

A Single-Atom Potential Confinement Strategy for Stabilizing Rhodium Nanocatalysts in Methane Oxidation

Corresponding Author: Professor Xingfu Tang

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Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

In this study, Xu et al used theoretical calculations to reveal that prefilling surface vacancies with suitable single metal atoms renders the subsequent anchoring of Rh atoms on supports energetically unfavourable. Guided by this insight, they propose a strategy that pre-anchors guest atoms to generate a high-potential confinement field that suppresses atom release and redeposition, thereby stabilizing Rh nano-catalysts across a wide temperature range during methane oxidation while maintaining high activity. Catalytic tests of simulated engine methane emissions and ESTEM characterizations reveal that both supported rhodium nanoparticles, with and without pre-anchored single atoms, show initial activity below 200 °C. However, only single-atom-confined nano-particles retain structural integrity and full activity after 800 °C aging, while unprotected ones transform into single atoms and lose low-temperature reactivity, confirming the strategy's effectiveness. Further theoretical calculations indicate that low-temperature activity arises from Rh nanoparticles with pronounced electron delocalization, whereas high-temperature activity results from Rh single-atom interacting with CeO₂, resembling the support's intrinsic behavior. This work could be considered for publication after addressing the following questions.

1. According to DFT calculations, the impact of the chosen U on the relative energy barriers should be discussed.
2. According to the adsorption energy formula ($E_{\text{ads}}(X)$) provided by the authors, it appears that the more strongly the adsorbate X binds to the surface. However, this interpretation is not strictly true. First, "exothermic" and "endothermic" refer to the ΔH of a process (e.g., a chemical reaction), not a ΔE like E_{ads} . Second, IUPAC defines an exothermic process as one with $\Delta H < 0$. Therefore, the authors should change their sign convention for E_{ads} .
3. The "constrained optimization scheme" employed by the authors may have limitations in reliably locating the lowest saddle points for the C–H bond activation transition states in CH₄. Since several bonds are broken and formed during these steps, and Ce may change its oxidation state along the pathway, it would be very helpful if the authors could provide further clarification to support the reliability of their transition-state calculations in this context.
4. Entropy effects are ignored. At the high temperatures of methane oxidation, entropy is an important factor and could be simply incorporated for the gas phase species. Incorporating these contributions would improve the completeness of the thermodynamic description and thereby strengthen the manuscript.
5. The authors highlight the activation of the first C–H bond as the key step in methane activation. It would be useful to indicate whether this has been experimentally validated, for example by infrared spectroscopy that characterize relevant intermediates during methane oxidation. In addition, a comparison between theoretically predicted intermediates and available experimental results would enhance the robustness and credibility of the proposed mechanism.

Reviewer #2

(Remarks to the Author)

This manuscript reports the synthesis and characterization of Rh catalysts, where single atoms on the CeO₂ support are introduced to prevent the deactivation of Rh nanoparticles which occurs when the particles fragment to form single atoms.

The work is very interesting, since it presents an approach to prevent this form of deactivation (transforming into atomically dispersed species) which has been documented with other transition metals such as Pt and Pd, so the work could have impact beyond the Rh catalysts that were described here.

The authors showed clearly that a conventional Rh/CeO₂ will transform into single atoms where heated to high temperatures and lose activity for methane oxidation. On the other hand, when Rh nanoparticles are deposited on a ceria support pre-populated with Rh single atoms, the deactivation does not occur. To extend the concept further, the authors also populated the ceria with Zr single atoms, and observed similar stabilization of the performance of Rh nanoparticles.

The characterization of the catalysts is quite extensive and includes DRIFTS, EXAFS and in-situ TEM. The HR SEM imaging is very helpful since there is no atomic number contrast for imaging Rh single atoms on CeO₂ supports. There are aspects of the characterization that need to be added to provide better context for others to be able to reproduce and build on this work, as listed below:

- 1) "Rh NPs well-dispersed on CeO₂ (111).." on line 157 is not correct. They observe (111) lattice fringes, but the surface on which the particles are located is undefined and cannot be determined from the TEM images they report. They could state that this is the most likely situation, but they have shown only through the particle views, which cannot define the orientation, and this is clear from the SE images which show undulating surface structures.
- 2) The Rh(n)/Rh(1) catalyst contains 1.55 wt% Rh while the Rh(n) contains 0.96 wt%. Did they prepare a Rh(n) catalyst with the same weight loading as the other catalyst, to get an apples to apples comparison similar to that in Figure 2.
- 3) The authors do not report BET surface areas of their catalysts, before and after use. In addition to this information, the authors should report the concentration of their single atom catalysts in terms of atoms per nm². This will make it easier to compare with other single atom catalysts.
- 4) Was this loading of Rh on the ceria designed to reach saturation capacity? It would be helpful if the authors reported any experiments they did with different metal loadings to arrive at the actual metal loading they used to prepare their single atom catalyst.
- 5) They term their strategy 'potential confinement strategy.' I am not sure I understand the origin of this term. Is it meant to be the saturation, or monolayer capacity of their ceria support after 800 C aging in air?
- 6) In previous work by Figueroba et al. (Catal. Sci. Technol., 2016, 6, 6806–6813), the Rh was postulated to sit on 4-fold (100) pockets, which can be found on steps of ceria. The binding energy of the Rh was reported to be -678 kJ/mol which is considerably stronger than the 1 eV reported here. Also, Rh atoms were shown to be trapped on ceria when heated in air at 800 C (Alcala et al., Atomically Dispersed Dopants for Stabilizing Ceria Surface Area. Applied Catalysis B: Environmental, 2021. 284: p. 119722 DOI: <https://doi.org/10.1016/j.apcatb.2020.119722>.) suggesting much stronger binding to the ceria. Can the authors explain their assignment of the charge of the Rh and its location (see question 5 below).
- 7) Can the authors provide more details on the site where the Rh is anchored. They call it a Ce cluster vacancy site. Is this a vacancy of Ce or of O? Can they provide atomic coordinates and also how they are able to fit the Rh in a four-fold site on a ceria (111) surface which has 3-fold symmetry. They report the oxidation state of Rh to be 3+. In this state, the Rh should not be active, or be able to adsorb CO. The previous work by Figueroba et al. (Catal. Sci. Technol., 2016, 6, 6806–6813) implied a Rh²⁺ oxidation state. The reported DRIFTS spectrum of Rh¹ (Figure 1c) does not appear to be consistent with Rh (3+) but rather with Rh(1+) based on the literature.
- 8) Related to this question, I would like to know the charge on the ceria when Rh is anchored in the 3+ oxidation state.
- 9) Methane oxidation is typically affected by water vapor, which is generated when methane is oxidized. Did the authors perform longer term tests at temperatures below 500 C where poisoning by water vapor causes loss of activity.

Also, there are several typographical errors which need to be corrected. I will point out a few:

- "preapred" on line 130
- "appearsd" on line 144
- "activation" on line 182

Reviewer #3

(Remarks to the Author)

The work is interesting and potentially relevant. However, the following aspects needs attention and revisions.

Experimental: the authors investigate catalytic activity under 20% O₂ concentration. This is a favorable atmospheric condition that however does not represent real exhaust conditions (more realistic 5-10 % O₂). Comments are expected.

Results: the authors discuss "a vacancy site (Vsite) on the CeO₂(111) surface," that is able to stabilize single atom Rh species. It is important to expand and clarify this aspect. A pioneer work underlines that many Oxygen vacancies can be formed in CeO₂(111), such single, double, linear, surface and subsurface Oxygen vacances associated to appropriate numbers of Ce(III) ions (see Electron localization determines defect formation on ceria substrates F Esch, et. al. Science 309 (2005), 752-755.) Would be relevant to characterize the vacancies by Raman spectroscopy for instance. Ce(III) could be also used to discuss associated vacancies.

The authors discuss an "extraordinary stability in methane oxidation", while extraordinary can not refers to few hrs activity. Furthermore, since deactivation is a kinetic phenomenon, it must be studied under kinetically controlled conditions (typically low conversion). See A Matter of Life(time) and Death, ACS Catal. 2018, 8, 9, 8597–8599) Under flow conditions, working at full or equilibrium conversion, the amount of time elapsed before a decrease in conversion is observed does not necessarily reflect stability. The rate may be far higher than is needed to achieve full or equilibrium conversion in the reactor, masking the initial presence of deactivation.

Fig 5 B Why not compare also Rhn/Zr1@CeO₂ and Rhn/Rh1@CeO₂.

Table S2, even if the authors uses the table only to indicate that their light off are in the range of literature data, I underline that correct comparison can be made only on identical space velocity.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors have addressed all my previous concerns comprehensively in this revised version. The manuscript now presents an outstanding study with novel findings that constitute a significant contribution to the field. I recommend acceptance without any further changes.

Reviewer #2

(Remarks to the Author)

The authors have adequately addressed my concerns. I would like them to check the calculation of the Rh surface concentration in terms of atoms/nm². Since their metal loading is 0.96 wt% and BET surface area 37 m²/g my calculation suggests 1.52 atoms/nm² as follows:

$0.96 \text{ g Rh}/100 \text{ g of support} \times 100 \text{ g}/3700 \text{ m}^2 \times 1 \text{ E}18 \text{ nm}^2/\text{m}^2 /102.91 \text{ g/gmol} \times 6.02 \text{ E}23 \text{ atoms/mol}$

Also, why does the surface area of Rhn/Rh1@CeO₂ go up from 37 m²/g to 60 m²/g?

Reviewer #3

(Remarks to the Author)

The authors avoided my comments

O₂ concentration reply is unsatisfactory! Either demonstrate examples of exhaust where 20% O₂ concentration is normal (is what you have in air!! and any combustion decrease this value significantly...

Regarding the generic use of "oxygen vacancies" the reply ... "limitations of experimental resources, it is difficult for..." is not professional when Nature family journal are the target! Not even an adequate discussion is added...

The reply on stability is shocking! It must be studied at low conversion! This is a basic concept in catalysis!

Version 2:

Reviewer comments:

Reviewer #2

(Remarks to the Author)

The authors have addressed one of my comments, about the Rh surface coverage but have not adequately addressed the other one concerning the BET surface area. The Rhn/Rh1 catalyst is prepared by depositing Rh nanoparticles via a colloidal synthesis. Would the amount of Rh added to the catalyst justify the increase in BET surface area? The TEM images do not show a low concentration of added Rh nanoparticles.

Reviewer #3

(Remarks to the Author)

The reviewers finally clarified the points raised by the reviewer in the previous evaluation step and now I can recommend the acceptance of the manuscript in the present form

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Reviewer's comments:

Reviewer #1

Comments:

In this study, Xu et al used theoretical calculations to reveal that prefilling surface vacancies with suitable single metal atoms renders the subsequent anchoring of Rh atoms on supports energetically unfavourable. Guided by this insight, they propose a strategy that pre-anchors guest atoms to generate a high-potential confinement field that suppresses atom release and redeposition, thereby stabilizing Rh nano-catalysts across a wide temperature range during methane oxidation while maintaining high activity. Catalytic tests of simulated engine methane emissions and ESTEM characterizations reveal that both supported rhodium nanoparticles, with and without pre-anchored single atoms, show initial activity below 200 °C. However, only single-atom-confined nanoparticles retain structural integrity and full activity after 800 °C aging, while unprotected ones transform into single atoms and lose low-temperature reactivity, confirming the strategy's effectiveness. Further theoretical calculations indicate that low-temperature activity arises from Rh nanoparticles with pronounced electron delocalization, whereas high-temperature activity results from Rh single-atom interacting with CeO₂, resembling the support's intrinsic behavior. This work could be considered for publication after addressing the following questions.

1. According to DFT calculations, the impact of the chosen U on the relative energy barriers should be discussed.

[Reply] Thanks for raising this concern. In many theoretical DFT+ U studies on the CeO₂-based systems, the U value of 5 eV was used to accurately describe the localized 4f orbitals of Ce. Specifically, previous studies have shown the $U = 5$ eV is appropriate to describe the atomic, electronic, and reaction properties of the CeO₂ bulk as well as CeO₂ surfaces. For example, Nolan et al. studied CeO₂ by using GGA + U with the U value of 5 eV, and they found that the 4f electrons can be correctly localized on Ce and the electronic structure of CeO₂ largely agrees with that observed in the experimental

UPS spectra; for the CeO₂(111), the calculated gap between the valence band maximum and the 4f band minimum is 1.1 eV, which agrees well with the available experimental value of 1.2 eV (*Surf. Sci.*, 2005, 576, 217–229).

In addition, we also fully agree with the reviewer that the Hubbard U parameter may affect the calculated activation barriers and thermodynamic values. Following the reviewer suggestion, we have also tested three representative U values ($U = 5, 4.5$, and 2 eV) by systematically evaluating the reaction of CH₄ heterolytic dissociation to form CH₃* and H* species on the Rh₁@CeO₂ and Rh_n/CeO₂ surfaces (**Table S6**). The results showed that the calculated activation energies and reaction energies exhibit only minor variations across the different U values, thereby supporting the GGA + U with the U value of 5 eV can also give correct energy barriers for catalytic reactions in the present study.

Table S6. Calculated activation and reaction energies for the CH₄ → CH₃* + H* reaction on Rh₁@CeO₂ and Rh_n/CeO₂ surfaces under different U values applied to the Ce-4f orbital.

	U value / eV	E_a / eV	ΔE / eV
Rh₁@CeO₂	5	0.91	-0.78
	4.5	0.74	-0.79
	2	1.15	-0.77
Rh_n/CeO₂	5	0.76	-1.21
	4.5	0.77	-1.19
	2	0.74	-1.18

In the revised manuscript, we have added **Table S6** in supporting materials and a relevant discussion in paragraph 1 on Page 14 in manuscript: “and the results have shown that $U = 5$ eV is appropriate to describe the atomic, electronic, and reaction properties of ceria. It should be noted that the choice of the U parameter may affect the calculated kinetic and thermodynamic results (Table S6). Nevertheless, our brief tests showed that the value of 5 eV may still represent the relative activities of different surface species at various CeO₂ surfaces in a reliable way.”

2. According to the adsorption energy formula ($E_{\text{ads}}(\text{X})$) provided by the authors, it appears that the more strongly the adsorbate X binds to the surface. However, this interpretation is not strictly true. First, “exothermic” and “endothermic” refer to the ΔH of a process (e.g., a chemical reaction), not a ΔE like E_{ads} . Second, IUPAC defines an exothermic process as one with $\Delta H < 0$. Therefore, the authors should change their sign convention for E_{ads} .

[Reply] Thanks for your suggestion. We totally agree with the referee that “exothermic” and “endothermic” are not appropriate for the discussion on ΔE , so we replaced "exothermic" and "endothermic" with "exergonic" and "endergonic" in the revised manuscript. Notably, the surface adsorption process is inconsistent with the chemical reaction process. In our manuscript, we take the definition of the adsorption energy from the textbook of “*Introduction to Surface Chemistry and Catalysis*” by G. A. Somorjai et al. (Verlag: Wiley-VCH, 2010.), as quoted from the Chapter One of the book, “*The process that involves trapping of atoms or molecules that are incident on the surface is called adsorption. It is always an exothermic process. For historic reasons, the heat of adsorption ΔH_{ads} is always denoted as having a positive sign-unlike the enthalpy ΔH , which for an exothermic process would be negative according to the usual thermodynamic convention.*” Accordingly, in our manuscript we defined that a positive E_{ads} indicates an exergonic adsorption process, and the more positive (larger) the E_{ads} is, the more strongly the adsorbate molecule binds on the surface. This kind of definition can be found in our previous studies and many other literatures (*Phys. Rev. Lett.*, 1998, 80, 3650-3653; *J. Am. Chem. Soc.*, 1999, 121, 7931-7932; *Adv. Chem. Eng.*, 2014, 44, 1-60; *J. Am. Chem. Soc.*, 2003, 125, 1958-1967).

3. The “constrained optimization scheme” employed by the authors may have limitations in reliably locating the lowest saddle points for the C–H bond activation transition states in CH_4 . Since several bonds are broken and formed during these steps, and Ce may change its oxidation state along the pathway, it would be very helpful if the authors could provide further clarification to support the reliability of their transition-state calculations in this context.

[Reply] Thanks for your suggestion. The commonly used methods for transition state (TS) calculations include *CI-NEB*, *Dimer*, and *Constrained* approaches. In our present work, we primarily adopted the Constrained method, as described in our original manuscript (*The transition states (TSs) of surface reactions were located using a constrained optimization scheme and were verified when (i) all forces on the relaxed atoms vanish and (ii) the total energy is a maximum along the reaction coordination but a minimum with respect to the rest of the degrees of freedom*). Furthermore, to validate the rationality of the calculated transition states, we first compared the C–H bond distances of CH₄ before and after C–H bond dissociation (**Table R1**). The results show that the C–H bond length in the transition state is longer than that in the CH₄, but shorter than that in the dissociated CH₄ species (**Table R1**). In addition, we further calculated the vibrational frequencies of the CH₄ dissociation transition states on the Rh₁@CeO₂ and Rh_n/CeO₂ surfaces. The results reveal that there is one and only one imaginary frequency (the corresponding frequencies are –795.14 and –1112.87 cm^{–1}, respectively). These findings clearly demonstrate that the transition states obtained in this work are reasonable.

Table R1. Calculated C-H bond distances (Å) of the key structures involved in CH₄ dissociation on the Rh₁@CeO₂ and Rh_n/CeO₂ surfaces, and calculated vibrational frequencies (cm^{–1}) of the corresponding transition states.

	C-H Bond distance / Å			Frequency / cm ^{–1}
	*CH ₄	[CH ₄] [‡]	*CH ₃ +*H	
Rh₁@CeO₂	1.098	1.264	2.489	-795.14
Rh_n/CeO₂	1.097	1.313	3.983	-1112.87

4. Entropy effects are ignored. At the high temperatures of methane oxidation, entropy is an important factor and could be simply incorporated for the gas phase species. Incorporating these contributions would improve the completeness of the thermodynamic description and thereby strengthen the manuscript.

[Reply] Thanks for your suggestion. We agree with the referee that the entropy effect of the adsorption/desorption of gaseous molecules may have strong impact on the

calculated energy profile, particularly under high temperatures. In **Figure S17**, we calculated the methane dissociation on the Rh₁@CeO₂ and Rh_n/CeO₂ surfaces to show this effect on reaction energetics at the reaction temperature of 523 K. The Gibbs free energy change ΔG of each elementary step in the methane dissociation process was calculated as follows:

$$\Delta G = \Delta E + \Delta ZPE - T \times \Delta S \quad (1)$$

where ΔE is the reaction energy calculated by DFT, and the changes of zero-point energy (ΔZPE) and entropy contribution ($T \times \Delta S$) were obtained by calculating the frequency of the related system, and we set the reaction temperature as 523 K. The ZPE was calculated as follows (Atkins' Physical Chemistry. Oxford University Press: 2018):

$$ZPE = \sum h\nu / 2 \quad (2)$$

The partition function (pf) and entropy (S) were calculated as follows:

$$x_i = \frac{100ch\nu_i}{k_B T} \quad (3)$$

$$pf_i = \frac{x_i}{e^{x_i}-1} - \log(1 - e^{-x_i}) \quad (4)$$

$$S = \frac{\sum(R \times pf_i)}{1000 \times 96.485} \quad (5)$$

where c , h , ν , k_B , T and R are the light speed ($m \times s^{-1}$), Plank constant, frequency (cm^{-1}), Boltzman constant, temperature (523 K) and gas constant, respectively. The units of ZPE and S are eV and eV/K, respectively. i is the number of vibration frequencies, and each adsorbed molecule has $3n$ vibration frequencies (n is the number of atoms). In addition, the frequency of small gas phase molecule (CH₄) was calculated using the Gaussian 16 program package (*Gaussian 16 Rev. A.03*, Wallingford, CT, 2016) and 6-311G* basis sets (*Can. J. Phys.* 1980, 58, 1200-1211) were used to obtain their ZPE and S values.

By comparing the Gibbs free energy profiles of methane dissociation on the Rh₁@CeO₂ and Rh_n/CeO₂ surfaces at 523 K (**Figure S17**), the calculated results show that the adsorption strength of key intermediate states involved in the methane activation process becomes relatively weaker, especially for methane molecular adsorption, which turns significantly endothermic by 0.46 and 0.56 eV, respectively. Notably, after considering the entropy correction, methane dissociation on the

Rh_1/CeO_2 surface requires overcoming an energy barrier of 0.98 eV and exothermic by 0.59 eV, while on the Rh_n/CeO_2 surface, the process proceeds with a reaction barrier of 0.50 eV and exothermic of 1.31 eV. This can be attributed to the similar entropy effects during methane activation on different catalyst surfaces. Therefore, it is reasonable and reliable to compare the catalytic performance of different catalysts merely based on the calculated enthalpic energetics.

Nevertheless, in the resubmitted manuscript, we have provided relevant discussions on the entropy effect and incorporated **Figure S17** in the Supporting Information. See page 8: “Moreover, we also calculated the Gibbs free energy profile of methane dissociation at 523 K (Fig. S17), and the results indicate that the methane adsorption becomes significantly more difficult; however, since the entropy effect operates similarly in the methane activation process on the Rh_1/CeO_2 and Rh_n/CeO_2 surfaces, the overall activity trend of methane dissociation on different surfaces remains unchanged.”

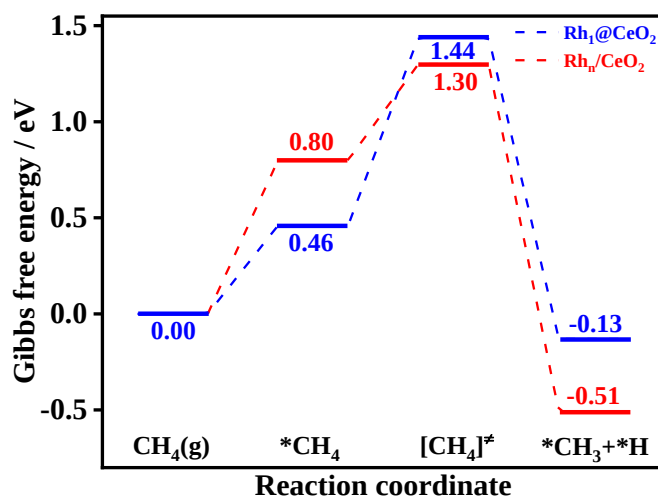


Figure S17. Calculated energy profiles of methane dissociation with the enthalpy changes and the Gibbs free energies at the 523 K on the Rh_1/CeO_2 and Rh_n/CeO_2 surfaces.

5. The authors highlight the activation of the first C–H bond as the key step in methane activation. It would be useful to indicate whether this has been experimentally validated, for example by infrared spectroscopy that characterize relevant intermediates during methane oxidation. In addition, a comparison between theoretically predicted

intermediates and available experimental results would enhance the robustness and credibility of the proposed mechanism.

[Reply] Thanks for your valuable suggestion. As pointed out by the reviewer, comparing the theoretically predicted intermediates with the experimental results would indeed greatly strengthen the reliability of the proposed reaction mechanism. However, methane catalytic combustion is a complex multistep process, in which the cleavage of the first C–H bond represents one of the key steps in methane activation. Therefore, in our original manuscript, we focused on systematic calculations of the activation and dissociation of the first C–H bond in methane on the Rh₁@CeO₂ and Rh_n/CeO₂ surfaces. We found that the calculated activation barrier for the first C–H bond cleavage over Rh_n/CeO₂ was 0.76 eV, which is in excellent agreement with the experimentally determined apparent activation energy ($E_a \approx 0.7$ eV). In contrast, the same process on Rh₁@CeO₂ exhibited a higher activation barrier of 0.91 eV, accompanied by an exothermic energy release of 0.78 eV.

Furthermore, we found that methane activation on Rh₁@CeO₂ mainly depends on the role of the CeO₂ support, and its reactivity closely resembles that of CeO₂ itself, thus requiring elevated temperatures for effective methane activation. In contrast, the low-temperature catalytic activity of the Rh_n/@CeO₂ system primarily originates from the highly active Rh species in the nanoparticles, thereby effectively lowering the activation temperature for methane.

Nevertheless, following the reviewer's suggestion, we additionally performed *in situ* infrared spectroscopy to identify the key surface intermediates during the CH₄ + O₂ reaction on Rh/CeO₂. The main signal peaks were observed in the range of 1200–1600 cm⁻¹ and were primarily assigned to CO₃²⁻ and HCOO⁻ species (Figure R1), which are consistent with previously reported results (*Nat. Commun.*, 2024, 15, 6494; *ACS Catal.*, 2025, 15, 6150–6164).

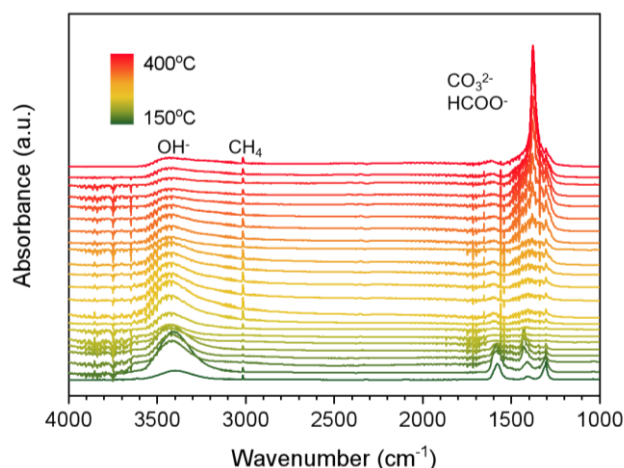


Figure R1. *In-situ* FT-IR spectra of Rh/CeO₂.

Reviewer #2

Comments:

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The authors showed clearly that a conventional Rh/CeO₂ will transform into single atoms where heated to high temperatures and lose activity for methane oxidation. On the other hand, when Rh nanoparticles are deposited on a ceria support pre-populated with Rh single atoms, the deactivation does not occur. To extend the concept further, the authors also populated the ceria with Zr single atoms, and observed similar stabilization of the performance of Rh nanoparticles.

The characterization of the catalysts is quite extensive and includes DRIFTS, EXAFS and in-situ TEM. The HR SEM imaging is very helpful since there is no atomic number contrast for imaging Rh single atoms on CeO₂ supports. There are aspects of the characterization that need to be added to provide better context for others to be able to reproduce and build on this work, as listed below:

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[Reply] Thank you for your advice. The surface of CeO₂ shows an undulating structure, although we observed (111) lattice fringes, we cannot generalize that all Rh nanoparticles are located on (111) crystal plane. Therefore, we made some revisions in paragraph 2 in page 7: “At 460 °C, the Rh NPs were clearly observed in the ESTEM-SE (secondary electron) images of both samples (insets of Fig. 3A and 3C), showing the Rh NPs well-dispersed on CeO₂, as confirmed by high-resolution ESTEM-ADF (annular dark field) images (Fig. 3A and 3C). A large difference between both samples appeared in the ESTEM images taken at the aging temperature of 800 °C.”

2. The Rh(n)/Rh(1) catalyst contains 1.55 wt% Rh while the Rh(n) contains 0.96 wt%. Did they prepare a Rh(n) catalyst with the same weight loading as the other catalyst, to get an apples to apples comparison similar to that in Figure 2.

[Reply] Thanks for your suggestion. We prepared Rh/CeO₂ with the loading of 1.5% by wet impregnation method. After aging at 800 °C, it was subjected to methane oxidation test under the same experimental condition of Rh_n/Rh₁@CeO₂. The test result showed that even with a similar loading amount, it would still deactivate after aging at 800 °C without using the single-atom potential confinement strategy, its activity was much lower than that of Rh_n/Rh₁@CeO₂.

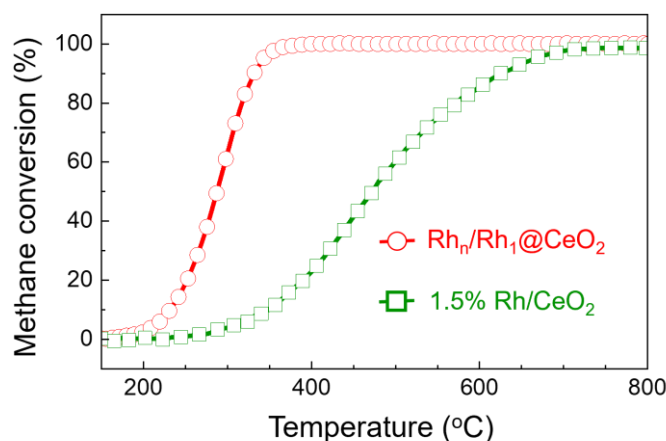


Figure S8. The comparison of activity between 1.5% Rh/CeO₂ aged after 800 °C and Rh_n/Rh₁@CeO₂.

Thus, we add several sentences to paragraph 1 in page 7: “As expected, the cooling light-off curve of Rh_n/Rh₁@CeO₂ nearly overlaps with the heating curve (Fig. 2A), providing strong evidence for the validity of the single-atom potential confinement strategy in preventing this form of catalyst deactivation. The comparison of activity between 1.5% Rh/CeO₂ aged after 800 °C and Rh_n/Rh₁@CeO₂ also confirms the effectiveness of the strategy (Fig. S8), where the Rh loading in both catalysts was similar.”

3. The authors do not report BET surface areas of their catalysts, before and after use. In addition to this information, the authors should report the concentration of their single atom catalysts in terms of atoms per nm². This will make it easier to compare with other single atom catalysts.

[Reply] Thanks for your suggestion. We tested the BET surface areas of catalysts and added its data to the supporting information.

Table S8. BET surface areas of samples.

Catalyst	CeO ₂	Rh _n /CeO ₂	Rh ₁ @CeO ₂	Rh _n /Rh ₁ @CeO ₂
BET surface ares	81	85	37	60

However, since the particle sizes of the catalysts and diluent used in experiment

were both relatively small, it is difficult to separate them. Moreover, the catalysts collected after the reaction were coated with diluent, which would interfere with the BET test and make it difficult to obtain accurate data. Therefore, there are difficulties in testing the BET data after the reaction.

The specific surface area of Rh₁@CeO₂ is ~37 m²/g. Assume that all the exposed surface is CeO₂(111) and the concentration of Rh₁@CeO₂ in terms of atoms per nm² is calculated to be ~15.9 atom/nm². We add some description in supporting note S2: “The concentration of Rh₁@CeO₂ in terms of atoms per nm² can be calculated from the specific surface area of Rh₁@CeO₂ and the loading amount of Rh atoms. The specific surface area of Rh₁@CeO₂ is about 37 m²/g (Table S8), thus the concentration of Rh₁@CeO₂ in terms of atoms per nm² is calculated to be ~15.9 atom/nm².”

4. Was this loading of Rh on the ceria designed to reach saturation capacity? It would be helpful if the authors reported any experiments they did with different metal loadings to arrive at the actual metal loading they used to prepare their single atom catalyst.

[Reply] Thanks for your suggestion. In our study, the Rh loading of Rh₁@CeO₂ is 0.96%, which is designed based to reach saturation capacity. Besides, we prepared Rh/CeO₂ with a Rh loading amount of 0.3%, and further loaded Rh nanoparticles to obtain Rh_n/0.3Rh₁@CeO₂. The results of methane oxidation activity tests conducted under the same conditions indicate that if the loading amount is insufficient, the negative ‘peak’ still appears.

However, since the Rh nanoparticles are the main active species, the differences in activity caused by different single-atom loading are relatively small. The slow increase in activity near 460 °C in below figure is due to the slower heating rate we applied here. Given such a small range of activity difference, it is difficult to set different metal loading to reflect the attainment of the saturation loading level.

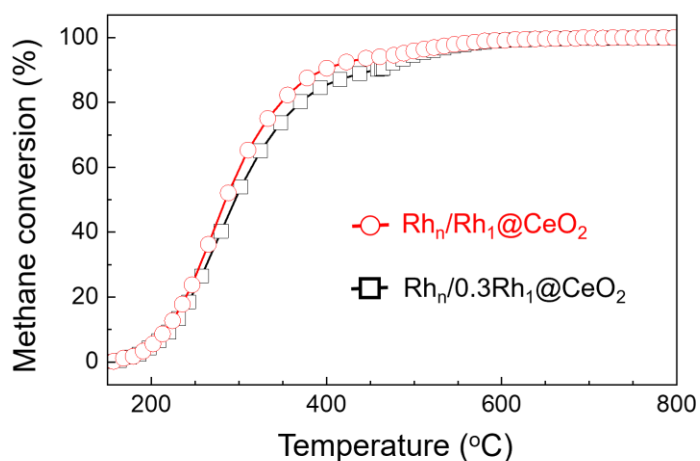


Figure R2. Light-off curves of methane conversion over $\text{Rh}_n/\text{Rh}_1@\text{CeO}_2$ and $\text{Rh}_n/0.3\text{Rh}_1@\text{CeO}_2$.

5. They term their strategy ‘potential confinement strategy.’ I am not sure I understand the origin of this term. Is it meant to be the saturation, or monolayer capacity of their ceria support after 800 °C aging in air?

[Reply] Thank you for your question. The term “potential confinement” does not simply refer to the physical blockage caused by a fully covered support surface. Over the past few decades, the spatial confinement effect has attracted considerable attention and has been widely applied in catalyst design and optimization (*Science*, 2012, 337, 6095; *ACS Catal.*, 2024, 14, 12991-13014; *Angew. Chem. Int. Ed.*, 2025, 64, e202503898). In such studies, “confinement” typically describes spatial restrictions that hinder the diffusion of guest atoms or molecules.

In our system, when noble metal species are supported on ceria surfaces without Zr atoms anchoring, they tend to undergo redispersion into single-atoms driven by volatilization or other process under harsh reaction conditions. However, once Zr single atoms are anchored to the surface, the redispersion of metal particles is markedly suppressed. This phenomenon cannot be fully rationalized by spatial limitation alone, as our catalyst lacks a well-defined porous structure. Supported by our DFT calculations, we propose that the migration process is essentially energy-directed. Therefore, we introduced the term “potential confinement” to emphasize the critical role of the altered

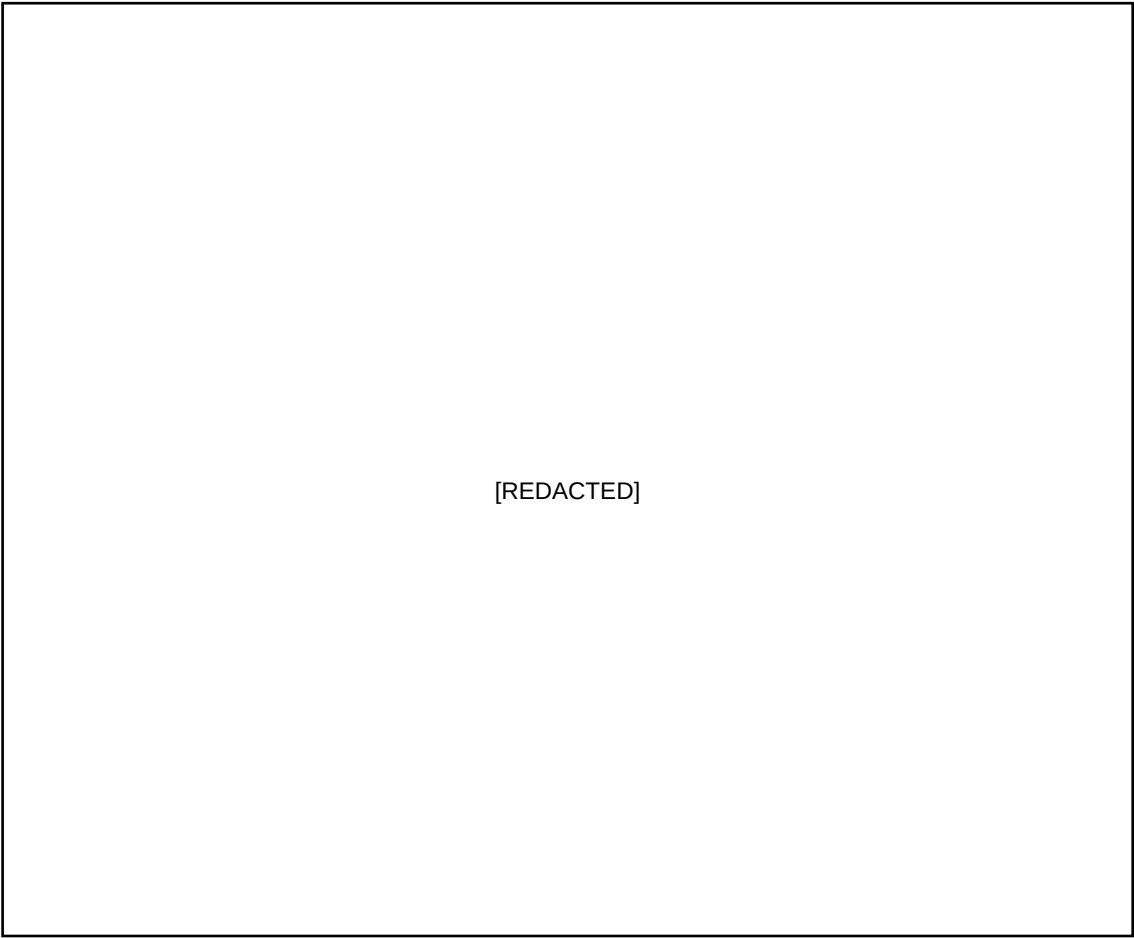
energy potential landscape in restricting atomic mobility. In our study, this concept was realized by constructing a monolayer, fully anchored configuration of Rh atoms on the CeO₂ surface.

6. In previous work by Figueroba et al. (*Catal. Sci. Technol.*, 2016, 6, 6806–6813), the Rh was postulated to sit on 4-fold (100) pockets, which can be found on steps of ceria. The binding energy of the Rh was reported to be -678 kJ/mol which is considerably stronger than the 1 eV reported here. Also, Rh atoms were shown to be trapped on ceria when heated in air at 800 °C (Alcala et al., Atomically Dispersed Dopants for Stabilizing Ceria Surface Area. *Appl. Catal. B: Environ.*, 2021, 284, 119722) suggesting much stronger binding to the ceria. Can the authors explain their assignment of the charge of the Rh and its location (see question 5 below).

[Reply] Thanks for your valuable question.

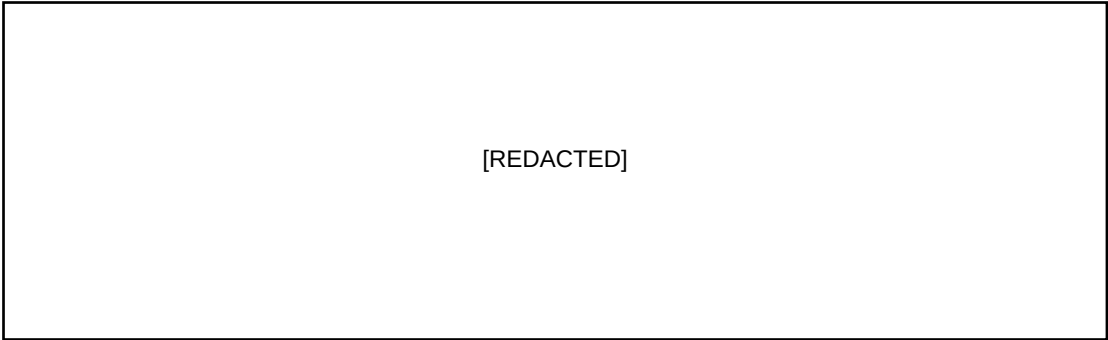
①In previous work by Figueroba et al. (*Catal. Sci. Technol.*, 2016, 6, 6806-6813), the adsorption energy of a metal atom M on Ceria NP was calculated as $E_{ad} = E(M_1-Ce_{40}O_{80}) - E(M_1) - E(Ce_{40}O_{80})$, where $E(M_1)$ is the total ground-state energy of an isolated metal atom and $E(M_1-Ce_{40}O_{80})$ and $E(Ce_{40}O_{80})$ are the total energies of the ceria NP with and without the adsorbed metal atom, respectively. However, in our study, the binding energy of metal M on the surface, $E_b(M)$, was calculated with $E_b(M) = E_{M/slabb} - E_{slab} - 1/nE_M$, where $E_{M/slabb}$ is the calculated total energy of the binding system, while E_{slab} and E_M are the calculated energies of the clean surface and the bulk metal, and n is the number of atoms in the bulk, respectively. There are differences in the selection of initial state of the metal and support model, which consequently leads to differences in the calculated binding energy.

②The charge of Rh was determined by combining XPS and CO IR data with references. The binding energy of Rh 3d_{5/2} is around 309 eV, similar to the reported position of the Rh³⁺ species in the literature. The CO DRIFT spectrum shows two peaks of asymmetric vibration peak and symmetric vibration peak of Rh(CO)₂ at 2019 and 2087 cm⁻¹, which locate in a position similar to that reported in the literature.



[REDACTED]

[Haifeng Xiong, et al. Nature and dynamic evolution of Rh single atom trapped by CeO₂ in CO hydrogenation. *ACS Catal.* 2022, 12, 12253-12267. Fig. 2 and Fig. 3 in p12257.]



[REDACTED]

[Hyunjoo Lee, et al. Selective activation of methane on single-atom catalyst of Rhodium dispersed on Zirconia for direct conversion. *J. Am. Chem. Soc.* 2017, 139, 17694-17699. Fig. 2 in p17696 and Fig. 3 in p17697.]

[REDACTED]

[Xiaoqing Huang, et al. High-efficiency direct methane conversion to oxygenates on a ceria dioxide nanowires supported rhodium single-atom catalyst. *Nat. Commun.* 2020, 11, 954. Fig. S5.]

③ The location of Rh is determined through a combined analysis of DFT calculations and experimental data. We selected five structure for calculating the binding energy of Rh on CeO₂ (CeO₂(111), CeO₂(111)-O_v, CeO₂(111)-Ce_v, CeO₂(111)-(CeO)_v and CeO₂(111)-(CeO₂)_v), and obtained the relevant parameters related to the anchoring of Rh atoms on each of above surface structure. Then, we compared the relevant parameters of the Rh single atom obtained from the experimental analysis with the calculated values, and arrived at what we consider to be a more reasonable location of Rh atom.

We add detail description in paragraph 2 on page 4: “The specific structure of Rh anchoring position is determined through comprehensive analysis of DFT calculation and the above experimental data. We compared the coordination, bond lengths, and oxidation states of Rh when anchored in different vacancy sites (Fig. S3 and Table S2), and finally selected the structure that most closely matched the actual situation for subsequent calculations (Fig. S3d).”

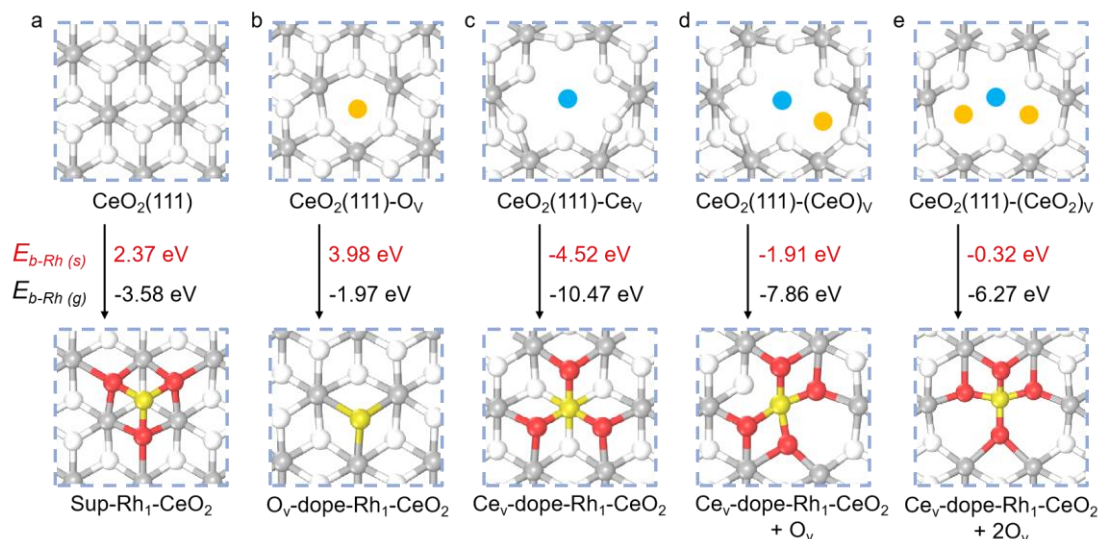


Figure S3. Binding energy of Rh atom on (a) $\text{CeO}_2(111)$, (b) $\text{CeO}_2(111)\text{-O}_v$, (c) $\text{CeO}_2(111)\text{-Ce}_v$, (d) $\text{CeO}_2(111)\text{-(CeO)}_v$ and (e) $\text{CeO}_2(111)\text{-(CeO}_2)_v$ surfaces.

Table S2. Parameters of the stable state of the Rh atom on each surface.

Structure	CN	Rh-O	Valance state
<i>Experimental data</i>	<i>4.4</i>	<i>2.037</i>	<i>+3</i>
$\text{Rh}_1/\text{CeO}_2(111)$	3	2.16	+1
$\text{Rh}_1/\text{CeO}_2(111)\text{-O}_v$	3	2.77	+1
$\text{Rh}_1\text{-CeO}_2(111)$	6	2.15	+4
<i>$\text{Rh}_1\text{-CeO}_2(111)\text{-O}_v$</i>	<i>4</i>	<i>2.15</i>	<i>+3</i>
$\text{Rh}_1\text{-CeO}_2(111)\text{-2O}_v$	5	2.01	+3

Thus, the bottom structure in Figure S3d is more likely to be the location of Rh atom.

7. Can the authors provide more details on the site where the Rh is anchored. They call it a Ce cluster vacancy site. Is this a vacancy of Ce or of O? Can they provide atomic coordinates and also how they are able to fit the Rh in a four-fold site on a ceria (111) surface which has 3-fold symmetry. They report the oxidation state of Rh to be 3+. In

this state, the Rh should not be active, or be able to adsorb CO. The previous work by Figueroba et al. (*Catal. Sci. Technol.*, 2016, 6, 6806–6813) implied a Rh^{2+} oxidation state. The reported DRIFTS spectrum of Rh_1 (Figure 1c) does not appear to be consistent with Rh (3+) but rather with Rh (1+) based on the literature.

[Reply] Thanks for you meaningful questions.

Firstly, the Ce cluster vacancy site mentioned in our study is a CeO_2 vacancy, as shown in the upper structure in Figure S3e *in the Reply to question 6*. Under oxidative conditions, as Rh is anchored at the vacancy site, the CeO_2 surface undergoes structural reconfiguration, and ultimately Rh assumes a tetrahedral coordination structure.

Secondly, Rh^{3+} may not strongly or actively adsorb CO, the intensity of the CO-DRIFT spectrum in our study is also not very strong. However, Rh^{3+} is reported to be highly active in activating methane (*J. Am. Chem. Soc.* 2017, 139, 17694-17699; *Nat. Commun.*, 2020, 11(1), 954).

Thirdly, the charge of Rh was determined by combining XPS and CO IR data with references, the details are presented in the second point of the reply to the question 6.

8. Related to this question, I would like to know the charge on the ceria when Rh is anchored in the 3+ oxidation state.

[Reply] Thanks for your question. In our study, from the perspective of DFT calculation, when Rh is anchored on CeO_2 under oxidative atmosphere, there is a position lacking one Ce atom and one O atom that is filled by Rh atom and O atom (the bottom structure in Figure S3e). Theoretically, the proportion of Ce^{3+} should decrease, and the XPS result indeed conform to this outcome (Figure S2).

9. Methane oxidation is typically affected by water vapor, which is generated when methane is oxidized. Did the authors perform longer term tests at temperatures below 500 °C where poisoning by water vapor causes loss of activity.

[Reply] Thanks for your suggestion. We conducted a 24-hour stability test at 460 °C, the result showed that, below 500 °C, the water vapor produced by methane oxidation would not poison the activity. We add some sentences in paragraph 1 in page 11: “The

activity of $\text{Rh}_n/\text{Rh}_1@\text{CeO}_2$ and $\text{Rh}_n/\text{Zr}_1@\text{CeO}_2$ is not be affected by the water vapor generated from the methane oxidation even below 500 °C (Fig. S21)”

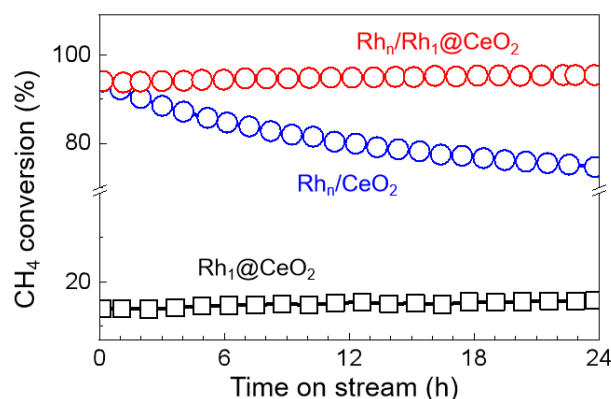


Figure S21. 24-hour stability test of $\text{Rh}_n/\text{Rh}_1@\text{CeO}_2$, Rh_n/CeO_2 and $\text{Rh}_1@\text{CeO}_2$ at 460 °C

Also, there are several typographical errors which need to be corrected. I will point out a few:

“preapred” on line 130

“appearsd” on line 144

“activation” on line 182

[Reply] Thanks for pointing out our error. We have all made corresponding revisions.

Line 130: Rh_n/CeO_2 was prepared by the same method as $\text{Rh}_n/\text{Rh}_1@\text{CeO}_2$

Line 144: Unlike $\text{Rh}_n/\text{Rh}_1@\text{CeO}_2$, a negative 'peak' unexpectedly appeared in the 460-800 °C range in the heating light-off curve of Rh_n/CeO_2

Line 182: Furthermore, we systematically calculated the activation of the first C-H bond in CH_4 for both single-atom Rh and Rh_n clusters using DFT^{24,26} (Figs. 4A and S16).

Reviewer #3

Comments:

The work is interesting and potentially relevant. However, the following aspects needs attention and revisions.

Experimental: the authors investigate catalytic activity under 20% O_2 concentration. This is a favorable atmospheric condition that however does not

represent real exhaust conditions (more realistic 5-10 % O₂). Comments are expected.

[Reply] Thanks for raising the concern. 5-10% O₂ does indeed better reflect the actual exhaust condition. Our choice of 20% O₂ is based on two aspects. Firstly, it is in line with the selection of oxygen concentration in the references that a concentration of around 20% is commonly used (*Angew. Chem. Int. Ed.* 2018, 57, 8953-8957; *Nat. Commun.* 2019, 10, 1611). Secondly, 20% O₂ can cover more application scenarios and enhance the applicability of the conclusion.

Results: the authors discuss “a vacancy site (V_{site}) on the CeO₂(111) surface,” that is able to stabilize single atom Rh species. It is important to expand and clarify this aspect. A pioneer work underlines that many Oxygen vacancies can be formed in CeO₂(111), such single, double, linear, surface and subsurface Oxygen vacancies associated to appropriate numbers of Ce(III) ions (see Electron localization determines defect formation on ceria substrates F Esch, et. al. *Science*, 309 (2005), 752-755.) Would be relevant to characterize the vacancies by Raman spectroscopy for instance. Ce(III) could be also used to discuss associated vacancies.

[Reply] Thanks for your suggestion. In our study, the anchor site of Rh atom was determined through a structural analysis that combined EXFAS, XPS data and DFT calculations. The detailed analysis process is showed *in the third point of the reply to the question 6 of reviewer #2*. Eventually, under oxidation atmosphere, Rh atom is anchored in “CeO₂” vacancy to fill one Ce and one O site. Regrettably, due to the limitations of experimental resources, it is difficult for us to analyze the characteristics of the vacancies through methods such as Raman spectroscopy.

The Ce(III) indeed helps in analyzing vacancy changes. The XPS data indicates that the content of Ce(III) in the catalyst after Rh anchoring has decreased, which is consistent with the result we obtained from the structural analysis that the part of oxygen vacancies have been filled.

The authors discuss an “extraordinary stability in methane oxidation”, while extraordinary can not refers to few hours activity. Furthermore, since deactivation is a

kinetic phenomenon, it must be studied under kinetically controlled conditions (typically low conversion). See A Matter of Life (time) and Death, *ACS Catal.* 2018, 8, 9, 8597–8599) Under flow conditions, working at full or equilibrium conversion, the amount of time elapsed before a decrease in conversion is observed does not necessarily reflect stability. The rate may be far higher than is needed to achieve full or equilibrium conversion in the reactor, masking the initial presence of deactivation.

[Reply] Thanks for your advice. The stability mentioned in our study refers to the high-temperature stability of the catalyst, which means its activity will not decrease under or after high-temperature conditions. However, it does not reflect the initial stability in the equilibrium conversion state. Therefore, we have revised this statement to make it more precise in paragraph 1 in page 11: “simultaneously achieving both high catalytic activity and extraordinary **thermal** stability in methane oxidation.”

Fig 5 B Why not compare also $\text{Rh}_n/\text{Zr}_1@\text{CeO}_2$ and $\text{Rh}_n/\text{Rh}_1@\text{CeO}_2$.

[Reply] Thanks for your question. In Fig. 5A, the comparison of methane conversion rates of $\text{Rh}_n/\text{Rh}_1@\text{CeO}_2$ and $\text{Rh}_n/\text{Zr}_1@\text{CeO}_2$ is made to confirm that the effect of Zr anchoring to the activity is consistent with that of Rh anchoring. In Fig. 5B, it compares the activity changes before and after aging and shows the thermal stability after aging, further demonstrating the effectiveness of the single-atom potential confinement strategy. Since the activity and aging experiment results of $\text{Rh}_n/\text{Rh}_1@\text{CeO}_2$ and $\text{Rh}_n/\text{Zr}_1@\text{CeO}_2$ are similar, only the comparison of $\text{Rh}_n/\text{Zr}_1@\text{CeO}_2$ and Rh_n/CeO_2 is presented in Fig. 5B. However, the differences in the main comparison subject is Fig. 5A and 5B may cause confusion. Therefore, we have supplemented the comparison of aging experiment of $\text{Rh}_n/\text{Rh}_1@\text{CeO}_2$ and $\text{Rh}_n/\text{Zr}_1@\text{CeO}_2$ in supporting information and mentioned in paragraph 2 in page 10: “ $\text{Rh}_n/\text{Zr}_1@\text{CeO}_2$ showed the same conversion before and after aging, **similar to $\text{Rh}_n/\text{Rh}_1@\text{CeO}_2$** (Fig. S20), whereas Rh_n/CeO_2 almost completely lose its low-temperature activity following aging”.

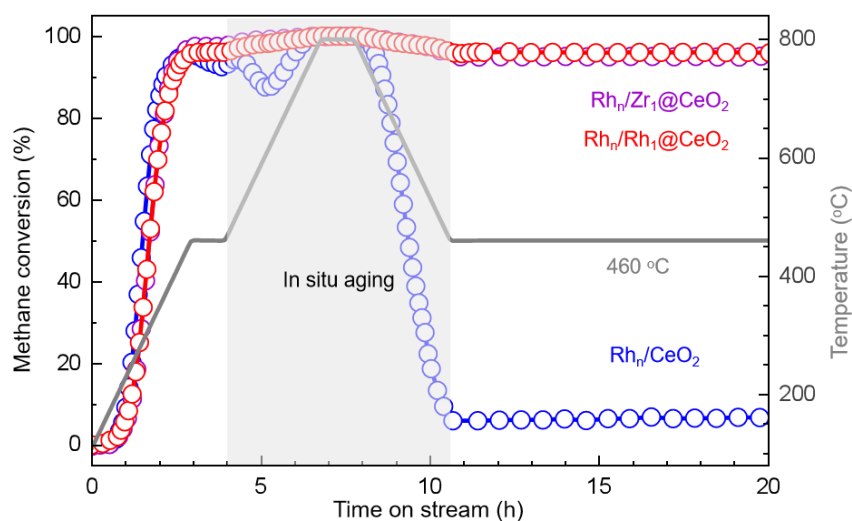


Figure S20. Time-on-stream methane conversion profiles for $\text{Rh}_n/\text{Rh}_1@\text{CeO}_2$, $\text{Rh}_n/\text{Zr}_1@\text{CeO}_2$ and Rh_n/CeO_2 with *in situ* aging procedure.

Table S2, even if the authors uses the table only to indicate that their light off are in the range of literature data, I underline that correct comparison can be made only on identical space velocity.

[Reply] Thanks for your suggestion. We selected some references and calculated the specific rate per gram of Rh taking into account the space velocity, the results show that the activity of our catalysts is within the range reported. We add some information in both the manuscript and supporting information: “For the heating light-off curves in Fig. 2, both $\text{Rh}_n/\text{Rh}_1@\text{CeO}_2$ and Rh_n/CeO_2 exhibit almost identical activity below $\sim 400^\circ\text{C}$ and initiate methane oxidation at a temperature as low as 200°C , which is comparable to the activity of well-known palladium-based catalysts^{3,20,21}(Table S3 and S4)

Table S4. Comparison of catalysts activity of Rh catalysts and Pd supported catalysts in methane-catalyzed combustion in literature considering space velocity.

Catalysts	M (wt.%)	Reaction conditions	Conversion	Specific rate on per gram of Rh (mmol _{CH₄} g _M ⁻¹ h ⁻¹)	Ref
Rh_n/CeO₂	0.69% Rh	150 ppm CH ₄ , 20 vol% O ₂ in Ar	55% (300 °C)	1.92	This work
Rh_n/Rh₁@CeO₂	1.55% Rh	150 ppm CH ₄ , 20 vol% O ₂ in Ar	40% (300 °C)	0.62	This work
Rh_n/Zr₁@CeO₂	0.69% Rh	150 ppm CH ₄ , 20 vol% O ₂ in Ar	40% (300 °C)	1.40	This work
1Pd/2Pt@CeO ₂	1% Pd +2% Pt	680 ppm CH ₄ , 14 vol% O ₂ , 5 vol% CO ₂ in N ₂	22% (300 °C)	3.33	1
Pd/NA-Al ₂ O ₃	5% Pd	1 vol% CH ₄ , 20 vol% O ₂ in Ar	53% (300 °C)	1.41	4
Pd/SnO ₂	0.15% Pd	1 vol% CH ₄ , 20 vol% O ₂ in N ₂	30% (300 °C)	4.01	7
PdW ₁ /Al ₂ O ₃	1% Pd	0.5 % CH ₄ , 20 vol% O ₂ in N ₂	40% (300 °C)	7.16	10

Reviewer's comments:

Reviewer #1

The authors have addressed all my previous concerns comprehensively in this revised version. The manuscript now presents an outstanding study with novel findings that constitute a significant contribution to the field. I recommend acceptance without any further changes.

[Reply] Thank you for your comments.

Reviewer #2

The authors have adequately addressed my concerns.

1. I would like them to check the calculation of the Rh surface concentration in terms of atoms/nm². Since their metal loading is 0.96 wt% and BET surface area 37 m²/g my calculation suggests 1.52 atoms/nm² as follows:

$$0.96 \text{ g Rh}/100\text{g of support} \times 100\text{g}/3700 \text{ m}^2 \times 1\text{E}18 \text{ nm}^2/\text{m}^2 / 102.91 \text{ g/gmol} \times 6.02\text{E}23 \text{ atoms/mol}$$

[Reply] Thank you for pointing out our mistake. There was an error in the order of magnitude calculation in the previous calculation. We have recalculated and the concentration of Rh₁@CeO₂ in terms of atoms per nm² is indeed calculated to be ~1.52 atom/nm². We made some modifications to Note S1 in supporting information: “The specific surface area of Rh₁@CeO₂ is about 37 m²/g (Table S8), thus the concentration of Rh₁@CeO₂ in terms of atoms per nm² is calculated to be ~1.52 atom/nm².”

2. Also, why does the surface area of Rh_n/Rh₁@CeO₂ go up from 37 m²/g to 60 m²/g?

[Reply] Rh₁@CeO₂ exhibits a relatively small specific surface area after being calcined at 800 °C, despite the inhibitory effect of Rh atoms on the reduction of the surface area of CeO₂. This result (37 m²/g) is similar to those reported in the literature (Applied Catalysis B-environmental, 2021, 284: 119722). Rh_n/Rh₁@CeO₂ contains more Rh nanoparticles compared to Rh₁@CeO₂, and the catalyst is prepared by colloidal

deposition. This might be the reason for the difference in specific surface area.

Reviewer #3

The authors avoided my comments

1.O₂ concentration reply is unsatisfactory! Either demonstrate examples of exhaust where 20% O₂ concentration is normal (is what you have in air!! and any combustion decrease this value significantly...

[Reply] Thank you for your suggestion. Regarding the issue of O₂ concentration, we have conducted the experiments of methane oxidation combustion under 7%-15% O₂ concentration. The experimental result shows that within the reaction kinetics range, the catalytic activity is not influenced by the O₂ concentration, especially considering that the CH₄ concentration is only 150 ppm.

Table R1. Reaction order test data.

Reaction condition: the reaction gas (150 ml min ⁻¹) containing 150 ppm CH ₄ and x vol% O ₂ balanced with Ar.	
O ₂ concentration	CH ₄ conversion
7%	10.51%
9%	10.60%
11%	10.63%
13%	10.50%
15%	10.72%

We calculated the reaction order based on the data, and reaction order is 0.02 (see the right figure).

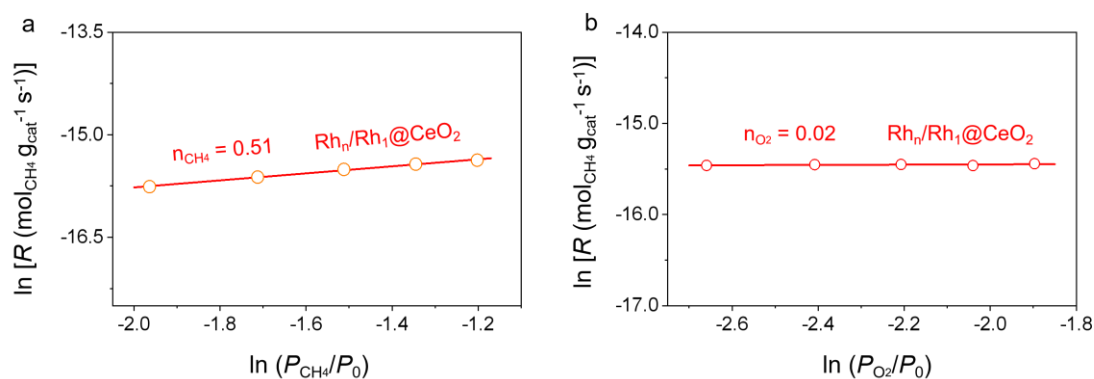


Figure S24. Reaction rates (R) as a function of (a) CH_4 partial pressure and (b) O_2 partial pressure over $\text{Rh}_n/\text{Rh}_1@\text{CeO}_2$ at 350 °C. Catalyst mass: 4 mg. When the CH_4 concentration was changed (70-150 ppm), the O_2 concentration remained at 10%. When the O_2 concentration was changed (7-15%), the CH_4 concentration remained at 150 ppm.

2.Regarding the generic use of “oxygen vacancies” the reply ...”limitations of experimental resources, it is difficult for...” is not professional when Nature family journal are the target! Not even an adequate discussion is added...

[Reply] Sorry for not providing sufficient explanations. In our study, it was inferred that Rh was anchored in the oxygen vacancy structure by comparing the changes in O_β and Ce^{3+} content of CeO_2 and aged $\text{Rh}_1@\text{CeO}_2$. It can be observed that the contents of O_β and Ce^{3+} after Rh anchoring have decreased significantly (Figure S2).

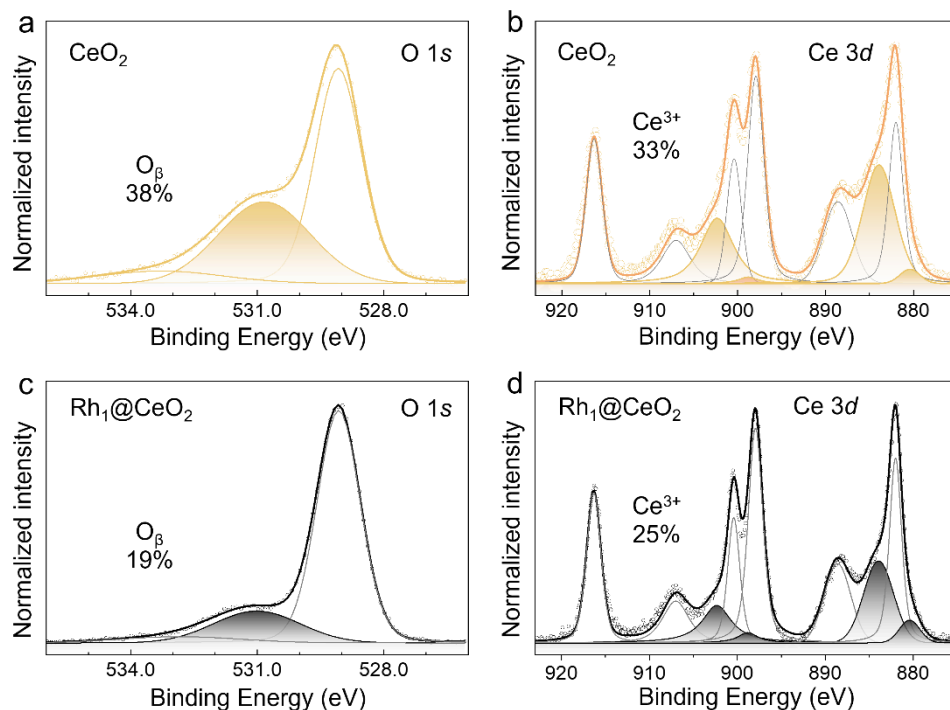


Figure S2. O 1s and Ce 3d XPS spectra of CeO₂ (a,b) and Rh₁@CeO₂ (c,d).

As you stated, in previous studies, there were various types of oxygen vacancy structures in CeO₂(111). We determined the oxygen structure that anchors the Rh atoms through DFT calculations. By comparing the structure information presented after Rh atom anchoring to different vacancy structure with the experimentally measured structural information, we can confirm the vacancy structure that best conforms to the actual situation, which is shown in Fig. S3d (Figure S3 and Table S2).

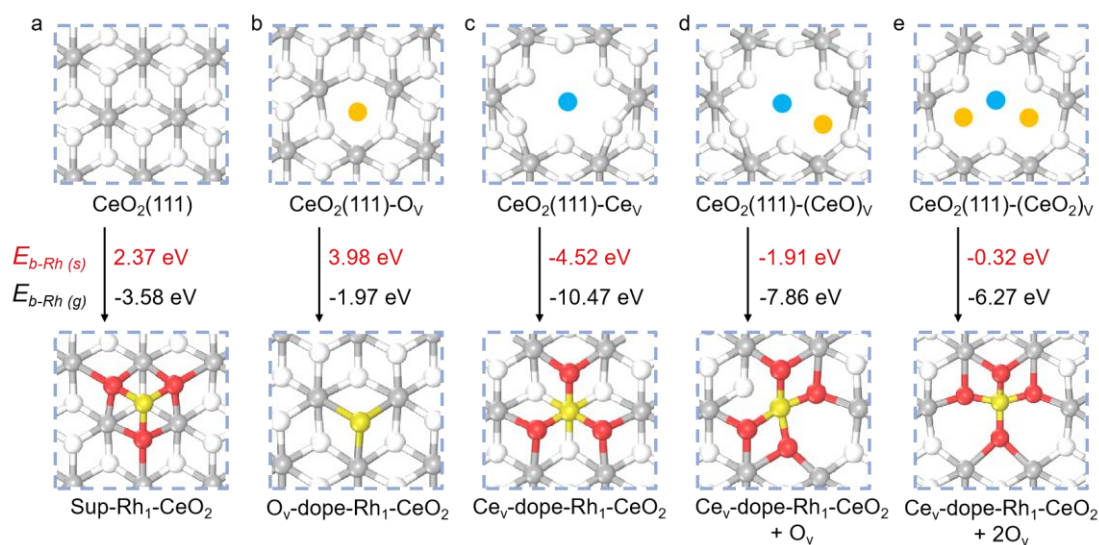


Figure S3. Binding energy of Rh atom on (a) CeO₂(111), (b) CeO₂(111)-O_v, (c) CeO₂(111)-Ce_v, (d) CeO₂(111)-(CeO)_v and (e) CeO₂(111)-(CeO₂)_v surfaces.

Table S2. Parameters of the stable state of the Rh atom on each surface.

Structure	CN	Rh-O	Valance state
<i>Experimental data</i>	<i>4.4</i>	<i>2.037</i>	<i>+3</i>
Rh ₁ /CeO ₂ (111)	3	2.16	+1
Rh ₁ /CeO ₂ (111)-O _v	3	2.77	+1
Rh ₁ -CeO ₂ (111)	6	2.15	+4
<i>Rh₁-CeO₂(111)-O_v</i>	<i>4</i>	<i>2.15</i>	<i>+3</i>
Rh ₁ -CeO ₂ (111)-2O _v	5	2.01	+3

To enhance the clarity, we added some revisions to manuscript in paragraph 2 in page 4: “X-ray photoelectron spectra (XPS) revealed that the concentration of surface defect oxygen species and Ce³⁺ sharply decrease after the single Rh atom anchoring (Fig. S2), evidencing that the single Rh atoms have occupied the CeO₂ surface V_{sites}. A pioneer work underlines that many oxygen vacancies can be formed in CeO₂(111), such single, double, linear, surface and subsurface¹⁵. Therefore, it is important to clearly define the vacancy structure. The specific structure of Rh anchoring position is determined through comprehensive analysis of DFT calculation and the above experimental data.”

3.The reply on stability is shocking! It must be studied at low conversion! This is a basic concept in catalysis!

[Reply] Thanks for your advice. We initially conducted the stability test at 460 °C because the activity dropping point of Rh_n/CeO₂ is at 460 °C. Therefore, we chose this temperature point to compare the differences in high-temperature activity stability among different catalysts.

In the current paper-revision stage, we conducted a stability test on Rh_n/Rh₁@CeO₂ at 260 °C. The results indicated that Rh_n/Rh₁@CeO₂ exhibited good

stability. We have included the stability data in the supporting information and mentioned in manuscript: “The activity of $\text{Rh}_n/\text{Rh}_1@\text{CeO}_2$ and $\text{Rh}_n/\text{Zr}_1@\text{CeO}_2$ is not be affected by the water vapor generated from the methane oxidation even below 500 °C (Fig. S21 and Fig. S22).”.

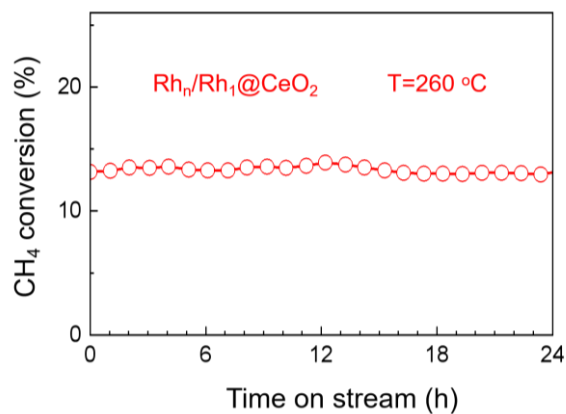


Figure S22. 24-hour stability test of $\text{Rh}_n/\text{Rh}_1@\text{CeO}_2$ at 260 °C.

REVIEWERS' COMMENTS

Reviewer #2 (Remarks to the Author):

The authors have addressed one of my comments, about the Rh surface coverage but have not adequately addressed the other one concerning the BET surface area. The Rh_n/Rh₁ catalyst is prepared by depositing Rh nanoparticles via a colloidal synthesis. Would the amount of Rh added to the catalyst justify the increase in BET surface area? The TEM images do not show a low concentration of added Rh nanoparticles.

[Reply] Thank you very much! You are right: In principle, the deposition of Rh nanoparticles will not increase the BET surface area especially when the concentration of added Rh nanoparticles is low. The difference in the surface areas of Rh₁@CeO₂ and Rh_n/Rh₁@CeO₂ is because Rh_n/Rh₁@CeO₂ was prepared using Rh₁@CeO₂ support (coming from another batch). Such difference in surface area is understandable, and that is not a big deal.

Reviewer #3 (Remarks to the Author):

The reviewers finally clarified the points raised by the reviewer in the previous evaluation step and now I can recommend the acceptance of the manuscript in the present form.

[Reply] Thank you very much for recommending publication!