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Article

Catalytic performance of highly dispersed WO_3 loaded on CeO_2 in the selective catalytic reduction of NO by NH_3

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ABSTRACT

The influence of tungsten trioxide (WO_3) loading on the selective catalytic reduction (SCR) of nitric oxide (NO) by ammonia (NH_3) over WO_3 /cerium dioxide (CeO_2) was investigated. The NO conversion first rose and then declined with increasing WO_3 loading. It was found that the crystalline WO_3 in the $1.6\text{WO}_3/\text{CeO}_2$ sample could be removed in 25 wt% ammonium hydroxide at 70 °C, which improved the catalytic activity of the sample. The obtained samples were characterized by X-ray diffraction, Raman spectroscopy, X-ray photoelectron spectroscopy, hydrogen (H_2) temperature programmed reduction, NH_3 temperature programmed desorption, and in situ diffuse reflectance infrared Fourier transform spectroscopy. The results revealed that the dispersed WO_3 promoted the catalytic activity of WO_3/CeO_2 while the crystalline WO_3 inhibited catalytic activity. The oxygen activation of CeO_2 was inhibited by the coverage of WO_3 , which weakened NO oxidation and adsorption of nitrate species over WO_3/CeO_2 . In addition, the NH_3 adsorption performance on CeO_2 was improved by modification with WO_3 . NH_3 was the most stable adsorbed species under NH_3 SCR reaction conditions. In situ DRIFT spectra suggested that the NH_3 SCR reaction proceeded via the Eley-Rideal mechanism over WO_3/CeO_2 . Thus, when the loading of WO_3 was close to the dispersion capacity, the effects of NH_3 adsorption and activation were maximized to promote the reaction via the Eley-Rideal route.

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1. Introduction

The selective catalytic reduction of NO_x by NH_3 (NH_3 SCR) has been widely investigated because of its ability to control NO_x pollutant emissions from mobile and stationary sources. Among NH_3 -SCR catalysts, CeO_2 -based materials have received increasing attention because they are considered as potential environmentally friendly non-vanadium catalysts for use in place of commercial $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts, which contain toxic V_2O_5 [1,2]. It is well known that CeO_2 has unique redox

ability and high oxygen storage capacity, which can easily result in a synergistic catalytic effect with many other metals or metal oxides in catalytic processes [3,4]. Although pure CeO_2 itself is unsuitable as a catalyst for NH_3 SCR, CeO_2 -based catalysts including $\text{CeO}_2\text{-MnO}_x$ [5–7], $\text{CeO}_2\text{-MoO}_3$ [8], $\text{CeO}_2\text{-SnO}_2$ [9], $\text{CeO}_2\text{-TiO}_2$ [10–12], and $\text{CeO}_2\text{-WO}_3$ [13,14] exhibit desirable catalytic activity in the temperature range from 100 to 450 °C. In particular, the $\text{CeO}_2\text{-WO}_3$ catalyst displays excellent NO conversion and N_2 selectivity over a wide temperature range from 200 to 450 °C and retains its catalytic activity in the presence of

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H₂O and SO₂ [14]. Thus, CeO₂-WO₃-based catalysts are a promising choice for industrial NO_x degradation by NH₃ SCR at both low and medium-high temperature.

A recent study found that adsorbed NH₃ could be oxidized by the surface oxygen of CeO₂ at high temperature, forming surface NO_x species [15]. This resulted in poor N₂ selectivity of pure CeO₂ at high temperature because of the competitive reactions of NO and O₂ with NH₃. It has been reported that WO₃ could improve the catalytic activity and N₂ selectivity of CeO₂-based catalysts at high temperature by suppressing the nonselective catalytic oxidation of NH₃ to NO_x and enhancing NH₃ adsorption [16]. In situ infrared (IR) and Raman spectroscopy results suggested that a CeO₂-WO₃ catalyst prepared via a co-precipitation method involved a reaction mechanism consisting of two independent cycles for the NH₃ SCR reaction [17]. These cycles included a redox cycle induced by the excellent oxygen storage capability and reducibility of cubic fluorite CeO₂ and an acid site cycle resulting from Brönsted acid sites provided by the W-O-W species of Ce₂(WO₄)₃. The addition of WO₃ to CeO₂ can increase its surface acidity [13,17], which plays an important role in promoting the NH₃ SCR performance of CeO₂. However, it has been reported that when MoO₃, which is related to WO₃, was supported on ZrO₂, the amount of nitrate species adsorbed obviously decreased with increasing coverage of MoO₃ [18]. The influence of the coverage of WO₃ on CeO₂ on NO adsorption and further effects on NH₃ adsorption in the NH₃ SCR reaction have not been elucidated.

In this work, a series of WO₃/CeO₂ supported catalysts are prepared via impregnation and characterized by X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), H₂ temperature programmed reduction (H₂-TPR), NH₃ temperature programmed desorption (NH₃-TPD), and in situ diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. We systemically investigate how the WO₃ loading affects the catalytic performance of WO₃/CeO₂ in NH₃ SCR, mainly focusing on (1) studying the relationships between the states of WO₃ on the surface of CeO₂ and the catalytic activity of WO₃/CeO₂, and (2) further exploring how NH₃ and/or NO adsorption on CeO₂ is influenced by surface modification with WO₃.

2. Experimental

2.1. Sample preparation

CeO₂ as a support was prepared by thermal decomposition of Ce(NO₃)₃·6H₂O at 550 °C for 4 h in flowing air. WO₃/CeO₂ was prepared by wet impregnation. The requisite quantities of ammonium tungstate and oxalic acid (molar ratio of 1:1.5) was added dropwise into water under stirring and then an appropriate amount of CeO₂ was added to the mixture. The solvent was evaporated at 100 °C, and then the remaining material was dried at 110 °C for 3 h before being calcined at 500 °C for 4 h in flowing air. For simplicity, xWO₃/CeO₂ samples are denoted as xW/Ce, where x is the loading amount of WO₃. For example, 0.8W/Ce represents 0.8 mmol WO₃ per 100 m² CeO₂ (0.8 mmol/(100 m²)). WO₃ and CeO₂ were mechanically mixed with

the same components as 0.8W/Ce; the mechanically mixed sample is denoted as 0.8W/Ce-MM. In addition, the 1.6W/Ce sample was immersed in 25 wt% ammonium hydroxide at 70 °C for 2 h, filtered, dried at 110 °C for 3 h, and then calcined at 500 °C for 4 h in flowing air to give a sample denoted as 1.6W/Ce-N (N represents ammonium hydroxide washing).

2.2. Characterization

Specific surface areas of samples were measured by nitrogen adsorption at –196 °C on a Micrometrics ASAP-2020 analyzer (Micromeritics, USA) by the Brunauer-Emmet-Teller method. Before each adsorption measurement, the catalyst sample (about 0.1 g) was degassed in a N₂/He mixture at 300 °C for 4 h.

Powder XRD patterns were collected using a Philips X'pert Pro diffractometer (APL, Switzerland) with Ni-filtered Cu K_α radiation (0.15408 nm). The X-ray tube was operated at 40 kV and 40 mA.

Raman spectroscopy analysis was performed on a LabRAM Aramis (Horiba, Japan) laser Raman spectrometer using an Ar⁺ laser beam. Raman spectra were recorded with an excitation wavelength of 532 nm and laser power of 10 mW.

XPS experiments were performed on a PHI 5000 Versa Probe high-performance electron spectrometer (ULVAC-PHI, Japan) using monochromatic Al K_α radiation (1486.6 eV) and operating at an accelerating power of 15 kW. Before each measurement, the sample was outgassed at room temperature in an ultra-high vacuum chamber (< 5×10^{–7} Pa). Sample charging effects were compensated for by calibrating all binding energies (BE) with the C 1s peak of adventitious carbon at 284.6 eV. This reference gave BE values with an accuracy of ± 0.1 eV.

H₂-TPR measurements were carried out in a quartz U-tube reactor connected to a thermal conductivity detector (TCD) using a 7% H₂/93% Ar mixture as the reductant. Before switching to the H₂/Ar stream, each sample (50 mg) was pretreated in a N₂ stream at 200 °C for 1 h. TPR was performed from room temperature to 850 °C at a rate of 10 °C/min.

NH₃-TPD experiments were carried out on a multifunction chemisorption analyzer (Tianjin Pengxiang, China) with a quartz U-tube reactor and detected by a TCD. Each sample (about 0.1 g) was pretreated in high-purity N₂ (40 mL/min) at 450 °C for 1 h. After pretreatment, each sample was saturated with 1 vol% NH₃ (10 mL/min) at 100 °C for 1 h and subsequently flushed with high-purity N₂ at the same temperature for 1 h to remove gaseous and weakly adsorbed NH₃. The sample was then heated to 600 °C at a rate of 10 °C/min in flowing high-purity N₂ (40 mL/min).

In situ DRIFT experiments were performed on a Nicolet Nexus 5700 FTIR spectrometer (Nicolet, USA) using a diffuse reflectance attachment (Harrick) equipped with a reaction cell with ZnSe windows. Thirty-two scans at a resolution of 4 cm^{–1} were obtained and spectra were presented as Kubelka-Munk functions with reference to background spectra recorded for the catalyst in N₂. Powder samples were pretreated in N₂ at 400 °C for 1 h prior to the collection of background spectra and

adsorption experiments. The reaction conditions were: 1000 ppm NH₃, 1000 ppm NO, 5 vol% O₂, and N₂ balance. All adsorption-desorption experiments were conducted at 200 °C. To achieve saturated adsorption, samples were preadsorbed by introduction of NH₃ and/or NO and O₂ for 1 h, purged with N₂ for 15 min, and then relative spectra were collected.

2.3. Catalytic activity tests

Catalytic reactions were performed in a fixed-bed quartz reactor tube. The reaction conditions were: 500 ppm NO, 500 ppm NH₃, 5 vol% O₂, 200 ppm SO₂ (when used), and 5 vol% H₂O (when used) with the balance N₂, gas flow rate of 100 mL/min, and 0.1 g of catalyst. Prior to catalytic testing, samples were pretreated in N₂ at 200 °C for 1 h. The effluent gases including NO, NH₃, NO₂, and N₂O were continuously analyzed by an online Nicolet IS10 IR spectrometer (Nicolet, USA) equipped with a gas cell. IR data were collected at the required temperature to keep the reaction at a steady state for 15 min. The NO conversion and N₂ selectivity were calculated using the following equations:

$$\text{NO conversion (\%)} = 100 \times ([\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}) / [\text{NO}]_{\text{in}}$$

$$\text{N}_2 \text{ selectivity (\%)} = 100 \times ([\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}} + [\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}} - [\text{NO}_2]_{\text{out}} - 2[\text{N}_2\text{O}]_{\text{out}}) / ([\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}} + [\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}})$$

3. Results and discussion

3.1. Catalytic activity results

The NH₃ SCR performance of W/Ce samples was evaluated as a function of temperature. As shown in Fig. 1(a), both pure CeO₂ and WO₃ displayed low catalytic activity. However, when WO₃ was supported on CeO₂, the supported W/Ce samples exhibited much higher NO conversion than that of pure CeO₂. Overall, NO conversion over W/Ce samples increased first and then decreased with increasing WO₃ loading. 0.8W/Ce displayed the highest catalytic activity of the samples, with more than 88% NO conversion from 200 to 450 °C. As shown in Fig. 1(b), the N₂ selectivity of W/Ce increased with the WO₃ loading. More than 95% N₂ selectivity was obtained over the whole temperature range when the WO₃ loading was higher than 0.4 mmol/(100 m²). Thus, it can be concluded that the catalytic performance of W/Ce depends on WO₃ loading. Interestingly, when 1.6W/Ce was washed with 25 wt% ammonium hydroxide, as illustrated in Fig. 1(c), NO conversion over 1.6W/Ce-N was higher than that of 1.6W/Ce and almost at the same level as that of 0.65W/Ce. The effect of washing with ammonium hydroxide on the catalytic activity of 1.6W/Ce needs to be investigated further to be fully understood. In addition, the cata-

Fig. 1. (a) NO conversion and (b) N₂ selectivity over W/Ce samples as a function of temperature; (c) NO conversion of 0.65W/Ce and 1.6W/Ce pretreated in ammonium hydroxide; (d) Lifetime testing over 0.8W/Ce in the presence of SO₂ + H₂O at 300 °C.

lytic activity of 0.8W/Ce in the presence of H₂O and SO₂ was investigated at 300 °C. As presented in Fig. 1(d), NO conversion remained unchanged at ca. 94% during 25 h of continuous testing, indicating that the supported WO₃/CeO₂ catalyst had the same excellent ability to tolerate H₂O and SO₂ as a reported WO₃-CeO₂ catalyst prepared via co-precipitation [11].

3.2. Characterization

3.2.1. XRD and Raman results

Fig. 2 shows XRD patterns of the W/Ce samples. When the WO₃ loading was lower than 0.8 mmol/(100 m²), all peaks were assigned to the cubic fluorite-type CeO₂ (PDF-ICDD 34-0394), which indicates that WO₃ was highly dispersed on the CeO₂ surface. However, when the WO₃ loading was higher than 0.8 mmol/(100 m²), new peaks appeared at $2\theta = 23.2^\circ$, 23.6° , and 24.4° originating from monoclinic WO₃ (PDF-ICDD 83-0591). This result is consistent with the reported experimental dispersion capacity of 4.8 W⁶⁺ per nm² over CeO₂ (equal to 0.8 mmol/(100 m²)) [19,20]. Interestingly, 0.8W/Ce-MM also displayed peaks from WO₃.

Meanwhile, Raman spectroscopy effectively discriminated the states of WO₃ supported on CeO₂. As shown in Fig. 3, the band at 463 cm⁻¹ was the characteristic F_{2g} vibration of CeO₂ and that at 259 cm⁻¹ could be assigned to the tetrahedral displacement of oxygen from the ideal fluorite lattice [21]. Pure WO₃ exhibited five major bands at 270, 325, 712, 806, and 900–970 cm⁻¹ originating from W–O–W deformation (F_{2g} mode), W–O–W bending vibration (E mode), W–O–W stretching vibrations (A_{1g}/E_g modes), and W=O stretching, respectively [22,23]. With regard to W/Ce samples, the band at 900–1000 cm⁻¹ could be assigned to the stretching of terminal W=O, and shifted to higher wavenumber with increasing WO₃ loading because of the weaker interaction between WO₃ and CeO₂ at higher WO₃ loading [24]. When the WO₃ loading was lower than 0.4 mmol/(100 m²), only bands at 900–1000 cm⁻¹ arising

Fig. 2. XRD patterns of W/Ce samples.

Fig. 3. Raman spectra of W/Ce samples.

from W=O stretching could be detected, which indicates that isolated tungstate species formed. However, when the WO₃ loading was higher than 0.4 mmol/(100 m²), a new band attributed to W–O–W deformation at 806 cm⁻¹ appeared, indicating the formation of polytungstate species. The intensity of the band at 806 cm⁻¹ strengthened when the WO₃ loading exceeded 0.8 mmol/(100 m²), which was caused by the formation of crystalline WO₃, as confirmed by XRD. Increasing WO₃ surface density on a ZrO₂ support caused the states of WO₃ to change from a submonolayer of isolated tungstate to polytungstate and then to crystalline WO₃ [25]. Thus, WO₃ loading should decide the states of WO₃ on both CeO₂ and ZrO₂. Isolated WO₃ existed below its dispersion capacity on CeO₂ and polytungstate/crystalline WO₃ formed above this dispersion capacity.

Combined with the results of catalytic activity testing, the NO_x degradation efficiency of the supported W/Ce catalysts gradually increased with WO₃ loading below the dispersion capacity of WO₃ on CeO₂, and then decreased above the dispersion capacity. Thus, the catalytic performance of W/Ce depended on the state of WO₃ on the CeO₂ surface. It is worth noting that the XRD and Raman results of 1.6W/Ce-N were different from those of 1.6W/Ce. As illustrated in Fig. 2, only the peaks of CeO₂ were observed in the XRD pattern of 1.6W/Ce-N. Meanwhile, Fig. 3 shows that the bands at 325, 712, and 806 cm⁻¹ originating from the crystalline WO₃ disappeared and only a band at 965 cm⁻¹ assigned to dispersed WO₃ was detected. Both XRD and Raman results indicate that crystalline WO₃ in 1.6W/Ce was removed by ammonium hydroxide so that only dispersed WO₃ was left on the CeO₂ surface. Combined with the results of catalytic activity testing, crystalline WO₃ had the lowest catalytic activity, with less than 20% NO conversion over the whole temperature range. Once the crystalline WO₃ was removed from 1.6W/Ce, NO conversion improved. In addi-

tion, although 0.8W/Ce-MM had the same components as those of 0.8W/Ce, as depicted in Fig. 1(a), 0.8W/Ce-MM displayed much lower NO conversion than 0.8W/Ce, and XRD analysis also revealed that crystalline WO₃ formed over 0.8W/Ce-MM. Therefore, we conclude that crystalline WO₃ inhibited the catalytic activity of the W/Ce catalysts.

3.2.2. XPS results

XPS was carried out to determine the surface components and chemical states of elements of the W/Ce samples. As shown in Fig. 4(a), Ce 3d spectra were composed of two multiplets (labelled as v and u) assigned to 3d_{3/2} and 3d_{5/2}, respectively, because of spin-orbit coupling. Through Gaussian-Lorentz fitting, the bands labelled u' and v' were ascribed to the primary photoemission of Ce³⁺ and the other six bands (u'', v'', u''', v''', u'', v'', u, and v) were assigned to Ce⁴⁺ [26–28]. Ce³⁺ content was calculated by the formula:

$$\text{Ce(III) (\%)} = 100 \times [S(u) + S(v)] / \sum [S(u) + S(v)]$$

As listed in Table 1, the relative content of Ce³⁺ did not obviously change with increasing WO₃ loading. In addition, as depicted in Fig. 4(b), for the W 4f spectra of W/Ce samples, the BE of W 4f_{5/2} and W 4f_{7/2} were fixed at 37.4 and 35.2 eV, respectively, indicating W was in the +6 oxidation state in all the W/Ce samples [29]. Therefore, the electronic interaction between CeO₂ and WO₃ can be ignored in the W/Ce samples.

It has been reported that the XPS peak intensity ratio

I_{W4f}/I_{Ce3d} is proportional to WO₃ loading in WO₃/CeO₂ samples when the WO₃ loading is lower than the dispersion capacity of WO₃ on CeO₂ [20]. To calculate the amount of WO₃ in 1.6W/Ce-N, the linear fitting between I_{W4f}/I_{Ce3d} for (0.2, 0.4, and 0.8)W/Ce (denoted as y) and the corresponding WO₃ loading (denoted as x) was carried out by the least squares method, which gave the linear equation $y = 0.336x + 0.034$ (Fig. 4(c)). Table 1 reveals that I_{W4f}/I_{Ce3d} of 1.6W/Ce-N was 0.252, thus its WO₃ loading was 0.65 mmol/(100 m²), which could explain why the NO conversion over 1.6W/Ce-N was as good as that over 0.65W/Ce. This analysis reveals that crystalline WO₃ inhibited the catalytic activity of the W/Ce samples.

Fig. 4(d) displays the O 1s spectra fitted by Gaussian-Lorentz curves. Bands labelled O' and O'' were attributed to surface oxygen species and lattice oxygen, respectively [21,30]. The O'' bands of 1.6W/Ce and 1.2W/Ce were shifted to higher BE compared with those of the other samples, reflecting the contribution of the lattice oxygen of crystalline WO₃ [29]. In fact, compared with that of the 1.6W/Ce sample, the O'' band of 1.6W/Ce-N shifted to lower BE because of the removal of crystalline WO₃. As listed in Table 1, the relative content of surface oxygen species decreased with increasing WO₃ loading. It has been reported that superoxide and peroxide species could form on the surface of CeO₂ [31,32]. Thus, it is likely that the adsorption of active oxygen species on CeO₂ was inhibited when the CeO₂ surface was covered with dispersed WO₃.

Fig. 4. XPS results for W/Ce samples. (a) Ce 3d; (b) W 4f; (c) Linear fitting between WO₃ loading and surface concentration ratio of W/Ce; (d) O 1s.

Table 1

Surface components, number of acid sites, and specific surface area of W/Ce samples.

Sample	Atomic concentration (%)			Atomic ratio (%)		Acid amount (a.u.)	Specific surface area (m ² /g)
	Ce	W	O	Ce ³⁺ /(Ce ³⁺ +Ce ⁴⁺)	O'/(O'+O'')		
CeO ₂	23.4	0.0	76.6	15.4	33.4	2051	69.5
0.2W/Ce	24.1	2.3	73.6	15.2	32.0	5242	60.2
0.4W/Ce	24.0	4.2	71.8	14.6	30.0	6657	60.0
0.8W/Ce	20.9	6.3	72.8	14.9	26.7	5320	59.8
1.2W/Ce	19.7	7.3	73.0	14.8	25.1	5300	55.3
1.6W/Ce	17.7	8.0	74.3	15.2	24.9	4739	43.5
1.6W/Ce-N	20.4	5.1	74.5	14.9	27.8	5930	61.2
0.8W/Ce-MM	—	—	—	—	—	1098	60.8

3.2.3. H₂-TPR results

The influence of WO₃ loading on the redox performance of the catalysts was investigated by H₂-TPR measurements. As shown in Fig. 5, pure WO₃ was reduced by H₂ above 700 °C. Pure CeO₂ and W/Ce samples displayed three reduction peaks: α at ca. 400 °C, β at 500–640 °C, and γ at 760 °C, which were ascribed to the reduction of surface active oxygen species, surface or subsurface layers of CeO₂, and bulk CeO₂, respectively [33,34]. With increasing WO₃ loading, the intensity of α peaks obviously decreased compared with those for pure CeO₂, indicating that the amount of surface active oxygen species decreased with increasing WO₃ loading, which was in accordance with the XPS results. Meanwhile, β peaks shifted to higher temperature with increasing WO₃ loading. Considering that WO₃ was not reduced below 700 °C and inhibited the adsorption of active oxygen species, it can be inferred that WO₃ supported on CeO₂ would prevent H₂ from reducing CeO₂, which weakened the redox activity of the W/Ce catalysts compared with that of CeO₂. In addition, compared with 1.6W/Ce, the reduction temperature of β peaks in 1.6W/Ce-N shifted to lower temperature by ca. 70 °C, which further indicates that crystalline WO₃ could inhibit the redox ability of the W/Ce catalysts. This is one of the reasons why 1.6W/Ce exhibited lower catalytic activity than that of 1.6W/Ce-N.

Fig. 5. H₂-TPR results of W/Ce samples.

3.2.4. NH₃-TPD results

NH₃-TPD experiments were conducted to investigate the intensity and amount of acid sites on pure CeO₂ and W/Ce samples. As illustrated in Fig. 6, pure CeO₂ displayed a peak from 100 to 300 °C, indicating that adsorbed NH₃ was totally desorbed at ca. 300 °C. Meanwhile, the W/Ce samples exhibited a broader peak and adsorbed NH₃ was totally desorbed at ca. 370 °C. Thus, modification with WO₃ could increase the adsorption strength of NH₃ on the W/Ce catalysts. Peak areas in NH₃-TPD curves were calculated and are listed in Table 1. Compared with that of pure CeO₂, the number of acid sites increased considerably in W/Ce samples, which was caused by the new acid sites provided by dispersed WO₃, as reported elsewhere [35]. For the W/Ce samples, the content of acid sites first increased and then decreased with increasing WO₃ loading. Interestingly, 0.8W/Ce-MM had the lowest content of acid sites in all the samples. Combined with the XRD results, these findings suggest that crystalline WO₃ covered the surface of W/Ce and could block the adsorption of NH₃, which inhibited the catalytic activity of the W/Ce samples.

3.2.5. In situ DRIFT spectroscopy analysis

NH₃ adsorption was measured by in situ DRIFT spectroscopy to further investigate the influence of WO₃ loading on the

Fig. 6. NH₃-TPD results of W/Ce samples.

content of surface acid sites of W/Ce samples. As shown in Fig. 7, for pure CeO_2 , bands at 1123 and 1570 cm^{-1} were ascribed to the adsorption of NH_3 on Lewis acid sites of CeO_2 [36]. For 0.2W/Ce, as well as bands at 1123 and 1570 cm^{-1} , new bands at 1175 and 1600 cm^{-1} were attributed to the adsorption of NH_3 at Lewis acid sites provided by W^{6+} of isolated tungstate species [16]. When the WO_3 loading exceeded 0.4 $\text{mmol}/(100 \text{ m}^2)$, new bands at 1423 and 1664 cm^{-1} assigned to the adsorption of NH_3 on Brönsted acid sites were formed. The Brönsted acid sites were mainly provided by the W–OH–W motif of polytungstate species [16,37]. The peak intensity of Lewis acid sites at 1123 and 1570 cm^{-1} decreased with increasing WO_3 loading and totally disappeared when the WO_3 loading was higher than 0.8 $\text{mmol}/(100 \text{ m}^2)$; this was because the dispersed WO_3 prevented NH_3 adsorption on the CeO_2 surface. At the same time, the ratio of Brönsted to Lewis acid sites provided by WO_3 species increased with WO_3 loading, consistent with the results reported for WO_3/TiO_2 and WO_3/ZrO_2 [35,37]. Considering these findings along with XRD and Raman results, isolated WO_3 species mainly provided Lewis acid sites and polytungstate species provided Brönsted acid sites over WO_3/CeO_2 . Thus, it can be concluded that the states of WO_3 played an important role in determining the surface acid properties of the W/Ce samples.

DRIFT spectra were measured following $\text{NO} + \text{O}_2$ adsorption by the W/Ce samples to investigate the influence of WO_3 on the adsorption of nitrate species. As shown in Fig. 8, bands at 1606, 1583, and 1230 cm^{-1} were assigned to bridging nitrate species, those at 1505 and 1270 cm^{-1} were attributed to monodentate nitrate species, and a weak band at 1305 cm^{-1} was attributed to nitrite species [18,38]. The intensity of bands originating from nitrate species decreased and even disappeared with increasing WO_3 loading. Only nitrite species formed when the WO_3 loading exceeded 0.8 $\text{mmol}/(100 \text{ m}^2)$. Supporting WO_3 inhibited the adsorption of nitrate on WO_3/ZrO_2 catalysts [18]. For W/Ce samples, considering the H_2 -TPR results and O 1s spectra, increased coverage of WO_3 not only weakened the oxida-

Fig. 8. In situ DRIFT spectra of W/Ce samples after adsorption of NO and O_2 .

tion ability of the W/Ce catalysts but also diminished their content of surface active oxygen species. Thus, O_2 activation and NO oxidation were more difficult over W/Ce compared with the case over pure CeO_2 . When WO_3 loading was higher than the dispersion capacity of WO_3 on CeO_2 , the samples oxidized NO to nitrite instead of nitrate. Thus, increasing WO_3 loading can inhibit NO oxidation and nitrate species adsorption on the W/Ce samples.

DRIFT spectra were also measured following adsorption of NO , NH_3 , and O_2 to study surface adsorption on W/Ce samples under real reaction conditions. As illustrated in Fig. 9, for pure CeO_2 , bands at 1275 and 1256 cm^{-1} were respectively assigned to monodentate and bidentate nitrate species, which indicates that nitrates were the stable adsorbed species in the NH_3 SCR reaction process. With regard to the W/Ce samples, bands observed at 1423, 1175, and 1123 cm^{-1} were attributed to adsorbed NH_3 species, and no nitrate species were found (bands

Fig. 7. In situ DRIFT spectra of W/Ce samples after NH_3 adsorption.

Fig. 9. In situ DRIFT spectra of W/Ce samples after adsorption of NH_3 , NO , and O_2 .

at 1275 and 1256 cm^{-1} were very weak for 0.2W/Ce). These findings further confirm that supporting WO_3 could inhibit NO adsorption, and the stable adsorbed species on W/Ce was NH_3 under the reaction conditions. Both Fig. 7 and Fig. 9 show that only pure CeO_2 , 0.2W/Ce, and 0.4W/Ce had a peak from Lewis acid sites at 1123 cm^{-1} related to the adsorption of NH_3 at CeO_2 sites. Interestingly, these three samples displayed much lower NO conversion and N_2 selectivity than those of 0.8W/Ce, following the order $\text{CeO}_2 < 0.2\text{W/Ce} < 0.4\text{W/Ce} < 0.8\text{W/Ce}$. The TPR and XPS results revealed that the redox ability and oxygen activation ability of the CeO_2 surface were inhibited by modification with WO_3 . Thus, we infer that NH_3 adsorbed at CeO_2 sites would induce the nonselective oxidation of NH_3 more easily than that at WO_3 sites because of the higher redox activity of CeO_2 sites than that of WO_3 ones under real reaction conditions, which was unfavorable to improve catalytic performance.

In situ DRIFT spectroscopy is helpful to study the mechanism of surface reactions. In this experiment, NH_3 was preadsorbed on 0.4W/Ce by introduction of NH_3 for 1 h, purged with N_2 for 15 min, and then introducing NO and O_2 . Spectra were collected as a function of time. As shown in Fig. 10(a), when NO and O_2 were introduced, with increasing reaction time from 0 to 6 min, bands from adsorbed NH_3 species (Lewis acid at 1173 cm^{-1} and Brönsted acid at 1421 cm^{-1}) gradually decreased in intensity and finally disappeared. In the meantime, no nitrate species were formed. It can therefore be inferred that adsorbed NH_3 species were not replaced by nitrate species via competitive adsorption, but reacted with NO and O_2 , which suggests that the NH_3 SCR reaction proceeded by the Eley-Rideal mechanism over the W/Ce samples.

In a different experiment, NO and O_2 were preadsorbed on 0.4W/Ce by introduction of NO and O_2 for 1 h, followed by purging with N_2 for 15 min. Figure 10(b) indicates that the main adsorbed species were bridging nitrate species (1606, 1583, and 1230 cm^{-1}) on the surface of the sample. When in-

troducing NH_3 , the intensity of bands from bridging nitrate species gradually decreased and those of bands from monodentate (1506 and 1264 cm^{-1}) and bidentate (1552 cm^{-1}) nitrate species gradually increased. In addition, bands from adsorbed NH_3 species (Brönsted acid at 1438 cm^{-1} and Lewis acid at 1175 cm^{-1}) appeared. In our previous studies [39,40], we found that bridging nitrate species adsorbed on Ce/TiSn and Ti-Cu/ CeO_2 catalysts also disappeared and new monodentate and bidentate nitrate species formed when NH_3 was introduced. We propose that one NH_3 molecule could snatch an adsorption site from a bridging nitrate to form one Lewis acid, and then the bridging nitrate is transformed to a monodentate or bidentate nitrate. In terms of the present results, competitive adsorption between NH_3 gas and adsorbed bridging nitrates also occurred on 0.4W/Ce, similar to that observed on Ce/TiSn and Ti-Cu/ CeO_2 . Figure 10(b) shows that after introducing NH_3 for 10 min, the band intensity of adsorbed NH_3 and nitrate species was nearly unchanged, which indicates that adsorbed NH_3 and adsorbed nitrate species did not react with each other. Moreover, the DRIFT spectra for both NO and O_2 adsorption and NO, NH_3 , and O_2 adsorption indicated that no nitrate species were adsorbed on 0.8W/Ce. However, 0.8W/Ce exhibited the highest catalytic activity in the samples. Therefore, we infer that the NH_3 SCR reaction over the W/Ce samples did not occur via the Langmuir-Hinshelwood mechanism. Our present results were not in accord with the literature finding that adsorbed nitrate species could react with adsorbed NH_3 species over WO_3 - CeO_2 prepared by a coprecipitation method [41]. It is possible that the preparation method of the WO_3 - CeO_2 catalyst influenced its reaction mechanism.

Based on the above in situ DRIFT spectral results, the adsorption behavior on the W/Ce samples included the following factors: (1) WO_3 loading affected surface acid properties, and the relative content of Brönsted acid sites rose with increasing WO_3 loading; (2) the adsorption ability of nitrate species was

Fig. 10. In situ DRIFT spectra of the 0.4W/Ce sample after (a) introducing NO + O_2 after saturated preadsorption of NH_3 and N_2 purging and (b) introducing NH_3 after saturated preadsorption of NO + O_2 and subsequent N_2 purging.

inhibited by the increased coverage of WO_3 and only nitrite formed when the WO_3 loading exceeded the dispersion capacity of WO_3 on CeO_2 ; (3) NH_3 was most stable adsorbed species in the NH_3 SCR reaction; (4) the NH_3 SCR reaction proceeded via the Eley-Rideal reaction route. Thus, when WO_3 loading was close to the dispersion capacity of WO_3 on CeO_2 , the effect of NH_3 adsorption and activation was maximized to promote the Eley-Rideal reaction route. As a result, the 0.8W/Ce sample displayed the highest catalytic activity of those investigated.

4. Conclusions

We studied the influence of WO_3 loading on the performance of WO_3/CeO_2 catalysts in NO_x degradation. Several major conclusions were obtained. (1) Dispersed WO_3 was beneficial to improve catalytic activity while crystalline WO_3 inhibited catalytic activity. The 0.8W/Ce sample displayed the highest catalytic activity in the SCR reaction. (2) Crystalline WO_3 could be removed in 25% ammonium hydroxide to recover the catalytic activity of 1.6W/Ce. (3) Supporting WO_3 could inhibit the redox ability of CeO_2 , which blocked NO oxidation and nitrate adsorption, while the modification of CeO_2 with WO_3 enhanced the content of surface acid sites. (4) In situ DRIFT spectra suggested that the NH_3 SCR reaction over the supported WO_3/CeO_2 catalysts mainly proceeded via the Eley-Rideal mechanism. As a result, when WO_3 loading was lower than the dispersion capacity of WO_3 on CeO_2 , the oxidation-adsorption performance of NO was inhibited and the adsorption-activation performance of NH_3 was improved to promote the NH_3 SCR reaction via the Eley-Rideal route with increasing WO_3 loading.

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Graphical Abstract

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Catalytic performance of highly dispersed WO_3 loaded on CeO_2 in the selective catalytic reduction of NO by NH_3

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WO_3 dispersed on the CeO_2 surface inhibits adsorption of NO_x species and promotes NH_3 adsorption on supported WO_3/CeO_2 catalysts, which promotes the NH_3 selective catalytic reduction reaction via the Eley-Rideal (E-R) route.

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CeO₂表面分散态WO₃的氨选择性催化还原性能

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摘要: 铈基材料在氨选择性催化还原氮氧化物(NH₃-SCR)的研究中备受关注, 亦被认为是潜在的新型环境友好型催化剂。CeO₂具有独特的氧化还原性能和优良的储释氧性能, 易与其它金属氧化物发生协同催化而有利于提高催化剂的催化反应性能, 而WO₃可以改善催化剂的表面酸性。研究亦报道了WO₃可以改善CeO₂的NH₃-SCR反应的高温活性和N₂选择性, 其原因在于WO₃增加了铈基催化剂NH₃的吸附性能且抑制了NH₃非选择性氧化成NO_x。我们采用浸渍法制备了一系列负载型WO₃/CeO₂催化剂, 并利用XRD, Raman, XPS, H₂-TPR, NH₃-TPD和*in situ* DRIFT对其理化性质进行了表征, 系统研究了WO₃负载量对WO₃/CeO₂催化剂NH₃-SCR催化性能的影响, 主要研究的内容包括: (1) WO₃/CeO₂催化剂中WO₃的状态与催化性能之间的关系; (2) WO₃负载量对WO₃/CeO₂催化剂的NH₃和NO吸附行为的影响。

NH₃-SCR反应测试表明WO₃负载量对WO₃/CeO₂催化剂有显著影响, 优化的WO₃/CeO₂催化剂在200–450 °C具有良好的脱硝性能, 且在300 °C通入SO₂ + H₂O条件下依然保持优异的催化活性。XPS和H₂-TPR结果表明, WO₃分散在CeO₂表面抑制了CeO₂表面活性氧和表面晶格氧的氧化能力, 这导致催化剂对NO的氧化以及对硝酸盐的吸附性能相比于纯CeO₂显著降低, 同时, *in situ* DRIFT也证实, 随着WO₃负载量的增加, WO₃/CeO₂催化剂表面吸附硝酸盐能力下降。因此, 我们认为, 由于低活性的晶相WO₃覆盖在催化剂表面, 阻碍了催化剂的表面活性位, 降低了催化剂的氧化还原能力和表面酸量, 从而晶相WO₃抑制了WO₃/CeO₂催化剂的催化活性。同时, 我们发现在70 °C下采用氨水可以洗掉WO₃/CeO₂催化剂中的晶相WO₃, 且洗涤后的样品催化活性有所提升, 这进一步验证了晶相WO₃对催化活性的抑制作用。

In situ DRIFT结果表明WO₃/CeO₂催化剂上NH₃-SCR反应是通过Eley-Rideal机理进行, 即吸附NH₃物种与气相NO之间发生反应。随着WO₃负载量的增加, WO₃/CeO₂催化剂中NH₃的吸附能力先增强后减弱, 而NO吸附能力持续减弱, 这有利于表面酸位在反应过程中不被硝酸盐阻碍, 当WO₃负载量在分散容量附近时, 这种吸附特性的效果发挥到最大, 从而最大限度地促进NH₃-SCR反应按照Eley-Rideal机理顺利进行。

关键词: 氨选择性催化还原; WO₃/CeO₂催化剂; WO₃状态; 分散容量; 红外光谱

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