碱土金属对 $\text{ZrO}_2\text{-Al}_2\text{O}_3$ 及其负载 Pd-Rh 密偶催化剂的影响

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摘要: 采用胶溶法制备了一系列碱土金属改性的 $\text{ZrO}_2\text{-Al}_2\text{O}_3$, 并以其为载体采用等体积浸渍法制备了 Pd-Rh 密偶催化剂. 采用低温 N_2 吸附-脱附、X 射线衍射(XRD)、氨气程序升温脱附($\text{NH}_3\text{-TPD}$)对载体样品进行了表征. 结果表明, 碱土金属的添加增大了 $\text{ZrO}_2\text{-Al}_2\text{O}_3$ 的比表面积, Sr-Zr-Al 样品经 $1000\text{ }^\circ\text{C}$ 焙烧 5 h 后具有最大的比表面积, 为 $164\text{ m}^2\cdot\text{g}^{-1}$. 对催化剂进行了 H_2 程序升温还原($\text{H}_2\text{-TPR}$)、X 射线光电子能谱(XPS)和活性表征, 考察了催化剂对 C_3H_8 的转化活性. 测试结果表明, 添加碱土金属能有效提高催化剂上丙烷的转化活性.

关键词: 碱土金属; $\text{ZrO}_2\text{-Al}_2\text{O}_3$; Pd-Rh; 密偶催化剂; 丙烷

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Effects of Alkaline Earth Metal on Performance of $\text{ZrO}_2\text{-Al}_2\text{O}_3$ Support and Pd-Rh Close-Coupled Catalyst

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Abstract: A series of alumina supports stabilized by alkaline earth metals and zirconia were prepared by the peptizing method. Pd-Rh close-coupled catalysts supported on modified alumina were prepared by the impregnation method. The supports were characterized by low temperature nitrogen adsorption-desorption method, X-ray diffraction (XRD), and NH_3 -temperature programmed desorption ($\text{NH}_3\text{-TPD}$). For the catalysts, H_2 -temperature programmed reduction ($\text{H}_2\text{-TPR}$) and X-ray photoelectron spectroscopy (XPS) were carried out. We also carried out catalytic activity tests for C_3H_8 conversion. Results show that the addition of alkaline earth metals increases the surface area of the supports and the surface area of Sr-Zr-Al reaches $164\text{ m}^2\cdot\text{g}^{-1}$ after calcination at $1000\text{ }^\circ\text{C}$ for 5 h. The introduction of alkaline earth metals into the $\text{ZrO}_2\text{-Al}_2\text{O}_3$ supports also improves their catalytic activity toward propane oxidation and the activities of the Pd-Rh catalysts containing alkaline earth metals are higher than that of the catalyst prepared with a $\text{ZrO}_2\text{-Al}_2\text{O}_3$ support.

Key Words: Alkaline earth metal; $\text{ZrO}_2\text{-Al}_2\text{O}_3$; Pd-Rh; Close-coupled catalyst; Propane

1 Introduction

Automobile exhaust gas is one of the major sources of atmosphere pollution. Since 1970s, the automobile exhaust catalysts have been widely used to purify exhaust gas.^{1,2} Currently cata-

lysts that meet more stringent emission standards generally consist of two parts: three-way catalysts (TWCs) and close-coupled catalysts (CCCs). The CCC is mainly to remove the hydrocarbons (HCs) during the cold start, because the majority

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(more than 80%) of the HCs is released during the cold start.³ Moreover as the CCC is close to the engine, the catalyst support and active washcoat should be kept stable at high temperature when the engine works at high speed.

Researchers have tried many methods to improve catalytic activity, such as improving noble metal dispersion with high surface area supports, improving thermal stability of supports and so on.⁴ As well known, Al_2O_3 is widely used as catalyst support. Due to long time exposed to high temperature (sometimes even above 1000 °C) exhaust gas and the high humidity atmosphere, Al_2O_3 would gradually sinter and translate from γ -phase to α -phase and the surface area and thermal stability are all decreased. In order to stabilize Al_2O_3 , some stabilizers need to be added. Researches showed that introducing alkali metals, alkaline earth metals, and rare earth elements can increase the thermal stability and surface area of alumina.⁵⁻⁹ The alkaline earth metals which can stabilize Al_2O_3 are Ba^{2+} , Sr^{2+} , and Ca^{2+} .¹⁰ Ba^{2+} is the best. In addition, zirconia can stabilize alumina as well. Horiuchi *et al.*¹¹ have reported that the surface area of zirconia stabilized alumina, calcined at 1200 °C, kept at $50 \text{ m}^2 \cdot \text{g}^{-1}$. However, using the alkaline earth metals and zirconia co-stabilized Al_2O_3 as support for automotive exhaust catalyst in CCC has not been reported.

In this study, M-Zr-stabilized (M=Mg, Ca, Sr, Ba) Al_2O_3 were prepared by peptizing method, and used as support to prepare Pd-Rh close-coupled catalysts. The influence of alkaline earth metals on textural properties of ZrO_2 - Al_2O_3 was studied and catalytic activities of Pd-Rh close-coupled catalysts on C_3H_8 conversion were investigated.

2 Experimental

2.1 Modified alumina preparation

A series of alumina stabilized by alkaline earth metals and zirconia (AR) were prepared by peptizing method,¹² using boehmite as precursor and nitric acid as peptizer. The mass fraction (*w*) of alkaline earth metal was 4% and that of zirconia was 6%. The products were dried at 105 °C overnight and calcined at 600 °C for 3 h in muffle furnace. In order to compare their thermal stabilities, the samples were calcined at 1000 °C for 5 h. The products are referred as Zr-Al, Mg-Zr-Al, Ca-Zr-Al, Sr-Zr-Al, and Ba-Zr-Al.

2.2 Catalyst preparation

Catalysts were prepared by the impregnation method.¹³ Different supports calcined at 1000 °C were impregnated with the desired amounts of $\text{Pd}(\text{NO}_3)_2$ and $\text{Rh}(\text{NO}_3)_3$ aqueous solutions. And then some deionized water was added to the catalyst powders which were prepared above, the mixture was ground to form slurry. The resulting slurry was spread to a honeycomb cordierite (2.5 cm^3 , Corning, China), and then excessive slurry was blown away with compression air. Fresh catalysts were obtained by calcining at 550 °C for 3 h in muffle furnace, and the aged catalysts were obtained by calcining at 1000 °C for 5 h. The catalysts were denoted respectively as Pd-Rh/Zr-Al, Pd-Rh/

Mg-Zr-Al, Pd-Rh/Ca-Zr-Al, Pd-Rh/Sr-Zr-Al, and Pd-Rh/Ba-Zr-Al. The precious metal content was $2 \text{ g} \cdot \text{L}^{-1}$ ($n_{\text{Pd}}:n_{\text{Rh}}=19:1$).

2.3 Characterization of supports and catalysts

2.3.1 Support characterization

The BET specific surface area and pore volume measurement were performed on a ZXF-5 automatic surface analyzer (Xibei Chemical Institute, China). The BET specific surface areas and pore volumes of samples were determined by using a N_2 adsorption technique at liquid nitrogen temperature. In order to desorb surface impurities, samples were degassed at 350 °C for 1 h before the measurement.

The crystal structures of the samples were determined by a powder X-ray diffraction (XRD) (Rigaku International Corp., Japan) on a D/MaX-rA rotary diffractometer using $\text{Cu } K_\alpha$ radiation ($\lambda=0.154 \text{ nm}$) and operated at 40 kV and 25 mA. The XRD data were tested for 2θ values between 10° and 90° with a rate of $0.03 (^\circ) \cdot \text{s}^{-1}$. The crystalline phases were compared with the reference data from the International Center for Diffraction Data (ICDD). The particle size calculations were performed using peak-broadening analysis.

The NH_3 -TPD experiments were performed for supports. The sample (80 mg) was pretreated in a flow of Ar ($30 \text{ mL} \cdot \text{min}^{-1}$) at a temperature ranging from room temperature to 400 °C and was maintained at 400 °C for 60 min. Then samples adsorbed NH_3 at the flow of $20 \text{ mL} \cdot \text{min}^{-1}$ for 60 min after they were cooled to room temperature. Excessive NH_3 was blown off in Ar ($30 \text{ mL} \cdot \text{min}^{-1}$). At last the temperature of the sample was increased to 500 °C at the rate of $8 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$, NH_3 was measured by a thermal conductivity detector (TCD).

2.3.2 Catalyst characterization

The CCC catalytic activity was evaluated in a multiple fixed-bed continuum flow micro-reactor by passing a gas mixture from a gasoline engine, which was similar to that of an exhaust from a gasoline engine. Before entering a blender, the gases were regulated using mass-flow controllers. The simulated exhaust contained a mixture of O_2 (adjustable), CO (0.86%), C_3H_8 (0.06%), NO (0.12%), CO_2 (12%), H_2O (10%), and N_2 (remaining). The gas space velocity was 34000 h^{-1} . The concentration of C_3H_8 was analyzed by a five-component analyzer (FGA-4100, Foshan) before and after the stimulated gas passed the micro-reactor.

The H_2 -TPR tests were performed for catalysts and detected by TCD-GC (gas chromatography). Each catalyst (100 mg) was put into a U-type quartz reaction tube and covered with quartz sand. After being preheated in N_2 atmosphere at 400 °C for 60 min, it was cooled to room temperature, and then subjected to a flow of mixed gases of 5% H_2 -95% N_2 at the rate of $30 \text{ mL} \cdot \text{min}^{-1}$. The temperature of the sample was increased to 600 °C at the rate of $8 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$.

The X-ray photoelectron spectroscopy (XPS) experiments were carried out on a spectrometer (XSAM-800, KRATOS Co) with $\text{Mg } K_\alpha$ radiation under ultra-high vacuum condition. All samples were pretreated in a stream of 5% H_2 -95% N_2 at 400 °C

for 60 min, and cooled to room temperature. The binding energy was determined by reference to the C 1s binding energy of 284.8 eV.

3 Results and discussion

3.1 Textural properties of supports

The textural properties of alkaline earth modified zirconia-alumina after being calcined at 1000 °C for 5 h are shown in Table 1. It can be seen from Table 1 that the addition of alkaline earth metals increases the surface area of alumina samples. The surface area can even reach 164 m²·g⁻¹ when Sr is added. The surface area of Ba-Zr-Al is almost the same as that of Sr-Zr-Al, only the pore volume is a little smaller, 0.45 cm³·g⁻¹. It is to say that the addition of alkaline earth metal plays an important role in stabilizing alumina, especially Sr and Ba. The ionic radii of the alkaline earth metals increase in turn from Mg to Ba (0.065, 0.099, 0.113, and 0.135 nm, respectively). In a certain amount range, the introduction of doped ions in alumina can prevent the migration of O²⁻ ions and Al³⁺ ions thus stabilize alumina at high temperature. And the larger the ionic radius is, the better the stability effect is. So the surface areas of the samples from Mg to Ba increase in turn. However, introducing alkaline earth metals into Zr-Al has little influence on their pore volumes.

3.2 XRD analysis

The powder XRD patterns of the alumina samples are shown in Fig.1. The 2θ angles of 37.5°, 45.5°, and 67.2° display the diffraction peaks of γ-Al₂O₃. The 2θ angles of 25.5°, 43.4°, and 57.5° show the diffraction peaks of α-Al₂O₃. And the diffraction peaks of ZrO₂ appear in the 2θ angles of 30.2°, 35.2°, 50.3°, 60.2°, and 81.8°. Zr-Al samples mainly display

Fig.1 X-ray diffraction patterns of alkaline earth metal modified zirconia-alumina after calcination at 1000 °C for 5 h

γ-Al₂O₃ and small amount of α-Al₂O₃ and ZrO₂. It demonstrates that the Al₂O₃ and ZrO₂ did not fully form to solid solution, but separate into two phases. ZrO₂ plays a role in stabilizing Al₂O₃, which is mainly due to the fact that ZrO₂ grains disperse in the surface of Al₂O₃ grains, and they prevent particle agglomeration rather than forming solid solution to stabilize the alumina.¹¹ After the introduction of alkaline earth metals, none of the diffraction peaks is observed in the XRD patterns of all samples. And this is mainly owe to two reasons, one is that alkaline earth metal oxide grains are too small and scatter better, and can not show a diffraction peak. The other is that the alkaline earth metal ions enter into the alumina grains or the zirconia grains to form alumina or zirconia solid solution. No matter what form they consist, these two factors can all stabilize alumina. They can prevent particle agglomeration sintering and the migration of Al³⁺ ions. So the alumina with a high surface area and pore volume can be maintained at high temperature with the addition of them. It is consistent with the BET results.

Fig.2 shows the X-ray diffraction patterns of alkaline earth metal modified zirconia-alumina after calcination at 1000 °C for 5 h. As shown in Fig.2(a), the peak at 2θ angle of 30.2° is the diffraction peak of zirconia(111). The diffraction peak intensity decreases and peak width increases after the introduction of the alkaline earth metal, but there is no obvious shift. Results indicate that ZrO₂ grains become smaller with the addition of alkaline earth metals, and the alkaline earth metal ions do not enter into the lattice of zirconia.

Table 1 Textural properties of alkaline earth metal modified zirconia-alumina after calcination at 1000 °C for 5 h

Sample	$S_{\text{BET}}/(\text{m}^2 \cdot \text{g}^{-1})$	$V_p/(\text{cm}^3 \cdot \text{g}^{-1})$
Al ₂ O ₃	126	0.28
Zr-Al	145	0.44
Mg-Zr-Al	148	0.44
Ca-Zr-Al	157	0.46
Sr-Zr-Al	164	0.46
Ba-Zr-Al	163	0.45

Fig.2 Powder X-ray diffraction patterns of alkaline earth metal modified zirconia-alumina after calcination at 1000 °C for 5 h
2θ: (a) 25°–35°, (b) 60°–70°

As seen from Fig.2(b), the peak at the 2θ angle of 67.2° is the diffraction peak of $\gamma\text{-Al}_2\text{O}_3(440)$. And the peak shows an apparent shift to small angle when the alkaline earth metal is introduced. Especially, the $\gamma\text{-Al}_2\text{O}_3$ diffraction peak of Mg-Zr-Al offset relatively larger, the 2θ angle deviates nearly 0.5° ; besides, the other three samples also have a different degree of deviation. It indicates that the alkaline earth metal ions have entered the lattice of alumina and changed lattice parameters. The ion radii of alkaline earth metals are larger than that of aluminum, as a result, the lattice of alumina will be expand, and the peak moves forward to smaller diffraction angle. The ion radius of Mg and Al is similar to each other. It is easy to form solid solution. So the Mg-Zr-Al has the maximum diffraction angle deviation.

3.3 NH_3 -TPD analysis

Fig.3 shows the NH_3 -TPD of the alumina samples calcined at 1000°C for 5 h. The desorption peak of the Zr-Al samples not only has the most wide temperature range from 130 to 450°C , but also has the largest peak area. When alkaline earth metal is introduced, both the peak temperature and the peak area all decrease from Mg to Ba, and their highest peak temperatures are 180 , 175 , 149 , and 147°C , respectively. Looking at the peak from another view, the desorption peak is asymmetric. It indicates that the desorption peak is formed by two overlapping peaks, while both the Sr-Zr-Al and Ba-Zr-Al show two separate peaks. All of these indicate that the surface of alumina samples have two acidic sites. One is a weak acid place; another is a middle strong acid site.

Alkaline earth metal oxides are basic compounds, and the alkaline increases gradually with the atomic number increasing. In addition, the surface acid sites of alumina are mainly determined by the number of hydroxyl groups on the surface of aluminum and the aluminum atoms, the more hydroxyl groups and aluminum atoms, the more H^+ and empty electron orbital. Besides, the surface acidity of alumina will be enhanced with the acidic oxide ZrO_2 accession. The addition of alkaline earth metal oxides will first neutralize some strong and middle strong acid sites on the surface, and then neutralize the weak acid sites, resulting in a decline in the surface acidity. What is

Fig.3 NH_3 -temperature programmed desorption profiles of alkaline earth metal modified zirconia-alumina after calcination at 1000°C for 5 h

more, with the atomic number of alkaline additive enhancing the middle strong acid sites of alumina decrease, and the weak acid peak shifts to low temperature range.

3.4 Catalytic performance

The close-coupled catalytic performances for the C_3H_8 oxidation are shown in Fig.4 and Fig.5. The catalytic properties of the C_3H_8 conversion temperature are presented in Table 2. The order of the fresh catalytic activity is $\text{Pd-Rh/Ba-Zr-Al} > \text{Pd-Rh/Sr-Zr-Al} > \text{Pd-Rh/Ca-Zr-Al} > \text{Pd-Rh/Mg-Zr-Al} > \text{Pd-Rh/Zr-Al}$. It indicates that the catalytic activity will increase with the addition of alkaline earth metal. Obviously, the complete conversion temperature (T_{90}) of catalysts with alkaline earth element is nearly 20°C lower than that of the Pd-Rh/Zr-Al catalyst. And the corresponding light-off temperature (T_{50}) and T_{90} of the Pd-Rh/M-Zr-Al catalysts were around 275 and 313°C , respectively; the ΔT ($\Delta T = T_{90} - T_{50}$) is nearly 35°C . The activity increases rapidly with the temperature increasing and it can quickly reach conversion of the C_3H_8 . That is, the Pd-Rh/M-Zr-Al catalysts have excellent temperature characteristics. It can also conclude from Fig.5 that the Pd-Rh/M-Zr-Al catalysts have better activity than the Pd-Rh/Zr-Al catalyst after they are all aged. Unfortunately, the temperature characteristics of aged catalysts declined a little with respect to the fresh catalysts. The catalysts were prepared with the same conditions except for the use of different supports. It is obviously that the supports led to the difference in activity.

The catalysts with the addition of alkaline earth metal have higher activity and thermal stability than the Pd-Rh/Zr-Al catalyst. The reasons are as follows: (1) the textural property

Fig.4 Conversion of C_3H_8 on fresh catalysts

Fig.5 Conversion of C_3H_8 on aged catalysts

Table 2 T_{50} and T_{90} for the conversion of C₃H₈ on different catalysts

Catalyst	Fresh			Aged		
	$T_{50}/^{\circ}\text{C}$	$T_{90}/^{\circ}\text{C}$	$\Delta T/^{\circ}\text{C}$	$T_{50}/^{\circ}\text{C}$	$T_{90}/^{\circ}\text{C}$	$\Delta T/^{\circ}\text{C}$
Pd-Rh/Zr-Al	284	327	43	357	394	37
Pd-Rh/Mg-Zr-Al	278	316	38	328	371	43
Pd-Rh/Ca-Zr-Al	279	314	35	332	381	49
Pd-Rh/Sr-Zr-Al	276	312	36	344	382	38
Pd-Rh/Ba-Zr-Al	274	310	36	335	380	45

plays an important role in the performance of catalyst, and the large surface area and pore volume are in favor for the better dispersion of noble metal, in addition, they are also in favor for mass and heat transfer. According to the textural property results, the Zr-Al with the alkaline earth metal has larger surface area, pore volume and better thermal stability than pure Zr-Al support after calcination at 1000 °C. (2) The alkaline earth metal changes the support surface acid centers, resulting in a decline in the surface acidity and an increase in the basicity, thus, affecting the distribution of Pd, Rh active component. And the TPR results in the following text show that the introduction of alkaline earth metal increases the distribution of Pd, Rh, so that the number of catalyst active sites and catalytic activity increase.

Although the support alumina is calcined at the high temperature of 1000 °C, the catalytic activity declined a little after being aged at 1000 °C. Aging progress led to accumulating and sintering of precious metal. The introduction of Rh is easy to generate RhAlO₃.^{14,15} These results would give rise to the decline of the dispersion of precious metals. Therefore, the effective area of active component contacting with reactant molecules is reduced. As a result, the activity declines.

3.5 H₂-TPR analysis

The reducibility of support Pd-Rh catalyst plays an important role in its catalytic property. It is generally acknowledged that the reduction temperature of precious metals is lower and the reduction peak area is larger (peak area corresponding to the adsorbed hydrogen consumption; and when the peak area is larger, the adsorbed hydrogen is more), thus the catalysts have better activity for catalytic reaction.¹³

Fig.6 TPR profiles of the catalysts calcined at 550 °C

(a) Pd-Rh/Zr-Al, (b) Pd-Rh/Mg-Zr-Al, (c) Pd-Rh/Ca-Zr-Al, (d) Pd-Rh/Sr-Zr-Al, (e) Pd-Rh/Ba-Zr-Al

For α peak of catalysts, it is commonly attributed to reduction of PdO due to the interaction of Pd and ZrO₂.^{16,17} It can be seen from Fig.6 that the addition of alkaline earth metals makes the α peak shift to lower temperature, indicating that the addition of alkaline earths increases the reducibility of PdO species, and the peak area is larger than that in Pd-Rh/Zr-Al catalyst, that is, the amount of active component distribution in Pd-Rh/M-Zr-Al catalyst is larger than that of Pd-Rh/Zr-Al catalyst. So the Pd-Rh/M-Zr-Al catalyst has better catalytic activity than Pd-Rh/Zr-Al catalyst. In addition, the peak temperature decreases and peak area increases all from Mg to Ba in turn, that is, the order of Pd-Rh/M-Zr-Al catalytic activity is Pd-Rh/Ba-Zr-Al>Pd-Rh/Sr-Zr-Al>Pd-Rh/Ca-Zr-Al>Pd-Rh/Mg-Zr-Al. For the β peak, the reduction temperature of Rh of all the catalysts is almost at the same temperature of 301 °C. But the peak area increases with the addition of alkaline earths.

On the basis of the above results, the reduction temperature and peak area of the precious species in the catalysts decreases in the following order: Pd-Rh/Ba-Zr-Al>Pd-Rh/Sr-Zr-Al>Pd-Rh/Ca-Zr-Al>Pd-Rh/Mg-Zr-Al>Pd-Rh/Zr-Al. This order is also in accordance with that of their catalytic activity.

3.6 XPS analysis

In order to investigate the changes in the chemical states of Pd ions and Rh ions, the fresh catalysts were studied by XPS. Fig.7 presents the Pd 3d photoelectron peaks of the catalysts. No Rh peaks are detected on the catalyst surface due to its low content.

We got the values of Pd 3d_{5/2} level in an attempt to identify the chemical state of Pd. By comparing to the reference¹⁸ where the Pd 3d binding energies have been measured both for metallic Pd, PdO, PdO₂, and Pd_xO (x>1), the binding energy is about 336.2 eV for the impregnation catalyst.¹⁹ It can be seen from Fig.7 that, on one hand, the Pd has different binding energies in different catalysts. That is, Pd has different oxidation states. The Pd 3d_{5/2} has the highest oxidation state in Pd-Rh/Zr-Al catalyst among all the catalysts, its Pd 3d_{5/2} is 336.60 eV which is assigned to PdO (336.6 eV).²⁰ The Pd 3d_{5/2} of the remaining four catalysts are 336.39, 336.40, 336.35, and 336.30 eV, which are between Pd⁰ (335.0 eV)²¹ and PdO (336.6 eV)

Fig.7 XPS profiles of Pd 3d of the catalysts calcined at 550 °C

(a) Pd-Rh/Zr-Al, (b) Pd-Rh/Mg-Zr-Al, (c) Pd-Rh/Ca-Zr-Al, (d) Pd-Rh/Sr-Zr-Al, (e) Pd-Rh/Ba-Zr-Al

and are more near to PdO. It indicates that the Pd is at lower oxidation states in those catalysts which include alkaline earth metal. As we all know, the lower the Pd binding energy, the higher the catalytic properties,²² so the activity of the Pd-Rh catalyst with alkaline earth metal is higher than that of Pd-Rh/Zr-Al catalyst. This is also consistent with catalytic activity test results. On the other hand, there is a decrease in the Pd 3d intensity of Pd-Rh/Zr-Al catalyst in comparison to the other four catalysts. It may be accounted for the possible PdO diffusion to the washcoat, sintering of Pd particles, and the structural changes in Al₂O₃ support.

4 Conclusions

Addition of alkaline earth metal plays an important role in stabilizing ZrO₂-Al₂O₃. The surface area of support containing Sr or Ba reaches 160 m² · g⁻¹ after being calcined at 1000 °C. XRD results indicate that the alkaline earth metal ions have entered into the lattice of alumina. They prevent the migration and diffusion of O²⁻ ions and Al³⁺ ions, so the γ phase of alumina is maintained. In addition, the Pd-Rh close-coupled catalysts doping with alkaline earth metal have better catalytic activity than the catalyst prepared with ZrO₂-Al₂O₃ as a support.

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