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Thermal Stable Pd/$Ce_{0.2}Y_{0.8}O_{2-\delta}$ Catalysts for CO and CH_4 Oxidation

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Abstract A series of Pd/$Ce_{0.2}Y_{0.8}O_{2-\delta}$ catalysts were prepared and tested for CO and CH_4 oxidation. It is found that the Pd/$Ce_{0.2}Y_{0.8}O_{2-\delta}$ catalysts are thermal stable, and the catalytic activity enhances with increasing calcination temperature. The enhancement of the activity is due to the decomposition of surface carbonate species and the increase in average oxidation state of Pd.

Keywords Pd/$Ce_{0.2}Y_{0.8}O_{2-\delta}$ catalysts · Thermal stable · CO oxidation · CH_4 oxidation · CO-TPR

1 Introduction

Catalytic combustion has been demonstrated as one of the most attractive technologies for the exhaust gas treatment and environment-friendly combustion of gaseous fuels [1–3]. In recent decades, the oxidation of CO and methane has been drawn great attention because of the interests arising from pollution abatement and power generation. Noble metal catalysts are most active for CO and methane oxidation, and Pd-containing catalysts are widely used for the oxidation reactions [4–6]. The supported Pd catalyst has been reported to possess the highest catalytic active for methane oxidation [7, 8], and its catalytic behavior has been extensively investigated [9–11].

However, there is no general agreement on many questions concerning the active phase for the reaction. Ribeiro et al. [12] reported that bulk PdO phase formed on the metallic Pd particles had the highest per site activity, while Oh et al. [13, 14] and Lyubovsky and Pfefferle [15] concluded that metallic Pd was more active than PdO in the methane combustion reaction at higher temperatures. In contrast, Burch and Urbano [16], Farrauto et al. [17], and McCarty [18] considered the metal phase to be less active or completely inactive. Moreover, regarding the structure-sensitivity of methane oxidation over Pd catalysts, Hicks et al. [19, 20] reported methane combustion was a structure sensitivity reaction and higher turnover rate (TOR) for larger Pd crystallites. Likewise, Oh and Hoflund [21] found the larger size Pd powder was about three times more active for CO oxidation than the smaller size Pd powder on a surface area basis. However, Cullis and Willatt [22] did not observe strong effects of crystallite size on the reaction turnover rate.

Generally, the high-temperature calcination leads to the decrease in the catalytic activity of the catalyst. Methane is a well known greenhouse gas and its strong C–H bonds are the most difficult to be broken, its catalytic oxidation requires higher temperatures. Therefore, it is necessary that the catalyst possesses a fairly good stability at higher temperatures. In this work, Pd/$Ce_{0.2}Y_{0.8}O_{2-\delta}$ catalysts were prepared, and the effect of the calcination temperature on the performance of the catalysts for the oxidation of CO and CH_4 was investigated.

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2 Experimental

2.1 Preparation of Catalysts

$Ce_{0.2}Y_{0.8}O_{2-\delta}$ mixed oxides was prepared by a citrate sol–gel method. A mixture of CeO_2, $Y(OH)_3$ and citric acid was dissolved into deionized water, where the Ce/Y molar ratio was 1/4 and the citric acid was added with equal mole with respect to the sum of metal salts. The solution was heated in water bath until a viscous gel was obtained. Then the gel was dried at 120 °C overnight and calcined in air at 550 °C for 4 h, the resulting sample was denoted as $Ce_{0.2}Y_{0.8}O_{2-\delta}$.

Supported Pd catalysts were prepared using a conventional impregnation method with an aqueous solution of H_2PdCl_4 (Pd content is 8.85 g L^{-1}). The catalysts were dried at 120 °C over night, and then calcined at different temperatures (500–1,200 °C) in air for 4 h. The resulting catalyst was denoted as $Pd/Ce_{0.2}Y_{0.8}O_{2-\delta}$, and the Pd loading was 3 wt.%. Also, reference Pd/Al_2O_3 catalysts with the same Pd content was prepared in a similar manner, using γ-Al_2O_3 as the support. These catalysts were calcined at 500 and 1,200 °C, denoted as Pd/Al_2O_3-500 and Pd/Al_2O_3-1200, respectively.

2.2 Characterization

X-ray diffraction (XRD) patterns were collected on a PANalytical X'Pert PRO MPD powder diffractometer using Cu $K\alpha$ radiation. The working voltage of the instrument was 40 kV and the current was 40 mA. The intensity data were collected at room temperature in a 2θ range from 15 to 110° with a scan rate of 0.6° min^{-1}.

Raman spectra were obtained with a Renishaw RM1000 confocal microscope. The exciting wavelength was 514.5 nm from an Ar laser with a power of ca. 3 mw.

The redox properties of the $Pd/Ce_{0.2}Y_{0.8}O_{2-\delta}$ catalysts were measured by CO temperature-programmed reduction (CO-TPR). 50 mg of the catalyst was located in a quartz tube and pretreated in O_2 at 500 °C for 1 h. When the catalyst cooled down to 100 °C, a gas mixture of 5% CO in Ar (30 mL min^{-1}) was introduced. The sample was then heated from 100 °C to 900 °C with a heating rate of 20 °C min^{-1}. The signal of CO_2 was monitored by a Balzers Omnistar 200 mass spectrometer at $m/e = 44$.

CO_2-TPD was also performed with a Balzers Omnistar-200 mass spectrometer, monitoring $m/e = 44$ (CO_2). A 50 mg of sample was pretreatmented in O_2 at 500 °C for 1 h and cooled down to room temperature, and then it was purged with He for 1 h. Finally, the sample was conducted in He flow (20 mL min^{-1}) from room temperature to 900 °C with a linear heating rate of 20 °C min^{-1}.

X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250 high performance electron spectrometer using nonmonochromatized Al $K\alpha$ excitation source ($h\nu = 1486.6$ eV). Binding energies were calibrated by using the contaminant carbon ($C_{1s} = 284.6$ eV).

2.3 Catalytic Testing

The catalytic activity measurements of CO and CH_4 were carried out in a fixed bed reactor (i.d. = 6 mm). 250 mg of the catalyst (20–40 meshes) was used for reaction without any pretreatment. For both reactions, the total gas flow rate was 40 mL min^{-1} and the reaction was stabilized for 1 h. For CO oxidation, the composition of inlet gas mixture was 1% CO, 1% O_2 in N_2. The inlet and outlet gas mixture was analyzed on a Agilent 6850 gas chromatograph equipped with a TCD detector attached with a HP PLOT column (30 m × 0.32 mm × 12.0 μm). For methane oxidation, the inlet gas was 0.5% CH_4, 3% O_2 in volume and with N_2 as balance gas. CH_4 was analyzed on a Shimadzu GC-14C gas chromatograph equipped with a FID detector attached with a supelcowax-10 column (30 m × 0.25 mm × 0.25 μm).

3 Results and Discussion

3.1 Catalytic Activity for CO and CH_4 Oxidation

Figure 1 shows the effect of calcination temperature on the catalytic activity of the CO oxidation over the $Pd/Ce_{0.2}Y_{0.8}O_{2-\delta}$ catalysts. As seen in Fig. 1a, for catalysts calcined at 500 °C and 1,200 °C, the T_{99} (the temperature when the conversion is 99%) of CO oxidation are 230 and 190 °C, respectively. It is clearly seen that the catalytic activity enhances with increasing calcination temperature. Also, from Fig. 1b, it can be seen that the reference Pd/Al_2O_3 catalyst calcined at low temperature (e.g. 500 °C) shows higher activity than that of the $Pd/Ce_{0.2}Y_{0.8}O_{2-\delta}$ catalyst. However, when calcined at high temperature (e.g. 1,200 °C), its reactivity hardly changes. Compared with the Pd/Al_2O_3 catalyst, higher calcination temperatures is more favorable for the catalytic performance of the $Pd/Ce_{0.2}Y_{0.8}O_{2-\delta}$ catalyst. Moreover, the bare support $Ce_{0.2}Y_{0.8}O_{2-\delta}$ (calcined at 900 °C, denoted as CeYO-900) is much less active for the reaction, implying that the Pd species is the main active composition in the $Pd/Ce_{0.2}Y_{0.8}O_{2-\delta}$ catalysts.

Figure 2 shows the CH_4 oxidation over the $Pd/Ce_{0.2}Y_{0.8}O_{2-\delta}$ catalysts. It is seen that the effect of calcination temperature on the catalytic activity is consistent with that for CO oxidation. The catalytic activity enhances with increasing calcination temperature, suggesting that the

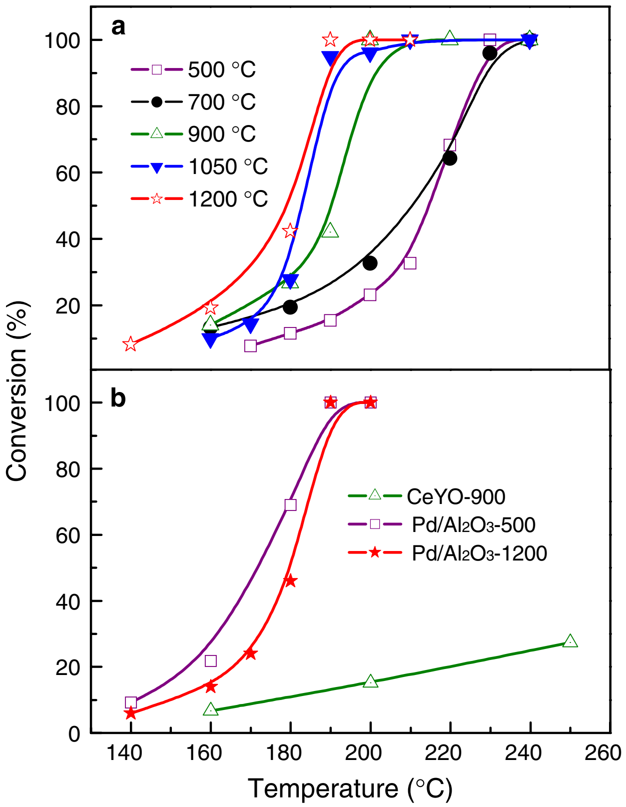

Fig. 1 CO oxidation over **a** Pd/$Ce_{0.2}Y_{0.8}O_{2-\delta}$ catalysts calcined at different temperatures; **b** Pd/Al_2O_3 catalysts and CeYO support

higher calcination temperature is favorable for the formation of the activity site and the catalytic activity increases. Moreover, it is noticed that when the calcination temperature increases, the activity of the catalyst for CH_4 oxidation enhances more obviously than that for CO oxidation, suggesting the catalyst running at higher temperatures exhibits better performance and is suitable for such high temperature reactions as the CH_4 oxidation. As seen in Fig. 2b, the reference catalysts Pd/Al_2O_3 catalyst and the $Ce_{0.2}Y_{0.8}O_{2-\delta}$ support exhibit the same catalytic behavior as the CO oxidation (Fig. 1b). Higher calcination temperatures can not improve the activity of the Pd/Al_2O_3 catalyst, and the $Ce_{0.2}Y_{0.8}O_{2-\delta}$ support is much less active than the Pd/$Ce_{0.2}Y_{0.8}O_{2-\delta}$ catalyst.

In order to investigate the stability of the catalyst, CH_4 oxidation at 550 °C over the Pd/$Ce_{0.2}Y_{0.8}O_{2-\delta}$ catalyst calcined at 1,050 °C under reaction conditions was tested and the results are shown in Fig. 3. It can be seen that the CH_4 conversion hardly changes in the 12 h continuous reaction, implying a good stability of this catalyst.

3.2 Structure Analysis of Catalysts

The XRD patterns of Pd/$Ce_{0.2}Y_{0.8}O_{2-\delta}$ catalysts calcined at different temperatures is shown in Fig. 4. For the catalyst calcined at 500 °C, only the diffraction peak associated with CeO_2 appears. For catalysts calcined at 700, 900, 1,050 and 1,200 °C, besides the peaks due to CeO_2, diffraction peaks assigned to Y_2O_3 are observed. As seen in the figure, the intensity of the CeO_2 and Y_2O_3 peaks become stronger with the increasing calcination temperature, suggesting sintering of the CeO_2 and Y_2O_3 crystallites and the crystallite size increase. However, it is difficult to analyze PdO and Pd phases, as their diffraction peaks are in the same position as those of Y_2O_3.

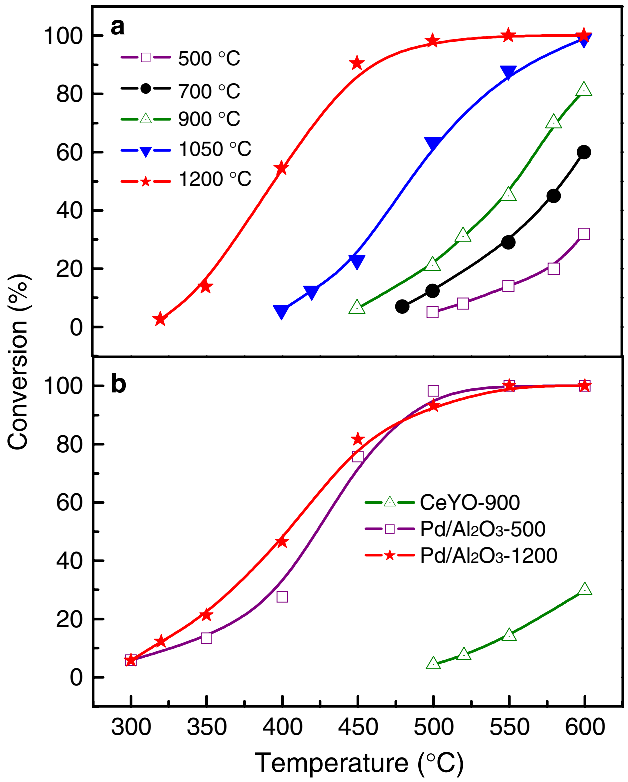

Fig. 2 CH_4 oxidation over **a** Pd/$Ce_{0.2}Y_{0.8}O_{2-\delta}$ catalysts calcined at different temperatures; **b** Pd/Al_2O_3 catalysts and CeYO support

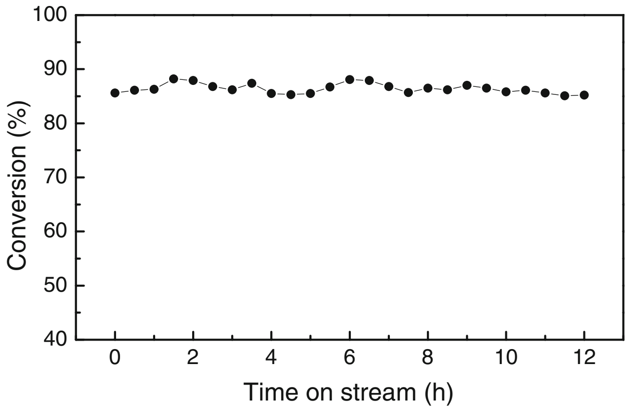

Fig. 3 CH_4 oxidation at 550 °C over Pd/$Ce_{0.2}Y_{0.8}O_{2-\delta}$ catalyst calcined at 1,050 °C

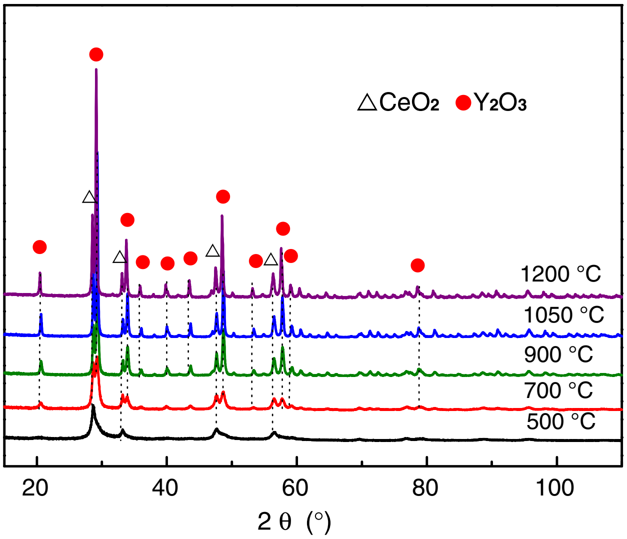

Fig. 4 XRD patterns of Pd/$Ce_{0.2}Y_{0.8}O_{2-\delta}$ catalysts calcined at different temperatures

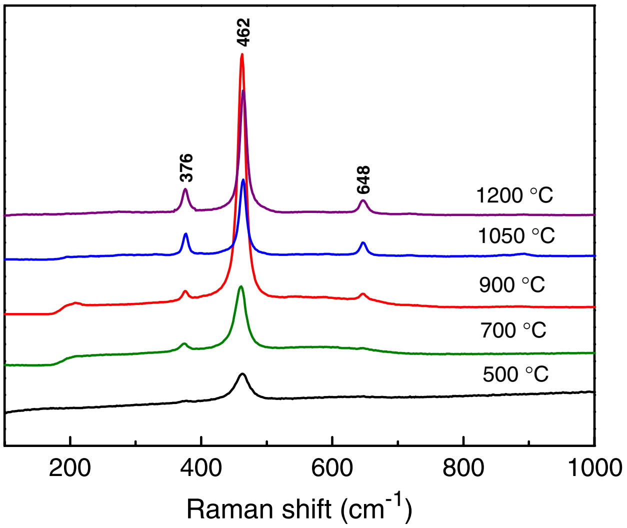

Fig. 5 Raman spectra of the Pd/$Ce_{0.2}Y_{0.8}O_{2-\delta}$ catalysts calcined at different temperatures

Figure 5 shows the Raman spectra of Pd/$Ce_{0.2}Y_{0.8}O_{2-\delta}$ catalysts calcined at different temperatures. It can be seen that for all the catalysts, there is a band at 462 cm^{-1} corresponding to CeO_2 [23], and a band at 376 cm^{-1} associated with Y_2O_3 [24] except for the catalyst calcined at 500 °C. For catalyst calcined at 700, 900, 1,050 and 1,200 °C, a band at 648 cm^{-1} corresponding to PdO [25] appears. With the increasing calcination temperatures, the intensities of the PdO, Y_2O_3 and CeO_2 bands become stronger, implying the growth of PdO and Y_2O_3 crystallites.

It is generally believed that for catalysts calcined at higher temperatures, the crystallite size of the activity species (Pd/PdO) increases and the catalytic activity declines, such as toluene combustion over Pd catalysts [26] and CO oxidation on Pd metal powders (although the TOR is higher on a surface area basis) [21]. However, combined with the activity performance of the catalysts (Figs. 1 and 2), it is found that the larger is the crystallite size of PdO, the higher is the activity of the catalyst. Therefore, there might be other factors that improve the activity of these catalysts.

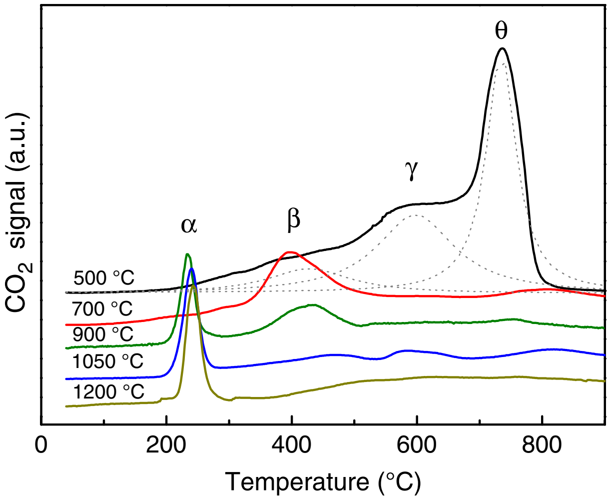

Fig. 6 CO-TPR profiles of Pd/$Ce_{0.2}Y_{0.8}O_{2-\delta}$ catalysts calcined at different temperatures

3.3 Redox Properties of Catalysts

CO-TPR profiles of Pd/$Ce_{0.2}Y_{0.8}O_{2-\delta}$ catalysts calcined at different temperatures are shown in Fig. 6. It is seen there are α peaks at 235 °C for catalysts calcined at higher temperatures (900, 1,050 and 1,200 °C); β peaks at 400 °C for catalysts calcined at 500, 700 and 900 °C are observed; γ and θ peak respectively appears at 600 and 735 °C only for the catalyst calcined at 500 °C. Combined with the Raman spectra (Fig. 5) that the crystalline PdO forms for catalysts calcined at higher temperatures and highly dispersed PdO forms for lower calcination temperatures, so the α peaks are attributed to the reduction of crystalline PdO and β peaks are attributed to the reduction of highly dispersed PdO. For catalysts calcined at higher temperatures, the crystallite size of PdO increases and the β peak disappears. It further confirms that the higher calcination temperature brings the phase change of PdO from high dispersion to crystalline phase. However, the reduction peaks at higher temperatures (γ and θ peaks) can not be ascribed to the reduction of PdO, because based on the calculation (the specific details is shown in the following paragraph), the average oxidation state of Pd is above +2, it is obviously unreasonable.

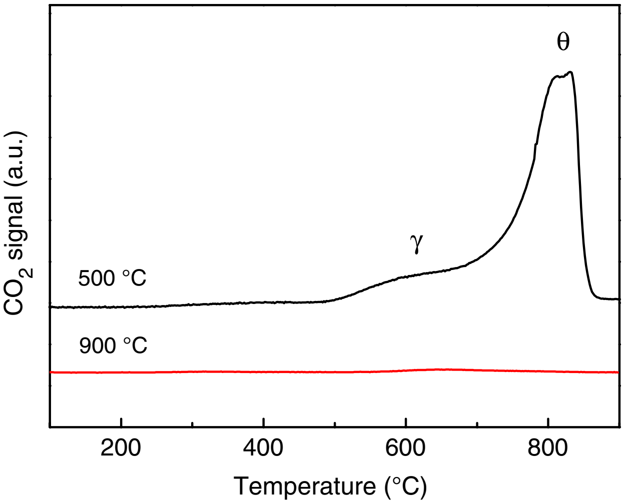

Fig. 7 CO_2-TPD profiles of Pd/$Ce_{0.2}Y_{0.8}O_{2-\delta}$ catalysts calcined at 500 and 900 °C

In order to interpret the presence of γ and θ peaks appear, CO_2-TPD of the Pd/$Ce_{0.2}Y_{0.8}O_{2-\delta}$ catalysts calcined at 500 and 900 °C were conducted, and the profile is shown in Fig. 7. As seen in the figure, for CO_2-TPD of the catalyst calcined at lower temperature (500 °C), γ and θ peaks are observed at 600 and 815 °C respectively. The desorption peaks of CO_2 only come from the decomposition of CO_3^{2-} existed on the surface of the catalyst. Compared with γ and θ peaks in Fig. 6, except the peak temperatures are slightly different, the shape and the area of these peaks are quite similar. Therefore, it is considered that γ and θ peaks in CO-TPR are ascribed to the formation of CO_2 by the decomposition of CO_3^{2-} existed on the surface of the catalyst. For the CO_2-TPD profile of the catalyst calcined at higher temperature (900 °C), no signal is observed, implying the absence of CO_3^{2-} species. This is because for the catalyst with a higher calcination temperature, CO_3^{2-} has decomposed and this decomposition is irreversible. It is reported CO_3^{2-} easily forms on the surface of Y_2O_3 and removes after heat-treating [27]. The absence of CO_3^{2-} maybe contributes to the higher activity of the catalyst calcined at higher temperature.

Based on the CO-TPR results of the catalysts (Fig. 6) and the peak area of the CO-TPR of CuO with known amount taken as a calibration, average oxidation state of Pd in the Pd/$Ce_{0.2}Y_{0.8}O_{2-\delta}$ catalysts calcined at different temperatures were calculated by the peak area of the reduction of PdO, the result is listed in Table 1. It can be seen that the average oxidation state of Pd declines with the increasing calcination temperature. Combined with the activity performance of the Pd/$Ce_{0.2}Y_{0.8}O_{2-\delta}$ catalysts for CO and CH_4 oxidation (Figs. 1 and 2), it is found that the average oxidation state of Pd drops to 0.99 from 1.92 with the increasing calcination temperature, and the activity of the catalyst increases. The decline of the average oxidation state indicates that besides Pd^{2+}, there is metallic Pd in the catalysts, and the decreasing oxidation state suggests the increase in the content of metallic Pd. For the catalyst calcined at 500 °C, the average oxidation state of Pd is 1.92, indicating that the catalyst consists mostly of Pd^{2+}; and for the catalyst calcined at 1,200 °C, the average oxidation state of Pd is 0.99, implying the content of each of Pd species (metallic Pd and Pd^{2+}) is about 50%. It is possible that the formation of metallic Pd on the PdO phase is favorable for the catalytic activity [28], that is, the lower is the average oxidation state of Pd, the higher is the activity of the catalyst.

Table 1 Average oxidation state of Pd in Pd/$Ce_{0.2}Y_{0.8}O_{2-\delta}$ catalysts calcined at different temperatures

Calcination temperature (°C)	Pd average oxidation state
500	1.92
700	1.71
900	1.56
1,050	1.03
1,200	0.99

In order to further study the chemical state of Pd species in the Pd/$Ce_{0.2}Y_{0.8}O_{2-\delta}$ catalysts, X-ray photoelectron spectroscopy measurements were performed. Figure 8 shows XPS spectra and curve-fitting of Pd $3d_{5/2}$ for the

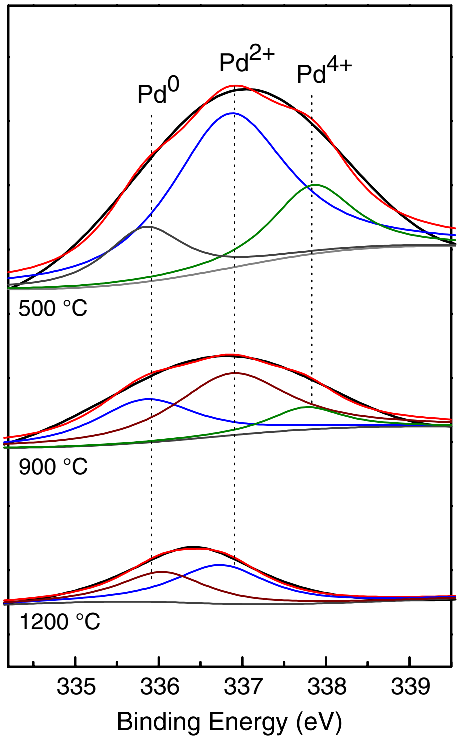

Fig. 8 XPS spectra and curve-fitting of Pd $3d_{5/2}$ for Pd/$Ce_{0.2}Y_{0.8}O_{2-\delta}$ catalysts calined at different temperatures

Table 2 Content of Pd species in Pd/$Ce_{0.2}Y_{0.8}O_{2-\delta}$ catalysts calcined at different temperatures

Calcination temperature (°C)	Content of Pd species (wt.%)		
	Pd^{4+}	Pd^{2+}	Pd
500	19.9	65.2	14.9
900	11.8	54.1	34.1
1,200	0	56.7	43.3

catalysts calcined at 500, 900 and 1,200 °C. The peaks at 335.9, 336.9 and 337.8 eV can be ascribed to Pd^0, Pd^{2+} and Pd^{4+} [28]. The contents of different Pd species calculated by the XPS spectra are listed in Table 2. For the catalyst calcined at 500 °C, the contents of Pd^0 and Pd^{4+} are 14.9% and 19.9% in the total amount of Pd species, respectively. For catalysts calcined at 900 and 1,200 °C, the contents of Pd^0 are 34.1% and 43.3%, and those of Pd^{4+} are 11.8% and 0, respectively. It can be seen, the content of metallic Pd increases and that of Pd^{4+} decreases with increasing calcination temperatures, implying the decline of the average oxidation state of Pd. It is consistent with the analysis results of the CO-TPR, and combined with the activity performance of the catalysts, it further indicates that the Pd species with lower oxidation state are more favorable for the oxidation of CO and CH_4.

4 Conclusions

A series of Pd/$Ce_{0.2}Y_{0.8}O_{2-\delta}$ catalysts calcined at different temperatures were prepared and characterized. It is found that for CO and CH_4 oxidation, the Pd/$Ce_{0.2}Y_{0.8}O_{2-\delta}$ catalyst possesses a fairly good thermal stability. With elevated calcination temperature, crystalline PdO forms and the crystallite size of PdO increases. For the catalysts calcined at lower temperature, there are CO_3^{2-} species on the surface of the catalyst, which possibly depresses the catalytic activity. With increasing calcination temperature, the CO_3^{2-} species decompose and the average oxidation state of Pd decreases, which are two main reasons for the enhancement of the reactivity for CO and CH_4 oxidation.

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References

1. McCarty JG, Gusman M, Lowe DM, Hidenbrand DL, Lau KN (1999) Catal Today 47:5
2. Forzatti P, Groppi G (1999) Catal Today 54:165
3. Pecchi G, Reyes P, Gomez R, Lopez T, Fierro JLG (1998) Appl Catal B 17:7
4. Epling WS, Hoflund GB (1999) J Catal 182:5
5. Gandhi HS, Graham GW, McCabe RW (2003) J Catal 216:433
6. Ibashi W, Groppi G, Forzatti P (2003) Catal Today 83:115
7. Choudhary TV, Banerjee S, Choudhary VR (2002) Appl Catal A 234:1
8. Reyes P, Figueroa A, Pecchi G, Fierro JLG (2000) Catal Today 62:209
9. Ciuparu D, Pfefferle L (2001) Appl Catal A 218:197
10. Faticanti M, Cioffi N, Rossi SD, Ditaranto N, Porta P, Sabbatini L, Bleve-Zacheo T (2005) Appl Catal B 60:73
11. Luo MF, Pu ZY, He M, Jin J, Jin LY (2006) J Mol Catal A 260:152
12. Ribeiro FH, Chow M, Dalla Betta RA (1994) J Catal 537–544:146
13. Oh SH, Mitchell PJ, Siewert RM (1991) J Catal 132:287
14. Oh SH, Mitchell PJ (1994) Appl Catal B 5:165
15. Lyubovsky M, Pfefferle L (1999) Catal Today 47:29
16. Burch R, Urbano FJ (1995) Appl Catal A 124:121
17. Farrauto RJ, Hobson MC, Kennelly T, Waterman EM (1992) Appl Catal A 81:227
18. McCarty JG (1995) Catal Today 26:283
19. Hicks RF, Young ML, Lee RG, Qi H (1990) J Catal 122:280
20. Hicks RF, Young ML, Lee RG, Qi H (1990) J Catal 122:295
21. Oh SH, Hoflund GB (2006) J Phys Chem A 110:7609
22. Cullis CF, Willatt BM (1983) J Catal 83:267
23. Trovarelli A, Zamar F, Llorca J, de Leitenburg C, Dolcetti G, Kiss JT (1997) J Catal 169:490
24. Yashima M, Lee JH, Kakihana M, Yoshimur M (1997) J Phys Chem Solids 58:1593
25. Su SC, Carstens JN, Bell AT (1998) J Catal 176:125
26. Luo MF, He M, Xie YL, Fang P, Jin LY (2007) Appl Catal B 69:213
27. Li X, Li Q, Wang J, Li J (2007) J Lumin 124:351
28. Cimino S, Casaletto MP, Lisi L, Russo G (2007) Appl Catal A 327:238