Effect of MoO₃ on vanadium based catalysts for the selective catalytic reduction of NOₓ with NH₃ at low temperature

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ABSTRACT

The selective catalytic reduction (SCR) activities of the MoO₃ doped V/WTi catalysts prepared by the incipient wetness impregnation method at low temperature were investigated. The results showed that the addition of MoO₃ could enhance the NOₓ conversion at low temperature and the best SCR activity was obtained when the dosage of MoO₃ reached 5 wt.%. The NH₃-TPD and DRIFTS experiments indicated that the addition of MoO₃ changed the type and number of acid sites on the surface of catalysts and reaction activities of acid sites were altered at the same time. The redox capacity and amount of active oxygen species got improved for V₃Mo₅/WTi catalyst, which could be confirmed by the H₂-TPR and transient response experiments. Water vapor inhibited the NOₓ conversion at low temperature. Deposition of ammonium sulfate or bisulfate might be main reason for the loss of catalytic activity in the presence of SO₂ at low temperature. Choosing the suitable NH₃/NO ratio and elevation of reaction temperature both could weaken the influence of SO₂ on the SCR activity of the V₃Mo₅/WTi catalyst. Thermal treatment of the deactivated catalyst at 350°C could get the low temperature activity recovered. The decrease of GHSV improved the deNOₓ efficiency at low temperature and we speculated that the rational technological process and operation parameters could contribute to the application of this kind of catalysts in real industrial environment.

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Introduction

The selective catalytic reduction (SCR) of NOₓ by NH₃ is to date the best developed and wide-spread technology for NOₓ removal from stationary sources (Forzatti, 2001; Busca et al., 1998; Li et al., 2011). The commercial catalysts for coal-fired power plants are mainly the V₂O₅–WO₃/TiO₂ in the form of monolith in China. Due to the undesired oxidation of SO₂ to SO₃ for V₂O₅, its content is generally kept at 0.3–1.5 wt% limiting its operation temperature window between 300°C and 400°C. The SCR unit is usually located upstream of electrostatic precipitator in order to avoid reheating the flue gas. However, the flue gas temperature for grate furnace and rotary kiln in many industrial occasions could not satisfy the need of this kind of catalysts in China. The dust in the flue gas for glass furnace and cement kiln contained the harmful species poisoning the SCR catalyst. Therefore, the ideal position of SCR reactor is behind the electrostatic precipitator. The catalyst with good low temperature activity is the important aspect for the realization of this design.

A lot of novel catalysts with great SCR activity without H₂O and SO₂ at low temperature, such as Fe–Mn/TiO₂ (Wu et al.,...
2008), Mn–Ce mixed oxide (Shen et al., 2013), CeO2/TiO2 (Gao et al., 2010), Ce–W–Ti oxide (Jiang et al., 2015) and CeWO3 (Shan et al., 2011, 2015) have been reported recently. The resistance for water vapor and sulfur dioxide are the main barrier for the application of these catalysts in the industrial environment (Li et al., 2011; Shan and Song, 2015). Vanadia is the active species that could not be poisoned by SO2. Ciambelli et al. (1996) investigated the effect of sulfate on the catalytic properties of V2O5/TiO2 and found the presence of sulfate resulted in the enhancement of catalytic activity. Guo et al. (2009) reported that sulfate did not form on vanadia sites but rather on titania sites and the sulfation enhanced NO reduction activity by increasing the number of active sites without changing the activation energy or acid site strength.

The SCR activities of vanadium based catalysts are directly related with the content of vanadia. Wang et al. (2013) and Kompio et al. (2012) both reported that the temperature window of SCR activity shifted to low temperature range with the increasing content of vanadium oxide for V2O5–WO3/TiO2 or V2O5/TiO2. Went et al. (1992) investigated the effect of structure on the SCR activity and selectivity of V2O5/TiO2. They found that the vanadia is present in the form of monomeric vanadyl and polymeric vanadate species at the vanadia loading less than a theoretical monolayer and the specific activity of the polymeric vanadates species is about 10 times greater than that of the monomeric vanadyl species. Kristensen et al. (2011) prepared the novel nanoparticle SCR catalysts by loading 20 wt.% vanadia on the crystalline anatase, which exhibited unprecedented high deNOx SCR activity comparing with an industrial reference. Djerad et al. (2011) prepared the novel nanoparticle SCR catalysts with high loading of V2O5 are possible to retro-fit low temperature range (150–170°C) (Djerad et al., 2006). The catalysts with high loading of V2O5 are possible to retro-fit the NH3–SCR technology to lower temperature (e.g., 250°C) (Due-Hansen et al., 2011). Compared with the literatures reported, the content of 3 wt.% for V2O5 is a suitable proportion for design of the low temperature catalyst.

WO3 is employed as the ‘chemical’ and ‘structural’ promoter, which could enlarge the temperature window for SCR reaction and improve the thermal stability of catalysts. Catalysts containing WO3 have been fully investigated and widely used in practical engineering. V2O5–MoO3/TiO2 catalysts were proposed to improve the toleration to As (Hums et al., 1991). Nova et al. (1998) compared the WO3/TiO2 and MoO3/TiO2 catalysts with similar molar composition and their results showed that the MoO3/TiO2 is more active but less selective in the SCR reaction. The similar conclusion was reported for TiO2-supported V2O5–WO3 and V2O5–MoO3 catalysts (Lietti et al., 2000). Dall’Acqua et al. (2000) investigated the MoO3/TiO2 by the spectroscopic technology and found there are strong parent interactions between the TiO2-supported V and Mo oxides. The activities of novel SCR catalysts have been improved by addition of molybdenum recently, such as Ce–Zr mixed oxide (Ding et al., 2015), CeO2/TiO2 (Liu et al., 2014).

The researches of V2O5–MoO3/TiO2 were mainly for the catalysts with low loading of V2O5 and less emphasis was put on the SCR activity at low temperature. The effect of MoO3 with different loadings on the activity of vanadium catalyst containing 3 wt.% V2O5 was investigated in this paper. The change of acid sites and redox capacity due to the addition of MoO3 were both studied. At last, the influence of H2O, SO2 and GHSV was evaluated for the catalyst with the best catalytic performance.

1. Experimental

1.1. Catalyst preparation

The commercial WTi supporter was purchased from Henan Billions Chemicals Co., Ltd. (China). The main chemical compositions of WTi supporter are: 92.45 wt.% TiO2, 4.61 wt.% WO3, and 2.56 wt.% SO3. V2O5–MoO3/WTi catalysts containing 3 wt.% V2O5 and different MoO3 (0, 1 wt.%, 3 wt.%, 5 wt.%, 7 wt.%) were synthesized via incipient wetness impregnation method. Ammonium metavanadate was dissolved in the deionized water with oxalic acid as promoter and the molar ratio was kept at 1:2 (NH4VO3:2H2O:2H2O). The corresponding ammonium heptamolybdate as the precursor of MoO3 was dissolved in the same solution. Considering the solubility of the precursors, the preparation processes were completed by twice co-impregnation. The final samples were dried at 105°C for 12 hr and then calcined in the muffle furnace at 500°C (heating rate 5°C/min) for 3 hr in air. The calcined powder samples were pelleted, crushed and sieved to 40–60 mesh for performance evaluation and characterization. The series of catalysts are denoted as V3Mo:x/WTi (x = 0, 1, 3, 5, 7). For comparison, 5 wt.% MoO3/WTi and WTi catalysts were prepared by the same method and labeled as Mo5/WTi and WTi.

1.2. Catalyst characterization

The N2 adsorption–desorption isotherms were obtained at −196°C using a V-Sorb 2800P instrument (GOLD APP instruments, China). Prior to N2 adsorption, the catalyst samples were degassed at 250°C for 5 hr. The surface areas were calculated by the multipoint BET method in 0.05–0.35 partial pressure range and the average pore sizes were determined by the BJH method. Powder X Ray Diffraction (XRD) measurements were carried out on a computerized DX-2700 Diffractometer (China, Cu Kα as radiation resource).

NH3-Temperature Programmed Desorption (TPD) was carried out using FineSorb 3010D chemisorption analyzer (FINETEC instruments, China). Prior to TPD experiments, the samples (100 mg) were pretreated at 400°C in a flow of helium (20 mL/min) for 1 hr and cooled down to 80°C. Then the samples were exposed to a flow of 5 vol.% NH3/N2 (20 mL/min) for 30 min, followed by He purge for another 1 hr. Finally, the temperature was raised to 600°C in He flow.
at the rate of 10°C/min. The amount of ammonia desorbed from the catalysts was monitored by a thermal conductivity detector (TCD). H2-Temperature Programmed Reduction (TPR) was also performed using the same instrument. Before the experiment, the catalysts (50 mg) were pretreated at 400°C in a flow of Ar (20 mL/min) for 1 hr and cooled down to 50°C. Then the temperature was raised linearly to 800°C at the rate of 10°C/min in a flow of 10 vol.% H2/Ar (20 mL/min). The H2 consumption was monitored by TCD.

In situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) spectra were measured by an Fourier Transform Infrared Spectroscopy (FTIR) spectrometer (Thermo Nicolet 6700) equipped with a diffuse reflectance optics accessory (DRP-NIR) and a DTGS detector. An in situ DRIFTS reactor cell (HVC-DRP-4) with the KBr windows was connected to a purging/adsorption gas control system for the in situ DRIFTS experiments. Prior to NH3/NOx adsorption, the catalysts were pretreated at 450°C in a flow of 5 vol.% O2/N2 for 0.5 hr and cooled down to 200°C. Thereafter, the background spectra were recorded, which were automatically subtracted to get the final spectra during the dynamic experiment process. The total flow rate was 30 mL/min and the inlet gas concentrations were kept at 1000 ppm NH3 or NO, 5 vol.% O2 when used. All spectra were collected by accumulating 32 scans with a resolution of 4 cm−1.

1.3. Activity tests

Catalytic activity tests of NOx reduction by NH3 were carried out in a fixed-bed stainless steel reactor (i.d 10 mm) containing 1.5 mL of catalyst under atmosphere pressure. The typical composition of the reactant gas was: 500 ppm NO, 500 ppm NH3, 3.0 vol.% O2, 5 vol.% H2O (when used), 500 ppm SO2 (when used) and N2 as the balance gas. The total flow rate was 1.5 L/min (refers to 1 atm and 298 K) which corresponded to a gas hourly space velocity (GHSV) of 60,000 hr−1. The NO, NOx, and O2 concentration were measured online by the flue gas analyzer (NOVA PLUS, MRU, Germany) and the N2O formation was monitored by a N2O IR analyzer (G200, Geotechnical Instruments Ltd., UK). The analysis of the product was performed after the reaction system reached a steady state for at least 0.5 hr. The NOx conversion was calculated as follows:

\[
\text{NOx conversion} = \left(1 - \frac{[\text{NOx}_{\text{out}}]}{[\text{NOx}_{\text{in}}]}\right) \times 100\%
\]

2. Results and discussion

2.1. Catalytic activity

The NOx conversion and N2O concentration in the exhaust of different catalysts are shown in Fig. 1. The temperature for tests was below 300°C in order to avoid the possible undesired oxidation of SO2. The temperature window between 150°C and 300°C is the applicable range for the design of low temperature SCR catalysts. It was obvious that the addition of MoO3 for vanadium based catalysts improved the SCR activity in the temperature region of 150–250°C. There was little difference between V3Mo3/WTi catalyst and V3Mo5/WTi catalyst. The V3Mo5/WTi sample exhibited the best catalytic performance at low temperature among all the catalysts investigated. When the loading of MoO3 reached 5 wt.%, the NOx conversion was 51.36% at 175°C while there was only 29.82% for V3Mo0/WTi sample. The deNOx efficiency improved from 58.66% to 83.36% at 200°C for V3Mo5/WTi catalyst, comparing with the sample without MoO3. The order of the activities was as follows: V3Mo5/WTi > V3Mo3/WTi > V3Mo7/WTi > V3Mo1/WTi > V3Mo0/WTi. The activity for NOx removal decreased when the amount of MoO3 reached 7 wt.%.

According to a large amount of researches, N2O is the main by-product formed during the SCR process. N2O concentration in the exhaust increased slightly with the elevation of amount

![Fig. 1 – NOx conversion and N2O concentration in the exhaust of the different catalysts. Reaction conditions: [NO] = [NH3] = 500 ppm, [O2] = 3 vol.%, balance N2 and GHSV = 60,000 hr−1.](image)
of MoO$_3$. Nevertheless, the amount of N$_2$O was still at a low level and less than 15 ppm at 300°C. Based on the phenomenon that the NO$_x$ conversion kept stable between 250°C and 300°C, the over-oxidation of ammonia can be excluded for the formation of N$_2$O. We speculated that the non-selective catalytic reduction of NO with NH$_3$ was the main reason for the slight decrease of N$_2$ selectivity at higher temperatures.

2.2. Characterization of catalysts

2.2.1. N$_2$ physisorption and XRD

Table 1 shows the structural parameters of the V$_3$Mo$_x$/WTi catalysts from N$_2$ physisorption results. The BET surface area increased slightly when the loading of MoO$_3$ increased from 1 wt.% to 5 wt.%. The special surface area of V$_3$Mo$_7$/WTi catalyst showed a decrease, which might account for the decline of SCR activity partly. There were not obvious tendencies for the change of pore volumes and average pore diameters, indicating that the influence of structural parameters was weaker in contrast with the chemical interaction.

Powder XRD patterns for the series of catalysts are shown in Fig. 2. Only TiO$_2$ anatase (JCPDS card 21-1272) has been detected by XRD and the intensities of diffraction peaks were not affected by the loading of MoO$_3$. None of diffraction peak signals for crystallites of V$_2$O$_5$, MoO$_3$, and WO$_3$ were detected, indicating that these metal oxides were dispersed well on the surface of supporter or the sizes of crystal particles were too small to be detected by XRD technology.

2.2.2. NH$_3$-TPD and DIRFTS study

The surface acidity for the catalysts is the crucial factor for NH$_3$ adsorption and activation, which is the key process for SCR reaction (Busca et al., 1998). The NH$_3$-TPD profiles for different catalysts are revealed in Fig. 3. It could be seen that the WTi supporter owned abundant surface acidities. The board peak between 100 and 400°C was due to the desorption of ionic NH$_4^+$ bound to Brønsted acid sites and coordinated NH$_3$ bound to Lewis acid sites with low thermal stability, while the peak at 525°C was caused by the desorption of coordinated NH$_3$ bound to stronger Lewis acid sites (Ramis et al., 1996; Wang et al., 2013). The desorption temperature shifted toward the low temperature along with the addition of vanadium, which attributed to the coverage of WO$_3$ and TiO$_2$ by weaker Lewis and Brønsted acid sites of vanadium oxide or strong interaction between vanadium species and supporter. When the loading of MoO$_3$ reached 3 wt.%, the desorption temperature and amount for strong acid sites both decreased. Combining the NH$_3$-TPD profile of the Mo5/WTi catalyst, it was easy to speculate that the strong Lewis acid sites for TiO$_2$ or WO$_3$ might be covered by Mo surface species, forming the new Lewis or Brønsted acid sites with lower acid strength (Nova et al., 1998). The desorption peak at high temperature totally disappeared for V3Mo5/WTi and V3Mo7/WTi catalysts and the strongest peak signal at low temperature was observed for V3Mo7/WTi sample. Comparing the change of SCR activity and acid sites with the loading of MoO$_3$, it could be concluded that the SCR activity was determined by the reaction characteristic of acid sites rather than the amount of acid sites.

In order to further clarify the influence of acid sites on the reaction activities brought by MoO$_3$, the in situ DIRFTS experiments were performed. A lot of researches have proved that the deNO$_x$ mechanism for vanadium based catalysts follows the Eley–Rideal mechanism (Busca et al., 1998; Topsøe et al., 1995a, 1995b) and we also found that there were not obvious NO$_x$ adsorbed species on the surface of the investigated catalysts during our experimental process. The in situ DRIFTS experiments of reaction between NO + O$_2$ and preadsorbed NH$_3$ species at 200°C were carried out and the results are shown in Fig. 4. After NH$_3$ adsorption and N$_2$ purge (as shown in Fig. 4A), the surface of V3Mo5/WTi catalyst was mainly covered by ionic

| Table 1 – Structural parameters of different catalysts. |
| Sample | BET surface area (m$^2$/g) | Total pore volume (cm$^3$/g) | Average pore diameter (nm) |
| V3Mo0/WTi | 80.98 | 0.343 | 12.21 |
| V3Mo1/WTi | 80.25 | 0.361 | 12.46 |
| V3Mo3/WTi | 82.62 | 0.333 | 12.05 |
| V3Mo5/WTi | 83.50 | 0.358 | 12.18 |
| V3Mo7/WTi | 79.08 | 0.342 | 12.55 |

Fig. 2 – XRD patterns for the different catalysts.

Fig. 3 – NH$_3$-TPD profiles for different catalysts.
NH$_4^+$ bound to Brønsted acid sites (1427 cm$^{-1}$ for $\delta_{as}$NH$_4^+$ and 1665 cm$^{-1}$ for $\delta_{as}$NH$_4^+$) and only weak bands for coordinated NH$_3$ bound to Lewis acid sites were detected at 1243 cm$^{-1}$ ($\delta_{as}$NH$_3$) and 1603 cm$^{-1}$ ($\delta_{as}$NH$_3$) (Ding et al., 2015; Liu et al., 2014; Dall’Acqua et al., 2000; Ramis et al., 1996). The bands at 3400–3100 cm$^{-1}$ (3385 cm$^{-1}$, 3246 cm$^{-1}$ and 3165 cm$^{-1}$) were attributed to N–H stretching vibration modes of coordinated NH$_3$ and the associated stretching bands connected to the Brønsted acid sites were in the region of 3100–2600 cm$^{-1}$ (3005 and 2794 cm$^{-1}$) (Ramis et al., 1996; Topsøe et al., 1995a). The negative band around 3643 cm$^{-1}$ was due to the surface O–H stretching. Once NO + O$_2$ passed over the NH$_3$-pretreated V$_3$Mo$_5$/WTi catalyst, the IR bands of coordinated NH$_3$ (1243 and 1603 cm$^{-1}$) and ionic NH$_4^+$ (1427 and 1665 cm$^{-1}$) both showed the decrease in intensity. The peak signals for Lewis acid sites disappeared after 25 min, while the intensity for Brønsted acid sites kept on decreasing until 50 min. We could draw the conclusion that the NH$_3$ adsorbed species on Lewis acid sites and Brønsted acid sites all exhibited the reaction activity for NO$_x$ removal. The IR band at 1617 cm$^{-1}$ assigned to bridging nitrate or NO$_2$ species (Liu et al., 2011; Ruggeri et al., 2015) appeared at 35 min. It was interesting that the N–H stretching vibration band for coordinated NH$_3$ bound to Lewis acid sites still existed after the IR band at 1243 cm$^{-1}$ and 1603 cm$^{-1}$ associated to the asymmetric and symmetric deformation of ammonia coordinated disappeared at 25 min. The transform from NH$_4^+$ on Brønsted acid sites to coordinated NH$_3$ on Lewis acid sites might happen during the process for NO reduction.

**Fig. 4** – In situ DRIFTS spectra of the catalysts for the reaction between NO + O$_2$ and pre-adsorbed NH$_3$ species at 200°C. (A) V$_3$Mo$_5$/WTi, (B) V$_3$Mo$_0$/WTi.
Similar with the spectrum of V3Mo5/WTi catalysts, the coordinated NH$_3$ bound to Lewis acid sites (1243 cm$^{-1}$ for $\delta$$_{\text{NH}_3}$, 1601 cm$^{-1}$ for $\delta$$_{\text{asNH}_3}$ and 3385, 3230, 3165 cm$^{-1}$ for N–H stretching vibration) and ionic NH$_4^+$ bound to Brønsted acid sites (1436 cm$^{-1}$ for $\delta$$_{\text{asNH}_4^+}$, 1675 cm$^{-1}$ for $\delta$$_{\text{NH}_4^+}$ and 3005 cm$^{-1}$, 2795 cm$^{-1}$ for N–H stretching vibration) (Dall’Acqua et al., 2000; Ramis et al., 1996; Topsoe et al., 1995a) were observed for V3Mo6/WTi after pretreatment of NH$_3$ (as shown in Fig. 4B). The intensity for the IR band of NH$_3$ (as shown in Fig. 4B). The intensity for the IR band of NH$_3$ adsorbed species decreased gradually and the surface hydroxyls got recover at 50 min. Different from the performance of V3Mo5/WTi catalyst, the coordinated NH$_3$ at Lewis acid sites and ionic NH$_4^+$ at Brønsted acid sites for V3Mo6/WTi almost disappeared at the same time. The negative IR bands at 1436 cm$^{-1}$ and 1292 cm$^{-1}$ after 90 min were assigned to ammonia adsorbed species bound to the strong acid sites, which could not be removed by the pretreatment at 450°C. The shift of symmetric deformation of coordinated NH$_3$ from 1243 cm$^{-1}$ to 1292 cm$^{-1}$ suggested that there were different kinds of Lewis acid sites on the surface of V3Mo6/WTi catalyst. The change of IR spectra indicated that NH$_3$ adsorbed species at Lewis and Brønsted acid sites both could take part in the process for NO reduction. It was observed that the negative signal for $\ddagger$NH$_2$ started to decrease after 50 min, manifesting that the acid sites brought by sulfate species might act as the reservoir of reductant NH$_3$ merely. The time of this reaction process for V3Mo6/WTi catalyst extended to 100 min, which was due to the increase of amount of acid sites and the difference of reaction rate between the two kinds of catalysts.

Comparing the profiles of NH$_3$-TPD and IR spectra of the in situ DRIFTS, we speculated that the addition of MoO$_3$ altered the type of acid sites on the catalysts surfaces, decreasing the amount of Lewis acid sites and forming the new Brønsted acid sites. The sulfate ion from the WTi supporter was removed or covered during the preparation process for the V3Mo5/WTi catalyst. The NH$_3$ adsorbed species on the different acid sites exhibited the different reaction activity.

2.2.3. H$_2$-TPR and transient respond study

The H$_2$-TPR (temperature-programmed reduction) measurements were conducted to investigate the reduction characteristic and the interactions between surface species of the different catalysts. The H$_2$-TPR profiles of different catalysts are shown in Fig. 5. In the profile of WTi sample, the double peaks at 580°C and 598°C were assigned to the reduction of W$^{6+}$ to W$^{4+}$, which was superimposed with the reduction of sulfates (Kompio et al., 2012). The reduction signal at 665°C was attributed to the reduction of W$^{6+}$ to W$^{4+}$ on the surface of crystalline WO$_3$ (Wang et al., 2013) and the peak above 750°C corresponded to the further reduction of W$^{4+}$ to W$^{0}$ (Kompio et al., 2012). When vanadium was introduced to WTi supporter, the peaks at 426°C and 455°C were caused by the superimposed reduction of V$^{5+}$, W$^{6+}$ and sulfate species (Wang et al., 2013). Meanwhile, the reduction of crystalline WO$_3$ shifted from 665°C to 650°C. A sharp single peak at 413°C was attributed to the co-reduction of Mo$^{5+}$ to Mo$^{4+}$ and sulfate and the reduction peak at 528°C might be caused by the reduction of polymeric Mo species (Cedeño Caero et al., 2003). Due to existence of sulfate, the qualitative analysis could not be carried out. The reduction temperature of sulfate shifted toward lower temperature by the influence of MoO$_3$. The first peaks were weakened continually for V3Mo1/WTi and V3Mo3/WTi catalysts, which were attributed to the decrease of the volume of materials content during the calcining process under the co-effect of V and Mo. The peaks at 413°C for the reduction of octahedral well dispersed Mo species appeared and were strengthened when the loading of MoO$_3$ was above 3 wt.%. The reduction peaks at 596°C were due to the superimposed reduction of polymeric Mo and W species. The second step reduction of octahedral Mo species and tetrahedral Mo species accounted for the reduction peak above 700°C (Cedeño Caero et al., 2003). The intensities of them kept increasing with the loading of MoO$_3$. The reduction peaks around 470°C corresponded to the reduction of vanadium species mainly (Putluru et al., 2014; Seo et al., 2009). V3Mo5/WTi exhibited the lowest reduction temperature at 486°C for VOx, which was in harmony with its highest SCR activity. The change of the reduction peaks suggested that the interaction between V and Mo existed when the catalysts were prepared. The more Mo species occupied more specific surface area of supporter and influenced the dispersion of V species. This might account for the slightly increase of reduction temperature (478°C) for V3Mo7/WTi.

According to the abundant mechanism study for vanadium based catalysts (Busca et al., 1998; Topsoe et al., 1995a), the
redox cycle of active species was important for the catalytic process. Zhao et al. (2010) found that the monomeric vanadia species are easier to reduce but more difficult to oxidize than the polymeric and crystalline species. Therefore, we performed the transient response experiment during the process for activity test. In the first step, 500 ppm NO and 3 vol.% O2 with N2 as the balance gas were introduced to the reactor at 150°C. When the NOx concentration in the outlet became stable, 500 ppm NH3 was added into the simulated flue gas. The trend for NOx change was recorded along with time and the profiles are shown in Fig. 6. It was interesting that the NO concentration decreased in the first 15–20 min and then rebounded again to reach the stable condition. Based on this phenomenon, we speculated that the re-oxidization of active sites or the amount of active species under the oxidation state was the key factor for SCR activity at low temperature. At the beginning of ammonia injection, enough active species under the oxidation state improved the NOx conversion to a higher level. Along with more active species reduced by ammonia, the NOx removal efficiency decreased. The series of catalysts exhibited the similar trend and no obvious difference of SCR activity was observed at 150°C.

The O2 transient response reaction at 175°C was employed to investigate the function of O2 during the reaction process. The transient response experiments were carried out without O2 firstly and then 3 vol.% O2 was added to the reaction system. The changes of NOx concentration under different conditions are revealed in Fig. 7. More NOx were reduced for V3Mo5/WTi catalyst in the first stage without O2, which suggested that the more active oxygen species existing on V3Mo5/WTi catalyst could participate in the NOx reduction reaction. When the 3 vol.% O2 was introduced, the NOx concentration reached the level of steady test quickly. The more time needed for V3Mo5/WTi catalyst might be caused by the consumption of lattice oxygen during the first stage. The NOx conversions for the two kinds of catalysts were not affected significantly by the elevation of O2 concentration. The results of H2-TPR and transient response experiments indicated the addition of MoO3 changed the redox capacity of catalyst, which contributed to elevate the SCR activity at low temperature.

2.3. Influence of H2O, SO2 and GHSV

The effects of H2O, SO2 and GHSV were the important factors for the application of SCR catalysts in the industrial occasion. The influence of 5 vol.% H2O on the SCR activity for the V3Mo5/WTi catalyst is shown in Fig. 8. The deionized water was injected into the preheating section by the micro syringe pump, which was vaporized and mixed with other gas components. In accordance with the literatures published (Lian et al., 2014, 2015; Shen et al., 2013), the introduction of water vapor inhibited the SCR activity at low temperature. The NOx conversion declined from 83.36% in absence of H2O to 63.88% under the wet condition at 200°C. The inhibition for V3Mo5/WTi catalyst brought by water vapor was reversible and the activity could recover after cutting off the H2O. The influence of water vapor became weaker along with the elevation of reaction temperature.
When the NOx conversion reached the stable condition at different temperature, 500 ppm SO2 was added in the feed gas to investigate its impact on the catalytic activity of V3Mo5/WTi catalyst. No obvious change of NOx conversion was observed after 500 ppm SO2 was introduced to the feed gas for half an hour as shown in Fig. 9. The SO2 in the outlet could be monitored as soon as it was added in. It is worth to note that the concentration of SO2 detected by the flue gas analyzer in the outlet was less than the theoretical value (500 ppm) and the amount of SO2 detected increased with the elevation of reaction temperature. This loss might be caused by the deposition of ammonium sulfate or ammonium bisulfite at low temperature in the exhaust pipe formed by the excess ammonia and sulfur dioxide and the unreacted ammonia determined the degree for the loss of SO2. When the water vapor was added in the reaction system, the NOx conversion decreased to the level under the condition with 5 vol.% H2O alone (Fig. 8). The introduction of water vapor leaded to the fluctuation of NO concentration in the outlet at lower temperature. The synergy effect of H2O and SO2 could not be observed distinctly. However, when the supply of H2O was cut off, the catalytic activity decreased to a certain extent at the temperature below 225°C and the activity could not recover as SO2 was stopped. The inactivation was more serious at 175°C than at 200°C. We guessed that adsorbed ammonia species might postpone the effect of SO2 on the catalytic activity and the deactivation of catalyst in presence of SO2 was a slow process.

In order to judge whether the competitive adsorption of NH3 and SO2 leaded to the decrease of activity, the transient response experiment at 175°C with SO2 was carried out and the result was shown in Fig. 10. The catalyst was pretreated at 175°C with 500 ppm SO2 and 500 ppm NO for 1 hr before injecting NH3. The change of NOx concentration at first 30 min was similar with the result without SO2, suggesting that the loss of activity was not due to the competitive adsorption of NH3 and SO2. The NOx concentration in the outlet increased gradually along with time after the NO concentration reached the minimum. The denitration efficiency decreased 10% approximately in 5 hr and the stop of SO2 did not get the activity recovered. It is well-known that for commercial V2O5–WO3/TiO2 catalysts, the formations of ammonium bisulfate (ABS) and ammonium sulfate could lead to the deactivation of the catalysts. Recently, Yang et al. (2016) investigated the heterogeneous reactions of SO2 and NH3 on typical mineral oxides and they found that the synergistic effect between SO2 and NH3 was significant and the formation of sulfate and ammonium was enhanced. Shi et al. (2016) reported that ammonium bisulfate (ABS) could be generated from the adsorption of NH3 with SO2 in the presence of O2 on the surface of catalysts or be produced by the direct reaction between NH3 and the intermediate metal sulfates on the surface of the catalysts. We speculated that the deposition of ammonium sulfate or bisulfate species on the surface of catalysts accounted for the loss of catalytic activity at low temperature. When the reaction temperature was raised to 200°C later, the NOx conversion kept stable at 68%, which was still less than the NOx conversion tested without SO2 in Fig. 1. Nevertheless, the catalytic activity at 225°C was closed to the used catalyst at different temperatures (300°C, 350°C and 400°C) in the air for half an hour. The result showed that the thermal treatment of inactivated catalyst at the temperature above 350°C could recover the catalytic activity at low temperature, which was in agreement with the conclusion of Shi et al., 2016.

Due to the low NOx conversion at 175°C, there was excess ammonia in the exhaust when the ratio of NH3/NO was 1 which might affect the deposition of ammonium and sulfate. We reduced the dose of reductant NH3 to conduct a long time test in the presence of SO2 as shown in Fig. 11. The effect of NH3/NO ratio on the NOx conversion are exhibited in the inserted figure of Fig. 11. According to the NOx conversion at 175°C, only 50% reductant was consumed by the reduction of NOx. The increase of NH3/NO ratio below 0.75 improved the
NOx conversion, while there was little enhancement when the NH3/NO ratio was above 0.75. There was no obvious decline of NOx conversion during 6 hr test when the NH3/NO ratio was set at 0.6 at 175°C, which indicated that rational choice of NH3/NO ratio could reduce the rate of catalyst deactivation. Except for the reaction temperature, the less residual ammonia might be another reason for the better resistance to SO2 at 225°C in Fig. 9. It could be concluded that the rational technological process and choices of operation parameters could contribute to the application of this kind of catalysts in real industrial environment. The accurate parameters need to be investigated further for the monolith catalyst under the real flue gas condition in a long time run.

The activities of the V3Mo5/WTi catalyst were measured at different gas hourly space velocities (GHSV) and the results are shown in Fig. 12. It can be seen that the NOx conversion at low temperature below 200°C increased dramatically as the GHSV decreased to 30,000 hr⁻¹. The longer contact time for reactant gases to react on the surface of catalysts accounted for the increase of NOx conversion (Cheng et al., 2014). The SCR reactors installed in power plants usually work under the low GHSV range (2000–4000 hr⁻¹) with the catalysts in the monolith form (Wu et al., 2015). The NOx conversion reached 86.56% and 99.34% at 175°C and 200°C for the granule catalyst under 30,000 hr⁻¹ respectively, which indicated that it was technically feasible to use the V3Mo5/WTi catalyst to catalyze NOx reduction at low temperature.

3. Conclusions

The SCR activities of the MoO3 doped V/WTi catalysts prepared by the incipient wetness impregnation method at low temperature were investigated. The results showed that the addition of MoO3 could enhance the NOx conversion at low temperature and the loading of 5 wt.% was the best dosage for performance improvement. The NH3-TPD and DRIFTS experiments indicated that the addition of MoO3 changed the type and number of acid sites on the surface of catalysts and reaction activities of acid sites were altered at the same time. The redox capacity and amount of active oxygen species got improved for V3Mo5/WTi catalyst, which could be confirmed by the H2-TPR and transient response experiments. Water vapor inhibited the NOx conversion at low temperature and the suppression of water vapor became weaker along with the elevation of reaction temperature. Deposition of ammonium sulfate or bisulfate might be the main reason for the loss of catalytic activity in the presence of SO2 at low temperature and the deactivation of this catalyst was a slow process. Choosing the suitable NH3/NO ratio and elevation of reaction temperature both could weaken the influence of SO2 on the SCR activity of the V3Mo5/WTi catalyst. The thermal treatment of the deactivated catalyst at 350°C could get the low temperature activity recovered. The decrease of GHSV improved the deNOx efficiency at low temperature and we speculated the rational technological process and operation parameters could contribute to the application of this kind of catalysts in real industrial environment.

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REFERENCES


