Surface properties and catalytic activities of PdO/CeO$_2$, PdO/TiO$_2$ and PdO/γ-Al$_2$O$_3$ catalysts

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Received 28 January 1999; revised 5 April 1999

The surface species and dispersion of PdO on CeO$_2$, TiO$_2$ and γ-Al$_2$O$_3$ have been studied by means of XRD, XPS and SEM techniques. The results obtained show that there is a great difference between CeO$_2$ support and other kinds of supports in the crystal phase structure and particle size, which are responsible for CO and CH$_4$ oxidation. The order of catalytic activity for the CH$_4$ oxidation is: PdO/CeO$_2$ > PdO/TiO$_2$ > PdO/γ-Al$_2$O$_3$ and that for CO oxidation is: PdO/CeO$_2$ > PdO/γ-Al$_2$O$_3$ > PdO/TiO$_2$. It is interesting to find that the PdO/CeO$_2$ catalyst exhibits high catalytic activity for CO oxidation even at a low temperature of 50°C. Due to strong interaction between ceria and palladium, excellent results are obtained in the oxidation reaction of CO or CH$_4$. The high dispersion of PdO is found to be the main factor for the high catalytic oxidation activity observed.

With the application of rare earth oxide catalysts in chemical research, their character has been examined extensively. Hamada$^3$ reported that many rare earth oxides were also active for the reduction of nitrogen monoxide (NO) to N$_2$. Noble metals (Pt, Pd and Rh) supported on ceria or as promoter are particularly important, because of their possible application in three-way automotive emission control catalysts$^4$.$^5$. Many researchers suggested that the nature of the support can strongly affect the catalytic properties$^6$.$^7$. Bond et al.$^8$ and Bajus et al.$^9$ have reported that supports not only provide high surface area to metal catalysts, but also drastically modify the catalytic properties of the metals. Many previous investigations have attempted to identify the ceria oxide-containing catalysts, especially from the point of view of oxygen storage capability$^{10}$. The present work was designed, in principle, to examine the dispersion state of PdO on CeO$_2$ support and that of the other two kinds of supports, such as TiO$_2$ and γ-Al$_2$O$_3$, and to explore the differences in catalytic properties between rare earth oxides and other supports.

Materials and Methods

Catalysts preparation

Supported palladium catalysts were prepared by the conventional impregnation method. Three kinds of supports used in the experiment were CeO$_2$, TiO$_2$ and γ-Al$_2$O$_3$. CeO$_2$ was obtained from Ce(NO$_3$)$_3$, by calcination at 650°C in air for 4 h. TiO$_2$ was supplied by Institute of Alum, Zhejiang, China and γ-Al$_2$O$_3$ was supplied by Wenzhou Aluminium Oxide Chemical Factory, Zhejiang, China. The loading of PdO is 2% in weight.

Structure and surface characterization

The BET surface area of the samples was determined by nitrogen adsorption on a Carlo-Erba instrument. X-ray diffraction (XRD) analysis were carried out on a Rigaku D/max—III B instrument using CuKα radiation. X-ray photoelectron spectra (XPS) was recorded on PHI-550 instrument using AlKα excitation source. Corrections related to charge on the samples were made with respect to the position of the C1s peak at 284.6 eV.

Activity measurement

The catalytic oxidation of CO and CH$_4$ was carried out in a fixed-bed flow reactor. The reaction mixture for CO oxidation contained CO:5.0%, O$_2$:3.5% in N$_2$; the reaction gases for CH$_4$ oxidation were CH$_4$:3.0%, O$_2$:8.0% in N$_2$. The amount of catalyst used in the reaction was 150 mg. The analyses of the effluent from the reactor were monitored with a SP-2304 model gas chromatograph.
Results and Discussion

X-ray diffraction (XRD) analysis

XRD patterns of the catalysts were shown in Fig. 1. It can be seen that the PdO diffraction lines cannot be detected in PdO/CeO₂ catalyst, while in PdO/TiO₂ and PdO/γ-Al₂O₃ catalysts, the PdO phase can be clearly observed. This indicates that PdO was well dispersed on the surface of CeO₂ support. Although the surface area of γ-Al₂O₃ (~220 m²/g) is higher than that of CeO₂ (~55 m²/g), the dispersion of PdO on CeO₂ was higher than that on γ-Al₂O₃. So the dispersion of PdO on the catalysts surface did not depend on the surface area of supports. Step scan has also been used to analyze the PdO (002, 101) peak for PdO particle size calculation on these three supports (shown in the right top in Fig. 1). The time of step count was 20 s, the range of 2θ was 32°-35°. The result indicated that the 002, 101 diffraction signals of PdO can be detected on TiO₂ support, but on γ-Al₂O₃ support, besides the 002, 101 diffraction, the 110, 112, 102, 200 diffraction also could be detected. The larger the PdO particle sizes are, the lower the dispersion of the PdO on supports is. The PdO dispersion over these catalysts follows the order: PdO/CeO₂ > PdO/TiO₂ > PdO/γ-Al₂O₃.

Comparison of the particle sizes of PdO on 002, 101 directions is given in Table 1. Data in Table 1 indicate that the PdO average particle size of PdO/γ-Al₂O₃ catalyst on (002, 101) two directions is obviously bigger than that on the PdO/TiO₂ catalyst, and the FWHW (full width of half maximum intensity) is also larger. Since the PdO is highly dispersed on the surface of CeO₂ support (PdO in this condition would not be visible through XRD) it could not be detected by the step scan technique. It is suggested that the difference among the supports also affected the PdO dispersion on the surface of catalyst.

SEM results

The morphologies of PdO on various supports were observed with scanning electron microscopy, and micrographs are shown in Fig. 2. It showed that there were great differences in particle sizes among these three catalysts. PdO particle sizes on PdO/CeO₂ catalyst are smaller than the other two. It has been found that PdO/CeO₂ catalyst was represented by finer PdO particles, which highly dispersed on support surface and the PdO particle size is the minimum (d<0.05 μm), and the particle sizes of PdO on PdO/γ-Al₂O₃ or PdO/TiO₂ catalyst are large. It was detected by SEM that PdO particle sizes of PdO/γ-Al₂O₃ are about 0.5-1.5 μm, and for PdO/TiO₂ are about 0.1-0.3 μm. The particle size of PdO from SEM agreed reasonably well with those results from XRD measurement. All these observations point to the fact that the PdO dispersion depends on the nature of the support.

XPS results

Shalvoy and co-workers¹¹ had reported that the interaction between support and active species can be studied by examining the value of the chemical shift. Data in Table 2 show the binding energy shift of the Pd 3d level of the two supported palladium catalysts. Comparing with
the data from literature\textsuperscript{12}, it has been found that the difference of the two shifts of PdO/CeO\textsubscript{2} and PdO/TiO\textsubscript{2} catalysts are 0.58 and 0.27 respectively, which shows clearly that the chemical shift of PdO/CeO\textsubscript{2} catalyst was obviously larger than that of PdO/TiO\textsubscript{2} catalyst. Such a difference should be attributed to the interaction between PdO and support, which causes an increase of electron density around the palladium\textsuperscript{13,14}. According to the standard XPS spectrum of PdO\textsuperscript{12}, it can be found that the existing state of palladium in the two supported catalysts is Pd\textsuperscript{2+}. This type of PdO-support interaction has different strengths with different supports, for surface oxygen atoms of different supports possess different electron donor properties and therefore they give Pd\textsuperscript{2+} different electronic environment. On TiO\textsubscript{2} support, the Ti-O bond is stronger, so that the interaction between Pd and support is weaker, and the chemical shift is less than that on PdO/CeO\textsubscript{2} catalyst. On the rare earth oxide support, the oxygen in ceria was more active than the other

Fig. 2 - SEM micrographs of catalysts (a) Pd/CeO\textsubscript{2}, (b) Pd/TiO\textsubscript{2} and (c) Pt/Al\textsubscript{2}O\textsubscript{3}

Fig. 3 - O1s spectra of catalysts (a) Pt/Al\textsubscript{2}O\textsubscript{3}, (b) Pd/TiO\textsubscript{2}, and (c) Pd/CeO\textsubscript{2}

Fig. 4 - Relationship between reaction temperature and CH\textsubscript{4} conversion
Catalytic activity for CO and CH$_4$ oxidation

Figures 4 and 5 show the relationship between the conversion of CH$_4$ and CO oxidation and reaction temperature. From Fig. 5, it can be seen the reaction temperature for CO oxidation decreases in the order: PdO/CeO$_2$<PdO/$\gamma$-Al$_2$O$_3$<PdO/TiO$_2$. The lower the reaction temperature is, the higher the reaction activity for CO oxidation. As to the CH$_4$ oxidation the temperature order is: PdO/CeO$_2$<PdO/TiO$_2$<PdO/$\gamma$-Al$_2$O$_3$. The most exciting result is that CO can be oxidized almost completely (98%) even at 50°C on PdO/CeO$_2$ catalyst. It indicates that the catalytic activity depends on the nature of support. The activity of PdO/CeO$_2$ catalyst is higher than that of others. The high activity of PdO/CeO$_2$ catalyst may be considered as follows: (i)CeO$_2$ support was more suitable for the PdO dispersed on catalyst surface. Obviously, there was a strong interaction between PdO and CeO$_2$, which plays an important role in CO and CH$_4$ oxidation. (ii)CeO$_2$ has electron-donor property and oxygen storage capability, which is helpful to improve the surrounding of PdO and support also account for the high activity of the catalysts. On the basis of the activity results, we can see clearly that the finely dispersed PdO species are the active sites for the oxidation reaction and they are identified to the main attribute for PdO/CeO$_2$ catalyst at low temperature oxidation reaction. CH$_4$ is more stable than CO and the oxidation mechanism is different from CO oxidation, which showed that the temperature of CH$_4$ oxidation is obviously higher than that of CO oxidation.

Conclusions

From the results mentioned above, we conclude that CeO$_2$ supported PdO catalyst shows the high activity for CO and CH$_4$ oxidation. The CO and CH$_4$ oxidation on PdO/CeO$_2$ catalyst is related to the surface species of PdO. In the present work, XPS, XRD and SEM techniques were used to identify the structure and surface species of PdO on three different kinds of supports. The PdO particle sizes on these catalysts were also calculated. The characteristics of CeO$_2$ support were compared with those of the other two kinds of supports (TiO$_2$ and $\gamma$-Al$_2$O$_3$). It is also suggested that PdO which highly dispersed on CeO$_2$ surface was the main reason for the low temperature of CO catalysis oxidation.

Acknowledgement

This research project was supported by the Zhejiang Provincial Natural Science Foundation of China.

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