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CO oxidation at low temperature over Pd supported on CeO_2-TiO_2 composite oxide

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Abstract

Low temperature CO oxidation was carried out over CeO_2-TiO_2 composite oxide and thereon supported Pd catalysts. The effects of Ce/Ti ratio and pre-treatments of calcination and reduction on the catalytic behaviour were investigated. The CO oxidation starts at about 220 °C over CeO_2-TiO_2 and the pre-reduction treatment has little influence on the catalytic activity. Pd supported on CeO_2-TiO_2 (Pd/CeO_2-TiO_2) exhibits high activity for CO oxidation and a complete conversion of CO to CO_2 can be achieved even at ambient temperature, which suggests a synergistic effect between Pd and CeO_2-TiO_2. The activity and stability of Pd/CeO_2-TiO_2 can be further improved by the pre-reduction treatment. Ce/Ti ratio influences the catalytic behaviour significantly; the catalyst Pd/CeO_2-TiO_2 with a Ce/Ti mole ratio of 0.20 (Pd/Ce20Ti) owns the highest activity and stability, which suggests an optimization of the Pd-Ce-Ti interaction in Pd/Ce20Ti. The calcined Pd/CeO_2-TiO_2 with a Ce/Ti mole ratio higher than 0.10 shows a distorted light-off profile with the temperature, which implies an alternation of the reaction mechanism with increasing temperature.

Keywords: CO oxidation; Palladium; Ceria; Titania; DRIFTS; Composite oxide; CeO_2-TiO_2

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1. Introduction

The catalytic oxidation of CO has wide applications in CO_2 laser exhaust abatement, trace CO removal in the enclosed atmospheres, the automotive emission control, and CO preferential oxidation for proton exchange membrane fuel cells (PEMFC). The supported Pd catalyst has been proposed as an alternative to the traditional three way catalysts (TWC), because it exhibits the excellent activity for the low temperature oxidation of CO and hydrocarbons compared with the supported Pt and Rh catalysts [1].

Noble metal catalysts for CO oxidation can be promoted by ceria. The addition of CeO_2 in the TWC may improve the noble metal dispersion and thermal stability of support alumina, promote the CO oxidation and water–gas shift reactions, and enhance the Ce^{4+}/Ce^{3+} redox activity for the oxygen storage/release capacity (OSC) [2,3]. The presence of ceria may induce a change in the reaction kinetics of CO oxidation, which is often interpreted by the mechanism involving interactions between CO adsorbed on noble metal and the surface oxygen from CeO_2 that occurred on the interface of noble metal and cerium [4–6].

The thermal stability, oxygen storage capacity, redox behaviour and catalytic activity of catalysts can be improved dramatically by the incorporation of transition-metal elements into CeO_2 lattice to form solid solutions [7–10]. Among them, CeO_2-ZrO_2 is widely investigated [11–15]. However, only a few studies concerned the CeO_2-TiO_2 composite oxide and its performance on the low temperature CO oxidation [16,17].

In our previous work, Pd supported on ceria-titania composite oxide prepared by the sol–gel precipitation followed with supercritical fluid dry (SCFD) exhibited high activity for the CO oxidation at low temperature [18]. The temperature-programmed reduction (TPR) using H_2 and CO as reducing agents suggested that the Pd/Ce interaction in Pd/CeO_2-TiO_2 favors the reduction of both PdO and CeO_2, which contributes to the high activity for CO oxidation at low temperature [19]. It was also found that the pre-treatment has significant effects on the catalytic behaviour [20,21].

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In this work, low temperature CO oxidation was carried out over CeO_2-TiO_2 composite oxide and thereon supported Pd catalysts to examine the effects of Ce/Ti ratio and pre-treatments on the catalytic behaviour. The interaction between CeO_2 and TiO_2 in CeO_2-TiO_2 with various Ce/Ti ratios, the synergistic effect between Pd and supports and their influence on the performance of low temperature CO oxidation were then investigated.

2. Experimental

2.1. Catalyst preparation

The CeO_2-TiO_2 composite oxide was prepared by sol–gel precipitation followed by SCFD, and Pd supported catalysts by the incipient wetness impregnation with aqueous $PdCl_2$ solution as Pd precursor, as described elsewhere [19]. The Ce/Ti mole ratio in the support is from 0.05 to 0.40 (denoted as Ce05Ti to Ce40Ti), and Pd loading is 1 wt% for the supported Pd catalysts.

2.2. Catalytic tests

As described previously, the catalytic oxidation of CO was carried out in a quartz tubular flow microreactor at atmospheric pressure [20]. Briefly, the light-off test was processed as an on-line temperature-programmed reaction from ambient temperature with a heating rate of 2 °C/min. The reacting stream consisted of 1.0% CO + 1.0% O_2 (by volume) balanced with argon and the space velocity was 39,000 ml g^{-1} h^{-1}. Before the light-off test, catalysts might endure the on-line pre-treatments of calcination in air at 500 °C for 2 h (calcined), reduction by H_2 at 500 °C for 2 h (HTR), and reduction by H_2 at 150 °C for 2 h (LTR). The produced CO_2 and unreacted CO were periodically analyzed on-line with a gas chromatograph equipped with a carbon molecule sieve column, a post-column methanator and a flame ionization detector (FID). CO conversion (x_{CO}) could then be determined as $C_{CO_2}/(C_{CO}+C_{CO_2})$, where C_{CO} and C_{CO_2} denote the contents of CO and CO_2 in the effluent, respectively.

2.3. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)

DRIFTS of CO adsorption was measured with a Vector 22 spectrometer (Bruker) as described previously [19,20]. A stream of CO (5.01% by volume) in argon was used to determine the initial states of Pd species, while another stream of CO (1.05%) + O_2 (1.01%) in nitrogen was used to measure the states of Pd species under the reaction conditions.

3. Results and discussion

3.1. Effects of cerium content and pre-treatment on the catalytic behaviour

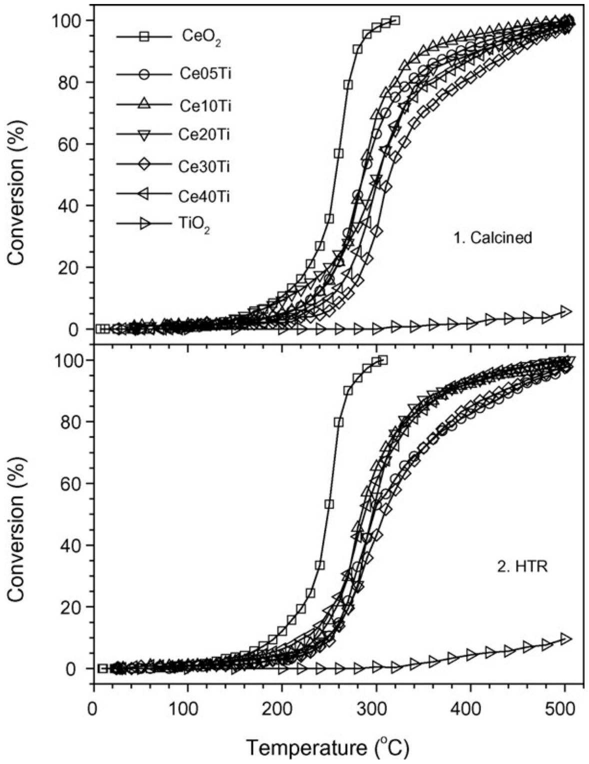

Fig. 1. Light-off profiles of CO oxidation over CeO_2-TiO_2 with various Ce contents and pre-treatments of calcination (1) and HTR (2).

The light-off profiles of CeO_2-TiO_2 composite oxide after calcination and HTR pre-treatments were shown in Fig. 1 and Table 1. For the calcined CeO_2-TiO_2 with Ce/Ti mole ratio from 0.05 to 0.40, the light-off temperature (where the CO conversion x_{CO} reaches 50%) is about 300 °C. It suggested that the pre-reduction treatment has little effect on the catalytic activity. The catalytic activity of CeO_2-TiO_2 is much higher than that of individual TiO_2 but a little lower than that of individual CeO_2. However, it is difficult to deduce a simple

Table 1
Light-off performance of CO oxidation on CeO_2-TiO_2 composite oxides with various Ce contents and pre-treatments

Sample	Pre-treatment	Temperature (°C)[a]		
		$x_{CO} = 10\%$	$x_{CO} = 50\%$	$x_{CO} = 90\%$
TiO_2	Calcined	>500		
	HTR	>500		
Ce05Ti	Calcined	232	286	390
	HTR	248	295	450
Ce10Ti	Calcined	232	286	350
	HTR	238	285	380
Ce20Ti	Calcined	200	300	405
	LTR	220	288	365
	HTR	246	295	370
Ce30Ti	Calcined	264	314	445
	HTR	252	307	432
Ce40Ti	Calcined	250	302	416
	HTR	225	287	375
CeO_2	Calcined	197	257	279
	HTR	192	249	270

[a] Temperatures at certain CO conversion (x_{CO}) during the light-off tests.

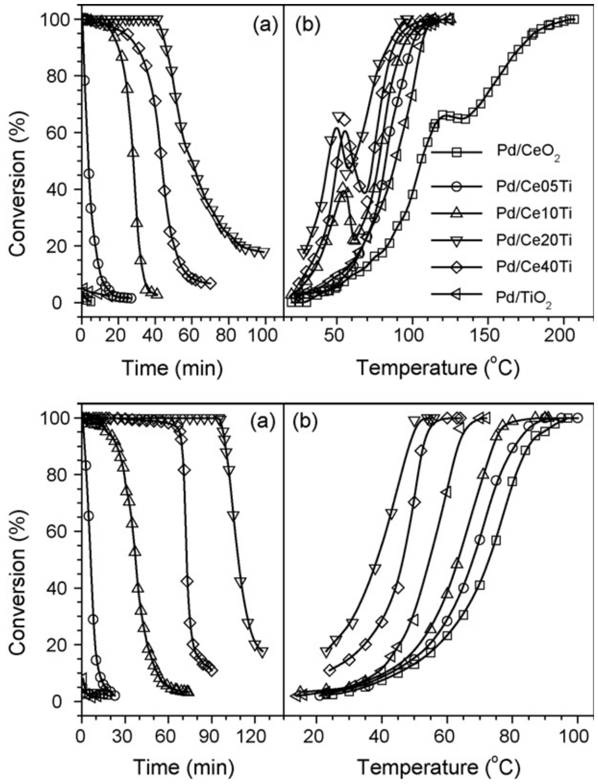

Fig. 2. Light-off profiles of CO oxidation over Pd/CeO_2-TiO_2 with various Ce contents and pre-treatments of calcination (upper) and LTR (lower): (a) activity at ambient temperature with time before heating-up and (b) CO conversion with the increase of temperature at a heating rate of 2 °C/min.

linear relationship between the activity and Ce content in CeO_2-TiO_2.

With introducing Pd, the catalyst Pd/CeO_2-TiO_2 exhibits high activity for CO oxidation and a complete conversion of CO to CO_2 can be achieved even at ambient temperature, which suggests a synergistic effect between Pd and CeO_2-TiO_2. Therefore, the catalytic tests were carried out both at room temperature until the preliminary activity diminished to a stable value and thereafter as a temperature-programmed reaction process at a heating rate of 2 °C/min until CO conversion reached 100%. The comparisons of CO oxidation over Pd/CeO_2-TiO_2 catalysts with different pre-treatments were shown in Fig. 2. For the catalysts either in the calcined state or in the reduced state, CO can be completely converted to CO_2 at ambient temperature, but the duration for a complete CO conversion depends on the Ce/Ti ratios and pre-treatments. Among them, Pd/Ce20Ti (Ce/Ti = 0.20) exhibits the highest stability at ambient temperature and activity in the light-off test. The activity and stability of all the catalysts can be improved by the pre-reduction treatments.

The CO conversion determined through the CO_2 and CO contents in the effluent may be affected by the adsorption of CO on the catalyst, but this occurs only at the very initial period of the catalytic test and is negligible for longer time on stream, because the catalytic test was carried out at a high space velocity in this work. Moreover, it was proved that the overall content of CO + CO_2 in the effluent kept stable during the entire process of catalytic tests. The DRIFTS of CO adsorption also indicated that CO adsorption on the catalysts reached a saturated state after the samples were exposed to the reacting stream for 3–5 min.

The catalyst activity decreases with the time on stream. Such a deactivation may originate from two reasons, the sintering of Pd species and the aggregation of carbonates on the supports. However, the sintering of Pd particles was not evident on the deactivated catalyst, as revealed by XRD. It seems that the aggregation of carbonates on the supports might be the major reason for the catalyst deactivation, although further detailed work is necessary to confirm it.

The calcined Pd/CeO_2-TiO_2 with low Ce content (Ce/Ti = 0.05) shows a normal light-off profile like that of Pd/TiO_2, while the light-off profiles of the calcined Pd/CeO_2 and Pd/CeO_2-TiO_2 with higher Ce content (Ce/Ti $\geq$ 0.10) show a distortion before CO conversion achieves 100%. This implies an alternation of the reaction mechanism with increasing temperature. The alteration of reaction mechanism with temperature and the involvement of the oxygen activation at different sites were employed to explain the light-off profiles of the calcined Pd/CeO_2-TiO_2 [20]. At lower temperature, the reaction is mainly performed between the adsorbed CO on Pd sites and the lattice oxygen of surface CeO_2 at the Pd/Ce interface, while at higher temperature it is carried out between the weakly adsorbed CO and O_2 (Langmuir–Hinshelwood mechanism). The activity of the reduced Pd/CeO_2-TiO_2 is much higher than that of the calcined sample due to both the enhancement of CO activation caused by Pd^0 and the enhancement of oxygen activation by the high active Ce^{3+} and oxygen vacancies.

3.2. DRIFTS of CO adsorption

The initial Pd species in the catalysts was determined by CO adsorption at 25 °C using 5.01% CO in argon, while no Pd species was detected either in the calcined state or in the reduced state [19,20,22] by XRD. The DRIFTS of CO adsorption for Pd/CeO_2-TiO_2 with various Ce contents and pre-treatments are shown in Fig. 3. For all the samples, the band in the region of 2300–2400 cm^{-1} is assigned to the gaseous CO_2. It is revealed that the calcined Pd/CeO_2-TiO_2 catalysts with various Ce contents are different in the reducibility of PdO. Pd^{2+} (linearly bonded CO around 2156 cm^{-1}), and Pd^0 (linearly bonded CO around 2085 cm^{-1} and bridge-bonded CO below 2000 cm^{-1}) species coexist in the calcined Pd/CeO_2, Pd/Ce05Ti and Pd/Ce40Ti, corresponding to a partial reduction of PdO. However, only Pd^0 is detected in the calcined Pd/TiO_2 and Pd/Ce20Ti, indicating a complete reduction of PdO by CO at ambient temperature. On the other hand, only metallic Pd is observed in the pre-reduced catalysts, indicating a complete reduction can be realized with the LTR pre-treatment, which is consistent with the H_2-TPR results [22].

It is generally considered that CO activation over the supported noble metal catalysts takes place on the noble metal sites (M), which is initiated through the formation of a metal-CO covalent adduct that transfers electron density into the anti

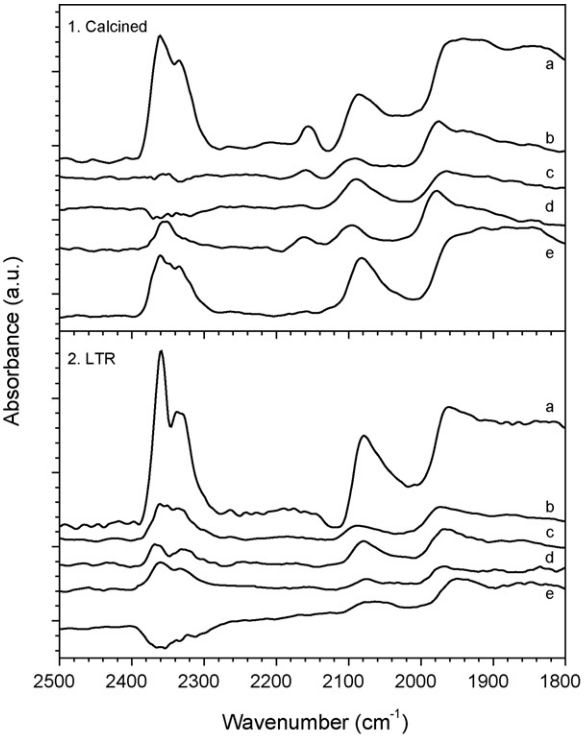

Fig. 3. DRIFTS of CO adsorbed at 25 °C after purging with He on Pd/CeO_2-TiO_2 with different pre-treatments of calcination (1) and LTR (2) and Ce contents: (a) Pd/CeO_2, (b) Pd/Ce05Ti, (c) Pd/Ce20Ti, (d) Pd/Ce40Ti, and (e) Pd/TiO_2.

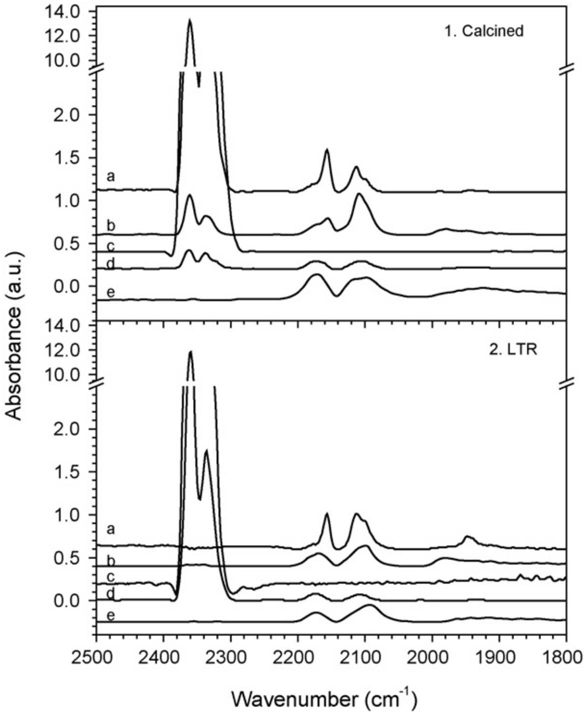

Fig. 4. DRIFTS of CO adsorbed at 25 °C in (1.05% CO + 1.01% O_2)/N_2 flow on Pd/CeO_2-TiO_2 with different pre-treatments of calcination (1) and LTR (2) and Ce contents: (a) Pd/CeO_2, (b) Pd/Ce05Ti, (c) Pd/Ce20Ti, (d) Pd/Ce40Ti, and (e) Pd/TiO_2.

bonding 2θ* orbits and weakens the C–O bond. The low valent state with higher electron density benefits the strengthening of M–C bond and the weakening of C–O bond. Therefore, the reductive Pd species is more active than oxidative Pd species for the CO activation. Meanwhile, because oxygen activation and dissociation are related with the electron transfer from Ce ions to oxygen molecule, the quantity of reducible ceria surface (Ce^{3+}) may be related to the ability of oxygen activation; on the other hand, the active oxygen species can also oxidize the interfacial Pd^0 into Pd^{2+}. Therefore, there exists an optimized Ce content to get a balance between the ability of oxygen activation/dissociation and the ability of maintaining Pd in the metallic state at the metal–support interface, and then to achieve the best catalytic activity for CO oxidation. As revealed by CO adsorption, the metallic Pd in Pd/Ce20Ti with a Ce/Ti mole ratio of 0.20 is more stable than those with other Ce/Ti ratios.

3.3. In situ DRIFTS of CO + O_2 coadsorption

The DRIFTS of CO adsorption in the flow of 1.05% CO + 1.01% O_2 (by volume) balanced with nitrogen at 25 °C on Pd/CeO_2-TiO_2 with various Ce/Ti mole ratios after calcination and LTR pre-treatments are shown in Fig. 4. The spectra of the calcined Pd/CeO_2 and Pd/Ce05Ti show three peaks at ca. 2156, 2110 and 2096 cm^{-1}, which should be ascribed to the linearly bonded CO on Pd^{2+}, Pd^{+} and Pd^0, respectively. They are overlapped by the gaseous CO absorption at 2175 and 2120 cm^{-1}. The bridge-bonded CO on Pd^0 below 2000 cm^{-1} is also identified. These results indicate that PdO in the calcined Pd/CeO_2 and Pd/Ce05Ti can be partially reduced into Pd species at low valence (Pd^+ and Pd^0) in the oxygen-extra atmosphere. Moreover, Pd^{2+} is the dominating species in the calcined Pd/CeO_2 under the reaction condition, while Pd^+ and Pd^0 are the dominating species in Pd/Ce05Ti, corresponding to its higher catalytic activity. For the calcined Pd/TiO_2, the peak at 2094 cm^{-1} overlapped by the bands of gaseous CO is ascribed to the linearly bonded CO on Pd^0. The bridge-bonded CO on Pd^0 at about 1960 cm^{-1} is evident. Pd^0 is the only palladium species detected at room temperature. The spectra of the calcined Pd/Ce20Ti and Pd/Ce40Ti show neither linear nor bridged CO adsorption species, indicating that both linearly and bridged adsorbed CO has been completely converted into CO_2 at ambient temperature, as revealed in light-off profiles shown in Fig. 2.

The DRIFTS of LTR pretreated Pd/CeO_2-TiO_2 are also shown in Fig. 4. Compared with the calcined samples, Pd^{2+}, Pd^+ and Pd^0 are still co-present in the reduced Pd/CeO_2 at room temperature, indicating that Pd can be partially oxidized to Pd species at high valence (Pd^{2+} and Pd^+) in the oxidative atmosphere. However, only Pd^0 was detected in the reduced Pd/Ce05Ti, indicating that Pd in the reduced sample still presents as metallic state in the oxidative atmosphere. The spectra for Pd/Ce20Ti, Pd/Ce40Ti and Pd/TiO_2 with LTR pre-treatments are similar to those for the corresponding calcined samples. Metallic Pd in Pd/Ce20Ti is more stable than that in Pd/CeO_2-TiO_2 with other Ce contents. All these contribute to the high activity and stability of Pd/Ce20Ti.

4. Conclusions

Low temperature CO oxidation was carried out over CeO_2-TiO_2 composite oxide and thereon supported Pd catalysts. The CO oxidation starts at about 220 °C over CeO_2-TiO_2 with Ce/Ti mole ratio from 0.05 to 0.40 and the light-off temperature ($x_{CO} = 50\%$) is about 300 °C. Pre-reduction treatment has little effect on the catalytic activity.

Pd supported on CeO_2-TiO_2 (Pd/CeO_2-TiO_2) exhibits high activity for CO oxidation and a complete conversion of CO to CO_2 can be achieved even at ambient temperature, which suggests a synergistic effect between Pd and CeO_2-TiO_2. The activity and stability of Pd/CeO_2-TiO_2 can be further improved by the pre-reduction treatment.

Ce/Ti ratio influences the catalytic behaviour significantly; the catalyst Pd/CeO_2-TiO_2 with a Ce/Ti mole ratio of 0.20 (Pd/Ce20Ti) owns the highest activity and stability, which suggests an optimization of the Pd-Ce-Ti interaction in Pd/Ce20Ti. The calcined Pd/CeO_2-TiO_2 with a Ce/Ti mole ratio higher than 0.10 shows a distorted light-off profile with the temperature, which implies an alternation of the reaction mechanism.

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