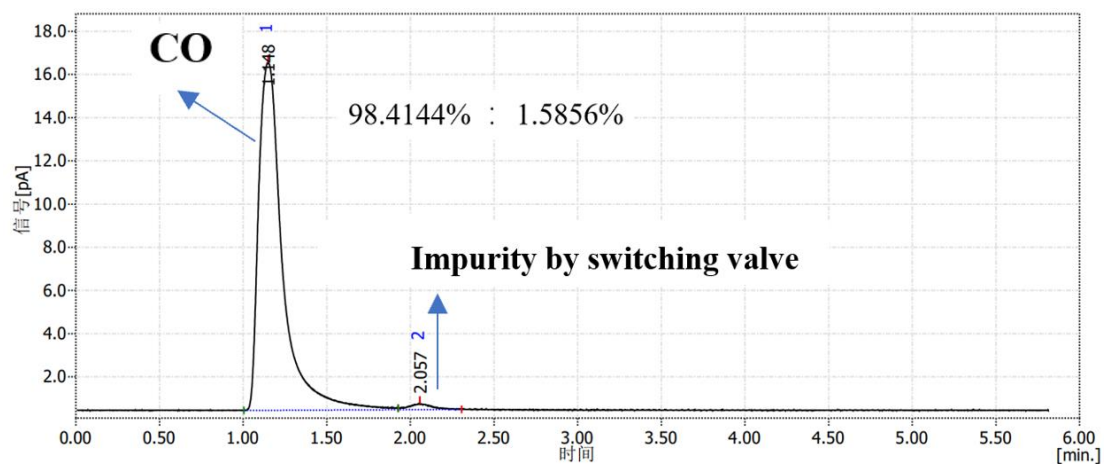


Figure S49 Original GC spectrum. (The raw gas contains 10ppm CO and the remaining is air).

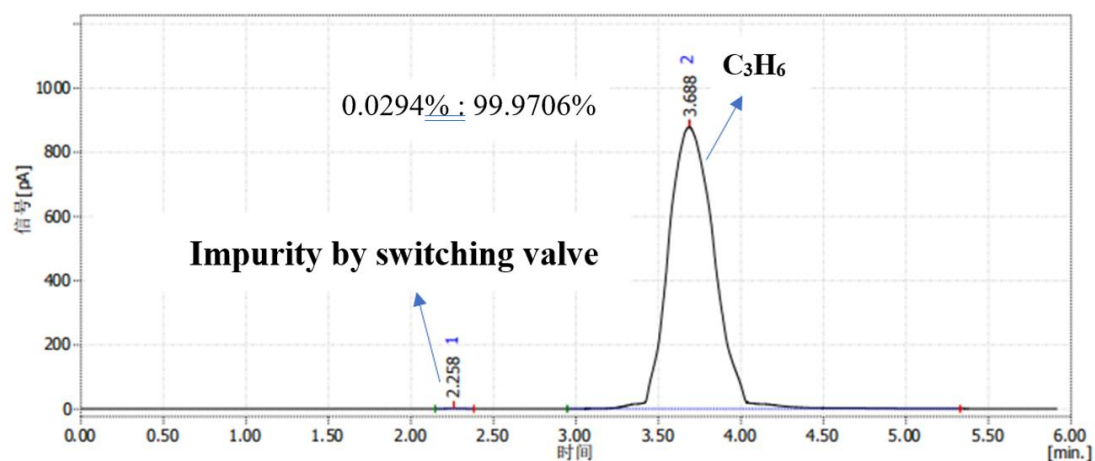


Figure S50 Original GC spectra with no catalysts at 50°C (10 mL/min , Feed gas ratio: 1vol % C₃H₆ and 99vol% air)



Figure S51. Photo about chromatography column. Porapak Q column used in the GC.

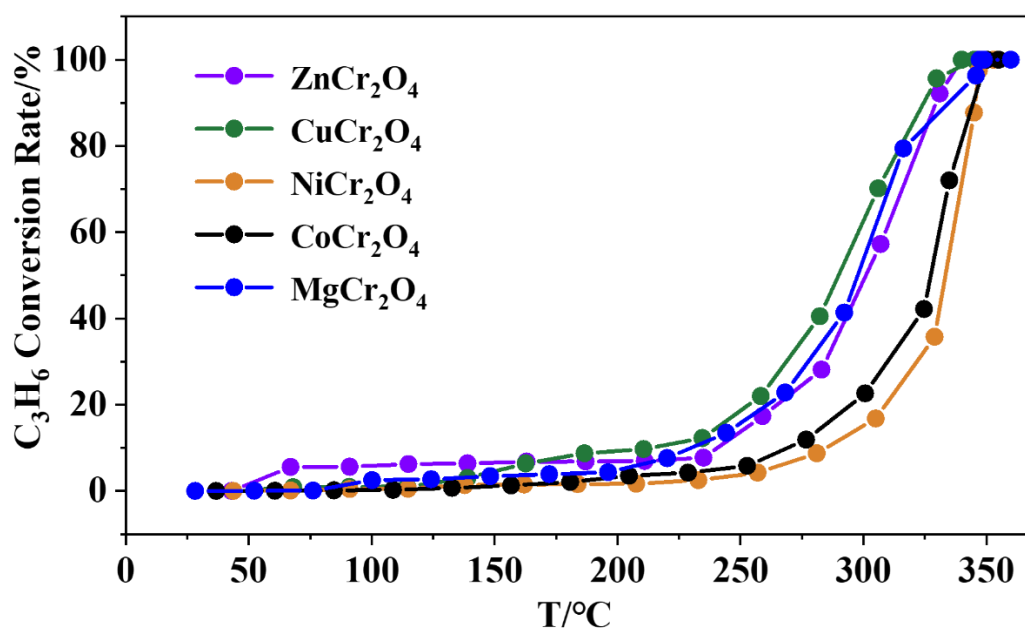


Figure S52 Catalytic performance. (a) C_3H_6 light-off curve of control samples $NiCr_2O_4$, $MgCr_2O_4$, $CuCr_2O_4$, $CoCr_2O_4$ and $ZnCr_2O_4$. (20000 mL h⁻¹g⁻¹; the feed gases contain 1 vol % C_3H_6 and 99 vol % air)

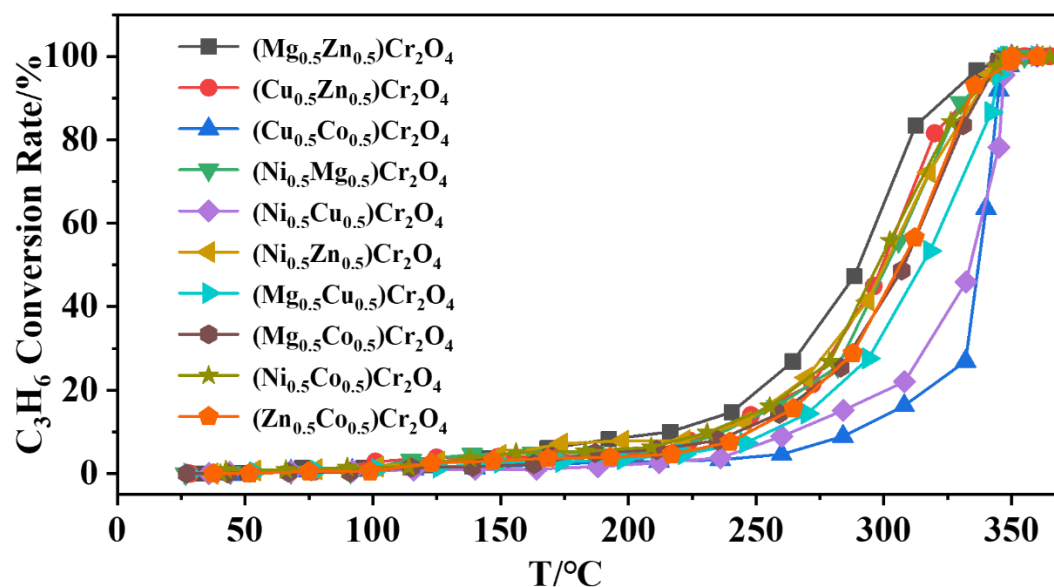


Figure S53 Catalytic performance. C_3H_6 light-off curves of 10 control ternary oxide samples (20000 mL h⁻¹g⁻¹; the feed gases contain 1vol % C_3H_6 and 99vol% air)



Figure S54 Mass spectrometry characterization. Mass spectrometry in this work.

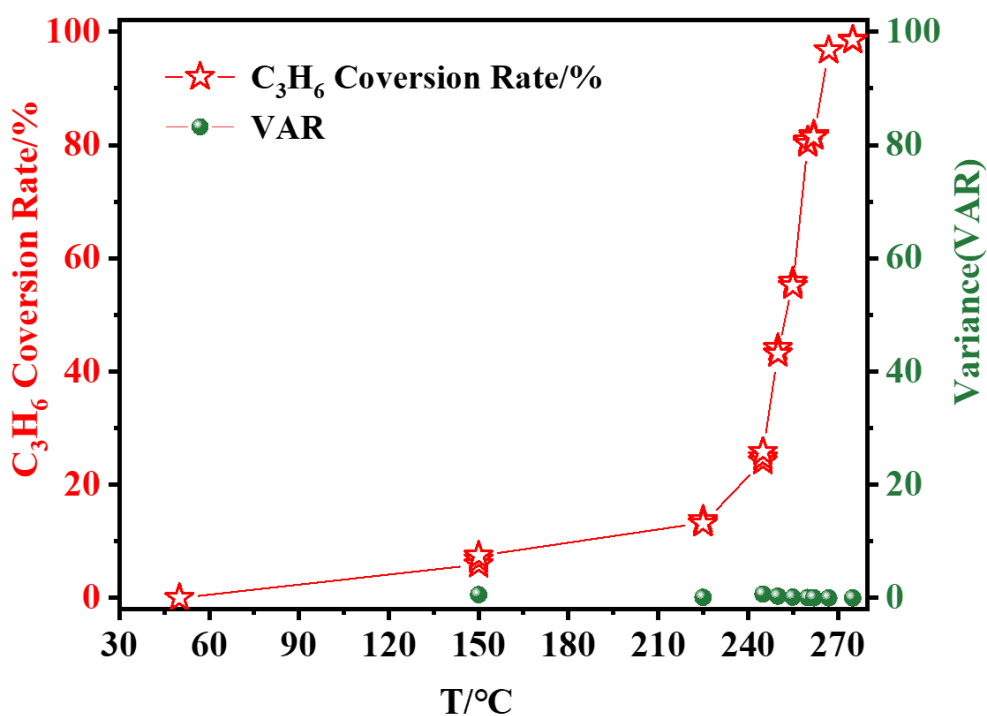


Figure S55. Variance measurement. C₃H₆ light-off curve and variance (VAR) of a- (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄, b-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ and c-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄(20000 mL h⁻¹g⁻¹; the feed gases contain 1 vol % C₃H₆ and 99vol% air)

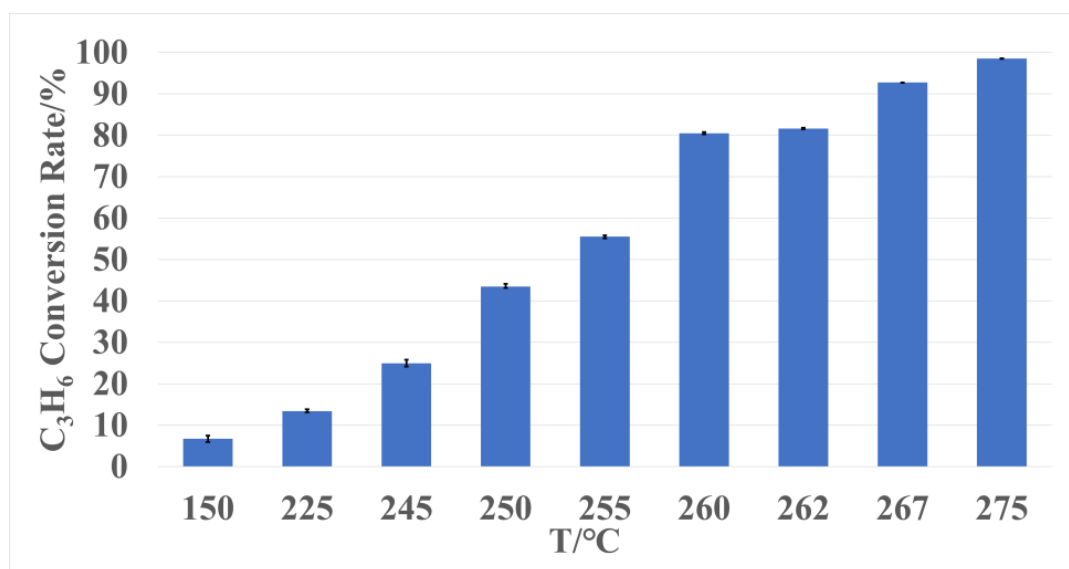


Figure S56. Variance measurement. C₃H₆ light-off curves and variance (VAR) of a- (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄, b-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ and c-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄(20000 mL h⁻¹g⁻¹; the feed gases contain 1 vol % C₃H₆ and 99vol% air)

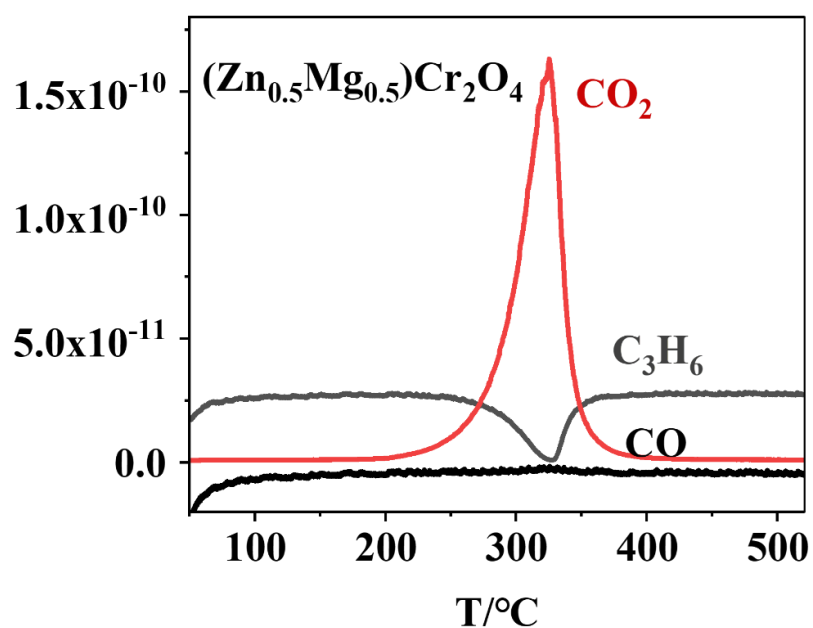


Figure S57. Mass spectrometry measurement. Mass spectrometry data in the light off process of $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{Cr}_2\text{O}_4$ sample(20000 $\text{mL h}^{-1}\text{g}^{-1}$; the feed gases contain 1vol % C_3H_6 and 99vol% air; 5 $^{\circ}\text{C}/\text{min}$)

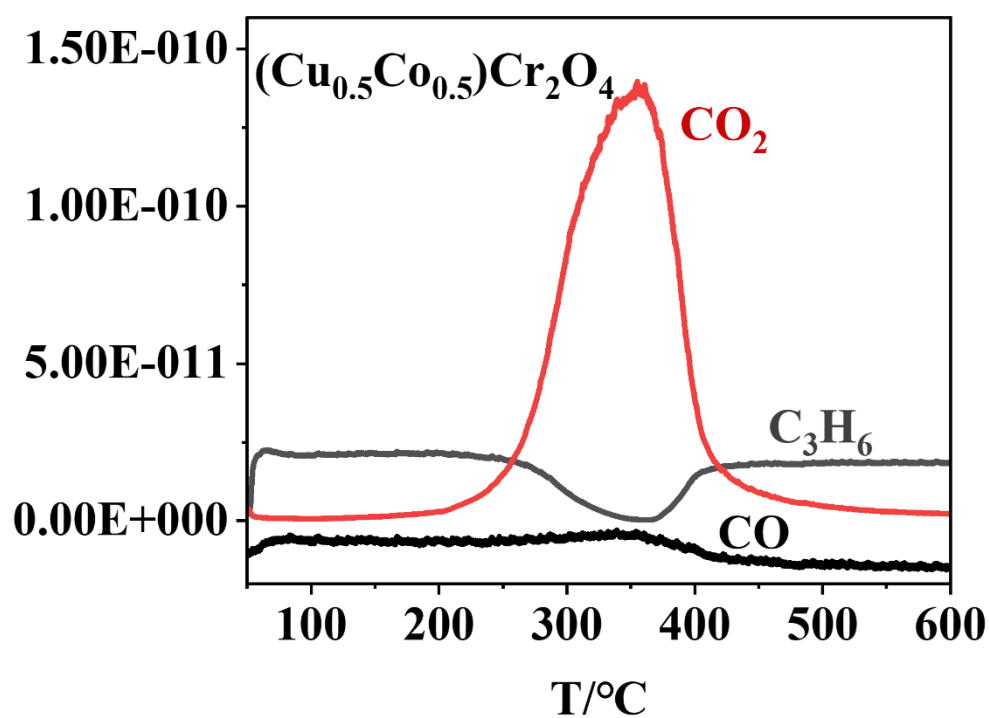


Figure S58. Mass spectrometry measurement. Mass spectrometry data in the light off process of $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Cr}_2\text{O}_4$ sample(20000 $\text{mL h}^{-1}\text{g}^{-1}$; the feed gases contain 1vol % C_3H_6 and 99vol% air; 5 $^{\circ}\text{C}/\text{min}$)



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

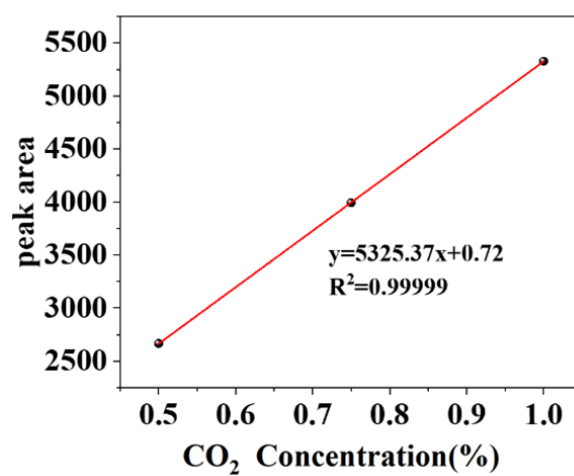
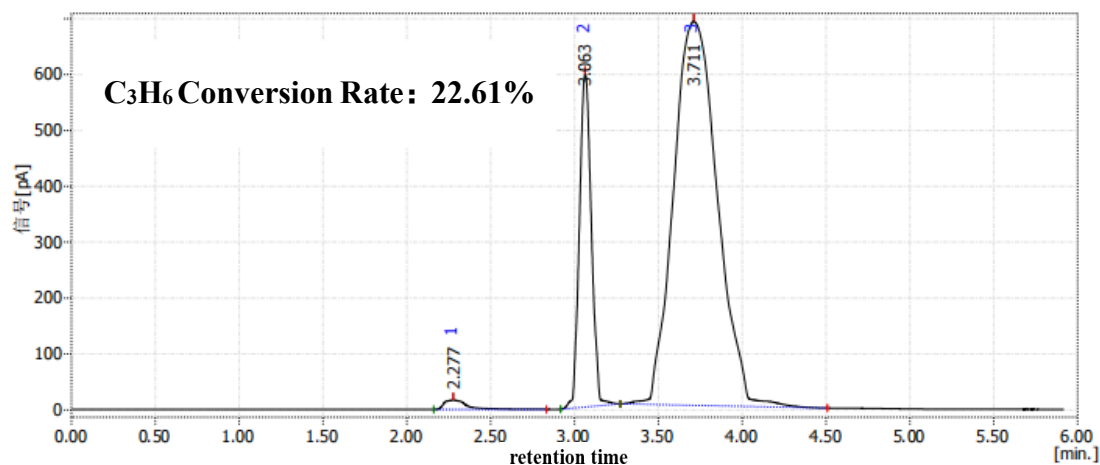
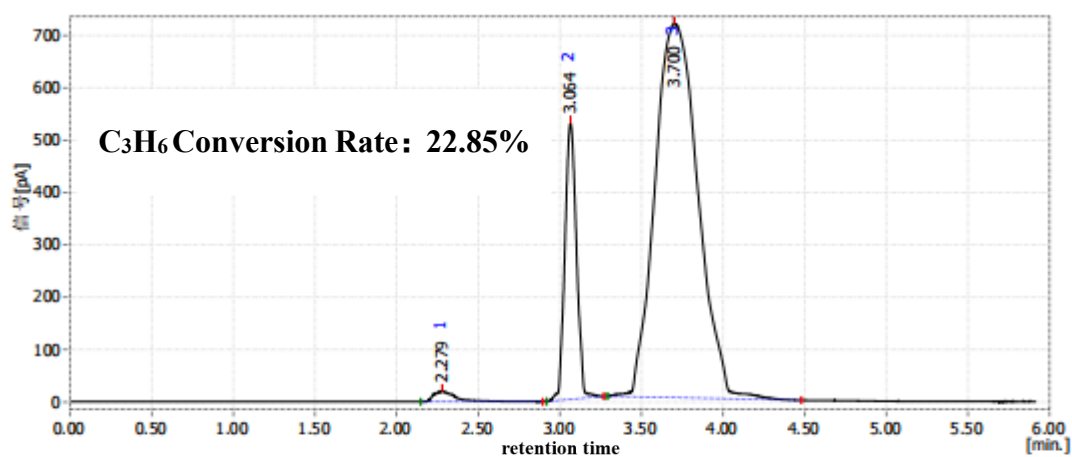


Figure S60 The standard curve measurement. The standard curve of CO₂ within the concentration range of 0.5%~1% at room temperature.



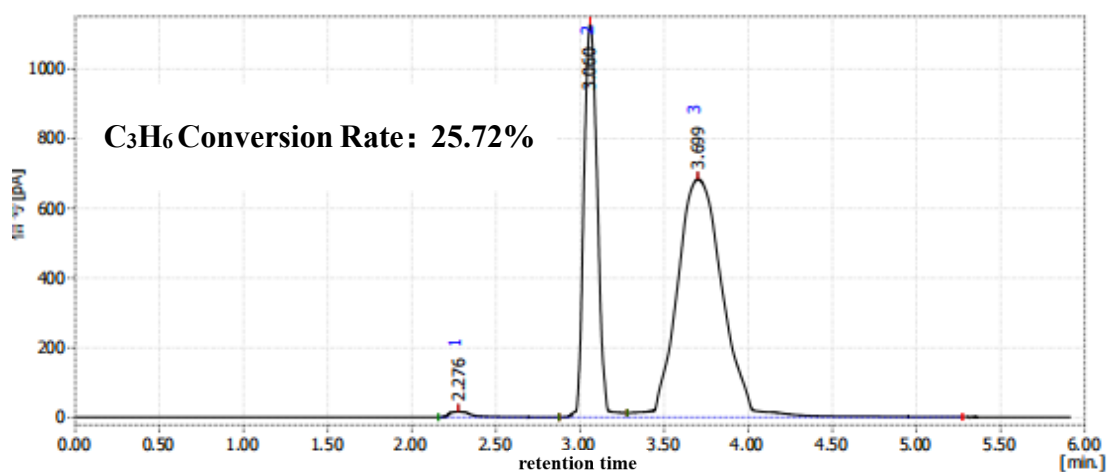
	retention time	peak area	concentration	Area percentage
1	2.2767	158.1006		1.0115
2	3.0625	2960.2470		18.9392
3	3.7108	12511.9300		80.0493

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



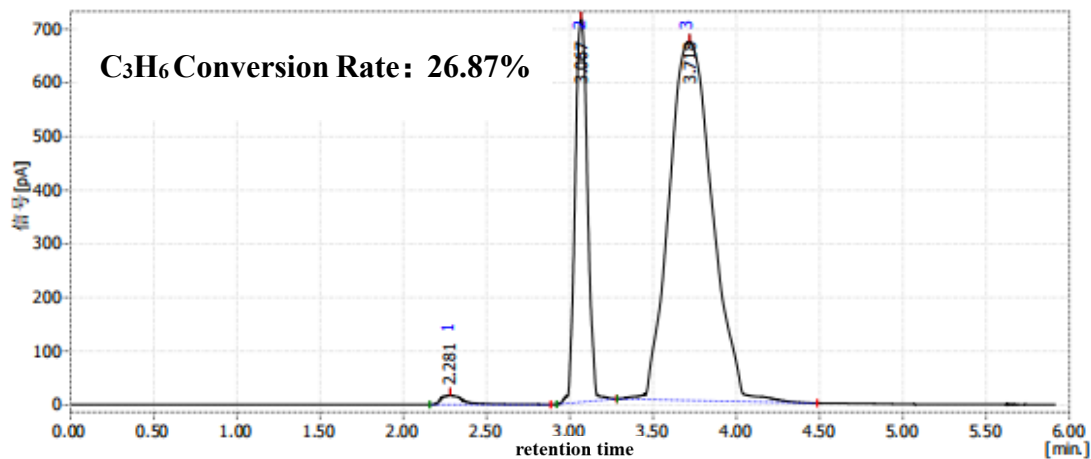
	retention time	peak area	concentration	Area percentage
1	2.2792	184.0992		1.1585
2	3.0642	2599.5460		16.3582
3	3.7000	13107.7100		82.4833

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



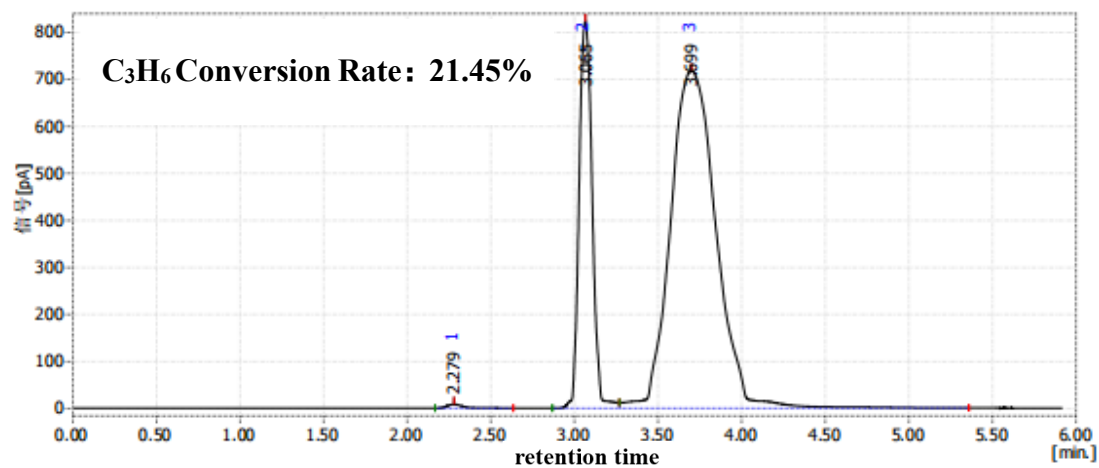
	retention time	peak area	concentration	Area percentage
1	2.2759	147.1126		0.7670
2	3.0600	6281.9720		32.7519
3	3.6992	12751.3900		66.4811

Figure S63 Original GC spectra. 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)



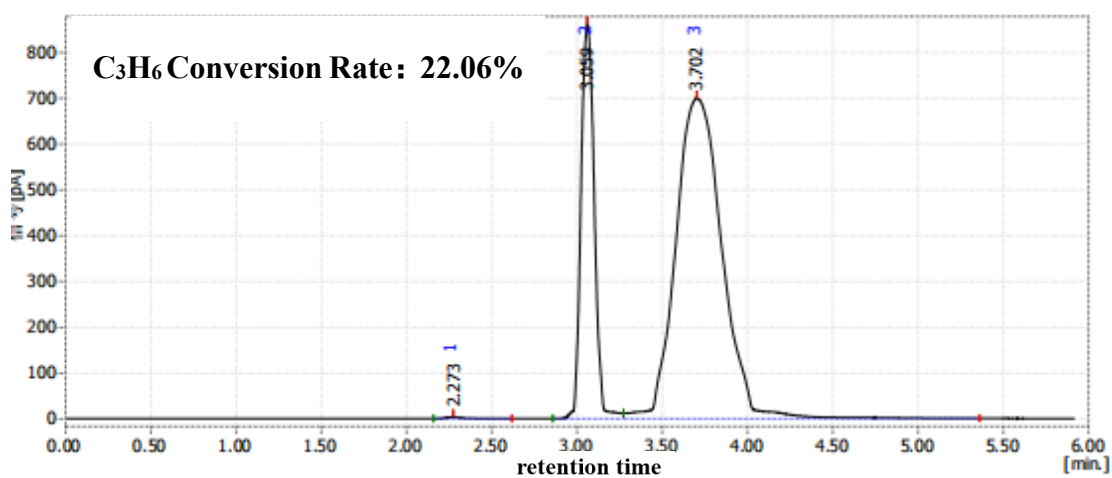
	retention time	peak area	concentration	Area percentage
1	2.2809	159.3673		1.0018
2	3.0667	3692.8800		23.2139
3	3.7175	12055.8300		75.7843
总计		15908.0800	0.0000	100

Figure S64 Original GC spectra. 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)



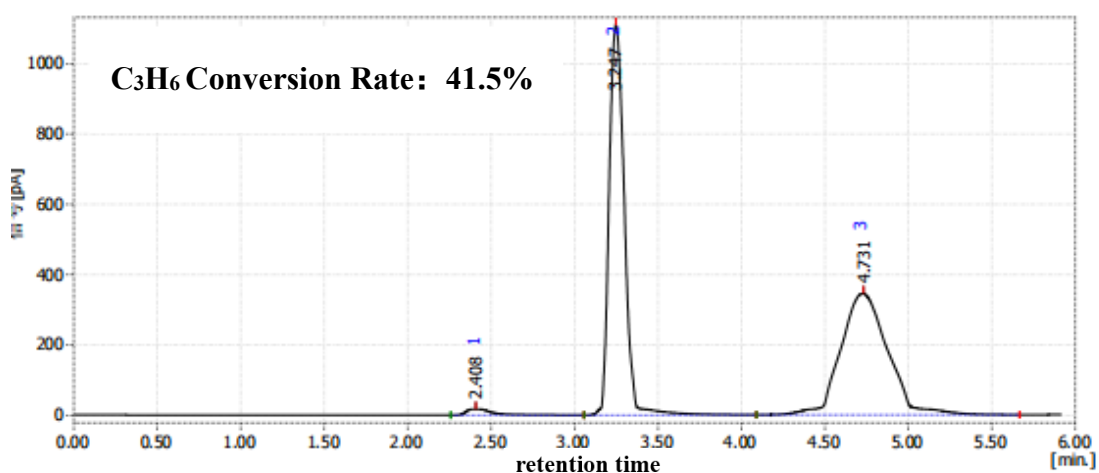
	retention time	peak area	concentration	Area percentage
1	2.2792	50.9346		0.2814
2	3.0650	4478.7630		24.7410
3	3.6992	13572.9100		74.9777
总计		18102.6000	0.0000	100

Figure S65 Original GC spectra. 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)



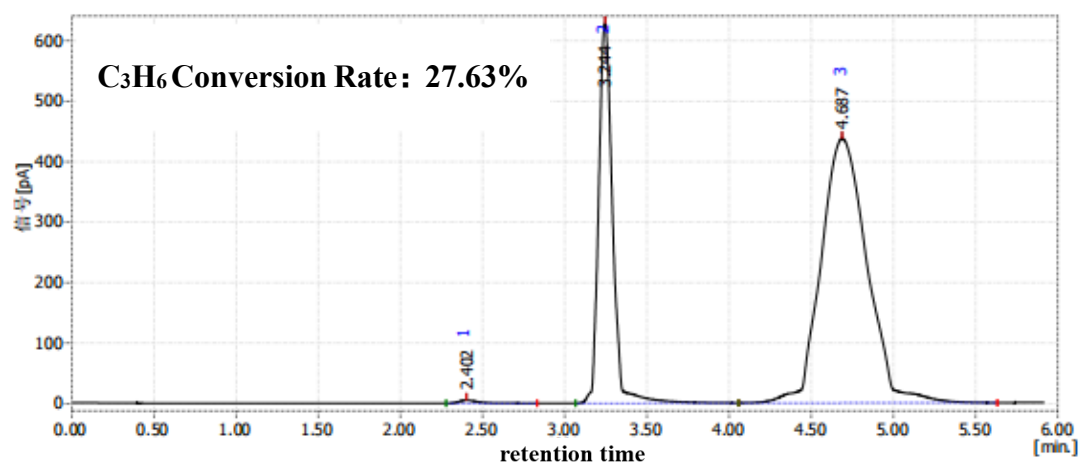
	retention time	peak area	concentration	Area percentage
1	2.2734	19.6187		0.1097
2	3.0592	4682.0840		26.1862
3	3.7017	13178.2800		73.7041
总计		17879.9800	0.0000	100

Figure S66 Original GC spectra. 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)



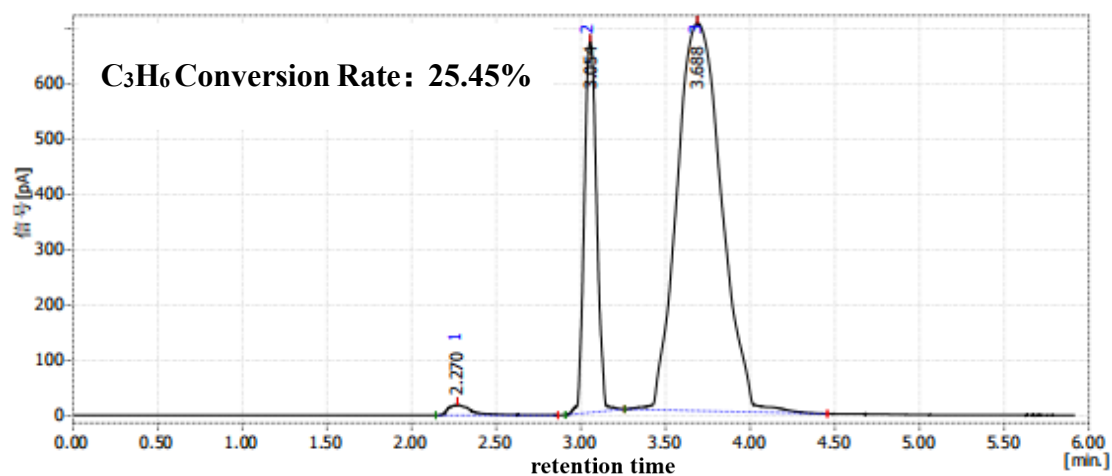
	retention time	peak area	concentration	Area percentage
1	2.4084	177.2897	0.0000	1.2729
2	3.2467	7030.2690	0.0000	50.4771
3	4.7310	6720.0930	0.0000	48.2500
总计		13927.6500	0.0000	100

Figure S67 Original GC spectra.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)



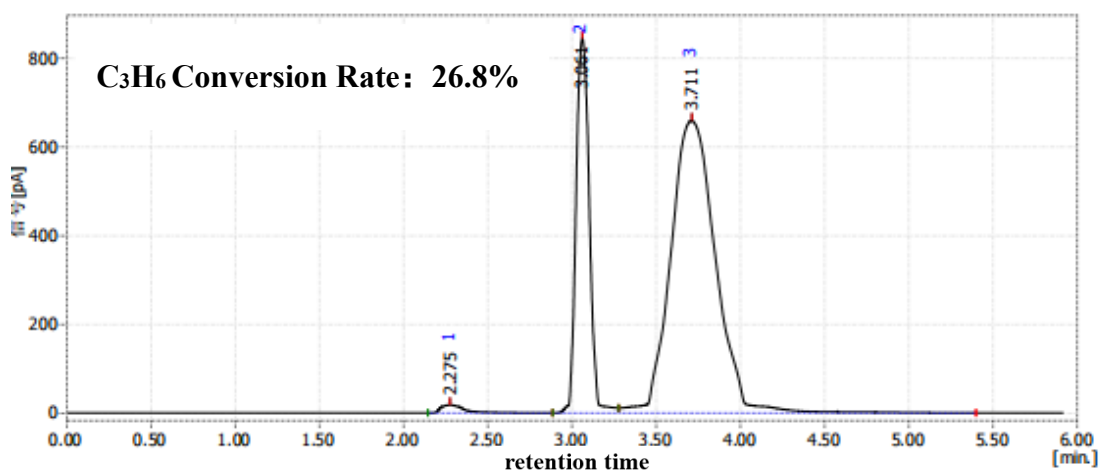
	retention time	peak area	concentration	Area percentage
1	2.4017	39.3101	0.0000	0.3221
2	3.2442	3704.2210	0.0000	30.3486
3	4.6868	8462.0510	0.0000	69.3294

Figure S68 Original GC spectra. 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)



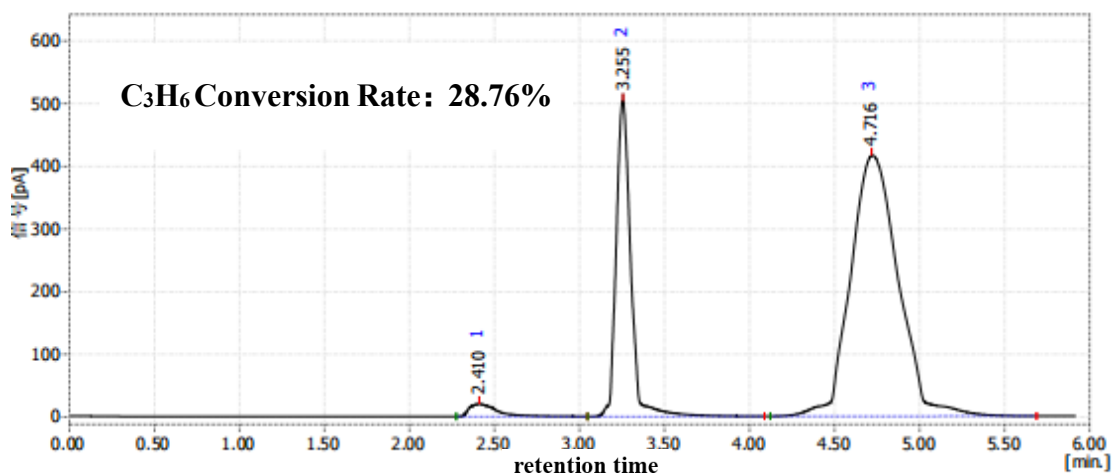
	retention time	peak area	concentration	Area percentage	
1	2.2701	175.6855		1.0692	
2	3.0542	3415.8770		20.7890	
3	3.6875	12839.6400		78.1418	
总计		16431.2000	0.0000	100	0.0000

Figure S69 Original GC spectra. 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)



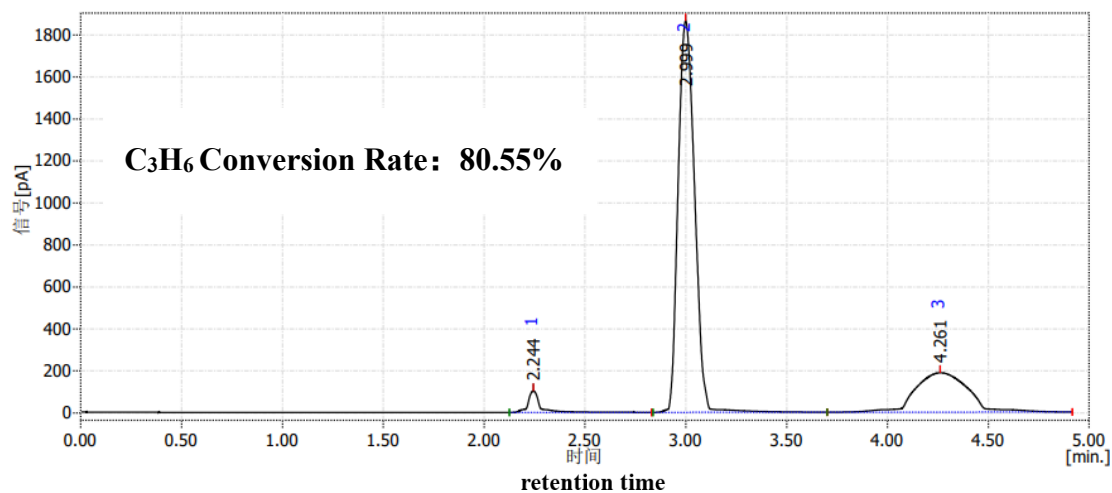
	retention time	peak area	concentration	Area percentage	
1	2.2751	176.7150		1.0398	
2	3.0608	4622.9270		27.2006	
3	3.7108	12196.0700		71.7597	
总计		16995.7100	0.0000	100	0.0000

Figure S70 Original GC spectra. 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

Figure S71 Original GC spectra. 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

Figure S72 Original GC spectra. 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)

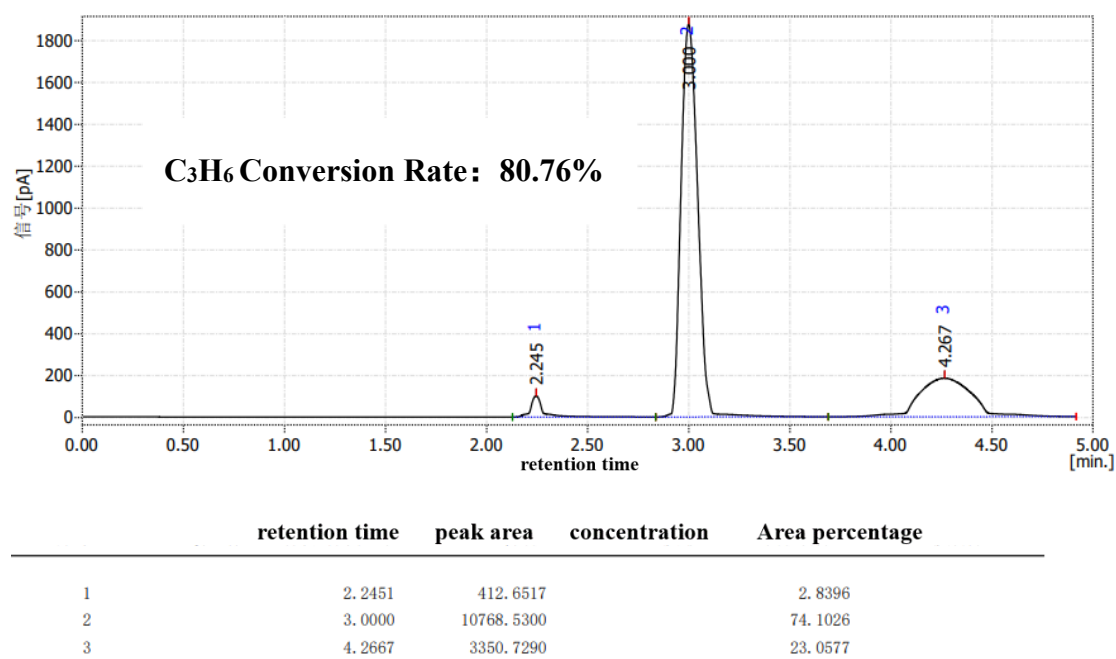


Figure S73 Original GC spectra. Original GC spectra of b-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ at 258°C (10 mL/min , Feed gas ratio:1vol % C₃H₆ and 99vol% air)

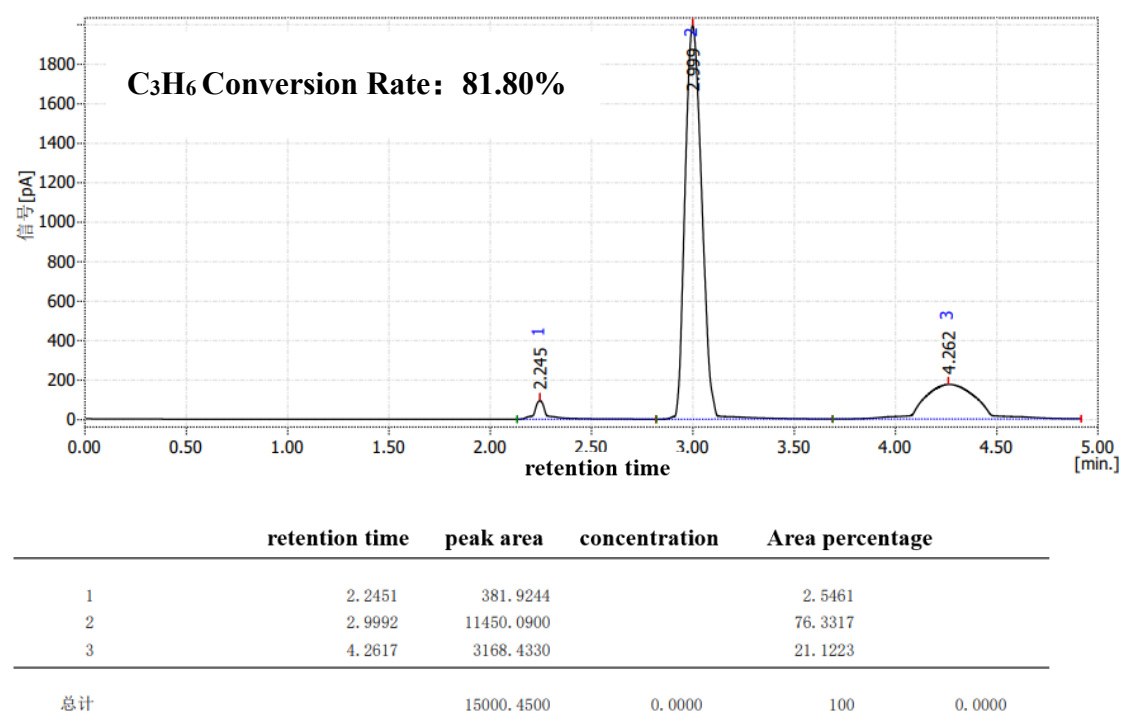


Figure S74 Original GC spectra. Original GC spectra of a-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ at 262°C (10 mL/min , Feed gas ratio:1vol % C₃H₆ and 99vol% air)

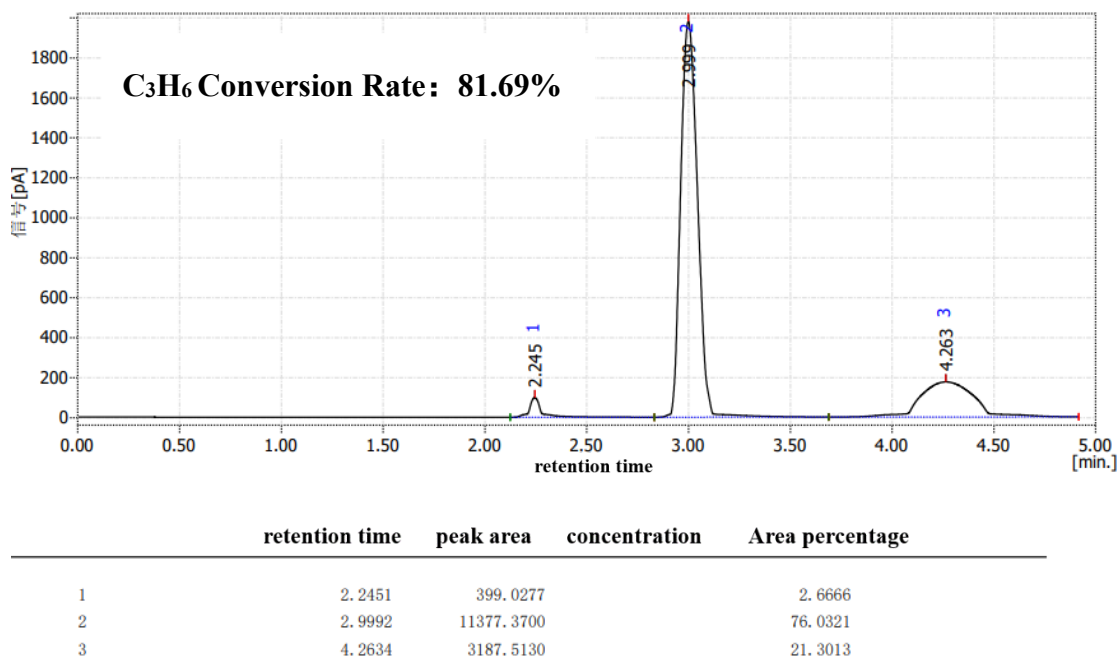


Figure S75 Original GC spectra. Original GC spectra of b-(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ at 262°C (10 mL/min , Feed gas ratio:1vol % C₃H₆ and 99vol% air)

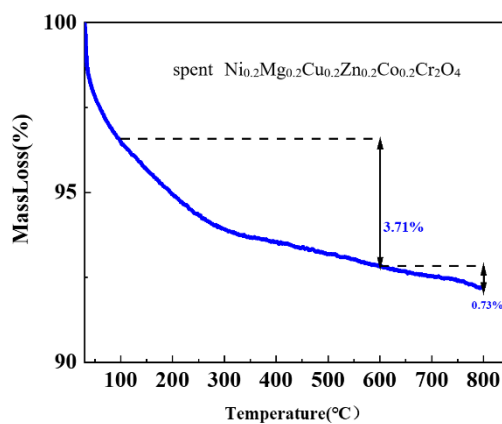


Figure S76 TGA measurement. TGA spectra of spent Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2}Cr₂O₄ catalysts after 100 hours of C₃H₆ combustion stability experiments at T₇₀ (temperatures that C₃H₆ conversion was 70%) in the presence of 4.2 vol% moisture.

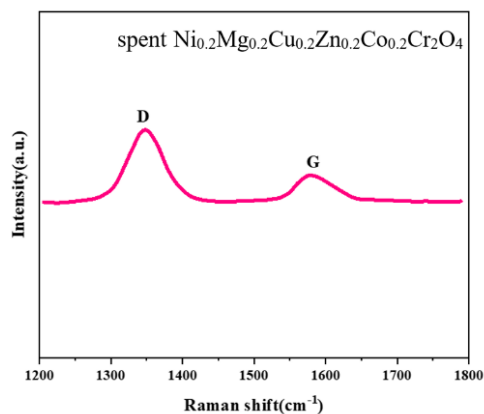


Figure S77 Raman measurement. Raman spectra of spent $\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2}\text{Cr}_2\text{O}_4$ catalysts after 100 hours of C_3H_6 combustion stability experiments at T_{70} (temperatures that C_3H_6 conversion was 70%) in the presence of 4.2 vol% moisture.

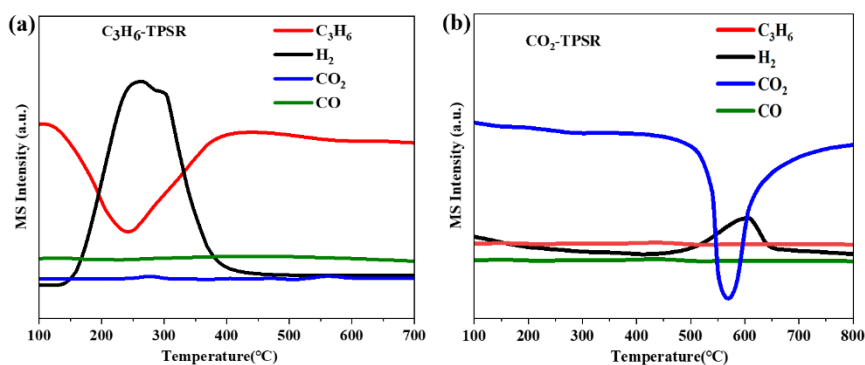


Figure S78. TPSR measurement. TPSR profiles of $\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2}\text{Cr}_2\text{O}_4$ catalyst from 100 to 800°C and maintained at 800°C for 60 min: (a) C_3H_6 -TPSR profiles of the reduced $\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2}\text{Cr}_2\text{O}_4$ 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.

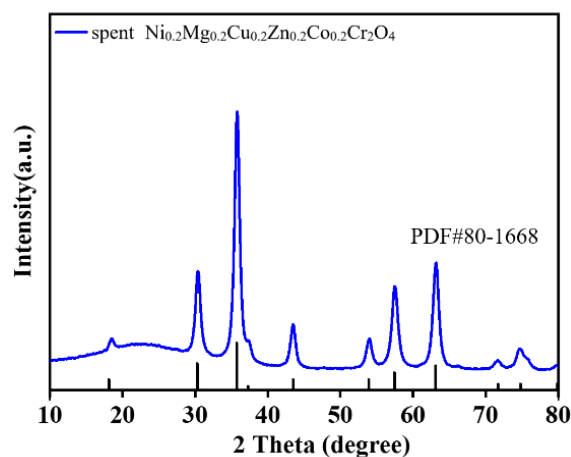


Figure S79 XRD measurement. XRD spectra of spent Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2}Cr₂O₄ catalysts after 100 hours of C₃H₆ combustion stability experiments at T₇₀ (temperatures that C₃H₆ conversion was 70%) in the presence of 4.2 vol% moisture.

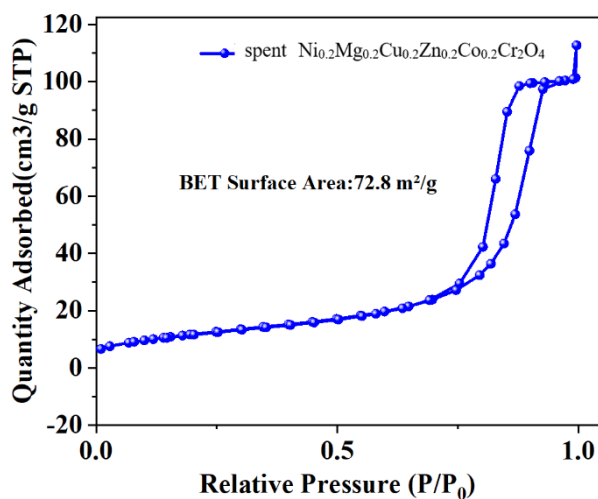


Figure S80. Nitrogen adsorption–desorption measurement. Nitrogen adsorption–desorption isotherms of spent Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2}Cr₂O₄ catalysts after 100 hours of C₃H₆ combustion stability experiments at T₇₀ (temperatures that C₃H₆ conversion was 70%) in the presence of 4.2 vol% moisture.

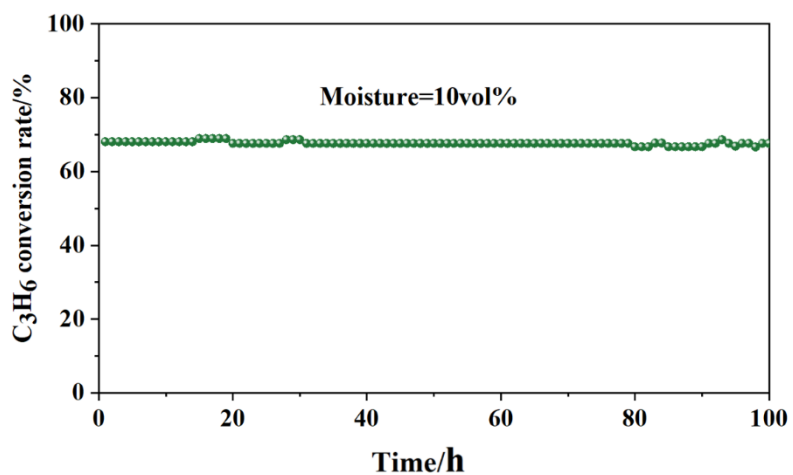


Figure S81. Stability measurement. Stability experiments of $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ at T_{70} (temperatures that C_3H_6 conversion was 70%) in the presence of 10vol% moisture.

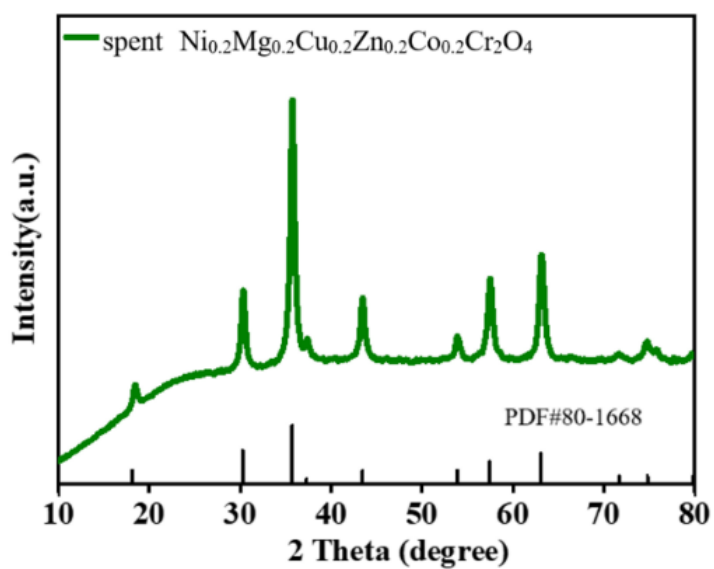


Figure S82. XRD measurement. XRD spectra of spent $\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2}\text{Cr}_2\text{O}_4$ catalyst after hydrothermal aging at 800°C for 30h in the presence of 4.2 vol% moisture.

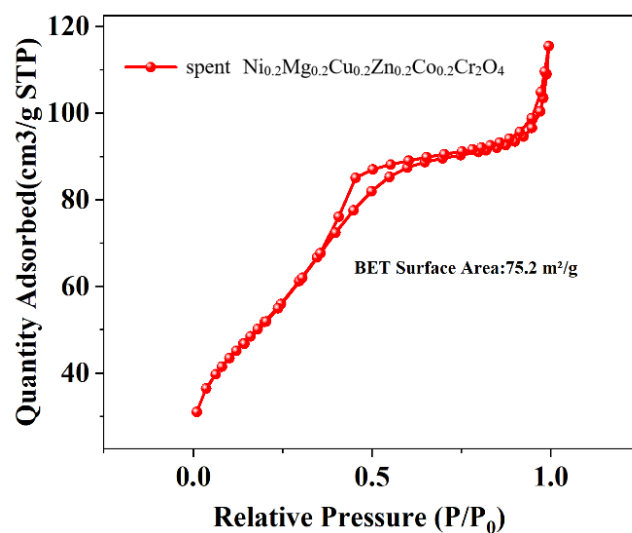


Figure S83. Nitrogen adsorption–desorption measurement. Nitrogen adsorption–desorption isotherms of spent Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2}Cr₂O₄ catalyst after hydrothermal aging at 800°C for 30h in the presence of 4.2 vol% moisture.

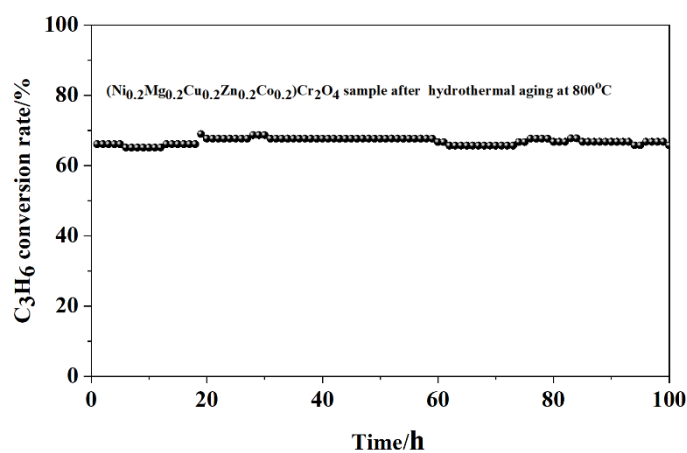


Figure S84. Stability experiments. After hydrothermal aging at 800°C for 30h and then stability experiments of (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ was conducted in the presence of 4.2vol% moisture.

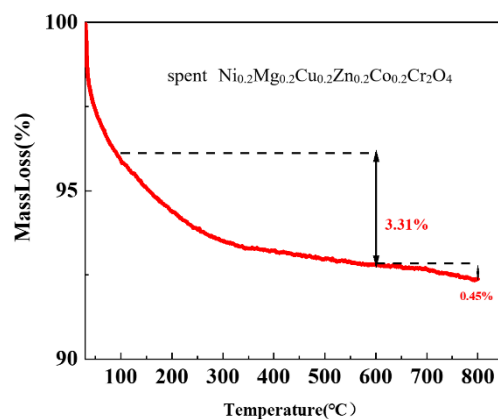


Figure S85. TGA experiments. TGA isotherms of spent $\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2}\text{Cr}_2\text{O}_4$ catalyst after hydrothermal aging at 800°C for 30h in the presence of 4.2 vol% moisture.

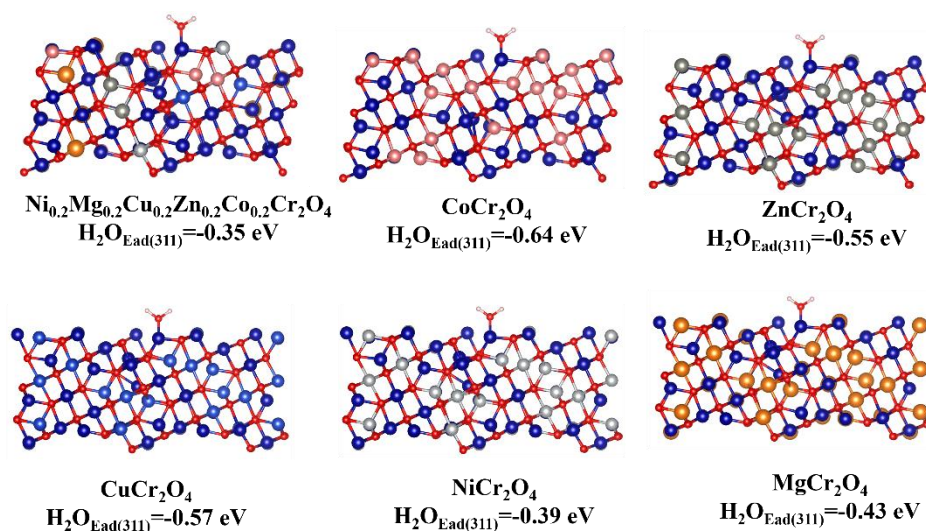


Figure S86. The adsorption energy of H_2O by DFT calculation. The adsorption energy of H_2O on the surface (311 plane) of high entropy $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ and single metal ACr_2O_4 (A=Ni, Mg, Cu, Zn, Co).

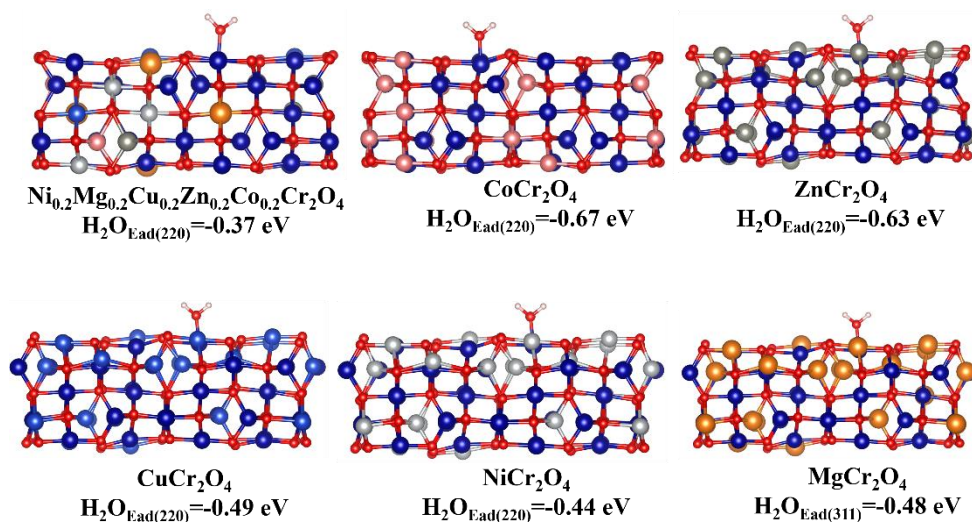


Figure S87. The adsorption energy of H_2O by DFT calculation. The adsorption energy of H_2O on the surface (220 plane) of high entropy $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ and single metal ACr_2O_4 (A=Ni, Mg, Cu, Zn, Co).

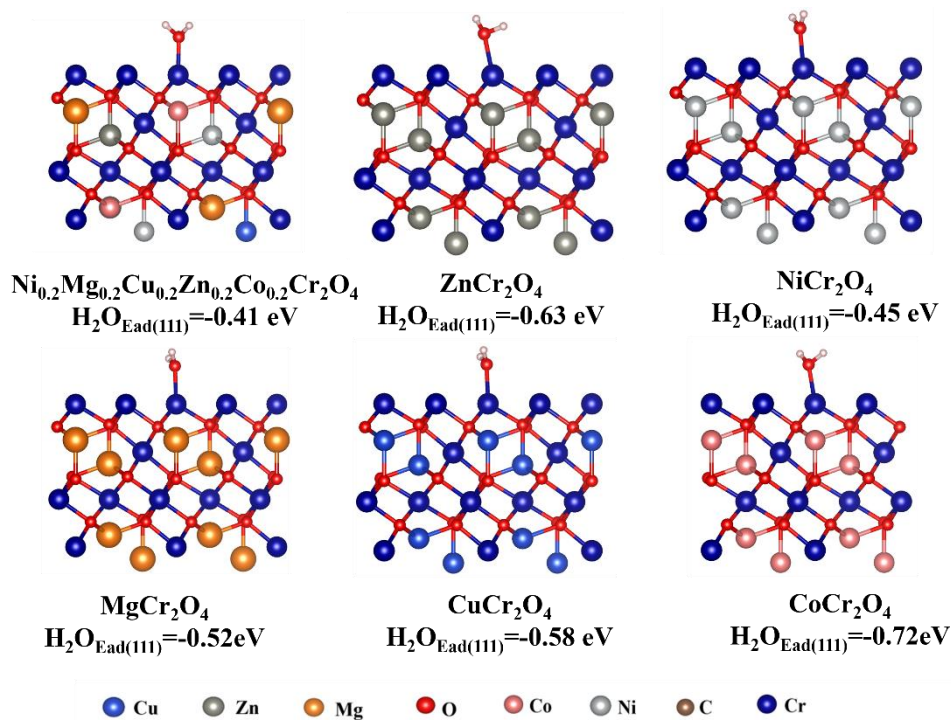


Figure S88. The adsorption energy of H_2O by DFT calculation. The adsorption energy of H_2O on the surface (111 plane) of high entropy $(\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2})\text{Cr}_2\text{O}_4$ and single metal ACr_2O_4 (A=Ni, Mg, Cu, Zn, Co).

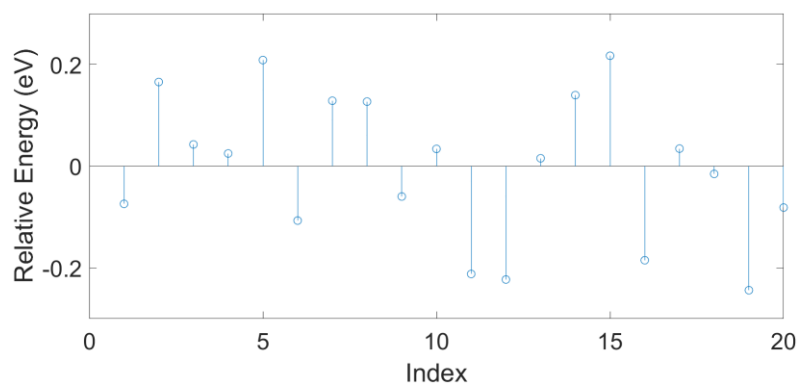


Figure S89. DFT calculation. Relative energy of 20 SQS, where the mean energy is set to zero.

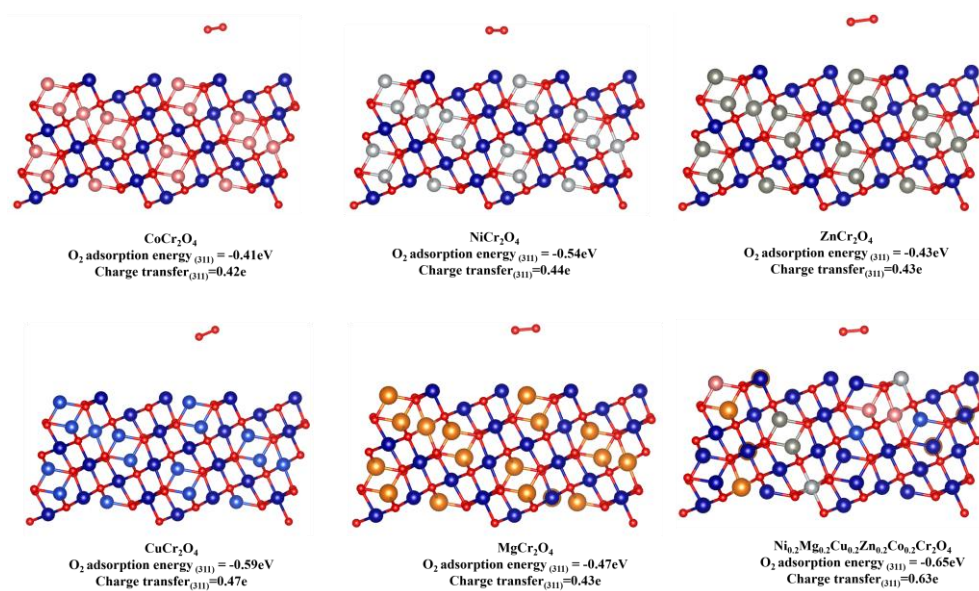


Figure S90 O_2 adsorption energy and charge transfer. O_2 adsorption energy and charge transfer on the surface (311 plane) of high entropy $(Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr_2O_4$ and single metal ACr_2O_4 (A=Ni, Mg, Cu, Zn, Co).

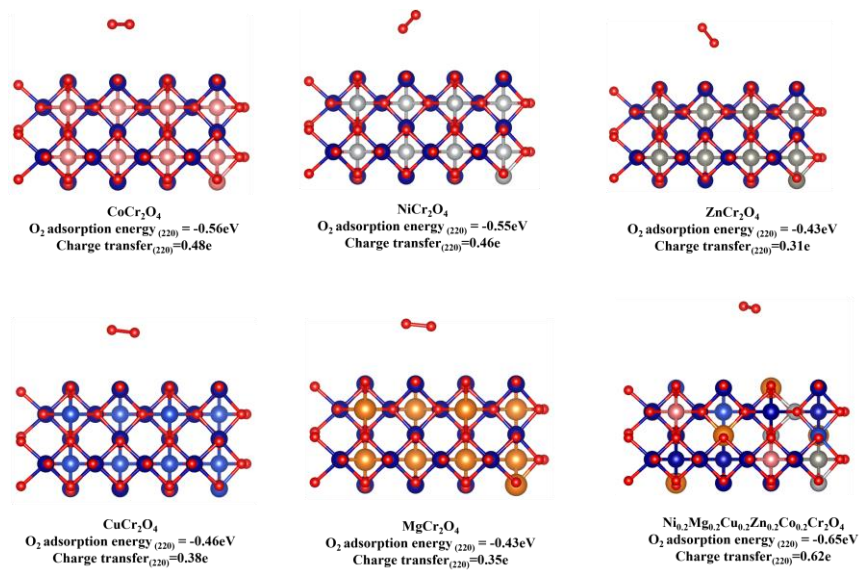


Figure S91 O₂ adsorption energy and charge transfer. O₂ adsorption energy and charge transfer on the surface (220 plane) of high entropy (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ and single metal ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co).

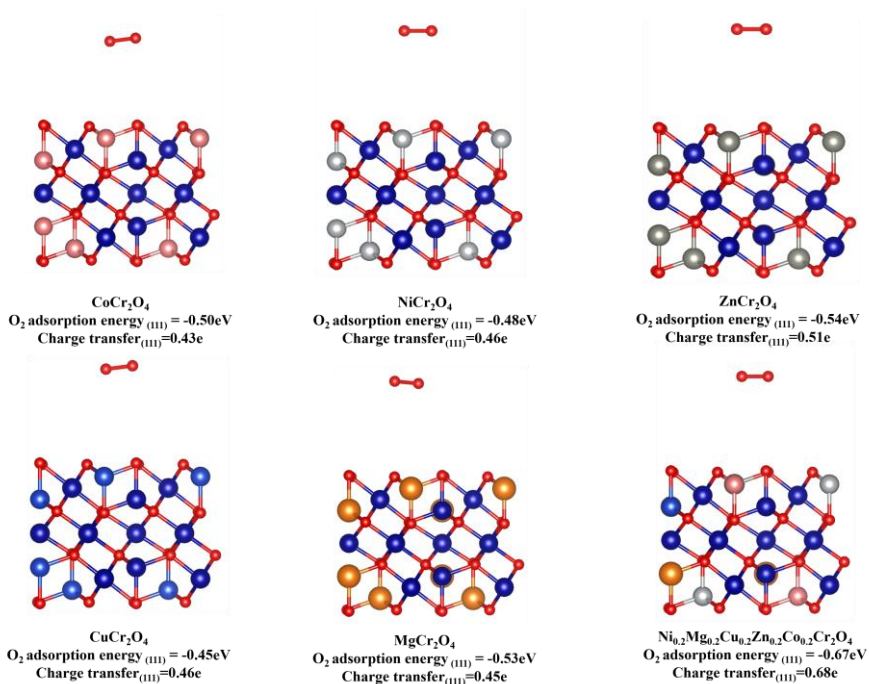


Figure S92 O₂ adsorption energy and charge transfer. O₂ adsorption energy and charge transfer on the surface (111 plane) of high entropy (Ni_{0.2}Mg_{0.2}Cu_{0.2}Zn_{0.2}Co_{0.2})Cr₂O₄ and single metal ACr₂O₄ (A=Ni, Mg, Cu, Zn, Co).

Supplementary Tables

Table S1 The adsorption energy of C₃H₆ by DFT calculation. 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	Ead(311) (4.2vol% water) /eV	Ead(311) (4.2vol% water) /eV	^a Δ _{Ead (311)} /eV	Ead (220) (4.2vol% water) /eV	Ead (220) (4.2vol% water) /eV	^b Δ _{Ead (220)} /eV	Ead (111) (4.2vol% water) /eV	Ead (111) (4.2vol% water) /eV	^c Δ _{Ead (111)} /eV
NiCr ₂ O ₄	-0.892	-0.615	0.277	-0.855	-0.571	-0.284	-0.74	-0.57	-0.17
MgCr ₂ O ₄	-0.865	-0.593	0.272	-0.802	-0.537	-0.265	-0.80	-0.49	-0.31
CuCr ₂ O ₄	-0.813	-0.527	0.286	-0.769	-0.491	-0.278	-0.72	-0.49	-0.23
ZnCr ₂ O ₄	-0.744	-0.384	0.36	-0.682	-0.349	-0.333	-0.71	-0.37	-0.34
CoCr ₂ O ₄	-0.852	-0.471	0.381	-0.749	-0.352	-0.397	-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	-1.051	-0.963	0.088	-0.974	-0.879	-0.095	-0.98	-0.87	-0.11

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

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

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

Table S2 The dissociation energy 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).

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	2.294	2.412	2.62
MgCr ₂ O ₄	2.691	2.731	2.75
CuCr ₂ O ₄	2.385	2.582	2.90
ZnCr ₂ O ₄	2.148	2.379	2.74
CoCr ₂ O ₄	2.336	2.532	2.80
(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	2.834	2.752	2.97

Table S3 The dissociation energy by DFT calculation. 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 E _{di} (311)/eV	H ₂ O E _{di} (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

Table S4 Formation energy of oxygen vacancy (Eov). 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) at crystal plane (220) , (311) and (111).

Sample	Eov (311)/eV	Eov (220) /eV	Eov (111) /eV
NiCr ₂ O ₄	4.916	5.637	5.96
MgCr ₂ O ₄	4.517	5.639	5.59
CuCr ₂ O ₄	4.695	5.748	5.83
ZnCr ₂ O ₄	4.773	5.271	5.49
CoCr ₂ O ₄	4.843	5.369	5.63
(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	4.166	4.562	4.32

Table S5 Feed ratio. Molar ratio of ACr_2O_4 (A=Ni, Mg, Cu, Zn, Co) and ($\text{Ni}_{0.2}\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{Co}_{0.2}$) Cr_2O_4 prepared by ball milling.

Sample	Ni(OAC) ₂ • 4H ₂ O/mmol	Mg(OAC) ₂ •4 H ₂ O/mmol	Cu(OAC) ₂ / mmol	Zn(OAC) ₂ / mmol	Co(OAC) ₂ •4H ₂ O/mmol	Cr(OAC) ₃ / mmol
NiCr ₂ O ₄	5	-	-	-	-	10
MgCr ₂ O ₄	-	5	-	-	-	10
CuCr ₂ O ₄	-	-	5	-	-	10
ZnCr ₂ O ₄	-	-	-	5	-	10
CoCr ₂ O ₄	-	-	-	-	5	10
(Ni _{0.2} Mg _{0.2} Cu 0.2Zn _{0.2} Co _{0.2}) Cr ₂ O ₄	1	1	1	1	1	10

Table S6 Measurement of specific surface area. The specific surface areas of the samples calculated using the Brunauer-Emmett-Teller (BET) method.

Sample	S _{BET} (m ² g ⁻¹)
NiCr ₂ O ₄	71
MgCr ₂ O ₄	69
CuCr ₂ O ₄	68
ZnCr ₂ O ₄	73
CoCr ₂ O ₄	70
(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	75

Table S7 Catalytic performance. T₉₀ in C₃H₆ oxidation (C₃H₆ conversion was 90%) of the samples under dry conditions

Sample	T ₉₀ /°C
NiCr ₂ O ₄	350
MgCr ₂ O ₄	332
CuCr ₂ O ₄	318
ZnCr ₂ O ₄	320
CoCr ₂ O ₄	345
(Ni _{0.2} Mg _{0.2} Cu _{0.2} Zn _{0.2} Co _{0.2})Cr ₂ O ₄	265

Table S8. ICP-MS experiment. 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	20.64	0	41.82
					%		%
MgCr ₂ O ₄	MgCr _{2.15} O ₄	0	0	0	0	18.22	39.13
						%	%
CuCr ₂ O ₄	CuCr _{1.98} O ₄	21.93	0	0	0	0	43.50
		%					%
ZnCr ₂ O ₄	ZnCr _{2.03} O ₄	0	19.06	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 _{10.26} O ₄	4.85	4.93	5.03	5.11	4.76	48.85
		%	%	%	%	%	%

Table S9. ICP-MS experiment. 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}O₄}	4.87%	4.83%	4.79%	4.89%	4.80%	48.96%

Table S10. ICP-MS experiment. 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%

Table S11. The dissociation energy of molecular H₂O by DFT calculation. 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). 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

Table S13 The adsorption energy of C₃H₆. 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 Ead (111) /eV	C ₃ H ₆ Ead (111) (4.2vol% water)/eV	^a Δ _{Ead} (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 S14 Feed ratio. Molar ratio of ternary control samples prepared by ball milling.

Sample	Ni(OAc) ₂ •4 H ₂ O/mmol	Mg(OAc) ₂ • 4H ₂ O/mmol	Cu(OAc) ₂ / mmol	Zn(OAc) ₂ / mmol	Co(OAc) ₂ •4 H ₂ O/mmol	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 S15 VAR experiment. 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	

The carbon balance original spectrum in supporting information

Table S16 Carbon Balance calculation. 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 Standard Curve. 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

Supplementary References

- 1 Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys Rev B Condens Matter* **54**, 11169-11186 (1996).
- 2 Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys Rev B* **59**, 1758-1775 (1999).
- 3 Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865-3868 (1996).
- 4 Perdew, J. P., Burke, K. & Ernzerhof, M. Erratum: Generalized gradient approximation made simple (Physical Review Letters (1996) 77 (3865)). *Phys. Rev. Lett.* **78**, 1396 (1997).
- 5 Grimme, S., Ehrlich, S. & Goerigk, L. Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.* **32**, 1456-1465 (2011).
- 6 Momma, K. & Izumi, F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *J. Appl. Crystallogr.* **44**, 1272-1276 (2011).
- 7 Zunger, A., Wei, S., Ferreira, L. G. & Bernard, J. E. Special quasirandom structures. *Phys. Rev. Lett.* **65**, 353-356 (1990).
- 8 Ångqvist, M. *et al.* ICET – A Python library for constructing and sampling alloy cluster expansions. *Adv. Theory Simul* **2**, 1900015 (2019).
- 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).
- 12 Zhang, Y. *et al.* A rhodium-based methane oxidation catalyst with high tolerance to H₂O and SO₂. *ACS Catal.* **10**, 1821-1827 (2020).
- 13 Zhao, S. *et al.* Remarkable active-site dependent H₂O promoting effect in CO oxidation. *Nat*

Commun **10**, 3824 (2019).

- 14 Zhang, N. *et al.* A MnO₂-based catalyst with H₂O resistance for NH₃-SCR: Study of catalytic activity and reactants-H₂O competitive adsorption. *Applied Catalysis B: Environmental* **270**, 118860 (2020).
- 15 García-Hernández, M. *et al.* Hydrothermal synthesis and characterization of europium-doped barium titanate nanocrystallites. *Nano-Micro Lett* **5**, 57-65 (2013).
- 16 Gati, E. *et al.* Breakdown of Hooke's law of elasticity at the Mott critical endpoint in an organic conductor. *Sci Adv* **2**, e1601646 (2016).
- 17 Liu, L. *et al.* A Universal lab-on-salt-particle approach to 2D single-layer ordered mesoporous materials. *Adv. Mater.* **32**, e1906653 (2020).