

Characterization study of CeO₂ supported Pd catalyst for low-temperature carbon monoxide oxidation

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Catalysts consisting of palladium supported on cerium dioxide (Pd/CeO₂) were prepared and used for carbon monoxide oxidation in a stoichiometric mixture of carbon monoxide and oxygen. Pd/CeO₂ exhibits high catalytic activity for the oxidation of CO, showing markedly enhanced catalytic activities due to the combined effect of palladium and cerium dioxide. The Pd/CeO₂ catalyst is superior to Pd/ZrO₂, Pd/Al₂O₃, Pd/TiO₂, Pd/ZSM-5 and Pd/SiO₂ catalysts with regard to the activity under the conditions examined. The catalysts were characterized by means of XRD and TPR. The position of the H₂-TPR peak shifts to lower temperature with increasing Pd loading from 0.25 to 2.0%. CeO₂ inhibits the hydrogen reduction of PdO. CO-TPR measurements have shown the existence of three peaks. The low-temperature peak (α) is due to the Pd hydroxide species. The β peak has been attributed to finely dispersed PdO. The high-temperature peak (γ) has been attributed to crystal phase PdO. Crystal phase PdO is more difficult to reduce by CO than finely dispersed PdO. On the basis of the catalytic activity and CO-TPR results, we conclude α species (Pd hydroxide) mainly contribute to the catalytic activity for low-temperature CO oxidation.

Keywords: CO oxidation, TPR, palladium, cerium dioxide

1. Introduction

Complete oxidation of carbon monoxide and gaseous hydrocarbons to carbon dioxide and water by catalysis has been used for emission of car exhaust, odor and toxic gas. Precious metals (Pt and Pd) are well-known complete oxidation catalysts with high activity and stability. The complete oxidation is recently studied from another point of view, i.e., the low-temperature carbon monoxide oxidation, which is widely used for carbon dioxide lasers that require recombination of carbon monoxide and oxygen produced in the laser to maintain higher power output [1]. Many different catalysts have been prepared and tested for low-temperature carbon monoxide oxidation. For carbon monoxide oxidation, noble metal catalysts, such as Pd/SnO₂, Pt/SnO₂, Au/MnO_x, Au/ γ -Fe₂O₃ and Au/Co₃O₄ have been demonstrated to be very effective [1–5]. In the past several years, much interest has arisen in the use of ceria, CeO₂, as a precious metal support. For example, the Pt/CeO₂ catalyst has been used for oxidation of CO [6,7] and ethylene [8], and for the water–gas shift reaction of CO [9]. Lin and co-workers [10,11] have found that the Au–CeO₂ composite catalyst is active for carbon monoxide oxidation, complete oxidation in air occurring at room temperature. However, nearly no study on CeO₂ as a support of palladium catalyst for low-temperature (near room temperature) carbon monoxide oxidation has been reported.

The present work is concerned with TPR of Pd/CeO₂ catalysts and with their oxidation activity for car-

bon monoxide. Our aim is to gain a direct evidence of the synergism between the Pd and CeO₂, and to aid the development of Pd/CeO₂ catalysts for the low-temperature carbon monoxide oxidation.

2. Experimental

2.1. Preparation of catalysts

CeO₂ was prepared by thermal decomposition of cerous nitrate, Ce(NO₃)₃, for 4 h at 650°C in air. The BET surface area of the obtained CeO₂ material is 55 m² g⁻¹. The supported Pd/CeO₂ catalysts were prepared by the conventional wet impregnation method using an aqueous solution of H₂PdCl₄. Prepared samples were dried overnight in an oven at 120°C and then heated in air at 650°C for 4 h. The loading of Pd (nominal value) is 0.25, 0.75, 2.0, 5.0%, respectively. The catalysts are denoted as Pd/CeO₂(X%). The amount of chlorine included in the catalysts is too small to be detected by spectrophotometry [12].

2.2. Activity measurements

Catalytic activity measurements were carried out in a fixed-bed reactor (0.6 cm i.d.) using 150 mg of catalyst of 20–60 mesh size. The total rate was set at 80 sccm consisting of 2.4% CO and 1.2% O₂ in N₂. The catalysts were directly exposed to 80 sccm of reaction gas as the reactor temperature stabilized at reaction temperature, without any pretreatment. The analyses of the reactor effluent

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were performed with an online SP-2304 model gas chromatograph with a thermal conductivity detector (TCD).

2.3. H₂-TPR

H₂-TPR measurements were made in a flow system. 10 mg catalyst was pretreated in air at 200°C and placed in a TPR cell at 20°C through which H₂-N₂ (5 : 95) mixed gas flowed. The temperature of the sample was programmed to rise at a constant rate of 10°C/min and the amount of H₂ uptake during the reduction was measured by a TCD.

2.4. CO-TPR

CO-TPR measurements were made in a flow system. 30 mg catalyst was pretreated in air at 200°C and placed in a TPR cell at 20°C through which CO-He (10 : 90) mixed gas flowed. The temperature of the sample was programmed to rise at a constant rate of 10°C/min and the amount of CO uptake during the reduction was measured by a TCD. The effluent CO₂ during CO-TPR was adsorbed with 5 Å molecular sieve.

3. Results and discussion

3.1. Catalytic activity for CO oxidation

Figure 1 shows the light-off curves over Pd/CeO₂ catalysts prepared by impregnation. None of these catalysts were pretreated before running the reaction. This is particularly important in applications where pretreatment is not possible or when the catalysts must be stored before exposed to air before use. The reaction was kept at each temperature for about 1 h to achieve steady activity.

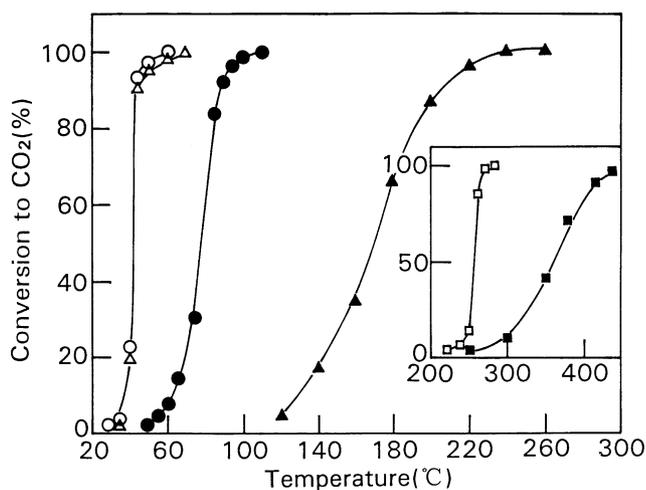


Figure 1. Effect of palladium loading in Pd/CeO₂ catalyst on CO oxidation activity. (○) 5%; (△) 2%; (●) 0.75%; (▲) 0.25%; (□) PdO(PdO 5% + quartz sand); (■) CeO₂.

From figure 1, it can be seen that the activities of pure PdO and CeO₂ are quite low, and the activity of Pd/CeO₂ catalysts is much higher than those of pure PdO and CeO₂. The activity of Pd/CeO₂ catalysts increases with Pd loading from 0.25 to 2%, but a larger amount of Pd (from 2 to 5%) does not affect the catalytic activity. The light-off temperature of Pd/CeO₂ (2 and 5%) is about 45°C. The light-off temperature of the Pd(5%)-CeO₂ catalyst prepared by coprecipitation (NaOH) is also about 45°C. Since pure PdO and CeO₂ support exhibit a very low activity, there is a synergistic interaction between the Pd and CeO₂ support that is responsible for the high activity of carbon monoxide oxidation at low temperature. The promotion of the CO oxidation activity of transition metals by ceria is well known. For example, Oh et al. [13] demonstrated the strong enhancement of the catalytic activity of Rh by ceria and suggested that the increased activity was due to the reaction of CO adsorbed on Rh with lattice oxygen supplied by neighbouring ceria. Lin et al. [10,11] reported the synergistic effect of Cu-Ce-O and Au-Ce-O catalysts, and suggested the enhanced catalytic activity was attributed to the concerted effect of CO adsorption on Au or CuO and activity of oxygen provided by cerium oxide. The studies of Hoflund et al. [14–16] and Schryer et al. [4] demonstrate that the activity of Pt/SnO₂ catalysts toward CO oxidation is strongly dependent on pretreatment conditions, and their paper also indicates that the Pt is initially present as PtO and PtO₂ and a small amount of Pt(OH)₂ and metallic Pt. Pt hydroxide is the active species on Pt/SnO₂ catalysts for low-temperature CO oxidation. Since pure PdO exhibits a very low activity, this implies that PdO is not the surface species responsible for the catalytic activity of CO at low temperature. We suppose that Pd hydroxide species is the active phase. Figure 2 shows the XRD patterns of these catalysts. From figure 2, no visible PdO or Pd crystal phase peak is observed at low Pd loading (< 2%). As the Pd loading increased to 5%, the weak crystal phase PdO peaks are observed. This implies that Pd species (PdO or Pd) on the CeO₂ surface exist in both crystalline and noncrystalline form. The amount of noncrystalline Pd species has a threshold limit value which is determined by the properties of the support. Only when the Pd species are in excess of the threshold limit value, will they exist in crystalline form. The noncrystalline form does not show the diffraction peaks. On the basis of the activity results, we propose that only a small amount of palladium (2%) is needed to form active sites for the CO oxidation, and that excess Pd forms bulk PdO particles contributing little to the activity.

The CO oxidation activity of the Pd/CeO₂(5%) catalyst as function of reaction time is shown in figure 3. The activity of the Pd/CeO₂ catalyst apparently does not decay with reaction time. Figure 4 shows the effect of support on CO oxidation activity. The support has a significant effect on the catalytic activity of the supported Pd catalysts. Activity of the Pd/CeO₂ catalyst is much

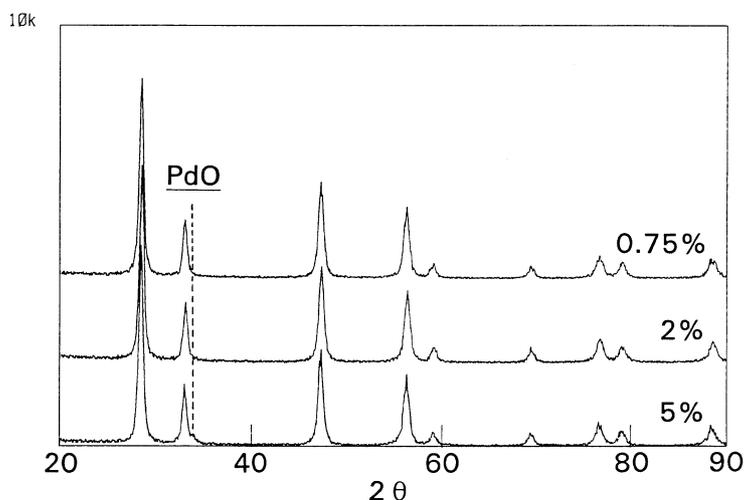


Figure 2. XRD pattern of the Pd/CeO₂ catalyst (Cu K α).

higher than that of Pd/ZrO₂, Pd/Al₂O₃, Pd/TiO₂, Pd/ZSM-5 and Pd/SiO₂ catalysts.

3.2. H₂-TPR

The H₂-TPR profiles for these Pd/CeO₂ catalyst are shown in figure 5. The reduction of pure CeO₂ began at 400°C (not shown in figure 5), and its TPR signal is much weaker than that of Pd/CeO₂(0.25%). The reduction profile of pure PdO is characterized by a single peak at 55°C. Only one reduction profile is observed for all Pd/CeO₂ catalysts. The TPR peak temperature of Pd/CeO₂ catalysts is higher than that of pure PdO. This indicates that CeO₂ inhibits the reduction of PdO. The position of the peak shifts to lower temperature and becomes narrow with increasing Pd loading from 0.25 to 2.0%; the intensity also increases with the loading. However, as Pd loading is further increased to 5%, the peak position

remains unchanged. The order of CO oxidation activity of Pd/CeO₂ is consistent with the temperature of the TPR peak of catalysts. Pure PdO is easier to reduce than Pd/CeO₂ catalyst, but the activity of pure PdO is much lower. The XRD shows that both the crystalline and noncrystalline form exist on the CeO₂ surface. The temperature of reduction of the Pd/CeO₂ catalyst shifts to lower temperature with increasing Pd loading, resembling the reduction of Pt/ γ -Al₂O₃ catalyst [17]. The large increase of the reduction temperature with dilution of PdO in the dispersed phase indicates that all the dispersed PdO molecules are in close contact with the support and they are probably separated from each other. The larger this separation, the stronger is the PdO–CeO₂ interaction. The dispersed phase where the PdO interacts more strongly with the support, is thus reduced at higher temperature. This is a reason that the temperature of

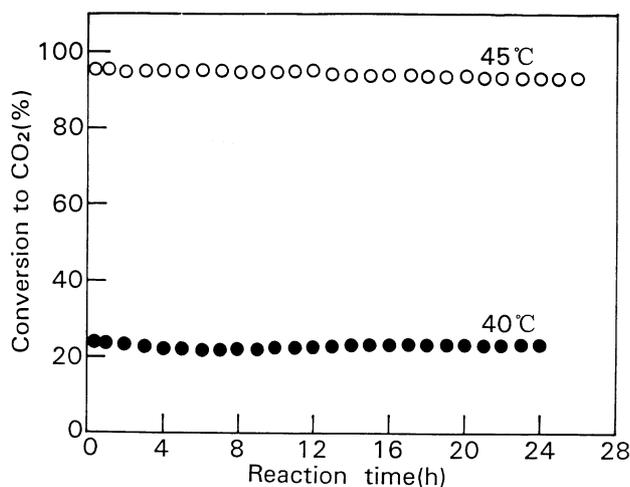


Figure 3. The percentage yield of CO₂ over Pd/CeO₂(5%) catalyst as a function of reaction time.

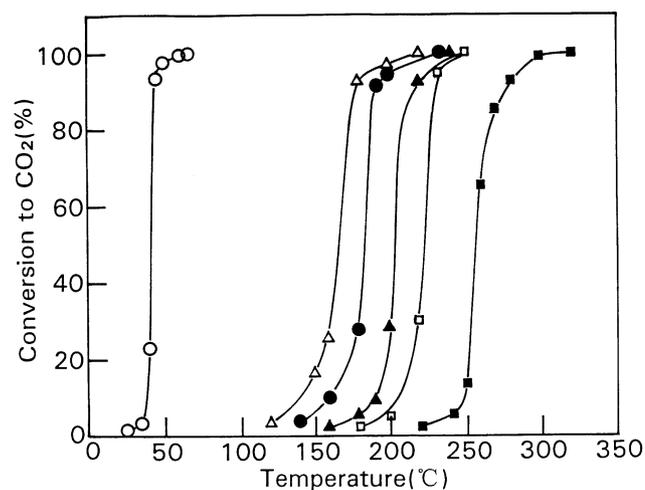


Figure 4. Effect of support on CO oxidation activity of Pd catalyst. (○) Pd/CeO₂(5%); (△) Pd/ZrO₂(5%); (●) Pd/TiO₂(2%); (▲) Pd/Al₂O₃(5%); (□) Pd/ZSM-5(5%); (■) Pd/SiO₂(5%).

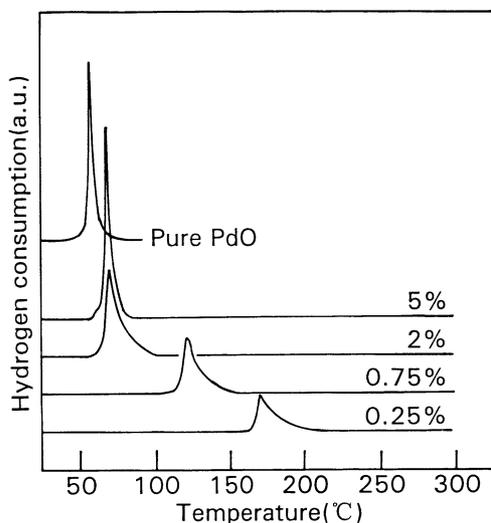


Figure 5. H₂-TPR profiles of Pd/CeO₂ catalyst.

reduction of Pd/CeO₂ catalyst shifts to lower temperature with increasing Pd loading. According to studies by Hoflund and coworkers [14–16], we suppose that other states of Pd such as Pd metal, PdO₂, and Pd hydroxide are present on these catalysts, and other states of Pd also influence the reduction temperature.

On the basis of the H₂-TPR result, we do not differentiate directly the finely dispersed PdO from the crystal phase PdO, because only one reduction peak is observed over all Pd/CeO₂ catalysts. Numerous studies have reported that the reduction temperature of metal oxide by H₂ can be lowered by the addition of transition metals, with Pt and Pd being the most efficient metals [18]. For example, surface hydrogen atoms formed on Pt, Pd, Cu and Ni can increase the rate of reduction of CuO, NiO and Co₃O₄. In the case of hydrogen reduction, the effect of Pt and Pd can be attributed to hydrogen spillover from Pt particles, and leading to activated hydrogen atoms which can reduce metal oxides more easily. We suppose that crystal phase PdO is first reduced to form Pd atoms at lower temperature and then H₂ is dissociated over these Pd atoms and hydrogen atoms spill over to the surface of finely dispersed PdO. Thus the reduction temperature of the finely dispersed PdO by H₂ can be decreased. In other words, the metallic palladium formed is thought to dissociate the hydrogen so that the reduction is autocatalytic [19]. Therefore, only one reduction peak is observed in figure 5 and the peak temperature shifts to lower temperature with increasing Pd loading.

3.3. CO-TPR

In order to differentiate the finely dispersed PdO from the crystal phase PdO, we have investigated CO-TPR of Pd/CeO₂ catalysts, since carbon monoxide is not dissociated [20]. The CO-TPR profiles for these Pd/CeO₂ cat-

alysts are shown in figure 6. The pure CeO₂ cannot be reduced below 400°C (not shown in figure 6). The reduction profile of pure PdO is characterized by a single peak at about 320°C. It is very interesting that when carbon monoxide is used as reducing agent, there are three peaks (α , β and γ), while only one peak when H₂ is used as reducing agent. When the Pd loading is 5 and 10%, three peaks (α , β and γ) are observed, when the Pd loading is 2%, the γ peak disappears, and when the Pd loading is lower than 0.75%, only the α peak is observed. The α peak temperature shifts to lower temperature with increasing Pd loading, while the temperature of the γ peak shifts to higher temperature with increasing Pd loading, but the temperature of the β peak does not change. The area of α peak increases with increasing Pd loading from 0.25 to 2%. However, as Pd loading is further increased to 10%, the area of the α peak does not change. This implies that the amount of α -peak reduction species is limited by a certain factor. In other words, it seems to exhibit a saturation phenomenon occurring at about 2.0% Pd loading. From figure 6, it can be seen that γ peak temperature of the Pd/CeO₂ (5%) catalyst is similar to pure PdO. According to studies by Hoflund and coworkers [14–16], we think that other states of Pd such as Pd metal, PdO₂, and Pd hydroxide are present on Pd/CeO₂ catalyst besides the PdO species in this paper. We suppose that the α form is due to Pd hydroxide and this is the active phase on Pd/CeO₂ catalyst for low-temperature CO oxidation. This is consistent with the fact that this feature occurs at a low temperature and the Pt hydroxide is the active phase on Pt/SnO₂ catalyst [14–16]. We suggest that the β peak can be contributed to finely dispersed PdO and the γ peak can be contributed to crystal phase PdO. This indicates that the crystal phase PdO is more difficult to reduce by CO than finely dispersed PdO. On the basis of the catalytic activity and CO-TPR results, we conclude that α peak species (Pd

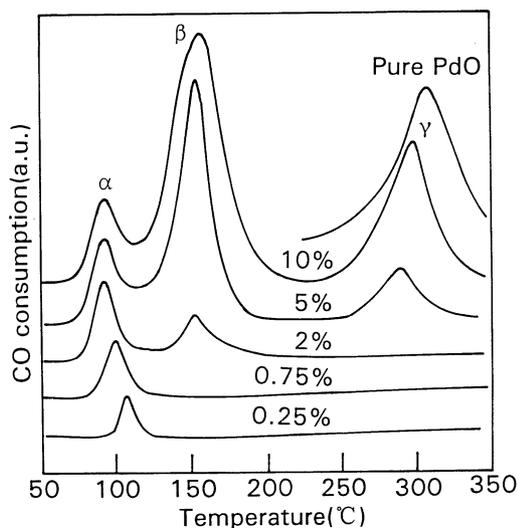


Figure 6. CO-TPR profiles of Pd/CeO₂ catalyst.

hydroxide) mainly contribute to the catalytic activity for low-temperature CO oxidation.

4. Conclusions

Pd/CeO₂ catalysts of different Pd loading have been prepared and tested for low-temperature carbon monoxide oxidation in stoichiometric mixtures of carbon monoxide and oxygen. The Pd/CeO₂ catalyst shows higher CO oxidation activity and does not exhibit the activity decay. The H₂-TPR investigation of Pd/CeO₂ catalyst showed that CeO₂ inhibits the reduction of PdO species. Therefore, CeO₂ promotes the CO oxidation activity of palladium catalyst. In the CO-TPR measurement three peaks could be observed. The low-temperature peak (α) is due to the Pd hydroxide species. The β peak has been attributed to the finely dispersed PdO. The high-temperature peak (γ) has been attributed to crystal phase PdO. The crystal phase PdO is more difficult to reduce by CO than finely dispersed PdO. On the basis of the catalytic activity and CO-TPR results, we conclude α peak species (Pd hydroxide) mainly contribute to the catalytic activity for low-temperature CO oxidation.

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