

CO and C₃H₈ total oxidation over Pd/La-Al₂O₃ catalysts: Effect of calcination temperature and hydrothermal treatment

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Abstract: A series of Pd/La-Al₂O₃ (PLA) catalysts with La-Al₂O₃ (LA) support calcined at different temperatures (500, 700, 900 and 1050 °C) were prepared using an incipient wetness impregnation method. The activity of the fresh and hydrothermally aged PLA catalysts were tested for total oxidation of CO and C₃H₈. The activity of the fresh PLA catalysts for CO and C₃H₈ oxidation increased with increasing calcination temperature of the support, while the activities of the aged catalysts declined and became essentially the same. CO chemisorption results revealed that the suppressed activities of the aged catalysts were mainly due to the decline of palladium dispersion. The turnover frequency (TOF) of CO oxidation increased with increasing reduction ability of the catalysts, with a fresh catalyst calcined at 1050 °C having the highest value (0.048 s⁻¹). However, the TOF of C₃H₈ total oxidation was affected by not only the redox properties of catalysts but also the size of Pd particle, and large Pd particles possessed higher TOF value of C₃H₈ oxidation, with the highest value (0.125 s⁻¹) being obtained on an aged catalyst calcined at 500 °C.

Keywords: Pd/La-Al₂O₃ catalysts; stability; turnover frequencies; hydrothermal ageing; rare earths

Automobile exhaust has become one of the main pollution sources in last several decades, causing many serious environmental problems, such as stratospheric ozone layer depletion, acidic rain, green house effect and photo-induced chemical smog^[1,2]. Three-way catalysts (TWCs) have been widely used to control gasoline engine exhaust. A typical three-way catalysts are composed of mainly three parts, including noble metals (Pt, Rh and Pd) serving as active components, γ -Al₂O₃ as a support, and Ce-Zr mixed oxide as promoters^[3-7]. The efficiency of the catalysts towards CO oxidation, hydrocarbons oxidation and NO_x reduction mainly depends on the dispersion of the active precious metal on the catalysts^[8]. However, the rate of active precious metal sintering increases dramatically with the elevation of temperature, which leads to a decrease in the catalytic activity. Although the alloy of these noble metals is typically more stable and more active than either alone, the possibility of reducing precious metals cost by developing Pd-only catalysts without Pt and Rh has prompted the study of the hydrothermal stability of Pd^[9]. Thus, the resistance to thermal aging becomes one of the main concerns for the catalysts design, especially in the case that the catalysts serve in the environment with high steam content (up to 10%) and temperature (up to 1050 °C) during normal operation in the catalytic converter.

The TWCs need to be aged under simulated conditions

to investigate the hydrothermal stability of the catalysts^[3,10]. Generally, the catalysts deactivate at high temperature^[11,12]. It has been found that the deactivation of the catalysts after the hydrothermal treatment mainly relates to the increase of Pd particles and the weakness of the Pd-support interaction during ageing process. The dispersion, crystallite size and the oxidation state of Pd are extremely important parameters in the catalytic performance. In addition, Cao et al.^[3] studied the effects of ageing condition on the Pd/Ce_{0.5}Zr_{0.5}O₂ and Pd/Al₂O₃ catalysts and found that the Pd/Ce_{0.5}Zr_{0.5}O₂ catalysts aged in air and cyclic conditions exhibited much better catalytic activities than those aged in N₂ and H₂, but the activities of Pd/Al₂O₃ catalysts were merely affected by the aged atmospheres.

In order to obtain TWCs with high activity and stability, it is fundamental to avoid the sintering processes to maintain the dispersion of the active phase and improve the support stability. It is well known that the calcination temperature plays an important role in determining the activity and stability of the catalysts. Zhao et al.^[13] found that the catalytic activity and Pd dispersion of Pd/(Ce,Zr)O_x-Al₂O₃ catalyst are affected by thermal treatment of the support. Gao et al.^[14] studied the catalytic activity of Pd/Al₂O₃ toward the combustion of methane and found that the excellent performance of the catalyst was attributed to high hydrothermal stability of

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the support calcined at 1100 °C. However, the hydrothermal stability of the catalyst is still not sufficient for practical application and the main influencing factors for Pd/Al₂O₃ catalytic activity are still unclear. In addition, the deactivating mechanism of Pd/Al₂O₃ catalysts is yet far from being understood.

In this work, the effect of hydrothermal ageing and the calcination temperature to the support on the activity of Pd/La-Al₂O₃ catalysts for CO and C₃H₈ total oxidation were studied. Various characterizations were employed to compare the different chemical nature of the fresh and aged catalysts, which could be correlated with their catalytic behavior.

1 Experimental

1.1 Catalyst preparation

The commercial La₂O₃ stabilized Al₂O₃ support was obtained from Shanghai Huaming Gona Rare Earth New Materials Co., Ltd. (Shanghai, China.) and a nominal content of La₂O₃ is 5 wt.%. The support was calcined at different temperatures (500, 700, 900 and 1050 °C) for 4 h in air before being used and denoted as LAx, where *x* refers to the calcination temperature of the support.

Supported Pd catalysts were prepared by incipient wetness impregnation of the obtained LAx support with an aqueous solution of Pd(NO₃)₂ for 12 h, and the Pd loadings in the catalysts were 0.5 wt.%. The catalysts were dried overnight at 120 °C and then calcined in air at 600 °C for 4 h. The catalysts were denoted as PLA500, PLA700, PLA900 and PLA1050. Aged samples were obtained by treating the fresh samples with 10% steam/N₂ atmosphere at 1050 °C for 4 h.

1.2 Catalyst characterization

X-ray diffraction (XRD) patterns were recorded using a PANalytic X'Pert PW3040 diffractometer with Cu K α radiation operating at 40 kV and 40 mA. The patterns were collected in a 2 θ range from 10° to 90°, with a scanning step of 0.15(°)/s.

Surface areas of the catalysts were determined by the modified BET method from the N₂ adsorption isotherms at liquid nitrogen temperature (−195.7 °C) on an NOVA 40000e Surface Area & Pore Size Analyzer. Before the measurement, the samples were out-gassed at 120 °C for 4 h under vacuum.

Transmission electron microscopy (TEM) investigations were carried out using a JEM-2100F field emission electron microscope operated at 200 kV.

CO chemisorption experiments were carried out on a Quantachrome CHEMBET-3000 instrument in order to determine the dispersion of Pd. The sample (50 mg) was placed in a U-shaped quartz reactor and a high-purity He (99.999%) gas flow of 70 mL/min was used as the carrier

gas. Before CO chemisorption, the samples were reduced in a H₂-N₂ mixture (5 vol.% H₂) stream at 300 °C for 1 h, cooled down to 30 °C, and then purged with pure He for 1 h at the same temperature. Then pulses of CO were fed into the stream of carrier gas with a precision analytical syringe.

Reducibility of the catalysts was measured by the hydrogen temperature programmed reduction (H₂-TPR) technique. 50 mg of the sample was placed in a quartz reactor connected to a homemade TPR apparatus and the reactor was heated from 40 to 900 °C with a heating rate of 10 °C/min, in a reducing atmosphere of mixed H₂ (5 vol.%) and N₂ (95 vol.%) with a total flow rate of 30 mL/min. The amount of H₂ uptake during the reduction was measured by a thermal conductivity detector (TCD). The water produced in TPR was trapped on a 0.5 nm molecular sieve.

1.3 Catalytic testing

The catalytic performance test was carried out in a quartz tubular (i.d.=6 mm) fixed-bed reactor under atmospheric pressure. 100 mg of the catalyst in 60–80 mesh was diluted with 250 mg quartz sands, and then the mixture was loaded into the reactor and the reaction temperature was monitored by a thermocouple placed in the middle of the catalyst bed. The feed gas mixture, consisting of 1% CO and 1% O₂, or 0.2% C₃H₈ and 1.5% O₂, balanced by N₂, was introduced at a flow rate of 40 mL/min, equivalent to a gas hourly space velocity (GHSV) of 9600 mL/(g·h). The catalyst was directly exposed to the reaction without any pretreatment. The CO concentration in the reactor effluent was analyzed using an Agilent 6850 gas chromatograph equipped with a TCD detector and an HP PLOT (30 m×0.32 mm×12 μ m) column and the C₃H₈ concentration in the reactor effluent was analyzed by a GC (GC-14C, Shimadzu) equipped with a flame ionization detector (FID). Before analysis, the reaction at each temperature over the catalyst was stabilized for least 30 min to obtain steady-state reaction data. The activities of the catalysts were then evaluated on the basis of CO and C₃H₈ conversion, which can be calculated with the CO and C₃H₈ concentrations in the reactant gas and in the effluent gas. The equation is as follows:

$$\text{CO conversion} = \frac{[\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}}{[\text{CO}]_{\text{in}}} \times 100\% \quad (1)$$

$$\text{C}_3\text{H}_8 \text{ conversion} = \frac{[\text{C}_3\text{H}_8]_{\text{in}} - [\text{C}_3\text{H}_8]_{\text{out}}}{[\text{C}_3\text{H}_8]_{\text{in}}} \times 100\% \quad (2)$$

where [CO]_{in} and [C₃H₈]_{in} refer to the CO and C₃H₈ concentrations in the feed stream, and [CO]_{out} and [C₃H₈]_{out} refer to the corresponding concentrations in the effluent gases, respectively.

The calculation of turnover frequency (TOF) was based on the conversion of CO or C₃H₈ and the amount

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