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Article

A highly efficient Rh-modified Pd/Al₂O₃ close-coupled catalyst

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ABSTRACT

The close-coupled catalysts Pd/Al₂O₃ and Rh-Pd/Al₂O₃ were prepared by the impregnation method and characterized by H₂ temperature-programmed reduction, CO chemisorption, and X-ray photoelectron spectroscopy. Both overall catalytic activity and specific reactions associated with C₃H₈ elimination were assessed. The light-off temperature and complete conversion temperature decreased by 23 and 18 °C, respectively, upon addition of Rh to the Pd/Al₂O₃ catalyst. The addition of Rh promotes the catalytic activity during C₃H₈ reactions, particularly in the presence of NO. The introduction of Rh not only inhibits sintering of PdO_x and increases the dispersion of these same species, but also changes the electronic state of the PdO_x in the catalyst.

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1. Introduction

Automobile exhaust gas has been a major source of environmental pollutions over the last several decades. Hydrocarbons (HCs), CO, and nitrogen oxides (NO_x) are the three major toxic components of vehicle exhaust emissions. In recent years, there has been significant research directed towards the purification of exhaust gases [1–3], typically based on the use of catalysts [4,5]. To meet emission standards that are becoming increasingly stringent, two kinds of catalysts are usually installed in the engine exhaust system [6]. One is the

close-coupled catalyst (CCC) used to eliminate the majority of hydrocarbon emissions (60%–80% of the total emitted) during cold starts [4]. To ensure that this unit quickly achieves the appropriate light-off temperature (*T*₅₀), the CCC is often installed close to the engine [7]. The other is the three-way catalyst (TWC), typically installed behind the CCC and used to simultaneously eliminate all three primary toxic emissions [8].

Because the CCC is installed very close to the engine, which can operate over 1050 °C, the catalyst must exhibit good thermal stability over prolonged exposure to high temperatures while still maintaining excellent low-temperature activity [7].

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Therefore, the ideal support material for a CCC should show not only good hydrocarbon purification efficiency but also superior anti-aging performance. Al_2O_3 is regarded as a promising candidate for anti-aging supports and has been widely used as such in CCC units [9,10]. However, at above 1000 °C, pure Al_2O_3 will gradually sinter and transition from a γ -phase to an α -phase, resulting in severe agglomeration of the active components. Modification of Al_2O_3 by one or more stabilizers is considered to be a viable means of suppressing this phase transition, and introducing alkali metals, alkaline earth metals, or rare earth elements has been shown to improve the thermal stability and surface area of Al_2O_3 [11–14]. In the present study, La was applied as the stabilizer in an Al_2O_3 support. Palladium is often used in CCC as the active component due to its superior activity for the oxidation of HCs [5,15]. Moreover, Pd currently also has lower price among the precious metals. PdO_x species exhibit considerably higher activity for the purification of C_3H_8 compared to metallic Pd, even in the form of large particles formed by sintering at high temperatures [16,17]. However, pure PdO_x decomposes into metallic Pd particles above 750 °C, even in oxygen-containing atmospheres, which can greatly lower the catalytic efficiency [18]. As a result, it is necessary to find techniques to either maintain or increase the decomposition temperature of PdO_x . One approach is to alter the support materials; according to Farrauto et al. [19], adding TiO_2 or CeO_2 to the support material can increase the decomposition temperature of PdO_x by about 130 °C. Another approach is more direct and involves synthesizing bimetallic catalysts by introducing other noble metals such as Pt and Rh. For example, the introduction of Pt increases catalytic activity and prevents deactivation of the catalyst [20,21]. Rassoul et al. [18] reported that the addition of Rh to form a $\text{Pd}_{0.75}\text{Rh}_{0.25}/\text{Al}_2\text{O}_3$ catalyst by stepwise impregnation can increase the temperature at which the PdO_x species are stable by ~230 °C, and demonstrated strong interactions between RhO_x and PdO_x on the surface of the catalyst based on temperature-programmed reduction (TPR) measurements. The addition of Rh to a Pd-based catalyst may also improve the activity of Pd during methane combustion due to the increased pore diffusion resistance at higher temperatures, while the effect of Rh-doping is most significant below 400 °C [21]. Due to its superior NO_x reduction activity, Rh is widely used in CCCs and TWCs. However, there is no evidence in the literature of the additive effect of Rh on the catalytic activity of a Pd-based CCC meant primarily for the removal of C_3H_8 , or on the specific reactions of C_3H_8 over a CCC.

We study the effects of introducing Rh into a $\text{Pd}/\text{Al}_2\text{O}_3$ CCC intended for the elimination of C_3H_8 . To investigate the influence of Rh on the overall activity of the Pd catalyst, single reactions associated with the conversion of C_3H_8 were also studied.

2. Experimental

2.1. Catalyst preparation

La-stabilized Al_2O_3 was prepared by the peptizing method, dried at 105 °C overnight, and then calcined at 600 °C for 3 h in a muffle furnace. After calcination at 1000 °C for 5 h, the Al_2O_3

had a surface area of 138 m^2/g and a pore volume of 0.47 mL/g .

The close-coupled catalysts $\text{Pd}/\text{Al}_2\text{O}_3$ and bimetallic $\text{Rh-Pd}/\text{Al}_2\text{O}_3$ were prepared by the impregnation method, employing $\text{Pd}(\text{NO}_3)_2$ and RhCl_3 in the aqueous precursor solutions. The Pd and Rh contents of the finished products were 2.5 and 0.12 g/L, respectively. Deionized water was added to these materials to form homogeneous slurries, and the resulting slurry was spread over honeycomb cordierite (2.5 cm^3 , Corning, China). Excess slurry was blown off using compressed air. These materials were dried at 120 °C and calcined at 1000 °C for 5 h in a muffle furnace, generating the final monolithic catalysts.

2.2. Catalyst characterization

The textural properties of the support materials were assessed using a Quantachrome SI instrument. To remove surface impurities, the samples were first degassed under vacuum at 300 °C for 3 h prior to the measurements.

The overall activity for C_3H_8 and the individual reactions of C_3H_8 were evaluated in a multiple fixed-bed continuum flow micro-reactor, by passing a gas mixture similar to gasoline engine exhaust through the reactor. These gases were regulated with mass flow controllers before entering a blender. The simulated exhaust gas used to assess C_3H_8 activity contained 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 isolated reactions of interest consisted of direct oxidation, reduction, and steam reforming of C_3H_8 . The C_3H_8 concentration was analyzed online by a five-component analyzer (FGA-4100, Foshan Analytical Instrument Co., Ltd., China) before and after the simulated gas was passed through the micro-reactor.

H_2 -TPR measurements were performed in a quartz tubular micro-reactor. Each sample (100 mg, 40–60 mesh) was pre-treated in N_2 (20 mL/min) from room temperature to 400 °C, maintained at this temperature for 60 min, and then cooled to room temperature under N_2 (20 mL/min). The reduction was carried out under a flow of a 5% H_2 –95% N_2 (v/v) gas mixture (20 mL/min) between room temperature and 900 °C at a heating rate of 8 °C/min. The consumption of H_2 was assessed by thermal conductivity detector (TCD).

X-ray photoelectron spectroscopy (XPS) data were obtained using a spectrometer (XSAM-800, Kratos Co) with Mg K_α radiation under ultra-high vacuum. XPS measurements were conducted with a resolution of 0.9 eV and a step size of 0.05 eV. The X-ray source was powered at 13 kV and 20 mA. The electron binding energy was referenced to the C 1s line of adventitious carbon at 284.8 eV to correct for the effects of charging on the XPS spectra.

The degree of Pd dispersion was determined by CO chemisorption measurements. In these tests, catalyst samples of approximately 200 mg were placed in a U-shaped quartz tube, reduced under H_2 (20 mL/min) at 500 °C for 60 min, and then purged with pure He (30 mL/min). After cooling to room temperature, pulses of CO were passed through the tube, and the level of adsorption was assessed by TCD.

3. Results and discussion

3.1. Total catalytic activity for C_3H_8

Figure 1 shows the total catalytic activity for the simulated C_3H_8 -based exhaust gas over both the Pd/Al_2O_3 and $Rh-Pd/Al_2O_3$ catalysts. The C_3H_8 conversions over both catalysts increased with increasing temperature, and complete conversion was rapidly achieved. The T_{50} obtained with Pd/Al_2O_3 and $Rh-Pd/Al_2O_3$ were 356 and 333 °C, respectively, meaning that T_{50} decreased by 23 °C when Rh was included in the catalyst. A lower T_{50} indicates superior low-temperature activity of the catalyst [22]. The complete conversion temperature (T_{90}) for the $Rh-Pd/Al_2O_3$ catalyst was 361 °C, while that of Pd/Al_2O_3 catalyst was 379 °C. In contrast, the C_3H_8 conversion over the Rh-treated catalyst was already 100% at 380 °C. In summary, the addition of Rh as a promoter to the Pd-based catalyst had a positive effect on the catalytic performance, especially with regard to the low-temperature activity. This improvement may be attributed to the ability of Rh to facilitate the start-up process [21].

3.2. TPR results

The reducibility of a catalyst plays an important role in its catalytic activity. A lower reduction temperature as well as a larger area of the active component reduction peaks are associated with improved catalytic activity because these peak areas correspond to the adsorbed hydrogen consumption and thus increased areas indicate a greater amount of adsorption [23]. The TPR profiles of the Pd/Al_2O_3 and $Rh-Pd/Al_2O_3$ catalysts are shown in Fig. 2. Due to the low levels of RhO_x species in the $Rh-Pd/Al_2O_3$ catalyst, no peaks associated with the reduction of RhO_x species, expected in the vicinity of 180 °C [18], are observed. The negative α peak at about 68 °C seen solely in the profile of the Pd-only catalyst corresponds to the decomposition of palladium hydrides [7,24]. Metallic Pd can dissociate H_2 molecules into H atoms that subsequently generate large crystallites of palladium hydrides at room temperature, although this effect is greatly suppressed if the Pd is highly dispersed [25]. These results indicate that, compared with the

Fig. 2. TPR profiles of Pd/Al_2O_3 and $Rh-Pd/Al_2O_3$ catalysts.

$Rh-Pd/Al_2O_3$ catalyst, the Pd/Al_2O_3 contained a greater amount of metallic Pd, which has much lower activity for C_3H_8 conversion than PdO_x . The β peak is attributed to the reduction of highly dispersed PdO_x species, while the χ peak is ascribed to the reduction of stable PdO_x species having strong interactions with the support [26]. No χ peak is evident in the profile of the Pd/Al_2O_3 catalyst, while a χ peak appears at approximately 90 °C in the Rh-treated catalyst, indicating that the introduction of Rh promoted interactions between the active components and the support. Other researchers have suggested that one effect of Rh doping may be the stabilization of Pd in an oxidized form, and that the re-oxidation of Pd to PdO_x species may also be accelerated due to Rh doping [21]. The reduction temperatures of the β peaks in the Pd/Al_2O_3 and $Rh-Pd/Al_2O_3$ profiles are 85 and 79 °C, respectively. From Fig. 2 the peak area of the $Rh-Pd/Al_2O_3$ catalyst is larger than that of the Pd/Al_2O_3 catalyst, meaning that the addition of Rh into the Pd/Al_2O_3 catalyst both increased the amount of PdO_x and inhibited the sintering of PdO_x species, both of which favor improved catalytic activity.

3.3. XPS results

Figure 3 presents the Pd 3d photoelectron peaks of the catalysts. No Rh peaks are seen on the surface of the Rh-treated catalyst due to the low concentration of Rh added. It has been reported that the binding energies of metallic Pd^0 and PdO are

Fig. 1. C_3H_8 conversion at varying temperatures over Pd/Al_2O_3 and $Rh-Pd/Al_2O_3$ catalysts.

Fig. 3. Pd 3d XPS spectra of Pd/Al_2O_3 and $Rh-Pd/Al_2O_3$ catalysts.

335.2 and 336.8 eV [27], respectively, and it is evident that the binding energies of the Pd 3d_{5/2} electrons of all the catalysts fall between 335.2 and 336.8 eV. This result indicates that the Pd species in these catalysts were in a partially oxidized state, Pd^{δ+} (0 < δ < 2), that was more active than metallic Pd [28]. Compared with the Pd-only catalyst, the Pd 3d_{5/2} binding energy of the Rh-treated catalyst is shifted to a higher value, likely due to the electronic effect of Rh, leading to the transferring of electrons from PdO_x to RhO_x. Various additives may be used to modify the active phase by changing the oxidation state and by modifying the electronic environment of the active components [29]. Considering the observed changes in the total catalytic activity, the higher oxidation state of the active PdO_x species may be one of the reasons for the superior activity of the Rh-treated catalyst.

3.4. CO chemisorption

The dispersion of active metal components is an important factor affecting catalytic activity, and the dispersions of active PdO_x in the Pd/Al₂O₃ and Rh-Pd/Al₂O₃ catalysts were determined by CO chemisorption. The average Pd particle size, *d* (nm), was approximated by 1.1/*D* [30], where *D* (%) is the dispersion of Pd. The active Pd surface area, *S* (m²/g), was found using the formula $V_0 N \delta / 22.4 w p$, where *V*₀ is the consumption of CO (L), *N* is Avogadro's constant (6.023 × 10²³), δ is the atomic cross section of Pd (0.06 nm²) [31], *w* (g) is the mass of catalyst, and *p* (%) is the mass fraction of Pd.

The results, listed in Table 1, show that the Rh-Pd/Al₂O₃ catalyst exhibited higher Pd dispersion and a larger Pd active surface area compared with the Pd-only catalyst, and that the active Pd particle size in Rh-Pd/Al₂O₃ was smaller than that in the Pd/Al₂O₃ catalyst. Higher dispersion and smaller active component particle size both produce a higher active surface area, and thus improve the activity of the catalyst. The measured extents of Pd dispersion are in good agreement with the catalytic activity, and the lower dispersion of Pd in the Pd-only catalyst is one reason for its poor activity in this study. These data indicate that the addition of Rh to the Pd/Al₂O₃ catalyst increased the stability and dispersion of PdO_x species.

3.5. Direct oxidation reaction of C₃H₈

To fully investigate the effects of Rh on the overall catalytic activity of the Pd catalyst, specific reactions of C₃H₈ were assessed and compared at different temperatures. The main single reactions relevant to the elimination of HCs over a CCC consist of direct oxidation (HC + O₂ → CO₂ + H₂O), reduction (NO_x + HC → N₂ + CO₂ + H₂O), and steam reforming (SR, HC + H₂O → CO + H₂). The oxidation reaction of C₃H₈ was studied in a simu-

lated exhaust gas consisting of a mixture of O₂ (adjustable), C₃H₈ (0.06%), and N₂ (balance).

Figure 4 shows the extent of C₃H₈ conversion by direct oxidation over the two catalysts, as well as the C₃H₈ conversion achieved upon the injection of NO and/or H₂O. The concurrent changes in *T*₅₀ and *T*₉₀ are summarized in Table 2. C₃H₈ conversion by direct oxidation did not increase as rapidly as the overall reaction with increasing temperature: the Δ*T* values (Δ*T* = *T*₉₀ – *T*₅₀) obtained for the Pd/Al₂O₃ and Rh-Pd/Al₂O₃ catalysts were 46 and 48 °C, respectively. Shinjoh et al. [32] suggested that either C₃H₈ or intermediate species (such as partial oxidation products) strongly adsorbed on the catalyst surface can result in self-inhibition by limiting the adsorption of oxygen. However, the Rh-Pd/Al₂O₃ catalyst still presented better activity than the Pd/Al₂O₃. The *T*₅₀ of the Pd/Al₂O₃ and Rh-Pd/Al₂O₃ catalysts were 404 and 385 °C, respectively, indicating the superior low-temperature activity of the Rh-treated catalyst. The *T*₉₀ of the Pd/Al₂O₃ and Rh-Pd/Al₂O₃ catalysts were 450 and 433 °C, respectively. In addition, the conversion of C₃H₈ over the Rh-treated catalyst was already 100% at 450 °C, while at 450 °C the Pd/Al₂O₃ catalyst was only 90%. With regard to the oxidation reaction, therefore, the Rh-Pd/Al₂O₃ catalyst presented superior catalytic activity and low-temperature properties compared to the Pd/Al₂O₃ catalyst, because the addition of Rh increased the oxidation state of the PdO_x species and/or accelerated the re-oxidation of Pd to PdO_x [21], both of which are helpful to the adsorption of O₂.

To investigate the effect of NO on the direct oxidation reaction of C₃H₈, conversions were assessed in a C₃H₈/O₂/NO/N₂

Fig. 4. C₃H₈ conversion by direct oxidation at varying temperatures and in response to the addition of NO and/or H₂O to a C₃H₈/O₂/N₂ atmosphere over Pd/Al₂O₃ (a) and Rh-Pd/Al₂O₃ (b) catalysts.

Table 1

CO chemisorption data for Pd/Al₂O₃ and Rh-Pd/Al₂O₃ catalysts.

Catalyst	Pd dispersion (%)	Pd particle size (nm)	Pd active surface area (m ² /g)
Pd/Al ₂ O ₃	4.5	24.9	15.2
Rh-Pd/Al ₂ O ₃	5.4	20.7	18.3

Table 2 T_{50} and T_{90} values for C_3H_8 conversion in various atmospheres over Pd/Al₂O₃ and Rh-Pd/Al₂O₃ catalysts.

Atmosphere	$T_{50}/^{\circ}\text{C}$		$\Delta T_{50}/^{\circ}\text{C}$	$T_{90}/^{\circ}\text{C}$		$\Delta T_{90}/^{\circ}\text{C}$
	Pd/Al ₂ O ₃	Rh-Pd/Al ₂ O ₃		Pd/Al ₂ O ₃	Rh-Pd/Al ₂ O ₃	
C_3H_8/O_2	404	385	19	450	433	17
C_3H_8/NO	—	431	—	—	—	—
$C_3H_8/O_2/NO$	425	396	29	—	440	—
C_3H_8/H_2O	374	363	11	399	392	7
$C_3H_8/H_2O/O_2$	361	351	10	394	377	17
$C_3H_8/H_2O/NO$	376	354	22	409	389	19
$C_3H_8/H_2O/NO/O_2$	378	368	10	397	379	18

atmosphere. Figure 4 shows that the effect of NO on the oxidation reaction over both the Pd/Al₂O₃ and Rh-Pd/Al₂O₃ catalysts is negative; the T_{50} of the Pd/Al₂O₃ catalyst under a $C_3H_8/O_2/NO/N_2$ atmosphere was 425 °C, and thus was increased by 21 °C, while the conversion at 450 °C was only about 70% with the inclusion of NO. However, from Fig. 4(b) the T_{50} and T_{90} of the Rh-Pd/Al₂O₃ catalyst under the same conditions were 396 and 440 °C, respectively, and thus increased by only 11 and 7 °C subsequent to the addition of NO. These results indicate that the presence of NO inhibits the oxidation of C_3H_8 due to the competition between NO and O₂, and that the inhibiting effect of NO on the Rh-treated catalyst was less than that on the Pd-only catalyst, which may result from the superior activity of Rh for NO_x.

Figure 4 summarizes the positive effect of H₂O on the oxidation reaction over both Pd/Al₂O₃ and Rh-Pd/Al₂O₃ catalysts. The T_{50} and T_{90} values of both catalysts decreased while the conversions at similar temperatures were higher with the addition of H₂O. The Rh-treated catalyst also showed superior low-temperature activity. The T_{50} of the Pd/Al₂O₃ and Rh-Pd/Al₂O₃ catalysts were 361 and 351 °C, respectively. After H₂O was injected, the T_{50} and T_{90} of the Pd/Al₂O₃ catalyst decreased by 43 and 56 °C, respectively, while the T_{50} and T_{90} of the Rh-Pd/Al₂O₃ catalyst decreased by 34 and 56 °C. The presence of H₂O enhanced the direct oxidation of C_3H_8 by weakening the adsorption of C_3H_8 or its intermediates, leading to lower complete conversion temperatures. The SR reaction also takes place under these conditions.

The C_3H_8 conversions before and after the injection of NO and H₂O to the oxidation reaction environment are compared in Fig. 4. Compared to the C_3H_8 conversions obtained from the direct oxidation reaction, the conversions increased at similar temperatures with the addition of NO and H₂O due to the positive effect of H₂O in terms of weakening the adsorption of C_3H_8 or its intermediates. The T_{50} and T_{90} of the Pd/Al₂O₃ catalyst decreased by 26 and 53 °C after NO and H₂O were injected, and the T_{50} and T_{90} of the Rh-Pd/Al₂O₃ catalyst decreased from 385 and 433 °C to 368 and 379 °C, respectively. Under the same conditions, the Rh-treated catalyst thus exhibited better activity than the Pd-only catalyst. The positive effect of H₂O on the oxidation reaction plays an important role at higher temperatures and results in complete conversion being achieved rapidly. Comparing the C_3H_8 conversions in $C_3H_8/O_2/H_2O/N_2$ and $C_3H_8/O_2/NO/H_2O/N_2$ atmospheres, we conclude that, at similar

temperature below 380 °C, the addition of NO dramatically decreases conversion due to the inhibiting effect of NO.

In summation, the presence of Rh increases the promotional effect of H₂O and also inhibits the negative effects of NO on the oxidation reaction. The catalytic activity of the Rh-treated catalyst under different atmospheres remains superior to that of the Pd-only catalyst, which is in good agreement with the overall activity results.

3.6. Reduction reaction of C_3H_8

To study the reduction reaction of C_3H_8 , catalysts were assessed in a $C_3H_8/NO/N_2$ atmosphere at different temperatures. According to Fig. 5, the reduction activity is weak compared with the direct oxidation reaction. Mannila et al. [33] have reported that the oxidation of alkenes proceeds through one or

Fig. 5. C_3H_8 conversion by reduction at varying temperatures and in response to the addition of NO and/or H₂O to a $C_3H_8/O_2/N_2$ atmosphere over Pd/Al₂O₃ (a) and Rh-Pd/Al₂O₃ (b) catalysts.

more cracking steps to give surface precursors such as CH_3^* and CH_2^* , and that the partial oxidation product CO may be produced with increasing temperatures. CO is able to strongly adsorb on active sites, and this results in a self-inhibition effect that can inhibit the reduction reaction of C_3H_8 . The conversion over the Pd/ Al_2O_3 catalyst at 450 °C was only about 35%, while the T_{50} of the Rh-Pd/ Al_2O_3 catalyst was 431 °C and the conversion at 450 °C was about 68%, a value that is much higher than that of the Pd/ Al_2O_3 catalyst. This result is attributed to the superior activity of Rh for NO_x as well as the higher oxidation state of the PdO_x species in the Rh-Pd/ Al_2O_3 catalyst.

It is evident from Fig. 5 that the conversion of C_3H_8 increases at similar temperatures in the presence of O_2 because O_2 can react with C_3H_8 or its intermediates strongly adsorbed on active metal sites more easily than NO, and thus regenerate the active sites. As an example, the intermediate species CO can react with O_2 below 200 °C. The conversions over the Pd/ Al_2O_3 and Rh-Pd/ Al_2O_3 catalysts at 450 °C reached 75% and 96%, respectively, and the T_{50} of the catalysts were 425 and 396 °C.

The activity increased dramatically at similar temperatures after the injection of H_2O to the $\text{C}_3\text{H}_8/\text{NO}/\text{N}_2$ atmosphere because H_2O weakens the adsorption of reactants. The T_{50} of the Rh-Pd/ Al_2O_3 catalyst decreased from 431 to 354 °C, and the conversion was already 100% at 400 °C. However, the T_{50} and T_{90} of the Pd/ Al_2O_3 catalyst remained at 376 and 409 °C, both of which are much higher than the Rh-additive values.

Unfortunately, C_3H_8 conversions over the Pd/ Al_2O_3 catalyst below 385 °C and over Rh-Pd/ Al_2O_3 below 375 °C decrease after O_2 was included in the $\text{C}_3\text{H}_8/\text{NO}/\text{H}_2\text{O}/\text{N}_2$ atmosphere. Keeping in mind the previous discussion of the oxidation activity of C_3H_8 , we conclude that the low-temperature activities of both catalysts are reduced when O_2 and NO are both present in the $\text{C}_3\text{H}_8/\text{O}_2/\text{H}_2\text{O}/\text{NO}/\text{N}_2$ atmosphere.

3.7. SR reaction of C_3H_8

To study the SR reaction of C_3H_8 , the conversions at different temperatures were determined under a $\text{C}_3\text{H}_8/\text{H}_2\text{O}/\text{N}_2$ environment, with the results shown in Fig. 6. The T_{50} of the Pd/ Al_2O_3 and Rh-Pd/ Al_2O_3 catalysts were 374 and 363 °C, respectively (Table 2). The Rh-treated catalyst exhibited far superior low-temperature activity compared to the Pd-only catalyst. The T_{90} of the Pd/ Al_2O_3 catalyst was 399 °C, while the conversion of the Rh-treated catalyst at this temperature was already 100%. The addition of Rh to the catalyst thus dramatically increases the catalytic activity for the SR reaction. The support is the principal site for water activation, and the metal sites are responsible for the activation of hydrocarbons in SR reactions [34]. In addition, H_2O weakens the adsorption of C_3H_8 or its intermediates. With the addition of Rh, not only is the activation of C_3H_8 adsorbed on Pd sites enhanced, but the conversion of C_3H_8 due to the SR reaction increases.

It is interesting to see from Fig. 6(b) that the inclusion of NO promotes the SR reaction over the Rh-Pd/ Al_2O_3 catalyst, especially for low-temperature activity (T_{50} decreases from 363 to 354 °C). However, the effect of NO on the SR reaction over the Pd/ Al_2O_3 catalyst is negative (Fig. 6(a)): T_{90} increases from 399

to 409 °C. The superior activity of Rh for NO_x and the higher dispersion of PdO_x species may result in the promotional effect of NO on the SR reaction over the Rh-Pd/ Al_2O_3 catalyst.

It can also be concluded from Fig. 6 that the C_3H_8 conversion due to the SR reaction increases dramatically with the addition of O_2 , such that the C_3H_8 conversions over these two catalysts are much higher than with O_2 at similar temperatures. The T_{50} and T_{90} of the Rh-Pd/ Al_2O_3 catalyst decreased by 12 and 15 °C, respectively, after O_2 was injected, while the T_{50} and T_{90} of the Pd/ Al_2O_3 catalyst decreased by 13 and 5 °C. Thus, in the case of these close-coupled catalysts, the oxidation and SR reactions appear to proceed synergistically.

According to Fig. 6, the low-temperature performance of both catalysts declined with the injection of NO to the $\text{C}_3\text{H}_8/\text{H}_2\text{O}/\text{O}_2/\text{N}_2$ atmosphere. The conversion over the Pd/ Al_2O_3 catalyst at 370 °C fell from 41.9% to 26.7% after NO was added, and the conversion over the Rh-treated catalyst at 360 °C decreased from 43.7% to 14.4%. This may be the reason for the poor overall catalytic activity for C_3H_8 at temperatures below T_{50} . These results indicate that the inhibiting effect of NO plays a major role in the low-temperature activity of these catalysts, while the positive effect of O_2 has a significant effect in terms of achieving complete conversion at higher temperatures.

In summary, two main factors affect the catalyst activity. Firstly, the textural properties of the support material play an important role in the dispersion of active components and also affect both mass and heat transfer [35]. The support materials for both the Pd/ Al_2O_3 and Rh-Pd/ Al_2O_3 catalysts were the

Fig. 6. C_3H_8 conversion by steam reforming at varying temperatures and in response to the addition of NO and/or H_2O to a $\text{C}_3\text{H}_8/\text{O}_2/\text{N}_2$ atmosphere over Pd/ Al_2O_3 (a) and Rh-Pd/ Al_2O_3 (b) catalysts.

Graphical Abstract

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A highly efficient Rh-modified Pd/Al₂O₃ close-coupled catalystRuimei Fang, Yajuan Cui, Sijie Chen, Hongyan Shang, Zhonghua Shi*, Maochu Gong, Yaoqiang Chen*
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Introducing Rh into a Pd/Al₂O₃ close-coupled catalyst increases the dispersion of active PdO_x species and improves the catalytic activity for propane elimination. The figure shows C₃H₈ conversion over Pd/Al₂O₃ and Rh-Pd/Al₂O₃ close-coupled catalysts.

same, so the effects of the support texture on the dispersion of noble metals are similar. Secondly, the high dispersion and stability of PdO_x species directly improve the catalytic activity, and the addition of Rh increases the catalytic performance of a Pd-based catalyst by inducing superior dispersion and higher oxidation states of these PdO_x species.

4. Conclusions

The addition of Rh plays an important role in the total catalytic activity for C₃H₈ elimination and in the performance of specific reactions of C₃H₈ over Pd/Al₂O₃ catalyst. The introduction of Rh can increase the dispersion of active PdO_x species and change this electronic states of these species. Comparing the performance of single reactions between the Pd-only catalyst and the Rh-treated catalyst, we conclude that the inclusion of Rh enhances the conversion of C₃H₈ due to specific reactions, especially those reactions involving NO.

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性能优异的Rh改性的Pd/Al₂O₃密偶催化剂

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摘要: 采用等体积浸渍法制备了Pd/Al₂O₃和Rh-Pd/Al₂O₃密偶催化剂, 运用H₂程序升温还原、CO化学吸附和X射线光电子能谱等手段对催化剂进行了表征, 并考察了催化剂对丙烷总包反应和单反应的转化活性。总包反应结果表明, Rh的添加使起燃温度和完全转化温度分别降低了23和18℃。单反应结果证明, 添加Rh能提高各单反应丙烷的转化活性, 尤其是有NO参与的反应。表征结果证明, 掺杂Rh不仅可以抑制活性组分PdO_x的烧结, 提高PdO_x的分散度, 而且可以改变其电子状态。

关键词: 密偶催化剂; 钯; 铑; 丙烷; 直接氧化反应; 还原反应; 蒸汽重整反应

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