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Effects of the addition of small quantities of ceria on the catalytic behavior of Pd-only close-coupled catalysts during automobile exhaust elimination

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ABSTRACT

A series of La-Al₂O₃ supported Pd-Ce close-coupled catalysts were synthesized by a co-adsorption impregnation method and subsequently investigated. In the case of fresh catalysts, the presence of an optimal concentration of ceria obviously promoted the catalytic activity during HC and NO_x eliminations, owing to the interaction between the palladium oxide species (PdO_x) and CeO₂ that improves the oxidation of Pd⁰ to PdO and enhances the adsorption of nitrite/nitrates and isocyanate intermediate species on the support under reaction conditions. Pd-Ce(2.0)/La-Al₂O₃ catalyst (where 2.0 is the wt% of CeO₂) exhibited the highest catalytic activity for HC and NO eliminations. Following aging at 1100 °C, the operational window for HC and NO_x conversions was broadened and the thermal stability of the catalysts was also improved as a result of the presence of an appropriate quantity of ceria (2.0–4.0 wt%). The enhanced interactions between PdO_x and CeO₂ evidently led to the formation of a Pd-O-Ce system, stabilizing PdO_x species with smaller particle sizes at high temperatures. This result is significant since it suggests a means of improving the catalytic performance of Pd-only close-coupled catalysts during automobile exhaust elimination.

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1. Introduction

Because of the growing concerns regarding pollution from vehicle exhaust, emissions regulations worldwide are becoming increasingly strict. Three-way catalytic converters (TWC) are currently the primary technology used to control the various regulated compounds emitted by cars [1] and TWC formulations containing Pt/Rh, Pt/Pd/Rh, Pd/Rh and Pd-only noble metal combinations are all in commercial use [2]. However, Pd-only TWCs have received considerable attention for automotive emissions catalytic conversion and the number of vehicles equipped with Pd-only TWCs is increasing on the basis of the remarkable activity of these systems during oxidation reac-

tions, as well as the availability of cleaner fuels and economic aspects [3]. It has long been recognized that 80%–90% of the hydrocarbon (HC) emissions from automobiles occur during cold-start conditions. Thus, a typical vehicle may fail stringent emission standards if the HC emissions from cold-start are not controlled [4]. Several potential solutions have been proposed to the cold-start problem, including HC traps, electrically heated catalysts, combustion heated catalysts, exhaust-gas ignition, microwave heating and close-coupled catalysts [5]. Among those solutions, close-coupled catalysts are the most direct and efficient, as no additional equipment or power inputs are needed. In such systems, the close-coupled catalyst is positioned close to the engine to allow for a rapid increase in the

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catalyst temperature. Unfortunately, the temperature in a close-coupled catalytic converter can reach in excess of 1000 °C during the practical application of the three-way catalytic conversion process, resulting in deactivation of Pd-based catalysts either through loss of the active surface by sintering or by transformation of the Pd to the metallic state [6].

Ce has traditionally been employed as a promoter [7–9] or as a support [10–12] and is well known as an excellent oxygen storage material because of its combination of facile redox cycling between the Ce³⁺ and Ce⁴⁺ oxidation states, good thermal stability, compatibility with noble metals and ease of insertion into alumina [2]. In addition, the ability of ceria to stabilize Pd in a highly dispersed state is well recognized, since the insertion of Pd into the cerium oxide lattice forms stable Pd–O–Ce bonds and thus leads to a high degree of dispersion [13]. Moreover, Ce can disperse on an alumina support in the form of two-dimensional regions when present at ≤ 10% by weight [14], thus serving as a bridge to connect Pd and Al₂O₃. Additionally, a strong interaction between CeO₂ and Al₂O₃ under oxidizing conditions leads to the formation of CeAlO₃ at the interface, which helps to stabilize the surface area of the Al₂O₃ [15,16], although overly large concentrations of Ce will encapsulate the metal nanoparticles, resulting in an irreversible loss of the metal's active sites [17]. We therefore chose to use Ce and to synthesize Pd–Ce nanoparticles supported on modified Al₂O₃, employing low ceria concentrations ranging from 0 to 4.0 wt%, in an attempt to determine the optimal ceria concentration.

Cargnello et al. [6,18,19] exploited the preorganization of variably functionalized thiol-protected Pd nanoparticles (with either 11-mercaptoundecanoic acid, 9-mercapto-1-nonanol or 1-dodecanethiol) and Ce(IV) alkoxide to form Pd@CeO₂ nanoparticles. This method, however, is not suitable for commercial applications, since the structure of Pd@CeO₂ is unstable at high temperatures. Wang et al. [20] prepared Pd–Ce catalysts by a stepwise impregnation method, in which the supports are first impregnated using PdCl₂ acidic aqueous solutions, after which they are calcined at 500 °C and then impregnated with a Ce(NO₃)₃ aqueous solution using the same method. In this method, Ce is not introduced within the first step. In our work, we employed a co-adsorption impregnation method to form a Pd–Ce system, in which the Pd is initially combined with the cerium oxide. A series of Pd–Ce close-coupled catalysts with varying CeO₂ contents were produced in this manner and have been characterized by means of three-way catalytic activity measurements, CO adsorption, high resolution transmission electron microscopy, hydrogen temperature programmed reduction and in situ DRIFTS. These techniques are all useful means of gaining insight into potentially important parameters involving the configuration of PdO_x particles on the surface of the support and the interaction of PdO_x with CeO₂, which may be responsible for enhancing the catalytic performance of TWCs.

2. Experimental

2.1. Catalyst preparation

The La-modified Al₂O₃ support was purchased from the Rhodia Company. Pd–Ce close-coupled catalysts were prepared by a co-adsorption impregnation method at 25 °C, with a theoretical Pd content of 1 wt%. In this process, aqueous Pd(NO₃)₂ and Ce(NO₃)₃ solutions were initially mixed for 20 min (applying CeO₂ contents of 0, 0.25, 0.5, 1.0, 2.0 and 4.0 wt%), following which the appropriate mass of La-modified Al₂O₃ was quickly added to the solution. After the mixture was stirred overnight, the powder was dried at 110 °C and then calcined at 500 °C for 2 h in static air. The resulting catalysts were termed Pd/La-A and Pd–Ce(x)/La-A (where x = 0.25, 0.5, 1.0, 2.0 and 4.0). A portion of each catalyst was further aged at 1100 °C for 4 h in static air to investigate the thermal stability of the samples, and these aged specimens were denoted as Pd/La-A-a and Pd–Ce(x)/La-A-a (x = 0.25, 0.5, 1.0, 2.0 and 4.0).

2.2. Catalytic activity tests

The catalytic activity tests were performed with a Bruker EQ55 FTIR spectrometer coupled with a multiple reflection transmission cell (Infrared Analysis, Inc.) before and after the simulated exhaust gas passed through the reactor. 0.2 ml catalyst was held in a quartz tube in the fixed-bed quartz reactor by packing quartz wool at both ends of the tube. The feed stream was regulated using special mass flow controllers and was composed of 0.12% NO, 0.03% NO₂, 0.066% C₃H₆, 0.033% C₃H₈, 0.6% CO and 0.745% O₂ with the balance Ar, at a GHSV of 43000 h^{−1} relative to the catalyst volume and the gas flow rate at room temperature (25 °C). Although a small quantity of H₂O was generated in the three-way catalytic reaction in our study, its presence would cause serious damage to the FTIR spectrometer and therefore H₂O was removed from the product stream before the gas passed through the multiple reflection transmission cell, and thus its concentration is not provided in the tabulation of results.

The air/fuel ratio (λ) was defined as equal to $(2V_{O_2} + V_{NO} + 2V_{NO_2}) / (V_{CO} + 9V_{C_3H_6} + 10V_{C_3H_8})$, where V is the concentration of each gas in units of volume percent, and a λ value of one was used in all the activity measurements. The operational window trials were carried out at 400 °C, applying different λ values by adjusting the concentration of O₂.

2.3. Characterization techniques

H₂-TPR measurements were carried out on a GC-1690 chromatograph to observe the reducibility of the catalysts. During these tests, 50 mg catalyst was pretreated at 200 °C in N₂ (30 ml/min) for 0.5 h and then cooled to −90 °C with liquid nitrogen. The reducing gas (5 vol% H₂/Ar at 40 ml/min) was passed through the sample and the temperature was raised to 900 °C at a rate of 10 °C/min. The consumption of hydrogen during the reduction was measured by a thermal conductivity detector (TCD).

Pd dispersion and particle sizes were determined by CO chemisorption at room temperature, using a CHEMBET-3000 (Quantachrome Co.). Prior to the experimental trials, each sample was reduced under a flow of 5% H₂/95% N₂ at 400 °C

for 1 h and then purged with He at the same temperature for 0.5 h. The sample was subsequently cooled to room temperature under an He flow and maintained at this temperature for another 0.5 h. Finally, CO pulses were injected into the sample bed every 5 min until no further consumption of CO could be detected. The Pd dispersion (D) was calculated using the following equation [21]:

$$D(\%) = 100 \times [(V_{\text{CO}} \times f) / (C_{\text{Pd}} \times m_{\text{Cat}} \times 22414)] \times m \quad (1)$$

Here V_{CO} is the CO volume adsorbed (mL), f is the stoichiometric factor, C_{Pd} is the Pd metal content (wt%), and m_{Cat} is the catalyst weight (g). The Pd particle size (d) was calculated according to the following equation:

$$d(\text{nm}) = 6 \times 10^5 \times M_{\text{Pd}} / (\rho_{\text{Pd}} \times D \times S_{\text{Pd}}) \quad (2)$$

Here M_{Pd} is the molar mass of Pd (106.42 g/mol), ρ_{Pd} is the Pd density (12 g/cm³), and S_{Pd} is the molar surface area of Pd assuming equidistribution of the low index faces ($S = 47780 \text{ m}^2/\text{mol}$ for Pd metal).

HRTEM images were obtained using a TECNAI G220 instrument operating at 200 kV with a perforated carbon film supported on a copper grid. Catalysts were crushed in an agate mortar and then ultrasonically dispersed in ethanol. EDS analysis was used to record elemental maps of samples, thus determining the chemical compositions of the catalysts.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) analyses were performed with a Nicolet 6700 FTIR spectrometer equipped with an MCT detector, a DRIFTS cell

fitted with CaF₂ windows and a heated reaction chamber for high-temperature trials. Spectra were collected by averaging 32 scans at a resolution of 4 cm⁻¹. Prior to analysis, catalysts were pretreated in Ar at 450 °C for 0.5 h and then cooled to 30 °C. The composition and flow rate of the feed stream were kept constant through each test.

3. Results and discussion

3.1. Catalytic performances

Fig. 1 presents the conversions of HC, CO, NO and NO₂ under stoichiometric CO + HC + NO_x + O₂ reaction conditions ($\lambda = 1$) over fresh Pd/La-A and Pd-Ce(x)/La-A catalysts. Over the temperature range from 150 to 200 °C, HC and NO did not take part in the reaction, while the reactions $\text{CO} + 1/2\text{O}_2 \rightarrow \text{CO}_2$ and $2\text{NO}_2 + 4\text{CO} \rightarrow \text{N}_2 + 4\text{CO}_2$ predominated. The light-off temperatures associated with CO and NO₂ conversions increased with increasing CeO₂ content, indicating that the addition of CeO₂ inhibited the conversion of CO and NO₂ when the temperature was below 200 °C. At 200–250 °C, the CO/O₂ and NO₂/CO reactions were still predominant, although NO₂ conversion over all catalysts decreased as the temperature increased and the CO conversion increased to 100%, suggesting that the CO/O₂ reaction occurred more rapidly than the NO₂/CO reaction. In contrast to the catalytic behavior below 200 °C, the conversion of

Fig. 1. Three-way conversion as a function of reaction temperature over Pd/La-A and Pd-Ce(x)/La-A catalysts calcined at 500 °C.

NO_2 in the higher temperature range was obviously enhanced with increasing CeO_2 content, and Pd-Ce(2.0)/La-A showed the highest activity.

Above 250 °C, the conversion of HC, NO and NO_2 increased as the temperature increased. It can be seen that HC conversion coincided with NO_x conversion in this range, since NO_x conversion is controlled via the reactions $10\text{NO} + 4\text{HC} \rightarrow 5\text{N}_2 + 4\text{CO}_2 + 2\text{H}_2\text{O}$ and $10\text{NO}_2 + 8\text{HC} \rightarrow 5\text{N}_2 + 4\text{CO}_2 + 4\text{H}_2\text{O}$ [22]. These results show that the presence of an optimum concentration of ceria promotes the catalytic activities associated with HC and NO_x removal. With increases in the CeO_2 content from 0.25 to 2.0 wt%, the catalytic activity first appeared to increase and then sharply decreased at 4.0 wt% of CeO_2 . Thus, the Pd-Ce(2.0)/La-A catalyst was also seen to exhibit better activity than the other catalysts.

Fig. 2 presents the conversions of HC, CO, NO and NO_2 under stoichiometric $\text{CO} + \text{HC} + \text{NO}_x + \text{O}_2$ reaction conditions ($\lambda = 1$) over Pd/La-A-a and Pd-Ce(x)/La-A-a catalysts calcined at 1100 °C. A large drop in catalytic activity was observed compared with the results obtained with the fresh catalysts (Fig. 1), because of the deteriorated structure and sintering of active components during the high-temperature pre-treatment [23]. In spite of this, the catalytic activity of the aged samples was still promoted with increasing CeO_2 content. Pd-Ce(4.0)/La-A-a exhibited the best catalytic activity for CO and HC oxidation while Pd-Ce(2.0)/La-A-a showed the best catalytic activity for

NO and NO_2 elimination. The results indicate that addition of the appropriate amount of CeO_2 promotes the thermal stability of the catalysts, and does not suggest any encapsulation of PdO_x species by ceria during the high-temperature pre-treatment, which could have important consequences in terms of improving the catalytic performance of close-coupled catalysts in automobile exhaust elimination.

In our experimental trials, we also evaluated the conversions of CO, HC and NO_x under different air/fuel ratios (λ) at 400 °C over fresh and aged catalysts. When using the fresh catalysts (data not shown here), there were no significant differences in the conversions of CO, HC and NO_x ; the HC conversion remained at 100% and the CO conversion was above 80% over the entire range of λ values. Moreover, the NO_x conversions only showed very slight differences from one another. However, the catalytic behavior did exhibit a noticeable change after the catalysts were aged at 1100 °C. As shown in Fig. 3, the conversion of CO dropped slightly with increasing ceria content under $\lambda < 1$ (lean oxygen) conditions. The HC conversion over Pd/La-A-a was also lower than 80% even at $\lambda > 1$ (rich oxygen) conditions, which may indicate a decrease in the catalytic activity for HC oxidation due to the reduction of PdO to Pd⁰ under the reaction conditions [24]. The NO_x conversion also dropped sharply when the λ value was above 0.95, demonstrating that the operational window of the Pd/La-A-a catalyst was significantly reduced after aging at 1100 °C. However, the operational

Fig. 2. Three-way conversion as a function of reaction temperature over Pd/La-A-a and Pd-Ce(x)/La-A-a catalysts calcined at 1100 °C.

Fig. 3. Conversions as a function of stoichiometric number (λ) over Pd/La-A-a and Pd-Ce(x)/La-A-a catalysts.

window was also broadened by the addition of CeO₂, and the conversions of HC and NO_x both obviously increased with increasing CeO₂ content, indicating that the presence of CeO₂ stabilizes PdO_x species in oxidized form because of the interaction between PdO_x and CeO₂. Pd-Ce(4.0)/La-A-a showed the widest operational window for HC conversion while Pd-Ce(2.0)/La-A-a exhibited the best catalytic behavior for NO_x

elimination. To obtain more information about the configuration of PdO_x particles on the surface of the support and the interactions between PdO_x and CeO₂, CO adsorption, HRTEM, H₂-TPR and in situ DRIFTS results obtained for the catalysts are analyzed below.

3.2. Structural properties

Pd dispersion and particle size results are presented in Table 1. For each fresh catalyst, Pd was well dispersed on the support and the calculated Pd particle sizes for these samples exhibited a slight increase with increasing CeO₂ contents. In contrast, the Pd particle sizes of the aged catalysts showed significant decreases as the CeO₂ content increased, demonstrating that the addition of CeO₂ enhances the stability of PdO_x species at high temperatures and helps to slow the sintering progress. The catalyst with a CeO₂ content of 2.0 wt% exhibited the highest Pd dispersion and smallest Pd particle size after being calcined at 1100 °C, results that are reflected in its catalytic performance.

Table 1 lists the calculated particle sizes of the metal Pd based on theoretical values, which will be somewhat different from the actual sizes of the PdO_x species in the catalysts. To further investigate the structural differences between Pd/La-A and Pd-Ce(2.0)/La-A on the atomic scale, the materials were further studied by TEM, and micrographs of the fresh samples are shown in Fig. 4. Only La₂O₃ and CeO₂ are observed in these samples, with interplanar distances of 0.307 and 0.312 nm, respectively. No PdO_x particles were found because of the low concentration and high dispersion of this species, and since the small Pd clusters are difficult to distinguish from the support. However, as demonstrated by Fig. 4(c) and Fig. 4(d), X-ray energy dispersive spectroscopy (EDS) line profile analysis confirmed that the bright spots in these images were composed of Pd and Ce, which clearly establishes the existence of a Pd-Ce structure in the Pd-Ce(2.0)/La-A catalyst.

The micrographs of aged samples are shown in Fig. 5. In Fig. 5(d), lattice fringes with interplanar spacings of 0.262 and 0.298 nm were determined to be associated with the (101) facet of PdO and the (011) facet of Ce₂O₃. As shown in Fig. 5(a) and Fig. 5(c), the PdO particle sizes exhibited growth after aging at 1100 °C because of significant agglomeration. It is obvious that the Pd-Ce(2.0)/La-A-a catalyst showed much smaller diameters for its Pd-Ce mixed oxides (20–50 nm) compared with the diameters of the PdO_x species in the Pd/La-A-a (70 nm). These results are consistent with the data presented in

Table 1
Pd dispersion and particle sizes.

Catalyst	n_{CO}^a (μmol/g)	D^b (%)	d^c (nm)	Catalyst	n_{CO}^a (μmol/g)	D^b (%)	d^c (nm)
Pd/La-A	24.06	25.60	4.4	Pd/La-A-a	1.35	1.44	77.3
Pd-Ce(0.25)/La-A	23.99	25.53	4.4	Pd-Ce(0.25)/La-A-a	1.97	2.10	53.0
Pd-Ce(0.5)/La-A	26.78	28.50	3.9	Pd-Ce(0.5)/La-A-a	2.52	2.68	41.5
Pd-Ce(1.0)/La-A	23.13	24.62	4.5	Pd-Ce(1.0)/La-A-a	2.51	2.67	41.7
Pd-Ce(2.0)/La-A	15.68	16.68	6.7	Pd-Ce(2.0)/La-A-a	2.68	2.85	39.1
Pd-Ce(4.0)/La-A	14.13	15.04	7.4	Pd-Ce(4.0)/La-A-a	2.43	2.59	43.0

^aThe amount of CO adsorbed on the Pd surface.

^bCalculated assuming the adsorption of one CO molecule on each Pd atom.

^cCalculated using Eq. (2).

Fig. 4. TEM images of Pd/La-A (a) and Pd-Ce(2.0)/La-A (b) as well as an HAADF-STEM image of Pd-Ce(2.0)/La-A (c) and the corresponding EDS line profile (d).

Fig. 5. TEM images of Pd/La-A-a (a, b) and Pd-Ce(2.0)/La-A-a (c, d).

Table 1, establishing that the addition of CeO_2 helps to stabilize PdO_x species with smaller particle sizes. This may be the main reason that the Pd-Ce(2.0)/La-A-a catalyst maintained good catalytic performance after the aging treatment.

3.3. H_2 -TPR results

Fig. 6 shows the H_2 -TPR profiles of fresh and aged catalysts. The fresh catalysts exhibit four hydrogen consumption peaks (α , β , γ and δ) in addition to a negative peak below 400 °C. According to our previous work [25], peak α is associated with the reduction of PdO_x species finely dispersed on the support, while the negative peak at 70 °C is generally attributed to the decomposition of palladium hydride when reduced Pd is ex-

posed to H_2 [10,23]. However, the negative peak disappears when the CeO_2 content reaches 0.5 wt% and peak β appears when the CeO_2 content further increases. Moreover, peak α undergoes a shift to a slightly higher temperature with increasing CeO_2 content. Osorio et al. [26] found that the addition of $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ mixed oxides to Al_2O_3 promoted the palladium-support interactions and some hard-to-reduce PdO_x species were formed when $x = 0.5$ and 0.33. Thus we suggest that there is a strong interaction between the metal and CeO_2 , leading to the catalysts having higher reduction temperatures, such that peak β can be attributed to the reduction of PdO_x species undergoing strong interactions with CeO_2 . Among these catalysts, there were no significant differences in the intensities and temperature locations of peaks γ and δ , indicating that these

Fig. 6. H₂-TPR profiles of fresh (a) and aged catalysts (b).

peaks may be related to the reduction of the La-modified Al₂O₃ support. According to the literature [27], contact between Pd and CeO₂ particles stabilizes the Pd clusters in an average Pd(I)-like oxidation state, and the presence of such oxidized Pd species serves as a source of oxygen to effectively decrease the light-off temperature during HC and NO conversions (Fig. 1). Additionally, the enhanced interactions between the PdO_x species and CeO₂, indicated by the shifts of both peaks α and β to higher temperatures, can be correlated to the decreased catalytic performance during CO and NO₂ conversions at low temperature.

After aging at 1100 °C, the H₂ consumption peaks α and β both decreased because of reduced dispersion of the active PdO_x species resulting from significant sintering during the aging process. Furthermore, this agglomeration of PdO_x species leads to weakening of the interactions between the PdO_x species and the support, thus shifting both peaks α and β to lower temperatures compared with the fresh catalysts. In the case of the aged catalysts, however, peaks α and β also shifted to higher temperatures with increasing CeO₂ content because of the strong interactions between the PdO_x and CeO₂.

3.4. In situ DRIFTS results

To assess the potential relationship between the presence of particular Pd phases and catalytic behaviors, in situ DRIFTS studies were performed under different reaction conditions. Fig. 7(a) and Fig. 7(b) present a set of in situ DRIFTS spectra obtained from fresh Pd/La-A and Pd-Ce(2.0)/La-A catalysts under a stoichiometric CO + HC + O₂ reaction mixture at 250 °C. Bands in the region of 1800–2100 cm⁻¹ can be attributed to carbonyls adsorbed on Pd⁰ sites. In these spectra, we can observe the presence of on-top-bonded (linear) Pd-CO at 2063 cm⁻¹ and a strong bridge-bonded Pd₂-CO peak at 1972 cm⁻¹ along with a three-fold hollow Pd₃-CO at 1909 cm⁻¹ [28,29], indicating that some PdO_x species are reduced to metallic Pd under these reaction conditions. However, the intensities of these features in the Pd/La-A spectra are much stronger than those obtained with Pd-Ce(2.0)/La-A, demonstrating that Pd-Ce(2.0)/La-A retains a large proportion of oxidized Pd spe-

cies and thus presenting fewer metallic Pd sites [28]. These results show that the presence of a small amount of CeO₂ promotes the reoxidation of Pd⁰ to PdO under reaction conditions. Furthermore, there is little evidence of the three-fold hollow Pd₃-CO species on the Pd-Ce(2.0)/La-A and the bridge/on-top-bonded CO bands are obviously shifted to lower wavenumbers. By analogy with observations reported for Pd-Au [30], the formation of Pd-Ce nanoparticles would cause the dilution of Pd in the CeO₂, thus limiting the extent of multi-bonded CO on Pd and further leading to the disappearance of the three-fold hollow Pd₃-CO band. The adsorption bands in the range of 1200–1800 cm⁻¹ can be attributed to surface carbonates/carboxylates species adsorbed on Al₂O₃ [31,32]. The intensities of these bands do not undergo visible changes over time, indicating that the concentration of carboxylates/carbonates species on the alumina surface is essentially saturated during the initial exposure to the CO + HC + O₂ reaction mixture because of the complete oxidation of CO at 250 °C.

Stoichiometric NO_x was abruptly added into the flow after 10 min exposure to a CO + HC + O₂ mixture at 250 °C and the corresponding spectra were collected as a function of time. As shown in Fig. 7(c) and (d), bands at 2253 and 2231 cm⁻¹ appear ascribed to isocyanate species adsorbing at octahedral and tetrahedral Al³⁺ cations, respectively [33]. These NCO species are formed by the interaction of unreacted CO with adsorbed N atoms (N_a) [34]. Two reaction mechanisms have been proposed for the formation of N_a; the first involves the unimolecular dissociative adsorption of NO to form N_a and O_a, while the second involves a direct bimolecular reaction between NO and CO to form N_a and CO₂ [35]. The significant intensity of the NCO band and its ready detection may be used to roughly determine the onset temperature for NO dissociation, and these bands are observed to reach a maximum after 2 min and then decrease slightly because of the NCO + NO + O₂ → N₂ reaction. However, it is noteworthy that the intensities of the NCO bands on the Pd-Ce(2.0)/La-A are much stronger than in the Pd/La-A, indicating that more NCO species are formed on the Pd-Ce(2.0)/La-A, and thus this process is responsible for the improved NO_x elimination performance seen for this catalyst at 250 °C, which is in accordance with the catalytic activity data

Fig. 7. DRIFTS spectra collected at varying time intervals during exposure of fresh Pd/La-A (a) and Pd-Ce(2.0)/La-A (b) to stoichiometric CO + HC + O₂ reaction conditions at 250 °C, and during exposure of Pd/La-A (c) and Pd-Ce(2.0)/La-A (d) to stoichiometric CO + HC + O₂ + NO_x reaction conditions at the same temperature.

shown in Fig. 1. Moreover, it is interesting that a new band is observed at 2175 cm⁻¹ in the Pd-Ce(2.0)/La-A spectra. According to the results of H₂-TPR analyses, there are two different PdO_x species dispersed in the catalyst and so this band may be related to NCO species produced on Pd⁰ sites having strong interactions with Ce atoms. Under such conditions, NCO species should be able to spill over onto CeO₂ sites because of the close contact of the PdO_x-CeO₂ particles. Simultaneously, three bands at 1610, 1575 and 1459 cm⁻¹ are also observed during the initial exposure to the CO + HC + NO_x + O₂ mixture, all of which reach a maximum after 5 min and then remain essentially constant. According to the literature, the band at 1610 cm⁻¹ can be assigned to bidentate nitrates species, while the 1575 and 1459 cm⁻¹ bands may be attributed to acetate species directly related to the reaction between surface nitrates species and HC [36]. The intensities of the nitrate/acetate bands in the Pd-Ce(2.0)/La-A spectra are also much stronger than those of the bands obtained from Pd/La-A, which is related to the superior NO/HC elimination performance of the Pd-Ce(2.0)/La-A at lower tem-

peratures. In addition, compared with Fig. 7(a) and (b), the intensities of the on-top/bridge-bonded CO species adsorbed on the Pd⁰ sites are obviously reduced under stoichiometric CO + HC + NO_x + O₂ reaction conditions, indicating that the presence of strongly oxidizing NO₂ species favors the stability of oxidized Pd species under these conditions, especially in the case of small Pd clusters.

To elucidate the reaction mechanism, a set of in situ DRIFTS spectra were obtained for the fresh catalysts under stoichiometric CO + NO_x + HC + O₂ reaction conditions from 50 to 400 °C. As shown in Fig. 8, three bands in the region of 1200–1800 cm⁻¹, assigned to nitrite/nitrates species in a variety of structures/configurations adsorbed on alumina [37,38], can be observed at 50 °C. The intensity of these features over the Pd-Ce(2.0)/La-A catalyst is much stronger than that over Pd/La-A and almost reaches an initial maximum at 50 °C, indicating better adsorption on the support after adding CeO₂, which may be favorable in terms of improving the NO reduction performance at lower temperatures. These bands decrease

Fig. 8. DRIFTS spectra of Pd/La-A (a) and Pd-Ce(2.0)/La-A (b) catalysts under stoichiometric CO + NO_x + HC + O₂ conditions from 50 to 400 °C.

in intensity with increasing reaction temperature. The band at 1319 cm⁻¹ assigned to monodentate nitrite species adsorbed on alumina [37] shifts to lower frequencies and disappears at about 270 °C, because of the effect of decreasing NO_x coverage caused by the thermodynamically favored desorption of NO_x and increasing CO-NO_x reaction activity. Bands in the region of 2100–2300 cm⁻¹, assigned to NCO species, and bands in the region of 1400–1800 cm⁻¹, because of acetate and nitrates species adsorbed on support, also appear and increase in intensity with increasing reaction temperature. As noted, the changes in those bands due to the conversion of NO_x and HC are in accordance with the observed catalytic performances. The intensities of the nitrate/acetate bands in the Pd-Ce(2.0)/La-A are much stronger than those in the Pd/La-A at the initial lower temperature, suggesting that the Pd-Ce(2.0)/La-A possesses better NO/HC elimination performance at lower temperatures. Moreover, in the case of the Pd/La-A catalyst, bands at 2061, 1972 and 1911 cm⁻¹, all assigned to the adsorption of CO on metallic Pd, begin to appear at 190 °C, indicating that a portion of the PdO_x species is reduced to metallic Pd under these stoichiometric reaction conditions. Also, very weak evidence of these Pd⁰-CO species can be observed in the Pd-Ce(2.0)/La-A catalyst at higher temperatures, demonstrating the improved stabilization of oxidized PdO_x species on the Pd-Ce catalysts.

4. Conclusions

A series of Pd-Ce/La-Al₂O₃ close-coupled catalysts were prepared by a co-adsorption impregnation method. In the case of each unaged catalyst, the presence of an appropriate quantity of CeO₂ obviously enhanced the catalytic activity during HC and NO eliminations because of interactions between PdO_x species and CeO₂ that improved the ability of Pd⁰ to reoxidize to PdO and enhanced the adsorption of nitrite/nitrates and isocyanate intermediate species under reaction conditions. The Pd-Ce(2.0)/La-A catalyst exhibited the best catalytic activity for

HC and NO eliminations and the addition of CeO₂ inhibited the conversions of CO and NO₂. The Pd-Ce(4.0)/La-A catalyst showed the lowest catalytic activity for CO, HC and NO_x eliminations, which may result from encapsulation of Pd particles by excess CeO₂ and associated inhibition of its catalytic performance. However, after aging treatment, the operational window for HC and NO_x conversions was obviously broadened because of the presence of optimal concentrations of CeO₂ (2.0–4.0 wt%), and the catalytic activities for CO, HC and NO_x eliminations were evidently promoted with increased levels of ceria content. These effects demonstrate that the presence of optimal CeO₂ concentrations favors stabilization of PdO_x species with smaller particle sizes because of the strong interactions between such PdO_x species and CeO₂.

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Graphical Abstract

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Effects of the addition of small quantities of ceria on the catalytic behavior of Pd-only close-coupled catalysts during automobile exhaust elimination

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The addition of an optimum concentration of ceria during the synthesis of Pd-only close-coupled catalysts by a co-adsorption impregnation method markedly improves the HC/NO conversions and the thermal stability of the Pd-Ce/La-Al₂O₃ catalyst.

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少量CeO₂的添加对Pd/La-Al₂O₃密偶催化剂三效性能的影响

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摘要: 以La改性的Al₂O₃为载体, 采用共吸附浸渍法制备了一系列不同CeO₂含量的单Pd密偶催化剂, 并对其进行了表征。PdO_x和CeO₂之间的强相互作用改善了Pd⁰再氧化为PdO的能力, 同时增强了反应条件下硝酸盐、亚硝酸盐和异氰酸盐在载体上的吸附。因

此适量CeO₂的添加明显改善了新鲜催化剂对HC和NO_x的催化性能,且当CeO₂添加量为2%时催化效果最佳。Pd-Ce界面上PdO_x和CeO₂间强相互作用也使得PdO_x物种在高温时仍能以小颗粒的形式分散在载体上,从而显著地提高催化剂的热稳定性。经1100 °C高温老化后,CeO₂ (2%–4%)的存在明显拓宽了HC和NO_x的操作窗口,这对于提高单Pd密偶催化剂在汽车尾气处理上的催化性能有重要意义。

关键词: 单钯密偶催化剂; 催化性能; 氧化铈; 热稳定性; 原位红外光谱

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1. 前言

随着汽车尾气污染排放的日益增加,各国相应的排放法规也越来越严苛。三效催化剂(TWC)是控制汽车尾气污染物排放的主要技术^[1]。目前投入商业应用的TWC包含了Pt/Rh, Pt/Pd/Rh, Pd/Rh和单Pd等贵金属催化剂^[2]。单Pd三效催化剂因为其显著的氧化反应活性和价格低廉等原因而广泛应用于汽车尾气的催化转化,配置单Pd三效催化剂的机动车数量也在增加^[3]。汽车尾气中HC排放物的80%–90%是在冷启动阶段生成的。因此,如果HC在冷启动阶段的排放量未得到有效控制,那传统的汽车将不能达到严格的排放标准^[4]。目前提出了众多解决冷启动问题的方案,包括HC捕集器,电加热催化剂,燃烧加热催化剂,废气点火,微波加热和密偶催化剂(CCC)^[5]。其中,CCC因为不需要配置附加装置和额外的能量输入而成为最直接有效的解决方法。CCC非常靠近汽车发动机,以便快速地提高催化剂的温度。然而,CCC催化转化器在实际的三效催化转化过程中温度可以达到1000 °C以上,导致Pd基催化剂在高温下烧结并从氧化态转变为金属态Pd从而失活^[6]。

众所周知,Ce通常被用作三效催化剂的助剂^[7–9]或载体^[10–12]。它由于具有在Ce³⁺和Ce⁴⁺之间灵活的转化能力,良好的热稳定性,与贵金属的兼容性和容易浸渍到氧化铝上等性能而被作为最主要的储氧材料^[2]。另一方面,Pd嵌入到CeO₂晶格中会形成Pd-O-Ce键,从而使Pd在载体表面高度分散^[13]。当Ce含量小于10 wt%时,Ce可以在氧化铝载体上以二维形式分布^[14],从而起到了联系Pd与Al₂O₃的桥梁作用。除此之外,氧化条件下CeO₂和Al₂O₃的强相互作用会使界面处生成CeAlO₃,有助于Al₂O₃表面的稳定^[15,16]。然而,Ce的添加量过大可能会对贵金属颗粒形成包覆,造成贵金属活性位点的不可逆流失^[17]。

Cargnello等^[6,18,19]利用巯基十一烷酸,巯基正醇和十二硫醇制备了不同巯基保护的Pd纳米颗粒,并将其与

Ce(IV)醇盐反应生成Pd@CeO₂纳米颗粒。但是这种方法并不适用于商业应用,而且Pd@CeO₂在高温下并不稳定。Wang等^[20]通过分布浸渍法制备了Pd-Ce催化剂: (1) 用PdCl₂的酸性水溶液作为前驱体将Pd浸渍在载体上; (2) 500 °C煅烧后,用同样的方法把Ce(NO₃)₃的水溶液浸渍在样品上。但是在这种方法中,Ce在第一步中没有引入。本文使用共吸附浸渍法来形成Pd-Ce系统,使Pd在初始阶段就可以稀释在Ce中,从而制备了一系列不同CeO₂含量的Pd-Ce密偶催化剂,并测量其三效催化活性。采用CO吸附,高分辨透射电镜, H₂-程序升温还原和原位红外(in situ DRIFTS)等手段进行表征,以期对PdO_x颗粒在载体表面的状态和PdO_x与CeO₂之间的相互作用进行深入研究。

2. 实验部分

2.1. 催化剂制备

La-Al₂O₃载体购买自Rhodia公司。Pd-Ce密偶催化剂在25 °C采用共吸附浸渍法来制备,Pd含量为1 wt%。Pd(NO₃)₂和Ce(NO₃)₃的水溶液先混合搅拌20 min (CeO₂含量分别为0, 0.25, 0.5, 1.0, 2.0和4.0 wt%),然后把适量的Al₂O₃载体快速加入溶液中。继续搅拌过夜后在110 °C干燥,500 °C焙烧2 h得到新鲜的催化剂样品,分别命名为Pd/La-A和Pd-Ce(x)/La-A (x = 0.25, 0.5, 1.0, 2.0, 4.0)。最后取部分催化剂在1100 °C焙烧4 h来研究样品的热稳定性。老化后的样品分别命名为Pd/La-A-a和Pd-Ce(x)/La-A-a (x = 0.25, 0.5, 1.0, 2.0, 4.0)。

2.2. 催化剂评价

催化剂活性评价仪器为自建的微反装置,Bruker EQ55型傅立叶气体红外分析仪在线检测进出反应器气体。在石英管中填装0.2 mL催化剂,并在其两端填充石英棉。反应气的流量由质量流量控制器来控制,其组成为NO 0.12%, NO₂ 0.03%, C₃H₆ 0.066%, C₃H₈ 0.033%, CO 0.6%和O₂ 0.745%,载气为Ar,空速为43000 h⁻¹ (计算于催化剂的体积与室温下的气体流速)。虽然在反应过

程中产生了少量的H₂O, 但它的存在会损坏FTIR分光仪. 因此在气体进入仪器之前便除去了H₂O, 它的浓度也没有列于图表中.

空燃比定义为 $\lambda = (2V_{O_2} + V_{NO} + 2V_{NO_2}) / (V_{CO} + 9V_{C_3H_6} + 10V_{C_3H_8})$, 其中 V 代表各气体组分的体积百分含量, $\lambda = 1$ 应用于所有的活性评价中. 催化剂窗口测试在400 °C下进行, 通过调节氧含量来设置不同的 λ 值.

2.3. 催化剂表征

H₂-TPR实验在GC-1690型色谱分析仪上进行. 将50 mg催化剂在N₂气氛下(30 ml/min) 200 °C处理30 min, 用液氮冷却至-90 °C后, 通入5 vol% H₂/Ar (40 ml/min)至基线稳定, 再以10 °C/min升温至900 °C. 还原过程中消耗的氢气通过热导检测器(TCD)进行检测.

CO吸附在室温下由CHEMBET-3000型(Quantachrome公司)化学吸附仪进行检测, 以此计算Pd的分散度和颗粒尺寸. 实验前, 样品在5% H₂-95% N₂气氛中400 °C还原1 h, 在He中保持30 min后, 样品在He中冷却至室温并保持30 min. 最后, CO每隔5 min脉冲入样品中直到没有检测到CO的消耗为止. Pd的分散度(D)计算如下^[21]:

$D(\%) = 100 \times [(V_{CO} \times f) / (C_{Pd} \times m_{Cat} \times 22414)] \times m$ (1)
 V_{CO} , CO吸附的体积(mL); f , 化学计量数; C_{Pd} , 金属Pd的含量(wt%); m_{Cat} , 催化剂的质量(g). Pd颗粒尺寸(d)计算如下:

$d(nm) = 6 \times 10^5 \times M_{Pd} / (\rho_{Pd} \times D \times S_{Pd})$ (2)
 M_{Pd} , Pd的摩尔质量(106.42 g/mol); ρ_{Pd} , Pd的密度(12 g/cm³); S_{Pd} , Pd的摩尔表面积($S = 47780$ m²/mol).

HRTEM照片由TECNAI G220型透射电镜表征获得, 工作电压为200 kV. 催化剂首先在研钵中碾碎, 无水乙醇中超声分散后担载在镀有碳膜的铜网上. EDS分析用来记录元素分布, 从而得到化学组成.

原位漫反射红外傅立叶变换光谱测试(In situ DRIFTS)在配置了MCT (merbury-cadmium-telluride)检测器的Nicolet 6700 FTIR分光仪上进行. 原位池窗片为CaF₂, 有一个可加热的反应室来进行高温反应, 扫描次数32, 分辨率4 cm⁻¹. 催化剂在Ar中450 °C下预处理30 min, 然后冷却至30 °C. 反应器的组成和流速在反应过程中保持稳定.

3. 结果与讨论

3.1. 催化剂的活性评价

图1给出了模拟汽车尾气气氛下($\lambda = 1$)新鲜Pd/La-A

和Pd-Ce(x)/La-A催化剂上HC, CO, NO和NO₂的转化率. 由图1可见, 在150–200 °C温度范围, HC和NO并未参与反应, 而 $CO + 1/2O_2 \rightarrow CO_2$ 和 $2NO_2 + 4CO \rightarrow N_2 + 4CO_2$ 在反应中占主导地位. CO和NO₂的起燃温度随着CeO₂添加量的增加而增高, 说明当温度低于200 °C时, CeO₂的添加抑制了CO和NO₂的转化. 在200–250 °C的温度范围, CO/O₂和NO₂/CO反应仍然是主要的. 各催化剂上CO转化率均达到100%, 而NO₂的转化率却随着温度的增加而降低, 可能是由于CO/O₂反应比NO₂/CO反应进行得更快. 不同的是, 在200–250 °C温度范围中各催化剂上NO₂转化率随CeO₂添加量的增加而增大, 其中Pd-Ce(2.0)/La-A表现出最好的NO₂还原的活性.

当温度大于250 °C时, HC, NO和NO₂的转化率随温度增加而增大, HC与NO转化曲线一致. 研究发现^[22], NO_x的转化由 $10NO + 4HC \rightarrow 5N_2 + 4CO_2 + 2H_2O$ 和 $10NO_2 + 8HC \rightarrow 5N_2 + 4CO_2 + 4H_2O$ 两个反应来控制. 以上结果表明, 适量CeO₂的添加可以提高HC和NO_x的反应活性. 随着CeO₂添加量从0.25增加到2.0 wt%, 催化活性明显增强, 至4.0 wt%时活性急剧下降. 其中Pd-Ce(2.0)/La-A表现出最好的催化活性.

图2为模拟汽车尾气气氛下($\lambda = 1$)老化后的Pd/La-A和Pd-Ce(x)/La-A催化剂上HC, CO, NO和NO₂的转化率. 与图1相比, 老化后催化剂的活性大大减弱, 这与催化剂在高温处理后(1100 °C)导致的活性组分烧结和载体结构塌陷有关^[23]. 尽管如此, 催化剂的活性仍随着CeO₂添加量的增加而增强, 其中Pd-Ce(4.0)/La-A-a呈现出最好的CO和HC的氧化活性, 而Pd-Ce(2.0)/La-A-a催化NO和NO₂还原活性最高. 这说明适量CeO₂的添加会在不包覆PdO_x物种的情况下提高催化剂的热稳定性, 这对改善密偶催化剂的活性有重要意义.

本文还评估了400 °C时不同空燃比窗口下CO, HC和NO_x在新鲜和老化催化剂上的转化. 对于所有的新鲜催化剂(数据未列出), CO, HC和NO_x的转化率并没有明显差异. HC均为100%转化, CO的转化率在整个 λ 范围都高于80%, NO_x的转化率也只有轻微的区别. 然而, 在1100 °C老化之后, 各催化剂的催化行为变化显著. 如图3所示, 在贫氧条件下($\lambda < 1$), CO的转化率随着CeO₂添加量的增加而有所下降. Pd/La-A-a上HC转化率在整个窗口中都低于80%, 这可能是因为PdO在老化过程中还原为Pd⁰而导致HC氧化活性的降低^[24]. 当 $\lambda > 0.95$ 时, Pd/La-A-a的NO_x转化率急剧减少. 由此可见, 1100 °C的高温老化明显破坏了Pd/La-A-a的操作窗口. 但是, CeO₂

的添加拓宽了催化剂的操作窗口, HC和NO_x的转化率也随着CeO₂添加量的增加而明显增大, 这表明PdO_x和CeO₂间的相互作用可以使PdO_x物种稳定在氧化态. Pd-Ce(4.0)/La-A-a有最宽的HC窗口, 而Pd-Ce(2.0)/La-A-a有最宽的NO_x窗口. 为得到关于PdO_x物种在载体表面的构型和PdO_x与CeO₂间相互作用的信息, 对催化剂进行了CO吸附, HRTEM, H₂-TPR和原位红外等表征.

3.2. 结构特性

各催化剂的Pd分散度及其颗粒尺寸列于表1. 对所有新鲜催化剂来说, Pd在载体表面分散度都较高, Pd颗粒尺寸随着CeO₂含量的增加而略有增大. 反之, 催化剂老化后Pd的颗粒尺寸随着CeO₂含量的增加而减小, 说明CeO₂的添加可以增强PdO_x物种的高温稳定性并减缓烧结的过程, 这可以与催化剂的活性变化趋势相关联. 含2% CeO₂的催化剂在1100 °C老化后呈现出最高的Pd分散度和最小的Pd颗粒尺寸.

如表1所示, 金属Pd颗粒尺寸的理论值与PdO_x颗粒的实际大小并不相同. 为了从原子尺度来研究Pd/La-A和Pd-Ce(2.0)/La-A结构上的不同, 我们对催化剂进行了TEM表征. 如图4所示, 新鲜催化剂上只能观测到La₂O₃ (0.307 nm)和CeO₂ (0.312 nm)的晶面间距. 由于PdO_x颗粒含量低, 分散度高以及小的Pd簇不易与载体区分等原因而无法在图中找到. 然而对Pd-Ce(2.0)/La-A进行的EDS线扫描分析显示(图4(c)和(d)), 图中的白点由Pd和Ce共同组成, 清晰地指出了Pd-Ce结构的存在.

图5是老化催化剂的TEM照片. Pd-Ce(2.0)/La-A上也能观察到PdO的(101)晶面($d = 0.262$ nm)和Ce₂O₃的(011)晶面($d = 0.298$ nm). 如图5(a)和(c)所示, 老化后PdO的颗粒尺寸因烧结作用而急剧增大. 但Pd-Ce(2.0)/La-A-a中的Pd-Ce复合氧化物颗粒尺寸(20–50 nm)明显比Pd/La-A-a的PdO颗粒尺寸(70 nm)更小, 这与表1结果一致, 证明CeO₂的添加有助于稳定PdO_x物种的颗粒尺寸. 这可能是Pd-Ce(2.0)/La-A-a在老化后也能保持良好的催化活性的主要原因.

3.3. H₂-TPR结果

图6为新鲜和老化后催化剂的H₂-TPR谱. 新鲜催化剂在400 °C以下出现了四个峰(α , β , γ 和 δ)以及一个负峰. α 峰可归属于高度分散在载体上PdO_x物种的还原, 70 °C左右的负峰则对应于氢化钯的分解^[25]. 其中, 氢化钯是由PdO还原生成的金属Pd与H₂进一步作用所形成^[10,23]. 当催化剂中CeO₂的添加量达到0.5 wt%时, 负峰消失. 随着CeO₂的添加量进一步增加, β 峰开始出现. 此外, α 峰

逐渐往高温偏移. Osorio等^[26]发现, Ce_xZr_{1-x}O₂复合氧化物的添加在可促进Pd与Al₂O₃间相互作用, 当 $x = 0.5$ 和0.33时, 会有部分难以被还原的PdO物种形成. 因此我们推测 α 峰往高温迁移与Pd和载体间相互作用增强有关, 而 β 峰也可归属于与CeO₂有强相互作用的PdO_x物种的还原. 对所有新鲜催化剂来说, γ 和 δ 峰的强度与峰温都没有明显的区别, 表明这两个峰的出现可能与La改性的Al₂O₃载体的还原有关. 研究发现^[27], Pd和CeO₂的相互作用可以使Pd簇稳定在Pd⁺氧化态, 而Pd⁺的存在可以有效地降低HC和NO的起燃温度(如图1). 除此之外, α 峰与 β 峰往高温偏移说明Pd和CeO₂的相互作用逐渐增强, 这也许是低温下CO和NO₂转化率随着CeO₂的添加而减少的原因.

1100 °C老化后, 催化剂的高温烧结造成活性PdO_x物种分散度降低, 使得 α 峰与 β 峰的耗氢量减少. PdO_x物种的烧结造成PdO_x与载体的相互作用减弱, 因此与新鲜催化剂相比, α 峰与 β 峰均移向较低温度. 但是在老化催化剂中, Pd和CeO₂的强相互作用仍然导致了 α 峰与 β 峰随着CeO₂的添加往高温偏移.

3.4. In situ DRIFTS结果

为了观察在催化反应中特定Pd物相的存在与催化反应之间的联系, 我们在不同反应条件下对催化剂进行了原位红外表征. 图7(a)和(b)为250 °C时新鲜催化剂Pd/La-A和Pd-Ce(2.0)/La-A在CO + HC + O₂气氛下采集的谱图. 1800–2100 cm⁻¹之间出现的峰归属于羰基物种在Pd⁰上的吸附. 其中2063 cm⁻¹是线式吸附Pd-CO, 1972 cm⁻¹是桥式吸附Pd₂-CO, 1909 cm⁻¹是三原子协同吸附Pd₃-CO^[28,29], 说明部分PdO_x物种在反应条件下会部分还原为金属态的Pd. Pd/La-A上这三种吸附峰强度明显大于在Pd-Ce(2.0)/La-A上的峰强, 表明Pd-Ce(2.0)/La-A被还原的金属Pd较少^[28], 这说明少量CeO₂的存在能促进反应条件下Pd⁰再氧化为PdO的过程. 此外, 我们很难在Pd-Ce(2.0)/La-A上看到Pd₃-CO吸附物种, 同时桥式吸附与线式吸附的峰也往低波数偏移. 从文献[30]类推, Pd-Ce复合氧化物纳米颗粒的形成使得Pd可以在CeO₂中稀释, 从而限制了Pd₂-CO的形成并导致Pd₃-CO的消失. 1200–1800 cm⁻¹之间的峰归属于在Al₂O₃表面吸附的碳酸盐与羧酸盐物种^[31,32]. 这些物种的吸附峰强度随着时间的增加并没有明显的变化, 可能是因为催化剂在250 °C刚暴露于CO + HC + O₂气氛中时, 碳酸盐与羧酸盐物种在Al₂O₃表面的吸附就几乎达到最大值. 这可能与CO在该温度下已经完全转化有关.

催化剂暴露在 $\text{CO} + \text{HC} + \text{O}_2$ 气氛中10 min后, 化学计量的 NO_x 也快速加入了反应气氛中. 如图7(c)和(d)所示, 2253与2231 cm^{-1} 处的吸收峰分别代表NCO在八面体的 Al^{3+} 与四面体的 Al^{3+} 上的峰^[33]. NCO物种是由吸附的N原子与未反应的CO相互作用而形成^[34]. N_a 的形成有两种机理: (1)由NO的单分子解离吸附形成 N_a 和 O_a ; (2)由NO与CO的双分子反应形成 N_a 和 CO_2 ^[35]. NCO的出现时机和峰强可以对NO分解的起燃温度作粗略考量. 两种NCO吸附峰的峰强在第2 min时就达到最大值, 然后随着反应 $\text{NCO} + \text{NO} + \text{O}_2 \rightarrow \text{N}_2$ 的出现而逐渐减弱. 值得注意的是, Pd-Ce(2.0)/La-A上NCO的吸附峰远远强于在Pd/La-A上的, 表明Pd-Ce(2.0)/La-A上形成了更多的NCO物种, 从而更有利于 NO_x 在250 °C的转化, 这与催化活性的数据一致(图1). Pd-Ce(2.0)/La-A在2175 cm^{-1} 处出现一个新峰. 由 H_2 -TPR结果可知催化剂中有两种不同的 PdO_x 物种, 而2175 cm^{-1} 处的峰可能是NCO吸附在与 CeO_2 有强相互作用的 Pd^0 上所致. 与此同时, 在1610, 1575和1459 cm^{-1} 处也出现了三个峰, 并且在第5 min达到最大峰强. 其中1610 cm^{-1} 归属于双配位的硝酸盐物种, 1575和1459 cm^{-1} 归属于表面硝酸盐物种与HC反应形成的醋酸盐^[36]. Pd-Ce(2.0)/La-A上硝酸盐和醋酸盐的吸附峰强度也大于在Pd/La-A上的峰强, 这与前者有更好的NO/HC催化活性相关. 此外, 与图7(a)和(b)相比, CO在 Pd^0 上的吸附峰强度在通入 NO_x 后变弱, 说明具有强氧化性的 NO_2 的存在有助于稳定氧化钯物种, 特别是小的Pd簇.

为了阐明催化剂的反应机理, 新鲜催化剂在汽车尾气气氛中从50到400 °C进行了一系列原位红外的表征. 如图8所示, 50 °C时可以观测到在1200–1800 cm^{-1} 出现三个主要的吸附峰, 归属于在 Al_2O_3 上形成的结构各不相同的亚硝酸盐/硝酸盐^[37,38]. Pd-Ce(2.0)/La-A上这三个峰的强度明显强于Pd/La-A, 并且在50 °C时就几乎达到最大峰强. 说明 CeO_2 的添加更利于载体对亚硝酸盐/硝

酸盐的吸附, 进而有利于NO在低温下的转化. 这些峰随着温度的升高而减弱. 温度的升高使CO- NO_x 活性增强, NO_x 的脱附也增多, 这使得 NO_x 在催化剂表面的吸附量减少, 因而单齿配位的亚硝酸盐物种(1319 cm^{-1})^[37]随着温度的升高逐渐迁移向低波数并且在270 °C消失. 亚硝酸盐物种消失的同时, NCO物种的吸附峰(2100–2300 cm^{-1})和醋酸盐与硝酸盐的吸附峰(1400–1800 cm^{-1})开始出现, 并且随着温度的升高而增强. 如前所述, 这些峰的变化与HC和 NO_x 的催化活性相关. 与Pd/La-A相比, Pd-Ce(2.0)/La-A上这些峰出现的温度更低, 峰更强, 表明其催化HC/ NO_x 反应的活性更高. Pd/La-A上, 三个归属于CO在 Pd^0 上吸附的峰(2061, 1972和1911 cm^{-1})出现于190 °C, 说明反应气氛中部分 PdO_x 物种被还原为金属态Pd. 然而在Pd-Ce(2.0)/La-A上几乎不能检测到CO的吸附峰, 说明 CeO_2 的添加有利于 PdO_x 物种的稳定.

4. 结论

以La- Al_2O_3 为载体, 采用共吸附浸渍法制备了一系列不同 CeO_2 含量的单Pd密偶催化剂. 结果表明, CeO_2 的添加明显提高了催化剂对HC和NO的催化活性. 这是由于 PdO_x 和 CeO_2 间的强相互作用改善了 Pd^0 再氧化为 PdO 的能力, 同时增强了反应条件下硝酸盐, 亚硝酸盐和异氰酸盐在载体上的吸附. Pd-Ce(2.0)/La-A呈现了最好的HC和 NO_x 的催化活性. 然而 CeO_2 的添加抑制了CO和 NO_2 的转化. Pd-Ce(4.0)/La-A对CO, HC和 NO_x 的催化活性均为最差, 这可能是由于过量的 CeO_2 会对Pd形成包覆, 从而抑制了其催化性能. 然而, 老化后的催化剂中, 适量的 CeO_2 (2%–4%)的添加明显拓宽了HC和 NO_x 的操作窗口. 同时, CeO_2 的添加明显提高了催化剂对三种反应物的催化活性. 这是因为Pd-Ce界面上 PdO_x 和 CeO_2 间的强相互作用使得 PdO_x 物种在1100 °C高温老化后仍能以小颗粒的形式分散在载体上, 从而显著地提高催化剂的热稳定性.