La₂O₃对Pd密偶催化剂性能的影响

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摘要: 采用浸渍法制备了不同 La₂O₃ 含量的 Pd 密偶催化剂. 使用低温 N₂ 吸附-脱附、X 射线衍射、H₂ 程序升温还原、CO 化学吸附和 X 射线光电子能谱等技术考察了 La₂O₃ 对催化剂性能的影响. 模拟汽车尾气条件考察了催化剂上丙烷的转化活性. 活性测试结果表明, La₂O₃ 的添加能显著提高催化剂对丙烷的转化活性和催化剂的热稳定性. H₂-TPR 结果表明 La₂O₃ 的添加降低了催化剂的还原温度, 提高了催化剂的氧化还原性能. CO 化学吸附和 XPS 结果表明, La₂O₃ 的添加提高了 Pd 物种的分散, 降低了 Pd 的平均颗粒度. La₂O₃ 的最佳添加量为 10%.

关键词: 氧化镧; 钯; 丙烷; 密偶催化剂; 热稳定性

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The Effect of La₂O₃ on Pd Close-Coupled Catalysts

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Abstract: Palladium close-coupled catalysts were prepared by impregnation method with different amounts of La₂O₃ as a promoter. Low temperature N₂ adsorption-desorption, X-ray diffraction, H₂-temperature programmed reduction (H₂-TPR), CO-chemisorption, and X-ray photoelectron spectroscopy (XPS) were used to characterize the effect of La₂O₃ on the physicochemical properties of the prepared catalysts. Their catalytic activities toward C₃H₈ conversion were evaluated using a gas mixture that simulates the emissions from a gasoline engine. The results of catalytic activity indicate that the presence of La₂O₃ significantly improves catalytic performance and enhances the thermal resistance of the catalysts. H₂-TPR results suggest that the addition of La₂O₃ increases the reductive ability of the catalysts and shifts the reduction temperature to a lower value. The XPS and CO-chemisorption results indicate that doping by La₂O₃ also improves the dispersion of the Pd species and decreases the mean particle size of palladium. The optimal loading amount of La₂O₃ is 10%.

Key words: lanthanum oxide; palladium; propane; close-coupled catalyst; thermal stability

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Exhaust gases that originate from the internal combustion of automobile engines are an important source of atmospheric contamination, particularly in urban areas. These gases mainly contain three toxic substances: hydrocarbons (HCs), carbon monoxide (CO), and nitrogen oxides (NO_x)

[1,2].

With the gradual improvement in environmental standards, controlling the HCs emitted during the cold-start of a vehicle is of particular interest and methods to quickly bring the catalyst up to the operating temperature are being ex-

ploded. One effective solution is to locate the catalyst close to the exhaust ports of the engine (close-coupled catalyst). However, this leads to the catalyst bed running at high temperature when the engine is operating normally, sometimes at higher than 1100 °C. Therefore, the thermal resistance property of the catalyst should also be suitable.

Lanthanum oxide, as a cheap and rich rare-earth element oxide has been widely used as a stabilizer, a sub-catalyst or a promoter in automobile exhaust catalysts. The addition of lanthanum oxide to alumina can impede the loss of surface area and raise the transformation temperature of alumina to enable a transformation from the γ -phase to the α -phase [3–9]. Sun et al. [10] reported that the addition of a small amount of La_2O_3 to Pd/CeO_2 significantly improved the catalytic activity toward methanol decomposition and also improved the surface area and dispersion of Pd. Koltsakis et al. [11] also reported that La^{3+} ions could increase the dispersion of active components and active sites, which results in a decrease in the light-off temperature of the catalyst and in an improvement of NO_x conversion. It has been further reported that the addition of La to the alumina-supported Pd catalysts increases its tolerance to thermal deactivation [12,13]. Therefore, the La species enhances the thermal stability of $\gamma\text{-Al}_2\text{O}_3$, improves its catalytic performance and impedes the sintering of the supported Pd catalysts. Shi et al. [14] investigated the catalytic performance of a Pt-Rh close-coupled catalyst supported on La-stabilized alumina and found high low-temperature catalytic activity. Li et al. [15] studied the effect of different supports on a close-coupled supported palladium catalyst and found that the support did influence the catalytic performance. However, there is still a lack of information about the catalytic functioning of lanthanum oxide as a promoter on Pd close-coupled catalysts.

In this work we investigated the influence of La_2O_3 as a promoter on the physicochemical properties and the catalytic activities of Pd close-coupled catalysts.

1 Experimental

1.1 Catalyst preparation

La-stabilized alumina and $\text{Ce}_{0.35}\text{Zr}_{0.55}\text{Y}_{0.07}\text{La}_{0.03}\text{O}_{1.95}$ (OSM) were used as catalyst supports. Before use, Al_2O_3 and OSM were calcined at 1000 and 900 °C for 5 h, respectively. After calcination, Al_2O_3 had a surface area of 145 m^2/g and a pore volume of 0.45 ml/g while the OSM had a surface area of 53 m^2/g and a pore volume 0.16 ml/g .

A series of La_2O_3 promoted Pd close-coupled catalysts were prepared by impregnating two different supports ($m(\text{OSM})/m(\text{Al}_2\text{O}_3) = 1/4$) with an aqueous solution of $\text{Pd}(\text{NO}_3)_2$, drying at 120 °C overnight and calcining at 550

°C for 3 h in a muffle furnace. The two obtained catalyst powders were mixed and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (La_2O_3 content was 0, 5%, 10%, and 20%) as well as a specific amount of deionized water was ground to form a homogeneous slurry. The resulting slurry was spread onto honeycomb cordierite (2.5 cm^3 , Corning), and excessive slurry was blown away with compressed air. The catalysts were dried and calcined at 550 °C for 3 h in a muffle furnace and the monolithic catalysts were thus obtained. The catalysts were denoted Cat.1, Cat.2, Cat.3, and Cat.4 for the La_2O_3 contents of 0, 5%, 10%, and 20%, respectively. To compare their thermal stability, the aged catalysts were obtained by calcining the fresh catalysts at 1000 °C for 5 h in air. The Pd content in all the catalysts was 2 g/L.

1.2 Catalyst characterization

The catalytic activity was evaluated in a multiple fixed bed continuum flow micro-reactor by passing a gas mixture similar to the exhaust gas from a gasoline engine. The gases were regulated with mass flow controllers before entering a blender. The simulated exhaust gas contained a mixture of O_2 , CO (0.6%), C_3H_8 (0.06%), NO (0.06%), CO_2 (12%), H_2O (10%), and N_2 (balance). The gas space velocity was 30000 h^{-1} . The concentration of C_3H_8 was analyzed online by a five-component analyzer (FGA-4100, Foshan Analytical Instrument Co., Ltd. China) before and after the simulated gas passed the micro-reactor.

The textural properties of the catalysts were determined by the adsorption-desorption of N_2 at the liquid nitrogen temperature (−196 °C) on a ZXF-06 automatic surface analyzer (Xibei Chemical Institute, China). To remove the surface impurities, the samples were degassed under vacuum for 2 h at 350 °C before obtaining a measurement.

The crystal structures of the catalysts were determined by powder X-ray diffraction (XRD) analysis on a computer-controlled DX-2500 diffractometer, using Cu K_α radiation ($\lambda = 0.15418 \text{ nm}$), operating at 40 kV and 25 mA. The XRD data were recorded for 2θ values between 20° and 90° with an interval of 0.03°.

H_2 temperature-programmed reduction (H_2 -TPR) experiments were performed on a quartz tubular micro-reactor. The sample (100 mg, 40–60 mesh) was pretreated in a flow of N_2 (20 ml/min) from room temperature to 400 °C, maintained at this temperature for 45 min and then cooled to room temperature in N_2 (20 ml/min). The reduction was carried out in a flow of a 5% H_2 -95% N_2 (V/V) gas mixture (20 ml/min) from room temperature to 700 °C with a heating rate of 8 °C/min. The consumption of H_2 was detected by thermal conductivity detector (TCD).

The metal dispersion and the mean particle size of Pd on the different catalysts were determined by

CO-chemisorption over the reduced catalysts. Approximately 300 mg (40–60 mesh) of the sample was placed in a U-shaped quartz tube. Before chemisorption, the catalyst was reduced in a flow of H_2 (30 ml/min) at 500 °C for 1 h, and then purged with pure N_2 (30 ml/min) at 550 °C for 1 h. After being allowed to cool to room temperature, CO was pulsed over the reduced catalyst until the TCD signal from the pulse was constant. The number of exposed Pd atoms was calculated assuming a chemisorption stoichiometry of $\text{CO}/\text{Pd} = 1$ and all CO was adsorbed on the exposed Pd atoms [16–18]. The mean particle size was determined by $d = (1.12/D) \times 10^{-9} \text{ m} = (1.12/D) \text{ nm}$ [19].

X-ray photoelectron spectroscopy (XPS) experiments were carried out using a spectrometer (XSAM-800, Kratos Co) with Mg K_α radiation under ultra-high voltage (UHV), calibrated internally by a carbon deposit C 1s binding energy at 284.8 eV.

2 Results and discussion

2.1 Catalytic activity

Figure 1 shows the results of the catalytic performance for C_3H_8 conversion over fresh and aged catalysts in the simulated exhaust gas. According to Fig. 1, C_3H_8 conversions over all the fresh and aged catalysts increases with an increase in the temperature and C_3H_8 can rapidly reach complete conversion. Furthermore, for the fresh catalysts the activities of the La_2O_3 -containing catalysts were better higher than that of the La_2O_3 -free catalyst, which suggests that La_2O_3 improves the catalytic performance of these catalysts. However, after high temperature calcination the activities of all the catalysts decreased compared with that of the fresh samples and we thus conclude that all the catalysts undergo different degrees of sintering. This phenomenon was explained in a previous study [20]. Kenevey et al found that during the high-temperature treatment process the surface area of the catalyst is reduced and the original porosity of the material was destroyed while the pore vol-

Table 1 Light-off temperatures and ΔT for C_3H_8 conversion over the different catalysts

Catalyst	$T_{50}/^\circ\text{C}$		$\Delta T/^\circ\text{C}$
	Fresh	Aged	
Cat.1	285	342	57
Cat.2	273	327	54
Cat.3	270	320	50
Cat.4	278	362	84

ume also decreased, which results in the degradation of catalytic performance.

A summary of changes in the light-off temperature T_{50} (T_{50} corresponding to the temperature at which 50% conversion of C_3H_8 is completed) values for the fresh and aged catalysts are listed in Table 1. In principle, a lower T_{50} value results in a higher low-temperature activity of the catalyst. From Table 1, the T_{50} values of the fresh Cat.1, Cat.2, Cat.3, and Cat.4 catalysts are 285, 273, 270, and 278 °C, respectively. The T_{50} for C_3H_8 oxidation increases as follows: Cat.3 < Cat.2 < Cat.4 < Cat.1. After aging at 1000 °C for 5 h, the T_{50} values increase to a value higher than that of the fresh catalysts, and are 342, 327, 320, and 362 °C for Cat.1, Cat.2, Cat.3, and Cat.4, respectively. The order of T_{50} values changes to: Cat.3 < Cat.2 < Cat.1 < Cat.4. Only Cat.1 and Cat.4 change positions. This may be the result of excessive La_2O_3 addition. From Table 1, the differences between the T_{50} of the fresh and the aged catalysts (ΔT) are 57, 54, 50, and 84 °C for Cat.1, Cat.2, Cat.3 and Cat.4, respectively. A lower ΔT indicates better catalyst thermal stability. With an increase in the La_2O_3 content, the catalytic activities increase initially, reach the highest value at 10% and then decrease. These results indicate that the introduction of La_2O_3 into the catalysts as a promoter improves the catalytic activity and the resistance to high temperature aging. The amount of La_2O_3 loading is very important for C_3H_8 conversion and an optimum loading amount exists for La_2O_3 . For the catalysts investigated in this study, Cat.3 exhibits the best low-temperature activity and high-temperature anti-aging performance, so the optimum La_2O_3 content is

Fig. 1. Conversion of C_3H_8 at different temperatures over various catalysts. (a) Fresh; (b) Aged.

Table 2 Surface areas and pore volumes of the catalysts

Sample	Specific surface area (m ² /g)		Pore volume (ml/g)	
	Fresh	Aged	Fresh	Aged
Cat.1	112	51	0.35	0.22
Cat.2	103	76	0.32	0.24
Cat.3	87	78	0.30	0.25
Cat.4	64	57	0.25	0.22

10%.

2.2 Textural properties

The BET surface areas and the pore volumes of the fresh and aged catalysts are summarized in Table 2. Significant differences exist between the surface areas and the pore volumes of the fresh catalysts. With an increase in the La₂O₃ content, the surface areas gradually decrease. The surface area and pore volume of Cat.4 is only 64 m²/g and 0.25 ml/g, which is the result of excessive La₂O₃ addition. Doping with La₂O₃ dilutes the mass fraction of the catalyst support, which gives a larger surface area than that of La₂O₃ and excessive La₂O₃ blocks the mesopores of alumina and/or the OSM. This is the main reason for the decrease in the surface area and the pore volume. After calcination at 1000 °C for 5 h, the specific surface areas and pore volumes decrease compared with those of the fresh catalysts. These results indicate that the catalysts experience a kind of sintering phenomenon. For the aged samples, the La₂O₃ containing catalysts were found to have larger specific surface areas and pore volumes compared with that of the La₂O₃-free catalyst. The surface area over the catalyst without La₂O₃ doping drops drastically by more than 50% from 112 m²/g to 51 m²/g. Although the surface areas of the La₂O₃ doped samples also decrease after high-temperature calcination, as shown in Table 2, their rate of decrease is far slower than that of the catalyst without La₂O₃ doping. Cat.2, Cat.3, and Cat.4 retain 74%, 90%, and 89% of their surface

areas. This indicates a stabilizing effect for La₂O₃. Among all the catalysts, Cat.3 has the largest specific surface area and pore volume while Cat.1 has the lowest. According to these results, the addition of La₂O₃ can help the catalysts retain their large surface areas and pore volumes and to improve their thermal resistance. Alternatively, we also found that the catalytic activities do not agree with the order of the surface areas. Therefore, apart from the surface area of the catalysts, other structural characteristics will affect the catalytic activity.

2.3 XRD analysis

XRD was used to determine the bulk crystalline phases of the catalysts. The diffraction patterns of the various catalysts are shown in Fig. 2. As shown in Fig. 2(a), the diffraction peaks of all the fresh samples are similar. The diffraction peaks appear at $2\theta = 29.20^\circ$, 33.87° , 48.76° , 57.70° , and 79.10° and they correspond to a structure similar to Ce_{0.50}Zr_{0.50}O₂, and it is specifically Ce_{0.35}Zr_{0.55}Y_{0.07}-La_{0.03}O_{1.95}. The diffraction peaks at $2\theta = 45.76^\circ$, 60.03° , and 67.24° are due to γ -Al₂O₃. According to the results of peak-broadening analysis (101 , $2\theta = 29.20^\circ$), the crystallite sizes of the Cat.1, Cat.2, Cat.3, and Cat.4 catalysts are 8.9, 8.3, 7.8, and 7.1 nm, respectively. Therefore, upon an increase in the La₂O₃ content the intensity of the diffraction peaks gradually weakens. The crystalline structure of La₂O₃ is not observed in any of the fresh catalysts, which indicates that La₂O₃ is well dispersed on the support surface.

From Fig. 2(b) the crystalline structures of all fresh catalysts are shown to change at different diffraction angles and the XRD peaks become sharper after calcination at 1000 °C for 5 h. Some α -Al₂O₃ is observed in Cat.1 and Cat.2 (Cat.1 has more α -Al₂O₃ than Cat.2), and for Cat.3 the catalyst has a highly stable crystalline structure but some LaAlO₃ is detected. However, for Cat.4 with a La₂O₃ loading of 20%, the crystalline structure changes obviously. Plenty of LaAlO₃ is present on the catalyst but no α -Al₂O₃ is detected.

Fig. 2. XRD patterns for the fresh (a) and aged (b) catalysts.

This demonstrates the stabilizing effect of La_2O_3 , which prevents the phase transformation of $\gamma\text{-Al}_2\text{O}_3$ into $\alpha\text{-Al}_2\text{O}_3$ but excessive La_2O_3 leads to the formation of LaAlO_3 . LaAlO_3 is a product of the high temperature solid-phase reaction between Al_2O_3 and La_2O_3 [5].

From the XRD results of the fresh catalysts, La_2O_3 is well dispersed on the support surface, which improves the dispersion of active sites. While excessive La_2O_3 addition leads to a drastic loss of the specific surface area of the catalyst, the catalytic performance of Cat.4 is lower than that of Cat.2 and Cat.3 and higher than that of Cat.1. For the aged catalysts, the α -phase transformation contributes to the surface area loss (confirmed by the BET results), which results in a decrease in active sites. Therefore, for Cat.1, Cat.2, and Cat.3, the activity increases with a decrease in $\alpha\text{-Al}_2\text{O}_3$ formation, in other words, with an increase in La_2O_3 content. However, for Cat.4 a large amount of LaAlO_3 forms and Cat.4 has the worst activity, therefore, the formation of LaAlO_3 has a negative effect on catalytic performance even though LaAlO_3 does impede the loss of surface area. Based on the above analysis, it is clear that the loss of surface area and the formation of LaAlO_3 are responsible for the decrease in catalytic activity.

No visible PdO or metallic Pd phases are present in the XRD patterns for all the catalysts, indicating that the content of Pd is too low for detection or that the Pd particles are well dispersed on the supports.

2.4 H_2 -TPR analysis

H_2 -TPR experiments were carried out to evaluate the relationship between the catalytic activity and the reducibility of the supported catalysts. The redox ability of the catalysts is closely related to the catalytic activity. The H_2 -TPR profiles of the catalysts are shown in Fig. 3.

From Fig. 3, although the H_2 -TPR profiles have similar spectra and some variations exist between the samples with different La_2O_3 content. The sharp peak between 50 and 200

Fig. 3. H_2 -TPR profiles of the catalysts.

$^{\circ}\text{C}$ is due to the reduction of the PdO species. The maximum reduction temperatures of the Cat.1, Cat.2, Cat.3, and Cat.4 catalysts were 139, 132, 115, and 135 $^{\circ}\text{C}$, respectively. This suggests a decrease in the PdO reduction temperature, indicating that the Pd-La interaction promotes the reduction of PdO. Kašpar et al. [2] reported that the active phase of Pd three-way catalysts is PdO. The transformation from PdO to Pd determines the catalytic performance of the catalysts. A lower reduction temperature for PdO can result in higher catalyst activity. We also calculated the H_2 -TPR peak areas of PdO and they were 2978, 3321, 3505, and 3037 for Cat.1, Cat.2, Cat.3, and Cat.4, respectively. This confirms that the addition of La_2O_3 increases the reduction ability of the catalysts and thus results in an improvement in the catalytic activity for C_3H_8 oxidation. The reducibility order follows the catalytic performance results. In addition, the reduction peaks from 250 to 350 $^{\circ}\text{C}$ are similar and this can be attributed to the reduction of the surface and/or bulk oxygen of CeO_2 . However, the peak has a low intensity after 900 $^{\circ}\text{C}$ calcination on the OSM.

2.5 CO chemisorption analysis

The results of the CO-chemisorption of the Pd close-coupled catalysts are listed in Table 3. Pd dispersion and particle size play an important role in the catalytic activity. Simplicio et al. [21] concluded that higher dispersion and smaller PdO particle sizes for Pd catalysts result in better catalytic activity. After the addition of La_2O_3 to the catalysts the Pd dispersion increases and the Pd mean particle size decreases, as given in Table 3. These results indicate that La_2O_3 addition can improve the Pd dispersion and maintain a small Pd particle size. A good correlation exists between Pd dispersion and catalytic activity, and a lower dispersion of Pd catalysts is one of the reasons for the poor activity obtained in this study. These results are in good agreement with the conclusions given in Ref. [20].

Table 3 CO chemisorption for the catalysts

Catalyst	Dispersion (%)	Mean particle size (nm)
Cat.1	29.9	3.7
Cat.2	31.9	3.5
Cat.3	34.2	3.3
Cat.4	31.1	3.6

2.6 XPS results

XPS measurements were carried out to investigate the electronic state of the Pd species to study the effect of La_2O_3 on the Pd close-coupled catalysts. Table 4 summarizes the binding energy values and the surface atomic ratio of Pd, as calculated from the XPS results of all four catalysts.

Table 4 Data from the XPS analysis of various catalysts

Catalyst	Binding energy of Pd 3d _{5/2} (eV)	Surface atomic ratio of Pd (%)
Cat.1	336.08	0.38
Cat.2	336.20	0.56
Cat.3	336.35	0.59
Cat.4	336.15	0.53

It has been reported that the binding energies of metallic Pd⁰ and PdO are 335.2 and 336.8 eV [22], respectively. As shown in Table 3, the binding energies of the Pd 3d_{5/2} electrons of all the catalysts fall between 336.08 and 336.35 eV, which is lower than that of PdO and higher than that of metallic Pd⁰. This indicates that the Pd species in the catalysts are in a partially oxidized state Pd^{δ+} (0 < δ < 2). This species is more active than Pd metal. Compared with Cat.1, doping with La₂O₃ results in the Pd 3d peaks shifting to higher values (Table 3). It has been reported that the addition of La could increase the electron density around PdO as an electron donor resulting in a decrease in the binding energy value [23], which is in contrast to our results. In this study, the surface atomic ratios of Pd on the Cat.1, Cat.2, Cat.3, and Cat.4 catalysts are 0.38%, 0.56%, 0.59%, and 0.53%, respectively. By combining the results of H₂-TPR and CO-chemisorption, we conclude that doping with La₂O₃ can improve the reduction ability and Pd species dispersion of the catalysts, leading to better catalytic activity toward propane oxidation. The most plausible explanation for the binding energy shift is that the dispersion of the Pd species increases as a result of La₂O₃ addition. Considering the catalytic activity, the dispersed higher oxidation state of Pd is more active toward the catalytic oxidation of propane.

3 Conclusions

XRD characterization results indicate that La₂O₃ is well dispersed on the supports, however, the formation of LaAlO₃ during high temperature treatment has a negative effect on the catalytic performance and LaAlO₃ impedes the surface area loss of the catalyst. In addition, the presence of La₂O₃ increases the reduction ability of the catalyst, improves the dispersion of the Pd species, decreases the mean particle size of Pd and stabilizes Pd in a more active high oxidation active. All these factors contribute to the improvement of catalytic activity and the high temperature tolerance of the catalyst. At a catalyst loading of 10% La₂O₃ the best catalytic performance was obtained and the light-off temperatures for the fresh and aged catalyst were found to be 270 and 320 °C, respectively.

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