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ARTICLE

Catalytic Activity of C_3H_8 over Fresh and Aged Pd/Al_2O_3 Close-Coupled Catalysts

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Abstract: The Pd/Al_2O_3 close-coupled catalysts supported on modified alumina were prepared by an impregnation method, and then characterized by H_2-temperature programmed reduction (H_2-TPR), CO chemisorption, and X-ray photoelectron spectroscopy (XPS). Both total catalytic activity and single reactions in related to C_3H_8 conversion were tested in simulated exhaust gas. The results show that the amount of active PdO_x decreases and negative metallic Pd^0 appears during aging treatment. The light-off temperature (T_{50}) and complete conversion temperature (T_{90}) increase by 76 ℃ and 64 ℃, respectively. After aging treatment, signifying that the low-temperature activity decreases more obviously than high temperature property. The results of comparison among single reactions indicate that the light-off activity of reactions which occur in atmosphere with the participation of NO but without H_2O injection decreases dramatically after the aging treatment. The inhibitive effect of NO on light-off activity and the positive effect of H_2O on high temperature property become obvious during the aging treatment.

Key words: close-coupled catalyst; Pd; Al_2O_3; propane; low-temperature activity

During the last several decades, the purification of exhaust gas has earned much attention[1,2], and two kinds of automobile exhaust catalysts have been widely used to meet stringent emission standards[3,4]. One kind is the close-coupled catalyst (CCC) which is used to eliminate the majority of hydrocarbon emissions (60%~80% of the total emitted) during the cold start[5,6]. In order to be heated to light-off temperature promptly, the CCC is usually installed nearer to the engine of automobile[7]. The other kind of catalyst is the three-way catalyst (TWC) which is installed behind the CCC[8-10].

Close-coupled catalyst presents high thermal stability and excellent low-temperature activity, because the catalyst is installed very near to the engine which is operated at temperature as high as or even above 1050 ℃[11]. Alumina-supported Pd close-coupled catalysts are always the most studied systems and widely used. During aging treatment, the main changes in the Al_2O_3 support were the loss of BET area and pore volume due to the transition of phase. The main deactivation mode of aging was loss of active Pd surface area with the sintering of metallic Pd, especially above the PdO decomposition temperature[12]. Much attention has been paid to the comparison of catalytic activity with or without aging treatment, suggesting that the degradation of low-temperature activity is more serious than that of high temperature activity[11,13,14]. Some authors have made some efforts to improve the light-off activity of CO oxidation and NO reduction, such as introducing of promoters to catalysts[15-17]. However, there are not too much reports on improving the light-off activity of reactions associated with C_3H_8 conversion in close-coupled catalyst. For this purpose, the total activity and the property of single reactions associated with C_3H_8 conversion before and after aging treatment were examined in the present study.

1 Experiment

La-stabilized alumina was prepared by a peptizing method and calcined at 600 ℃ for 3 h. After calcination at 1000 ℃ for 3 h, the surface area and pore volume of Al_2O_3 are 138 m^2/g

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and 0.47 mL/g, respectively.

The Pd/Al_2O_3 close-coupled catalysts were obtained by a conventional aqueous impregnation method, using an aqueous solution of $Pd(NO_3)_2$ as a precursor. The fresh and aged catalysts were calcined at 550 ℃ for 3 h and 1000 ℃ for 5 h, respectively. The academic loading content of Pd was 2.5 g/L (1.6 wt%).

H_2-TPR experiments were carried out in a flow system to measure the reducibility of the supported Pd catalysts. The sample (100 mg, 400~250 μm) was pretreated in a flow of N_2 (20 ml/min) from room temperature to 400 ℃ at a rate of 8 ℃ /min, held at this temperature for 60 min, and cooled down to room temperature in N_2 (20 mL/min). Then the sample was heated under a flow of 5% H_2/N_2 (20 mL/min) from room temperature to 300 ℃ at a heating rate of 8 ℃/min. The consumption of H_2 was detected by TCD.

The XPS experiments were performed on a spectrometer (XSAM-800, Kratos Co) with Mg *Kα* radiation under ultra-high vacuum (UHV), calibrated internally by a carbon deposit C 1s binding energy at 284.8 eV.

The dispersion of palladium was determined by CO chemisorption measurement. Prior to chemisorption, the catalyst was reduced under a flow of H_2 (20 mL/min) at 500 ℃ for 60 min and then purged with pure He (30 mL/min). After being cooled down to room temperature, carbon monoxide was pulsed and detected by TCD.

The catalytic activity were evaluated in simulated exhaust gas with a mixture of O_2 (adjustable), 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 40 000 h^{-1}. The concentrations of the gases were regulated with mass flow controllers before entering a blender.

2 Results and Discussion

2.1 TPR results

The H_2-TPR results are shown in Fig.1. In the TPR profile of aged Pd/Al_2O_3 catalyst, there are two peaks at 65~70 ℃ and 75~90 ℃, denoted as α and β, respectively. However, only β peak can be seen in the profile of fresh catalyst. The β peak arises from hydrogen consumption, and the negative α peak corresponds to the decomposition of palladium hydrides[7,18]. Metallic Pd^0 can dissociate H_2 molecule into smaller hydrogen atoms which can form palladium hydrides with larger crystallites of metallic Pd^0 at room temperature; however, the formation of palladium hydrides on the highly dispersed Pd is considerably suppressed[19]. It indicates that larger crystallites of metallic Pd^0 appears on the aged catalyst and the dispersion of active PdO_x decreases during aging treatment. Moreover, the reduction temperature and area of peak β of fresh Pd catalyst are lower and larger than those of aged catalyst. It demonstrates that the amount of active PdO_x species on the supported Pd catalyst decreases after the calcination at 1000 ℃ for 5 h, which is unfavorable to the catalytic performance.

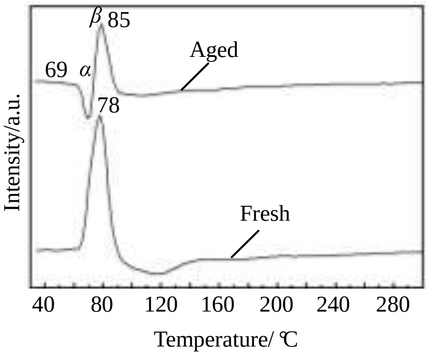

Fig.1 H_2-TPR profiles of fresh and aged Pd/Al_2O_3 close coupled catalysts

2.2 CO chemisorption analysis

Simplício et al.[20] have reported that higher dispersion of active component and smaller particle size produces higher active surface area, and thus enhanced catalytic performance of catalyst can be obtained. The results of CO chemisorption of fresh and aged Pd/Al_2O_3 close-coupled catalysts are shown in Table 1. It is assumed that the ratio of Pd to CO is 1:1. The average Pd particle size, d (nm), was obtained by $1.12/D$[21], where D (%) is the dispersion of Pd. The active Pd surface area, S (m^2/g), was approximated by

$$V_0N\delta/22.4wp \qquad (1)$$

where V_0 is the consumption of CO (L), N is Avogadro constant (6.023×10^{23}), δ is the atomic cross section of Pd ($0.06\ nm^2$)[22], w (g) is the mass of catalyst, and p (%) is the mass fraction of Pd.

As seen in Table 1, the dispersion of Pd decreases dramatically from 22.8% to 4.5%, and the active surface area declines from 77.4 to 15.2 m^2/g after aging treatment, possibly due to the sintering of Pd over support. The deterioration of Pd dispersion and increase of active species particle size are in acoordance with the TPR results. Meanwhile, the particle size of Pd increases obviously from 4.9 to 24.9 nm after calcination at 1000 ℃ for 5 h.

2.3 XPS results

The XPS spectra of Pd 3*d* for the fresh and aged catalysts are shown in Fig.2, and the BE values of Pd $3d_{5/2}$ are listed in Table 1. In general, the binding energy of Pd $3d_{5/2}$ for Pd^0 and Pd^{2+} are about (334.9±0.1) eV and (336.4±0.1) eV[23], respectively. As shown in Table 1, the binding energy of Pd $3d_{5/2}$ of fresh and aged catalysts falls in the range of 334.9~336.4 eV, indicating that the Pd species in fresh and aged

Table 1 Date from XPS analysis and CO chemisorption of fresh and aged catalysts

Cat.	D/%	d/nm	S/$m^2\ g^{-1}$	BE/eV	Pd/%	Pd^0/%
Fresh	22.8	4.9	77.4	336.3	0.36	0.03
Aged	4.5	24.9	15.2	335.9	0.50	0.11

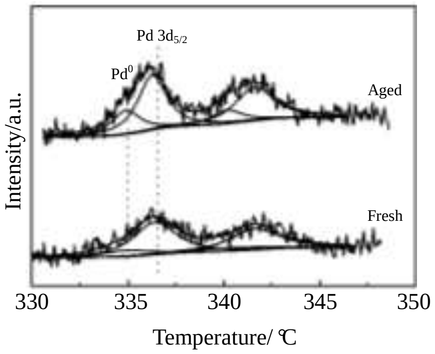

Fig.2 XPS spectra of Pd3d$_{5/2}$ of fresh and aged catalysts

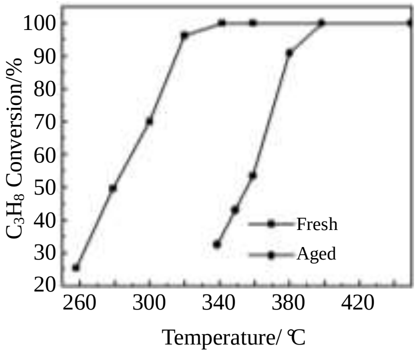

Fig.3 C_3H_8 conversion at different temperatures over fresh and aged catalysts

catalysts are in partially oxidized state $Pd^{\delta+}$ ($0<\delta<2$) which is more active than metallic Pd^0. Compared with the fresh catalyst, the Pd 3d$_{5/2}$ peaks of aged catalyst shift to lower values. Based on Ref. [24], the core-level binding energy of Pd mainly depends on the particle size of PdO_x and the energy value of Pd 3d$_{5/2}$ decreases with the rise of PdO_x particle size supported on Al_2O_3, indicating that the particle size of PdO_x become larger after aging treatment. This result is in good agreement with the conclusion given in CO chemisorption. Moreover, the spectra of metallic Pd^0 on aged catalyst profile can be observed obviously, but it can hardly be seen in the profile of fresh catalyst. It means that the metallic Pd^0 atoms gather on the surface of catalyst after aging treatment obviously, which is consistent with the H_2-TPR results. The surface atomic ratios of Pd on fresh and aged catalysts are 0.36% and 0.50%, respectively, indicating the sintering and aggregation of PdO_x species on the surface. Probably the main reason for this is the variation in textural property of support material, since the area density of Pd on the support surface must increases as the support material undergoes sintering[25].

2.4 Total catalytic activity

The results of total catalytic activity of fresh and aged Pd/Al_2O_3 catalysts are shown in Fig.3. The difference in activity seems obvious between these catalysts with or without aging treatment. The light-off temperature (T_{50}) and complete conversion temperature (T_{90}) of fresh catalyst are 280 ℃ and 315 ℃, respectively. And those of aged catalyst are 356 ℃ and 379 ℃, respectively. It is interesting to note that the T_{50} and T_{90} increase to higher values distinctly by 76 and 64 ℃ after aging treatment, respectively. As is well known, a lower T_{50} results in a higher low-temperature activity of the catalyst[26]. The low-temperature activity of catalyst declines more seriously than the high temperature activity after the aging treatment process, due to the generation of metallic Pd^0 which is disadvantageous to the catalytic activity for C_3H_8.

2.5 Single reactions over fresh and aged catalysts

2.5.1 Direct oxidation reaction of C_3H_8

In order to further investigate the deterioration of C_3H_8 activity after aging treatment, especially for the decline of low-temperature activity, the following single reactions were measured in corresponding simulated exhaust gas atmosphere.

The direct oxidation reaction of C_3H_8 ($HC+O_2 \rightarrow CO_2+H_2O$) was tested in $C_3H_8/O_2/N_2$ atmosphere and the results are shown in Fig.4. The T_{50} and T_{90} of fresh catalyst shown in Table 2 are 310 ℃ and 366 ℃, respectively. And the T_{50} and T_{90} of aged catalyst are 404 ℃ and 450 ℃, respectively. That is, the T_{50} and T_{90} increase by 94 ℃ and 84 ℃ after aging treatment, respectively. The property in low-temperature range declines more significantly than that in high temperature range. The decline of the amount of active PdO_x species during the aging treatment makes the competitive adsorption on active component sites between C_3H_8 and O_2 much fiercer, and thus the reaction occurs at higher temperature. On the other hand, either C_3H_8 or intermediates (such as partial oxidation products) which is strongly adsorbed on the catalyst surface can result in self-inhibition and their strong adsorption can also inhibit the oxygen adsorption[27].

Variations of C_3H_8 conversion of oxidation reaction with a rise of oxygen content were studied at 450 ℃ and compared in Fig.4b. The conversion of fresh catalyst increases rapidly to 100% with the rise of O_2 content and then maintains at 100%. Meanwhile, the conversion of aged catalyst increases to 90% with the rise of O_2 content before 15% and then decreases dramatically. It illustrates that the operation window of oxygen concentration which is useful for oxidation reaction becomes much narrower after aging treatment.

2.5.2 NO_x Reduction reaction

The C_3H_8 conversions of reduction reaction ($NO_x+HC \rightarrow N_2+CO_2+H_2O$) over fresh and aged catalysts were tested in $C_3H_8/O_2/N_2$ atmosphere and displayed in Fig.5. The catalytic performance on reduction reaction is much poorer than that of oxidation reaction since the desorption of NO is much more difficult than C_3H_8 on palladium[28]. The conversion over fresh catalyst increases slowly from 38% to 65% with the temperature rises from 340 ℃ to 400 ℃. And the catalytic activity decreases sharply after the aging treatment, the conversion at 450 ℃ is only 35% which is lower than 50%.

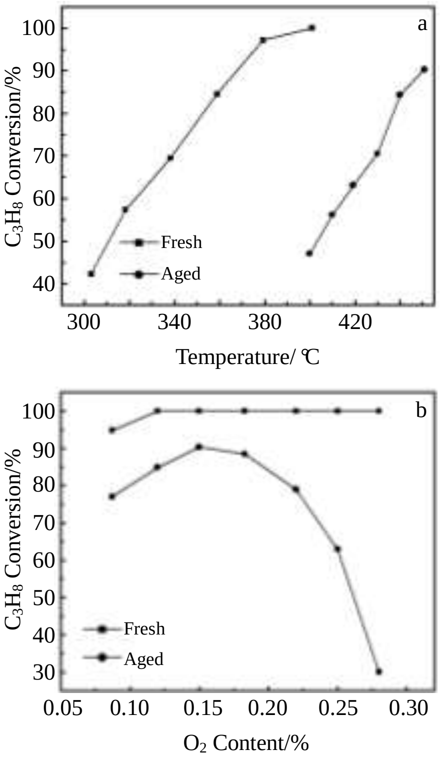

Fig.4 Conversions of C_3H_8 over fresh and aged catalysts: (a) C_3H_8 conversion of oxidation reaction at different temperatures and (b) conversion of C_3H_8 with different O_2 contents at 450 ℃

Table 2 T_{50} and T_{90} values for C_3H_8 conversion in various atmospheres over fresh and aged catalysts

Atmosphere	T_{50}/ ℃		ΔT_{50}/ ℃	T_{90}/ ℃		ΔT_{90}/ ℃
	Fresh	Aged		Fresh	Aged	
Total activity	280	356	76	315	379	64
HC/O_2	310	404	94	366	450	84
HC/NO	360	-	-	-	-	-
$HC/O_2/NO$	320	425	105	351	-	-
HC/H_2O	323	374	51	374	398	24
$HC/H_2O/O_2$	303	361	58	333	394	61
$HC/H_2O/NO$	307	376	69	358	409	51
$HC/H_2O/NO/O_2$	307	378	71	330	397	67

The strongly adsorption of NO and poorer activity of metallic Pd^0 may be the reasons for poor catalytic performance of reduction reaction.

2.5.3 Steam reforming (SR) reaction

The conversions of C_3H_8 ($HC+H_2O \rightarrow CO+H_2$) over fresh and aged catalysts in $C_3H_8/H_2O/N_2$ atmosphere are presented in Fig.6. As shown in Table 2, the conversion of C_3H_8 over both fresh and aged catalysts increases rapidly with the rise of temperature. The T_{50} and T_{90} of fresh catalyst are 323 ℃ and 374 ℃, respectively. And those of aged catalyst are 374 ℃ and 398 °C, respectively. The ΔT_{50} and ΔT_{90} are 51 ℃ and 24 ℃, respectively. It should be noted that the decline of catalytic activity over SR reaction is slighter than that of oxidation or reduction reaction, indicating that the SR reaction plays a more important role in total catalytic activity[29]. It is found that the support is the principal site for water activation and the metal sites are responsible for the activation of hydrocarbons in steam reforming reactions.

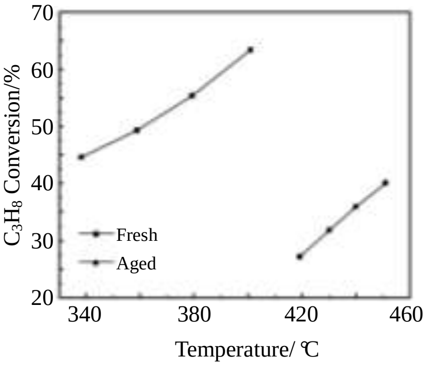

Fig.5 Variations of C_3H_8 conversion at different temperatures in C_3H_8/NO atmosphere over fresh and aged catalysts

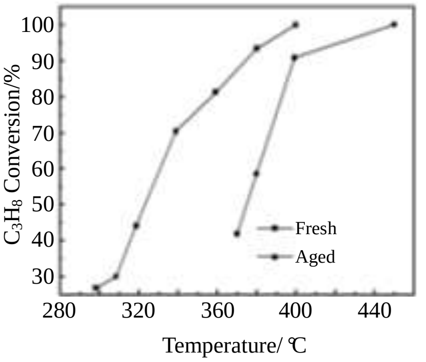

Fig.6 C_3H_8 conversion of steam reforming reaction at different temperatures over catalysts

2.6 Comparison of catalytic activity among single reactions

It can be seen that the performance of oxidation reaction is better than that of SR reaction over fresh catalyst, especially for low-temperature activity (ΔT_{50}=13 ℃). However, the performance of oxidation reaction is much poorer than that of SR reaction after aging treatment. And the activity in $HC/O_2/H_2O$ atmosphere is also much superior to that of oxidation reaction (ΔT_{50}=43 °C, ΔT_{90}=56 ℃).

For fresh catalyst, the property in $C_3H_8/NO/O_2$ atmosphere above 330 ℃ is better than that of oxidation reaction (ΔT_{90}=15 ℃), which may be due to the faster adsorption or desorption on enough active sites at high temperature. However, the property of aged catalyst in $C_3H_8/NO/O_2$

atmosphere is poorer than that of oxidation reaction, resulting from the fierce competition between O_2 and NO.

For fresh catalyst, the catalytic activity in HC/H_2O/NO atmosphere is superior to the performance of SR reaction (ΔT_{50}=16 °C, ΔT_{90}=16 ℃), resulting from the enough active sites for the coexistence of SR and reduction reaction. However, the catalytic activity in HC/H_2O/NO atmosphere is poorer than the performance of SR reaction (ΔT_{90}=11 ℃) due to the fierce competitive adsorption and/or desorption between C_3H_8 and NO after aging treatment.

For fresh catalyst, the oxidation reaction and SR reaction play a major role in total catalytic activity, and the coexistence of three single reactions promote the total property of fresh catalyst due to the existence of enough active sites, especially for the high temperature activity. After aging treatment, SR reaction plays an important role in total activity with the decline of active sites, and only the high temperature performance in HC/O_2/NO/H_2O atmosphere is a little better than that of the SR reaction (ΔT_{90}=1 ℃) due to the fierce competitive effect between oxidation reaction and reduction reaction. It is worth noting that the low-temperature catalytic activities over both fresh and aged catalysts in HC/O_2/NO/H_2O atmosphere are poorer than the performance of SR reaction and/or oxidation reaction, which is in good agreement with the changes in total activity.

3 Conclusions

1) The metallic Pd^0 which is negative for low-temperature activity appears during the aging treatment.

2) The low-temperature activity of oxidation reaction and reactions with the participation of NO decrease dramatically after the aging treatment, especially for the reactions occurring in atmosphere without H_2O injection.

3) Aging treatment makes the inhibition of NO for low-temperature activity and the positive effect on high temperature property is distinct.

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新鲜和老化 Pd/Al_2O_3 密偶催化剂上催化 C_3H_8 转化催化性能

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摘　要：采用等体积浸渍法制备了以改性氧化铝为载体材料的 Pd/Al_2O_3 密偶催化剂，并采用 H_2 程序升温还原(H_2-TPR)，CO 化学吸附和 X 射线光电子能谱(XPS)对催化剂进行了表征。在模拟尾气条件下对催化剂的总包反应及与 C_3H_8 相关的单反应活性进行了测试。结果表明，老化处理后活性 PdO_x 数量下降，并伴随有金属态 Pd^0 的产生。老化后，起燃温度(T_{50})和完全转化温度(T_{90})分别提高了 76 和 64 ℃，即催化剂低温活性比高温活性下降明显。对比新鲜和老化催化剂上单反应活性，结果表明，老化后无水条件下有 NO 参与的反应的低温活性下降显著。老化处理过程突出了 NO 对低温活性的抑制作用和 H_2O 对高温活性的促进作用。

关键词：密偶催化剂；钯；氧化铝；丙烷；低温活性

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