A novel catalyst for CO oxidation at low temperature

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Supported catalysts of palladium over ceria–titania mixed oxides (Pd/CeO_2–TiO_2) were prepared and tested for carbon monoxide oxidation. The catalysts exhibited high catalytic activity at room temperature. The Pd/CeO_2–TiO_2 catalyst was more active than Pd/CeO_2, Pd/SnO_2–TiO_2, Pd/ZrO_2–TiO_2, Pd/Al_2O_3–TiO_2 and Pd/TiO_2 catalysts under the same conditions examined. The effects of preparation methods of the support, the mole ratio of ceria and titania in mixed supports as well as Pd loading upon the catalytic activity of CO oxidation were investigated. Among the Pd/CeO_2–TiO_2 catalysts, the best one corresponds to the Pd loading of 1.0 wt% or above, and the mole ratio of ceria and titania ranging from 1 : 7 to 1 : 5. The steady-state catalytic performance of such catalyst was recorded without any deactivation over 8 h time-on-stream in the present study.

Keywords: carbon monoxide oxidation, palladium, titania-based mixed oxide, ceria, low temperature

1. Introduction

The catalytic oxidation of CO on numerous catalysts has been studied over the years and this subject has been well reviewed [1–3]. The earlier investigation was conducted mainly to get insight into the mechanism of the oxidation. Recently, however, special attention has been paid to low-temperature CO oxidation due to its potential applications. Particularly, these applications include air-purification devices for respiratory protection, pollution control devices for reducing industrial and environmental emission and removal of trace quantities of CO from the ambient air in enclosed atmospheres such as submarines and space crafts, and carbon dioxide lasers. Carbon monoxide gas sensors are also based on the catalytic materials used for CO oxidation.

Many different catalysts have been prepared and tested for low-temperature CO oxidation. Stark and coworkers [4–6] first reported that Pt/SnO_x is an effective catalyst for the oxidation of CO. But complicated pretreatments of the catalyst such as reduction and induction periods were needed before reaching maximum catalytic activities [7]. It has been also reported that Au particles dispersed on oxide supports, such as α-Fe_2O_3, Co_3O_4, TiO_2, NiO and MnO_x were active for CO oxidation at low temperature [8–13]. It has been substantiated that support and particle size had effects on the activity of Au catalysts [9,14]. Ultrafine Au particles may be prerequisite for the observation of Au–support interaction [15]. For the Au/TiO_2 catalyst, since TiO_2 is almost inert for CO oxidation as is bulk gold, it was regarded that there is a significant synergistic effect between gold and TiO_2 support [16].

In this paper, the CO oxidation on palladium supported titania-based mixed oxides at low temperatures below 100 °C was studied. The effects of preparation method of supports, the mole ratio of CeO_2 and TiO_2 as well as Pd loading upon the CO oxidation activity were investigated.

2. Experimental

2.1. Preparation and characterization of catalyst

Titania-based mixed supports were prepared by using the sol–gel technique. $TiCl_4$ was freshly distilled prior to use. An hydrosol of titanium hydroxide was obtained by controlled hydrolysis of $TiCl_4$, then a transition metal nitrate dissolved in water was poured into it under stirring. Following the basification by aqueous ammonia of mixed solution, the mixed hydrogel was obtained after drying at 110 °C for 24 h and calcining at 500 °C for 3 h in air. The alcohol was substituted for water in wet mixed hydrogel, leading to the mixed alcogel after conventional drying described above. Titania-based aerogel was produced when the wet alcogel was dried by the supercritical fluid (SCFD) method and calcined at 500 °C for 3 h. The textural and structural properties of ceria–titania mixed oxides were characterized as listed in table 1. Palladium impregnated (loading range from 0.05 to 1.0 wt%) mixed oxides were prepared with palladium chloride solution by using the incipient wet method. The Pd contents were determined by ICP-AES.

The individual oxide aerogels of titanium and cerium were also prepared separately by precipitating the hydroxides from their respective aqueous solutions using a similar procedure and drying by the supercritical method, then calcining the aerogels at 500 °C for 3 h in air. Pd metal was impregnated on these oxides in the same way as used for the mixed oxide system. For carrying out comparative studies, other preparation methods were used to prepare the mixed oxides. The urea combustion method (UCM),

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Table 1
The textural and structural properties of CeO_2–TiO_2 mixed oxides prepared by the sol–gel process.

CeO_2–TiO_2 mixed oxide	Calcination temperature (°C)	S_{BET} (m^2/g)	V_{PN} (cm^3/g)	Most propable pore diameter d (nm)	Average pore diameter d (nm)	Physical phase[a]
5% CeO_2–TiO_2 (aerogel)	500	67.3	0.306	35–38	18.1	A
10% CeO_2–TiO_2 (aerogel)	500	–	–	–	–	A
15% CeO_2–TiO_2 (aerogel)	as prepared at 260 °C	254.5	1.189	25–35	18.7	A
15% CeO_2–TiO_2 (aerogel)	500	182.5	1.024	35	22.4	A
15% CeO_2–TiO_2 (hydrogel)	500	193.8	0.305	4.2–5.0	6.3	No
15% CeO_2–TiO_2 (alcogel)	500	223.9	0.637	8.5	11.4	No
20% CeO_2–TiO_2 (alcogel)	500	224.3	0.779	11.0	13.9	No
20% CeO_2–TiO_2 (aerogel)	500	196.2	–	–	–	A
40% CeO_2–TiO_2 (aerogel)	500	219.4	0.716	2550	13.0	No

[a] A: anatase; No: amorphous.

organic complex decomposing (OCD) method and the sol–SCFD method were used to prepare the mixed oxides. Palladium metal was impregnated on these oxides in the same manner as used for the above. For all catalysts, the impregnation time was 48 h with subsequent drying for 24 h under an infrared lamp. Finally, the catalysts were calcined at 500 °C for 3 h in air.

2.2. Apparatus and method for activity test

The catalytic test for CO oxidation was carried out in a micro fixed-bed reactor at atmospheric pressure. The reactor was a 5 mm i.d. quartz U-tube, and a thermocouple was placed at the outside wall of the reactor to control the temperature of the furnace. About 200 mg of catalyst of 40–60 mesh was used for each run. The feed gases adjusted by mass flow controllers consisted of 0.57 vol% CO and 1.5 vol% O_2 passed though the catalyst bed with a total flow rate of 100 ml/min (space velocity is 3×10^4–4×10^4 h^{-1}). The product CO_2 and unreacted CO were measured by an on-line gas chromatograph equipped with a column packed with carbon molecular sieve, a methanator and a FID. The minimum detection level of CO was ca. 50 ppm.

The catalysts were reduced in flowing H_2 at 150 °C for 2 h before the activity measurements and then cooled to the ambient temperature in N_2 flow for 0.5 h. The N_2 flow was subsequently switched to the feed gas and product sampling was initiated. The conversions of CO obtained under the ambient temperature were plotted versus time to yield the CO oxidation activity curves, which is called preliminary activity test. When the conversion measured at the ambient temperature reached a constant, the temperature-programmed reaction was carried out at a heating rate of 1 °C/min, and then the catalytic activity was estimated by measuring the conversion as a function of temperature. These curves of the conversion versus temperature can serve as a convenient activity indicator for the practical application of the catalysts. During the test, the furnace temperature was controlled by a temperature controller.

3. Results and discussion

3.1. Effect of the support

Figure 1 shows the CO oxidation activity on different aerogel supports. It can be found that the activity of the Pd/CeO_2–TiO_2 catalyst is higher than that of the Pd/TiO_2 catalyst, and much higher than those of the other titania-based mixed-oxides-supported Pd catalysts. This Pd/CeO_2–TiO_2 catalyst is much more active than the 0.5 wt% Pd/γ-Al_2O_3 catalyst but less active than Au/Fe_2O_3 (Au/Fe $= 1/19$) reported by Haruta et al. [9]. For the bulk metal Pd and supports prepared, little activity for CO oxidation was determined at low temperature. But for the 0.4 wt% Pd/TiO_2 catalyst, the obvious catalytic activity for CO oxidation at lower temperature can be observed. Moreover, the addition of ceria can enhance the activity of the catalyst, particularly at low temperature. It could be considered that there is a synergistic interaction between the Pd and support which is responsible for the high activity of CO oxidation.

3.2. Effect of the preparation methods of ceria–titania mixed oxides

A series of 15% CeO_2–TiO_2 (mole ratio) supports were prepared by different methods: sol–gel–different drying

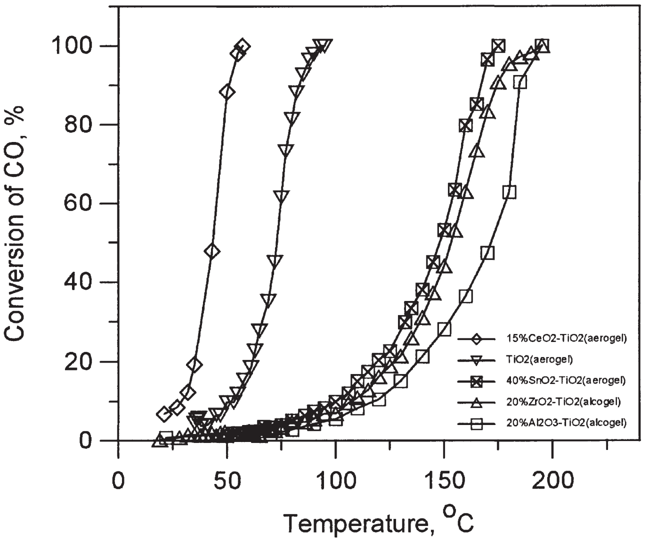

Figure 1. Effect of support on CO oxidation activity of 0.4 wt% Pd catalyst.

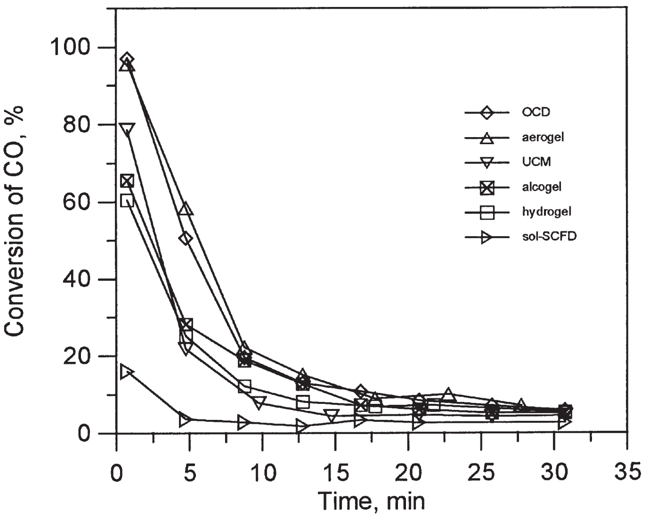

Figure 2. The preliminary activity of catalysts prepared by different methods at ambient temperature.

methods, UCM, OCD and sol–SCFD. The loading of metal palladium of these catalysts was 0.2 wt%. The comparison of the catalytic activity of these catalysts was carried out by measuring the conversion of CO oxidation as, on the one hand, a function of a time (preliminary activity test), on the other hand, a function of temperature, as shown in figures 2 and 3, respectively. All catalysts exhibit similar overall reaction profiles which are maximum at the onset of reaction but steeply decay with time. The catalysts supported on the mixed oxides prepared by the sol–gel process are obviously better than those prepared by UCM and sol–SCFD. The catalytic activity of the mixed oxides support was tested, and no activity for CO oxidation can be measured at temperature from ambient temperature to 560 °C. The synergistic effect between Pd and CeO_2–TiO_2 support could be responsible for the high catalytic CO oxidation activity at low temperature, as metioned above. For the same 15% CeO_2–TiO_2 mixed support, the catalytic activity of the catalysts varies with the preparation method. It is mainly due to the different textural properties of the supports. The different methods lead to different sizes of particle, different surface areas and different pore distributions and so on. These properties could affect the degree of dispersion of the active phase, further would affect the catalytic activities of the catalysts. So the catalytic activity of the catalysts is not only determined by its intrinsic properties, but also affected by its preparation method.

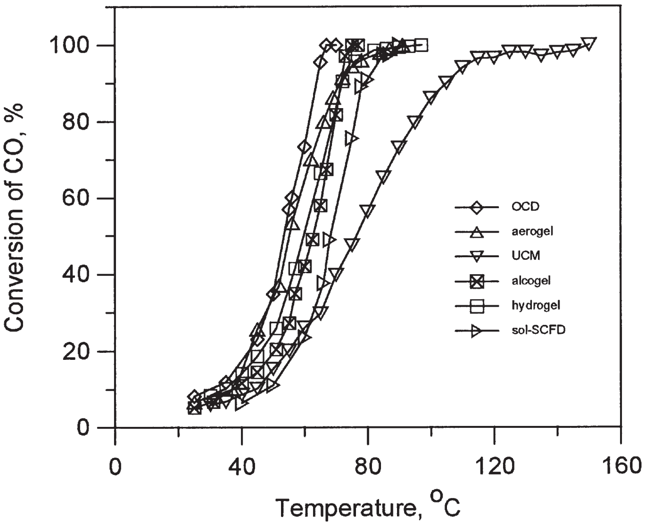

Figure 3. The effects of catalysts prepared by different methods on the activities of CO oxidation.

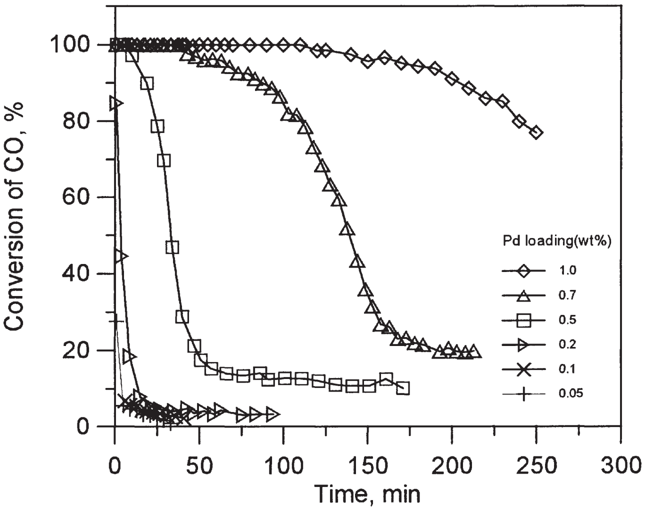

Figure 4. The effects of palladium loading on the preliminary activities of catalysts at ambient temperature.

3.3. *Effect of Pd loadings*

The effect of Pd loadings on the CO oxidation activities of Pd/20% CeO_2–TiO_2 (SCFD) catalysts is shown in figures 4 and 5. It can be seen that the activity of the Pd/20% CeO_2–TiO_2 catalyst increases with Pd loading from 0.05 to 1.0%. At low Pd loading, the dispersion is high and

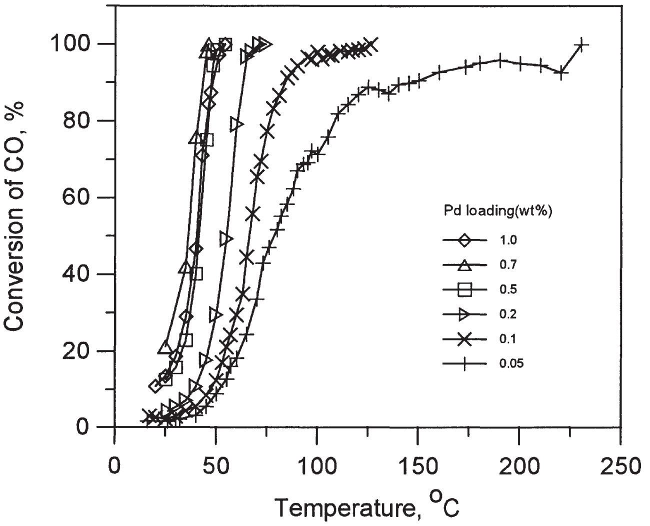

Figure 5. The effects of palladium loading on the activities of CO oxidation of catalysts.

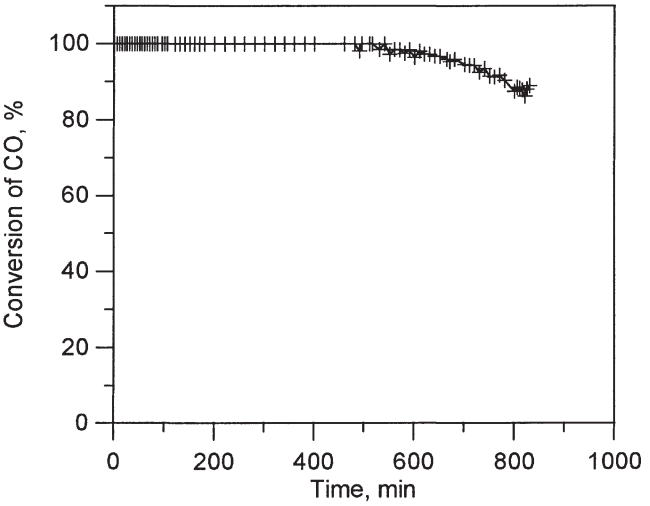

Figure 6. The CO conversion over 1.0 wt% Pd/20% CeO_2–TiO_2 (alcogel) catalyst as a function of reaction time at ambient temperature.

the activity increases as the Pd loading increases, and its decay rate of high loading is much smaller than that of low loading.

The CO oxidation activity of the 1.0 wt% Pd/CeO_2–TiO_2 (alcogel) catalyst as a function of reaction time is shown in figure 6. The activity of the Pd/CeO_2–TiO_2 catalyst does not decay over 8 h time-on-stream at ambient temperature.

3.4. Effect of mole ratio of CeO_2–TiO_2 mixed oxides

The effect of mole ratio of CeO_2–TiO_2 mixed oxides on the CO oxidation activity of 0.5 wt% Pd catalysts is given in figures 7 and 8. When the mole ratio of ceria and titania increases, the activity increases firstly then decreases. Table 1 gives the textural and structural properties of mixed oxides. It seems that the activity has no direct relationship with these properties.

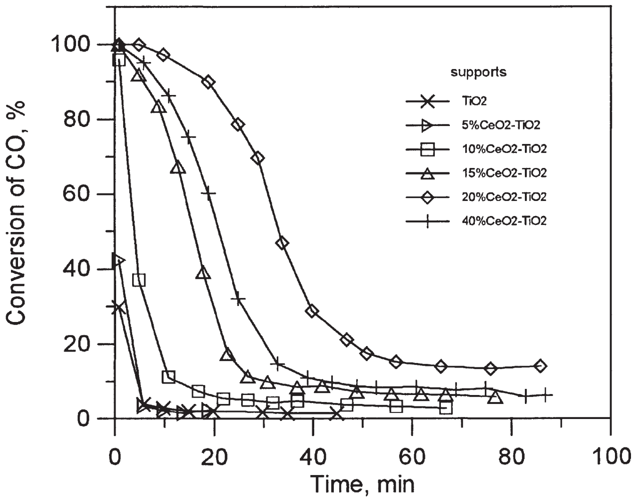

Figure 7. The effects of the mole ratio of Ce and Ti on the preliminary activities of catalysts at ambient temperature.

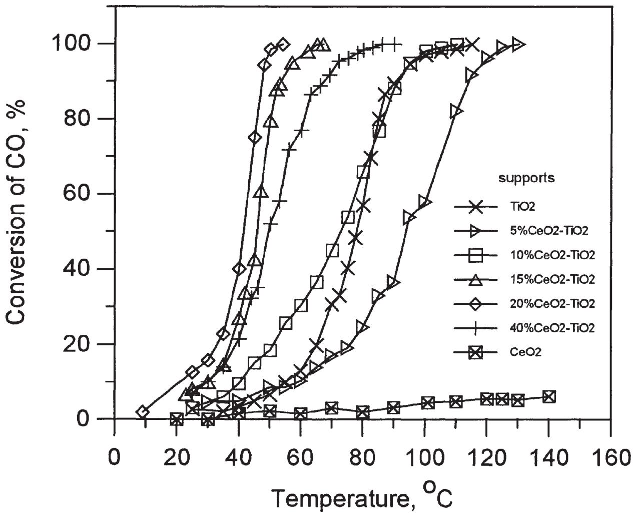

Figure 8. The effects of the mole ratio of Ce and Ti on the activities of CO oxidation of catalysts.

4. Conclusions

Catalysts consisting of palladium supported over ceria–titania mixed oxides (Pd/CeO_2–TiO_2) were prepared and used for carbon monoxide oxidation in mixtures of carbon monoxide and air in feed gases. The activity of the Pd/CeO_2–TiO_2 catalyst for CO oxidation is superior to that of Pd/CeO_2, Pd/SnO_2–TiO_2, Pd/ZrO_2–TiO_2, Pd/Al_2O_3–TiO_2 and Pd/TiO_2 catalysts under the same conditions tested. Among the Pd/CeO_2–TiO_2 catalysts prepared by the sol–gel process, which is better than other preparation methods, the best one was prepared with the Pd loading of 1.0 wt% or above, and the mole ratio of ceria and titania ranging from 1 : 7 to 1 : 5. Using the 1.0 wt% Pd/20% CeO_2–TiO_2 (alcogel) catalyst, CO in the stream (0.57 vol% CO, 1.5 vol% O_2, GHSV $= 3$–4×10^4 h^{-1}) could be fully converted to CO_2 at ambient temperature over 8 h without any deactivation. It is a novel CO oxidation catalyst at low temperature.

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