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The complex behavior of the Pd₇ cluster supported on TiO₂(110) during CO oxidation: adsorbate-driven promoting effect

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Using the TiO₂(110)-supported Pd₇ cluster as a model catalyst, we have identified from density functional theory calculations that the dynamics of supported metal nanoparticles, particularly at the sub-nanometer scale, can be complex under reactive environments. Increasing the CO coverage can induce a structural transformation from Pd₇-3D/TiO₂(110) at low coverage to Pd₇-2D/TiO₂(110) at the saturation coverage wherein CO saturation-driven Pd₇-2D/TiO₂(110) structure displays superior CO oxidation activity at the interfacial sites, which are highly active for catalyzing O₂ dissociation and CO oxidation *via* bifunctional synergy.

Metal nanoparticles (NPs) dispersed on a high surface-area support play an essential role in catalyzing many important chemical reactions.¹ In this regard, supported palladium (Pd) NPs have attracted enormous interest owing to their high catalytic activity for CO oxidation,²⁻⁴ which is also known as a benchmark reaction for studying fundamental issues in catalysis science.⁵ Particular attention has been paid to the sub-nanometer Pd clusters (up to 100 atoms) in both gas-phase and supported phase conditions, which are able to catalyze CO oxidation at the temperature of 300 K and below.^{4,6-9} The origin of such high activity has been proposed to be associated with the competing adsorption between CO and O₂, which varies depending on the support and particle size.

Using MgO(100) as a support, both experimental observations and theoretical calculations demonstrated that adsorbed CO molecules could promote adsorption and dissociation of O₂ on Pd_{13,30} clusters rather than block the active sites as on single crystals;¹⁰ in contrast to the case of

Pd₉/MgO, where adsorbed CO would inhibit O₂ dissociation as well as CO oxidation, which preferred to occur under O₂-rich conditions with the formation of Pd oxides.⁹ For Pd₁₋₂₅/TiO₂(110) model catalysts, the formation of reactive oxygen was suggested experimentally as an activated process for all sizes of clusters limiting their CO oxidation activity,⁴ while the observed activity from Pd₅/TiO₂(110) was not predicted theoretically due to the strong adsorption of CO and atomic O.¹¹ This disagreement is likely due to the lack of consideration of CO coverage effect in the modeling. According to our previous density functional theory (DFT) study on Pd₇/TiO₂,¹² one of the active catalysts for CO oxidation,⁴ strong CO–Pd binding, leads to not only the CO accumulation up to ~0.6 monolayer (ML) consistent with the experimental observations,¹³ but also the structural transformation of Pd₇ cluster from the 3D-bi-pyramidal to the 2D-hexagonal conformation as a result of the interplay between strong CO–Pd and Pd–TiO₂ interactions.¹²

Herein, we extend our previous study by investigating CO oxidation on a Pd₇/TiO₂(110) model catalyst. Our main focus is the comparative behavior of the Pd₇ sites and the Pd₇/TiO₂ interfacial sites, which have been previously reported to be active for the CO oxidation reaction.^{14–16} The key questions to be addressed include: (1) What are the structures of Pd₇/TiO₂(110) likely to be during CO oxidation? (2) What are the active sites? (3) How do CO and O₂ compete for the active sites? (4) How does the coverage of adsorbates influence the binding property and thereby the catalytic activity of Pd₇/TiO₂(110)? Our results highlight the importance of considering more realistic conditions for better describing the catalytic behavior of supported sub-nanometer clusters.

CO oxidation on Pd₇/TiO₂(110) was investigated under two different situations. One is on a clean surface, where the Pd₇ cluster adopts a bi-pyramidal cage-like structure (Fig. 1). A CO molecule is strongly adsorbed at a Pd 3-fold hollow site with adsorption energy (E_{ads}) of –2.15 eV, larger than that (–1.82 eV) on Pd(111).¹⁷ This is associated with the up-shift (0.30 eV) of the Pd 4d band center with respect to that of Pd(111),¹² which accordingly promotes the electron back-donation from Pd 4d orbitals to the CO 2 π^* anti-bonding orbital.¹⁸ The CO adsorption induces a slight distortion of the Pd₇ cluster, yet the 3D structure is mostly sustained.^{12,19} The other is on CO-saturated Pd₇/TiO₂(110), where four CO molecules are adsorbed at the hollow and bridge sites of Pd₇. As a consequence, the 3D structure of Pd₇ cannot be maintained, but rather is transformed into a 2D-like structure (Fig. 1). With the increase of CO coverage, the Pd

d-band center of supported Pd₇ is shifted down below that of Pd(111) until CO is saturated. Thus, the adsorption of 5th CO is not favored and only benefits in energy as low as −1.29 eV against the average energy of −2.26 eV for first four CO molecules.¹² Note also that the Pd 4d-band center of TiO₂(110)-supported Pd₇ is relatively insensitive to addition of up to three CO molecules, then is shifted downward as CO coverage is increased, passing through the value for Pd(111) and eventually toward that of PdO.¹²

Fig. 1 Optimized structures for CO and O₂ adsorption on the TiO₂(110)-supported Pd₇-3D and -2D clusters. O–O bond length labeled in Å.

On clean Pd₇/TiO₂(110) (Fig. 1), O₂ does not compete with CO for the adsorption sites, preferring to bind at the interface *via* the η²(O,O)μ³(Pd,Pd,Ti)-tri-σ-configuration ($E_{\text{ads}} = -1.97$ eV) with O–O bond perpendicular to the surface of TiO₂(110), rather than at the Pd sites of the Pd₇-3D cluster *via* the η²(O,O)μ²(Pd,Pd)-di-σ-configuration ($E_{\text{ads}} = -1.38$ eV). The former adsorption mode is similar to that obtained at the interface of the Au cluster/TiO₂(110),^{20,21} but is much more activated with a O–O bond length (d) of 1.4 Å ($d = 1.2$ Å for gas-phase O₂) and therefore, the O₂ dissociation is most likely to proceed readily.

For CO oxidation on metal NPs/TiO₂ systems, the Langmuir–Hinshelwood mechanism is often suggested, where O–O bond cleavage is *via* either direct O₂ dissociation or OO–CO-like intermediate.^{14–16} In our case, CO and O₂ prefer to adsorb at separate sites (Fig. 1), which are not close enough in space to form the OO–CO intermediate. Accordingly, O₂ adsorption at the Pd₇-3D/TiO₂(110) interface was considered in the presence of adsorbed CO(*CO) at the stable Pd hollow sites of Pd₇. In Fig. 2, O₂ is activated upon binding at the Pd–Ti(O₂) interface with a binding energy of −2.18 eV, higher than that (−1.97 eV) on clean Pd₇-3D/TiO₂(110). The O–O bond is stretched by 0.21 Å with respect to that in the gas-phase. The enhanced activation is

partially due to electron withdrawal from both the Pd 4d electron and the Ti^{3+} 3d electron to O_2 π_{2p}^* antibonding orbitals. Our Bader charge calculations on adsorbed O_2 show that the net charge on $^*\text{O}(\text{-Ti})$ and $^*\text{O}(\text{-Pd})$ at the interface of CO pre-adsorbed $\text{Pd}_7/\text{TiO}_2(110)$ is $-0.50 e^-$ and $-0.42 e^-$ respectively, against those ($-0.49 e^-$ and $-0.38 e^-$) on clean $\text{Pd}_7/\text{TiO}_2(110)$. Our calculations also show that $^*\text{CO}$ induces the down-shift in the Pd d-band center by 0.17 eV compared to that without $^*\text{CO}$ and accordingly, $\text{Pd-}^*\text{O}_2$ interaction should be weakened; however, $\text{Pd}_7\text{-3D}$ structure is also destabilized as a result of adsorbed $^*\text{CO}$.¹² Therefore, the interfacial Pd atoms are more flexible that are able to interact with $^*\text{O}_2$ considerably. As a consequence, $^*\text{O}_2$ -induced structural distortion in $\text{Pd}_7\text{-3D}$ is more significant in the presence of $^*\text{CO}$ (Fig. 2) than that without $^*\text{CO}$ (Fig. 1). Moreover, O_2 dissociation is slightly exothermic with a reaction energy (ΔE) of -0.19 eV and a negligible activation barrier (E_a) of 0.08 eV, where the dissociated $^*\text{O}$ atoms are adsorbed at the bridge sites of Pd–Ti and Pd–Pd respectively. That is to say, the bifunctional synergy of interfacial sites is able to greatly facilitate O_2 activation.

Fig. 2 Potential energy profile for CO oxidation on $\text{Pd}_7\text{-3D}/\text{TiO}_2(110)$. Bond lengths were labeled in Å. 0 eV refers to the total energy of the gas-phase $\text{CO} + \text{O}_2$ plus slab.

CO oxidation by dissociated $^*\text{O}$ on $\text{Pd}_7\text{-3D}/\text{TiO}_2(110)$ encounters an activation barrier of 1.01 eV with exothermic ΔE of -1.22 eV (Fig. 2). The transition state (TS) corresponds to the conformation in which $^*\text{O}$ at Pd–Pd bridge site approaches to $^*\text{CO}$ pre-adsorbed at the Pd 3-fold hollow site as a result of space separation (Fig. 2). It indicates that the strongly bound $^*\text{O}$ at Pd

sites essentially hinders the CO₂ formation, a manifestation of the Sabatier principle. Although *CO is stable on Pd₇-3D/TiO₂(110), the binding of *O at vicinal site can make a big difference in CO oxidation. The structure of TS and its energetics are close to those obtained from the graphene-supported Pd₇-3D cluster ($E_a = 0.67$ eV)²² and from the Pd₆O₄⁺ cluster ($E_a = 1.22$ eV),⁶ but in stark contrast to those obtained from larger-size metal clusters ($n > 10$) supported on oxide, where the adsorbed *CO is able to directly interact with the activated O₂ at the interface *via* the OO–CO intermediate.^{20,21,23,24} We speculate such a discrepancy may be attributed to the limited number of active sites available and the high structural flexibility of such small clusters. By comparison, CO oxidation solely at the Pd sites is unlikely in that O₂ adsorption at Pd–Pd bridge site of the supported Pd₇ cluster ($E_{\text{ads}} = -0.66$ eV, Fig. S1a, ESI[†]) is much less stable than that at the interface ($E_{\text{ads}} = -2.18$ eV) due to the repulsive interaction with *CO, and therefore, the O–O activation *via* the OO–CO intermediate is not plausible despite a similar barrier ($E_{\text{ads}} = 0.99$ eV, Fig. S1a, ESI[†]).

As CO predominantly occupies Pd sites and is adsorbed more strongly than O₂, the Pd₇ cluster of Pd₇/TiO₂(110) is more likely to be saturated by CO under typical CO oxidation conditions. Our previous study¹² showed that the saturation coverage of *CO on Pd₇/TiO₂(110) are four CO molecules per Pd₇ cluster. Such a model is hereby employed to describe the CO-saturated Pd₇/TiO₂(110). As shown in Fig. 1, upon adsorption of four CO molecules, Pd₇-3D → Pd₇-2D structural transformation occurs, where all Pd atoms strongly interact with TiO₂(110) *via* Pd–O bonds (see Fig. 3). Such a structural transformation allows the sequential binding energy of *CO of 4/7 ML coverage to stay the same (–2.15 eV) as that of 1/7 ML coverage on Pd₇-3D/TiO₂(110);¹² however, the binding strength of *O₂ is lowered ($E_{\text{ads}} = -0.90$ eV), and O–O bond is shortened ($d = 1.38$ Å), even that the interfacial sites are still preferred (Fig. 3). The decreased binding can be attributed to the further down-shifted Pd d-band center by 0.57 eV induced by CO saturation¹² and to the quenching of Pd free-bonding due to the formation of Pd–O bonds from TiO₂(110). In addition, the transformation to the 2D-Pd₇ structure lowers the flexibility of interfacial Pd atoms, and hence no obvious structural distortion is observed upon O₂ adsorption (Fig. 3). Overall, the decrease in the binding strength of *O₂ follows the down-shift of the Pd d-band center in this case.

Fig. 3 Potential energy profile for CO oxidation at the interface of CO-saturated Pd₇-2D/TiO₂(110). 0 eV refers to total energy of CO-adsorbed slab plus gas-phase O₂.

Despite the weaker binding of *O₂ on Pd₇-2D/TiO₂(110), O–O bond cleavage at the interface is facile ($E_a = 0.04$ eV, [Fig. 3](#)). The facile O₂ activation is associated with the unique structural motif of CO-saturated Pd₇-2D/TiO₂(110), which enables a superoxide-like TS with O–O bond parallel to the surface of TiO₂(110), rather than perpendicular to the surface as initial configuration of adsorbed *O₂. Such conformation can be effectively stabilized by the synergy of interfacial Pd and Ti^{δ+} sites ([Fig. 3](#)). This is however not the case for Pd₇-3D/TiO₂(110), where TS maintains the perpendicular orientation of O–O and one of O atoms sits on the top site of Pd₇ ([Fig. S1b](#), [ESI†](#)). More importantly, once the O–O bond is cleaved, the remaining elementary steps are not activated as in the case of Pd₇-3D/TiO₂(110), but rather going downhill. One of dissociated *O atoms approaches a vicinal *CO at the Pd hollow site forming stable *CO₂ ([Fig. 3](#)). In comparison, CO oxidation is unlikely to occur solely on Pd sites of CO-saturated Pd₇-2D/TiO₂(110) ($E_a = 1.42$ eV, [Fig. S1c](#), [ESI†](#)), where *O₂ is very weakly bound at Pd sites by ~1 eV and cannot compete with the interfacial sites.

From above, three key factors are identified that can influence CO oxidation activity: (1) CO coverage. It is apparent that CO coverage on Pd₇/TiO₂(110) has a substantial impact on the structural change of the Pd₇-cluster, the metal–support interaction, binding property and thereby

catalytic performance. The structural transformation occurs from Pd₇-3D/TiO₂(110) at low CO coverage to Pd₇-2D/TiO₂(110) at the saturation coverage. CO oxidation on Pd₇-3D/TiO₂(110) starts with a facile O–O bond cleavage, but is hindered by the activated removal of *CO due to the strong *O–Pd interaction. Consequently, the most difficult step is the diffusion of *O forming highly active *O at Pd atop, which can readily interact with *CO at an adjacent Pd site (Fig. 2). The unique Pd₇-2D/TiO₂(110) structure driven by CO saturation promotes CO oxidation significantly. On one hand, O–O bond scission of *O₂ remains facile, while effectively stabilizing the corresponding TS; on the other hand, the saturation of *CO prevents the difficult diffusion of *O and enables a facile O–CO bond formation towards CO₂. (2) Interfacial sites. It is certain that interfacial sites are highly active for O₂ dissociation on either Pd₇-3D/TiO₂(110) or Pd₇-2D/TiO₂(110). In particular, CO-saturated Pd₇-2D/TiO₂(110) enables a superoxide-like TS for O₂ dissociation, making the reaction as fast as that on Pd₇-3D/TiO₂(110) in spite of weaker binding with *O₂. (3) Bifunctional synergy. Independent of CO coverage, CO oxidation proceeds *via* CO adsorption at Pd site and O₂ activation at the interfacial Pd–Ti^{δ+} site, where *O approach to *CO forming CO₂. As such, CO oxidation is much faster than that solely on Pd sites. The synergy between Pd and Ti^{δ+} sites at the interface prevents the competition between CO and O₂ adsorption, while promotes the O–O bond scission of *O₂ and O–CO bond formation, in particular, on CO-saturated Pd₇-2D/TiO₂(110). Our results demonstrate that the dynamics of supported NPs, especially at the sub-nanometer scale, can be complex under reactive environments. The nanostructures can be flexible that allows the adsorbate-driven structural changes ranging from distortion in local arrangement,^{19,25} NP shape transformation as shown here, to phase transformation,²⁶ under reaction conditions which can greatly affect the catalytic performance of a catalyst.

In conclusion, we employed DFT calculations to investigate the detailed Langmuir–Hinshelwood mechanism of CO oxidation on the TiO₂(110)-supported Pd₇ cluster. The significant effect of CO coverage observed is that with the increase of CO coverage, the structural transformation occurs from Pd₇-3D/TiO₂(110) at low coverage to Pd₇-2D/TiO₂(110) at the saturation coverage. Moreover, CO saturation-driven Pd₇-2D/TiO₂(110) structure displays a much higher CO oxidation activity than Pd₇-3D/TiO₂(110), wherein the interfacial sites are highly active for catalyzing O₂ dissociation and CO oxidation *via* bifunctional synergy. Our

study provides a fine example for the adsorbate-driven promoting effect of the catalytic activity at the interface of supported metal nanoparticles.

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