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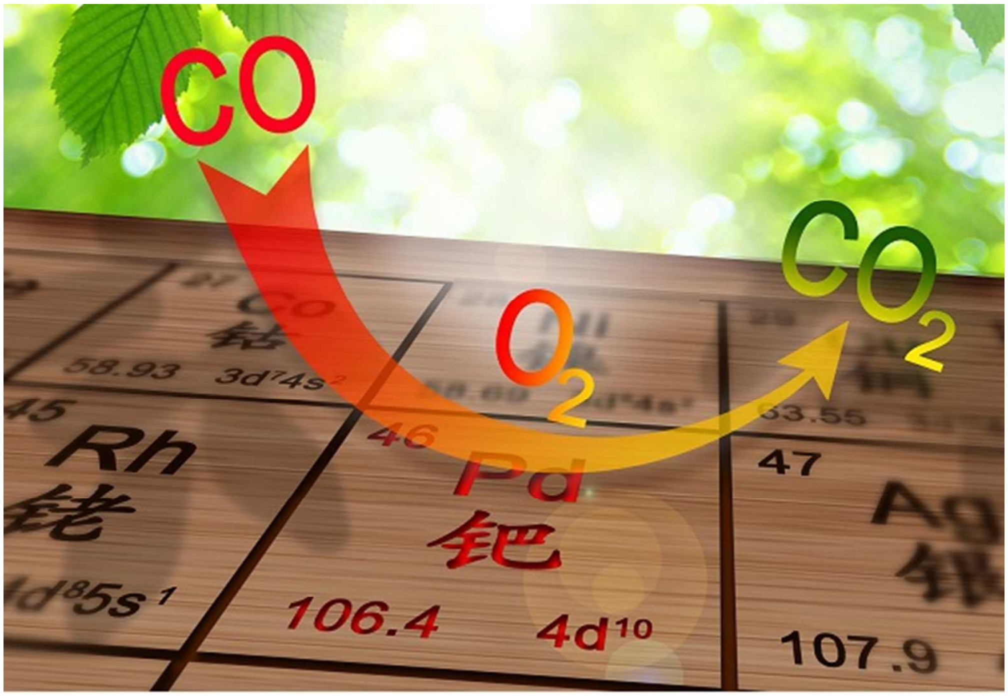

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ARTICLE TYPE

Perspective on CO oxidation over Pd-based catalysts

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CO oxidation is one of the most extensively investigated reactions in the field of heterogeneous catalysis because of its importance in both environmental protection and fundamental study. CO oxidation over Pd catalysts has attracted significant attentions not only because of their high activity. It is an excellent model reaction for the study of structure, metal-support interaction and other issues of various Pd based catalysts with many important applications beyond CO oxidation. It is simple and can be easily operated with low cost. Density functional theoretical study can be directly and easily combined with experimental investigations. Carbon monoxide itself is an excellent probe molecule for the catalyst characterization. In this perspective, we summarize the progress in the study of CO oxidation over Pd based catalysts. Various influencing factors will be discussed. Future challenges and opportunities will be addressed.

Introduction

CO oxidation is one of the most extensively investigated reactions in the field of heterogeneous catalysis because of its importance in both environmental protection and fundamental study.[1-8] According to the Web of Science (SCIE), 5498 papers have been published since 1995 (by the date of Sept. 10, 2014) with the title of 'CO oxidation'. These papers have attracted 97837 citations (19.87 citations per article). This is definitely a hot topic on such a simple molecule. [9-13]

Carbon monoxide or CO is a colourless, odourless but poisonous and even deadly gas. It is produced from the incomplete burning or partial oxidation of various fuels like coal, gasoline and natural gas. Some specific cases like CO_2 laser also generate CO. It is very necessary to remove CO from enclosed atmospheres and various residue gases. In addition, even trace CO is harmful to the Pt catalyst with applications like fuel cells. The purification of feed gases for these applications is of course mandatory.

From the aspect of fundamental studies, CO is exactly a frequently used probe molecule for studies of catalyst structure, adsorption/desorption and reaction mechanism. With the potential competitive adsorption and activation of oxygen, CO oxidation is an excellent reaction for the evaluation of catalysts with easy operation and low cost.

Catalysts for CO oxidation can be grouped into two main categories: non noble metal catalysts and supported noble metal catalysts. Non noble metal catalysts mainly include copper, cobalt, manganese based catalysts and their mixtures. The commercial Hopcalite catalyst, in which CuO and MnO_2 are principal components, is the representative of the samples.[14] In addition, the supported Cu catalyst has also been widely studied.[15-16] CuO can be highly dispersed on CeO_2, ZnO and Al_2O_3 with intense interaction. For example, Pillai *et al.*[17] prepared 60%CuO-40%ZnO catalyst by co-precipitation and aging treatment, which can complete the oxidation of CO into CO_2 at room temperature. They found that, CuO can be diluted by ZnO, and the surface morphology of CuO can be changed, resulting in an amorphous phase. It promotes the formation of more weakly adsorbed CO on the surface of the catalyst, and the evolution of active copper oxide species (CuO_x). Although non noble metal catalysts are cheap, they have some disadvantages that cannot be ignored. The activity is still not high in general. They are normally sensitive to H_2O.

Supported noble metal catalysts, especially Pt, Pd, Au and Ru based samples (and their mixtures as bi-metal or tri-metal catalysts), have been extensively studied for CO oxidation.[18-21] Among them, Au catalysts always exhibit excellent activity at lower temperatures, while Pd and Pt catalysts have higher turnover frequencies at relatively high temperature (no less than 100 ^oC). Normally, the adsorption of CO on Pd and Pt sites is very strong and almost exclusive at low temperature, leaving O_2 no active sites for activation. As temperature rise, O_2 adsorption and activation occur, then the reaction rate of CO oxidation increases. Therefore, over Pd and Pt catalysts, CO oxidation always proceeds in a competitive Langmuir-Hinshelwood mechanism with high apparent activation energies (E_a). Considering low activity of Pt catalysts, Pd based catalysts have drawn much more attention for their high activity and application for the interpretation of the metal-support interaction.

The property of Pd catalysts is influenced by many factors, such as promoters, preparation methods, supports, Pd structure, and so on. In this perspective, we attempt to summarize the studies on the influencing factors on CO oxidation over Pd-based catalysts. The future development will be discussed at the end of the article.

Effects of additives

As a promoter, ceria can improve the dispersion of the noble metal and the ability of oxygen storage and releasing. It can thereby enhance the activity of CO oxidation. As for Pd catalysts, CeO_2 is mostly applied as a support, for the specific metal-support interaction that allows synergistic oxidation/reduction of both the metal and CeO_2, and favours the catalytic performance.[22-25] Apart from ceria, many other species can also be used as additives to promote the performance of Pd catalysts in CO oxidation.

The addition of Zn to Pd catalysts can lower the binding energy of CO, which will be beneficial for CO oxidation. Even submonolayer quantities of Zn deposited onto Pd catalysts will change the CO binding energy, and the increased coverage brings more pronounced influence. Johnson *et al.*[26] reported PdZn bimetallic nanoparticles that are homogeneous in both phase and composition. The aerosol derived bimetallic samples were used to investigate the effect of the reduced binding energy of CO on Zn-modified Pd catalysts for CO oxidation. The activities of the Pd metal (fcc structure), α-PdZn (Zn solid solution in fcc Pd) and β-PdZn (50:50 intermetallic PdZn) powder samples were compared, as shown in Fig. 1. It was found that the initial CO oxidation reactivity (per Pd surface atom) is as much as 10 times higher on the α-PdZn surface and about 5 times higher on the β-PdZn surface, compared to metallic Pd. The weakening of the CO bond and easier binding of oxygen to Pd sites modified by Zn was considered as the reason for the higher reactivity. However, most of the initial CO oxidation enhancement is lost once the steady state is achieved, which is presumably caused by the disruption of the Zn-Pd interaction after the oxidation of Zn. Obviously, the addition of oxophilic metals such as Zn can modify the reactivity of Pd catalysts. It is important to prevent the oxidation of the oxophilic component in order to achieve stable high activities.

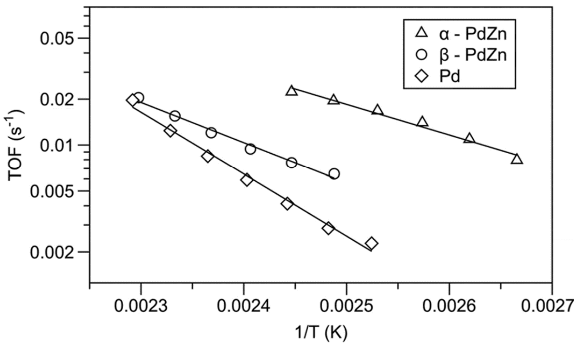


Fig. 1 Arrhenius plots for CO oxidation on Pd, α and β PdZn catalysts. [26]

Alkaline earth metals are also common additives for improving the activity of Pd based catalysts. Tanikawa and Egawa prepared barium fixed alumina (Pd/Ba/Al) and ceria-zirconia mixed oxide (Pd/Ba/CZ) supported Pd catalysts, and investigated the effect of barium on CO oxidation over these two catalysts.[27] As shown in Fig. 2, the properties of the support possess a significant influence on the barium addition. For the Pd/Ba/Al catalysts, the increasing barium loading gradually improves the CO oxidation activity. For the Pd/Ba/CZ catalysts, however, the presence of barium reduces the activity for CO oxidation. The higher barium loading causes lower activity. It was proposed that the CZ support could enhance the activation of oxygen at surface anion vacancies that are important for CO oxidation. When barium is added, the contact between Pd particles and CZ support may be prevented, and the oxygen supply from CZ to Pd would be inhibited, which results in the reducing activity of Pd/Ba/CZ for CO oxidation. Considering the results of XPS and DRIFT spectra, they concluded that the adsorption strength of CO on palladium could be weakened by barium in Pd/Ba/Al, while in Pd/Ba/CZ the oxygen mobility from CZ to palladium is inhibited by barium.

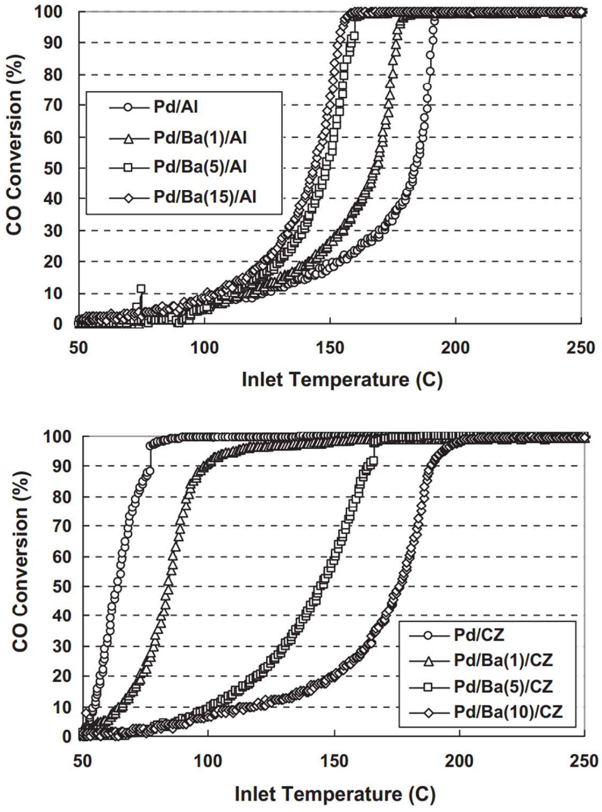


Fig. 2 CO conversion in CO oxidation as a function of the amount of Ba loading for (up) Pd/Ba/Al catalysts and (down) Pd/Ba/CZ catalysts. Reproduced with permission from ref. 27. Copyright 2011, Elsevier.

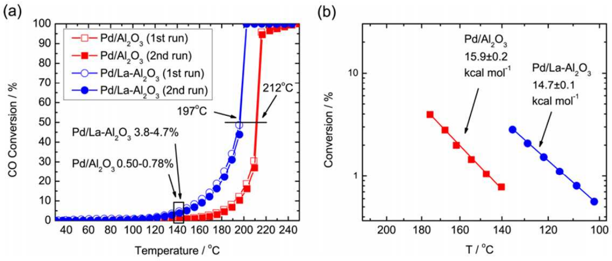
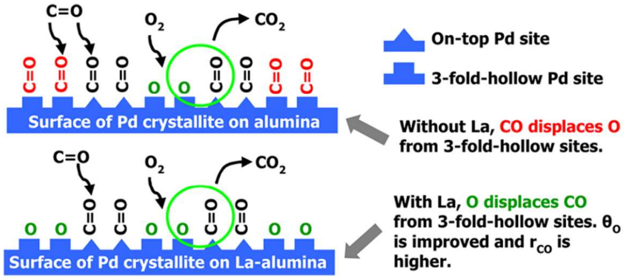


Fig. 3 (a) Light-off traces of 2.5% Pd/La-Al_2O_3 and 2.5% Pd/Al_2O_3 and (b) associated Arrhenius plot. Reproduced with permission from ref. 28. Copyright 2013, American Chemical Society.

Additives in the support can also lead to better performance for the supported Pd catalysts. In Gaudet's work, they found that the La-stabilized alumina improves the dispersion of Pd particles.[28] To investigate the role of the La-stabilized alumina support in the CO oxidation, they prepared 2.5% Pd/Al_2O_3 and 2.5% $Pd/La\text{-}Al_2O_3$, and found that the La-containing catalyst has higher CO conversion and lower onset temperature for CO oxidation. As shown in Fig. 3(a), the 2.5% $Pd/La\text{-}Al_2O_3$ sample is much more active for CO oxidation. Calculated from the data in Fig. 3(b), the apparent activation energies (E_A) are 16 kcal mol^{-1} for Pd/Al_2O_3 and 15 kcal mol^{-1} for $Pd/La\text{-}Al_2O_3$, respectively. What's more, the results of STEM and EXAFS analyses indicate that the addition of La increases not only Pd dispersion but also TOF, indicating that the factors that cause increased CO oxidation rate are other than improved dispersion. Further study shows that the presence of La is helpful for increasing the preference of oxygen adsorption. As shown in Scheme 1, for $Pd/La\text{-}Al_2O_3$, O could displace CO from 3-fold hollow sites, resulting in improved O coverage and higher TOF. Meanwhile, a bulk oxide or a passivation layer, which might deactivate the catalyst, would not form. The authors believe that the La species helps to modify the nucleation of Pd. The resulting smaller Pd clusters exhibit facile redox behaviour at low temperatures, which are less susceptible to poisoning by CO.



Scheme 1 CO oxidation on Pd/Al_2O_3 and $Pd/La\text{-}Al_2O_3$. Reproduced with permission from ref. 28. Copyright 2013, American Chemical Society.

In diesel applications, Pd-Pt bi-metal catalyst is more active than either alone. The synergistic effect between Pd and Pt is useful to weaken the adsorption of CO, which is helpful for improving the activity in low-temperature CO oxidation. We prepared Pd/MIL-101 and Pt-Pd/MIL-101 catalysts by impregnation method and electron reduction. For the bi-metal sample, Pd was loaded and reduced firstly, then Pt was added subsequently. As shown in Fig. 4, the Pt-Pd/MIL-101 sample exhibits much higher activity. From the results of DRIFT in Fig. 5, we found that the CO molecules are strongly absorbed on the Pd sites in the Pd/MIL-101 sample. Meanwhile, CO_2 and the formate species also keep strong interaction with the sample. It could be concluded that Pd/MIL-101 could strongly adsorb the carbon species, leading to the low efficiency of the active sites. As for Pt-Pd/MIL-101, the Pt adding significantly changes the adsorption properties of the sample. Comparing with Pd/MIL-101, the bands of the carbon species for the Pt-Pd/MIL-101 sample are much weaker. It indicates that, the interaction between Pt and Pd could weaken the adsorption capacity of the metal particles for carbon species. To further investigate the reason for better CO oxidation activity of Pt-Pd/MIL-101, we carried out CO-TPD on the two samples. As shown in Fig. 6, there are two distinct CO desorption peaks in the CO-TPD profiles, for both the two samples. Peak α, which is centred at 76°C for Pd/MIL-101 and 85°C for Pt-Pd/MIL-101, is attributed to the weakly adsorbed CO species. Although these CO species are not active for CO oxidation, they compete with O_2 to adsorb on the active sites in the low temperature region, resulting in poor reactive oxygen species as well as low activity of the samples. Peak β, centred at 262°C for both the samples, is assigned to the moderately adsorbed CO species on the samples, which plays the key role in CO oxidation. Obviously, peak β of Pt-Pd/MIL-101 has stronger intensity and larger area than that of Pd/MIL-101, which indicates that there are more active CO species adsorbed on the Pt-Pd/MIL-101 sample. The desorption of CO species in peak β part for Pt-Pd/MIL-101 starts at much lower temperature than that for Pd/MIL-101, which might count for the better activity of the bimetallic catalyst.

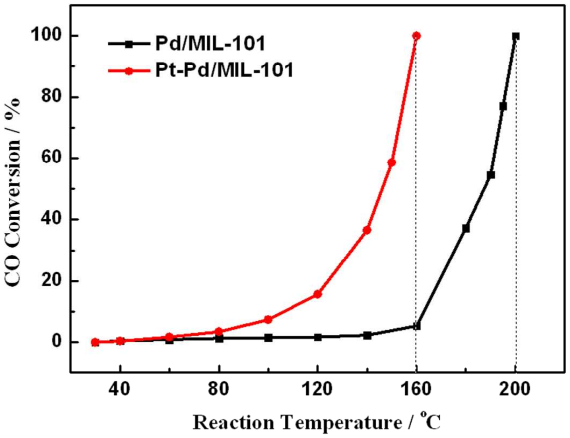


Fig. 4 Results of CO oxidation on Pd/MIL-101 (Pd 5%, 10 mg) and Pt-Pd/MIL-101 (Pd 1.8%, Pt 3.2%, 10 mg)

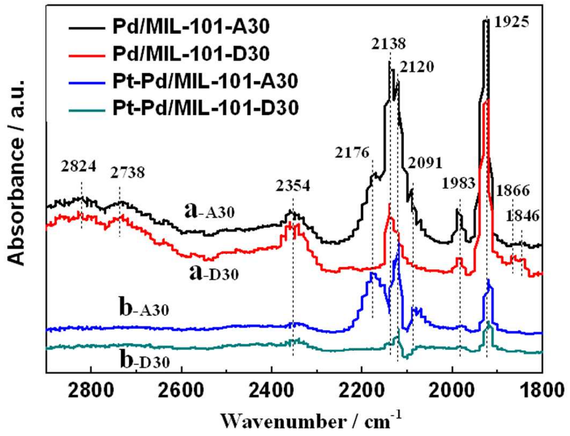


Fig. 5 DRIFT spectra of CO absorbed on (a) Pd/MIL-101 and (b) Pt-Pd/MIL-101 at 25°C (A30: absorbing for 30 min; D30: desorbing for 30 min)

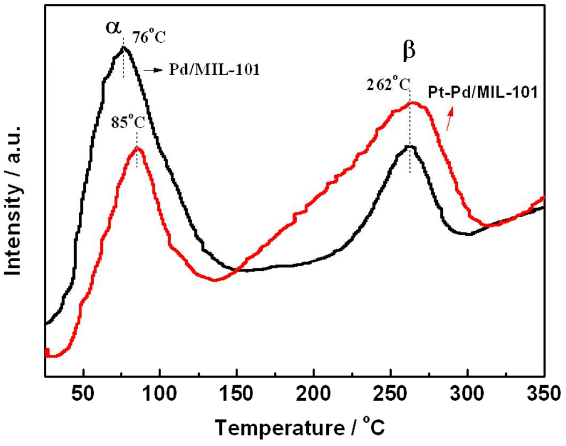


Fig. 6 CO-TPD profiles of Pd/MIL-101 and Pt-Pd/MIL-101. Experimental conditions: flow rate = 30 mL/min (He), heating rate = 5°C/min

Effect of alloyed catalysts

Regarding the bimetallic catalysts, the effect of alloyed catalysts should not be ignored.[29-31] A higher activity and enhanced stability of Pd-alloy based catalysts are always expected. Unfortunately, as indicated by Singh and Xu,[30] only a few reported works can be found in the literature on CO oxidation over alloyed Pd catalysts. However, these reported works indeed show improved activity with enhanced stability. Morfin *et al*.[32] found that, the IrPd catalysts revealed a marked superiority over their pure metal counterparts and an Ir + Pd mechanical mixture in terms of CO conversion and selectivity. Shan *et al*. [33] found that, PdNi nanoalloy catalysts exhibited remarkable tunability in terms of phase state, bimetallic composition, and atomic-scale structure, which were responsible for the origin of the structural synergy for CO oxidation reaction over the nanoalloy catalysts. There is also pronounced synergistic enhancement in supported bimetallic palladium-gold catalysts. The Pd-Au alloys are superior to pure palladium for CO oxidation.[34,35] Goodman and his co-workers postulated that Au atoms tune Pd-Pd bonds in model bimetallic compounds via an “ensemble effect” that enhances catalytic performance. However, the surface structure of gold-modified palladium remains conjectural. Furthermore, the precise mechanistic role of gold in accelerating low-temperature reactions remains ambiguous.

Ham *et al*.[36] present a theoretical explanation on how PdAu alloyed catalysts can enhance the oxidation of CO molecules based on density functional theory (DFT) studies of CO adsorption and oxidation on AuPd/Pd(111) surfaces. They suggested that the enhanced activity is principally attributed to the possible existence of “partially-poisoned” Pd ensembles that accommodate fewer CO molecules than Pd atoms. AuPd alloys resist CO poisoning. Kim *et al*.[37] also conducted a DFT study on CO-adsorption-induced Pd surface segregation in Au/Pd bimetallic surfaces, dynamics of Pd−Au swapping, defect effect on the swapping rate, and the reaction mechanism of CO oxidation. They found that Pd clusters consisting of at least four Pd atoms prefer to bind O_2 rather than CO. These clusters facilitate the rapid dissociation of O_2 and supply reactive oxygen species for CO oxidation. Their findings suggest that geometric, electronic, and dynamic effects should be considered in the function of bimetallic alloys or nanoparticles whose components asymmetrically interact with reacting molecules.

Xu *et al*.[38] synthesized a series of nanocrystalline biphasic Pd-Au nanoalloy catalysts with different compositions, supported on silica fume, in order to investigate the activity for CO oxidation as a function of bulk composition, and to understand the key role of modified surface chemistries in mixed metal catalysts. They found that, except for the pure metals, these materials invariably showed biphasic separation into palladium- and gold-rich components. Optimal performance is achieved for a catalyst of bulk composition Pd_4Au_1, a mixture of $Pd_{90}Au_{10}$ (72.5 at. %) and $Pd_{31}Au_{69}$ (27.5 at. %), that was remarkably active at 300 K and more stable than a pure Au catalyst. CO oxidation reaction was conducted on all catalysts. The activities from highest to lowest for all catalyst pairs are in sequence: Au > Pd:Au = 4:1 > 8:1 > 16:1 > Pd > 2:1 > 1:1.6 > 1:3.4. However, Pd_4Au_1 exhibits superior activity and stability as compared to pure gold, with the latter showing a 50% loss of activity after 10 h at 353 K as compared to 5% for Pd_4Au_1 in an ideal exhaust gas of 5.0 kPa CO, 5.0 kPa O_2, and Ar balance. In addition, in the simulated exhaust gas (5.0 kPa CO, 5.0 kPa O_2, 10.0 kPa H_2O, 20.0 kPa CO_2, and Ar balance), there was a substantial loss of activity for pure Au, while only a mild deterioration was observed for Pd_4Au_1. The catalyst characterization indicated that, at Pd-rich compositions, hollow spheres or annular morphologies are formed, while Au-rich crystals are often twinned. Pd atoms in the surface might be surrounded or separated by Au. Surface defects, ascribed as metal vacancies, are directly observed and contributed to enhanced low-temperature CO oxidation. Pd-Au alloy catalysts showed significant activity and stability toward low-temperature CO oxidation even at 300 K for bulk compositions from Pd to Pd_4Au_1, but showed degraded performance at higher Au contents due to higher activation that was accompanied by greater surface coverage by coverage of Au. These results demonstrate that gold-containing biphasic Pd nanoalloys are excellent catalysts for CO oxidation.

Influence of preparation method

To obtain supported noble metal catalysts with small particle size and high distribution, and then excellent performance in reaction, the preparation method plays a crucial role.

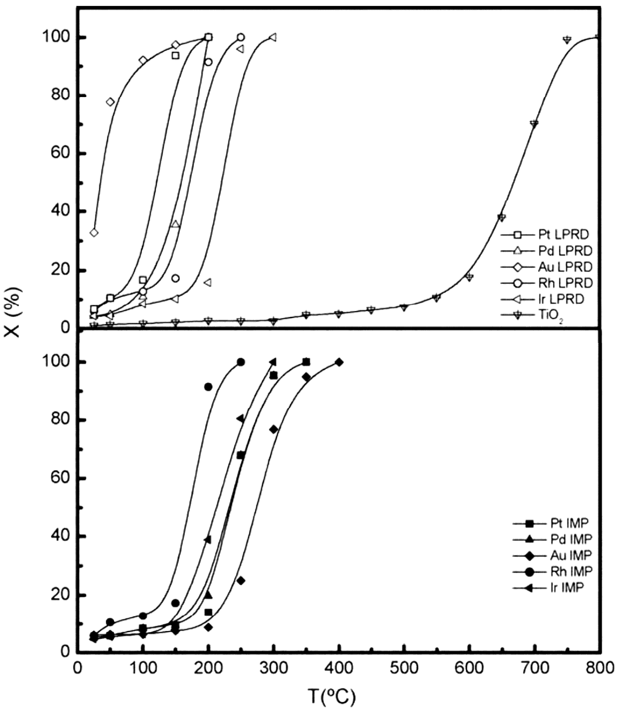


Fig. 7 Light-off curves for CO oxidation over supported noble metal catalysts prepared by different methods. Reproduced with permission from ref. 39. Copyright 2010, Elsevier.

Santos *et al.* [39] investigated the activity of noble metal catalysts (Pd, Pt, Ir, Rh and Au) supported on TiO_2 for the CO oxidation reaction. Two methods, liquid phase reduction deposition (LPRD) and incipient wetness impregnation (IMP), were used to prepare the catalysts for comparison. It was found that, the dispersion of the metallic phase was significantly affected by the preparation method. For example, the average size of Pd particle prepared by IMP was 8.0 nm, while that prepared by LPRD was 3.0 nm. Meanwhile, LPRD prepared Pd sample has a dispersion of 28%, much higher than that of IMP Pd sample (16%). Subsequently, the performance of the catalysts towards CO oxidation is different. LPRD makes better results, as shown in Fig. 7.

During the normal impregnation method, the use of different solvents would lead to distinguishing particle distribution and thereby different catalytic properties. We have found that the solvent applied in the impregnation method has a significant effect on CO oxidation over the covalent organic polymer-4 (COP-4, a new porous organic polymer) supported palladium catalyst.[40] N,N-dimethylformamide (DMF) and distilled water were used as the solvents, respectively, with a novel electron reduction to convert Pd ion into metallic species. As shown in Fig. 8, when DMF was used as the solvent, Pd particles are distributed in the pores of COP-4 with uniform size of 1.1 nm. When water was used, the average size of Pd particles, obviously outside the pores, becomes 2.4±0.1 nm. In our experiment, DMF can easily infiltrate into the pores of COP-4, while water is kept outside the pores. Therefore, we can say that the Pd particles are confined into the pores after the metal ions in DMF are reduced, while the Pd ions in water are transferred to Pd particles outside the pores without confinement of the pores. The DRIFT spectra of CO at room temperature show that, there are different active sites on the two samples, which show different activity for CO oxidation.

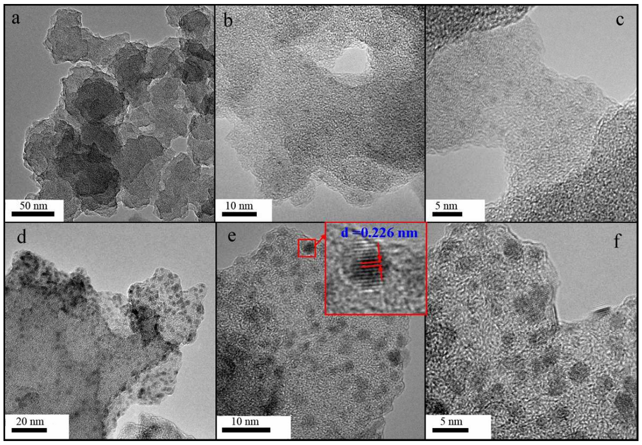


Fig. 8 TEM images of (a) COP-4; (b and c) Pd/COP-4-DE; (d–f) Pd/COP-4-WE. (D=DMF, W=Water, E = electron reduction).[40]

We further prepared two more Pd/COP-4 samples by hydrogen reduction,[41] compared with the samples reduced by electron reduction, to check the effect of the reduction method. The relatively high temperature (300°C) of hydrogen reduction leads to the formation of much larger Pd particles outside the pores of COP-4. The average size of the particles in Pd/COP-4-DH and Pd/COP-4-WH (H=hydrogen reduction) is 7.7±1.8 nm and 9.9 nm, respectively. However, the samples prepared by hydrogen reduction have better activity for CO oxidation than those prepared by electron reduction, as shown in Fig. 9. Comparing the DRIFT spectra of CO of the four Pd/COP-4 samples, we found that, the Pd/COP-4 samples prepared by electron reduction have much stronger interaction with the CO molecules and mainly show the Pd(111) lattice plane, which should be the reason for their relatively low activity for CO oxidation. The results indicated that, not only the solvents but also the reduction methods will influence the properties of the catalysts. What is more, the activities of the Pd/COP-4 samples prepared by hydrogen reduction are compared with that of MOF-5 supported Pd catalyst, as shown in Table 1. The TOF values of Pd/COP-4 samples are much higher than that of Pd/MOF-5, indicating the superiority of the COP-4 material with large amounts of nitrogen atoms.

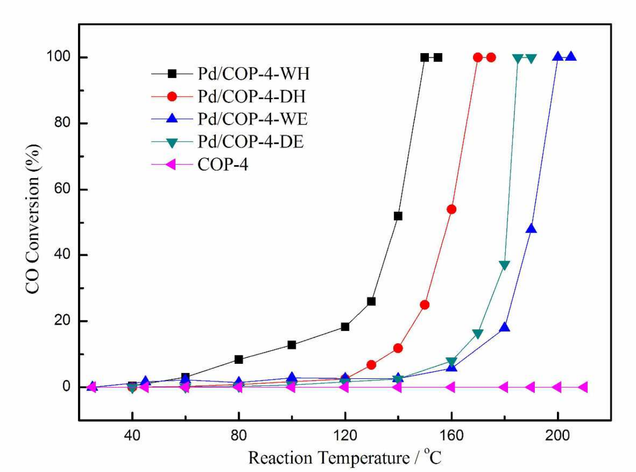


Fig. 9 Light-off curves for CO oxidation over COP-4 supported Pd catalysts. Reproduced with permission from ref. 41. Copyright 2014, American Chemical Society.

Table 1 Catalytic results of CO oxidation over different samples

	Dispersion	$TOF_{130^{o}C}\times10^{3}s^{-1}$	$TOF_{140^{o}C}\times10^{3}s^{-1}$
Pd/COP-4-DH	0.14	14.9	25.8
Pd/COP-4-WH	0.11	72.9	145.8
1%Pd/MOF-5-DH	0.45	1.8	3.2

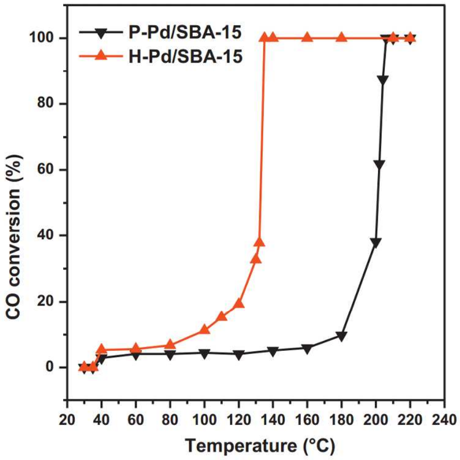


Fig. 10 Light-off curves for CO oxidation over Pd/SBA-15 samples. Reproduced with permission from ref. 42. Copyright 2011, Elsevier.

Wang *et al.* [42] reported the effect of preparation condition on the SBA-15 supported Pd catalysts for CO oxidation. Using electron reduction, they synthesized highly dispersed Pd nanoparticles within the uniform channel of SBA-15. The obtained Pd/SBA-15 catalyst shows good activity for CO oxidation. Then the electron reduced Pd/SBA-15 (P-Pd/SBA-15) is calcined under air and further reduced thermally with hydrogen. Apart from a slight increase in the particle size, the hydrogen reduced Pd/SBA-15 (H-Pd/SBA-15) has higher activity for CO oxidation compared with P-Pd/SBA-15, as shown in Fig. 10. It indicates that the preparation condition possesses a significant influence on the catalyst activity. This study suggests that CO oxidation over Pd/SBA-15 is a structure sensitive reaction. Structure change induced by the thermal treatment is the reason for the improvement in the activity, which is implied by the DRIFT studies. Normally, linear CO is preferentially formed on low-coordinated Pd atoms, while smaller particles always expose a larger fraction of low-coordinated atoms than larger ones. Therefore, the structure change can be induced by the preferential adsorption of CO at bridge sites. This is an advantage for reaction between CO and O adatoms. It changes the reaction rate, resulting in a higher activity for CO oxidation on the H-Pd/SBA-15 sample.

Ivanova *et al.* [43] used γ–Al_2O_3 as support to prepare Pd catalysts and investigated the effect of the calcination temperature. The properties of the catalysts, denoted as Pd/Al_2O_3(X)-Y (X—the calcination temperature of support, °C; Y—the calcination temperature of catalyst, °C), were studied. Palladium particles in the Pd/Al_2O_3 (550)-450 catalyst are almost completely decorated with a thin layer of an aluminate phase, which cannot be reduced by hydrogen in the temperature range of −15 to 450 °C. In Pd/Al_2O_3(800)-T catalysts, decorated metallic particles with a core-shell structure are formed. When the calcination temperature of the catalyst changes from 450°C to 1000°C gradually, the morphological form of the active component converts from the core-shell structure to the combination of two phases, Pd^0 and PdO, with the gradually decreasing Pd^0/PdO ratio. Meanwhile, the interaction between Pd phases and the support is weakened, and the palladium particles grow larger. After calcination of the Pd/Al_2O_3 catalyst at 1200 °C, the coarse PdO particles are reduced into Pd^o. However, the palladium particles lose interaction with the support, gathering into large agglomerates, and exhibit poor catalytic performance for CO oxidation. The light-off curves for CO oxidation over the Pd/Al_2O_3 catalysts are shown in Fig. 11. It could be found, the efficiency of the palladium catalysts for CO oxidation depends on the support calcination temperature. The increase of the support calcination temperature from 550 to 800 °C makes the catalyst more active (for the catalysts calcined at 450 °C). When the calcination temperature is no more than 800 ◦C, the character of CO oxidation has no big difference. If further increasing the calcination temperature, the CO conversion appears a sharp decrease.

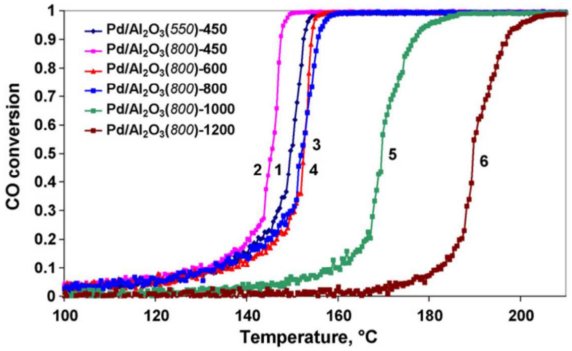


Fig. 11 Temperature dependence of the CO conversion for catalysts: Pd/Al_2O_3(550)-450 (1), Pd/Al_2O_3(800)-450 (2), Pd/Al_2O_3(800)- 600 (3), Pd/Al_2O_3(800)-800 (4), Pd/Al_2O_3(800)-1000 (5), Pd/Al_2O_3(800)-1200 (6). Reproduced with permission from ref. 43. Copyright 2010, Elsevier.

For supported metal catalysts, high-temperature aging always results in sintering or re-dispersion which is mastered by metal-support interaction and gas atmosphere. Hinokuma *et al.* [44] found that, the Pd/CeO_2 catalyst after thermal aging at 900 ^{o}C in air has obviously increased activity for ambient-temperature CO oxidation. Fig. 12a exhibits the temperature dependences of CO conversion to CO_2 before and after thermal aging at 900^{o}C, while Fig. 12b shows CO conversion measured at 50^{o}C versus the aging temperature. The activation is demonstrated to be driven by metal-support interactions followed by phase transformation. Details are discussed in the following mechanism in Fig. 13. Firstly, the bonding of Pd-O-Ce is formed at the PdO/CeO_2 interface, which allows high dispersion of Pd oxide into the surface structure of sintered CeO_2 crystallites. However, the surface Pd oxide species themselves should not be an active site for low-temperature CO oxidation. When the aging temperature reaches 800 ^{o}C or higher, the Pd-O-Ce moiety becomes instable. Finally, the PdO/Pd phase equilibration at 900 ^{o}C will cause the thermodynamic dissociation of Pd oxide species to yield metallic Pd nanoparticles, which can activate CO. Compared with other supported catalysts such as Pd/γ-Al_2O_3 and Pt/CeO_2 which are deactivated by sintering, the Pd/CeO_2 catalyst is an exceptional case that significant thermal sintering in the presence of O_2 converts it to be a very active catalyst for ambient-temperature CO oxidation.

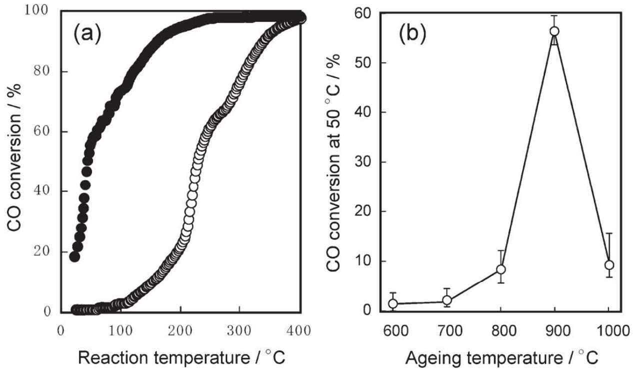


Fig. 12 (a) Light-off of CO oxidation on Pd/CeO_2 before (○) and after (●) aging at 900^{o}C; (b) CO conversion to CO_2 at 50^{o}C as a function of aging temperature. Reproduced with permission from ref. 44. Copyright 2010, American Chemical Society.

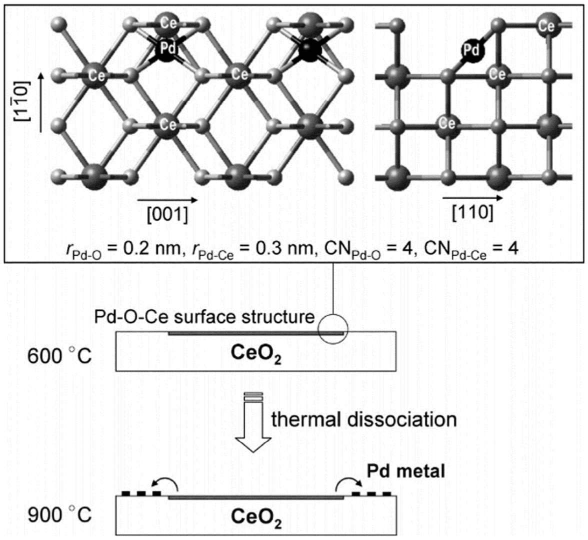


Fig. 13 Possible mechanism of sintering-induced activation of Pd/CeO_2. Reproduced with permission from ref. 44. Copyright 2010, American Chemical Society.

Effect of Pd structure

The shape or morphology of the nanoparticles is also an important factor which influences the catalytic performance of metal catalysts.[45] When the crystalline shape is tuned, the exposed facets on the surface of metallic nanocrystals will alter, and then the catalytic properties of metal nanocrystals will be different.

Wang *et al.* [46] synthesized palladium nanocrystals with cubic, octahedral, and spherical morphologies, and dispersed them onto the inert silica support, respectively. Carbon monoxide oxidation was chosen to investigate the activity of these catalysts. The results shown in Fig. 14 indicate that the catalytic activities of the Pd catalysts are influenced by the shape of Pd nanocrystals. The apparent activation energies of CO oxidation are calculated to be 76.5, 52.9 and 42.6 kJ mol^{-1} for the cubic, octahedral and spherical Pd catalysts, respectively. The spherical Pd/SiO_2 catalyst possesses the lowest activation energy and shows the best catalytic performance, while the cubic Pd/SiO_2 sample has the highest activation energy with the poorest activity. Their further investigations indicate that, the octahedral and spherical Pd nanocrystals with mainly exposed Pd(111) planes are more active for CO oxidation, compared with the cubic Pd nanocrystals which are enclosed by Pd(100) plane. It means that the exposed facets of Pd nanocrystals influence the adsorption and desorption properties of CO molecule and consequently the catalytic activity of CO oxidation. The results of CO-TPD and DRIFT indicate that the interaction between CO species and Pd(100) is weak, while CO molecule has much stronger interaction with Pd(111) under ambient conditions. It is inferred that the appropriate adsorption strength of CO molecule on Pd(111) planes is beneficial to the enhancement of the catalytic activity.

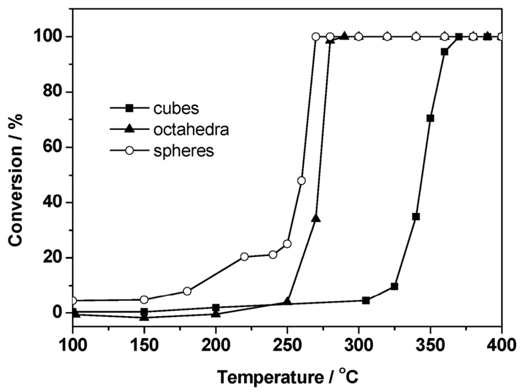


Fig. 14 CO oxidation activity over Pd/SiO_2 catalysts with different particle shapes. [46]

In addition to the facets exposed on the surface, the size of Pd nanocrystals is also important for the catalytic activity. As for the CO oxidation, many studies have demonstrated that the Pd(100) plane of Pd single crystals is superior in activity than the Pd(110) and Pd(111) planes. Manipulating the rate of reduction of the precursor, Jin *et al.* [47] successfully synthesized Pd nanocrystals enclosed by (100) facets with sizes controlled in the range of 6-18 nm. When the concentrations of Br^- and Cl^- ions added to the reaction mixture are adjusted, the rate of reduction of Na_2PdCl_4 can be controlled. They immobilized the Pd nanocrystals on ZnO nanowires and investigated their activity for CO oxidation. As shown in Fig. 15, the nanocrystal size shows great influence on the catalytic activity for CO oxidation. The 6-nm Pd cubes/bars have much higher CO conversion than the 10- and 18-nm Pd cubes/bars under the same reaction temperature. The activity can be remarkably enhanced by decreasing the size of the Pd cubes/bars. The complete conversion temperature and the intrinsic turnover frequency (TOF) are also affected by the size of the Pd cubes/bars in the same way. When the size is reduced from 18 nm to 6 nm, the complete conversion temperature is lowered by ~80 °C. The TOF at 140 °C of the 6-nm Pd cubes/bars is approximately 3 and 10 times higher, respectively, than those of the 10- and 18-nm Pd cubes/bars. It indicates that the size of the Pd nanocrystals determines their activity for CO oxidation.

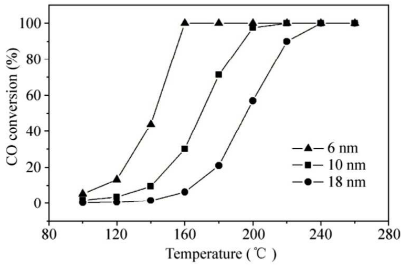


Fig. 15 CO conversion as a function of temperature for Pd cubes/bars with different sizes supported on ZnO nanowires. Reproduced with permission from ref. 47. Copyright 2011, Springer.

Study of the active sites

Pavlova *et al.* [48] reported that, at saturation coverages of carbon monoxide on supported palladium particles, the most reactive weakly bound forms of CO (both linear and bridge-bonded) appear to be mainly located at defect centres generated by reconstruction of the open (100) and (110) faces. There are some disputes on the oxidation state of active Pd species for CO oxidation. A common assertion exists that PdO is a poor CO oxidation catalyst. In addition, the case exists that lower dispersion of Pd is more preferable for higher activity to some degree. Highly dispersed Pd particles tend to be oxidized to PdO or ionic Pd^{2+}, which are less active than metallic Pd. It is believed that the metallic state of Pd is more important than Pd dispersion for improving the catalytic activity.

Satsuma *et al.* [49] prepared different oxides (CeO_2, TiO_2, Al_2O_3, ZrO_2, and SiO_2) supported Pd catalysts, in order to investigate the controlling factors on CO oxidation. As shown in Fig. 16, the Pd/CeO_2 sample shows the highest activity. Comparing the temperature at 50% conversion of CO, the light-off temperature follows the order of Pd/CeO_2 < Pd/TiO_2 < Pd/Al_2O_3 < Pd/ZrO_2 ≤ Pd/SiO_2. As shown in Table 2, Pd/TiO_2 with the lowest Pd dispersion has higher catalytic activity than Pd/Al_2O_3 at lower temperatures, indicating that Pd dispersion is not the most preferential activity-controlling factor of supported Pd catalysts. Further CO-TPR analysis indicates that the order of catalytic activity is fairly in agreement with the reduction temperature of supported Pd to metallic species. It suggests that the reduction of Pd ion to the metallic state is the most important controlling factor for CO oxidation. By using the series of Pd/SiO_2 as model catalysts, the metallic Pd can be sure to be the active sites for low temperature CO oxidation, and the reaction follows the typical Langmuir-Hinshelwood mechanism. Further research on contribution of supports shows that oxygen storage property of the samples and their catalytic activity for CO oxidation agrees well, which suggests the oxygen storage property of the support is another key factor for CO oxidation. Both CeO_2 and TiO_2 have outstanding oxygen release and storage capacities, then the activity of Pd/CeO_2 and Pd/TiO_2 are better. In conclusion, there are two controlling factors for CO oxidation on supported Pd catalysts. One is the reducibility of PdO to Pd, the other is the oxygen storage property of the support.

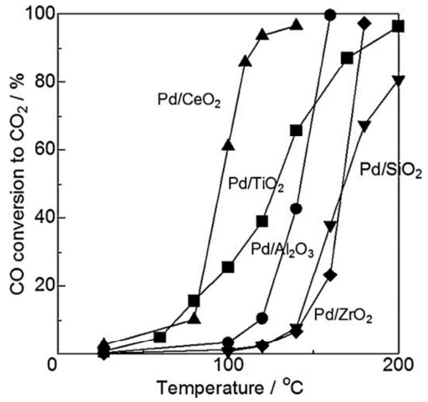


Fig. 16 CO conversion as a function of temperature for the Pd catalysts. Reproduced with permission from ref. 49. Copyright 2013, Elsevier.

Table 2 BET surface area and dispersion of Pd of the supported Pd catalysts [49]

Catalyst	Surface area (m^2g^{-1})	Pd dispersion (%)
Pd/CeO_2	26	25
Pd/TiO_2	39	8.9
Pd/Al_2O_3	111	54
Pd/ZrO_2	11	10
Pd/SiO_2	101	16

For its prominent redox property, the reducible support CeO_2 plays an important role in the catalytic oxidation of CO. Generally, the metal-support interface is believed to be where the reaction takes place. However, no final conclusion is made about the nature of the active sites/phase. As for the Pd/CeO_2 supported catalysts, the PdO species are considered as the active sites for the oxidation of CO.[50-52] The $PdO-CeO_2$ system may contain complex PdO species, such as surface free PdO species with different particle sizes and Pd^{2+} ions in the CeO_2 matrix. Therefore, it is also difficult for the identification of active sites in the $PdO-CeO_2$ catalysts. Meng *et al.* [53] prepared catalyst $PdO/Ce_{1-x}Pd_xO_{2-\delta}$ which contains both free surface PdO species and PdO species in $Ce_{1-x}Pd_xO_{2-\delta}$ solid solution, and PdO/CeO_2 catalyst which contains only free surface PdO species. After the removal of the free surface PdO species by nitric acid, the catalyst $Ce_{1-x}Pd_xO_{2-\delta}$ which contains only Pd^{2+} species in the CeO_2 matrix can also be obtained. Then the catalytic activities of the samples for CO oxidation were examined, with the results shown in Fig. 17. Obviously, the $PdO/Ce_{1-x}Pd_xO_{2-\delta}$ catalyst has the highest activity on which the complete CO conversion realizes at 160 °C. The $Ce_{1-x}Pd_xO_{2-\delta}$ and PdO/CeO_2 catalysts have similar activity, with a complete CO conversion at 220 °C. What's more, the results indicate that, as for the activity of the individual PdO species, the free PdO species on the surface of $PdO/Ce_{1-x}Pd_xO_{2-\delta}$ catalyst has the best performance with a reaction rate of 969.3 $\mu mol_{CO}\ g_{Pd}^{-1}s^{-1}$, and that on the surface of PdO/CeO_2 catalyst has a much lower reaction rate of 109.0 $\mu mol_{CO}\ g_{Pd}^{-1}s^{-1}$, while Pd^{2+} in the CeO_2 lattice shows the lowest activity with a reaction rate of 13.2 $\mu mol_{CO}\ g_{Pd}^{-1}s^{-1}$. As a simplified reaction model, Scheme 2 is used to demonstrate the CO oxidation pathways on the samples. For the catalytic cycle, CO chemisorbed on the surface of PdO firstly, then the chemisorbed CO migrated to the interface of PdO and support. After the activation of O_2 on the oxygen vacancies and the formation of active oxygen, the reaction between the chemisorbed CO at interface and the nearby active oxygen occurs. At last, the refilling of oxygen vacancies would be finished by gas phase O_2.

Effect of support

CO oxidation is a reaction that follows bi-functional reactions at the metal and support interface. The property of the support has a significant influence on the activity of supported Pd catalysts. For CO oxidation, the reported Pd catalysts are usually supported on metal oxides, like SiO_2, Al_2O_3, CeO_2, TiO_2, CoO_x and MnO_x. The metal oxides can be simply divided into two classes, active and inert ones. Known as oxygen storage materials, CeO_2 and TiO_2 possess redox properties. The Co-O bond in Co_3O_4 is relatively weak. The lattice oxygen makes Co_3O_4 show high reactivity for CO oxidation even at low temperature. As for Mn_2O_3, it contains a large amount of labile oxygen that is useful for CO oxidation. In comparison, SiO_2 and Al_2O_3 are always considered as inert supporting materials. In addition, some new materials have been employed as the support, such as graphene or graphene oxide, in which oxygen containing groups are rich. This would be helpful for CO oxidation. Apart from reactive oxygen, the basic-property of the support is an important factor too.

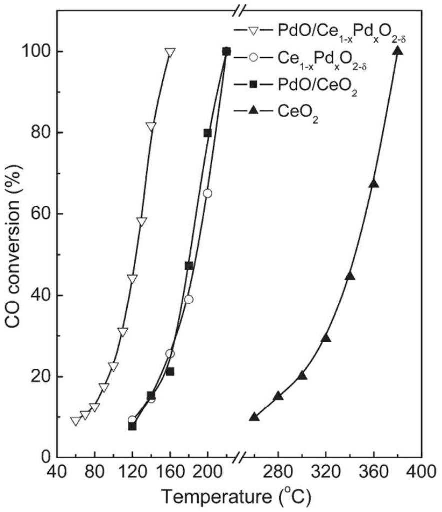
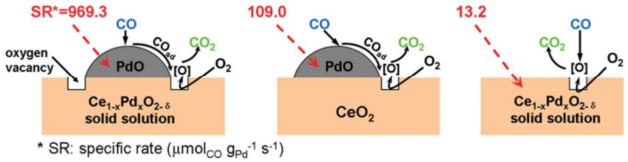


Fig. 17 Catalytic activities of the samples for CO oxidation. Reproduced with permission from ref. 53. Copyright 2011, American Chemical Society.



Scheme 2 Reaction Model of CO Oxidation over Catalysts. Reproduced with permission from ref. 53. Copyright 2011, American Chemical Society.

Kochubey *et al.* [54] prepared SiO_2, TiO_2 and Al_2O_3 supported Pd clusters and investigated the influence of support on the low-temperature activity of Pd. They found that the morphology and the spatial homogeneity of the Pd species on the support are different with different support. Pd on SiO_2 appears to have a fairly perfect structure, while the structure of Pd clusters on TiO_2 and γ-Al_2O_3 is strongly disturbed by the interaction with support. For Pd/TiO_2, flat clusters of Pd are probably stabilized due to a structural matching with this support. For Pd/Al_2O_3, the absence of any preferential shape for Pd clusters on alumina could indicate a strong interaction of Pd with defect centres on the surface of a disordered spinel support. Furthermore, at saturation coverages, weakly bound CO (both linear and bridge-bonded) are the most reactive. Obviously, this depends upon the type of the support.

Li *et al.* [55] prepared graphene supported palladium catalysts by the impregnation and hydrogen reduction method. Pd nano-particles are highly dispersed on the support. Through the density functional theory (DFT) study and the catalyst characterization using Raman and X-ray photoelectron spectroscopy, they found that the oxygen containing groups in graphene are useful for stabilizing Pd clusters. It was concluded that the Pd clusters tended to take on multilayer structure, with which the first layer mainly presented as PdO_x form, and the dominant composite of other layers is Pd metal. The resulting catalysts show excellent activity and high stability for CO oxidation, following the Langmuir-Hinshelwood mechanism. The Arrhenius plots of graphene supported palladium catalysts (Pd-GE) shown in Fig. 18 are basically consistent with the other Pd supported catalysts in the literature.[56]

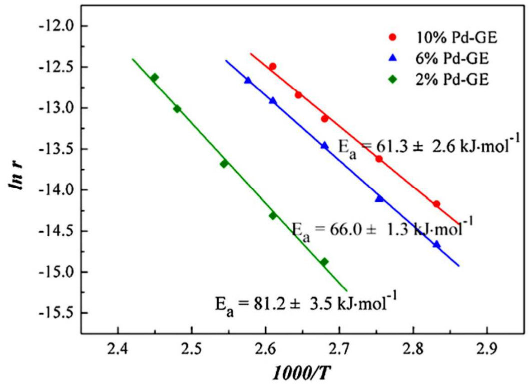


Fig. 18 Arrhenius plots for CO oxidation over Pd-GE catalysts. Reproduced with permission from ref. 55. Copyright 2012, Elsevier.

Liu *et al.* [57] prepared a series of FeO_x and Al_2O_3 supported Pd catalysts that exhibit high CO oxidation activity. They found that Pd catalysts on FeO_x and Al_2O_3 show different E_a. The values are 34 kJ/mol and 71 kJ/mol on FeO_x and Al_2O_3 supported Pd catalysts, respectively. Al_2O_3 can hardly activate O_2 for CO oxidation, while adsorption and activation of molecular oxygen occurs on FeO_x support. Furthermore, they found that the Fe_2O_3 supported Pd catalysts, calcined at high-temperature, exhibit similar E_a with Pd/FeO_x but far inferior catalytic activity. It means that different CO oxidation mechanisms or pathways might happen over FeO_x and Fe_2O_3 supported Pd catalysts. The characterization indicates that, Pd over $Fe(OH)_x$ can facilitate Fe^{3+} reduction and hydroxyl loss at relatively low temperature, resulting in the production of large numbers of oxygen vacancies. The partially reduced FeO_x support acts as an oxygen supply in CO oxidation. Then for CO oxidation over Pd/FeOx, Pd sites play the role for CO activation and FeO_x acts to supply active oxygen, which results in the low activation energy and high activity.

For CO oxidation, the basic-property of the support may induce the adjustment in electronic structure of the metallic NPs, and then directly alter the adsorption intensity of surface CO molecules. This will further change the catalytic activity over the supported catalysts. Liu *et al.* [58] prepared SiO_2, TiO_2 and MgO supported Pd nanocubes catalysts, and evaluated the effect of the basic-property of the support. As shown in Fig. 19, the Pd/MgO sample has the best catalytic activity in CO oxidation. To elucidate the origin of the difference, they investigated the surface acid-basic properties of the supports and the CO adsorption behaviours over the catalysts. The results of the "temperature-dependent" and the "time-dependent" DRIFT spectra indicate that CO adsorption on the Pd/MgO catalyst is the strongest with the largest adsorption amount. Among the three supports, MgO is the most basic, which can enhance the amount and stability of CO adsorption on (100) planes of the Pd nanocubes. In CO oxidation, an "volcano shape correlation" curve exists between CO adsorption behaviour and the catalytic activity. For Pd/MgO, the CO adsorption approaches the top of the "volcano shape" curve and the CO oxidation activity is better than that of the other two samples.

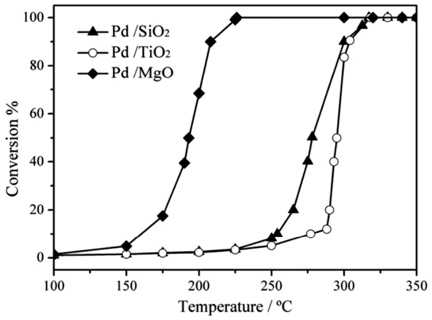


Fig. 19 CO oxidation activity over the supported Pd catalysts. Reproduced with permission from ref. 58. Copyright 2014, Elsevier.

Jin *et al.* [59] synthesized a serial of highly ordered mesoporous metal oxides (meso-MO_x) by a nano-replication method, such as CeO_2, Co_3O_4, Mn_2O_3,SnO_2 and TiO_2, and investigated the CO oxidation activity of meso-MO_x supported Pd catalysts (Pd/ meso-MO_x). As shown in Fig. 20, meso-Co_3O_4 and meso-Mn_2O_3 exhibit much higher catalytic activities in CO oxidation than meso-CeO_2, meso-SnO_2 and meso-TiO_2. The temperature at which CO is converted to CO_2 completely follows the order of Co_3O_4>Mn_2O_3>CeO_2>SnO_2>TiO_2. After the loading of Pd, the light-off curves for CO oxidation are shown in Fig. 21(a). Compared with the corresponding mesoporous metal oxides, the CO oxidation activities of the Pd/meso-MO_x samples are all increased, with Pd/meso-Co_3O_4 showing the highest activity. Meanwhile, resulting from the well-defined pore size and higher surface areas of meso-MO_x, the Pd/meso-MO_x samples also exhibit higher activities than the corresponding Pd/bulk-MO_x samples. It indicates that the property of support would affect the activity of the catalyst. However, the activity amplifications of Pd/meso-Co_3O_4 and Pd/meso-Mn_2O_3 are slight, while those of Pd/meso-CeO_2, Pd/meso-SnO_2 and Pd/meso-TiO_2 are significant. The results of XPS indicate that a strong interaction exists between Pd species and meso-CeO_2/meso-SnO_2/meso-TiO_2, while a weak interaction between Pd species and meso-Co_3O_4 and meso-Mn_2O_3. It suggests that there is a synergistic effect between Pd species and the supports. The nature of the support strongly affects the catalytic activities of the samples. Furthermore, the activities of the supported Pd catalysts can be improved by a pre-reduction treatment. As shown in Fig. 21(b), after H_2 pretreatment, the catalytic activities of the samples for CO oxidation are all increased. Among the samples, Pd/meso-CeO_2 exhibits the highest activity after the promotion via H_2 pretreatment. It was thought that the pretreatment can enhance the metal-support interaction, and facilitate the formation of oxygen vacancies and hydroxyl groups, which will influence the electronic state of surface active sites. From the above results, the authors estimated that the activity of supported Pd catalyst is dependant on the type of support and the interaction between metal and the support, and the H_2 pretreatment might enhance the metal-support interaction.

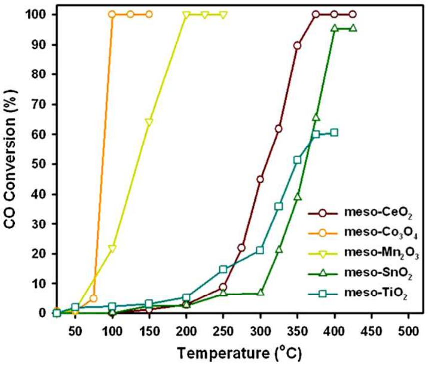


Fig. 20 CO conversion on meso-MOx catalysts. Reproduced with permission from ref. 59. Copyright 2012, Elsevier.

Conclusions and outlook

In this perspective, the influencing factors for the activity of supported Pd catalysts in CO oxidation are discussed. Additives such as ceria, zinc, alkaline earth metals, and so on, can be used as promoters, to enhance the activity of catalyst in CO oxidation. They may lower the binding energy of CO, enhance the thermal durability of the support, or improve the dispersion of Pd species. The preparation method also plays a crucial role. Different preparation methods will change the distribution of Pd particles, as well as the interaction between Pd species and the support. Pd structure decides the exposed facets on the surface, which strongly influences the performance in CO oxidation. The property of the support is another key role in deciding the activity of the catalyst. The basic-property and oxygen storage capacity both have important influence.

Pd based catalyst is a very active and important one for not only CO oxidation but many other reactions.[60-64] Pd based catalysts have been extensively applied in industrial productions. CO oxidation is an excellent model reaction for the study of structure, metal-support interaction and other issues of various Pd based catalysts. It is simple and can be easily operated with lost cost. Carbon monoxide itself is an excellent probe molecule for the catalyst characterization. Density functional theoretical study has been a convenient tool for the study.[64,65] We can expect further increasing publications and applications over Pd based catalyst.

However, even for simple CO oxidation, there are many challenges remained with Pd catalysts. The low temperature activity over Pd catalysts is not impressed. The role of metal-support interface is still not clear. The defect control is not easy. The geometrical and electronic roles of alloyed Pd catalysts are to be further studied. It is still very difficult to *in situ* characterize the reaction. A significant effort is being made towards the size and structure control of Pd catalysts but it still remains as a big challenge to the chemists worldwide. High activity of single atomic Pd catalyst or Pd cluster catalyst has been expected but we need to find a way to make it. The catalysts with one dimensional or two dimensional Pd nanoparticles have attracted many attentions but the progress is very slow. Innovation in the catalyst preparation is immediately needed.

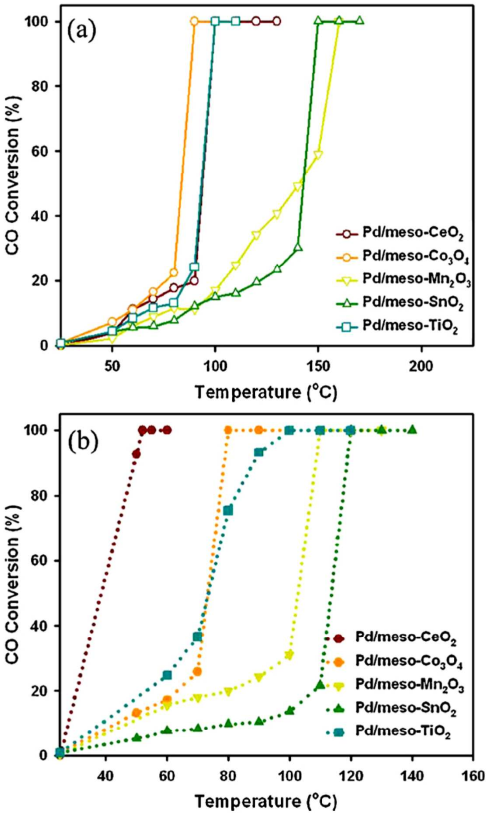


Fig. 21 Light-off curves for CO oxidation over Pd/meso-MO_x catalysts (a)without H_2 pretreatment and (b)with H_2 pretreatment. Reproduced with permission from ref. 59. Copyright 2012, Elsevier.

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Notes and references

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1 Y.X. Shen, Y. Guo, L. Wang, Y.Q. Wang, Y.L. Guo, X.Q. Gong, and G.Z. Lu, *Catal. Sci. Technol.*, 2011, **1**, 1202.
2 L.Q. Liu, F. Zhou, L.G. Wang, X.J. Qi, F. Shi and Y.Q. Deng, *J. Catal.*, 2010, **274**, 1-10.
3 Y. Zhao, C.L. Zhong and C.-J. Liu, *Catal. Commun.*, 2013, **38**, 74-76.
4 Q.X. Cai, X.D. Wang, Xinde and J.G. Wang, *J. Phys. Chem. C*, 2013, **117**, 21331.
5 H.B. Na, T. Zhu and Z.M. Liu, *Catal. Sci. Technol.*, 2014, **7**, 2051.
6 B.T. Qiao, A.Q. Wang, X.F. Yang, L.F. Allard, Z. Jiang, Y.T. Cui, J.Y. Liu, J. Li and T. Zhang, *Nature Chem.*, 2011, **3**, 634-641.
7 J.J. Wang, Z.Y. Wang and C.-J. Liu, *ACS Appl. Mater. Interfaces*, dx.doi.org/10.1021/am502807b

8 R.V. Gulyaev, E.M. Slavinskaya, S.A. Novopashin, D.V. Smovzh, A.V. Zaikovskii, D.Yu. Osadchii, O.A. Bulavchenko, S.V. Korenev and A.I. Boronin, *Appl. Catal. B: Environ.*, 2014, **147**, 132.

9 K. Shimizu, Y. Kamiya, K. Osaki, H. Yoshidad and A. Satsuma, *Catal. Sci. Technol.,* 2012, **2**, 767.

10 N. Li, Q.Y. Chen, L.F. Luo, W.X. Huang, M.F. Luo, G.S. Hu and J.Q. Lu, *Appl. Catal. B: Environ.,* 2013, **142-143**, 523.

11 Y.X. Shen, Y. Guo, L. Wang, Y.Q. Wang, Y.L. Guo, X.Q. Gong and G.Z. Lu, *Catal. Sci. Technol.*, 2011, **1**, 1202.

12 M. Kurnatowska, L. Kepinski and W. Mista, *Appl. Catal. B: Environ.*, 2012, **117-118**, 135.

13 S.T. Chen, R. Si, E. Taylor, J. Janzen and J.Y. Chen, *J. Phys. Chem. C*, 2012, **116**, 12969.

14 H. Chen, X.L. Tong and Y.D. Li, *Appl. Catal. A: Gen.*, 2009, **370**, 59.

15 C.J. Tang, J.F. Sun, X.J. Yao, Y. Cao, L.C. Liu, C.Y. Ge, F. Gao and Lin Dong, *Appl. Catal. B: Environ.*, 2014, **146**, 201.

16 J.Q. Lu, C.X. Sun, N. Li, A.P. Jia and M.F. Luo, *Appl. Surf. Sci.*, 2013, **287**, 124.

17 U.R. Pillai and S. Deevi, *Appl. Catal. B: Environ.,* 2006, **65**, 110.

18 E.M.C. Alayon, J. Singh, M. Nachtegaal, M. Harfouche and J.A. van Bokhoven, *J. Catal.*, 2009, **263**, 228.

19 P.J. Berlowitz, C.H.F. Peden and D.W. Goodman, *J. Phys. Chem.*, 1988, **92**, 5213.

20 M.S. Chen, Y. Cai, Z. Yan, K.K. Gath, S. Axnanda and D. Wayne Goodman, *Surf. Sci.*, 2007, **601**, 5326.

21 E.D. Park and J.S. Lee, *J. Catal.*, 1999, **186**, 1.

22 A.I. Boronin, E.M. Slavinskaya, I.G. Danilova, R.V. Gulyaev, Y.I. Amosov, P.A. Kuznetsov, I.A. Polukhina, S.V. Koscheev, V.I. Zaikovskii and A.S. Noskov, *Catal. Today*, 2009, **144**, 201.

23 E.L. Wilson, Q. Chen, W.A. Brown and G.J. Thornton, *J. Phys. Chem. C,* 2007, **111**, 14215.

24 H.Q. Zhu, Z.F. Qin, W.J. Shan, W.J. Shen and J.G. Wang, *J. Catal.*, 2004, **225**, 267.

25 R.J. Farrauto and R.M. Heck, *Catal. Today*, 1999, **51**, 351.

26 R.S. Johnson, A. DeLaRiva, V. Ashbacher, B. Halevi, C.J. Villanueva, G.K. Smith, S. Lin, A.K. Datye and H. Guo, *Phys. Chem. Chem. Phys.*, 2013, **15**, 7768.

27 K. Tanikawa and C. Egawa, *Appl. Catal. A: Gen.*, 2011, **403**, 12.

28 J.R. Gaudet, A. de la Riva, E.J. Peterson, T. Bolin and A.K. Datye, *ACS Catal.*, 2013, **3**, 846.

29 S.Y. Shan, J. Luo, L.F. Yang and C.J. Zhong, *Catal. Sci. Technol.*, 2014, DOI: 10.1039/c4cy00469h.

30 A.K. Singh and Q. Xu, *ChemCatChem*, 2013, **5**, 652.

31 F. Gao and D.W. Goodman, *Chem. Soc. Rev.*, 2012, **41**, 8009.

32 F. Morfin, S. Nassreddine, J.L. Rousset and L. Piccolo, *ACS Catal.*, 2012, **2**, 2161.

33 S.Y. Shan, V. Petkov, L.F. Yang, J. Luo, P. Joseph, D. Mayzel, B. Prasai, L.Y. Wang, M. Engelhard and C.J. Zhong, *J. Am. Chem. Soc.*, 2014, **136**, 7140.

34 R.W. Scott, C. Sivadinarayana, O.M. Wilson, Z. Yan, D.W. Goodman, R.M. Crooks, *J. Am. Chem. Soc.* , 2005, **127**, 1380.

35 A.M. Venezia, L.F. Liotta, G. Pantaleo, V. La Parola, G. Deganello, A. Beck, Zs. Koppany, K. Frey, D. Horvath, L. Guczi, *Appl. Catal., A*, 2003, **251**, 359.

36 H.C. Ham, J.A. Stephens, G.S. Hwang, J. Han, S.W. Nam and T.H. Lim, *J. Phys. Chem. Lett.*, 2012, **3**, 566.

37 H.Y. Kim and G. Henkelman, *ACS Catal.*, 2013, **3**, 2541.

38 J. Xu, T. White, P. Li, C.H. He, J.G. Yu, W.K. Yuan and Y.F. Han, *J. Am. Chem. Soc.* , 2010, **132**, 10398.

39 V.P. Santos, S.A.C. Carabineiro, P.B. Tavares, M.F.R. Pereira, J.J.M. Órfão and J.L. Figueiredo, *Appl. Catal. B: Environ.*, 2010, **99**, 198.

40 Y. Zhou, Z.H. Xiang, D.P. Cao and C.J. Liu, *Chem. Commun.*, 2013, **49**, 5633.

41 Y. Zhou, Z.H. Xiang, D.P. Cao and C.J. Liu, *Ind. Eng. Chem. Res.*, 2014, **53**, 1359.

42 H.P. Wang and C.J. Liu, *Appl. Catal. B: Environ.*, 2011, **106**, 672.

43 A.S. Ivanova, E.M. Slavinskaya, R.V. Gulyaev, V.I. Zaikovskii, O.A. Stonkus, I.G. Danilova, L.M. Plyasova, I.A. Polukhina and A.I. Boronin, *Appl. Catal. B: Environ.*, 2010, **97**, 57.

44 S. Hinokuma, H. Fujii, M. Okamoto, K. Ikeue and M. Machida, *Chem. Mater.*, 2010, **22**, 6183.

45 W.E. Kaden, W.A. Kunkel, M.D. Kane, F.S. Roberts and S.L. Anderson, *J. Am. Chem. Soc.*, 2010, **132**, 13097.

46 R. Wang, H. He, L.C. Liu, H.X. Dai and Z. Zhao, *Catal. Sci. Technol.,* 2012, **2**, 575.

47 M.S. Jin, H.Y. Liu, H. Zhang, Z.X. Xie, J.Y. Liu and Y.N. Xia, *Nano Res.,* 2011, **4**, 83.

48 S.N. Pavlova, V.A. Sadykov, V.A. Razdobarov and E.A. Paukshtis, *J. Catal.*, 1996, 161, 507.

49 A. Satsuma, K. Osaki, M. Yanagihara, J. Ohyama and K. Shimizu, *Appl. Catal. B: Environ.*, 2013, **132-133**, 511.

50 A. Hadi and I. I. Yaacob, *Catal. Today*, 2004, **96**, 165.

51 S.H. Oh and G.B. Hoflund, *J. Phys. Chem. A*, 2006, **110**, 7609.

52 M.F. Luo, Z.Y. Pu, M. He, J. Jin and L.Y. Jin, *J. Mol. Catal. A: Chem.,* 2006, **260**, 152.

53 L. Meng, A.P. Jia, J.Q. Lu, L.F. Luo, W.X. Huang and M.F. Luo, *J. Phys. Chem. C,* 2011, **115**, 19789.

54 D.I. Kochubey, S.N. Pavlova, B.N. Novgorodov, G.N. Kryukova and V.A. Sadykov, *J. Catal.*, 1996, **161**, 500.

55 Y.Z. Li, Y. Yu, J.G. Wang, J. Song, Q. Li, M.D. Dong and C.J. Liu, *Appl. Catal. B: Environ.,* 2012, **125**, 189.

56 L. Liu, F. Zhou, L. Wang, X. Qi, F. Shi and Y. Deng, *J. Catal.,* 2010, **274**, 1.

57 L.Q. Liu, F. Zhou, L.G. Wang, X.J. Qi, F. Shi and Y.Q. Deng, *J. Catal.*, 2010, **274**, 1.

58 X.J. Liu, R. Wang, L.Y. Song, H. He, G.Z Zhang, X.H. Zi and W.G. Qiu, *Catal. Commun.,* 2014, **46**, 213.

59 M.S. Jin, J.N. Park, J. K. Shon, J.H. Kim, Z.H. Li, Y.K. Park and J.M. Kim, *Catal. Today*, 2012, **185**, 183.

60 D.B. Pacardo and MR Knecht, *Catal. Sci. Technol.,* 2013, **3**, 745.

61 H.C. Ma, W. Cao, Z.K. Bao and Z.Q. Lei, *Catal. Sci. Technol.,* 2012, **2**, 2291.

62 F.F. Lu, D.H. Sun, J.L. Huang, M.M. Du, F. Yang, H.M. Chen, Y.L. Hong and Q.B. Li, *ACS Sustainable Chem. Eng*., 2014, **2**, 1212.

63 C.J. Liu, Y. Zhao, Y.Z. Li, D.S. Zhang, Z. Chang and X.H. Bu, *ACS Sustainable Chem. Eng*., 2014, **2**, 3.

64 J.Y. Ye, C.J. Liu and Q.F. Ge, *Phys. Chem. Chem. Phys*., 2012, **14**, 16660.

65 D. Vogel, C. Spiel, Y. Suchorski, A. Trinchero, R. Schlogl, H. Gronbeck, G. Rupprechter, *Angew. Chem., Int. Ed.*, 2012, **51**, 10041