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Article

Enhanced low-temperature NH₃-SCR performance of CeTiO_x catalyst via surface Mo modification

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ABSTRACT

The effect of molybdenum oxide on the activity and durability of CeO₂-TiO₂ catalyst for NO reduction by NH₃ was examined. It was found that the introduction of Mo could improve the low-temperature NH₃-SCR activity and SO₂/H₂O durability of the CeO₂-TiO₂ catalyst and an optimal loading of Mo was 4 wt.%. The best MoO₃/CeO₂-TiO₂ catalyst displayed over 90% NO conversion from 200 °C to 400 °C and obtained 4-fold increase in NO conversion compared to CeO₂-TiO₂ at 150 °C. The characterization results revealed that the number of Brønsted acid sites over MoO₃/CeO₂-TiO₂ was significantly increased, and the adsorption of nitrate species was dramatically weakened because of the coverage of MoO₃, which were favorable for the high NH₃-SCR performance. It is believed that the MoO₃/CeO₂-TiO₂ catalyst is a suitable substitute for the NH₃-SCR reaction.

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1. Introduction

Nitrogen oxides (NO_x) are major air pollution emission in industrial processes and human activities, which need to be tightly controlled under stringent environmental regulations. Selective catalytic reduction of NO with NH₃ (NH₃-SCR) over V₂O₅-WO₃/TiO₂ catalyst is an efficient and cost-effective technology for eliminating NO_x from stationary sources [1–3]. This process, however, can be operated only in a rather high and narrow temperature range of 300–400 °C [4,5]. Unlike the case in a coal-fired power plant, the temperature of NO_x-containing exhaust gases from other sources such as glass furnace, metal-

lurgy sintering furnace and cement plant is often lower than 300 °C [6–9]. Moreover, the biological toxicity caused by vanadium species also limits the application of vanadium-based DeNO_x catalysts. Hence, the design of vanadium-free SCR catalysts that are sufficiently active at low temperature is highly desired.

In the past few years, Ce-based oxides emerged as a promising candidate for vanadium-based NH₃-SCR catalysts because of the high oxygen storage capacity (OSC) and facile Ce⁴⁺/Ce³⁺ redox cycle of CeO₂ [6,10–13]. Among them, Ce-Ti mixed oxide catalyst has drawn much attention because of its large surface area and good redox ability [14–16]. For instance, CeO₂-TiO₂

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catalyst for NH_3 -SCR reaction was first synthesized by Xu *et al.* [17] and admirable catalytic performance was observed at 275–400 °C. Afterwards, Gao *et al.* [18] explored the influence of preparation methods on the NH_3 -SCR performance of CeO_2 - TiO_2 catalyst and found that the catalyst prepared by single step sol-gel showed better SCR activity. However, the poor low-temperature SCR activity and SO_2 durability of these Ce-Ti-based catalysts still limit their practical application. Much effort to improve the low-temperature SCR catalytic performance of Ce-Ti-based catalysts has been made over the last several years. Among them, the introduction of other metal oxides to enhance their SCR activity has received considerable attention. The studies have proved that CeO_2 - TiO_2 incorporated with various metals, such as Mn, W, Cu, Sn and Fe, achieved better NH_3 -SCR catalytic performance [19–23]. MoO_3 was employed to increase the activity of traditional V-based deNO_x catalyst [24]. Recently, Jiang *et al.* [25] prepared Ce-Mo-Ti oxide catalysts by a sol-gel method and found that the addition of Mo could improve the SCR activity of CeO_2 - TiO_2 catalyst and its resistance to SO_2 and H_2O . Our study found that the incorporation of MoO_3 into TiO_2 could enhance the low-temperature activity and SO_2 / H_2O resistance of CeO_2 / TiO_2 catalyst by improving the properties of carrier [26]. Li *et al.* [27,28] also revealed that the addition of MoO_3 has a promoting effect on the activity and arsenic resistance of supported CeO_2 / TiO_2 catalyst. Nevertheless, few studies have focused on supported MoO_3 / CeTiO_x catalysts for NH_3 -SCR reaction, which were obtained only by deposition of MoO_3 on CeTiO_x support. Based on these findings, we considered that not only the supported MoO_3 / CeTiO_x could be a novel promising NH_3 -SCR catalyst with high low-temperature activity and good durability of $\text{H}_2\text{O}/\text{SO}_2$, but also surface Mo modification alone is a good strategy to study the promoting effect of Mo on CeTiO_x catalyst. Therefore, in this work, we attempted to develop a novel non-vanadium low-temperature NH_3 -SCR catalyst by only loading MoO_3 on CeTiO_x support. It was found that the addition of MoO_3 has a noticeable promoting effect on the activity of CeO_2 - TiO_2 for the NH_3 -SCR reaction. On the basis of the characterization results, the reason for the distinct promoting effect of MoO_3 has been elucidated.

2. Experimental

2.1. Catalyst preparation

CeTiO_x mixed oxides with different Ce/Ti mole ratios (4:1, 1:1, 1:4) were prepared by an inverse co-precipitation method. In a typical synthesis, requisite amounts of ammonium cerium(IV) nitrate and titanium(IV) tetrachloride were dissolved in distilled water at room temperature and stirred for 1 h, and then the obtained slurry was added dropwise into excess ammonia (25%) under stirring until pH = 10. The milky solution was kept stirring for another 2 h, followed by aging for 24 h. The obtained precipitate was filtered and washed with deionized water until no pH change or Cl^- residual (detected by the solution of AgNO_3) was detected. The obtained powder was dried at 110 °C overnight and then calcined in flowing air at

550 °C for 3 h. The MoO_3 / CeTiO_x catalysts were prepared by incipient-wetness impregnating the obtained CeTiO_x supports with a proper amount of ammonium molybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$) solution, then dried at 110 °C and calcined at 500 °C for 3 h. For simplicity, the obtained MoO_3 / CeTiO_x catalysts were denoted as $y\text{Mo}/\text{CT}$, where y is the mass fraction of the loaded Mo.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) was performed on a Shimadzu XRD-6000 power X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The data were collected at $2\theta = 10^\circ$ – 80° with $8^\circ/\text{min}$ scanning rate. Nitrogen adsorption-desorption isotherms were measured on a Micrometrics ASAP-2020 adsorption analyzer via the Brunauer-Emmett-Teller (BET) method at -196°C . The samples (0.1 g) were activated for 4 h at 300 °C before each adsorption measurement. X-ray photoelectron spectroscopy (XPS) analysis was implemented on a PHI 5000 Versa Probe system at an accelerating power of 15 kW, equipped with monochromatic Al K (1486.6 eV) radiation. The adventitious C 1s peak at 284.6 eV was used as calibration to compensate the charging effect of the binding energies (BE, $\pm 0.1 \text{ eV}$ error) of the samples. H_2 -temperature-programmed reduction (H_2 -TPR) was carried out using a H_2 -Ar mixture (7 vol.% H_2) as reducing agent. Typically, 50 mg sample was used in a quartz U-tube reactor for each measurement. NH_3 -temperature-programmed desorption (NH_3 -TPD) experiments were performed on a multifunction chemisorption analyzer with a quartz U-tube reactor, detected by a thermal conductivity detector (TCD). Raman spectra were collected on a Spex 1877 D triplemate spectrograph with 2 cm^{-1} resolution. A 532 nm DPSS diode-pump solid semiconductor laser was used as the excitation source with power output of ca. 5 mW. The *in situ* DRIFT spectra were collected on a Nicolet Nexus 5700 FTIR spectrometer with a scanning number of 32 at a resolution of 4 cm^{-1} , and a diffuse reflectance reaction cell (HARRICK) was used. For the experiments of NH_3 or $\text{NO} + \text{O}_2$ adsorption-desorption, the IR cell with sample was saturated with NH_3 (1 vol.%) or $\text{NO} + \text{O}_2$ (500 ppm NO and 5 vol.% O_2) for 1 h at room temperature, then the sample was purged with N_2 for 30 min, and the spectra were recorded at target temperature by raising the temperature from 50 °C to 400 °C.

2.3. Catalytic performance measurements

The activity tests were carried out on a fixed-bed quartz reactor using a 0.25 g catalyst of 40–60 mesh. The feed gas mixture contained 500 ppm NO, 500 ppm NH_3 , 5% O_2 , 6% H_2O (when used), 200 ppm SO_2 (when used), and Ar as the balance gas. The total flow rate of the feed gas was 200 mL/min, corresponding to a GHSV of $48,000 \text{ mL g}^{-1} \text{ h}^{-1}$. The reaction temperature was increased from 100 to 400 °C. The composition of the gas in the inlet and outlet streams was measured with a quadrupole mass spectrometer (Dycor Dymaxion DM300M, AMETEK) when the catalytic reaction reached steady-state condition at each test temperature point.

Fig. 1. NO conversions on these Mo/CT catalysts with different Mo contents and CT support.

3. Results and discussion

3.1. NH_3 -SCR catalytic performance

3.1.1. Effect of Ce/Ti mole ratio and Mo loading on catalytic activity over Mo/CT catalysts

First, a series of Mo/C/T samples with different Ce/Ti mole ratios (f) were prepared to explore the influence of Ce/Ti molar ratio on NO conversion over Mo/C/T catalysts. Herein, the loading amount of Mo was fixed at 4 wt.%. As shown in Fig. S1, the order of NH_3 -SCR catalytic activity followed $\text{Mo/Ce}_4\text{TiO}_x > \text{Mo/Ce}_1\text{TiO}_x > \text{Mo/Ce}_{0.25}\text{TiO}_x$. The results of the catalytic activities indicated that Mo/CeTiO_x catalyst exhibited the optimal NO conversion when the molar ratio of Ce/Ti was 4:1. Then, a series of $y\text{Mo/Ce}_4\text{TiO}_x$ samples with different Mo loadings were prepared and the NH_3 -SCR activity was tested. As shown in Fig. 1, activity test results showed that the pristine Ce_4TiO_x support had rather poor SCR activity in the whole operation temperature range (100–400 °C) with the maximum NO conversion of 71% at 350 °C. In contrast, the $y\text{Mo/Ce}_4\text{TiO}_x$ catalysts displayed much higher SCR activity in the temperature range of 200–400 °C. Among which, 4Mo/Ce₄TiO_x sample exhibited a NO conver-

sion of more than 90% within a broad operation temperature window (200–400 °C) under the GHSV of 48000 mL g⁻¹ h⁻¹. Most notably, the addition of Mo significantly increased the activity of Ce_4TiO_x catalyst in the low-temperature range, obtaining 4-fold increase in NO conversion compared to Ce_4TiO_x at 150 °C (from ca. 20% to ca. 80%). These results indicated that loading Mo on Ce_4TiO_x surface had a remarkable promoting effect on NH_3 -SCR activity especially at low temperature and the optimal loading amount was 4 wt.% Mo. Therefore, comparative studies between 4Mo/Ce₄TiO_x catalyst (Mo/CT for short in the following chapters) and Ce_4TiO_x support (CT for short) were conducted to elucidate the effect of MoO₃ loading on NH_3 -SCR performance.

3.1.2. Influence of SO_2 and H_2O on the NH_3 -SCR activity over CT and Mo/CT

The existence of sulfur dioxide and water vapor was unavoidable in the industrial application of NH_3 -SCR catalysts, so it is important to evaluate the influence of SO_2 and H_2O on the catalytic performance of our deNO_x catalyst. Thus, the SO_2 and H_2O resistance of the Mo/CT catalyst during NH_3 -SCR reaction at 250 °C was evaluated through a long-time test, and the corresponding results are presented in Fig. 2. When 200 ppm SO_2 was injected at 250 °C (Fig. 2A), the NO conversion of the Mo/CT catalyst decreased slightly at first and then was kept at about 94% during the test period. Meanwhile, the NH_3 -SCR activity of the CT sample was also measured in the presence of 200 ppm SO_2 as a comparison. The results showed that the NO conversion over CT slowly decreased with an increase in time and was kept at ca. 40% after 24 h. Moreover, when 200 ppm SO_2 and 5 vol% H_2O were introduced into the reaction gas at the same time (Fig. 2B), the deactivation of the CT sample was much faster than that of Mo/CT. After 24 h, the NO conversion on the CT sample decreased from ca. 56% to ca. 29%, and the decline rate of the activity was 27%. However, the NO conversion over the Mo/CT sample still maintained at about 92%. The above results indicated that the Mo/CT catalyst exhibited above 90% NO conversion in the range of 200–400 °C and good $\text{H}_2\text{O}/\text{SO}_2$ resistance at 250 °C for NH_3 -SCR reaction. Therefore, the Mo/CT catalyst can be used to remove NO_x from stationary

Fig. 2. SO_2 (a) and $\text{H}_2\text{O}+\text{SO}_2$ (b) resistance of the CT and Mo/CT catalysts at 250 °C.

Fig. 3. XRD (A) and Raman (B) patterns of the CT and Mo/CT samples.

pollution sources containing a certain amount of SO₂ and H₂O vapor because of its great catalytic performance.

3.2. Catalyst characterization

3.2.1. Structural and textural characteristics (XRD, Raman and BET)

Fig. 3A presents the XRD patterns of CT and Mo/CT catalysts. Both samples exhibited the fluorite type crystalline structure without any phase segregation, characteristics of CeO₂ (PDF-ICDD 34-0394) [29]. Furthermore, no diffraction peak attributed to MoO₃ was detected in the XRD pattern of Mo/CT catalyst, which indicated that the molybdenum oxide was highly dispersed or presented as amorphous entities on the surface of CT [30]. To get further information of Mo species, Raman characterization was operated. It is well known that in comparison with XRD, Raman is more sensitive to distinguish the dispersion state of Mo. Fig. 3B displays Raman spectra of CT and Mo/CT samples. It shows that the two Raman spectra all exhibited a main band ascribed to the triply degenerate F_{2g} mode of fluorite ceria and no Raman bands corresponding to MoO₃ were detected, indicating that MoO₃ was indeed present in the form of highly dispersed state on the surface of the CT support [31,32]. Moreover, the Raman band intensity of the Mo/CT catalyst was weaker than that of the CT support, which also suggested that the highly dispersed MoO₃ species on the surface of CT covered the support and weakened the signal [33]. These Raman results are in good agreement with XRD. We also noted that the F_{2g} band of the Mo/CT catalyst shifted slightly from 451 to 444 cm⁻¹ owing to electronic interactions between MoO₃ and CT support.

N₂ adsorption/desorption isotherms of the samples were collected to understand the textural properties of CT and Mo/CT. It can be observed from Fig. 4A that both samples exhibit type-IV isotherms according to IUPAC classification, showing the presence of mesoporous structure [34]. Besides, the H3-type hysteresis loops (P/P_0 of 0.4–1.0) manifested the

presence of irregular pores, which was revealed by the BJH pore distribution curves (Fig. 4B). Table 1 shows BET surface area and pore structure results of the two catalysts. The specific surface area and total pore volume of CT was 135 m²/g and 0.303 cm³/g, while that of Mo/CT was 101 m²/g and 0.273 cm³/g, respectively. The specific surface area and total pore volume of Mo/CT decreased owing to the blocking effect of the CT support by the deposited molybdenum oxide. However, the A_{BET} values of CT and Mo/CT followed the opposite trend of the corresponding SCR activity. Therefore, we believe that the improvement of the SCR activity over Mo/CT catalyst cannot be attributed to the changes of specific surface area caused by

Fig. 4. N₂ adsorption/desorption isotherms of the CT and Mo/CT samples (inset is BJH pore distribution curves).

Table 1

The results of BET, XPS, and NH₃-TPD.

Sample	BET specific surface area (m ² /g)	Total pore volume (cm ³ /g)	Atomic ratio (%)	Acidity (mg/g)
CT	135	0.303	49.2	0.49
Mo/CT	101	0.273	33.1	0.68

Fig. 5. XPS spectra of Ce 3d (A), Mo 3d (B) and O 1s (C).

molybdenum addition.

3.2.2. Surface chemical states analysis (XPS)

XPS experiments were conducted to explore the chemical states of surface species and the types of oxygen species over CT and Mo/CT samples, as presented in Fig. 5. For the Ce 3d XPS spectra in Fig. 5A, the bands labeled μ , μ' , μ'' , ν , ν' and ν'' represented the $3d^{10}4f^0$ state of Ce^{4+} , whereas ν' and ν'' represented the $3d^{10}4f^1$ state, corresponding to Ce^{3+} [6,14]. It can be seen that the redox pair of $\text{Ce}^{3+}/\text{Ce}^{4+}$ was observed in the Mo/CT and CT catalysts. According to the area ratio of the peaks representing Ce^{3+} and Ce^{4+} , the percentage of Ce^{3+} in the total Ce (Ce^{3+} and Ce^{4+}) could be calculated. The addition of molybdenum to CT led to the slight increase in the percentage of $\text{Ce}^{3+}/(\text{Ce}^{3+} + \text{Ce}^{4+})$, which indicated there was interaction between the oxides of Mo and Ce. With regard to Mo 3d XPS spectra in Fig. 5B, two main peaks owing to Mo $3d_{5/2}$ and Mo $3d_{3/2}$ were observed at 232.2 and 235.6 eV, which were attributed to MoO_3 or Mo^{6+} oxide [35,36]. The O 1s XPS information of these samples was presented in Fig. 5C. The peak at 532.1 eV was considered as surface oxygen species (denoted as O_α), and the band of O_β at 529.2 eV was ascribed to lattice oxygen species. The $\text{O}_\alpha/(\text{O}_\alpha + \text{O}_\beta)$ ratio of all the samples were calculated by the area integral of O_α and O_β . It was found that the relative concentration ratio of O_α over Mo/CT catalyst was lower than that of CT (Table 1), suggesting that the number of surface oxygen species decreased after the introduction of molybdenum.

3.2.3. Redox properties

The redox properties of an NH_3 -SCR catalyst always play an important role in the NH_3 -SCR catalytic performance [37–39]. Thus, H_2 -TPR was carried out to evaluate the redox properties of CT and Mo/CT catalysts. As shown in Fig. 6, three reduction peaks were observed for the two samples, which were assigned to the reduction of the surface oxygen species of ceria (α), the reduction of surface Ce^{4+} (β), and the reduction of bulk of Ce^{4+} (γ), respectively [29,40,41]. In addition, the reduction of the well dispersed Mo species and surface Ti^{4+} was also likely to be included in peak β [28]. It is worth noting that loading Mo could slightly affect the reduction temperature for peak β . The β peak moved to higher temperature, from 570 °C for CT to 582 °C for Mo/CT, which was caused by the coverage of molybdenum

oxides. Similar results were also obtained for vanadium and tungsten dispersed on CeO_2 [42]. At the same time, the area of peak α over the Mo/CT sample attributed to the reduction of surface oxygen species obviously declined because of the loading of Mo. This phenomenon illustrated that Mo loaded on CT could decrease the number of labile surface oxygen and defect sites, leading to low reducibility of the catalysts. This deduction can be supported by the results of XPS spectra shown in Fig. 5. It is clear that the O_α signal representing surface chemisorbed oxygen was much higher for CT than for Mo/CT. These results were also in line with the observations of Li *et al.* [35]. In brief, the H_2 -TPR result manifested that the reducibility of Mo/CT was restrained compared with CT. According to the above characterization results and NH_3 -SCR activity in Fig. 1, the experiments of NH_3 -TPD and *in situ* DRIFTS were carried out to explore the reason for better catalytic activity of Mo/CT. The results may be more relevant for assessing the catalytic performance of the NH_3 -SCR catalysts because they were obtained under conditions very close to or even identical with those of the catalytic reaction.

3.3. Adsorption properties

3.3.1. NH_3 -TPD

Surface acid properties of NH_3 -SCR catalysts are another

Fig. 6. H_2 -TPR profiles of the CT and Mo/CT samples.

Fig. 7. NH_3 -TPD profiles of the CT and Mo/CT samples.

crucial aspect affecting the catalytic activity apart from the redox property. Accordingly, NH_3 -TPD and *in situ* NH_3 adsorption experiments were employed to evaluate the adsorption behavior of NH_3 on the surface of CT and Mo/CT catalysts. First, the NH_3 -TPD experiment was performed to probe the number of acid sites in the CT and Mo/CT catalysts, and the corresponding results are shown in Fig. 7. It can be seen that the NH_3 -TPD profiles of CT and Mo/CT catalysts both exhibited four desorption peaks in the temperature range of measurements, which are labeled as I, II, III, and IV. The Peak I around 150 °C was assigned to the desorption of physisorbed NH_3 species. Peak II was attributed to weak acid sites, and the peaks III and IV were ascribed to strong acid sites [14,43]. The quantitative analysis results of NH_3 -TPD are summarized in Table 1. It shows that the total acidity of CT and Mo/CT was 0.49 and 0.68 mg/g, respectively. Evidently, the Mo/CT catalyst exhibited a remarkably increased total acid amount compared with CT, which suggested that Mo surface modification can effectively improve the surface acidity of Mo/CT catalyst to promote the adsorption of NH_3 molecules, and finally enhance the NH_3 -SCR activity.

3.3.2. NH_3 -adsorption *in situ* DRIFTS

NH_3 -TPD can determine the total number of acid sites, but it fails to distinguish Brønsted acid sites and Lewis acid sites on catalyst surface. To ascertain the nature of acid sites and acquire more information of the increased acidity, NH_3 adsorption *in situ* DRIFTS was carried out, and the corresponding results are depicted in Fig. 8. For the CT catalyst in Fig. 8A, after NH_3 adsorption and N_2 purge, several bands were detected in the range of 1000–2000 cm^{-1} . The bands at 1579 and 1181 cm^{-1} were ascribed to coordinated NH_3 bound to Lewis acid sites, and the weak band at 1440 cm^{-1} could be related to the NH_4^+ species on Brønsted acid sites [19,28,44]. For the Mo/CT catalyst in Fig. 8B, the *in situ* DRIFT spectra of NH_3 adsorption were obviously different from that of the CT catalyst. In addition to the band at 1183 cm^{-1} attributed to the coordinated NH_3 linked to Lewis acid sites, a new band at 1672 cm^{-1} assigned to NH_4^+ species bound to Brønsted acid sites was observed [18,45,46]. Moreover, the intensity of the band at 1433 cm^{-1} ascribed to the NH_4^+ species bound to Brønsted acid sites was much stronger than that of the CT catalyst. With the temperature rising, all bands became weaker and the band intensity of Brønsted acid sites (1440, 1433, 1672 cm^{-1}) decreased faster than that of Lewis acid sites. This phenomenon indicated that NH_3 bonded to Lewis acid sites was more stable than that bonded to Brønsted acid sites on catalyst surface. Combining with the NH_3 -TPD results, the weak acid should be related to the Brønsted acid and the strong acid was related to the Lewis acid. This meant that the loading of Mo could result in more Brønsted acid sites on the Mo/CT catalyst surface, and similar results were found on $\text{CeO}_2\text{-MoO}_3$ catalyst in Li's work [35]. Moreover, we can find that the area ratio of Brønsted acid sites to total acid sites over Mo/CT was much higher than that on CT in the low-temperature range (< 300 °C) (Fig. S2). And, Mo/CT displayed the higher NO conversion in the same temperature range (Fig. 1). These phenomena suggested that the larger number of Brønsted acid sites caused by Mo addition played an important role in the improvement of catalytic activity in the low-temperature range over the Mo/CT catalyst for NH_3 -SCR reaction in the present work.

Fig. 8. NH_3 adsorption *in situ* DRIFTS of (A) CT and (B) Mo/CT catalyst.

Fig. 9. NO + O₂ adsorption *in situ* DRIFTS of (A) CT and (B) Mo/CT catalysts.

3.3.3. NO + O₂-adsorption *in situ* DRIFTS

The *in situ* DRIFT experiments of NO + O₂ co-adsorption were also employed to probe the surface adsorption the NO_x species over the two catalysts. For the CT catalyst (Fig. 9A), several vibration bands attributed to adsorbed nitrate species were observed when it was exposed to NO + O₂. According to the literature, the band at 1630 cm⁻¹ was ascribed to bridging bidentate nitrates, the bands at 1605 and 1217 cm⁻¹ were attributed to bridging monodentate nitrates, the band located at 1580 cm⁻¹ was assigned to bidentate nitrates, and the bands at 1530 and 1278 cm⁻¹ were assigned to monodentate nitrates. For the Mo/CT catalyst (Fig. 9B), when NO + O₂ were introduced into the DRIFTS cell at 150 °C, some bands attributed to adsorbed NO_x species were also observed: bridged nitrates (1628, 1601, and 1227 cm⁻¹), monodentate nitrates (1524 and 1271 cm⁻¹), and bidentate nitrates (1577 cm⁻¹) [47–52]. The bands at 1349 cm⁻¹ attributed to ionic nitrate also appeared [53–55]. Compared with the NO + O₂ spectra of the CT and Mo/CT samples, it is worth noting that the intensity of adsorbed NO_x species on Mo/CT was significantly weaker than that on CT. Moreover, with increasing temperature, the band intensities of adsorbed NO_x species became weaker gradually.

Especially, the adsorbed NO_x species on the Mo/CT catalyst disappeared completely at 300 °C. The above results suggested that the highly dispersed molybdenum on Mo/CT not only resulted in more Brønsted acid sites formed on the catalyst surface, but also reduced the thermal stability of the inactive nitrate species, leaving more active sites available for the adsorption of NH₃, both of which were favorable for the promotion of SCR activity.

3.4. Interaction with reactants (NH₃ + NO + O₂ co-adsorption *in situ* DRIFTS)

To investigate the reaction mechanism of NH₃-SCR reaction over the CT and Mo/CT catalysts, *in situ* DRIFTS of NH₃ + NO + O₂ co-adsorption was performed, and the results are displayed in Fig. 10. When the CT sample was exposed to the NH₃ + NO + O₂ mixed gas at room temperature, bidentate nitrate (1563 cm⁻¹), monodentate nitrate (1520 and 1278 cm⁻¹), and bridging nitrate (1624 and 1228 cm⁻¹) were observed over the catalyst. Furthermore, combining the results of NH₃ adsorption *in situ* DRIFTS, the band at 1444 cm⁻¹ related to NH₄⁺ ions bonded on Brønsted acid sites was also detected. Along with the rise of temperature, the band of Brønsted acid sites disappeared at

Fig. 10. NH₃ + NO + O₂ adsorption *in situ* DRIFTS of (A) CT and (B) Mo/CT catalysts.

200 °C due to the desorption of NH_3 and the reaction between the adsorbed NH_3 species and NO_x species. More importantly, some interesting phenomena about adsorbed NO_x species were observed during the heating process. The band of monodentate nitrate (1278 cm^{-1}) disappeared at 200 °C because of its poor thermal stability, and the band intensity of bidentate nitrate (1563 cm^{-1}) and bridging nitrate (1624 and 1228 cm^{-1}) increased with increasing temperature first and then decreased with a further increase in temperature, which was related to the reaction between the adsorbed NO_x and NH_3 species, as well as the transformation and dissociation of the adsorbed NO_x species. However, these bidentate and bridging nitrates did not disappear even at 400 °C owing to the strong adsorption. With regard to the Mo/CT catalyst, the bands of bridging nitrate (1626 and 1227 cm^{-1}), bidentate nitrate (1600 and 1565 cm^{-1}), monodentate nitrate (1515 and 1262 cm^{-1}), and Brönsted acid (1433 cm^{-1}) were also detected at corresponding positions. And the variation of these bands was similar to that of the CT catalyst with an increase in temperature. More significantly, however, a new band at 1342 cm^{-1} was observed, which was attributed to the intermediate species generated by the reaction of the adsorbed NH_3 and NO_x species [56]. This may be one reason that the Mo/CT catalyst displayed better catalytic performance than the CT catalyst for NH_3 -SCR reaction.

4. Conclusions

A novel Mo-promoted $\text{CeO}_2\text{-TiO}_2$ catalyst has been developed for the selective catalytic reduction of NO by NH_3 , which

showed high de NO_x efficiency from 150 to 400 °C. The redox properties and surface acidity of the $\text{MoO}_3/\text{CeO}_2\text{-TiO}_2$ catalyst were affected markedly by the addition of Mo species, thereby modified the adsorption of NH_3 and NO_x on the catalyst surface. The improvement of SCR activity over $\text{MoO}_3/\text{CeO}_2\text{-TiO}_2$ may be directly correlated to the increase in the number of Brönsted acid sites and weakly adsorbed NO_x species, as opposed to a decrease in the BET surface area and a change in the redox properties. Our results can provide a scientific reference for the development of CeO_2 -based catalysts for practical applications.

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Graphical Abstract

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Enhanced low-temperature NH_3 -SCR performance of CeTiO_x catalyst via surface Mo modification

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Mo surface modification improves the low-temperature NH_3 -SCR activity and SO_2 -poisoning resistance of the CeTiO_x catalyst because the acid site number is significantly increased and the adsorption of nitrate species is weakened.

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表面Mo修饰提高CeTiO_x催化剂低温脱硝性能

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摘要: 近年来, 以雾霾为代表的大气污染问题严重影响到经济社会的可持续发展。其中, 氮氧化物(NO_x)的大量排放是导致雾霾天气的重要原因之一。氨选择性催化还原(NH₃-SCR)是目前消除氮氧化物的主流技术, 低温NH₃-SCR更是广泛应用于钢铁、焦化、水泥、玻璃、陶瓷和垃圾焚烧等行业的烟气排放治理。传统的V₂O₅-WO₃/TiO₂催化剂活性温度高(300–400 °C)且钒具有生物毒性, 因此亟待开发环境友好的低温非钒基脱硝催化剂。

最近, CeTiO_x基催化剂由于在中高温段(250–400 °C)表现出优异的脱硝性能而得到广泛关注。然而, 该催化剂仍面临低温活性差及抗硫性能差的问题, 制约了其工业化应用。研究显示, 添加过渡金属可提高CeTiO_x基催化剂的脱硝活性和抗硫

中毒性能,这主要是因为过渡金属的添加可以有效改善催化剂的氧化还原性能和表面酸性。 MoO_3 作为一种可以提供大量酸性位的氧化物,常被用作助剂改善钒钨钛催化剂的活性。研究显示, MoO_3 的引入可以促进催化剂中钒物种的分散度以及提高表面酸性。基于此,我们制备了一系列不同Mo含量的 $\text{MoO}_3/\text{CeTiO}_x$ 催化剂,以期提高 CeTiO_x 催化剂的低温脱硝性能及抗 SO_2 中毒能力,并着重研究表面Mo的修饰对 CeTiO_x 催化剂物理化学性质的影响。

研究发现,表面Mo修饰可以显著提高 CeTiO_x 的低温催化活性,其脱硝效率在 $150\text{ }^\circ\text{C}$ 即可达到80%,同时抗 SO_2 中毒能力也得到增强。进一步借助X射线衍射、比表面积测定、氢气程序升温还原、氨气程序升温脱附和X射线光电子能谱等方法对催化剂进行了全面表征分析。结果显示,表面Mo修饰对 CeTiO_x 催化剂物理化学性质的影响与其脱硝性能有着密不可分的关系。首先,钒物种主要是以 MoO_3 的形式存在于 CeTiO_x 表面,其最佳的负载量为4 wt.%. 其次,表面Mo的沉积显著提高了催化剂的表面酸量,尤其是Brönsted酸位的数量,而表面酸位的增加有利于催化剂吸附与活化反应物种 NH_3 ;同时,表面Mo修饰还减弱了硝酸盐在催化剂表面的吸附,进一步促使 NH_3 -SCR反应按照Eley-Rideal机理顺利进行。最后,该催化剂在 H_2O 和 SO_2 存在的条件下仍具有最佳的脱硝性能,因而有望用于实际含 SO_2 的低温烟气脱硝。

关键词: 氮氧化物消除; 氧化铈-氧化钛催化剂; 氧化钼表面修饰; 二氧化硫中毒; 表面酸性

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