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Effect of pretreatment on Pd/Al_2O_3 catalyst for catalytic oxidation of *o*-xylene at low temperature

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Abstract

The effect of pretreatment on Pd/Al_2O_3 catalysts for the catalytic oxidation of *o*-xylene at low temperature was studied by changing the pretreatment and testing conditions. The fresh and pretreated Pd/Al_2O_3 catalysts were characterized by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). The results showed that the pretreatment dramatically changed the Pd/PdO ratio and then significantly affected the Pd/Al_2O_3 activity; while the pretreatment had not much influence on Pd particle size. The Pd/Al_2O_3 pre-reduced at 300°C/400°C, which has fully reduced Pd species, showed the highest activity; while the fresh Pd/Al_2O_3, which has fully oxidized Pd species, presented the worst performance, indicating the Pd chemical state plays an important role in the catalytic activity for the *o*-xylene oxidation. It is concluded that metallic Pd is the active species on the Pd/Al_2O_3 catalyst for the catalytic oxidation of *o*-xylene at low temperature.

Key words: Pd/Al_2O_3; *o*-xylene; catalytic oxidation; noble metal; VOC

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Introduction

Emissions control of volatile organic compounds (VOCs) is very important for environmental protection and human health, since VOCs are known to be a major contributor to air pollution and have a high toxic potential toward human beings (Finlayson-Pitts and Pitts Jr, 1997; Jones, 1999; Lan et al., 2004). Among several well-established removal techniques, the catalytic oxidation of VOCs to carbon dioxide and water is considered to be the most suitable method for their total removal, owing to its low production of thermal NO*x*, ease of application and high efficiency (Prasad et al., 1984; Zwinkels et al., 1993).

Supported noble metals such as Pd, Pt, Rh, are regarded as promising catalysts for the oxidation of VOCs (Everaert and Baeyens, 2004). Among them, the Pd-based catalysts have been widely studied due to their relatively high activity, thermal stability and tolerance toward moisture (Lampert et al., 1997; Centi, 2001; Huang et al., 2009; Fan et al., 2012). Much research has focused on the study of the existing Pd species state during the catalytic oxidation process. The variation of the catalytic activity was found to be closely related to the changes of Pd species, particle size, and morphology (Lyubovsky et al., 1999). It is commonly accepted that Pd species can be divided into three groups, namely the metallic (Pd^0) state, the oxidized state (PdO) and a mixture of both states (Pd^0/PdO), depending on the catalytic process (Zhu et al., 2005; Shim et al., 2007). Although the catalytic behavior of supported Pd catalysts has been widely investigated, disagreement still remains as to which Pd state is active for the catalytic oxidation of VOC. Some researchers (Hicks et al., 1990; Lyubovsky and Pfefferle, 1999) have found that metallic Pd (Pd^0) is the active species for methane oxidation. However, Demoulin et al. (2005) and Yoshida et al. (2007) reported that high activity for methane oxidation was attributed to the PdO species in a Pd/Al_2O_3 catalyst. On the other hand, Burch and Urbano (1995) and Yang et al. (2000) found a correlation between high efficiency of methane conversion and the mixed Pd/PdO_x ($0 < x \leq 1$) state of the Pd species.

BTX (benzene, toluene, xylene), as one of the major classes of VOCs, exist in air in a large scale. Many researchers have focused their studies on the removal of these kinds of pollutants (Wu et al., 2000; Okumura et al., 2003; Li et al., 2005; Perez-Cadenas et al., 2008; Shim et al., 2008; Kim and Shim, 2009). A few researches have been performed to study the behavior of Pd active species during the reaction of BTX oxidation (Shim et al., 2008;

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Kim and Shim, 2009). In particular, Kim and Shim (2009) studied the effect of the Pd state and particle size on BTX oxidation over Pd/Al_2O_3 catalysts. They found that metallic Pd favors the activity of Pd/Al_2O_3 catalysts, but the Pd particle size plays the more important role in the catalytic activity (Kim and Shim, 2009). In this article, we investigated the effect of pretreatment on Pd/Al_2O_3 catalysts for the catalytic oxidation of *o*-xylene at low temperature by changing the pretreatment and testing conditions. The relationship between the chemical Pd state, Pd particle size and the activity for the *o*-xylene oxidation was discussed. It was found that the Pd state plays the key role in the catalytic activity, while the Pd particle size shows little change during the pretreatment and activity testing.

1 Materials and methods

1.1 Catalyst preparation

The catalyst (1 wt.% Pd/Al_2O_3) was prepared via the wetness impregnation technique with Al_2O_3 (305 m^2/g) and an aqueous solution containing the appropriate amount of $Pd(NO_3)_2$ (Sigma-Aldrich). The required amount of $Pd(NO_3)_2$ solution was added in the ratio of 10 mL per gram of support. After stirring for 3 hr, the excess water was removed in a rotary evaporator at 60°C. The sample was dried overnight at 110°C and calcined at 500°C for 3 hr in air. Then the prepared catalyst was crushed and sieved to 40–60 mesh for use. This was defined as the fresh catalyst. To examine the influence of gas treatments on the Pd-based catalyst, the fresh catalyst was pretreated in a 30 mL/min flow rate of hydrogen or oxygen (10% H_2/Ar or 20% O_2/N_2) at different temperatures (100°C, 200°C, 300°C and 400°C) for 1 hr.

1.2 Catalyst characterization

The catalysts were analyzed using X-ray photoelectron spectroscopy (XPS) to identify the nature of the surface and the concentration of the active species. The spectra were recorded in an ESCALAB Mark II spectrometer (Vacuum Generators, UK) using Al $K\alpha$ radiation ($h\nu$ = 1486.6 eV) with a constant pass energy of 50 eV. The C 1s peak (285.0 eV) was used to calibrate the binding energy (BE) values. An approximate quantitative calculation was made by integrating the areas of the Pd and PdO peaks after curve peakfitting. The crystal phases of the catalysts were characterized by X-ray diffractometry using a computerized Rigaku D/max-RB X-ray diffractometer (Cu $K\alpha$ radiation, 0.154056 nm, Japan) with the X-ray tube operated at 40 kV and 100 mA. The samples were investigated in the 2θ range 10°–90° at a scanning speed of 4°/min. TEM images were obtained by employing a HITACHI H-7500 transmission electron microscope (Japan) with an acceleration voltage of 80 kV. The average particle size (d, mm) of the metallic Pd was determined from an arithmetical mean of ca. 200 Pd particles in the TEM images. On the basis of the average particle size, the dispersion (D, %) can be estimated from the expression $D = 112/d$, assuming spherical particles and a Pd surface atom density of 1.27×10^{19} atoms/m^2 (Ribeiro et al., 1994).

1.3 Catalytic test

The activity test for the catalytic oxidation of *o*-xylene over Pd/Al_2O_3 catalyst was performed in a continuous-flow fixed bed reactor under atmospheric pressure. The catalyst (40–60 mesh) was supported on a small plug of glass wool in the middle of a straight-tube quartz reactor. Before the activity tests, the Pd/Al_2O_3 catalysts were pretreated in a flow of 30 mL/min 10% H_2/Ar or 20% O_2/N_2 gas. The 100 ppm *o*-xylene gas was produced by a N_2 stream bubbling through a saturator filled with liquid *o*-xylene and the concentration of *o*-xylene was controlled by either the flow rate of nitrogen or the temperature of the water bath. The reaction feed consisted of 100 ppm *o*-xylene and 20 vol.% O_2 in N_2. The flow rate of the gas mixture through the reactor was 100 mL/min. The reactants and the products were analyzed on-line using a GC/MS (5973N-6890N, Agilent, USA) with a HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm) and another GC (GC-112A, Shangfen, China) with a carbon molecule sieve column.

2 Results and discussion

2.1 Catalytic performance

We first investigated the effect of pre-reduction on the activity of Pd/Al_2O_3. The catalyst was pre-reduced in a pure H_2 flow of 30 mL/min at 100°C, 200°C, 300°C and 400°C for 1 hr (denoted as H_{T1}, H_{T2}, H_{T3} and H_{T4}, respectively). **Figure 1** shows the *o*-xylene conversions over the fresh and pre-reduced Pd/Al_2O_3 catalysts. The results indicated that the activity of Pd/Al_2O_3 was closely related to the pre-reduction temperature. The conversion profiles shifted to lower temperatures with increasing reduction temperature. The catalytic activity followed the order of $H_{T4} \approx H_{T3} > H_{T2} > H_{T1}$. The H_{T3} and H_{T4} samples demonstrated similar excellent activity and the complete conversion of 100 ppm *o*-xylene could be obtained at 160°C. It is worth noting that all of the H_2 pretreated catalysts were much more active than the fresh one.

The reduced catalyst was further pretreated in various oxidative atmospheres following the pre-reduction at 300°C and then tested. The experimental details were as follows: the catalysts were pretreated with (a) H_2 at 300°C for 1 hr (H_{T3}), (b) H_2 at 300°C for 1 hr then with pure O_2 at 200°C for 1 hr ($H_{T3}O_{T2}$), (c) H_2 at 300°C for 1 hr then with O_2 at 300°C for 1 hr ($H_{T3}O_{T3}$), (d) H_2 at 300°C for 1 hr then with O_2 at 400°C for 1 hr ($H_{T3}O_{T4}$). **Figure 2** shows the activity comparison of the pretreated catalysts. The catalytic activities followed the order of H_{T3}

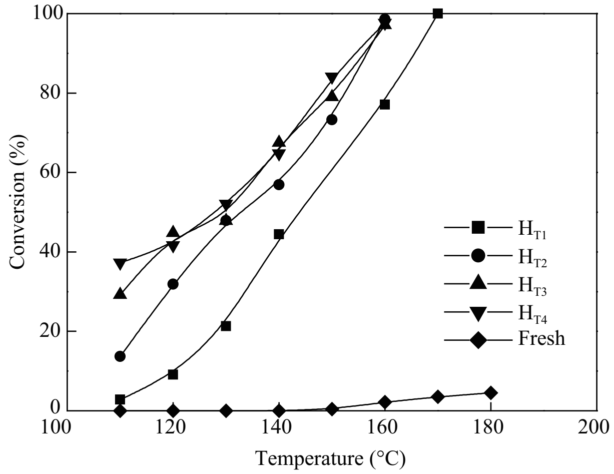

Fig. 1 *o*-Xylene conversion over fresh and pre-reduced 1% Pd/Al_2O_3 catalysts. Reaction conditions: *o*-xylene 100 ppm, 20 vol.% O_2, N_2 balance, total flow rate 100 mL/min, GHSV 50,000 hr^{-1}.

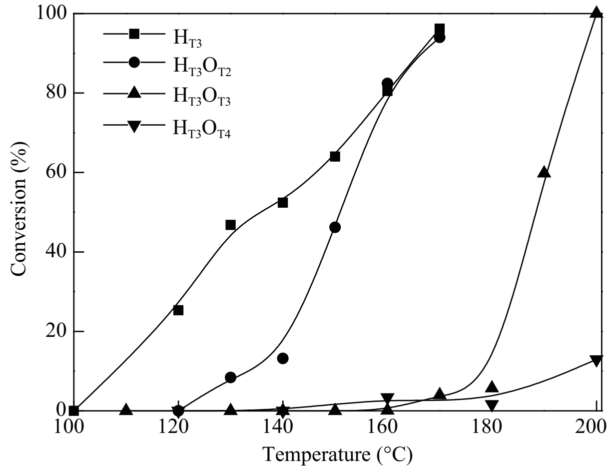

Fig. 2 *o*-Xylene conversion over 1% Pd/Al_2O_3 catalysts pretreated by different methods. Reaction conditions: *o*-xylene 100 ppm, 20 vol.% O_2, N_2 balance, total flow rate 100 mL/min, GHSV 50,000 hr^{-1}.

> $H_{T3}O_{T2}$ > $H_{T3}O_{T3}$ > $H_{T3}O_{T4}$. The activity decreased sharply with the increase of O_2 treatment temperature and the catalyst pretreated at 400°C presented the lowest activity. The T_{50} (temperature for 50% *o*-xylene conversion) increased from 130°C to 150°C and 189°C for the H_{T3}, $H_{T3}O_{T2}$, and $H_{T3}O_{T3}$ samples, respectively. For the $H_{T3}O_{T4}$ catalysts, the *o*-xylene conversion was not more than 20% at 200°C.

The stability of the pre-reduced catalyst was studied over the H_{T3} sample by repeating the test in the working condition of an oxidative atmosphere (20% O_2) (**Fig. 3**). The catalyst in the first run had the highest activity for *o*-xylene oxidation, especially at the low temperature range from 100 to 150°C. In contrast, the activity ($T < 160°C$) dramatically dropped in the 2nd, 3rd and 4th runs. A long-term test (time on stream (TOS) test) was also carried out over the H_{T3} sample at 160°C for 55 hr and the result is shown in **Fig. 4**. The catalyst showed a high *o*-xylene conversion in the first few hours and then the conversion slightly decreased from 98% to 94% in the following time, demonstrating that the Pd/Al_2O_3 is relatively stable at this temperature even in an oxidative atmosphere. In addition, a small oscillation of the *o*-xylene conversion was observed during the TOS test. This oscillation has frequently been explained by a mechanism whereby the metal is oxidized by oxygen and reduced by the hydrocarbon in a cyclic manner, so that it becomes successively less or more active, giving the oscillatory behavior (Tsou et al., 2004). Based on the results of both the four-run tests and the TOS test, it is suggested that the metallic Pd could be partially oxidized to PdO in a working atmosphere containing 20% O_2; however, it still maintained a relatively stable activity at 160°C.

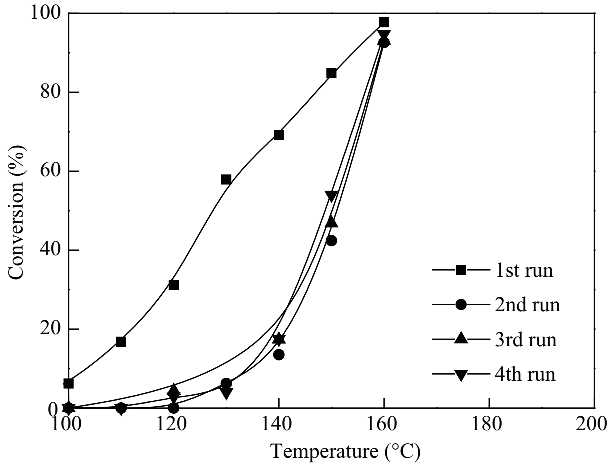

Fig. 3 Repeatability test for *o*-xylene catalytic oxidation over the pre-reduced 1% Pd/Al_2O_3 catalyst. Reaction conditions: catalyst pre-reduced at 300°C for 1 hr, *o*-xylene 100 ppm, 20 vol.% O_2, N_2 balance, total flow rate 100 mL/min, GHSV 50,000 hr^{-1}.

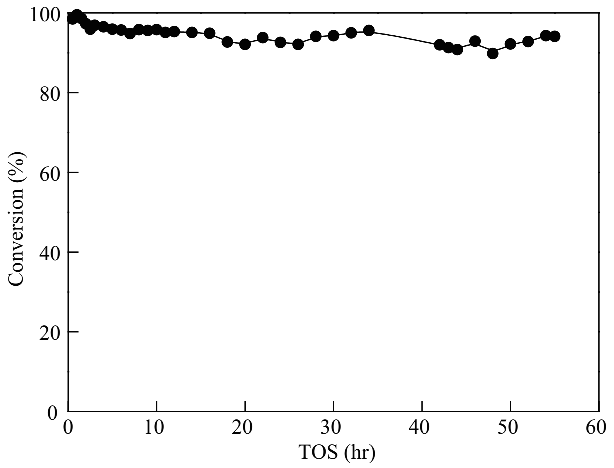

Fig. 4 *o*-Xylene conversion with time on stream (TOS) over the pre-reduced 1% Pd/Al_2O_3 catalyst at 160°C. Reaction conditions: catalyst pre-reduced at 300°C for 1 hr, *o*-xylene 100 ppm, 20 vol.% O_2, N_2 balance, total flow rate 100 mL/min, GHSV 50,000 hr^{-1}.

2.2 TEM

Figure 5 shows the TEM images of the Pd/Al_2O_3 catalysts pretreated at different temperatures. **Table 1** gives a sum-

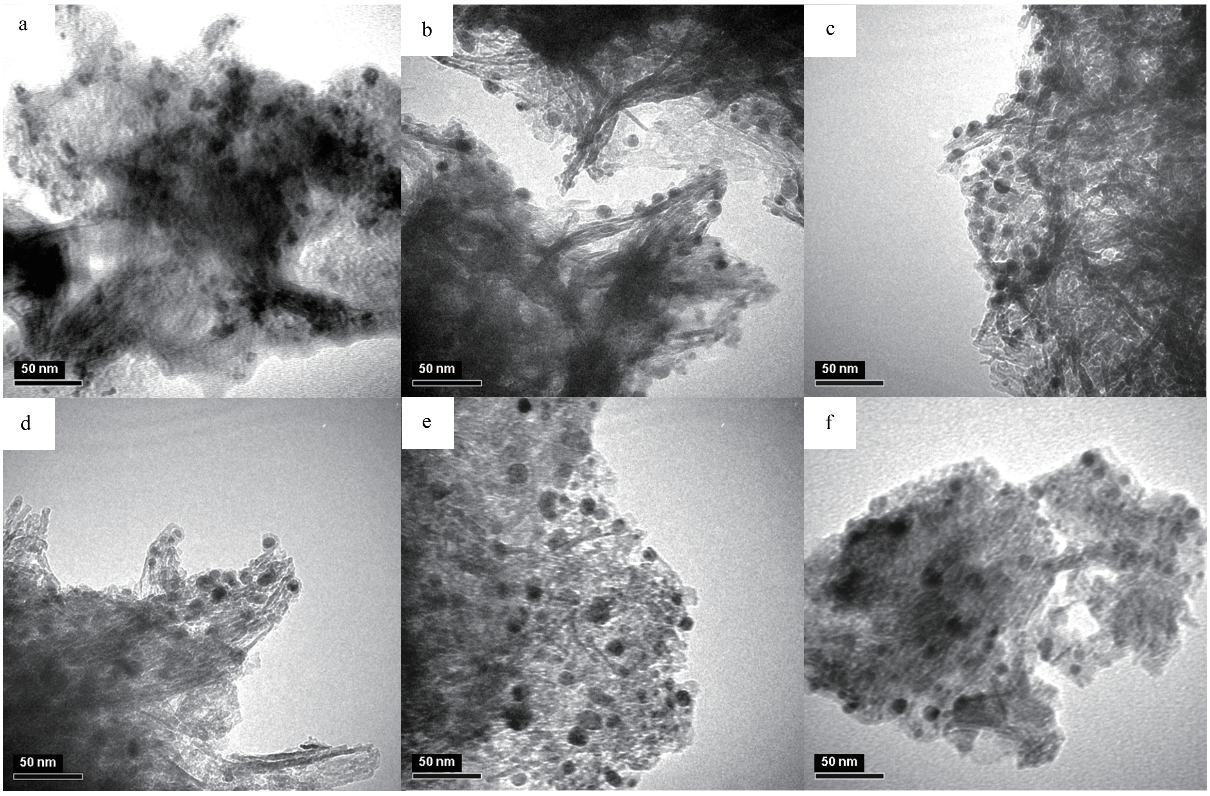

Fig. 5 TEM images of 1% Pd/Al$_2$O$_3$ catalysts after different pretreatment conditions. (a) fresh catalyst; (b) pre-reduced at 100°C for 1 hr; (c) pre-reduced at 200°C for 1 hr; (d) pre-reduced at 300°C for 1 hr; (e) pre-reduced at 400°C for 1 hr; (f) after the TOS test.

Table 1 Binding energy of Pd 3d$_{5/2}$, Pd dispersion, Pd particle sizes and Pd^0 content for Pd/Al$_2$O$_3$ catalysts pre-reduced under different conditions

Sample	Binding energy			
	3d$_{5/2}$ (eV)	Pd particle size^a (nm)	Pd dispersion^b (%)	Pd^{0c} (%)
Fresh	336.8	8.00	/	0
H$_{T1}$	336.0	7.80	/	32.6
H$_{T2}$	335.2	6.75	16.6	72.4
H$_{T3}$	335.1	7.68	14.6	100
H$_{T4}$	335.1	8.45	13.3	100

[a] Average value of 200 Pd particles in TEM image.

[b] Deduced from the expression $D_{\text{dispersion}} = 112/d$. Assumes spherical particles and a Pd surface atom density of 1.27×10^{19} atoms/m^2.

[c] An approximate quantitative calculation of Pd^0 content was made by integrating the areas of the Pd and PdO peaks after XPS curve peakfitting.

mary of the Pd particle sizes and Pd dispersion in these samples. The Pd particles had a spherical morphology and a crystalline particle diameter of around 6–9 nm. The Pd particles in fresh and H$_{T1}$ catalysts displayed the sizes of 8.0 nm (**Fig. 5a**) and 7.80 nm (**Fig. 5b**). The H$_{T2}$ catalyst showed a smaller particle size of 6.75 nm (**Fig. 5c**) due to Pd shrinkage during the H$_2$ reduction. Further increasing of the reduction temperature from 200 to 300 and 400°C (H$_{T3}$ and H$_{T4}$ catalysts) resulted in the slight increase of the Pd particle sizes from 6.75 to 7.68 (**Fig. 5d**) and 8.45 nm (**Fig. 5e**) and the decrease of Pd dispersion from 16.6% to14.6% and 13.3%, respectively. Fresh and H$_{T1}$ catalysts presented larger Pd particle sizes than H$_{T2}$ and H$_{T3}$ catalysts, possibly due to the fact that most of the Pd over the fresh and H$_{T1}$ catalysts still exists in the Pd oxide state, which has a larger particle size compared to the reduced catalyst. In addition, the TOS test did not induce any observable change in Pd particle size and shape, still presenting about 8 nm Pd particle size and also a sphere-like shape (**Fig. 5f**). These results indicated that pre-reduction and the TOS test at 160°C have little influence on the Pd particle size on Pd/Al$_2$O$_3$ catalysts.

Kim and Shim (2009) have previously investigated the particle size of Pd in fresh Pd/Al$_2$O$_3$, H$_2$-treated and tested samples. In their case, the Pd particle size in fresh samples was about 7–10 nm, similar to our result, but the H$_2$ treatment (300°C for 2 hr) resulted in a slight increase of the particle size to 10–16 nm. In addition, they found that the Pd particle size was significantly increased to 20–40 nm after being tested for 140 min at 240°C. Therefore, they attributed the improved activity of the H$_2$-treated sample to the increase of the Pd particle size. However, in our case, we did not observe a significant increase of the Pd particle size after the H$_2$ treatment and the TOS test for 55 hr at 160°C, possibly due to the different treating and testing conditions.

2.3 XPS

Figure 6 shows the Pd 3d XPS results of the Pd/Al$_2$O$_3$ catalysts pre-reduced at different temperatures. The fresh

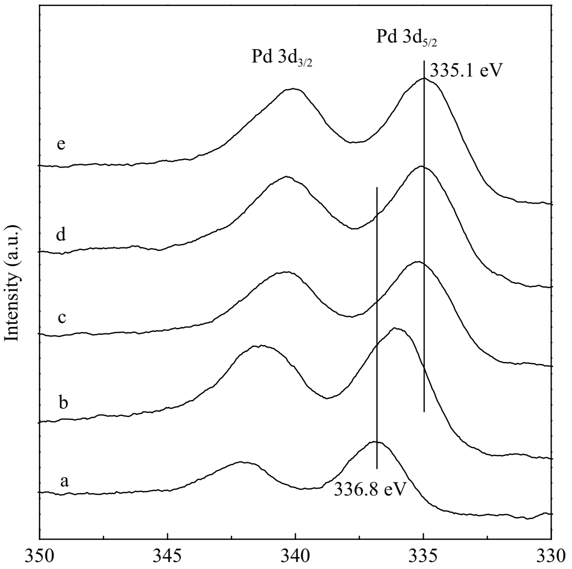

Fig. 6 XPS spectra of Pd/Al_2O_3 catalysts with different H_2 pre-reduction temperatures. (line a) fresh catalyst; (line b) pre-reduced at 100°C for 1 hr; (line c) pre-reduced at 200°C for 1 hr; (line d) pre-reduced at 300°C for 1 hr; (line e) pre-reduced at 400°C for 1 hr.

catalyst presented a Pd $3d_{5/2}$ photoemission line centered at 336.8 eV (**Fig. 6 line a**), indicating that the Pd species were all in the oxide state (Brun et al., 1999). When the catalysts were reduced at 100°C and 200°C, the BE peak of Pd $3d_{5/2}$ shifted from 336.8 to 336.0 and 335.2 eV (**Fig. 6 line b, c**), indicating that both metallic and oxide Pd co-existed on the H_{T1} and H_{T2} catalysts. After being reduced at 300°C and 400°C, the Pd species gave a Pd $3d_{5/2}$ BE of 335.1 eV (**Fig. 6 line d, e**), showing that Pd was in the metallic state on H_{T3} and H_{T4} catalysts (Schmal et al., 2006). **Table 2** summarizes the binding energy (BE) values of the Pd $3d_{5/2}$ core level and the metallic Pd content in these catalysts. It is indicated that Pd species on the catalyst could be completely (100%) reduced to metallic Pd when pre-reduced at temperatures higher than 300°C.

XPS spectra of Pd/Al_2O_3 catalysts treated and tested under different conditions were also measured. The results are shown in **Fig. 7** and a summary of the BE values and Pd/PdO ratios for these catalysts is given in **Table 2**. The fresh catalyst only presented the Pd oxide peak at 336.8 eV (**Fig. 7 line a**), and the H_{T3} sample only showed the metallic Pd peak at 335.1 eV (**Fig. 7 line e**). When the H_{T3} sample was further treated in oxygen or directly tested for *o*-xylene oxidation, a dramatic change of Pd state was observed. After the 1st test run, a part of the surface metallic Pd had been oxidized to PdO even at low temperatures (< 160°C) and the Pd peak shifted from 335.1 to 335.4 eV (**Fig. 7d**). After the 55 hr TOS test, the peak shifted to 335.6 eV (**Fig. 7c**), which is 0.2 eV higher than that of the 1st run catalyst. As for the $H_{T3}O_{T2}$ sample (pre-reduced at 300°C for 1 hr and then oxidized at 200°C for 1 hr in an oxygen atmosphere), the Pd $3d_{5/2}$ peak was at 336.2 eV (**Fig. 7b**). As shown in **Table 2**, about 23.8%, 33.3% and 44.4% of metallic Pd in the H_{T3} sample were changed into Pd oxide after the 1st test run, TOS and oxidation at 200°C, respectively. On the basis of these XPS results and activity test results in **Fig. 2**, it is suggested that the formation of Pd oxide during the tests accounts for the dramatic loss of the activity at low temperature.

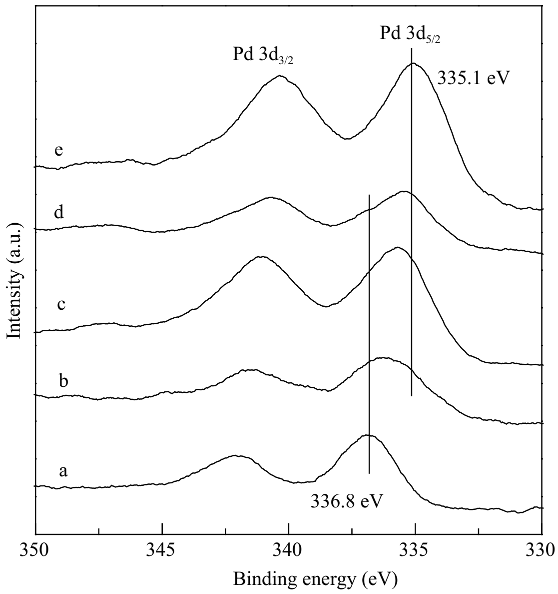

Fig. 7 XPS spectra of 1% Pd/Al_2O_3 catalysts with different pretreatments. (line a) fresh catalyst; (line b) pre-reduced at 300°C for 1 hr and then oxidized with pure O_2 at 200°C for 1 hr; (line c) after TOS test; (line d) 1st run; (line e) pre-reduced at 300°C for 1 hr.

Kim and Shim (2009) have also investigated the Pd state in fresh Pd/Al_2O_3, H_2-treated and tested samples using XPS measurement. They also found that the fresh catalyst only presented the Pd oxide peak and the H_2-treated sample only showed the metallic Pd peak; however, they did not observe an obvious change in the Pd state in the reduced sample during activity testing at a given temperature (240°C). Therefore, Kim and Shim (2009) conclude that the Pd state does not play an important role in the catalytic activity.

2.4 XRD

For a bulk crystalline analysis of the Pd/Al_2O_3 catalysts, the XRD technique was employed. **Figure 8** shows the XRD patterns of three kinds of catalysts. The diffraction

Table 2 Bingding energy (BE) value of Pd $3d_{5/2}$, Pd^0 content and Pd^0/Pd^{2+} atomic ratio in 1% Pd/Al_2O_3 catalysts pre-treated or tested under different conditions

Sample	BE Pd$3d_{5/2}$ (eV)	Pd^{0a} (%)	Pd/Pd^{2+}
Fresh	336.8	0	0
H_{T3}	335.1	100	\
After 1st run	335.4	76.2	3.20
After TOS	335.6	66.7	2.00
$H_{T3}O_{T2}$	336.2	55.6	1.25

[a] An approximate quantitative calculation of Pd^0 content was made by integrating the areas of the Pd and PdO peaks after XPS curve peakfitting.

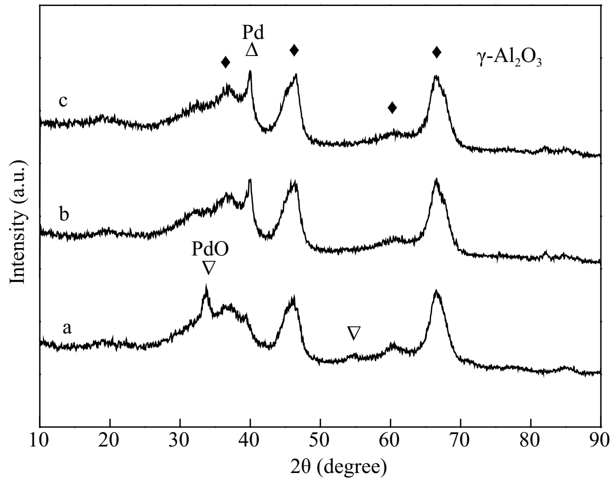

Fig. 8 X-ray diffraction patterns of 1% Pd/Al_2O_3 catalysts. (line a) fresh catalyst; (line b) pre-reduced at 300°C for 1 hr; (line c) after 55 hr TOS test.

lines at 2θ = 37.7°, 45.9°, and 66.9° (PDF 79–1558) were assigned to γ-Al_2O_3 and those at 2θ = 33.5°, 33.8° and 54.7° (PDF 41–1107) were attributed to the PdO species. In addition, the diffraction lines at 2θ = 40.2°, 46.8° and 68.3° (PDF 87–0639) are characteristic of the metallic Pd phase. PdO was the dominant phase in fresh catalyst (**Fig. 8 line a**) and no metallic Pd diffraction lines were detected. However, metallic Pd was the main species and no observable PdO phase appeared in both the H_{T3} sample (**Fig. 8 line b**) and used catalyst (**Fig. 8 line c**). The absence of the PdO peak in the used catalyst indicates that the amount of surface PdO species was below the XRD detection limit.

3 Conclusions

Pd state plays an important role in the catalytic activity of Pd/Al_2O_3 for *o*-xylene oxidation at low temperature. The Pd/Al_2O_3 catalyst fully reduced at 300°C/400°C in a flow of H_2 for 1 hr has the highest activity for the *o*-xylene oxidation. Further oxidizing treatment of the reduced catalysts sharply decreases the catalytic activity. It is confirmed that metallic Pd is the active species for *o*-xylene catalytic oxidation over the Pd/Al_2O_3 catalyst at low temperature; however, the metallic Pd is not stable during the activity test and could be partially oxidized into PdO, which is the reason for the dramatic loss of activity. Therefore, stabilizing the metallic Pd species on the catalyst surface during BTX oxidation process is critical for the Pd/Al_2O_3 catalyst to maintain high activity at low temperature.

Acknowledgments

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