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Mechanistic insight into N₂O formation during NO reduction by NH₃ over Pd/CeO₂ catalyst in the absence of O₂

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ABSTRACT

N₂O is a major by-product emitted during low-temperature selective catalytic reduction of NO with NH₃ (NH₃-SCR), which causes a series of serious environmental problems. A full understanding of the N₂O formation mechanism is essential to suppress the N₂O emission during the low-temperature NH₃-SCR, and requires an intensive study of this heterogeneous catalysis process. In this study, we investigated the reaction between NH₃ and NO over a Pd/CeO₂ catalyst in the absence of O₂, using X-ray photoelectron spectroscopy, NH₃-temperature-programmed desorption, NO-temperature-programmed desorption, and *in-situ* Fourier-transform infrared spectroscopy. Our results indicate that the N₂O formation mechanism is reaction-temperature-dependent. At temperatures below 250 °C, the dissociation of HON, which is produced from the reaction between surface H• adatoms and adsorbed NO, is the key process for N₂O formation. At temperatures above 250 °C, the reaction between NO and surface N•, which is produced by NO dissociation, is the only route for N₂O formation, and the dissociation of NO is the rate-determining step. Under optimal reaction conditions, a high performance with nearly 100% NO conversion and 100% N₂ selectivity could be achieved. These results provide important information to clarify the mechanism of N₂O formation and possible suppression of N₂O emission during low-temperature NH₃-SCR.

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1. Introduction

Nitrogen oxides (mainly NO and NO₂, named as NO_x) emitted during the combustion of fossil fuels cause serious environmental problems such as acid rain, photochemical smog, and ozone depletion [1,2]. Low-temperature selective catalytic reduction of NO with NH₃ (NH₃-SCR) was advocated to be a

preferential method for the abatement of NO_x emitted from the flue gas in steel, cement, glass, and other non-power-plant industries [3–6]. However, the formation of undesired by-products of N₂O during the low-temperature NH₃-SCR process is a great constraint because of their greenhouse effect and potential for the destruction of the stratospheric ozone layer [7]. Therefore, detailed knowledge of the mechanism of N₂O

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formation during the NO abatement by low-temperature NH₃-SCR is indispensable for the rational design of effective catalysts with good N₂ selectivity. Several reaction mechanisms for the formation of N₂O in the low-temperature NH₃-SCR process over metal-oxide-supported noble metal catalysts have been proposed. For example, Otto *et al.* [8] and Takoudis *et al.* [9] proposed that N₂O produced over Pt/Al₂O₃ is a combination of two nitroxyl species (HNO); however, the reaction intermediate HNO has never been observed experimentally. Pérez-Ramírez *et al.* [10] suggest that the coupling of ammonia intermediates (NH_x) and nitric oxide is the exclusive route for N₂O formation. The coupling of two adsorbed NO molecules, the recombination of an adsorbed NO molecule with an adsorbed NH_x fragment, and the coupling of un-dissociated NO molecules with N• adspecies were considered to be possible pathways for N₂O formation over a Pt–Ba/Al₂O₃ LNT catalyst, based on isotopic labeling experiments [11,12]. Due to the complexity of this reaction system, the reaction mechanisms of the whole system are complicated, and more fundamental studies are expected to provide further insights into the pathways involved in N₂O formation.

Cerium oxide (CeO₂) has been extensively investigated in the field of heterogeneous catalysis due to its unique redox properties and high oxygen storage capacity [13]. Although pure CeO₂ generally exhibits poor NH₃-SCR activity as an active component [14], the use of CeO₂ as a support can significantly enhance the catalytic activity via the increased dispersion and stabilization of the active species as well as the activation of the reaction gas [15–19]. Earlier studies revealed that Pd metal is capable of activating NO and enables the reduction of NO with H₂ [20], CO [21], and hydrocarbons [22]. However, research on the Pd-containing catalysts applied in the NO abatement by NH₃ is limited.

In this study, Pd nanoparticles were selected as the active components loaded on a CeO₂ support, and the activity for low-temperature NH₃-SCR of NO was studied; special attention was paid to N₂O formation and its related mechanisms. Our results indicated that the formation of N₂O was temperature-dependent; below 250 °C, N₂O was produced through the decomposition of the HON intermediate, and above 250 °C, N₂O resulted from the reaction of N• and NO in the absence of O₂.

2. Experimental

2.1. Catalyst preparation

CeO₂ nanorods were prepared via a hydrothermal method, according to the literature [23]. Typically, 20 ml Ce(NO₃)₃ solution (0.4 mol/L) was dropped into 140 ml NaOH solution (9 mol/L) and stirred for 30 min at room temperature. Then, the mixed solution was transferred into a 200 ml Teflon-lined stainless steel autoclave and heated at 100 °C for 24 h. After hydrothermal treatment, the precipitates were collected by centrifugation, washed with deionized water, and dried at 80 °C overnight. Finally, the product was calcined at 600 °C for 2 h under flowing air.

A Pd/CeO₂ catalyst was prepared using the solid grinding

method [24]. Pd(acac)₂ powder was mixed with the CeO₂ nanorods and ground in a mortar pestle for 30 min. Thereafter, the sample was calcined at 280 °C for 4 h under flowing air and then at 400 °C for 2 h under high-purity nitrogen.

2.2. Catalyst characterization

The amount of Pd loaded on the CeO₂ nanorods was measured to be 3%, via inductively coupled plasma analysis. The morphology, structure, and composition of the catalyst were identified using transmission electron microscopy (TEM; FEI Titan 80-300KV FEG TEM), X-ray diffractometry (XRD; Philips XD-98 X-ray diffractometer with Cu K_α radiation, λ = 0.15406 nm), and X-ray photoelectron spectroscopy (XPS; Thermo Scientific ESCALAB 250Xi system with Al K_α radiation of 1486.6 eV, using the C 1s binding energy of 284.8 eV as a reference).

NH₃-temperature-programmed desorption (NH₃-TPD) tests were carried out in a Micromeritics Autochem II 2920 apparatus with a thermal conductivity detector (TCD). A 100 mg sample was pretreated at 300 °C under helium atmosphere (40 ml/min) for 1 h, and subsequently cooled to 60 °C under the same airflow. Thereafter, the sample was exposed to 10% vol NH₃/He flow (20 ml/min) for 2 h, and the physisorbed NH₃ was purged with helium before the TPD test. TCD curves were recorded from 50 to 800 °C at a heating rate of 10 °C/min.

An NO-TPD experiment was carried out in a fixed-bed flow reactor. Prior to the experiment, the sample was treated at 400 °C for 1 h and then cooled to 100 °C. 800 ppm NO balanced with N₂ at a flow rate of 500 ml/min was passed through the sample for 2 h. After it reached a saturation stage, the sample was flushed with pure N₂ (500 ml/min) until the NO_x signal stabilized. Finally, the sample was heated up to 450 °C (ramp of 2 °C/min), and the concentrations of NO/NO₂ and N₂O desorbed from the catalyst surface were detected, with a temperature interval of 10 °C, using the Testo AG testo 335 and Medi-Gas G200 instruments, respectively.

In-situ transmission infrared (IR) spectra were recorded on a CRCP-7070 micro transient reaction integrated platform, which was built by the Tianjin Xianquan Company. The platform was equipped with an *in-situ* IR reaction cell containing a gas flow system and a liquid-nitrogen-cooled MCT detector. The catalyst was pretreated at 300 °C under flowing N₂ for 30 min before spectrum acquisition. The background spectrum recorded under flowing N₂ was subtracted from the sample spectrum.

2.3. Catalyst performance

Catalytic activity measurements were conducted in a fixed-bed flow reactor. 1.0 g catalyst powder was pasted on seven 4 cm × 10 cm aluminum plates. The plates were placed in a reactive tank, at 5 mm intervals. The reactant gas was composed of 800 ppm NO and 800 ppm NH₃ balanced with N₂ at a total flow rate of 500 ml/min, corresponding to a gas hourly space velocity (GHSV) of 36000 h⁻¹. In order to simplify the system, O₂ was removed intentionally in this study, and the reaction between NO and NH₃ could be studied without inter-

ference. The Testo AG testo 335 instrument was applied to monitor the inlet and outlet concentrations of NO/NO₂, whereas the N₂O concentration was monitored using the Medi-Gas G200 instrument. The conversion of NO was calculated using the following equation:

$$\text{NO}_x \text{ conv. (\%)} = \frac{[\text{NO}_x]_{\text{in}} - [\text{NO}_x]_{\text{out}}}{[\text{NO}_x]_{\text{in}}}$$

Where $[\text{NO}_x]_{\text{in}}$ and $[\text{NO}_x]_{\text{out}}$ represent the sums of the concentrations of NO and NO₂ at the inlet and outlet, respectively.

3. Results and discussion

The structure and morphology of the Pd/CeO₂ catalyst was characterized using TEM. As shown in Fig. 1(a), the CeO₂ support exhibited a nanorod morphology with an average diameter of about 20 nm. Fig. 1(b) is an enlarged image of the area marked by a white dashed rectangle in Fig. 1(a). The *d*-spacing of approximately 3.13 Å measured on the nanorod was indexed as CeO₂ {111}, and the supported nanoparticles on the catalyst surface, with a *d*-spacing of approximately 1.92 Å, could be attributed to the {200} planes of Pd. It is notable that there is no obvious interface between the Pd nanoparticles and CeO₂, which can result from the formation of a solid solution of Pd_xCe_{1-x}O₂ at the interface [25]. Moreover, many subnanometer Pd clusters (marked by white circles) are present in Fig. 1(a) and (b), indicating a good dispersion of Pd on CeO₂. The size distribution of Pd is shown in Fig. 1(c); almost all the clusters have a diameter less than 2 nm. The XRD pattern of the Pd/CeO₂ catalyst is displayed in Fig. 1(d), wherein all the diffraction peaks are consistent with the characteristic peaks of cubic phase CeO₂ (JCPDF 34-0394) and no diffraction peak can be identified for Pd, in good agreement with the TEM observation.

The atomic concentrations and element chemical states of

the catalyst surface were investigated using XPS, and the results are shown in Fig. 1(e) and (f). By performing peak-fitting deconvolutions, the Ce 3*d* spectrum can be divided into eight characteristic peaks: *v* (882.3 eV), *v'* (884.4 eV), *v''* (888.5 eV), *v'''* (898.2 eV), *u* (900.8 eV), *u'* (903.0 eV), *u''* (907.4 eV), and *u'''* (916.6 eV). The bands labeled as *v'* and *u'* were ascribed to Ce³⁺, and the other six bands were assigned to Ce⁴⁺ [26]. The relative surface content of Ce³⁺/(Ce³⁺+Ce⁴⁺) was measured to be about 12.6%; Ce³⁺ defects and oxygen vacancies in the CeO₂ nanorods are reported to play an important role in their catalytic performance [27]. The spectrum of Pd 3*d* was divided into four peaks, as shown in Fig. 1(e). The peaks at 335.5 and 340.7 eV can be assigned to metallic Pd⁰, and the other two peaks (337.5 and 342.6 eV) can be attributed to ionic Pd²⁺ located in the structure of the Pd_xCe_{1-x}O₂ solid solution at the surface and subsurface layers of the ceria lattice [25,28,29].

It is well-recognized that the adsorption of reaction gases on the catalyst surface always plays a crucial role in the catalyst performance. Therefore, NH₃-TPD and NO-TPD were performed to evaluate their adsorption (Fig. 2). The NH₃-TPD profile shows distinct desorption peaks located at 50–400 °C, belonging to NH₃ desorption from weak (60–180 °C) and medium (180–400 °C) acid sites distributed on the catalyst surface [30]. The small peak located at 488 °C belongs to the strong acid sites [31,32]. According to the NO-TPD profile shown in Fig. 2(b), NO started to desorb at 120 °C and showed a maximum concentration at 275 °C; even above 400 °C, NO desorption was detectable, suggesting that NO strongly adsorbed on the catalyst during the reaction. Moreover, N₂O was also found to be desorbed in the temperature range of 250–370 °C, with a maximum concentration of 18 ppm at 310 °C, which could be attributed to the dissociation of NO to N• and O• on the catalyst surface. The curve for N₂O formation in Fig. 2(b) also indicated

Fig. 1. (a) TEM image of Pd/CeO₂ catalyst; enlarged HRTEM image (b) and size distribution (c) of Pd clusters; (d) XRD pattern of the Pd/CeO₂ catalyst; XPS results for Ce 3*d* (e) and Pd 3*d* (f).

Fig. 2. NH_3 -TPD (a) and NO -TPD (b) profiles of the Pd/CeO_2 catalyst.

that the direct dissociation of NO only occurred at temperatures above 250°C . It is notable that the appearance of N_2O is accompanied by a decrease in NO desorption, which further indicates that the detected N_2O is attributable to the NO dissociation.

The *in-situ* transmission IR spectra for the reaction between NO and the adsorbed NH_3 species over the Pd/CeO_2 catalyst at 250°C are depicted in Fig. 3(a). The catalyst was firstly treated with NH_3 for 30 min and then purged with N_2 . The bands at 1124 and 1570 cm^{-1} originated from coordinated NH_3 on Lewis acid sites, whereas the other two bands at 1466 and 1635 cm^{-1} were ascribed to $\delta_{\text{as}}(\text{NH}_4^+)$ and $\delta_{\text{s}}(\text{NH}_4^+)$ bound to Brønsted acid sites, respectively [30,33]. Activated NH_3 species ($-\text{NH}_2$) were also indicated by the bands at 1315 and 1370 cm^{-1} [26]. Earlier studies suggested that both CeO_2 and Pd were the active sites for NH_3 adsorption and activation [34,35]. When NO was introduced into the system, all the adsorbed NH_3 species, including the coordinated NH_3 on Lewis acid sites, NH_4^+ , and $-\text{NH}_2$, were rapidly consumed within 5 min, implying that the adsorbed NH_3 , NH_4^+ , and $-\text{NH}_2$ species on the surface of the Pd/CeO_2 catalyst at 250°C reacted with NO quickly. Then, adsorbed NO_x species, including chelating nitrites (1210 cm^{-1}), NO_3^- (1326 and 1405 cm^{-1}) [12], and bidentate nitrate (1498 and 1530 cm^{-1}) [36], rapidly formed on the surface of the catalyst. It is worth noting that in addition to the aforementioned NO_x species formed with the aid of CeO_2 , NO adsorbed on Pd , including linear NO [$\text{Pd}^0\text{-NO}$] (1751 cm^{-1}) and bent NO

[Pd-NO] (1664 cm^{-1}), was also observed [21].

To investigate the reactivity of adsorbed NO_x species with NH_3 , an *in-situ* IR spectrum was also recorded as a function of time over Pd/CeO_2 catalyst at 250°C , as shown in Fig. 3(b). After the introduction of NO for 30 min and purging with N_2 , bands attributable to chelating nitrites (1210 cm^{-1}), NO_3^- (1326 and 1405 cm^{-1}) [12], bidentate nitrate (1498 and 1530 cm^{-1}) [36], and Pd-NO (1664 cm^{-1}) [21] appeared. The band at 1751 cm^{-1} for $\text{Pd}^0\text{-NO}$ was not detected; this may have been because of the oxidation of metallic Pd upon NO introduction. The follow-up introduction of NH_3 resulted in the disappearance of adsorbed chelating nitrites, bidentate nitrate, and Pd-NO , which was attributed to their reaction with NH_3 at 250°C ; however, there was hardly a decrease in the intensity of the peaks attributed to NO_3^- (1326 and 1405 cm^{-1}), suggesting that its reaction with NH_3 was slow at 250°C . Furthermore, new bands at 1556 , 1635 , and 1370 cm^{-1} , corresponding to coordinated NH_3 on Lewis acid sites, NH_4^+ , and $-\text{NH}_2$ species over Pd [26,30,33], respectively, were detected. Based on Fig. 3(b), it can be concluded that nitrites, nitrate species, as well as adsorbed NO on Pd participate in the reaction with adsorbed NH_3 on the surface of the Pd/CeO_2 catalyst at 250°C .

The catalyst was further investigated under a flow of $\text{NO} + \text{NH}_3$ with the temperature rising from 100 to 300°C , to gain an insight into the possible reaction routes versus temperature. As presented in Fig. 3(c), both NO and NH_3 adsorbed on the catalyst over the entire test temperature range. At 100°C adsorbed

Fig. 3. *In-situ* transmission IR spectra for reaction between NO and pre-adsorbed NH_3 species at 250°C (a), reaction between NH_3 and pre-adsorbed NO_x species at 250°C (b), and catalytic reduction of NO with NH_3 as the temperature rises from 100 to 300°C (c).

NO_x species, including NO_3^- (1326 and 1405 cm^{-1}), bidentate nitrate (1235 and 1550 cm^{-1}) [12,36], NH_3 species bound to Brønsted acid sites, with peaks at 1466 and 1635 cm^{-1} [30,33], and intermediates ($\text{N}_x\text{H}_y\text{NO}_3$) with an extremely weak peak at 1357 cm^{-1} [37], were simultaneously detectable. This indicated that the reaction between NH_3 and NO at 100 °C was slow, and only the reactions between $-\text{NH}_2 + \text{NH}_3\text{-L}$ and nitrates + Pd-NO occurred, accompanied by the formation of N_2O and N_2 . The other reactants still existed as adsorption species.

With an increase in temperature to 150 °C, the intensity of adsorbed bidentate nitrate at 1550 cm^{-1} decreased obviously, indicating that the reaction between bidentate nitrate and $-\text{NH}_2 + \text{NH}_3\text{-L}$ species was promoted. At 175 °C, the intensity of adsorbed bidentate nitrate (1550 cm^{-1}) further decreased and the peaks of bidentate nitrate at 1235 cm^{-1} started to get activated. Moreover, the peaks at 1326 and 1405 cm^{-1} weakened slightly, implying that NO_3^- ions were also activated and consumed by NH_3 species at this temperature. When the temperature reached 300 °C, the adsorbed nitrate species, both NO_3^- and bidentate nitrate, disappeared, which implied that all the reaction species were activated and contributed to the NO reduction. Moreover, the IR peak located at 1466 cm^{-1} , which was ascribed to NH_4^+ , was found to shift to 1484 cm^{-1} , and its intensity increased as the temperature increased from 200 to 300 °C; this could be attributed the transformation of Lewis acid sites to Brønsted acid sites after contact with the OH groups from the H_2O produced during the reaction [38]. Accordingly, it could be concluded from Fig. 3(c) that NO_3^- and bidentate nitrates only get activated above 175 °C, and are fully activated at 200 °C.

The catalytic performance of the Pd/CeO_2 catalyst for NO reduction by NH_3 is shown in Fig. 4. The catalyst exhibited a high performance for NO reduction with NH_3 in the absence of O_2 . The NO conversion increased rapidly with an increase in the temperature, and the light-off temperature (with 50% conversion of NO) was about 125 °C. A conversion of 100% was achieved throughout the temperature range of 175–400 °C. Interestingly, the concentration of N_2O firstly increased with the temperature and reached 160 ppm at 125 °C; it then decreased to 0 when the temperature increased beyond 175 °C,

Fig. 4. NO conversion and N_2O formation over Pd/CeO_2 catalyst. Reaction conditions: $[\text{NO}] = 800$ ppm, $[\text{NH}_3] = 800$ ppm, balance N_2 , and $\text{GHSV} = 36000$ h^{-1} .

indicating that the reaction between a 1:1 molar ratio of NO and NH_3 had a perfect N_2 selectivity above 175 °C. When the molar ratio of $\text{NO}:\text{NH}_3$ changed, the N_2O selectivity also changed, as shown in Fig. 5. With a decrease in the amount of NH_3 introduced, the NO conversion decreased obviously. In detail, for $\text{NO}:\text{NH}_3 = 0.4:1$, the NO reduction behavior was very similar to that of $\text{NO}:\text{NH}_3 = 1:1$, but the maximum concentration of N_2O (115 ppm) was produced at 120 °C. For $\text{NO}:\text{NH}_3 = 1.5:1$, 100% N_2 conversion could still be achieved; however, at temperatures below 200 °C, a relatively low NO conversion, compared with the result shown in Fig. 4, was observed. A further decrease in the NH_3 amount resulted in an evident decrease in NO conversion, as shown in Fig. 5(a). It should be pointed out that the theoretical NO conversion is 60% and 37.5% when $\text{NO}:\text{NH}_3$ equals 2.5:1 and 4:1, respectively. The measured NO conversion in these two cases was higher than the corresponding theoretical data (Fig. 5(a)), indicating a decrease in N_2 selectivity, which was in good agreement with the results shown in Fig. 5(b), according to which a high concentration of N_2O was detected at temperatures above 250 °C. Furthermore, even after the catalyst was tested for more than 50 h, no evident activity loss was found, indicating its good stability.

Based on the above results, the route of NO reduction by NH_3 over Pd/CeO_2 can be approximately described as follows.

Fig. 5. NO conversion and N_2O formation over Pd/CeO_2 catalyst with different molar ratios of NO/NH_3 . Reaction conditions: $\text{NO}/\text{NH}_3 = 800/2000$; $\text{NO}/\text{NH}_3 = 1200/800$; $\text{NO}/\text{NH}_3 = 1000/400$; $\text{NO}/\text{NH}_3 = 1600/400$; balance N_2 , and $\text{GHSV} = 36000$ h^{-1} .

It should be pointed out that in the absence of O₂, the reaction routes for nitrides and nitrates were similar because all the possible reducible [O] species came from NO, and the lattice [O²⁻] was not involved in the reactions.

The possible reaction routes for N₂O can be summarized as follows. (1) At low temperatures below 250 °C, Reactions (1)–(7) are the reaction routes for NO removal. HON from Reaction (6) is the intermediate for N₂O formation, which is in agreement with earlier reports [7,8]. (2) At high temperatures above 250 °C, Reactions (5) and (8)–(15) are the reaction routes for NO abatement, and Reaction (15) is the only route for N₂O formation.

In detail, the reaction can be discussed based on three temperature windows. (1) At temperature window I below 200 °C, the yield of HON is related to the H[•] species. When sufficient NH₃ is used, the H[•] species originating from NH₃ activation would preferentially react with adsorbed NO to form HON (Reaction (6)), and Reaction (10) is prohibited due to the energy barrier. The combination of two formed HON species through Reaction (7) leads to the formation of N₂O; simultaneously, HON can also react with H[•] to generate N₂, as described in Reaction (8). Thus, excessive H[•] species promote Reaction (8), reducing the formation of N₂O from Reaction (7); this is in good agreement with the catalytic performance tests under molar ratios of NO/NH₃ below 1.5:1, as presented in Figs. 4 and 5. When NH₃ is insufficient, H[•] is still produced, but Reaction (8) is suppressed; as a result, N₂O formation increases with a decrease in the NH₃/NO molar ratio (Fig. 5(b)). (2) At temperature window II between 200 and 250 °C, Reaction (10) gets activated and suppresses Reactions (6)–(8); hence, the quantitative analysis of the formation of N₂O was complicated, and no evident tendency could be observed. (3) At temperature window III above 250 °C, Reaction (6) is completely prevented because the H[•] species are completely trapped by Reaction (10); therefore, the N₂O formation through Reaction (7) is prohibited. However, NO dissociation through Reaction (13) gets activated. In this case, when sufficient NH₃ exists, adsorbed NO species preferentially react with activated –NH₂, which implies that reaction (13) is still prohibited, and the N₂O formation through reaction (15) is still suppressed (in the cases of NO:NH₃ = 0.4:1 and 1:1). However, when NH₃ is insufficient, direct NO dissociation through Reaction (13) occurs, activating Reaction (15)

between N[•] and –NO, and N₂O formation is favored again, as shown in Fig. 5(b). The direct dissociation of NO, occurring at high temperatures, is in accordance with the NO-TPD results shown in Fig. 2(b). Evidently, the dissociation of NO is the rate-determining step for N₂O formation at temperatures above 250 °C, and the trapping of O[•] (Reaction (14)) by surface NH₄⁺ further favors the formation of N₂O; the existence of NH₄⁺ at high temperatures was evidenced by the detection of the transformation of L-NH₃ to NH₄⁺ at these temperatures (Fig. 3(c)).

4. Conclusions

In summary, we investigated the mechanism of N₂O formation over Pd/CeO₂ catalyst during the catalytic reduction of NO using NH₃ as the reductant in the absence of O₂. The temperature-dependent formation mechanism of N₂O was confirmed. When NH₃ is sufficient for NO abatement, N₂O formation only takes place at low temperatures, through the dissociation of HON intermediates. However, when NH₃ is insufficient for NO removal, direct dissociation of NO into N[•] and O[•] takes place at high temperatures, and the combination of N[•] and NO[•] induces N₂O emission. Our results provide detailed knowledge on the mechanism of the N₂O formation, which is good reference for the suppression of N₂O emission in the low-temperature SCR of NO with NH₃.

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Graphical Abstract

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Mechanistic insight into N₂O formation during NO reduction by NH₃ over Pd/CeO₂ catalyst in the absence of O₂

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N₂O formation at low temperatures is through the reaction of two HON intermediates. However, at high temperatures, direct dissociation of NO into N• and O• takes place, and the combination of N• and NO_(ads) is the route for N₂O generation.

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无氧条件下Pd/CeO₂催化剂表面NH₃还原NO过程中N₂O形成机理研究

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摘要: 氮氧化物(NO_x, 主要包括NO和NO₂)是主要的大气污染物之一, 造成酸雨, 光化学烟雾和臭氧层破坏等环境问题, 甚至直接危害人体健康。化石燃料燃烧和汽车尾气排放是NO_x的主要来源, 严格控制火力发电厂, 大型锅炉, 汽车尾气等污染源中NO_x的排放刻不容缓。以NH₃为还原剂选择性催化还原NO_x(NH₃-SCR)是目前公认的最有效的NO_x脱除技术, 然而在催化NO_x还原为N₂的过程中往往伴随着副产物N₂O的生成, 降低了催化剂的选择性, 造成温室气体效应和破坏臭氧层等环境问题。因此充分理解NH₃-SCR过程中N₂O的形成机理对于抑制N₂O的产生、提高催化剂的选择性十分重要。本文将高度分散的Pd纳米团簇负载在CeO₂纳米棒上制成Pd/CeO₂催化剂, 结合NH₃-TPD, NO-TPD和原位傅里叶变换红外光谱等表征手段研究了无氧条件下该催化剂上利用NH₃催化还原NO过程中N₂O的产生路径。结果表明, N₂O的形成途径与反应温度和反应气体的浓度相关。当反应气体中NH₃含量大于化学计量比时, 在反应温度低于200 °C时, 由NH₃活化产生的吸附态H•自由基与催化剂表面吸附的NO反应先生成中间产物HON, 两个HON分子进一步反应生成N₂O; 过量的吸附态的H•自由基也可以与HON反应生成N₂, 所以低温下(<200 °C)随着反应气氛中NH₃的增加, 解离生成的H•也随之增加, 促进反应向着生成N₂

的方向进行,从而抑制了 N_2O 的产生.随着反应温度增加, NH_3 解离产生的 $\text{H}\cdot$ 被 CeO_2 表面的 O 捕获形成羟基,中间产物 HON 的生成被切断,从而阻断了 N_2O 的生成.同时由于体系中含有大量的 NH_3 ,吸附态的 NO 会优先与活化态的 NH_3 物种反应生成 N_2 ,阻碍了 NO 解离生成 N_2O 这一过程的发生,因此 NH_3 过量情况下在高温下观察不到 N_2O 的产生,可获得100%的 N_2 选择性.但是当反应气体中的 NH_3 含量不足时,即体系中含有过量的 NO ,当反应温度高于 $250\text{ }^\circ\text{C}$, NO 可在催化剂表面解离生成吸附态的 $\text{N}\cdot$ 自由基和 $\text{O}\cdot$ 自由基, $\text{N}\cdot$ 自由基可进一步与吸附态的 NO 反应生成 N_2O , NO 的解离是 N_2O 生成的速控步,还原性吸附物种对 $\text{O}\cdot$ 自由基的捕捉将有利于 N_2O 的生成.当反应温度介于 $200\text{--}250\text{ }^\circ\text{C}$, NH_3 解离产生的 $\text{H}\cdot$ 自由基既可以与 NO 结合生成 HON 中间产物,又能被 CeO_2 表面的 O 捕获形成羟基,两个反应之间存在竞争,此时 N_2O 产生与反应气体浓度之间的关系不再呈单调变化.

关键词: N_2O 形成; NO 还原; Pd/CeO_2 催化剂; 原位红外; 机理研究

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