

The Complete Oxidation of Ethanol at Low Temperature over a Novel Pd–Ce/ γ -Al₂O₃–TiO₂ Catalyst

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Pd–Ce/ γ -Al₂O₃–TiO₂ catalysts were prepared by combined sol–gel and impregnation methods. Transmission electron microscopy, X-ray diffraction, H₂-temperature-programmed reduction, O₂-temperature-programmed desorption, and ethanol oxidation experiments were conducted to determine the properties of the catalysts. Addition of an optimal amount of Ce improved the performance of the Pd/ γ -Al₂O₃–TiO₂ catalyst in promoting the complete oxidation of ethanol. The catalyst with 1% Ce exhibited the highest activity, and catalyzed complete oxidation of ethanol at 175 °C; its selectivity to CO₂ reached 87%. Characterization results show that addition of appropriate amount of Ce could enrich the PdO species, and weaken the Pd–O bonds, thus enhancing oxidation ability of the catalyst. Meanwhile, the introduction of CeO₂ could make PdO better dispersed on γ -Al₂O₃–TiO₂, which is beneficial for the improvement of the catalytic oxidation activity.

Key Words : Ethanol complete oxidation, CO₂ selectivity, γ -Al₂O₃–TiO₂, Pd dispersion, Pd–Ce/ γ -Al₂O₃–TiO₂

Introduction

As alternative fuel, ethanol could satisfy the demand for renewable energy sources with minimal environmental impact. However, unburned ethanol and by-products of ethanol combustion such as acetaldehyde and carbon monoxide are harmful to the environment and human health. This problem necessitates investigations on catalysts with stable performance and ability to effect complete oxidation of ethanol at low temperature.

Much attention has been devoted to single component carriers of catalysts or composite oxide catalysts used in purifying exhaust from vehicles running on ethanol fuel, but these catalysts can't satisfy the need to catalyze complete oxidation of ethanol at a lower temperature (≤ 200 °C), or they are unstable at a high temperature.^{1–4}

Al₂O₃–TiO₂ supports have received a lot of attention recently. Al₂O₃–TiO₂ mixed oxides can combine the advantages derived from the properties of Al₂O₃ and TiO₂, such as the high surface area and good thermal stability of alumina, the surface acidity of titania.⁵ A variety of organic oxidation reactions catalyzed by Al₂O₃–TiO₂ supported catalysts have been reported, and its catalytic performances are proved to be better than the single γ -Al₂O₃ or TiO₂ supported catalysts.^{6–8}

Noble metals such as Pt, Pd, Ag and Rh have been shown to be efficient catalysts for the complete oxidation of ethanol.^{9–11} Previous studies have demonstrated that the palladium component catalyzes oxidation reaction in form of PdO.¹² And many oxide supports could interact with PdO, which could retard the active component agglomerating on the surface of support and enhance the catalytic activity.¹³

A proper amount of metal oxide added to noble-metal catalysts may provide a richer source of oxygen for the

surface reactions, and an example of such metal oxide is cerium oxide,^{14,15} which possesses high oxygen storage capacity and improves dispersion of the noble metal in the catalyst.¹⁶ Meanwhile, the oxidation–reduction properties of Ce³⁺/Ce⁴⁺ and the capacity of Ce to deliver oxygen make Ce a good promoter of combustion reactions.¹⁷ These characteristics of cerium oxide catalysts not only provide tailored catalytic activity, but also reduce the cost.

Some studies suggest that complete oxidation of ethanol occurs by a surface reaction mechanism.^{18–20} The initial step of this mechanism is the production of ethoxy derivatives by ethanol dehydrogenation. This is followed by further oxidation to CO₂ and H₂O through the formation of various intermediates in the presence of adsorbed oxygen or lattice oxygen. However, whether adsorbed oxygen or lattice oxygen plays an important role in ethanol oxidation is still controversial. In addition, ethanol has been reported to undergo dehydrogenation to generate acetaldehyde, or dewater to produce ethylene and ether.²¹ These reactions are mainly attributed to the nature of the metal oxides and carriers. Therefore, further research and analyses are needed to determine what factors are related to the reaction pathway. These variables include the strength of molecular bonds in ethanol under various conditions, the nature and structure of carriers, the oxidation state of the metal surface, and the pH.

Using a procedure established in our previous work,²² Ce was added to Pd/ γ -Al₂O₃–TiO₂ catalyst to modify its properties. The selectivity of this catalyst to CO₂ produced by ethanol combustion was studied. Transmission electron microscopy (TEM), X-ray diffraction (XRD), O₂-temperature-programmed desorption (O₂-TPD), and H₂-temperature-programmed reduction (H₂-TPR) techniques were carried out to determine the physicochemical properties of the catalysts.

Experimental

Catalyst Preparation. The composite carrier γ -Al₂O₃-TiO₂ was prepared by a sol-gel method. Titania and alumina sols were prepared separately, and mixed together to obtain γ -Al₂O₃-TiO₂,²³ in which the content of TiO₂ was about 95%. The mixed sol was dried at 50 °C and 110 °C for 12 h, respectively, then calcined at 500 °C in air for 5 h. Pd-Ce/ γ -Al₂O₃-TiO₂ catalysts were prepared by a stepwise impregnation method, and all the samples contained 1 wt % Pd. Firstly, the γ -Al₂O₃-TiO₂ supports were impregnated with acidic aqueous solutions containing the requisite amount of PdCl₂. The impregnates were dried at 80 °C in a water bath and at 110 °C in a oven for 12 h, then calcined at 500 °C in air for 5 h. Using the same method, Pd/ γ -Al₂O₃-TiO₂ was impregnated with the aqueous solution of Ce(NO₃)₃·6H₂O, and the Pd-Ce/ γ -Al₂O₃-TiO₂ catalysts with different Ce contents were obtained and designed as 1-x/AT, where, x denotes the weight percentage of Ce.

Catalyst Evaluation. The catalytic properties of the catalysts were evaluated using a fixed-bed reactor connected with an online gas chromatograph. The compositions of ethanol and products were analyzed using a GC-950 apparatus with two FID detectors, one of which incorporated a methanator. Approximately 0.30 g of catalyst was used (40–60 mesh), and the feed gas consisted of 0.5 vol. % C₂H₅OH, 5 vol. % O₂, and a balance of N₂. The flow rate was 100 mL/min of total gas and the gas hourly space velocity (GHSV) was 24000 h⁻¹. Ethanol conversion (X_i) and the yields (Y_j) of by-products and carbon dioxide from ethanol combustion were calculated according to the formulas:

$$X_i = \frac{C_{i,\text{in}} - C_{i,\text{out}}}{C_{i,\text{in}}} \times 100\% \quad Y_j = \frac{C_{j,\text{out}}}{C_{i,\text{in}}} \times \frac{1}{n} \times 100\%$$

Where C_i and C_j are the concentrations of ethanol and products from ethanol combustion, respectively, n is the products and reactants carbon atom ratios. And

$$C_i = A_i \times f_i \quad C_j = A_j \times f_j$$

Where A and f are the peak areas and the relative correction factors of reactants (i) or products (j), respectively.

Characterization. X-ray diffraction (XRD) measurement of the samples was obtained on a Rigaku D/max 2500 diffractometer operated at 40 kV and 100 mA using Cu K_{α} radiation. Intensities of the diffraction peaks were recorded in the 2θ range 5–80° with a step size of 0.01°, and the scanning speed was 8°/min.

Transmission electron micrographs (TEM) were carried out on a Tecnai G²F20, operating at 200 kV. The sample was diluted in ethanol and dropped onto a copper grid coated with a thin film of carbon.

The O₂-TPD experiment was performed on a TP-5080. About 20 mg of catalyst was pretreated at 400 °C with He flow (50 mL/min) for 1 h. Adsorption of O₂ on the catalyst was allowed to proceed (30 min) at room temperature, and the He flow was maintained until the baseline reading was

stable. Afterward, the catalyst sample was heated to 800 °C at a heating rate of 10 °C/min.

The H₂-TPR measurement was performed in a quartz microreactor. Prior to the measurement, 20 mg of the catalyst was pretreated with N₂ flow (50 mL/min) at 500 °C for 40 min; subsequently, the sample was cooled to room temperature. Afterward, a gaseous mixture of 5 vol. % H₂ in N₂ was introduced into the system, and the sample was heated to 900 °C at a rate of 10 °C/min.

Results and Discussion

Catalytic Activity. The ethanol conversion over Pd-Ce/ γ -Al₂O₃-TiO₂ catalysts at various temperatures is shown in Figure 1. It can be seen that ethanol conversion over the catalysts changed with Ce content. At low Ce content ($\leq 1\%$), the catalytic activity strengthened with the increase in Ce content, whereas, further increase in Ce content resulted in deterioration of the catalytic activity. The catalyst with 1% Ce exhibited the highest activity, and catalyzed complete oxidation of ethanol at 175 °C.

Catalytic Selectivity. Figure 2 shows the selectivity of the Pd-Ce/ γ -Al₂O₃-TiO₂ catalysts to CO₂. From the results it

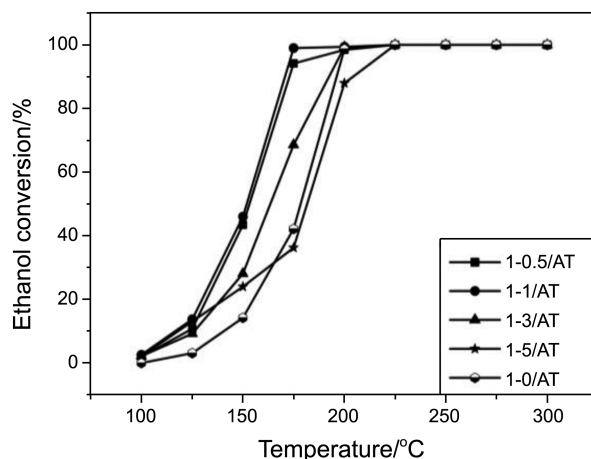


Figure 1. Ethanol conversion over Pd-Ce/ γ -Al₂O₃-TiO₂ catalysts.

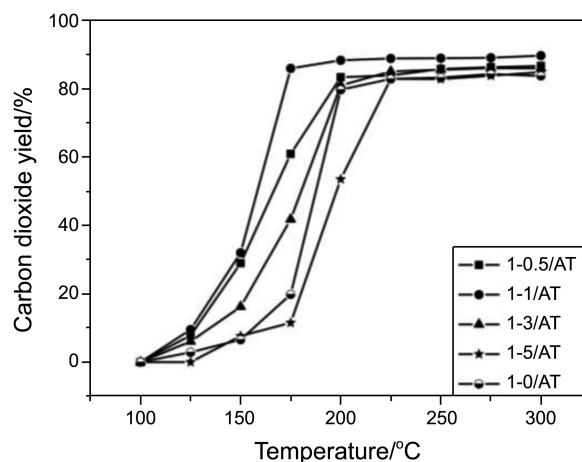


Figure 2. Selectivity to CO₂ from ethanol oxidation over Pd-Ce/ γ -Al₂O₃-TiO₂ catalysts.

Table 1. The yields of main by-products from ethanol oxidation over Pd–Ce/ γ -Al₂O₃–TiO₂ catalysts at 175 °C. Experiment conditions: 5 vol. % of O₂, 0.4–0.5 vol. % of CH₃CH₂OH, balanced by N₂, GHSV = 24000 h^{–1}

Sample	Yields of by-products /%				
	Acetaldehyde	Ethyl acetate	Methane	Carbon monoxide	Carbon dioxide
1-0.5/AT	5.17	18.71	11.32	0	59.95
1-1/AT	2.54	3.56	6.58	0	86.97
1-3/AT	5.01	13.74	6.89	0	41.78
1-5/AT	10.53	9.54	5.34	0	11.52
1-0/AT	6.90	14.12	7.23	1.05	17.83

can be deduced that Ce loadings had a significant impact on CO₂ selectivity. The CO₂ selectivity of sample 1-1/AT reached 87% at 175 °C, whereas the selectivity of 1-0/AT was only 17.8% at the same temperature. It was reported that CeO₂ could effectively reduce the reversion between PdO decomposition and Pd oxidation, resulting in better mobility and availability of lattice oxygen, which is beneficial to a oxidation reaction.²⁴ The degree of conversion of ethanol over 1-0.5/AT sample was approximately the same as that over 1-1/AT; however, the former catalyst had lower selectivity to CO₂. The results indicate that a minimum amount of Ce was required to promote complete oxidation of ethanol at low temperature.

The Distribution of the Main By-products. Table 1 exhibits the yields of the main reaction products obtained on the Pd–Ce/ γ -Al₂O₃–TiO₂ catalysts from ethanol oxidation at 175 °C. In the present work, when 1-0/AT was used as a catalyst for ethanol oxidation, the by-products were mainly acetaldehyde, ethyl acetate, methane, and carbon monoxide. However, the incorporation of Ce affects the resulting by-products,²⁵ and there was no CO generated. Han *et al.* reported that PdO species was easy to enrich on catalyst surface as optimal Ce were incorporated into the catalyst system, thus led to CO low-temperature oxidation.²⁶

Characterization of Catalyst. The XRD patterns of the

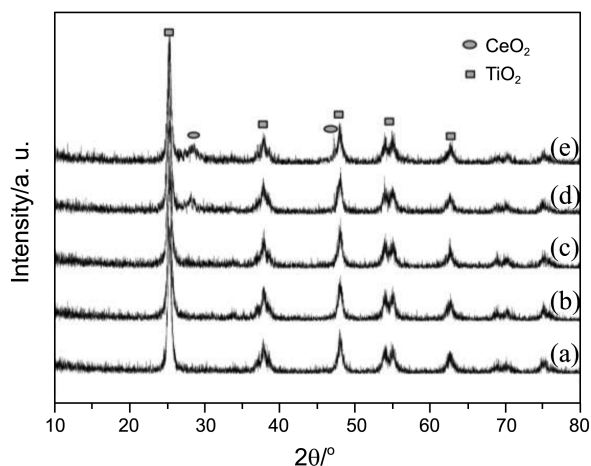


Figure 3. XRD patterns of Pd–Ce/ γ -Al₂O₃–TiO₂ catalysts. a: 1-0/AT b: 1-0.5/AT c: 1-1/AT d: 1-3/AT e: 1-5/AT

catalysts are presented in Figure 3. All of the patterns exhibited typical lines of the anatase structure in TiO₂ (2θ = 25.30°, 37.80°, 48.05°, 53.89°, 55.06°, and 62.69°, PDF 65-5714). No peak correlated to γ -Al₂O₃ or PdO was observed, probably due to the relatively low contents and/or the high dispersion of γ -Al₂O₃ and PdO over the catalysts. The CeO₂ fluorite structure (2θ = 28.55° and 47.48°, PDF 69-2975) was observed in the 1-3/AT and 1-5/AT samples, and the corresponding diffraction peak became stronger and broader as the amount of Ce increased. This is probably because of CeO₂ accumulation on the composite carrier surface. As a result, some activity sites were covered, and thus led to reduced catalytic activity. These observations are consistent with the results on catalytic activity.

TEM photographs of 1-0/AT, 1-1/AT are displayed in Figure 4. The dark spots are considered to be PdO particles against the lighter Al₂O₃–TiO₂ support. The photographs show that the sample without Ce showed very serious agglomeration, while PdO particles were found to be well dispersed in the 1-1/AT, demonstrating that addition of Ce is beneficial to the high dispersion of PdO particles.

The chemical states of PdO on the catalysts were studied by performing O₂-TPD measurements (Figure 5). The low temperature curves at about 85 °C and 200 °C for the 1-0/AT, 1-1/AT, 1-3/AT, and 1-5/AT catalysts correspond to the surface oxygen species.²⁷ It is clear that the intensity of

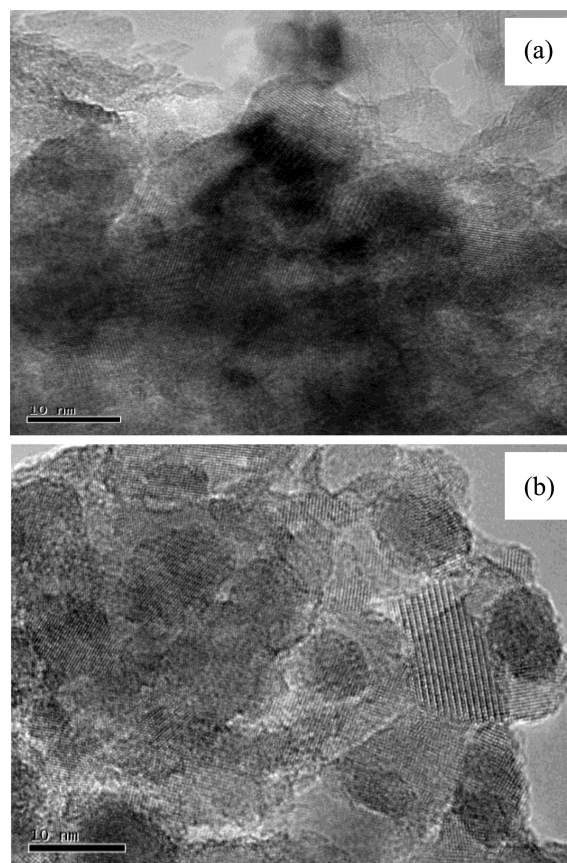


Figure 4. TEM images of Pd–Ce/ γ -Al₂O₃–TiO₂ catalysts. a: 1-0/AT b: 1-1/AT

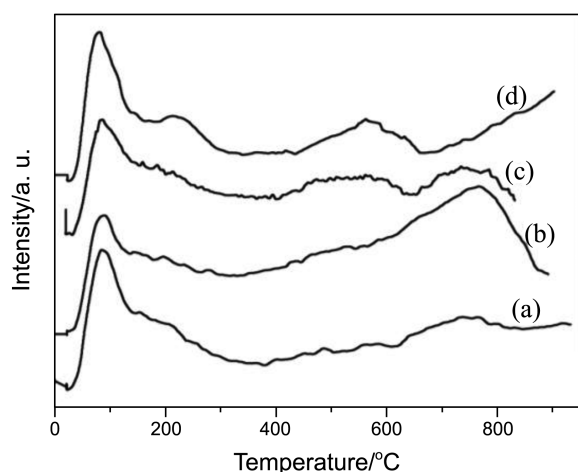


Figure 5. O₂-TPD profiles of Pd-Ce/γ-Al₂O₃-TiO₂ catalysts. a: 1-0/AT b: 1-1/AT c: 1-3/AT d: 1-5/AT

desorption peaks at 200 °C enhances with an increase in Ce content, which is ascribed to more CeO₂ was deposited on the catalyst surface. The peaks located at 750 °C represent the liberation of lattice oxygen of PdO. It was reported that the O₂ desorption peaks located between the temperatures 650 °C and 674 °C were ascribed to the decomposition of crystalline PdO, while the peaks appearing at a high temperatures (722–790 °C) mainly correspond to the decomposition of amorphous PdO.²⁸ Apparently, amorphous PdO possesses stronger Pd–O bonds than crystalline Pd–O, and stable PdO species are beneficial to the oxidation activity.²⁹ Compared with other samples, the initial desorption temperature of PdO lattice oxygen for 1-1/AT is far less than that of other samples, and the 1-1/AT has the largest desorption peak area of PdO lattice oxygen. According to Chen *et al.*, well-dispersed PdO was in intimate contact with the CeO₂, and subsequently promoted oxygen transfer from CeO₂ to PdO.³⁰ This implies that addition of appropriate Ce could weaken the Pd–O bonds, and enrich the PdO species, thus led to the improvement of the catalyst activity for ethanol combustion. And by further examining the O₂-TPD profiles, the peak at about 530 °C for 1-3/AT and 1-5/AT should be attributed to the surface oxygen species on CeO₂. Whereas, no desorption peak related to CeO₂ appeared for 1-1/AT at this temperature, which was ascribed to an interaction between PdO and CeO₂,²⁴ and CeO₂ could reduce the PdO decomposition temperature, but more addition of Ce would agglomerate on the catalyst surface.

H₂-TPR profiles are displayed in Figure 6. A negative peak around 70 °C for the 1-0/AT catalyst is attributed to the desorption of weakly adsorbed hydrogen or to palladium hydride decomposition at room temperature.³¹ In hydrogen atmosphere, PdO or PdCl₂ could be easily reduced to metallic Pd at ambient temperature, resulting in the formation of PdH_x.³² And the formation of PdH_x is normally accompanied by the presence of larger Pd particles.³¹ The TPR signals of 1-1/AT, 1-3/AT and 1-5/AT samples located at about 65 °C are observed owing to the reduction of dispersed PdO. The amount of dispersed PdO formed increased with an increase

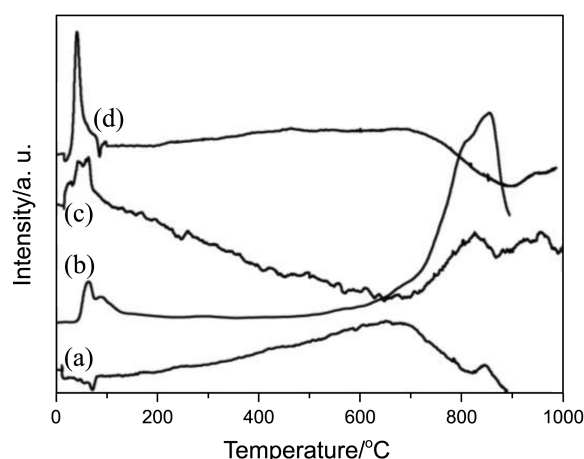


Figure 6. H₂-TPR profiles of Pd-Ce/γ-Al₂O₃-TiO₂ catalysts. a: 1-0/AT b: 1-1/AT c: 1-3/AT d: 1-5/AT

in CeO₂ content. The broad positive peak for 1-0/AT in the range 400–800 °C resulted from the reduction of Ti⁴⁺ to a nonstoichiometric amount of low-valency titanium ion.³³ The peaks at about 850 °C are considered to be the reduction of PdO lattice oxygen. Compared with TPR of other samples, the 1-1/AT catalyst exhibits the highest H₂ consumption for PdO lattice oxygen reduction, and its reduction peak moved to a lower temperature. This demonstrates that addition of proper amount Ce to the system leads to more PdO species and weakened Pd–O bonds, which is in accordance with the O₂-TPD result. The peak corresponding to TiO₂ reduction disappears for 1-1/AT and 1-3/AT catalysts, it emerges again on the 1-5/AT. This may be related with some Ce–O–Ti surface structures.³⁴

Conclusion

In this paper, the catalyst of Pd-Ce/γ-Al₂O₃-TiO₂ was prepared by stepwise impregnation method, and it was excellent catalyst for low temperature ethanol oxidation reaction. Through the research, the abundance of amorphous PdO species and the weakened Pd–O bonds are mainly contributed to the catalytic activity improvement. At 1 wt % Pd loading and 1% Ce loading, the Pd-Ce/γ-Al₂O₃-TiO₂ could completely oxidize ethanol at 175 °C, and its selectivity to CO₂ reached 87%. O₂-TPD, H₂-TPR showed that PdO species were easy to enrich on the surface of the catalyst with the addition of Ce, and PdO particles were highly dispersed on the surface of γ-Al₂O₃-TiO₂.

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