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Selective catalytic reduction of NO_x by H₂ over Pd/TiO₂ catalyst

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ABSTRACT

Pd/TiO₂ catalysts prepared by three different methods (impregnation, deposition-precipitation, and polyethylene glycol reduction) were investigated in the selective catalytic reduction of NO_x by H₂ (H₂-SCR). It was found that the preparation method exerted a significant effect on the activity of the Pd/TiO₂ catalyst, and that the catalyst prepared by the polyethylene glycol reduction method exhibited the highest activity in the reduction of NO_x. Characterization of the catalyst showed that, in the Pd/TiO₂ catalyst prepared by the polyethylene glycol reduction method, the existing Pd species was Pd⁰, which is the desirable species for the H₂-SCR of NO_x. In situ DRIFTS studies demonstrated that over this catalyst, more chelating nitrite and monodentate nitrite species formed, both of which are reactive intermediates in the H₂-SCR of NO_x. All of these factors account for the high activity of Pd/TiO₂ prepared by the polyethylene glycol reduction method.

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1. Introduction

Nitrogen oxides (NO_x), one of the major classes of air pollutants, can cause a series of environmental problems such as acid rain and photochemical smog [1]. Selective catalytic reduction (SCR) has been demonstrated to be one effective method for removing NO_x in the presence of oxygen, and different reducing agents have been employed in this process [2]. Currently, SCR of NO_x by ammonia (NH₃-SCR) has been widely adopted for the control of NO_x [3–5]. However, NH₃ slip and vanadia emissions associated with the NH₃-SCR process have restricted its application [6,7]. The SCR of NO_x by hydrocarbons (HC-SCR) also has some disadvantages such as poor activity at low temperatures [8]. As an alternative technology, selective catalytic reduction of NO_x by H₂ (H₂-SCR) has recently attracted increasing attention [9–12]. When H₂ is used as the reducing

agent, NO_x can be effectively removed at relatively low temperatures (100–300 °C) [13]. Moreover, the combustion product of H₂ is H₂O, which is environmentally benign, and corresponds with the goal of environmental protection.

In the process of H₂-SCR, noble metals, especially Pt and Pd, were found to be the active components [14–17]. Many studies have focused on the development of Pd-based catalysts for the H₂-SCR, due to the lower cost of Pd than that of Pt [18–22]. Lee et al. [23] reported that Pd/Al₂O₃ prepared using PdCl₂ as the precursor was more active than that prepared using Pd(NO₃)₂ as the precursor. Ueda et al. [24] found that Pd/TiO₂ was much more active than a Pd/Al₂O₃ catalyst. The activity of Pd-based catalysts in the H₂-SCR of NO_x is dependent upon the chemical nature of Pd (PdO, metallic Pd⁰, and Pd alloy). Wen [25] proposed that Pd⁰ plays a significant role in the H₂-SCR reaction. Xu et al. [26] investigated the activities of a series of Pd-doped

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aluminate spinel catalysts for the H₂-SCR reaction, and found that the activity decreased in the following sequence: Pd/CoAl > Pd/ZnAl > Pd/CuAl. Based on an XPS analysis, they proposed that the most-reduced state of Pd in Pd/CoAl was responsible for the highest activity.

The activity of a catalyst is closely related to the preparation method [8]. Chiarello et al. [21] found that Pd/LaCoO₃ prepared by the flame-spray pyrolysis method was more active than that prepared by the impregnation method. Pd/MFI prepared by the sublimation method also exhibited higher activity in the reduction of NO_x by H₂ than that prepared by the impregnation method [25]. However, little research has been reported on the effect of preparation method on the activity of Pd/TiO₂ catalysts for the H₂-SCR of NO_x. In the present study, Pd/TiO₂ catalysts were prepared by different preparation methods, and it was found that the catalyst prepared by the polyethylene glycol reduction method exhibited the highest activity in the reduction of NO_x. On the basis of the catalyst characterization, the reason for this difference in activity resulting from the different preparation methods has been revealed.

2. Experimental

2.1. Catalyst preparation

0.5% Pd/TiO₂ catalysts were prepared by the impregnation (abbreviated as Pd/TiO₂ (IM)), deposition-precipitation (abbreviated as Pd/TiO₂ (DP)), and polyethylene glycol reduction (abbreviated as Pd/TiO₂ (PR)) methods. Degussa AEROSIL TiO₂ P25 was used as the support.

For Pd/TiO₂ (IM), TiO₂ was impregnated with an appropriate amount of PdCl₂ solution, stirred for 4 h, dried at 120 °C, and then calcined in air at 500 °C for 4 h.

For Pd/TiO₂ (DP), TiO₂ was dispersed into an appropriate amount of PdCl₂ solution and mixed for 1 h, and then NaOH (10 mol/L) was added dropwise into the homogeneous mixture until the pH of the suspension reached 10. The suspension was filtered and washed thoroughly with deionized water, dried in an oven for 12 h at 120 °C, and finally calcined in air at 500 °C for 4 h.

For Pd/TiO₂ (PR), an appropriate amount of PdCl₂, polyethylene glycol (PEG), and polyvinylpyrrolidone (PVP) were combined in a beaker and mixed well, and then the mixture was transferred to a three-neck flask placed in an oil bath. An appropriate amount of TiO₂ was dispersed into the mixed solution in the three-neck flask. The mixed solution was heated at 150 °C under N₂ flow for 2 h, then allowed to cool to room temperature. The suspension was then centrifuged and washed thoroughly with ethanol. The obtained solid was dried under vacuum at 60 °C for 12 h.

2.2. Catalytic activity measurement

The H₂-SCR measurements were carried out in a fixed-bed quartz reactor using 0.2 g of 40–60 mesh catalyst. The typical reactant consisted of 2000 ppm NO, 8000 ppm H₂, 5% O₂, and the balance was He. The total flow rate was 200 cm³ min⁻¹

(GHSV = 35000 h⁻¹). The reaction temperature was increased from 100 °C to 400 °C. The compositions of the inlet and outlet gases were monitored by a NO/NO₂ chemiluminescence analyzer (Thermo Scientific, model 42i-HL) and an FTIR spectrometer (Gasmeter FTIR DX4000). The NO_x conversion and N₂ selectivity were calculated using equations reported previously [19]. At each temperature, the catalytic activity data were collected after the catalytic reaction reached a steady-state condition.

2.3. Catalyst characterization

N₂ adsorption and desorption isotherms were measured on a Quantachrome Autosorb AS-1 system. The specific surface area and the pore size distribution were calculated by BET plots and the BJH method, respectively. The Pd loading of the prepared catalyst was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a Plasma-Spec-I spectrometer. The particle size of Pd was measured with a JEOL JEM-2100 transmission electron microscope (TEM). The crystal structures were determined by X-ray diffraction (XRD; Bruker D8 ADVANCE system) with a Cu K_α radiation source (45 kV, 200 mA). XPS analysis was performed on an ESCALab220i-XL electron spectrometer (VG Scientific), using 300 W Mg K_α radiation. The binding energies were referenced against C 1s (284.8 eV).

A Thermo Scientific Nicolet 6700 spectrometer, which was equipped with a high-temperature environmental cell fitted with a ZnSe window as well as an MCT detector cooled with liquid N₂, was employed to explore the mechanism of the H₂-SCR. The catalyst was first pre-treated at 400 °C under helium at a total flow rate of 100 cm³ min⁻¹ for 1 h in order to remove impurities on the surface of the catalyst, and then cooled to the desired temperature. A background spectrum was collected under a helium atmosphere and was subtracted from the sample spectra. DRIFT spectra were recorded by accumulating 100 scans with a resolution of 4 cm⁻¹.

3. Results and discussion

3.1. Comparison of H₂-SCR performance

The effects of different catalyst preparation methods on the performance of a Pd/TiO₂ catalyst in the H₂-SCR are illustrated in Fig. 1. As shown in Fig. 1(a), both Pd/TiO₂ (IM) and Pd/TiO₂ (DP) were inactive at 100 °C. For the Pd/TiO₂ (IM) catalyst, the maximum NO_x conversion was achieved at 125 °C, with NO_x conversion decreasing as the temperature was increased further. Above 150 °C, Pd/TiO₂ (DP) was more active than Pd/TiO₂ (IM), and the maximum NO_x conversion was obtained at 250 °C. Compared to the Pd/TiO₂ (IM) and Pd/TiO₂ (DP) catalysts, Pd/TiO₂ (PR) exhibited the highest activity over the widest temperature window. From Fig. 1(b), it can be seen that Pd/TiO₂ (PR) exhibited much better N₂ selectivity than Pd/TiO₂ (IM) and Pd/TiO₂ (DP) in the low temperature range (100–200 °C). As shown in Fig. S1 (see the Supporting Information), over the Pd/TiO₂ (PR) catalyst, the main by-product was N₂O and only a small amount of NH₃ formed between 150 and 250 °C. In

Fig. 1. H₂-SCR performance of Pd/TiO₂ (IM), Pd/TiO₂ (DP), and Pd/TiO₂ (PR) in terms of (a) NO_x conversion and (b) N₂ selectivity. Reaction conditions: 2000 ppm NO, 8000 ppm H₂, 5% O₂, and He balance; space velocity = 35000 h⁻¹.

contrast, the amounts of NH₃ formed over Pd/TiO₂ (IM) and Pd/TiO₂ (DP) catalysts were higher than that over Pd/TiO₂ (PR). Therefore, the preparation method exerted a significant effect on the H₂-SCR performance, and the catalyst prepared by polyethylene glycol reduction method was found to be the most active.

3.2. Catalyst characterization

3.2.1. N₂ adsorption, XRD, and TEM

The physicochemical properties of TiO₂, Pd/TiO₂ (IM), Pd/TiO₂ (DP), and Pd/TiO₂ (PR) catalysts are summarized in Table 1. Compared to the bare TiO₂ support, the BET surface areas of the three Pd/TiO₂ catalysts were lower due to the introduction of Pd. The BET surface areas of Pd/TiO₂ (DP) and Pd/TiO₂ (PR) were similar, and larger than that of Pd/TiO₂ (IM). The Pd loading of Pd/TiO₂ (PR) was slightly lower than those of Pd/TiO₂ (IM) and Pd/TiO₂ (DP).

XRD patterns of the different Pd/TiO₂ catalysts are shown in Fig. 2. Strong characteristic diffraction peaks corresponding to the anatase phase and weak diffraction peaks ascribable to the rutile phase [5] were observed in all three catalysts. However, no diffraction peaks attributed to Pd species were observed, which suggests that Pd was highly dispersed on the TiO₂ support, or that the loading of Pd was so low that it could not be detected.

The TEM images and the particle size distributions of the Pd/TiO₂ (IM), Pd/TiO₂ (DP), and Pd/TiO₂ (PR) catalysts are displayed in Fig. 3. It can be seen that Pd was highly dispersed on the surface of TiO₂ in all the three catalysts. The average particle sizes of Pd on the Pd/TiO₂ (IM), Pd/TiO₂ (DP), and Pd/TiO₂ (PR) catalysts were 1.28, 1.50, and 1.02 nm, respec-

tively. The smallest Pd particle size, observed in Pd/TiO₂ (PR), may have contributed to its high H₂-SCR activity.

3.2.2. XPS analysis

The chemical nature of each of Pd/TiO₂ (IM), Pd/TiO₂ (DP), and Pd/TiO₂ (PR) was analyzed by XPS. Fig. 4(a) illustrates the Pd 3d XPS spectra of the Pd/TiO₂ (IM), Pd/TiO₂ (DP), and Pd/TiO₂ (PR) catalysts. For the Pd/TiO₂ (IM) catalyst, the Pd 3d_{3/2} and 3d_{5/2} peaks are observed at approximately 341.7 and 336.6 eV, respectively, which are the classical XPS peaks of Pd²⁺ [13,18,27]. Similar XPS spectra were also observed for the Pd/TiO₂ (DP) catalyst. In the case of the Pd/TiO₂ (PR) catalyst, the Pd 3d_{3/2} and 3d_{5/2} peaks were shifted to lower bonding energies by approximately 1.3 eV. The peaks at 340.2 and 335.1 eV were assigned to metallic Pd [18,27,28]. As shown in Fig. 4(b), two Ti 2p peaks at around 458.5 eV (Ti 2p_{3/2}) and 464.3 eV (Ti 2p_{1/2}), which were assigned to Ti⁴⁺ [29,30], appeared in the spectra of all three catalysts.

O 1s XPS spectra of Pd/TiO₂ (IM), Pd/TiO₂ (DP), and Pd/TiO₂ (PR) are exhibited in Fig. 4(c). Two remarkable characteristic peaks are present in the spectra of all three catalysts: the peak at 529.5–529.7 eV was attributed to lattice oxygen (denoted as O_β), and the other at 531.5–531.6 eV was ascribed to surface chemisorbed oxygen (denoted as O_α). It is worthwhile to note that the content of O_α in Pd/TiO₂ (PR) was 23.39%, which is much higher than those in Pd/TiO₂ (DP) and

Fig. 2. XRD patterns of three different Pd/TiO₂ catalysts.

Table 1
Physicochemical properties of TiO₂ and Pd/TiO₂ catalysts.

Sample	BET surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore size (nm)	Pd loading ^a (wt%)
TiO ₂	84	0.25	11.8	—
Pd/TiO ₂ (IM)	43	0.33	31.1	0.49
Pd/TiO ₂ (DP)	52	0.48	37.1	0.46
Pd/TiO ₂ (PR)	53	0.39	32.0	0.42

^a Determined by ICP-AES.

Fig. 3. TEM images of (a) Pd/TiO₂ (IM), (b) Pd/TiO₂ (DP), and (c) Pd/TiO₂ (PR); Particle size distributions of (d) Pd/TiO₂ (IM), (e) Pd/TiO₂ (DP), and (f) Pd/TiO₂ (PR).

Pd/TiO₂ (IM) (11.45% and 14.86%, respectively). It has been reported that O_α contributed to the adsorption and oxidation of NO [19], thus promoting the reduction of NO_x by H₂ [31].

3.3. In situ DRIFTS studies

3.3.1. Co-adsorption of NO and O₂

Fig. 5 shows the in situ DRIFTS spectra of NO+O₂ co-adsorption at different temperatures on Pd/TiO₂ (IM) and Pd/TiO₂ (PR). As can be seen in Fig. 5(a), a series of bands at 1851, 1815, 1749, 1612, 1581, 1498, 1290, and 1246 cm⁻¹ were observed for the Pd/TiO₂ (IM) catalyst, which were respectively assigned to physisorbed NO (1851 and 1815 cm⁻¹) [32], *trans*-(NO)₂ (1749 cm⁻¹) [5, 14], NO₂ (1612 cm⁻¹) [33], biden-

Fig. 4. XPS spectra of (a) Pd 3d, (b) Ti 2p, and (c) O 1s orbitals of Pd/TiO₂ (IM), Pd/TiO₂ (DP), and Pd/TiO₂ (PR) catalysts.

tate nitrate (1581 cm⁻¹) [34,35], monodentate nitrate (1498 cm⁻¹) [10,14], chelating nitrite (1290 cm⁻¹) [33,36], and monodentate nitrite (1246 cm⁻¹) species [14]. The peak ascribed to NO adsorption disappeared as the temperature reached 100 °C. On the contrary, the intensities of the peaks assigned to *trans*-(NO)₂ increased slightly in intensity with increasing temperature. With increasing temperature, new bands also appeared at 1529 and 1450 cm⁻¹, which correspond to biden-

Fig. 5. In situ DRIFTS spectra of NO+O₂ adsorption on (a) Pd/TiO₂ (IM) and (b) Pd/TiO₂ (PR) catalysts at different temperatures.

tate nitrate [37] and monodentate nitrate [14], respectively.

Fig. 5(b) illustrates the in situ DRIFT spectra of NO+O₂ co-adsorption on the Pd/TiO₂ (PR) catalyst at different temperatures. Compared with the spectra observed for Pd/TiO₂ (IM), the intensities of the peaks ascribed to *trans*-(NO)₂ (1759 cm⁻¹), chelating nitrite (1286 cm⁻¹), and monodentate nitrite (1246 cm⁻¹) species were stronger. Moreover, at 30 °C, a new band was observed due to a bent mono-nitrosyl adsorbed on metallic Pd⁰ (1681 cm⁻¹) [19,22], which further demonstrates the existence of metallic Pd on the Pd/TiO₂ (PR) catalyst.

3.3.2. Reaction of NO_x with H₂ (or H₂+O₂)

Fig. 6 shows the dynamic changes of the in situ DRIFTS spectra of adsorbed species on Pd/TiO₂ (PR) at 150 °C. As shown in Fig. 6(a), after exposure of Pd/TiO₂ (PR) to NO+O₂ at 150 °C, some bands assignable to NO₂ (1607 cm⁻¹), bidentate nitrate (1583 cm⁻¹), bidentate nitrate (1531 cm⁻¹), chelating nitrite (1283 cm⁻¹), and monodentate nitrite (1245 cm⁻¹) species appeared. After changing the gas to H₂, the bands assigned to adsorbed NO_x species disappeared in 20 min, during which time the band at 1200 cm⁻¹ appeared, which was attributed to NH₃ on Lewis acid sites [33,38]. This indicates that the adsorbed NO_x species can react with H₂ to form NH₃ species. When the gas was changed back to NO+O₂, the peaks assigned to the NH₃ species disappeared and the adsorbed NO_x species appeared again. This observation indicates that the NH₃ species formed were reactive intermediates in the H₂-SCR of NO_x over the Pd/TiO₂ (PR) catalyst. From Fig. 6(b), it can be seen that if the gas was switched to H₂+O₂ instead of H₂, the adsorbed NO_x species could also react with H₂+O₂. Meanwhile, the band assigned to NH₃ on Lewis acid sites also appeared, meaning that it is also reactive. Therefore, NH₃ species played an important role in the reduction of NO_x by H₂ over the Pd/TiO₂ (PR) catalyst.

In the H₂-SCR of NO_x, the catalytic activity is dependent on the nature of the noble metal, and the metallic state can contribute to improving the activity in the reduction of NO_x [25,39]. In the case of Pd/TiO₂-Al₂O₃, the added Sn led to the formation of Pd⁰, thus exerting a promoting effect on the activity of the catalyst in the H₂-SCR [40]. For a Pd-Au/TiO₂ catalyst, the in-

teraction between Pd and Au resulted in the formation of Pd⁰, leading to improved activity in the reduction of NO_x [18]. The activity of Pd/TiO₂ (IM) pretreated by H₂ at 400 °C for 1 h (denoted herein as Pd/TiO₂ (IM-H₂)) was also evaluated in this study, and the result is shown in Fig. S2. In comparison to Pd/TiO₂ (IM), the activity of Pd/TiO₂ (IM-H₂) at 100 °C was significantly improved. This confirms that Pd⁰ is active in the reduction of NO_x, which is consistent with previous reports [24,25]. The highly dispersed metallic Pd on the Pd/TiO₂ (PR) catalyst played a significant role in the high activity. With increased temperature, the NO_x conversion over Pd/TiO₂ (IM-H₂) decreased, even falling lower than that over Pd/TiO₂ (IM). TiO₂ is a reduced oxide, and during the 400 °C pretreatment of Pd/TiO₂ (IM-H₂), TiO₂ could be reduced along with Pd, thus leading to an improved oxidation activity as reported by Li et al. [41]. The improved oxidation activity would cause the combustion of H₂ with O₂ to become predominant at elevated temperatures over the Pd/TiO₂ (IM-H₂) catalyst, and thus less H₂ would remain for the reaction with NO_x. This is a possible reason for the decreased NO_x conversion over Pd/TiO₂ (IM-H₂) at high temperatures. In contrast to the pretreatment by H₂, in the polyethylene glycol reduction process, Pd⁰ was formed while TiO₂ was seldom reduced. Therefore, Pd/TiO₂ (PR) exhibited high activity in the H₂-SCR of NO_x.

4. Conclusions

In comparison to Pd/TiO₂ (IM) and Pd/TiO₂ (DP), Pd/TiO₂ (PR) exhibited superior catalytic activity in the H₂-SCR of NO_x over a wide temperature window. Characterization results showed that on Pd/TiO₂ (PR), Pd existed entirely in the form of Pd⁰, which is active in the reduction of NO_x. In situ DRIFTS results revealed that more chelating nitrite and monodentate nitrite species formed over the Pd/TiO₂ (PR) catalyst, both of which are reactive in the reduction of NO_x. DRIFTS studies also indicated that NH₃ species are reactive intermediates in the H₂-SCR of NO_x. The presence of metallic Pd and more reactive chelating nitrite and monodentate nitrite species on the Pd/TiO₂ (PR) catalyst was responsible for its high activity in the H₂-SCR of NO_x.

Fig. 6. In situ DRIFTS spectra of surface species adsorbed on Pd/TiO₂ (PR) at 150 °C after exposure to NO+O₂ mixed gas followed by (a) H₂ or (b) H₂+O₂, and then again to NO+O₂ mixed gas.

Graphical Abstract

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Selective catalytic reduction of NO_x by H₂ over Pd/TiO₂ catalyst

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A Pd/TiO₂ catalyst prepared by the polyethylene glycol reduction (PR) method exhibited high activity in the reduction of NO_x by H₂ because of the presence of highly dispersed Pd⁰ active sites on TiO₂.

Acknowledgments

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Pd/TiO₂催化剂上氢气选择性催化还原NO_x的研究

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摘要: 氮氧化物(NO_x)的控制是当前环境催化领域研究的热点。氢气选择性催化还原NO_x (H₂-SCR)近年来引起研究者的高度关注。在H₂-SCR反应中, NO_x可在较低的温度(100–300 °C)下被还原, 并且过量氢气会与氧气反应生成水, 不会导致二次污染。研究表明, Pd基催化剂在H₂-SCR反应中具有良好的活性, 并且其催化活性与Pd的化学价态密切相关, Pd⁰较Pd²⁺具有更高的催化活性。

鉴于Pd的化学价态与催化剂的制备方法密切相关, 本文通过浸渍法、沉积–沉淀法和聚乙二醇还原法分别制备了Pd/TiO₂ (IM)、Pd/TiO₂ (DP)和Pd/TiO₂ (PR)催化剂, 研究了不同方法制得的Pd/TiO₂催化剂对H₂-SCR的催化性能。实验结果表明, 与Pd/TiO₂ (IM)和Pd/TiO₂ (DP)相比, Pd/TiO₂ (PR)催化剂的催化活性明显提高, 并且温度窗口显著拓宽。

为了揭示Pd/TiO₂ (PR)催化剂具有高活性的原因, 对Pd/TiO₂ (IM)、Pd/TiO₂ (DP)和Pd/TiO₂ (PR)催化剂进行了一系列分析表征。XRD分析表明, 在三种不同方法制备的Pd/TiO₂催化剂上, 活性组分Pd高度分散在TiO₂表面。TEM结果也证实了Pd高度分散在TiO₂表面, 并且在Pd/TiO₂ (PR)催化剂上, Pd颗粒粒径(1.02 nm)最小, 这可能是Pd/TiO₂ (PR)催化剂具有高活性的原因之一。XPS分析表明, 在Pd/TiO₂ (IM)和Pd/TiO₂ (DP)催化剂中, Pd主要以Pd²⁺的形式存在; 而在Pd/TiO₂ (PR)中, Pd则以Pd⁰的形式存在, 高分散的Pd⁰有利于H₂-SCR反应的进行。同时, Pd/TiO₂ (PR)中表面吸附氧(O_{ad})含量明显高于Pd/TiO₂ (IM)和Pd/TiO₂ (DP), 较高含量的O_{ad}能有效促进NO_x的吸附与活化, 从而促进NO_x还原反应的进行。

通过原位漫反射红外光谱(In-situ DRIFTS)分析发现, 与Pd/TiO₂ (IM)催化剂上NO+O₂稳态吸附的光谱相比, Pd/TiO₂ (PR)催化剂上螯合亚硝酸根和单齿亚硝酸根的特征峰明显增强。同时观测到Pd⁰上吸附的单齿亚硝酸酯基特征峰, 由此进一步证实了在Pd/TiO₂ (PR)催化剂中Pd以Pd⁰的形式存在。NO + O₂ → H₂ (或H₂ + O₂) → NO + O₂瞬态吸附研究表明, Pd/TiO₂ (PR)催化剂上吸附的NO_x具有高的反应活性, 并且吸附态NO_x和H₂ (或H₂+O₂)反应可生成中间产物NH₃, NH₃可进一步与NO_x反应。Pd/TiO₂ (PR)催化剂上高分散的Pd⁰以及在反应条件下表面生成的更多螯合亚硝酸根和单齿亚硝酸根反应中间体是其具有高H₂-SCR催化性能的主要原因。

关键词: 氮氧化物; 氢气选择性催化还原; Pd/TiO₂; 原位漫反射红外光谱

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