

Simultaneously activating molecular oxygen and surface lattice oxygen on Pt/TiO₂ for low-temperature CO oxidation



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REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

Zhang et al., report a Pt-based catalyst with only a 0.15 wt% Pt loading, which consists of Pt-Ti intermetallic single-atom alloy (ISAA) and Pt nanoparticles co-supported on a defective TiO₂ support, achieving a record high turnover frequency of 11.95 s⁻¹ at 80 C and complete conversion of CO at 120 C for CO oxidation reaction. The characterization of the catalyst is thoroughly performed to support the authors' assertion. I am sure this manuscript can be published in Nature Communications. However, several issues should be addressed or modified before accepting the manuscript.

1. Reduction at 300 C would be the key to fabricate Pt-Ti ISAA. The reviewer has a question on the structure of Pt-Ti ISAA. It would be an intermetallic compound. Considering the change in ADF images, Pt and/or Ti atoms would be aligned along the observation directions. Do the authors have any justifications that the intermetallic compound consists of single Pt atoms?

2. It is well known that Pt is oxidized by calcination in a muffle furnace after loading them on TiO₂. Therefore, reduction treatment at low temperature is the key to enhance the catalytic activity. Detailed discussion on when Pt-Ti ISAA is formed is necessary. Do the authors changed the reduction temperature after loading for PtNP/TiO₂-R and PtNP/TiO₂ and the catalytic activities of such samples? At least, using control samples without reduction treatment after Pt loading seems not fair.

3. Pt nanoparticles can be easily broken to form single atoms during HAADF STEM observations when the probe current is high. The authors should describe the observation conditions such as probe current during the HAADF STEM observations.

Minor typos

This manuscript contains many typos. They should be carefully modified. Just to mention a few, Page 4, line 86, two control samples would not be PtNP/TiO₂-R and PtPt TiISAA+NP/TiO₂-R, but PtNP/TiO₂ and PtNP/TiO₂-R.

Page 8, line161, AC-HAADF-STEM is used before it is defined.

Page 6, line 115 and page 23, line 407, EELS is defined twice.

Page 23, line 409 and 414, HAADF is defined twice.

Reviewer #2 (Remarks to the Author):

Upon initial reading, this study appears comprehensive. The synthesis and post-structural analysis are generally well-executed, focusing on three types of Pt/TiO₂ catalysts with different reactive species and interface ensembles. The manuscript delves into the physicochemical properties of the catalysts in its early sections. However, significant issues arise in the performance test and DFT calculation parts, leading to a lack of alignment with the quality criteria of Nature Communications.

Comment #1

The authors pre-reduced TiO₂ to generate initial vacancies and induce the formation of ISAA. However, note that 0.15 wt.% of Pt content is slightly greater than the usual Pt content in general SA-only catalysts. Therefore, ISAA and NPs (clusters) naturally coexist in the current catalysts as the excess Pt forms NPs. If the Pt content exceeds 0.15 wt.%, the fraction and the size of Pt NPs will naturally increase. However, suppose the Pt-Pt cohesion becomes stronger than the Pt-Ti interaction in the large NPs. In that case, the ISAA will likely disappear, and the larger NPs will be a majority. In this manner, the morphological stability of the ISAA with the increased Pt content should be confirmed.

Comment #2

Interestingly, an unusually very high concentration of O₂ was supplied in the reaction feedstock. I strongly believe that supplying 16% of O₂ to oxidize 1% of CO significantly biases the results. The experimental activity test results should be performed again using a reasonable level of O₂ concentration (1~4 vol.%). Moreover, more importantly, any oxygen vacancy generated during the reaction by the first step of the MvK mechanism of CO oxidation cannot survive long under such highly oxygen-rich conditions. I think calculating the binding energy of O₂ on Pt in the presence of the reaction-generated oxygen vacancy is not reasonable because the life span of the

vacancy will be extremely short under the reaction conditions. The unusually high O₂ concentration makes comparing the TOF with others skeptical.

The authors may perform reaction order experiments with O₂ concentration to confirm that gas phase O₂ vigorously participates in the reaction. A highly positive correlation between the activity and O₂ concentration is a signature feature of the CO oxidation by the LH mechanism.

Comment #3

I am pretty sure that Pt NPs in Pt/TiO₂ and Pt/TiO₂-R differ in their average size. The authors may report the size distribution of Pt species and discuss how the size influences the performance.

Comment #4

The light-off profiles of the catalysts show that they differ in catalytic activity. The authors reported the activation energy barrier values and claimed that the one with the lowest barrier works better. The catalyst performance test results part should be revised and enriched. The authors may discuss how the initial vacancy or the difference in the Pt size affects the catalyst performance. The reason why E_a differs in three catalysts should be adequately discussed based on experimental results.

Comment #5

I believe that directly comparing the binding energy of the initial binding single molecule does not deduce any scientific insight into the catalytic mechanism or the performance of a model catalyst. The bottom line is that the data presented in Fig 5a to 5d present the available binding sites of CO and O₂ over the catalyst surface. These data are insufficient to state that one of the catalysts preferentially activates the MvK or the LH mechanism. Moreover, all the cases present that Pt (ISAA and NP) preferentially binds CO than O₂, meaning that the surface of all Pt species will be covered with CO under the real reaction conditions. I strongly believe that the CO-covered Pt NPs or ISAA should be the initial model structure before exploring the reaction pathways. A well-demonstrated example can be found in J. Chem. Phys. 2019, 151 (23), 234716.

In general, the MvK mechanism of CO oxidation denotes the interface-mediated oxidation reaction in which lattice oxygen of the oxide support directly oxidizes CO bound to the metal active sites. Of course, removing a lattice oxygen generates a vacancy, and the vacancy binds an O₂ molecule. The extruded O atom of the O₂ molecule again oxidizes the second CO, recovering to the initial structure of the catalyst. Based on the definition of catalysis, the above two parts comprise the MvK mechanism of CO oxidation.

On the other hand, the LH mechanism of CO oxidation by Pt occurs on Pt by utilizing coadsorbed CO and O₂ on Pt surface. Therefore, Pt should bind and activate CO and O₂ together. In this manner, to study CO oxidation by the LH mechanism at the surface of Pt NPs using DFT calculations, I think well-developed Pt facets, or at least a micro-facet, should be required to compare the CO and O₂ adsorption preferences of the surface active sites of Pt NPs. I am sure that directly comparing the binding energy of the first binding molecules does not give any significant insight into the equilibrium surface concentrations of CO and O₂ under the reaction conditions. From my experience, I think the surface of Pt₁₀ NP will be fully saturated with CO molecules. Coadsorbing CO and O₂ to activate the LH mechanism is energetically prohibited on Pt₁₀ because even the last binding CO will interact more strongly with Pt₁₀ than O₂ at that same site. In this manner, the CO oxidation activity of Pt₁₀ following the MvK mechanism should also be estimated using a fully-CO-saturated Pt₁₀ rather than the model presented in Figure 5.

I think that if a Pt(100) or a Pt(111) facet is developed on the surface of Pt NPs, the surface coverage of CO molecules will be limited to a specific value because of the steric hindrance between CO molecules. The residual open space will bind and dissociate O₂ for CO oxidation by the LH mechanism.

The DFT-calculated initial activation energy barrier (for the first step of the MvK mechanism) is very high. The geometry of ts1 and *CO-O presents why this is the case. I think the first CO oxidation process is misestimated. In general, CO oxidation by the MvK mechanism at the Pt-oxide interface accompanies the formation of a reaction intermediate that can be stabilized at the interface. The process reported in Figure 5e (from *CO to *CO-O) shows that the pre-adsorbed CO is rejected from Pt (desorbed) so that the barrier almost similar to the binding energy is required. I am not sure why the authors claim that the LH mechanism is operative based on Figure 5e. The following statement on page 19 is based on a misunderstanding of the MvK/LH mechanism.

"... oxygen atom from the chemisorbed O₂ molecule at the Ov site can engage with the CO adsorbed on the Pt NP via the L-H mechanism to synthesize CO₂."

The authors also should report the details of the reaction pathway catalyzed by PtNP/TiO₂.



Response to the comments of Reviewer 1

Overall Comment: Zhang et al., report a Pt-based catalyst with only a 0.15 wt% Pt loading, which consists of Pt-Ti intermetallic single-atom alloy (ISAA) and Pt nanoparticles co-supported on a defective TiO₂ support, achieving a record high turnover frequency of 11.95 s⁻¹ at 80 °C and complete conversion of CO at 120 °C for CO oxidation reaction. The characterization of the catalyst is thoroughly performed to support the authors' assertion. I am sure this manuscript can be published in Nature Communications. However, several issues should be addressed or modified before accepting the manuscript.

Response: Authors thank the reviewer for the good comments.

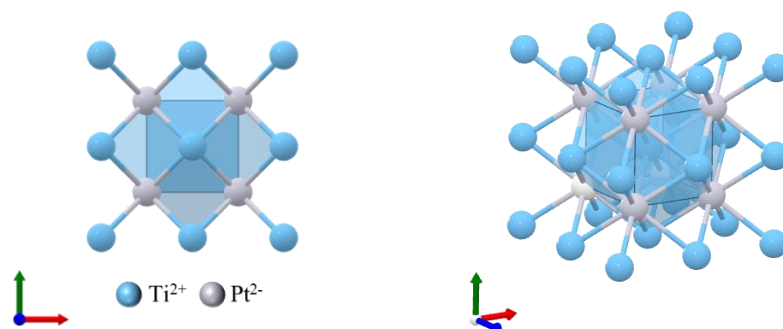
Comment 1: Reduction at 300 °C would be the key to fabricate Pt-Ti ISAA. The reviewer has a question on the structure of Pt-Ti ISAA. It would be an intermetallic compound. Considering the change in ADF images, Pt and/or Ti atoms would be aligned along the observation directions. Do the authors have any justifications that the intermetallic compound consists of single Pt atoms?

Response: The authors express their appreciation to the reviewer for asking good questions. In Fig. 1f, it is evident that the bright spots that represent Pt atoms are surrounded by dark spots corresponding to Ti atoms. The observed distribution of Pt and Ti atoms on the surface is attributed to the body-centered cubic (bcc) B₂ structure, which is of CsCl type and belongs to the *Pm3m* space group. In this arrangement, Pt atoms are surrounded by Ti atoms (see Supplementary Fig. 18).

In the section of Characterization of the Catalysts (page 6, bottom), we added:

The observed atomic distributions of Pt and Ti in the catalyst surface layer are ascribed to the body-centered cubic (bcc) B₂ structure, which belongs to the CsCl type and the *Pm3m* space group. In this arrangement, Pt atoms are isolated by Ti atoms (Supplementary Fig. 18).

In the section of Supporting Information, we added:



Supplementary Fig. 18 | Schematic diagram of Pd–Ti crystal structure.

Comment 2: It is well known that Pt is oxidized by calcination in a muffle furnace after loading them on TiO_2 . Therefore, reduction treatment at low temperature is the key to enhance the catalytic activity. Detailed discussion on when Pt–Ti ISAA is formed is necessary. Do the authors change the reduction temperature after loading for $\text{Pt}_{\text{NP}}/\text{TiO}_2\text{-R}$ and $\text{Pt}_{\text{NP}}/\text{TiO}_2$ and the catalytic activities of such samples? At least, using control samples without reduction treatment after Pt loading seems not fair.

Response: The authors express gratitude to the reviewer for the valuable suggestion. The $\text{Pt}_{\text{Pt-TiISAA+NP}}/\text{TiO}_2\text{-R}$ sample was synthesized through H_2 reduction of $\text{Pt}_{\text{NP}}/\text{TiO}_2\text{-R}$. It's important to note that the Pt–Ti ISAA structure was not present in the untreated $\text{Pt}_{\text{NP}}/\text{TiO}_2\text{-R}$, indicating the crucial role of hydrogen reduction in forming the Pt–Ti ISAA structure within $\text{Pt}_{\text{Pt-TiISAA+NP}}/\text{TiO}_2\text{-R}$. Additionally, following the reviewer's suggestion, $\text{Pt}_{\text{NP}}/\text{TiO}_2$ was treated with hydrogen at 300°C for 30 minutes, resulting in an additional control sample called $\text{Pt}_{\text{NP}}/\text{TiO}_2\text{-H}_2$, which was then evaluated for its catalytic performance.

In the section of Characterization of the Catalysts (page 7, middle), we added:

No Pt–Ti ISAA structure was detected in the Pt/TiO_2 catalyst ($\text{Pt}_{\text{NP}}/\text{TiO}_2\text{-H}_2$) treated at 300°C in a hydrogen atmosphere (Supplementary Fig. 21). This finding, when considered alongside the preceding analysis, underscores the crucial role of Ov in the TiO_2 support and the subsequent calcination in a hydrogen environment after Pt deposition in the formation of the Pt–Ti ISAA

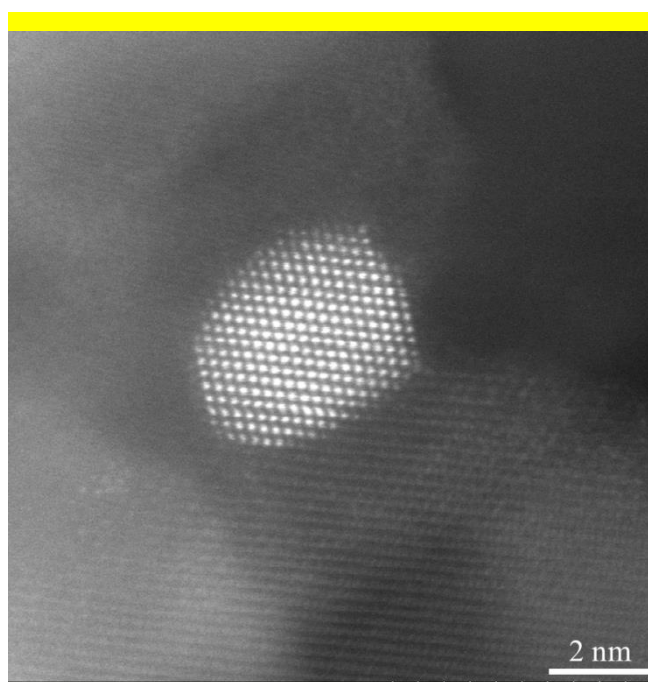


structure. Specifically, the Pt–Ti ISAA structure was formed during the calcination process in hydrogen after loading Pt onto the TiO_2 support.

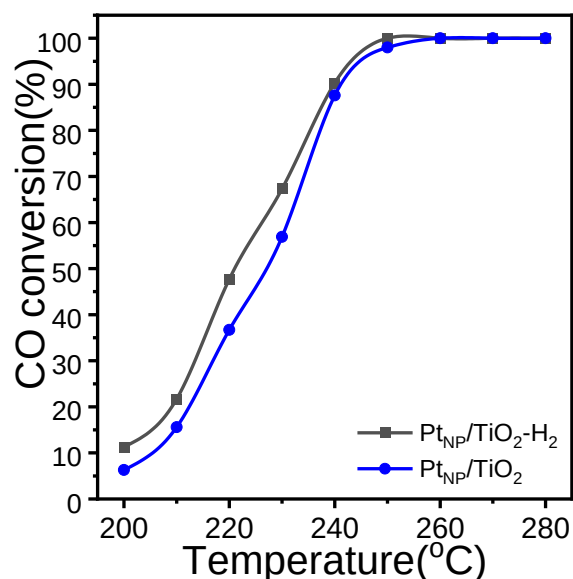
In the section of Performance of CO oxidation on the catalysts (page 18, top), we added:

To assess the impact of hydrogen treatment on catalytic performance, we evaluated the catalytic activity of $\text{Pt}_{\text{NP}}/\text{TiO}_2\text{-H}_2$, which was obtained via treatment in hydrogen at 300 °C for 30 min (Supplementary Fig. 37). The results indicated a negligible improvement in performance compared to $\text{Pt}_{\text{NP}}/\text{TiO}_2$. This finding supports the conclusion that the enhanced performance of $\text{Pt}_{\text{Pt-TiISAA+NP}}/\text{TiO}_2\text{-R}$ over $\text{Pt}_{\text{NP}}/\text{TiO}_2\text{-R}$ is not due to alterations in the valence state of Pt induced by hydrogen treatment. Instead, the superior performance is attributed to the presence of the Pt–Ti ISAA structure in $\text{Pt}_{\text{Pt-TiISAA+NP}}/\text{TiO}_2\text{-R}$.

In the section of Supporting Information, we added:



Supplementary Fig. 21 | AC-HAADF-STEM image of $\text{Pt}_{\text{NP}}/\text{TiO}_2\text{-H}_2$.



Supplementary Fig. 37 | CO conversion as a function of reaction temperature over Pt_{NP}/TiO₂-H₂ and Pt_{NP}/TiO₂. (Reaction conditions: 0.4 g of Cat., a gas mix containing 1 vol% CO and 16 vol% O₂ balanced with N₂.)

In the section of Preparations of Pt_{NP}/TiO₂ and Pt_{NP}/TiO₂-H₂ catalysts, we added:

Pt_{NP}/TiO₂ was synthesized with the same method as Pt_{NP}/TiO₂-R on pristine TiO₂ as the support.

Pt_{NP}/TiO₂-H₂ was obtained by treating Pt_{NP}/TiO₂ in H₂ atmosphere at 300 °C for 30 min.

Comment 3: Pt nanoparticles can be easily broken to form single atoms during HAADF STEM observations when the probe current is high. The authors should describe the observation conditions such as probe current during the HAADF STEM observations.

Response: The authors would like to thank the reviewer for bringing up this concern. The HAADF-STEM images were captured at 200 kV. We have gained extensive experience in using HAADF-STEM for high-resolution, non-destructive imaging of Pt NPs. Our studies consistently demonstrate that these particles are not damaged during imaging (<https://doi.org/10.1038/s41467-022-33250-8>, <https://doi.org/10.1038/s41467-022-30540-z>).

Comment 4: Minor typos

This manuscript contains many typos. They should be carefully modified. Just to mention a few,



Page 4, line 86, two control samples would not be $\text{Pt}_{\text{NP}}/\text{TiO}_2\text{-R}$ and $\text{Pt}_{\text{Pt-TiSAA+NP}}/\text{TiO}_2\text{-R}$, but $\text{Pt}_{\text{NP}}/\text{TiO}_2$ and $\text{Pt}_{\text{NP}}/\text{TiO}_2\text{-R}$.

Page 8, line 161, AC-HAADF-STEM is used before it is defined.

Page 6, line 115 and page 23, line 407, EELS is defined twice.

Page 23, line 409 and 414, HAADF is defined twice.

Response: The authors thank the reviewer for the kind reminder. We are very sorry for these typos, and we have corrected these errors in the revised manuscript.

In the section of Characterization of the Catalysts, we revised:

$\text{Pt}_{\text{NP}}/\text{TiO}_2$ and $\text{Pt}_{\text{NP}}/\text{TiO}_2\text{-R}$ were prepared with identical Pt loading and using TiO_2 and $\text{TiO}_2\text{-R}$ as the respective supports.

Fig. 1d illustrates an enlarged Aberration-corrected high-angle-annular-dark-field scanning transmission electron microscopy (AC-HAADF-STEM) image of the area marked by the red dashed boxes in Fig. 1b.

Aberration-corrected scanning transmission electron microscopy (AC-STEM) and EELS analyses were performed using a probe-corrected Hitachi HF5000 S/TEM, operating at 200 kV.

The instrument is equipped with a HAADF and a segmented DF4 detector for high spatial resolution for high spatial resolution STEM-HAADF and STEM-iDPC imaging experiments.



Response to the comments of Reviewer 2

Overall Comment: Upon initial reading, this study appears comprehensive. The synthesis and post-structural analysis are generally well-executed, focusing on three types of Pt/TiO₂ catalysts with different reactive species and interface ensembles. The manuscript delves into the physicochemical properties of the catalysts in its early sections. However, significant issues arise in the performance test and DFT calculation parts, leading to a lack of alignment with the quality criteria of Nature Communications.

Response: The authors thank the reviewer for the valuable comment. Following the kind and constructive suggestions of the reviewer, we thoroughly revised the manuscript. All the raised issues have been addressed below. We sincerely hope the reviewer will reconsider our manuscript.

Comment 1: The authors pre-reduced TiO₂ to generate initial vacancies and induce the formation of ISAA. However, note that 0.15 wt.% of Pt content is slightly greater than the usual Pt content in general SA-only catalysts. Therefore, ISAAs and NPs (clusters) naturally coexist in the current catalysts as the excess Pt forms NPs. If the Pt content exceeds 0.15 wt.%, the fraction and the size of Pt NPs will naturally increase. However, suppose the Pt-Pt cohesion becomes stronger than the Pt-Ti interaction in the large NPs. In that case, the ISAA will likely disappear, and the larger NPs will be a majority. In this manner, the morphological stability of the ISAA with the increased Pt content should be confirmed.

Response: The authors thank the reviewer for the good suggestions. We agree with the reviewer's assessment that when the cohesion between Pt atoms exceeds the interaction between Pt and Ti atoms in larger nanoparticles (NPs), the unique structure may not be preserved, leading to a prevalence of larger NPs. To minimize the effect of particle size on the ISAA structure, and considering the typically low Pt loading in Pt-based catalysts, we prepared Pt_{Pt-TiISAA+NP}/TiO₂-R with a Pt loading of 0.5 wt% using the same method as before. Subsequently, the catalysts were examined using AC-HAADF-STEM, which confirmed that even on larger Pt NPs, ISAA and NPs (clusters) can still coexist.

In the section of Characterization of the Catalysts (page 7, middle), we added:

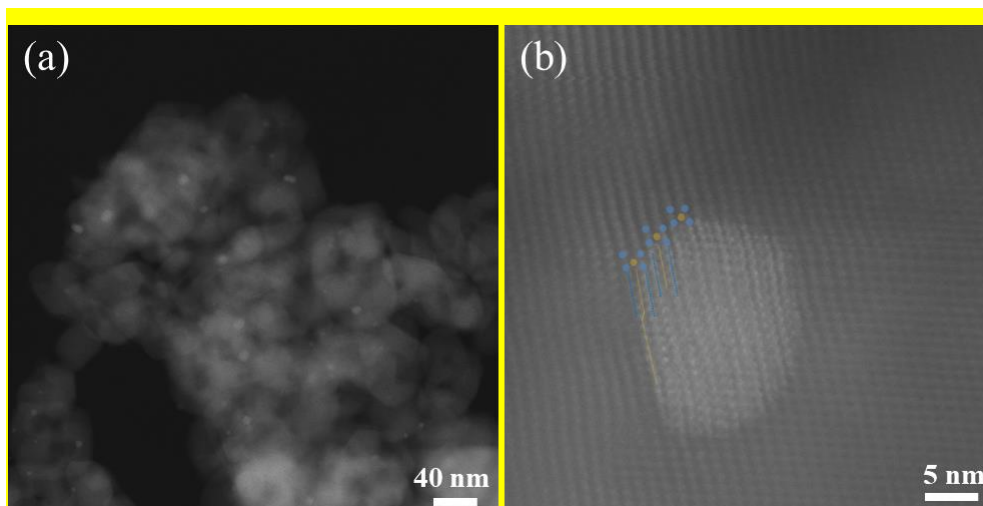


To investigate whether the cohesion between Pt atoms in larger NPs surpassed the Pt-Ti interactions that resulted in the disappearance of Pt-Ti ISAA, a sample of 0.5 wt% Pt_{Pt-TiISAA+NP}/TiO₂-R was prepared. The results, as presented in Supplementary Fig. 22, reveal that the Pt-Ti ISAA and Pt NPs can still coexist even in the presence of the larger Pt particles (~20 nm).

In the section of Preparations of 0.5 wt% Pt_{Pt-TiISAA+NP}/TiO₂-R, we added:

H₂PtCl₆ solution (0.05 g) was dissolved into 50 mL of ethanol, and then TiO₂-R (2.00 g) was added to the above solution. The mixture was stirred at 50 °C until ethanol evaporated and then calcined at 300 °C for 2 h after dried at 50 °C overnight, followed by reduction at 300 °C in H₂ for 30 min. This catalyst was denoted 0.5 wt% Pt_{Pt-TiISAA+NP}/TiO₂-R.

In the section of Supporting Information, we added:



Supplementary Fig. 22 | (a) and (b) AC-HAADF-STEM images of 0.5 wt% Pt_{Pt-TiISAA+NP}/TiO₂-R.

Comment 2: Interestingly, an unusually very high concentration of O₂ was supplied in the reaction feedstock. I strongly believe that supplying 16% of O₂ to oxidize 1% of CO significantly biases the results. The experimental activity test results should be performed again using a reasonable level of O₂ concentration (1~4 vol.%). Moreover, more importantly, any oxygen vacancy generated during the reaction by the first step of the MvK mechanism of CO oxidation cannot survive long under such highly oxygen-rich conditions. I think calculating the binding energy of O₂ on Pt in the presence of the reaction-generated oxygen vacancy is not reasonable because the life span of the vacancy will be extremely short under the reaction conditions. The unusually high O₂ concentration



makes comparing the TOF with others skeptical. The authors may perform reaction order experiments with O₂ concentration to confirm that gas phase O₂ vigorously participates in the reaction. A highly positive correlation between the activity and O₂ concentration is a signature feature of the CO oxidation by the LH mechanism.

Response: The authors thank the reviewer for the good questions. We conducted activity tests under reduced oxygen concentrations as recommended by the reviewer. The results confirm the reviewer's assertion that oxygen concentration impacts catalytic performance. Specifically, CO conversion decreased for all the three catalysts as the oxygen levels decreased, indicating that the Langmuir-Hinshelwood (L-H) reaction mechanism is at play in each case. Notably, the decrease in CO conversion for Pt_{Pt-TiISAA+NP}/TiO₂-R was less pronounced compared to those for Pt_{NP}/TiO₂-R and Pt_{NP}/TiO₂. When utilizing a gas mixture of 1% CO and 4% O₂, the CO conversion for Pt_{Pt-TiISAA+NP}/TiO₂-R was 50% at 106 °C, which is substantially lower by 118 °C and 162 °C than Pt_{NP}/TiO₂-R (T₅₀ = 224 °C) and Pt_{NP}/TiO₂ (T₅₀ = 268 °C), respectively. Under these conditions, the turnover frequency (TOF) of Pt_{Pt-TiISAA+NP}/TiO₂-R (5.94 s⁻¹) remained superior compared to other reported catalysts.

Also, we agree with the reviewer's assessment that calculating the binding energy of O₂ on Pt in the presence of oxygen vacancies generated by the reaction is not a sound approach. Therefore, we have removed this aspect of the calculation from our analysis.

In the section of Performance of CO oxidation on the catalysts (page 17, middle), we added and revised:

Fig. 4a shows the CO oxidation curves of Pt_{NP}/TiO₂-R, Pt_{Pt-TiISAA+NP}/TiO₂-R, and Pt_{NP}/TiO₂ under a high WHSV of 60000 mL g⁻¹ h⁻¹, utilizing gas mixtures comprising 1 vol% CO and 4 vol% O₂ balanced with N₂. Pt_{Pt-TiISAA+NP}/TiO₂-R exhibited significantly superior catalytic activity for CO oxidation. For Pt_{Pt-TiISAA+NP}/TiO₂-R, the CO conversion was 50% at 106 °C, which is substantially lower by 118 °C and 162 °C than Pt_{NP}/TiO₂-R (T₅₀ = 224 °C) and Pt_{NP}/TiO₂ (T₅₀ = 268 °C), respectively.

For the three catalysts examined, a decrease in the oxygen concentration was observed to correlate with a reduction in CO conversion. The strong correlation between the catalyst activity



and the O_2 concentration is indicative of the L-H mechanism that governs CO oxidation, which is applicable to all three catalysts. Notably, in the case of $Pt_{Pt-TiISAA+NP}/TiO_2-R$, the temperature required for 50% CO conversion rises by 35 °C (from 90 °C to 125 °C) as the oxygen content diminishes from 16% to 1% (Fig. 4b). This increase is significantly less pronounced than that observed for Pt_{NP}/TiO_2-R (110 °C) (Fig. 4c) and Pt_{NP}/TiO_2 (94 °C) (Fig. 4d), which is attributed to the presence of the MvK pathway on $Pt_{Pt-TiISAA+NP}/TiO_2-R$.

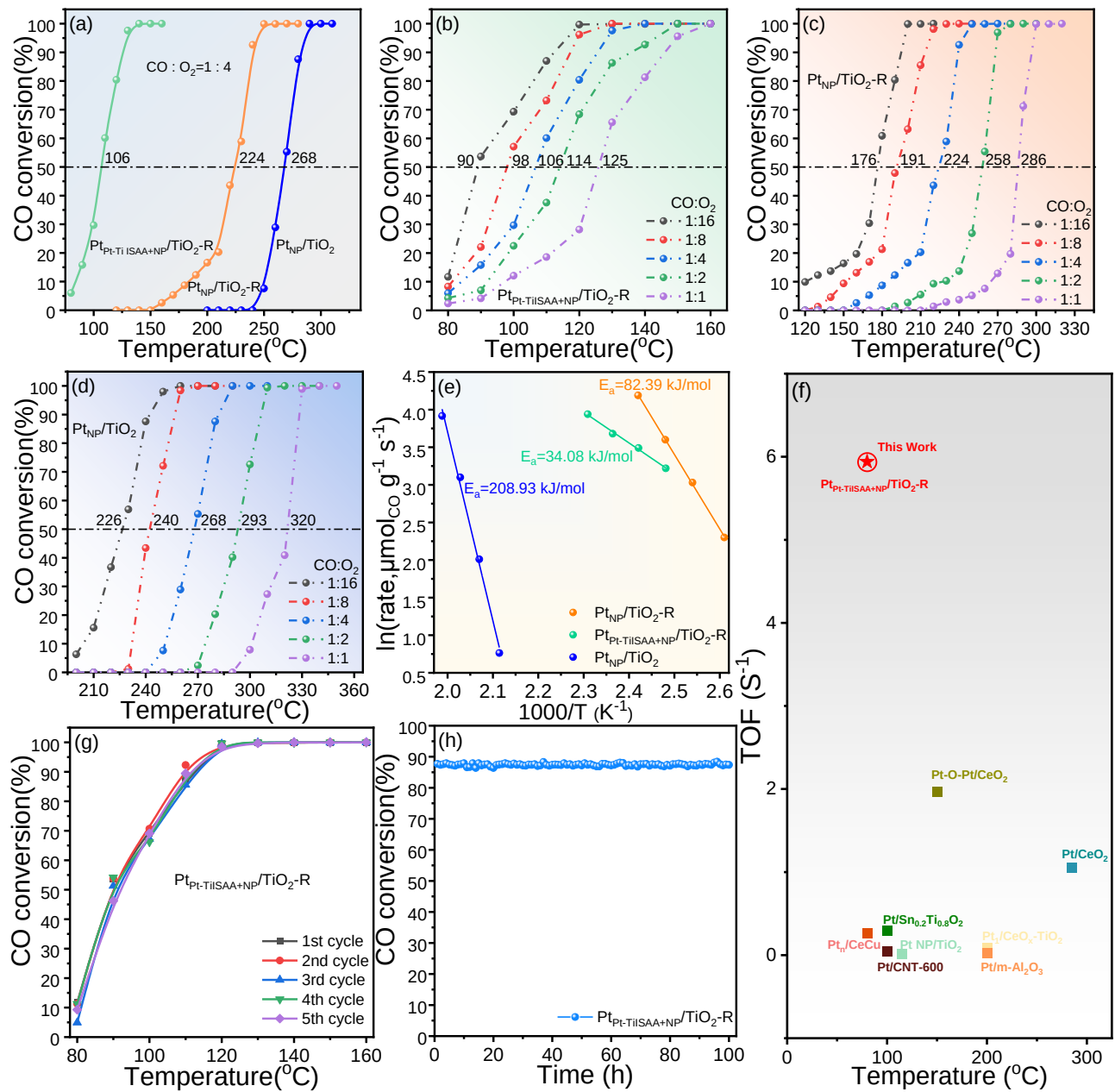


Fig. 4 | (a) CO conversion as a function of reaction temperature over all catalysts. Reaction conditions: 0.4 g of Cat., 1 vol% CO, 4 vol% O_2 , balanced with N_2 ; $v = 400$ mL min⁻¹, GHSV =



60000 mL g⁻¹ h⁻¹, (b) - (d) Activity test on all catalysts with different O₂ concentrations. Reaction conditions: 0.4 g of Cat., $v = 400 \text{ mL min}^{-1}$, GHSV = 60000 mL g⁻¹ h⁻¹, (e) Apparent activation energies (E_a) over different catalysts. (f) In comparison with the catalysts listed in Supplementary Table 2. (g) The cycling test of the CO oxidation activity of Pt_{Pt-TiISAA+NP}/TiO₂-R from 80 to 160 °C. Cyclic CO oxidation reaction condition: 0.4 g of Cat., a gas mix containing 1 vol% CO and 16 vol% O₂ balanced with N₂, $v = 400 \text{ mL min}^{-1}$. (h) A long-term test of Pt_{Pt-TiISAA+NP}/TiO₂-R, (0.4 g of Cat., 110°C, 1 vol% CO, 16 vol% O₂, balanced with N₂; $v = 400 \text{ mL min}^{-1}$, GHSV = 60000 mL g⁻¹ h⁻¹).

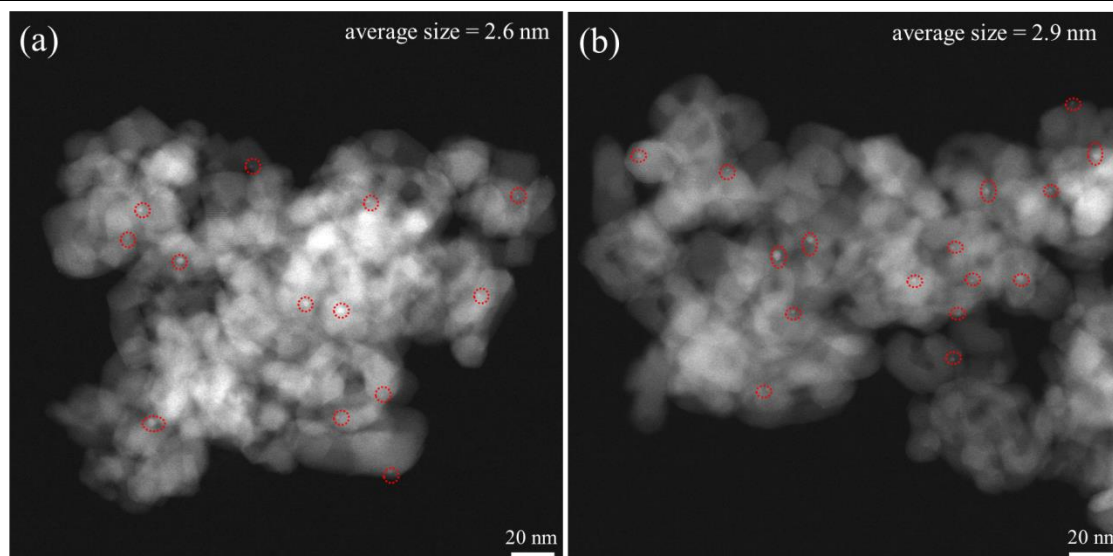
Comment 3: I am pretty sure that Pt NPs in Pt/TiO₂ and Pt/TiO₂-R differ in their average size. The authors may report the size distribution of Pt species and discuss how the size influences the performance.

Response: The authors thank the reviewer for the good comments. For Pt/TiO₂ and Pt/TiO₂-R, the Pt particles were analyzed in a single image. Due to the low Pt loading of 0.15 wt%, the count did not exceed 50 Pt NPs per image. Nevertheless, the observed Pt particles were taken into consideration, yielding average particle sizes of 2.9 and 2.6 nm, respectively. The slight difference in Pt particle sizes in these two catalysts is likely due to the similar anatase structure of the catalyst supports TiO₂ and TiO₂-R.

In the section of Characterization of the Catalysts (page 6, top), we added:

For Pt/TiO₂ and Pt/TiO₂-R, the average Pt particle sizes are very close, which are 2.9 nm and 2.6 nm, respectively (see Supplementary Fig. 17), probably related to the similar anatase structure of the two TiO₂ supports (Supplementary Fig. 4).

In the section of Supporting Information, we added:



Supplementary Fig. 17 | AC-HAADF-STEM images of (a) Pt_{NP}/TiO₂-R and (b) Pt_{NP}/TiO₂.

Comment 4: The light-off profiles of the catalysts show that they differ in catalytic activity. The authors reported the activation energy barrier values and claimed that the one with the lowest barrier works better. The catalyst performance test results part should be revised and enriched. The authors may discuss how the initial vacancy or the difference in the Pt size affects the catalyst performance. The reason why E_a differs in three catalysts should be adequately discussed based on experimental results.

Response: The authors express their sincere thanks to the reviewer for the insightful suggestions. The presence of isolated Pt and Ov, two critical factors, plays a pivotal role in the enhancement of the catalytic performance of the CO catalyst. Additionally, the variation in the E_a among the three catalysts can be attributed to the differing strengths of CO adsorption on the catalyst surfaces, with some showing excessively strong adsorption that impedes subsequent CO activation.

In the section of Performance of CO oxidation on the catalysts (page 17, middle), we added:

Pt_{NP}/TiO₂-R demonstrates superior catalytic performance compared to Pt_{NP}/TiO₂. It is because of the increased concentration of Ov (Fig. 2a), which facilitates more unpaired electron transfer and enhances the adsorption of oxygen molecules. Furthermore, Pt_{Pt-TiSAA+NP}/TiO₂-R exhibits a more significant interaction between the Pt species and the TiO₂ support than observed in Pt_{NP}/TiO₂-R



(Fig. 1i). This interaction leads to modified electronic properties of Pt, which in turn further improve the adsorption and activation of O₂.

As depicted in Fig. 4e, the measured apparent activation energy (E_a) value of CO oxidation for Pt_{NP}/TiO₂-R, Pt_{Pt-TiISAA+NP}/TiO₂-R, and Pt_{NP}/TiO₂ is 82.39, 34.08, and 208.93 kJ mol⁻¹, respectively. The intensity of CO adsorption on the catalyst surface influences the subsequent dissociation of CO and the desorption energy barrier of CO₂, which ultimately leads to the change of the activation energy barrier of CO. CO-TPD analysis reveals that the presence of Pt-Ti ISAA and Ov diminishes CO adsorption (Fig. 2b), thereby reducing the E_a for Pt_{Pt-TiISAA+NP}/TiO₂-R to the lowest value among the catalysts. Density Functional Theory (DFT) calculations will further discuss the activation energy barrier of CO over different catalysts.

Comment 5: I believe that directly comparing the binding energy of the initial binding single molecule does not deduce any scientific insight into the catalytic mechanism or the performance of a model catalyst. The bottom line is that the data presented in Fig 5a to 5d present the available binding sites of CO and O₂ over the catalyst surface. These data are insufficient to state that one of the catalysts preferentially activates the MvK or the LH mechanism. Moreover, all the cases present that Pt (ISAA and NP) preferentially binds CO than O₂, meaning that the surface of all Pt species will be covered with CO under the real reaction conditions. I strongly believe that the CO-covered Pt NPs or ISAA should be the initial model structure before exploring the reaction pathways. A well-demonstrated example can be found in J. Chem. Phys. 2019, 151 (23), 234716.

In general, the MvK mechanism of CO oxidation denotes the interface-mediated oxidation reaction in which lattice oxygen of the oxide support directly oxidizes CO bound to the metal active sites. Of course, removing a lattice oxygen generates a vacancy, and the vacancy binds an O₂ molecule. The extruded O atom of the O₂ molecule again oxidizes the second CO, recovering to the initial structure of the catalyst. Based on the definition of catalysis, the above two parts comprise the MvK mechanism of CO oxidation.

On the other hand, the LH mechanism of CO oxidation by Pt occurs on Pt by utilizing coadsorbed CO and O₂ on Pt surface. Therefore, Pt should bind and activate CO and O₂ together. In



this manner, to study CO oxidation by the LH mechanism at the surface of Pt NPs using DFT calculations, I think well-developed Pt facets, or at least a micro-facet, should be required to compare the CO and O₂ adsorption preferences of the surface active sites of Pt NPs. I am sure that directly comparing the binding energy of the first binding molecules does not give any significant insight into the equilibrium surface concentrations of CO and O₂ under the reaction conditions. From my experience, I think the surface of Pt₁₀ NP will be fully saturated with CO molecules. Coadsorbing CO and O₂ to activate the LH mechanism is energetically prohibited on Pt₁₀ because even the last binding CO will interact more strongly with Pt₁₀ than O₂ at that same site. In this manner, the CO oxidation activity of Pt₁₀ following the MvK mechanism should also be estimated using a fully-CO-saturated Pt₁₀ rather than the model presented in Figure 5.

I think that if a Pt(100) or a Pt(111) facet is developed on the surface of Pt NPs, the surface coverage of CO molecules will be limited to a specific value because of the steric hindrance between CO molecules. The residual open space will bind and dissociate O₂ for CO oxidation by the LH mechanism.

The DFT-calculated initial activation energy barrier (for the first step of the MvK mechanism) is very high. The geometry of ts1 and *CO-O presents why this is the case. I think the first CO oxidation process is misestimated. In general, CO oxidation by the MvK mechanism at the Pt-oxide interface accompanies the formation of a reaction intermediate that can be stabilized at the interface. The process reported in Figure 5e (from *CO to *CO-O) shows that the pre-adsorbed CO is rejected from Pt (desorbed) so that the barrier almost similar to the binding energy is required. I am not sure why the authors claim that the LH mechanism is operative based on Figure 5e. The following statement on page 19 is based on a misunderstanding of the MvK/LH mechanism.

“... oxygen atom from the chemisorbed O₂ molecule at the Ov site can engage with the CO adsorbed on the Pt NP via the L-H mechanism to synthesize CO₂.”

The authors also should report the details of the reaction pathway catalyzed by PtNP/TiO₂.

Response: The authors express gratitude to the reviewer for valuable suggestions. We have implemented the reviewer's advice to reconfigure the DFT calculations and have conducted the two reaction pathways as per the recommendations.



In the section of DFT study on the CO oxidation pathways (page 20, middle), we added and revised:

Based on the nearly identical catalyst structures of $\text{Pt}_{\text{NP}}/\text{TiO}_2\text{-R}$ and $\text{Pt}_{\text{NP}}/\text{TiO}_2$, the main difference being the varying concentrations of oxygen vacancies, and considering the experimental data on different oxygen concentrations, it is clear that these catalysts follow a similar reaction pathway. Consequently, we have selected $\text{Pt}_{\text{NP}}/\text{TiO}_2$ and $\text{Pt}_{\text{Pt-TiISAA+NP}}/\text{TiO}_2\text{-R}$ as model catalysts to calculate the reaction energies for each basic phase of CO oxidation as it occurs along the L-H and MvK pathways on their surfaces, as depicted in Fig. 5 and Supplementary Fig. 38. To align our established DFT computational model more closely with the catalyst structures during actual reactions, we employed a CO-covered NP model to depict the catalyst surface under CO oxidation conditions more accurately. In pursuit of determining the energetically optimal CO and O_2 coverage for the two Pt/TiO₂ models, we assessed the CO binding energy on the Pt NP of $\text{Pt}_{10}/\text{TiO}_2$. Our analysis reveals that within the 8CO saturated adsorption structure, O_2 can effectively compete for adsorption at the ninth Pt site, as its binding energy (E_{bind}) (-1.80 eV) surpasses that of the ninth CO molecule (-1.48 eV), particularly evident in the case of $\text{Pt}_{\text{Pt-TiISAA+NP}}/\text{TiO}_2\text{-R}$. This observation corroborates with previously reported findings⁵⁶. The adsorption energies of O_2 on both catalysts are comparable, measuring -1.80 eV for CO oxidation reactions along the L-H pathway on either catalyst (Fig. 5a). Although the energy barrier for CO_2 formation is marginally higher for $\text{Pt}_{\text{Pt-TiISAA+NP}}/\text{TiO}_2\text{-R}$ compared to $\text{Pt}_{\text{NP}}/\text{TiO}_2$, the critical rate-determining step is the subsequent desorption of CO_2 . Notably, $\text{Pt}_{\text{Pt-TiISAA+NP}}/\text{TiO}_2\text{-R}$ shows a superior capacity for CO_2 desorption, which facilitates easier CO_2 removal and thus facilitates the overall reaction.

In the course of the MvK pathway, the CO adsorption energy of the Pt NP on $\text{Pt}_{\text{Pt-TiISAA+NP}}/\text{TiO}_2\text{-R}$ is -1.48 eV, which is less negative than the -1.80 eV observed for the Pt NP on $\text{Pt}_{\text{NP}}/\text{TiO}_2$ (Fig. 5b). This suggests a reduction in the CO adsorption energy barrier due to the presence of single atoms. This finding aligns with the CO-TPD results. Furthermore, the adsorption energy of the Pt SA on $\text{Pt}_{\text{Pt-TiISAA+NP}}/\text{TiO}_2\text{-R}$ for CO is -2.03 eV, indicating that the Pt SA within the Pt-Ti ISAA configuration possesses the capability to adsorb CO effectively. The rate-determining step on $\text{Pt}_{\text{NP}}/\text{TiO}_2\text{-R}$ is the premier oxidation of CO by surface lattice oxygen,



necessitating overcoming an energy barrier of 1.59 eV. In contrast, for the $\text{Pt}_{\text{Pt-TiSAA+NP}}/\text{TiO}_2\text{-R}$ system, the surface lattice oxygen in proximity to the Pt–Ti ISAA markedly reduces the energy barrier of the initial step to 1.47 eV via oxidation with the CO adsorbed on Pt SA. The activation threshold for the foremost formation of CO_2 on $\text{Pt}_{\text{Pt-TiSAA+NP}}/\text{TiO}_2\text{-R}$ is adequately low, thereby facilitating the reaction at comparatively subdued temperatures, agreeing with the experimental results. This is because Pt substitution instigates lattice deformation, thus reducing the energy barrier for generating oxygen vacancies. For $\text{Pt}_{\text{NP}}/\text{TiO}_2$, the inaugural CO_2 molecule is synthesized through the interaction of CO with the lattice oxygen at the surface. The ensuing desorption of CO_2 gives rise to an oxygen vacancy at the surface, which is subsequently replenished via the adsorption of O_2 . Interestingly, the energy requisite for the secondary CO oxidation reaction on the $\text{Pt}_{\text{NP}}/\text{TiO}_2$ catalyst is 0.98 eV, significantly higher than its counterpart on $\text{Pt}_{\text{Pt-TiSAA+NP}}/\text{TiO}_2\text{-R}$ (0.61 eV). In this step, the extruded O atoms of the O_2 molecules oxidize the second CO again, directly precipitate to form the second CO_2 molecules, and the remaining oxygen atoms fill the oxygen vacancies and restore the initial structure of the catalyst. These findings contribute to a comprehensive understanding of catalytic CO oxidation processes and pave the way for designing improved catalysts for other oxidation reactions.

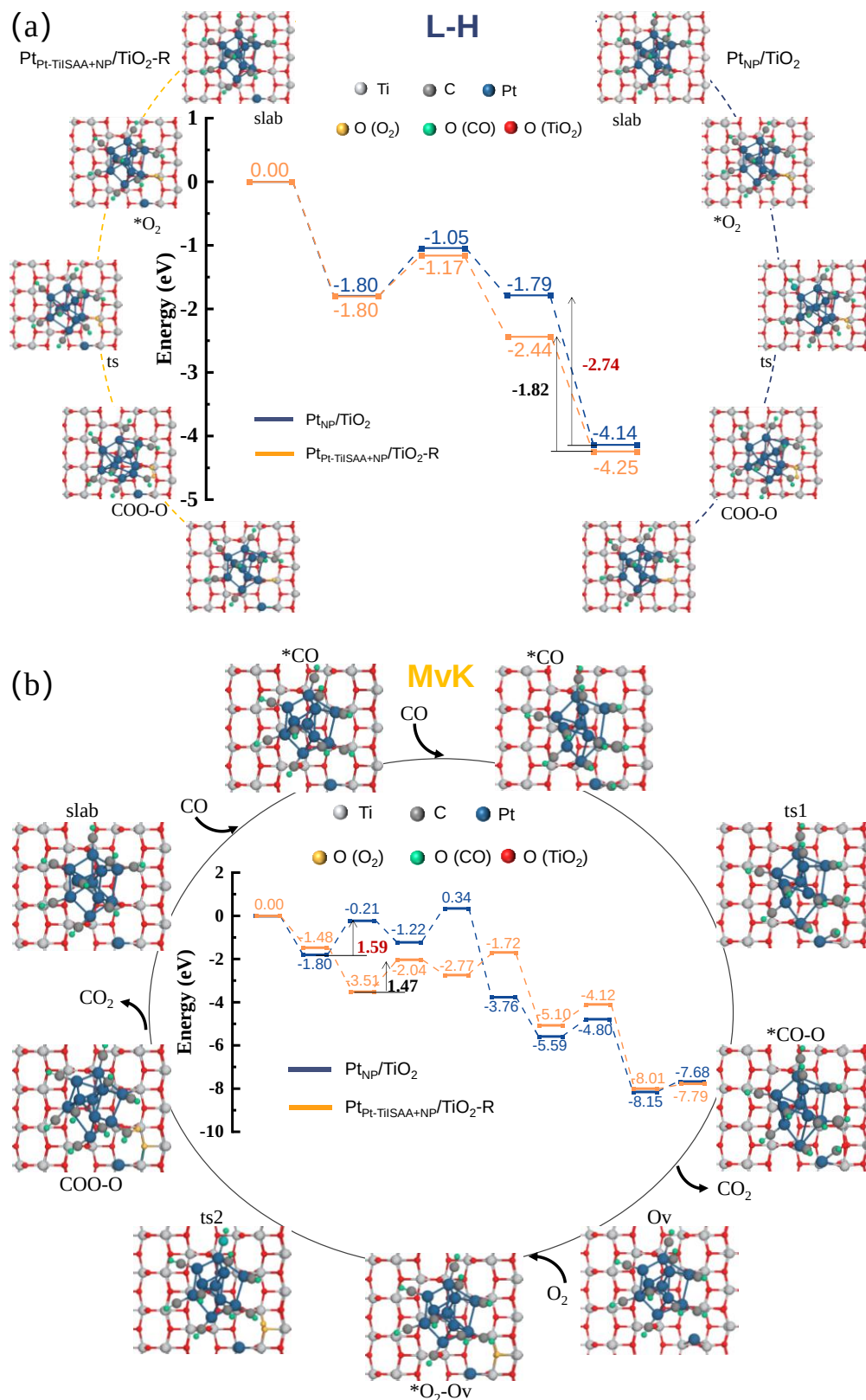


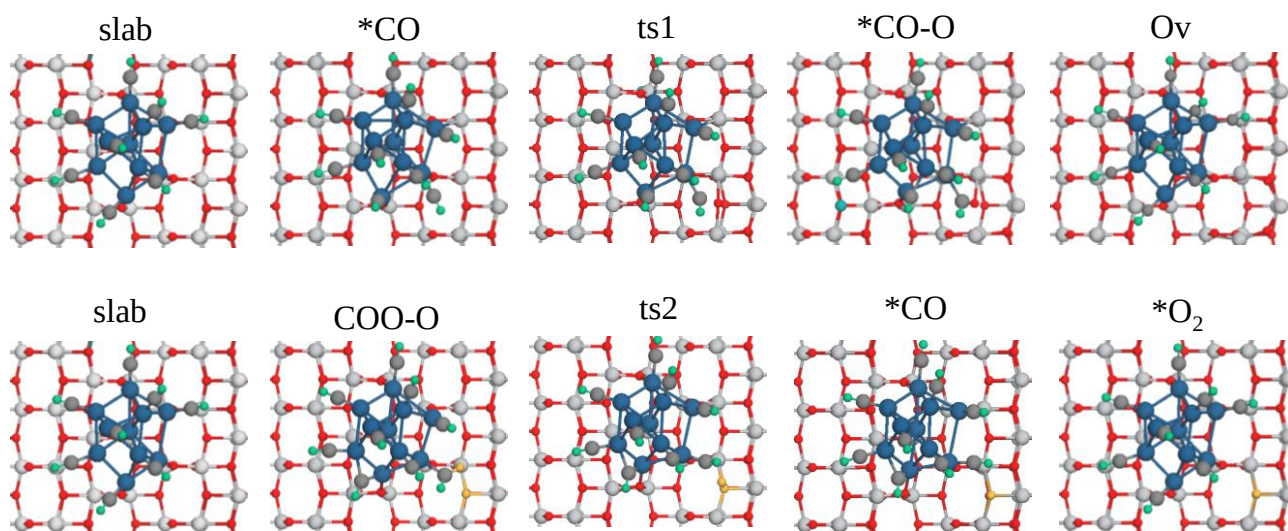
Fig. 5 Scheme of the CO oxidation (a) L-H and (b) MvK mechanisms and computed energies of intermediates and transition states for $\text{Pt}_{\text{Pt-TiISAA+NP}}/\text{TiO}_2\text{-R}$ and $\text{Pt}_{\text{NP}}/\text{TiO}_2$.



In the section of Reference, we added:

56 Oh, S. et al. Oxygen activation on the interface between Pt nanoparticles and mesoporous defective TiO₂ during CO oxidation. *J. Chem. Phys.* **151**, 234716 (2019).

In the section of Supporting Information, we added:



Supplementary Fig. 38 | Intermediates and transition states for Pt_{NP}/TiO₂.

REVIEWERS' COMMENTS

Reviewer #1 (Remarks to the Author):

I think that the authors have replied to all comments and questions in a satisfactory way, and that the manuscript is suitable for publication in Nature Communications.

Minor typo: The space group of CsCl structure is not Pm3m but Pm-3m.

Reviewer #2 (Remarks to the Author):

The authors adequately addressed my concern.

However, Figure 5 should be revised to be more informative and clearer. I recommend denoting the name of each reaction step.



Response to the comments of Reviewer 1

Overall Comment: I think that the authors have replied to all comments and questions in a satisfactory way, and that the manuscript is suitable for publication in Nature Communications.

Response: Authors thank the reviewer for the good comments.

Comment 1: Minor typo: The space group of CsCl structure is not $Pm3m$ but $Pm-3m$.

Response: The authors express gratitude to the reviewer for the valuable suggestion. We are very sorry for these typos, and we have corrected these errors in the revised manuscript.

In the section of Characterization of the Catalysts (page 6, bottom), we revised:

The observed atomic distributions of Pt and Ti in the catalyst surface layer are ascribed to the body-centered cubic (bcc) B_2 structure, which belongs to the CsCl type and the $Pm-3m$ space group.

Response to the comments of Reviewer 2

Overall Comment: The authors adequately addressed my concern.

Response: The authors thank the reviewer for the valuable comment.

Comment 1: However, Figure 5 should be revised to be more informative and clearer. I recommend denoting the name of each reaction step.

Response: The authors thank the reviewer for the good suggestions. In Fig. 5, we have added the name of each reaction step.

In the section of DFT study on the CO oxidation pathways (page 23), we revised:

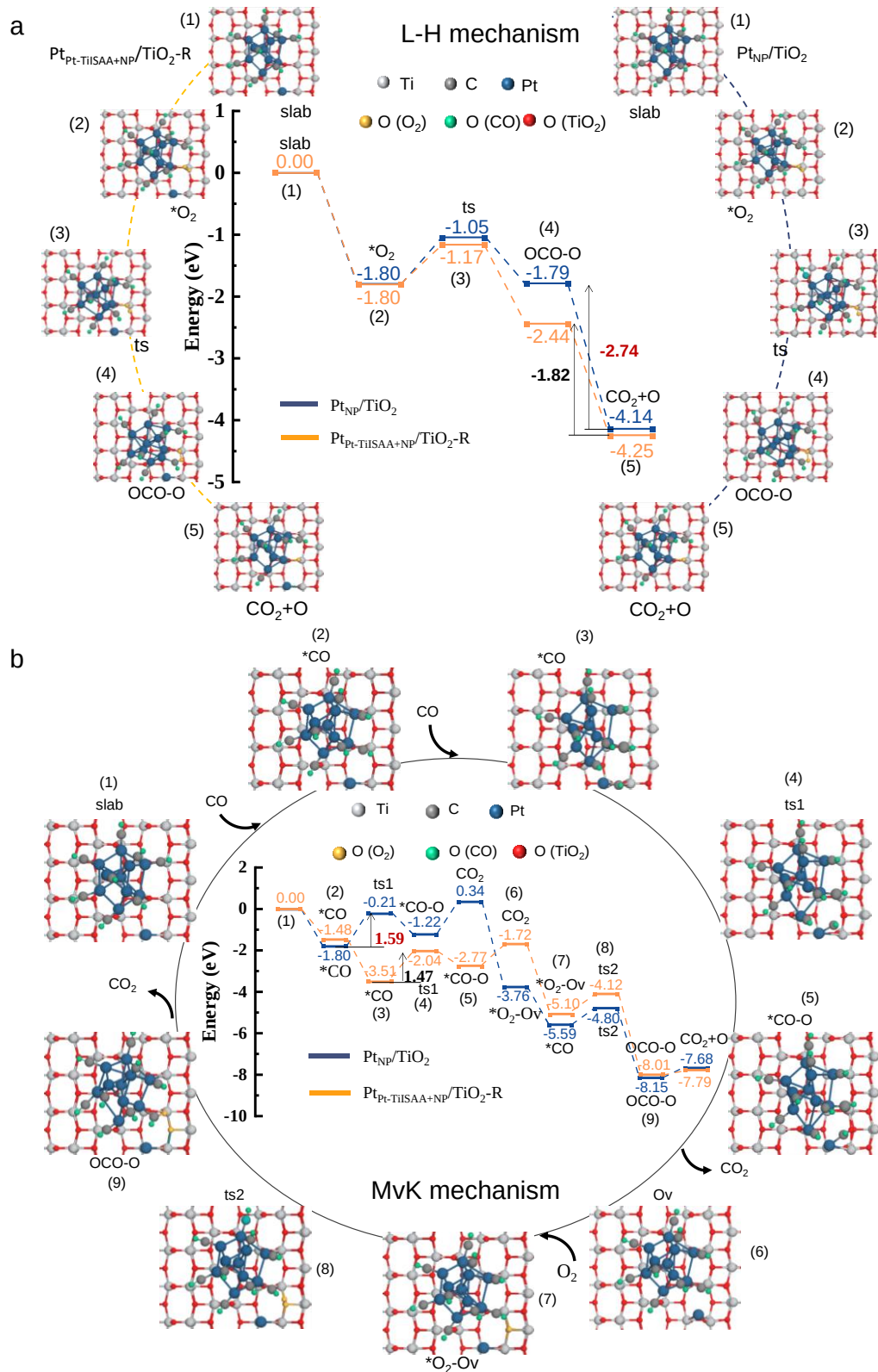


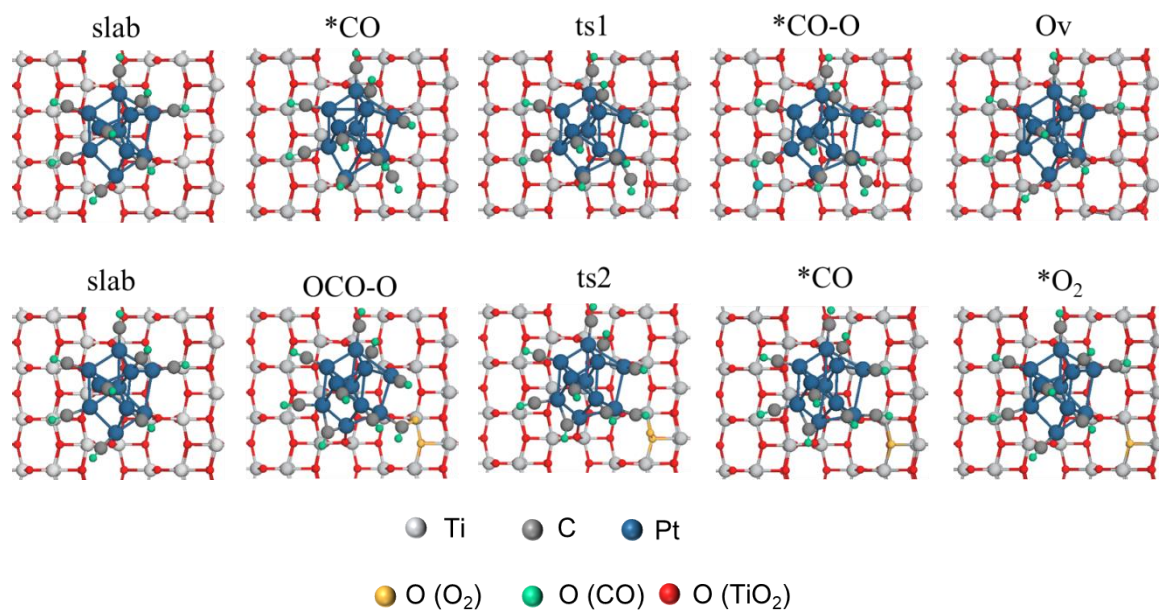
Fig. 5 | DFT calculations on the catalytic mechanism of CO oxidation over Pt_{NP}/TiO₂ and Pt_{Pt-TiISAA+NP}/TiO₂-R. Schematic illustration of the CO oxidation via (a) L-H and (b) MvK



mechanisms and the calculated energies of intermediates and transition states over

Pt_{Pt}-Ti_{ISAA}+NP/TiO₂-R and Pt_{NP}/TiO₂.

In the section of Supporting Information, we revised:



Supplementary Fig. 38 | Intermediates and transition states for Pt_{NP}/TiO₂.