available at www.sciencedirect.com journal homepage: www.elsevier.com/locate/chnjc

Article

Promotion of a Pd/Al₂O₃ close-coupled catalyst by Ni

Ruimei Fang ^{a,c}, Yajuan Cui ^{b,c}, Zhonghua Shi ^{c,#}, Maochu Gong ^c, Yaoqiang Chen ^{a,c,*}^a College of Chemical Engineering, Sichuan University, Chengdu 610064, Sichuan, China^b College of Architecture & Environment, Sichuan University, Chengdu 610064, Sichuan, China^c Key Laboratory of Green Chemistry & Technology of the Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, Sichuan, China

ARTICLE INFO

Article history:

Received 5 February 2015

Accepted 26 March 2015

Published 20 July 2015

Keywords:

Close-coupled catalyst

Palladium

Nickel

Alumina

Propane

ABSTRACT

The influence of a nickel promoter on the catalytic behavior of a modified alumina supported Pd close-coupled catalyst was investigated. Doping with nickel improved the catalytic activity for the reactions of C₃H₈, especially over the aged catalyst. *T*₅₀ and *T*₉₀ of the aged Pd catalyst were decreased by 31 and 30 °C, respectively. The single reaction results revealed that doping with Ni promoted the catalytic activity for the C₃H₈ + NO reaction. The fresh and aged catalysts were characterized by H₂-temperature-programmed reduction, CO chemisorption, high resolution transmission electron microscopy, and X-ray photoelectron spectroscopy, which revealed that the doping with Ni inhibited the sintering of active PdO_x species and the formation of undesired metallic Pd⁰, and led to improved reducibility of active PdO_x and increased the surface area of PdO_x species.

© 2015, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Pollutant emission from gasoline engine powered vehicles is a major source of environmental pollution which is becoming more severe [1,2]. Hydrocarbons (HCs), carbon monoxide (CO), and nitrogen oxides (NO_x) are the major components in exhaust emission from vehicles [3–5]. Since the third European emission standard was adopted in 2000, a close-coupled catalyst (CCC) has been widely used to eliminate the HCs emission (60%–80% of the total emitted) during the cold-start period [5,6]. In order to quickly achieve light-off temperature (*T*₅₀), the CCC is often installed close to the engine. However, the extremely high temperature (ca. 1100 °C) near the engine can readily lead to the sintering of catalysts. Therefore, a CCC should possess not only excellent catalytic activity but also excellent thermal stability.

The classical components of these systems include Rh, Pt, and Pd as active metal and high surface alumina as the support [7–9]. The use of Pd as a single active metal component in a CCC has received considerable attention on the basis of its economic aspects (lower cost and more supply of Pd than Rh and Pt) as well as the availability of cleaner fuels and its remarkable activity for oxidation [10]. Pd/Al₂O₃ is widely regarded as the most active CCC for the catalytic combustion of propane, with excellent activity in the oxidation of HCs. However, its poor stability and the insufficient Pd supply have limited its practical application [11]. During the past several years, considerable attention has been paid to the improvement of catalytic activity of the CCC. To promote the catalytic activity by improving the stability of the support using a stabilizer is a viable means. Besides, another interesting approach is to promote Pd with lower cost metals [12]. Promising results have been obtained with Mn, Cr,

* Corresponding author. Tel/Fax: +86-28-85418451; E-mail: nic7501@scu.edu.cn# Corresponding author. Tel/Fax: +86-28-85418451; E-mail: shizh96@scu.edu.cn

This work was supported by the National Natural Science Foundation of China (21173153) and the Sichuan Province Science and Technology Support Program (2014SZ0143).

DOI: 10.1016/S1872-2067(15)60850-6 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 36, No. 7, July 2015

or Cu, which have been attributed to the formation of the corresponding alloys (and consequent perturbation of Pd electronic properties) or, such as Mn, to a combination of the effects of alloy formation and Pd-MnO_x interaction [12–15]. Ni is also a potential promoter of Pd activity for these reactions despite legislative restrictions on its use in some countries. The effect of contact between Pd and Ni on promoting catalytic activity is positive, especially on enhancing NO_x conversion under stoichiometric or rich atmosphere, e.g., the remarkable activity of Rh for the conversion of NO_x that is due to that the nickel aluminate crystallites provide sites for NO adsorption and subsequent transfer to the active Pd sites [16,17]. Recent reports on the same Pd-Ni catalyst have revealed that Ni induces a promotion of CO oxidation as a consequence of an indirect effect favoring the establishment of contact between Pd and the nanostructured configuration of the Ce-Zr mixed oxide component [16,18,19]. In a previous work, it was found that the improvement of the activity of NO_x conversion promoted the total catalytic activity of the CCCs [20]. Therefore, the effect of Ni on the activity of HC conversion is worth studying for its lower cost and better activity in promoting NO_x conversion. For this purpose, the effects of introducing Ni into a Pd/Al₂O₃ CCC for the elimination of C₃H₈ was studied in the present work.

2. Experimental

2.1. Catalyst preparation

La₂O₃-stabilized Al₂O₃ was prepared by the peptizing method. This was calcined at 1000 °C for 5 h in a muffle furnace. The Al₂O₃ material obtained was used as the support. The CCCs Pd/Al₂O₃ and bimetallic PdNi/Al₂O₃ were prepared by the impregnation method employing Pd(NO₃)₂ (Pd(NO₃)₂ content of 14.21%, Herarus Holding) and Ni(NO₃)₂·6H₂O (Ni(NO₃)₂·6H₂O content of 98.0%, Kelong Chemical Company) as the aqueous precursor solution. Deionized water was added to these materials to form a homogeneous slurry. The resulting slurry was spread over a honeycomb cordierite (2.5 cm³, Corning, China). Excess slurry was blown away using compressed air. The sample was dried at 120 °C and calcined at 1000 °C for 5 h in a muffle furnace to give the final monolithic catalyst. The Pd and Ni contents were 2.5 and 0.18 g/L, respectively.

2.2. Catalyst characterization

The textural properties of La₂O₃-stabilized Al₂O₃ were assessed using a Quantachrome SI instrument. To remove surface impurities, the sample was first degassed under vacuum at 300 °C for 3 h prior to the measurement. The surface area and pore volume were 138 m²/g and 0.47 mL/g, respectively.

The activity for C₃H₈ and the single reactions of C₃H₈ were evaluated in a multiple fixed bed continuous flow microreactor by passing a gas mixture similar to gasoline engine exhaust through the reactor. The gas flows were regulated with mass flow controllers and sent to a blender. The simulated exhaust gas contained a mixture of O₂, CO (0.6%), C₃H₈ (0.06%), NO (0.06%), CO₂ (12%), H₂O (10%), and N₂ (balance). The gas

space velocity was 40000 h⁻¹. The individual reactions of C₃H₈ were the C₃H₈ + O₂, C₃H₈ + NO, and C₃H₈ + H₂O reactions. The oxidation of C₃H₈ was studied in an exhaust gas consisting of a mixture of O₂ (adjustable), C₃H₈ (0.06%), and N₂ (balance). The reduction of NO_x with C₃H₈ was studied with an exhaust gas including a mixture of NO (0.06%), C₃H₈ (0.06%), and N₂ (balance). The steam reforming reaction of C₃H₈ was studied in a mixture of H₂O (10%), C₃H₈ (0.06%), and N₂ (balance). The C₃H₈ 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 microreactor.

H₂ temperature-programmed reduction (H₂-TPR) measurement was performed in a quartz tubular microreactor. Each sample (100 mg, 20–40 mesh) was pretreated in a flow of N₂ (20 mL/min) from room temperature to 400 °C, maintained at this temperature for 60 min, and then cooled to room temperature under N₂ (20 mL/min). The reduction was carried out under a flow of a 5% H₂-95% N₂ (V/V) gas mixture (20 mL/min) between room temperature and 600 °C at a heating rate of 8 °C/min. The H₂ consumption was assessed by a thermal conductivity detector (TCD).

Pd dispersion was determined by CO chemisorption measurement. A catalyst sample of 200 mg was placed in a U-shaped quartz tube, reduced under a flow of H₂ (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 gas were passed through the tube and the amount of adsorption was assessed by TCD.

X-ray photoelectron spectroscopy (XPS) data were obtained using a spectrometer (XSAM-800, Kratos Co) with Mg K_α radiation under ultrahigh vacuum (UHV). 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. Surface morphology analysis was carried out using high-resolution transmission electron microscopy (HRTEM) on a JEM-2010 instrument operated at 200 kV. The sample for the HRTEM study was ultrasonically dispersed in ethanol and deposited onto a perforated carbon film supported on a copper grid.

3. Results and discussion

3.1. Catalytic performance of catalysts

The catalytic activity of the Pd/Al₂O₃ and PdNi/Al₂O₃ catalysts before and after aging treatment was tested with the simulated exhaust gas. The results are shown in Fig. 1. Fig. 1(a) presents the C₃H₈ conversion over all catalysts at different temperatures. Fig. 1(b) shows the light-off temperature (*T*₅₀) and full conversion temperature (*T*₉₀) over the different catalysts.

According to Fig. 1(a), the C₃H₈ conversion increased with the rise of temperature and C₃H₈ rapidly reached complete conversion. The difference in activity between the catalysts

Fig. 1. Catalytic activity of fresh and aged catalysts. (a) C₃H₈ conversion at different temperatures over different catalysts; (b) T₅₀ and T₉₀ values of different catalysts.

with and without Ni addition was obvious. From Fig. 1(b), the T₅₀ of the fresh Pd/Al₂O₃ and PdNi/Al₂O₃ catalysts were 280 and 274 °C, respectively. After the aging treatment, the catalytic activity declined dramatically, and T₅₀ increased to 356 and 325 °C, respectively. The ΔT_{50} (T_{50-Aged}–T_{50-Fresh}) of the Pd/Al₂O₃ and PdNi/Al₂O₃ catalysts were 76 and 51 °C, respectively. A lower T₅₀ represents a higher low-temperature activity of the catalyst. This indicated that the introduction of Ni not only promoted the light-off property but also inhibited the deterioration of light-off activity, promoting the stability of catalytic activity. A superior light-off property is vital to a CCC.

The T₉₀ of the fresh Pd/Al₂O₃ and PdNi/Al₂O₃ catalysts were 315 and 305 °C, respectively. Those of the aged catalysts were 379 and 349 °C, respectively. It is interesting to note that the T₉₀ of Pd-only and Ni-added catalysts were increased by 64 and 44 °C, respectively, after the aging treatment. To summarize, the introduction of Ni promoted the catalytic activity dramatically and also increased the stability of the catalytic property during the aging treatment, especially the light-off property.

3.2. TPR results

One of the most important characteristics of the catalyst is its reducibility of active PdO_x species, which impacts the catalytic property of the catalyst. The H₂-TPR measurements of the Pd/Al₂O₃ and PdNi/Al₂O₃ catalysts before and after the aging treatment are shown in Fig. 2. There were two peaks in the TPR profiles, which were denoted as α and β , respectively. However, the α peak was only seen in the profile of the aged Pd/Al₂O₃ catalyst. The β peak is from hydrogen consumption, and the negative α peak corresponds to the decomposition of palladium hydride [21]. A larger area reduction peak of the active component is beneficial for the superior catalytic activity of the catalyst (the peak area corresponds to the adsorbed H₂ consumption, and a larger peak area means a larger amount of the active component) [22].

For the fresh catalysts, the reduction temperature of peak β was similar (around 115 °C), but the peak area of the PdNi/Al₂O₃ catalyst was larger than that of the Pd/Al₂O₃ cata-

lyst. This demonstrated that the amount of active PdO_x species on the supported PdNi/Al₂O₃ catalyst was larger, which is beneficial for enhanced catalytic performance. After the aging treatment, significant changes in the reduction characteristics occurred for the catalysts. The area and reduction temperature of the β peak of the aged catalysts became smaller and lower than the fresh catalysts, indicating that the amount of active species decreased and the catalyst was sintered during the aging treatment. However, the area of the β peak of the PdNi/Al₂O₃ catalyst was still larger than that of the aged Pd/Al₂O₃ catalyst, implying a larger amount of active PdO_x species. Another obvious change after the aging treatment was that the negative α peak from the decomposition of palladium hydride appeared in the profile of the aged Pd/Al₂O₃ catalyst at 93 °C. Metallic Pd⁰ can dissociate H₂ molecules into H atoms, which can form palladium hydride with the large crystallites of metallic Pd⁰ at room temperature. However, the formation of palladium hydride on the highly dispersed Pd was considerably suppressed [23]. Moreover, metallic Pd⁰, which showed poorer activity for C₃H₈ than the active PdO_x species, was generated through the reduction or decomposition of PdO_x after the aging treatment. To summarize, large crystallites of metallic Pd⁰ ap-

Fig. 2. H₂-TPR profiles of fresh and aged catalysts.

peared only on the aged Pd/Al₂O₃ catalyst, indicating that the doping with Ni effectively inhibited the sintering of the active component and the formation of metallic Pd⁰.

3.3. CO chemisorption analysis

The dispersion of the active component on the supported catalyst is vital to the catalytic performance of the catalyst. CO chemisorption is effective for determining the dispersion of metal Pd over the support. The dispersion of active Pd on the Pd/Al₂O₃ and PdNi/Al₂O₃ catalysts before and after the aging treatment was determined by CO chemisorption. Simplício et al. [24] reported that a higher dispersion of the active component and smaller particle size produce a higher active surface area, therefore enhanced catalytic performance of catalyst can be obtained. It was assumed that the stoichiometry of Pd to CO is 1:1. The average particle size, d (nm), was approximated by $1.12/D$ [25], where D (%) is the dispersion of Pd. The Pd active surface area, S (m²/g), was obtained 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 (6.023×10^{23}), δ is the atomic cross section of Pd (0.06 nm²) [26], w (g) is the mass of catalyst, and p (%) is the mass fraction of Pd.

The results listed in Table 1 show that both the fresh and aged PdNi/Al₂O₃ catalysts exhibited higher Pd dispersion and Pd active surface area compared with the Pd-only catalyst. The active Pd particle size in PdNi/Al₂O₃ was also smaller than that in the Pd/Al₂O₃ catalyst. Moreover, the decline of active Pd dispersion in the PdNi/Al₂O₃ catalyst was less than that in the Pd/Al₂O₃ catalyst during the aging treatment. These results are in good agreement with the above TPR results. These data indicated that the addition of Ni to the Pd/Al₂O₃ catalyst increased the stability and dispersion of the active PdO_x species.

3.4. XPS studies

In order to investigate the changes in the chemical state of Pd element, the fresh and aged catalysts were studied by XPS. Fig. 3 presents the Pd 3d photoelectron peaks of the catalysts. No Ni peak was seen on the surface of the Ni-promoted catalyst due to the low concentration of Ni added.

The binding energy of metallic Pd⁰ and PdO is 335.3 and 336.8 eV, respectively, according to the references [27,28]. From the results given in Fig. 3, it can be seen that the binding energy of the Pd 3d_{5/2} electrons of all the catalysts was between 335.3 and 336.8 eV. This result indicated that the Pd species in these catalysts were in a partially oxidized state, Pd ^{δ +} ($0 < \delta < 2$), which is more active than metallic Pd⁰ [29]. Compared with the Pd-only catalysts, the Pd 3d_{5/2} binding energy of both the

Fig. 3. Pd 3d XPS spectra for the fresh and aged catalysts.

fresh and aged PdNi/Al₂O₃ catalysts was shifted to a higher value by 0.2 and 0.5 eV, respectively. This was likely due to the electronic effect of Ni, leading to the transfer of electrons from PdO_x to NiO_x. Various additives can be used to modify the active phase by changing the oxidation state and by modifying the electronic environment of the active component [30]. By considering the observed changes in the total catalytic activity, the higher oxidation state of the active PdO_x species may be one reason for the superior activity of the Ni-promoted catalyst. After the aging treatment, the binding energy of the Pd-only catalyst and Ni-promoted catalyst decreased by 0.4 and 0.1 eV, respectively. The decrease in the binding energy of Pd 3d_{5/2} due to aging can be explained by particle growth [31], indicating that the introduction of Ni to the Pd-only catalyst inhibited the sintering and growth of active PdO_x species during the aging treatment. By considering the observed changes in the above catalytic activity, the higher oxidation state and smaller particle size of the active PdO_x species may be one reason for the superior activity of the Ni-promoted catalyst.

3.5. HRTEM results

HRTEM studies play a relevant role in the nanostructure characterization of noble metal dispersed on a support [32]. Fig. 4 presents HRTEM micrographs of the aged catalysts. The corresponding elemental mapping of Pd is inserted in the images. As presented in Table 1, the fresh catalysts showed a higher dispersion of Pd species, especially the Ni-promoted catalyst. Therefore, the highly dispersed Pd species were hard to observe owing to a lack of contrast with the support. Only the aged catalysts were examined by HRTEM. It can be seen from the following micrographs that the promoting effect of Ni on inhibiting the sintering of the catalyst was positive. After the aging treatment, PdO_x particles (labeled by the arrows) were observed on the images owing to the lower dispersion (shown in Table 1). It can be seen from Fig. 4 that the Ni-promoted catalyst showed smaller PdO_x particles compared with the Pd-only catalyst, which is in accordance with the CO chemisorption results. A smaller particle size and higher dispersion of the active PdO_x species were the main reasons that the PdNi/Al₂O₃

Table 1
CO chemisorption for fresh and aged catalysts.

Catalyst	Pd dispersion (%)	Pd particle size (nm)	Pd active surface area (m ² /g)
Pd-Fresh	22.8	4.9	77.4
PdNi-Fresh	30.3	3.7	102.8
Pd-Aged	11.6	9.7	39.4
PdNi-Aged	13.1	8.5	44.5

Fig. 4. HRTEM photographs of aged Pd/Al₂O₃ (a) and PdNi/Al₂O₃ (b) catalysts.

catalyst still has good catalytic activity after the aging treatment.

3.6. Catalytic activity for the single reactions

In order to further study the effect of Ni on the overall catalytic activity of the Pd-only catalyst, specific reactions of C₃H₈ were assessed at different temperatures. These are shown in Fig. 5. The main single reactions relevant to the elimination of C₃H₈ are direct oxidation (HC + O₂ → CO₂ + H₂O) and steam reforming (HC + H₂O → CO + H₂) of C₃H₈, and the reduction of NO_x with C₃H₈ (NO_x + HC → N₂ + CO₂ + H₂O).

Fig. 5(a) presents the C₃H₈ conversion of the C₃H₈ + O₂ reaction at different temperatures. The oxidation reaction of C₃H₈ was studied in a C₃H₈/O₂/N₂ atmosphere. The changes in the

light-off and full conversion temperatures are summarized in Table 2. The conversion of C₃H₈ by direct oxidation did not increase as rapidly as that of the overall reaction with increasing temperature: the ΔT values ($\Delta T = T_{90} - T_{50}$) obtained for the fresh Pd/Al₂O₃ and PdNi/Al₂O₃ catalysts were 57 and 55 °C, respectively. Shinjoh et al. [33] proposed that either C₃H₈ or an intermediate species (such as partial oxidation products) strongly adsorbed on the catalyst surface result in self-inhibition by restricting the adsorption of O₂. For the fresh catalysts, the catalytic activity of PdNi/Al₂O₃ catalyst was similar to that of the Pd/Al₂O₃ catalyst due to sufficient active sites. However, the aged PdNi/Al₂O₃ catalyst presented better activity than the aged Pd/Al₂O₃ catalyst, in accordance with the discussion above. The T_{50} of the aged Pd/Al₂O₃ and PdNi/Al₂O₃ catalysts was 404 and 398 °C, respectively. T_{90} of the aged Pd/Al₂O₃ and

Fig. 5. Catalytic activity for the single reactions over fresh and aged catalysts at different temperatures. (a) C₃H₈ + O₂; (b) C₃H₈ + H₂O; (c) C₃H₈ + NO.

Table 2

T_{50} and T_{90} values for C_3H_8 conversion on single reactions over fresh and aged catalysts.

Catalyst	$C_3H_8+O_2$		C_3H_8+NO		$C_3H_8+H_2O$	
	$T_{50}/^{\circ}C$	$T_{90}/^{\circ}C$	$T_{50}/^{\circ}C$	$T_{90}/^{\circ}C$	$T_{50}/^{\circ}C$	$T_{90}/^{\circ}C$
Pd-Fresh	310	367	374	— ^a	323	372
PdNi-Fresh	314	369	367	— ^a	320	353
Pd-Aged	404	450	— ^b	— ^b	375	397
PdNi-Aged	398	435	436	— ^b	369	394

^a C_3H_8 over fresh catalysts cannot reach full conversion before 400 °C.

^b C_3H_8 over aged catalysts cannot achieve light-off or full conversion before 450 °C.

PdNi/Al₂O₃ catalysts was 450 and 435 °C, respectively. In addition, the conversion of C_3H_8 over the Ni-promoted catalyst was already 100% at 450 °C, while the conversion over the Pd/Al₂O₃ catalyst was only 90%. With regard to the oxidation reaction, therefore, the PdNi/Al₂O₃ catalyst presented a better catalytic activity and low temperature property compared to the Pd/Al₂O₃ catalyst. This was because the addition of Ni increased the oxidation state of the PdO_x species and accelerated the re-oxidation of Pd to PdO_x, as discussed in XPS results, both of which are helpful to the adsorption of O₂.

To study the steam reforming reaction of C_3H_8 , the conversion at different temperatures was determined under a $C_3H_8/H_2O/N_2$ environment. The results are shown in Fig. 5(b). The activity for the $C_3H_8 + H_2O$ reaction was different from those for the $C_3H_8 + O_2$ and $C_3H_8 + NO$ reactions (Fig. 5(c)). C_3H_8 can reach full conversion more quickly and the deterioration during the aging treatment was much less. For the fresh catalysts, the T_{50} of the Pd/Al₂O₃ catalyst was similar to that of PdNi/Al₂O₃ catalyst, as shown in Table 2. However, the Ni-promoted catalyst exhibited superior high temperature activity compared to the Pd-only catalyst, which was in good agreement with the total catalytic activity. T_{90} of the Pd/Al₂O₃ and PdNi/Al₂O₃ catalysts was 372 and 353 °C, respectively. After the aging treatment, T_{50} and T_{90} increased to higher values due to the sintering of catalysts. T_{50} of the aged Pd/Al₂O₃ and PdNi/Al₂O₃ catalysts increased to 375 and 369 °C, respectively. T_{90} of the aged Pd/Al₂O₃ and PdNi/Al₂O₃ catalysts increased to 397 and 394 °C, respectively. The activity of the Ni-promoted catalyst was still better than that of Pd-only catalyst due to more active sites, especially at temperatures higher than 400 °C. The support is the principal site for water activation, and the metal sites are responsible for the activation of the HC in the steam reforming reactions [34]. In addition, H₂O weakens the adsorption of C_3H_8 or its intermediates. With the addition of Ni, not only was the activation of C_3H_8 adsorbed on Pd sites enhanced, but the conversion of C_3H_8 due to the SR reaction increased.

Fig. 5(c) shows the catalytic activity of the $C_3H_8 + NO$ reaction, which was tested in a $C_3H_8/NO/N_2$ atmosphere at different temperatures. According to Fig. 5(c), the reduction activity of all the catalysts was weaker compared with the direct oxidation (Fig. 5(a)) and steam reforming reaction (Fig. 5(b)). The reactions between adsorbed species on the noble metal surface and desorption of the product are the key steps [35]. The more difficult desorption of NO, C_3H_8 or an intermediate species, and

insufficient active sites are the complicated reasons for the lower catalytic activity of the $C_3H_8 + NO$ reaction. For the fresh catalysts, T_{50} of the Pd/Al₂O₃ and PdNi/Al₂O₃ catalysts was 374 and 367 °C, respectively. However, when the temperature increased to 400 °C, the conversion over Pd/Al₂O₃ and PdNi/Al₂O₃ catalyst was only 59.1% and 63.4%, respectively. After the aging treatment, the activity of both the Pd/Al₂O₃ and PdNi/Al₂O₃ catalysts decreased dramatically, although the activity of the Ni-promoted catalyst was still superior to that of the Pd-only catalyst. T_{50} of the PdNi/Al₂O₃ catalyst was 436 °C and the conversion at 450 °C was 58%, much higher than that of the Pd/Al₂O₃ catalyst (40%). The positive effect of Ni on improving the activity for the reduction reaction may be attributed to that the nickel aluminate crystals provided sites for NO adsorption [17].

To summarize, the doping with Ni obviously promoted the C_3H_8 conversion over the aged catalyst, especially for the single reaction of $C_3H_8 + NO$. This result was attributed to the superior activity of Ni for NO_x conversion, and the higher oxidation state of the PdO_x species in the PdNi/Al₂O₃ catalyst [16].

4. Conclusions

Addition of Ni to a Pd/Al₂O₃ catalyst plays a promoting role in the total activity of C_3H_8 conversion as well as the single reactions of C_3H_8 , especially the $C_3H_8 + NO$ reaction. TPR, XPS, HRTEM, and CO chemisorption results revealed that the addition of Ni improved the stability of the active PdO_x species and increased the oxidation state of the active component.

References

- [1] Gandhi H S, Graham G W, McCabe R W. *J Catal*, 2003, 216: 433
- [2] Kašpar J, Fornasiero P, Hickey N. *Catal Today*, 2003, 77: 419
- [3] Li M, Wu X D, Wan J, Liu S, Ran R, Weng D. *Catal Today*, 2015, 242: 322
- [4] Lan L, Chen S H, Zhao M, Gong M C, Chen Y Q. *J Mol Catal A*, 2014, 394: 10
- [5] Yao Y L, Fang R M, Shi Z H, Gong M C, Chen Y Q. *Chin J Catal* (姚艳玲, 方瑞梅, 史忠华, 龚茂初, 陈耀强. 催化学报), 2011, 32: 589
- [6] Wang G, You R, Meng M. *Fuel*, 2013, 103: 799
- [7] Neyertz C, Volpe M, Gigola C. *Appl Catal A*, 2004, 277: 137
- [8] Spinicci R, Tofanari A. *Appl Catal A*, 2002, 227: 159
- [9] Dong L. *Chin J Catal* (董林. 催化学报), 2009, 30: 1150
- [10] Hungria A B, Calvino J J, Anderson J A, Martínez-Arias A. *Appl Catal B*, 2006, 62: 359
- [11] Pan X Q, Zhang Y B, Zhang B, Miao Z Z, Wu T X, Yang X G. *Chem Res Chin Univ*, 2013, 29: 952
- [12] Fernández-García M, Martínez-Arias A, Beller C, Anderson J A, Conesa J C, Soria J. *J Catal*, 2000, 190: 387
- [13] Trillat J F, Massardier J, Moraweck B, Praliaud H, Renouprez A J. *Stud Surf Sci Catal*, 1998, 116: 103
- [14] Elhamdaoui A, Bergeret G, Massardier J, Primet M, Renouprez A. *J Catal*, 1994, 148: 47
- [15] Hungria A B, Iglesias-Juez A, Martínez-Arias A, Fernández-García M, Anderson J A, Conesa J C, Soria J. *J Catal*, 2002, 206: 281
- [16] Hungria A B, Browning N D, Erni R P, Fernández-García M, Conesa J C, Pérez-Omil J A, Martínez-Arias A. *J Catal*, 2005, 235: 251
- [17] Zhang S J, Li L D, Zhang F X, Xue B, Guan N J. *Chin J Catal* (张淑娟,

Graphical Abstract

Chin. J. Catal., 2015, 36: 994–1000 doi: 10.1016/S1872-2067(15)60850-6

Promotion of a Pd/Al₂O₃ close-coupled catalyst by Ni

Ruimei Fang, Yajuan Cui, Zhonghua Shi *, Maochu Gong, Yaoqiang Chen *
Sichuan University

Addition of Ni to a Pd/Al₂O₃ close-coupled catalyst improved the catalytic activity for C₃H₈ conversion and increased the amount of active PdO_x species. The figure describes how C₃H₈ conversion over the aged Pd/Al₂O₃ and PdNi/Al₂O₃ close-coupled catalysts occurs.

- 李兰冬, 章福祥, 薛斌, 关乃佳. 催化学报, 2005, 26: 929
- [18] Hungria A B, Fernández-García M, Anderson J A, Martínez-Arias A. *J Catal*, 2005, 235: 262
- [19] Martínez-Arias A, Fernández-García M, Hungria A B, Iglesias-Juez A, Anderson J A. *Catal Today*, 2007, 126: 90
- [20] Fang R M, Cui Y J, Chen S J, Shang H Y, Shi Z H, Gong M C, Chen Y Q. *Chin J Catal* (方瑞梅, 崔亚娟, 陈思洁, 尚鸿燕, 史忠华, 龚茂初, 陈耀强. 催化学报), 2015, 36: 229
- [21] Zhao B, Wang Q Y, Li G F, Zhou R X. *J Environ Chem Eng*, 2013, 1: 534
- [22] Narui K, Furuta K, Yata H, Nishida A, Kohtoku Y, Matsuzaki T. *Catal Today*, 1998, 45: 173
- [23] Bonarowska M, Pielaszek J, Juszczak W, Karpiński Z. *J Catal*, 2000, 195: 304
- [24] Simplício L M T, Brandão S T, Sales E A, Lietti L, Bozon-Verduraz F. *Appl Catal B*, 2006, 63: 9
- [25] Bourane A, Derrouiche S, Bianchi D. *J Catal*, 2004, 228: 288
- [26] Usami Y, Kagawa K, Kawazoe M, Matsumura Y, Sakurai H, Haruta M. *Appl Catal A*, 1998, 171: 123
- [27] Xiao L H, Sun K P, Xu X L, Li X N. *Catal Commun*, 2005, 6: 796
- [28] Liu J Y, Zhao M, Xu C H, Liu S Y, Zhang X Q, Chen Y Q. *Chin J Catal* (刘建英, 赵明, 徐成华, 刘盛余, 张雪乔, 陈耀强. 催化学报), 2013, 34: 751
- [29] Kobayashi T, Yamada T, Kayano K. *Appl Catal B*, 2001, 30: 287
- [30] Zhao M, Zhang H L, Li X, Chen Y Q. *J Energy Chem*, 2014, 23: 755
- [31] Talo A, Lahtinen J, Hautajärvi P. *Appl Catal B*, 1995, 5: 221
- [32] Yang L Y, Lin S Y, Yang X, Fang W M, Zhou R X. *J Hazard Mater*, 2014, 279: 226
- [33] Shinjoh H, Muraki H, Fujitani Y. *Appl Catal*, 1989, 49: 195
- [34] Li Y, Wang X X, Xie C, Song C S. *Appl Catal A*, 2009, 357: 213
- [35] Tanabe T, Nagai Y, Dohmae K, Takagi N, Takahashi N, Matsumoto S, Shinjoh H. *Appl Catal B*, 2011, 105: 41

Ni对Pd/Al₂O₃密偶催化剂催化性能的影响

方瑞梅^{a,c}, 崔亚娟^{b,c}, 史忠华^{c, #}, 龚茂初^c, 陈耀强^{a,c,*}

^a四川大学化学工程学院, 四川成都610064

^b四川大学环境与工程学院, 四川成都610064

^c四川大学化学学院, 绿色化学与技术教育部重点实验室, 四川成都610064

摘要: 考察了助剂Ni对以改性氧化铝为载体的单Pd密偶催化剂的影响。结果表明, 掺杂Ni可以明显改善对C₃H₈的催化性能, 尤其对老化催化剂效果显著。此外, Ni的添加使老化催化剂Pd/Al₂O₃的起燃温度(*T*₅₀)和完全转化温度(*T*₉₀)分别降低31和30 °C。单反应测试结果表明, 添加Ni能明显提高对C₃H₈ + NO反应的催化性能。采用H₂程序升温还原、CO吸附、高倍透射电镜和X射线光电子能谱等手段对新鲜和老化催化剂进行了表征。结果表明, 掺杂Ni不仅可以抑制活性组分PdO_x的烧结, 减少金属态Pd⁰的产生, 而且可以提高PdO_x物种的可还原能力和有效比表面积。

关键词: 密偶催化剂; 钯; 镍; 氧化铝; 丙烷

收稿日期: 2015-02-05. 接受日期: 2015-03-26. 出版日期: 2015-07-20.

*通讯联系人. 电话/传真: (028)85418451; 电子信箱: nic7501@scu.edu.cn

#通讯联系人. 电话/传真: (028)85418451; 电子信箱: shizh96@scu.edu.cn

基金来源: 国家自然科学基金(21173153); 四川省科技厅科技支撑项目(2014SZ0143).

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).