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Article (Special Issue on Environmental Catalysis and Materials)

Resistance to SO₂ poisoning of V₂O₅/TiO₂-PILC catalyst for the selective catalytic reduction of NO by NH₃Simiao Zang, Guizhen Zhang, Wenge Qiu [#], Liyun Song, Ran Zhang, Hong He ^{*}

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ARTICLE INFO

Article history:

Received 29 January 2016

Accepted 5 March 2016

Published 5 June 2016

Keywords:

Selective catalytic reduction

TiO₂-pillared clay

Nitrogen oxide

Vanadia catalyst

In situ diffuse reflectance infrared

Fourier transform spectroscopy

ABSTRACT

A titania pillared interlayered clay (Ti-PILC) supported vanadia catalyst (V₂O₅/TiO₂-PILC) was prepared by wet impregnation for the selective catalytic reduction (SCR) of NO with ammonia. Compared to the traditional V₂O₅/TiO₂ and V₂O₅-MoO₃/TiO₂ catalysts, the V₂O₅/TiO₂-PILC catalyst exhibited a higher activity and better SO₂ and H₂O resistance in the NH₃-SCR reaction. Characterization using TPD, *in situ* DRIFT and XPS showed that surface sulfate and/or sulfite species and ionic SO₄²⁻ species were formed on the catalyst in the presence of SO₂. The ionic SO₄²⁻ species on the catalyst surface was one reason for deactivation of the catalyst in SCR. The formation of the ionic SO₄²⁻ species was correlated with the amount of surface adsorbed oxygen species. Less adsorbed oxygen species gave less ionic SO₄²⁻ species on the catalyst.

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1. Introduction

Nitrogen oxides (NO_x) from the combustion of fossil fuels in vehicles or coke in the electrical power plants have resulted in serious environmental problems due to their promotion of acid rain, photochemical smog, ozone depletion, and greenhouse gases. The selective catalytic reduction (SCR) of NO_x with NH₃ is the most effective method for the removal of NO_x from stationary sources and diesel engines [1–3]. V₂O₅/TiO₂-based catalysts have been widely used in industry to eliminate NO_x for their high NO_x removal efficiency and strong resistance to poisoning by SO₂ that is common in flue gases [3–5]. Nevertheless, these catalysts still suffer from the high activity for SO₂ oxidation to SO₃, which cause corrosion and plugging of the reactor [6], and the high operating temperatures (300–400 °C) that cause high

energy consumption. Low temperature SCR has aroused great interest in the past two decades [7–10]. Transition metal oxides like Fe₂O₃ [11], MnO_x [12–14], CuO [15] and V₂O₅ [16,17] have shown good activity for low temperature SCR reaction. However, these catalysts are easily deactivated in the presence of SO₂ and H₂O by the blocking of the active sites. Therefore, a high resistance to SO₂ and H₂O poisoning is of concern for low temperature SCR catalysts for NO_x removal.

Pillared interlayer clays (PILCs) are unique two dimensional zeolite-like materials prepared by intercalation of inorganic cationic clusters into clay layers followed by heating. Researchers have paid much attention to PILCs because of their large specific surface area, high surface acidity and good thermal stability. A series of PILCs were synthesized and used as catalysts for the SCR reaction of NO_x with NH₃ by Yang et al.

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This work was supported by the National Natural Science Foundation of China (21277009, 21577005).

DOI: 10.1016/S1872-2067(15)61083-X | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 37, No. 6, June 2016

[18,19]. These showed high activity in the SCR reaction that was better than the traditional V_2O_5 -based catalysts. TiO_2 -PILC has a large surface area and pore size, high thermal and hydrothermal stability as well as high resistance to SO_2 [20]. The activity of V_2O_5/TiO_2 -PILC [21] and Fe/TiO_2 -PILC [22] catalysts can be improved by the presence of H_2O and SO_2 . Although PILCs-based catalysts showed high sulfur resistance in the NH_3 -SCR reaction, there are no reports on the mechanisms of the resistance to SO_2 over the V_2O_5/TiO_2 -PILC catalysts. Even the investigations of SO_2 interaction with vanadia/titania catalysts are not comprehensive. Orsenigo et al. [23] studied the role of sulfates in NO_x reduction and SO_2 oxidation, and suggested that the buildup of sulfates at the catalyst surface likely occurred first at or near the vanadyl sites and increased both the Brönsted and Lewis acidity of the catalyst and enhanced the reactivity in the de- NO_x reaction. However, their work did not include confirming experimental evidence from surface science methods. Baxter's group [24] used *in situ* FTIR and XPS to prove that a stable sulfate species was formed on titania but not on vanadia. In summary, there was no exact determination on the interaction between SO_2 and the vanadia/titania catalysts.

Understanding the effects of SO_2 on SCR activity over PILCs catalysts is important for the development and application of the appropriate catalysts. In this study, the effects of SO_2 on the NH_3 -SCR reaction over a V_2O_5/TiO_2 -PILC catalyst were investigated. X-ray fluorescence (XRF), X-ray diffraction (XRD), N_2 adsorption-desorption measurements, temperature-programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), and *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) were used to characterize the catalysts and identify the interaction between SO_2 and the catalysts.

2. Experimental

2.1. Catalyst preparation

TiO_2 -PILCs were synthesized by the established procedures [25,26]. The starting clay was a purified grade montmorillonite powder from Nanocor Company. The cation exchange capacity (CEC) of the clay was 145 meq/100 g. The pillaring agent, a solution of partially hydrolyzed Ti polycations, was prepared by adding $TiCl_4$ into HCl solution (2 mol/L). The mixture was then diluted by the slow addition of distilled water with stirring to reach a final Ti concentration of 0.82 mol/L. The amount of HCl solution corresponded to the final concentration of 0.11 mol/L. The solution was aged for 8 h at room temperature, which was the pillaring solution. Clay (10 g) was dispersed in 2.0 L of deionized water and the slurry was stirred for 24 h. The pillaring solution was then slowly added into the suspension of clay with vigorous stirring until the amount of pillaring solution reached the required Ti/clay ratio of 10 mmol/g. The product was left in the solution for 24 h. Subsequently, the mixture was separated by centrifugation and washed with deionized water until the liquid was free of chloride ions as indicated by the silver nitrate test. The samples were dried at 120 °C for 12 h and then calcined at 400 °C for 4 h.

The TiO_2 -PILCs supported vanadia catalysts were prepared by the impregnation of TiO_2 -PILCs with aqueous solutions of NH_4VO_3 in oxalic acid. The samples were dried at 105 °C for 4 h and then calcined at 250 °C for 1 h and 450 °C for 3 h. The obtained V_2O_5/TiO_2 -PILC catalysts were labeled as nV/TiO_2 -PILC, where n referred to the vanadium amount (mass fraction, %) on the support. Besides the pillared clay catalysts, V_2O_5/TiO_2 and $V_2O_5-MoO_3/TiO_2$ catalysts were also prepared using a similar method for comparison. These catalysts contained 4% V_2O_5 and 6% MoO_3 and were denoted as 4V/ TiO_2 and 4V6Mo/ TiO_2 , respectively.

2.2. Catalytic activity measurement

The SCR activity measurement was carried out in a fixed bed quartz microreactor (i.d. = 8 mm) with 0.2 mL catalyst (40–60 mesh) at atmospheric pressure. The flue gas was simulated by blending different gaseous reactants that contained 0.1% NO , 0.1% NH_3 , 8% O_2 , 0.05% SO_2 (when used), 10% H_2O (when used), and balanced with He. The total flow was 100 mL/min with the GHSV of 30 000 h⁻¹. The gas mixtures in the reactor outlet that contained NO , NO_2 , N_2O , and N_2 was analyzed by a gas chromatograph (GC-2014C, Shimadzu) equipped with a TCD detector and a Fourier transform infrared (FT-IR) spectrometer (Tensor 27, Bruker). The NO conversion (X) was calculated by

$$X = \frac{[NO]_{in} + [NO_2]_{in} - [NO]_{out} - [NO_2]_{out}}{[NO]_{in} + [NO_2]_{in}} \times 100\%$$

where “in” and “out” represented inlet and outlet of the reactor, respectively.

2.3. Characterization

Elemental analysis of the samples was carried out on an X-ray fluorescence spectrometer (Magix PW2403, PANalytical). The XRD patterns were measured on a Bruker D8 Advance diffractometer operated at 50 kV and 40 mA using $Cu K\alpha$ radiation ($\lambda = 0.154$ nm) for $2\theta = 5^\circ$ – 80° with a step size of 7.2° /min. The specific surface areas, pore volumes and micropore volumes of the samples were measured by a physical adsorption instrument (Micromeritics ASAP 2020). Specific surface areas were calculated by the Brunauer-Emmett-Teller (BET) method. All the samples were degassed at 250 °C under vacuum for 12 h, and N_2 was adsorbed at -196 °C. *In situ* DRIFTS were carried out using an FT-IR spectrometer (Nicolet 6700, Thermo) equipped with an *in situ* diffuse reaction chamber and a high sensitivity mercury cadmium telluride (MCT) detector cooled by liquid nitrogen. The samples were first treated at 110 °C in N_2 flow for 30 min to remove water and impurities on the surface of the catalysts. All spectra were collected at a resolution of 4 cm^{-1} by an accumulation of 32 scans. The TPD spectra were obtained by a quantitative gas analysis (QGA) system (HIDEN analytical). For each experiment, the catalyst was preconditioned at 110 °C in N_2 at a flow rate of 30 mL/min and then cooled to 40 °C. The catalyst samples were then treated with 1% SO_2/N_2 or (1% SO_2 +8% O_2)/ N_2 at 40 °C for 1 h. The total flow rate was 30 mL/min. Subsequently, the samples were

purged with N₂ for 0.5 h before the TPD experiments. The TPD run was conducted from 50 to 900 °C at a heating rate of 10 °C/min.

3. Results and discussion

3.1. Characterization of the catalysts

XRD patterns of the montmorillonite and *n*V/TiO₂-PILC catalysts are shown in Fig. 1. The XRD pattern of the parent clay exhibited a peak at $2\theta = 7.1^\circ$, which was assigned to the basal (001) reflection, indicating the order of the clay layers [20]. The diffraction at $2\theta = 19.7^\circ$ was assigned to the summation of *hk* indices of (02) and (11), and the diffraction at $2\theta = 35.0^\circ$ was the summation of *hk* indices of (13) and (20) [19]. The peaks at $2\theta = 26.5^\circ$ and 28.0° were reflections of a quartz impurity [27]. No reflection was observed at $2\theta = 7.1^\circ$ over the TiO₂-PILC support and *n*V/TiO₂-PILC catalysts. The disappearance of the regular basal spacing was attributed to the delaminated clay, which generated a “house card” structure as previously reported [19,27]. The XRD patterns of the *n*V/TiO₂-PILC catalysts also showed the characteristic diffraction peaks of the anatase phase of titania (JCPDS No. 24-0913). The crystalline phase of V₂O₅ was not observed on the catalysts, suggesting that vanadia existed in amorphous or highly dispersed state on the surface of the support [28].

The N₂ adsorption isotherms and the pore size distributions of the clay (1), 4V/TiO₂-PILC (2), 4V/TiO₂ (3) and 4V6Mo/TiO₂ (4) catalysts are shown in Fig. 2. The BET surface areas and pore volumes are summarized in Table 1. The adsorption isotherm of the clay was type II, which was characteristic of macroporous solids. The adsorption-desorption isotherms formed a hysteresis loop of the H3 type, which was typical of non-uniform slit-like pores according to IUPAC classification [29]. The 4V/TiO₂-PILC catalyst showed a type I N₂ adsorption isotherm and type H4 hysteresis loops, implying a typical microporous solid that had uniform slit-like pores. The transformation of the adsorption isotherm and hysteresis loops illustrated that TiO₂ was successfully pillared in the interlayers of the clay. There was a sharp peak at the pore diameter of ap-

Fig. 1. XRD patterns of the clay (1), TiO₂-PILC (2), 3V/TiO₂-PILC (3), 4V/TiO₂-PILC (4), 5V/TiO₂-PILC (5), 4V/TiO₂ (6), and 4V6Mo/TiO₂ (7) catalysts.

proximately 4 nm for the 4V/TiO₂-PILC catalyst (Fig. 2(b-2)), suggesting that there were mesopores with a uniform pore size in the pillared clay. From Table 1, one can see that the elemental composition changed after pillaring modification, indicating that TiO₂ was exchanged into the clay. The BET surface area (*A*_{BET}) was increased greatly from 9 m²/g of the clay to approximately 210 m²/g of the 4V/TiO₂-PILC catalysts, which was also much larger than that of the traditional V₂O₅/TiO₂ catalysts.

3.2. Catalytic performance

The catalytic performance of the *n*V/TiO₂-PILC catalysts for the SCR reaction of NO by NH₃ is shown in Fig. 3. The pure TiO₂-PILC support showed a low activity for NO removal (Fig. 3(a)), and only 60% NO was converted at 500 °C. When vanadia was loaded on the TiO₂-PILC, its activity was enhanced significantly under the same reaction conditions, attaining nearly total NO conversion at 300 °C. The 4V/TiO₂-PILC catalyst ex-

Fig. 2. N₂ adsorption isotherms (a) and pore size distributions (b) of the clay (1), 4V/TiO₂-PILC (2), 4V/TiO₂ (3), and 4V6Mo/TiO₂ (4) catalysts.

Table 1Elemental composition, BET surface area and pore volume of the clay, $n\text{V}/\text{TiO}_2\text{-PILC}$, $4\text{V}/\text{TiO}_2$, and $4\text{V}6\text{Mo}/\text{TiO}_2$ catalysts.

Sample	Content ^a (wt%)								A_{BET} (m ² /g)	V_p (cm ³ /g)
	V_2O_5	TiO_2	MoO_3	SiO_2	Al_2O_3	MgO	Fe_2O_3	SO_3		
Clay	—	—	—	65.6	22.4	3.6	2.34	—	9	0.036
$\text{TiO}_2\text{-PILC}$	—	43.7	—	39.0	15.0	1.96	1.34	—	223	0.24
$3\text{V}/\text{TiO}_2\text{-PILC}$	2.65	38.8	—	40.6	13.6	2.14	1.51	—	213	0.24
$4\text{V}/\text{TiO}_2\text{-PILC}$	3.47	38.6	—	40.9	13.4	2.11	1.43	—	210	0.24
$5\text{V}/\text{TiO}_2\text{-PILC}$	4.76	38.0	—	39.9	13.2	2.07	1.50	—	211	0.24
$4\text{V}/\text{TiO}_2$	3.57	94.5	—	0.221	—	—	—	0.861	75	0.28
$4\text{V}6\text{Mo}/\text{TiO}_2$	3.51	91.1	5.02	0.149	—	—	—	0.0726	77	0.31

^a Determined by the ICP-AES technique. **Fig. 3.** (a) Catalytic performance of $n\text{V}/\text{TiO}_2\text{-PILC}$ catalysts in the $\text{NH}_3\text{-SCR}$ reaction; (b) NO conversion over $4\text{V}/\text{TiO}_2\text{-PILC}$, $4\text{V}/\text{TiO}_2$, and $4\text{V}6\text{Mo}/\text{TiO}_2$ catalysts with (hollow) or without (solid) $\text{SO}_2 + \text{H}_2\text{O}$; (c) Effects of SO_2 and H_2O on NO conversions over $4\text{V}/\text{TiO}_2\text{-PILC}$ and $4\text{V}6\text{Mo}/\text{TiO}_2$ at 260°C .

hibited a higher catalytic performance and displayed a wider operating temperature window from 260 to 500°C than that of the $3\text{V}/\text{TiO}_2\text{-PILC}$ and $5\text{V}/\text{TiO}_2\text{-PILC}$ catalysts, revealing that 4% vanadia loading was the optimum amount. The NO conversion over the $4\text{V}/\text{TiO}_2\text{-PILC}$ catalyst reached 80% at 160°C , and maintained at a high level ($>90\%$) in the temperature range of 260 – 500°C .

Fig. 3(b) shows the effects of SO_2 and H_2O on the catalytic performance of the pillared clay catalyst and the traditional vanadia-based catalysts. The $4\text{V}/\text{TiO}_2\text{-PILC}$, $4\text{V}/\text{TiO}_2$ and $4\text{V}6\text{Mo}/\text{TiO}_2$ catalysts exhibited a similar catalytic activity in the absence of SO_2 or H_2O between 100 and 350°C . After the addition of 0.05% SO_2 and 10% H_2O , the NO conversion over all the samples increased slightly at the low temperature range ($<150^\circ\text{C}$), which was attributed to sulfation of the catalyst surface that increased the Brönsted acid site density, which correlated well with the increase in SCR catalytic activity [24]. For the $4\text{V}/\text{TiO}_2$ and $4\text{V}6\text{Mo}/\text{TiO}_2$ catalysts, obvious decreases of the NO conversion were observed in the presence of SO_2 and H_2O in the temperature range of 160 – 400°C . However, the inhibition effect of SO_2 and H_2O on the $4\text{V}/\text{TiO}_2\text{-PILC}$ catalyst was negligible when the temperature was above 160°C . The NO conversion maintained a high level ($>96\%$) in the range of 250 – 400°C (Fig. 3(b)). The tolerance to SO_2 and H_2O of the three catalysts was in order of $4\text{V}/\text{TiO}_2\text{-PILC} > 4\text{V}6\text{Mo}/\text{TiO}_2 >$

$4\text{V}/\text{TiO}_2$. The concentrations of N_2O formed over the $4\text{V}/\text{TiO}_2\text{-PILC}$ catalyst above 300°C were lower compared with the other two catalysts, implying that the $4\text{V}/\text{TiO}_2\text{-PILC}$ catalyst had high N_2 selectivity at high temperature.

The effects of SO_2 and H_2O on the activities of the $4\text{V}/\text{TiO}_2\text{-PILC}$ and $4\text{V}6\text{Mo}/\text{TiO}_2$ catalysts are shown in Fig. 3(c). In the presence of SO_2 and H_2O , the NO conversion over $4\text{V}/\text{TiO}_2\text{-PILC}$ and $4\text{V}6\text{Mo}/\text{TiO}_2$ gradually decreased with time from 97% to 65% and from 84% to 69% , respectively, after 25 h. During the first 10 h on stream, the NO conversion over the $4\text{V}/\text{TiO}_2\text{-PILC}$ catalyst was higher than that of $4\text{V}6\text{Mo}/\text{TiO}_2$ catalyst. After 11 h, the NO conversion over the $4\text{V}/\text{TiO}_2\text{-PILC}$ catalyst was lower than that of the $4\text{V}6\text{Mo}/\text{TiO}_2$ catalyst. These results showed that the stability of the $4\text{V}/\text{TiO}_2\text{-PILC}$ catalyst was still not to our satisfaction, although it had good initial activity for the $\text{NH}_3\text{-SCR}$ reaction in the presence of SO_2 and H_2O .

3.3. $\text{SO}_2\text{-TPD}$ analysis

In order to investigate SO_2 adsorption on the catalysts, temperature-programmed desorption of SO_2 ($\text{SO}_2\text{-TPD}$) experiments were conducted. Fig. 4 shows the profiles of SO_2 ($m/z = 64$) signals with temperature. For the $4\text{V}/\text{TiO}_2$ and $4\text{V}/\text{TiO}_2\text{-PILC}$ catalysts, a weak peak at 92 and 108°C was de-

tected, respectively (Fig. 4(a)), which was attributed to the physisorption of SO_2 on the catalyst [30]. There was also a broad SO_2 desorption band at 550–850 °C for each catalyst, which was assigned to the decomposition of bulk sulfate species on titania formed by the interaction of SO_2 with lattice oxygen. For the 4V6Mo/TiO₂ catalyst, no obvious SO_2 desorption peak at low temperature was observed. Moreover, the intensity of the SO_2 desorption band at high temperature was much weaker than that of the two others. The 4V6Mo/TiO₂ catalyst exhibited the least SO_2 desorbed amount, which was possibly due to the inhibition by Mo of SO_2 adsorption [31]. When the three catalysts were exposed to (1% SO_2 + 8% O_2)/N₂ at 40 °C for 1 h, their SO_2 desorption behavior changed (Fig. 4(b)). The SO_2 desorption peak at low temperature disappeared and a new broad SO_2 desorption band at 350–600 °C appeared for each catalyst, which were due to the decomposition of chemisorbed sulfate and/or sulfite species on the titania surface [23,29]. These results indicated that the presence of O_2 promoted the oxidation of SO_2 and reduced physisorbed SO_2 . The significant decrease of the SO_2 desorption band at high temperature (> 700 °C) suggested that the interaction between SO_2 and the lattice oxygen of the catalyst was inhibited by the presence of O_2 , which reduced the formation of sulfate species on the catalyst. The SO_2 desorption amount from the 4V/TiO₂-PILC catalyst was comparative more than that from the 4V6Mo/TiO₂ catalyst, possibly due to the adsorption of SO_2 molecules on the clay.

3.4. In situ DRIFT studies

To investigate SO_2 poisoning of the SCR catalysts, the *in situ* DRIFT technique was used. The adsorption mechanism of sulfate species on metal oxides has been reported in the literature [32–34]. The sulfate infrared spectra show the interaction modes of the sulfate species with the surface, from the change of the number of S=O bonds in the sulfate species. Normally, the $\nu(\text{S=O})$ stretching mode of ionic sulfate with a bond number of 1.5 is observed at 1100 cm^{-1} . However, with increasing bond number, the stretching frequency shifts from 1300–1200 cm^{-1} for bond numbers of 1.6–1.7 to 1400 cm^{-1} for double bonds.

Corresponding to the increasing bond number, the binding character of sulfate changes from ionic to covalent [35]. Fig. 5(a) shows the DRIFT spectra of the 4V/TiO₂-PILC catalyst as a function of exposure time. After exposing the 4V/TiO₂-PILC catalyst to SO_2 , four peaks at 1373, 1359, 1344, and 1275 cm^{-1} appeared. Their intensities increased with exposure time. In other studies [36–38], the peaks at 1373, 1359 and 1344 cm^{-1} were attributed to the S=O stretching frequencies of chemisorbed sulfate and/or sulfite species, which indicated covalently bonded sulfate species on the surface of TiO₂ [39]. The band at 1275 cm^{-1} was assigned to ionic SO_4^{2-} species [36]. The band shift to lower frequencies indicated that the bond number of S=O decreased, implying that the binding mode of the sulfate species with the catalyst changed from covalent to ionic.

A broad band in the range of 1200–1100 cm^{-1} over the 4V/TiO₂ and 4V6Mo/TiO₂ catalysts was observed (Fig. 5(b)), which was assigned to bulk sulfate species. For the 4V/TiO₂ and 4V6Mo/TiO₂ catalysts, the DRIFT results were consistent with the SO_2 -TPD data. However, no bulk sulfate species was detected on the 4V/TiO₂-PILC catalyst. Compared to the other two catalysts, the intensity of the bands at 1359 and 1344 cm^{-1} over the 4V/TiO₂-PILC catalyst was higher (Fig. 5(b)), indicating more chemisorbed sulfate and/or sulfite species on the 4V/TiO₂-PILC catalyst. This would explain the larger SO_2 desorption band of the 4V/TiO₂-PILC catalyst in the SO_2 -TPD profile.

Fig. 6 shows the interaction of SO_2 and NH_3 on the catalyst. In the absence of SO_2 , four bands were observed for the 4V/TiO₂-PILC catalyst at 260 °C (Fig. 6(a)). The weak bands at 1598 and 1256 cm^{-1} were attributed to the asymmetric and symmetric bending vibrations of the N–H bonds in NH_3 coordinately linked to Lewis acid sites. The bands at 1674 and 1430 cm^{-1} were due to the asymmetric and symmetric deformation vibrations of the N–H bonds in ammonium ions formed by the chemisorption of NH_3 on Brønsted acid sites [22,40,41]. After the addition of 0.05% SO_2 to the feed, four new peaks at 1377, 1359, 1344, and 1270 cm^{-1} appeared. Their intensities increased with time in the SO_2 atmosphere. All these peaks were characteristic peaks of surface sulfate and/or sulfite species, indicating the adsorption of SO_2 on the catalyst. From Fig. 6(b),

Fig. 4. SO_2 -TPD profiles of the 4V/TiO₂-PILC (1), 4V/TiO₂ (2), and 4V6Mo/TiO₂ (3) catalysts pretreated under 1% SO_2 /N₂ (a) and (1% SO_2 + 8% O_2)/N₂ (b) atmospheres, respectively.

Fig. 5. (a) DRIFT spectra of 4V/TiO₂-PILC in SO₂ flow at 260 °C for different SO₂ exposure times; (b) DRIFT spectra of the three catalysts exposed to SO₂ for 150 min at 260 °C. Gas phase composition: 0.05% SO₂ and balanced by N₂.

Fig. 6. (a) DRIFT spectra of 4V/TiO₂-PILC in NH₃ + O₂ before and after the addition of 0.05% SO₂ at 260 °C for different times; (b) DRIFT spectra of the three catalysts in NH₃ + O₂ + SO₂ atmosphere for 150 min at 260 °C. Gas phase composition: 0.1% NH₃, 8% O₂, 0.05% SO₂ and balanced by N₂.

one can see that the intensity of the peak at 1272 cm⁻¹ over the 4V/TiO₂ and 4V6Mo/TiO₂ catalysts was stronger than that on the 4V/TiO₂-PILC catalyst, revealing the existence of more ionic SO₄²⁻ species on both the 4V/TiO₂ and 4V6Mo/TiO₂ catalysts. In other words, less ionic SO₄²⁻ species were formed on the surface of the 4V/TiO₂-PILC catalyst than on the 4V/TiO₂ and 4V6Mo/TiO₂ catalysts, implying that the conversion of chemisorbed SO₂ to SO₄²⁻ was inhibited on the 4V/TiO₂-PILC catalyst in the presence of NH₃. The amounts of ionic SO₄²⁻ species on the three catalyst were in the order of 4V/TiO₂-PILC < 4V6Mo/TiO₂ < 4V/TiO₂, which was reversed to that of NH₃-SCR activity over the three catalysts in the presence of SO₂ and H₂O. This showed that the accumulation of ionic SO₄²⁻ species on the

catalyst was one reason that led to the deactivation of the catalyst in the SCR reaction. In addition, for the 4V/TiO₂ catalyst, the bands at 1359 and 1344 cm⁻¹ were very weak, indicating that part of the sulfate species on the 4V/TiO₂ catalyst surface was transformed to ionic SO₄²⁻ species due to the presence of a hydrogen donor (NH₃). Weak bands at 1160 and 1140 cm⁻¹ over the 4V/TiO₂ and 4V6Mo/TiO₂ catalysts were also observed, showing the formation of the bulk sulfate species, but this band was not detected on the 4V/TiO₂-PILC catalyst.

The DRIFT experiments of the 4V/TiO₂-PILC catalyst were also conducted in a NO + O₂ + SO₂ atmosphere. As shown in Fig. 7, three peaks at 1629, 1600 and 1348 cm⁻¹ appeared in the absence of SO₂, which were all assigned to the formation of nitrate

species on the surface [42–44]. The addition of SO_2 resulted in the appearance of sulfate species bands at 1371, 1348 (overlapped with the band of nitrate species) and 1278 cm^{-1} . Moreover, their intensity increased with exposure time. In contrast, the intensity of the bands of the nitrate species decreased gradually with the introducing of SO_2 . The results showed that the existence of SO_2 promoted the reduction of the nitrate species.

We also investigated the interaction of SO_2 and the reaction gases. The DRIFT spectra of the catalysts in a flow of $\text{NO} + \text{NH}_3 + \text{O}_2$ with and without SO_2 at 260°C are illustrated in Fig. 8. The experiment was carried out by treating the catalysts in a flow of $\text{NO} + \text{NH}_3 + \text{O}_2$ for 60 min first, and then 0.05% SO_2 was introduced into the feed. From Fig. 8(a), one can see that the characteristic bands of nitrate species at 1630, 1600, and 1385 cm^{-1} were detected in the absence of SO_2 , but almost no N–H vibration band related to ammonia species was detected, which was possibly due to the consumption by the reaction between NO and NH_3 . New bands appeared at 1362 and 1277 cm^{-1} after the introduction of SO_2 and their intensity increased with time. Meanwhile, the bands at 1630, 1600, and 1385 cm^{-1} assigned to nitrate species disappeared gradually, further illustrating that the existence of SO_2 improved the reduction of nitrate species, which could be correlated with the good resistance of $4\text{V}/\text{TiO}_2\text{-PILC}$ to SO_2 poisoning. From Fig. 8(b), one can see that there were obvious differences among the DRIFT spectra of the three catalysts. For the $4\text{V}/\text{TiO}_2$ and $4\text{V}6\text{Mo}/\text{TiO}_2$ catalysts, the bands due to the nitrate species (1629 and 1600 cm^{-1}) still could be detected in the presence of SO_2 , revealing that the nitrate species could be maintained for some time on the surface under the reaction atmosphere. The intensity of the band at 1277 cm^{-1} attributed to ionic SO_4^{2-} species over the $4\text{V}/\text{TiO}_2\text{-PILC}$ catalyst was much weaker than that over the others, showing that the amount of ionic SO_4^{2-} species over the $4\text{V}/\text{TiO}_2\text{-PILC}$ catalyst was negligible. The broad bands at 1115 cm^{-1}

Fig. 7. DRIFT spectra of $4\text{V}/\text{TiO}_2\text{-PILC}$ in $\text{NO} + \text{O}_2$ before and after addition of 0.05% SO_2 at 260°C for different times. Gas phase composition: 0.1% NO , 8% O_2 , 0.05% SO_2 and balanced by N_2 .

cm^{-1} for the $4\text{V}/\text{TiO}_2$ and $4\text{V}6\text{Mo}/\text{TiO}_2$ catalysts also illustrated the existence of bulk sulfate species on the surface. The results were consistent with the other results in the above experiments.

From the *in situ* DRIFTs experiments, it was found that surface sulfate and/or sulfite species and ionic SO_4^{2-} species were formed on the catalysts, but the amount of ionic SO_4^{2-} species on the surface of the $4\text{V}/\text{TiO}_2\text{-PILC}$ catalyst was the least among the three catalysts. This was one reason why the $4\text{V}/\text{TiO}_2\text{-PILC}$ catalyst had better resistance to SO_2 poisoning than the two others.

Fig. 8. (a) DRIFTs spectra of $4\text{V}/\text{TiO}_2\text{-PILC}$ in $\text{NO} + \text{NH}_3 + \text{O}_2$ before and after addition of 0.05% SO_2 at 260°C for different times; (b) DRIFTs spectra of the three catalysts in $\text{NO} + \text{NH}_3 + \text{O}_2 + \text{SO}_2$ for 150 min at 260°C . Gas phase composition: 0.1% NO , 8% O_2 , 0.05% SO_2 and balanced by N_2 .

3.5. Surface oxygen species

In order to further explain the formation of surface ionic SO_4^{2-} species on the catalysts, XPS experiments were carried out to analyze the surface oxygen species of the catalysts. According to Fig. 9, the O 1s spectra exhibited two peaks due to different oxygen-containing chemical bonds. The first peak at 530.3 eV was attributed to the lattice oxygen O^{2-} (expressed by O_β) and the peak at 531.8 eV was assigned to surface adsorbed oxygen (O_α), including O_2^- , O_2^{2-} and O^- . The strong and broad peak at 532.3 eV over the 4V/TiO₂-PILC catalyst was attributed to surface hydroxyl, which existed on the interlayer of the clay [45,46]. The XPS data showed that the molar ratios of $\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$ on the three catalysts surface increased in the order of 4V/TiO₂-PILC < 4V6Mo/TiO₂ < 4V/TiO₂. The surface with more adsorbed oxygen species was more susceptible to sulfur poisoning than the surface without adsorbed oxygen species [47]. The surface oxygen species oxidize adsorbed SO_2 to SO_4^{2-} . When less O_α species existed on the surface, less ionic SO_4^{2-} species were formed on the catalyst. This is a plausible interpretation of the formation of less ionic SO_4^{2-} species on the 4V/TiO₂-PILC catalyst than the two others. On the other hand, surface adsorbed oxygen (O_{ads}) is often thought to be more reactive in oxidation reactions due to its higher mobility than lattice oxygen (O_{latt}), and it is beneficial for NO oxidation to NO_2 in the SCR reaction and facilitates the “fast SCR” reaction, which improve the catalytic performance of the catalyst [46,48].

In order to further identify the amounts of surface adsorbed oxygen over the catalysts, O₂-TPD experiments were carried out. It was known that physically adsorbed oxygen O_2 and chemically adsorbed oxygen $\text{O}_2^{2-}/\text{O}_2^-/\text{O}^-$ species are much easier to desorb than lattice O^{2-} species [49]. As shown in Fig. 10, the O₂-TPD profiles of the three catalysts displayed several broad oxygen desorption peaks from 100 to 850 °C. Based on the results reported in the literature [50,51], we attributed the peaks in the range of 100 to 500 °C to the desorption of chemisorbed oxygen (O_{ads}). The oxygen desorption peak at 750 °C over the 4V6Mo/TiO₂ catalyst was assigned to the decomposi-

Fig. 9. O 1s XPS spectra of the 4V/TiO₂-PILC (1), 4V/TiO₂ (2) and 4V6Mo/TiO₂ (3) catalysts.

Fig. 10. O₂-TPD profiles of the 4V/TiO₂-PILC (1), 4V/TiO₂ (2) and 4V6Mo/TiO₂ (3) catalysts.

tion of MoO_3 [52]. From Fig. 10, one can see that the intensity of the oxygen desorption peak over the 4V/TiO₂-PILC catalyst was much weaker than that over 4V/TiO₂ and 4V6Mo/TiO₂, indicating that the amount of oxygen species on its surface was much less than that over the others. The results agreed with the XPS analysis, further illustrating that the formation of ionic SO_4^{2-} species was correlated with the amount of surface adsorbed oxygen on the catalyst.

4. Conclusions

$\text{V}_2\text{O}_5/\text{TiO}_2$ -PILC, 4V/TiO₂ and 4V6Mo/TiO₂ catalysts were prepared and used in the SCR reaction of NO by NH_3 . The 4V/TiO₂-PILC catalyst showed higher catalytic activity with a broader operating temperature window and higher N_2 selectivity, as well as higher tolerance to SO_2 and H_2O in the SCR of NO by NH_3 . The accumulation of ionic SO_4^{2-} species on the catalyst was one reason for the deactivation of the catalyst, and the formation of ionic SO_4^{2-} species was correlated with the amount of surface adsorbed oxygen species on the catalyst.

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Graphical Abstract

Chin. J. Catal., 2016, 37: 888–897 doi: 10.1016/S1872-2067(15)61083-X

Resistance to SO₂ poisoning of V₂O₅/TiO₂-PILC catalyst for the selective catalytic reduction of NO by NH₃

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The accumulation of ionic SO₄²⁻ species on the V₂O₅/TiO₂-PILC catalyst surface might be one of the main reason that led to the deactivation of catalyst in SCR reaction in the presence of SO₂ and H₂O. The formation of ionic SO₄²⁻ species might correlate with the amount of surface adsorbed oxygen species on the catalyst.

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氨法选择性还原氮氧化物 V₂O₅/TiO₂-PILC 催化剂的抗硫性能

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摘要: 选择性催化还原 (SCR) 是目前去除氮氧化物最有效的方法之一。V₂O₅/TiO₂ 催化剂被广泛应用于氨法选择性还原氮氧化物 (NH₃-SCR) 反应, 但该催化剂存在工作温度高 (300–400 °C) 及 SO₂ 氧化率高引起设备腐蚀和管路堵塞等问题, 开发

低温 SCR 催化剂具有重要意义. 过渡金属氧化物 (如 Fe_2O_3 , MnO_x 和 CuO 等) 催化剂用于低温 SCR 先后见诸文献报道, 但这些催化剂在 SO_2 和 H_2O 存在下易失活. 近年来柱撑黏土 (PILC) 引起科学家广泛关注, Yang 等首次将 $\text{V}_2\text{O}_5/\text{TiO}_2$ -PILC 催化剂应用于 NH_3 -SCR 反应, 发现其催化活性高于传统 $\text{V}_2\text{O}_5/\text{TiO}_2$ 催化剂. 柱撑黏土基催化剂在 NH_3 -SCR 反应中也显示出良好抗硫性能, 但 $\text{V}_2\text{O}_5/\text{TiO}_2$ -PILC 催化剂的抗硫机理至今尚未见深入研究. 因此我们制备了一系列 $\text{V}_2\text{O}_5/\text{TiO}_2$ -PILC 催化剂, 采用原位漫反射红外等方法详细研究了其抗硫性能较好的原因.

首先采用离子交换法制备出 TiO_2 -PILC 载体, 之后采用浸渍法制备了不同钒含量 (质量分数 $x/\% = 0, 3, 4, 5$) 的 $x\text{V}_2\text{O}_5/\text{TiO}_2$ -PILC 催化剂. 同时, 制备了传统 $\text{V}_2\text{O}_5/\text{TiO}_2$ 和 $\text{V}_2\text{O}_5\text{-MoO}_3/\text{TiO}_2$ 催化剂作为对比. 活性评价结果显示, $4\text{V}/\text{TiO}_2$ -PILC 催化剂具有最高的催化活性, 其催化性能与传统钒钛催化剂相当. 在 160°C 时, NO 转化率可达 80% 以上. 同时, $4\text{V}/\text{TiO}_2$ -PILC 催化剂还具有较宽的反应温度窗口, 在 $260\text{--}500^\circ\text{C}$ 范围内, NO 转化率保持在 90% 以上. 向反应体系中加入 0.05% SO_2 和 10% H_2O 后, 在低温 (160°C 以下) 时所有催化剂的反应活性都有一定提高, 可能是由于 SO_2 的加入提高了催化剂的表面酸性. 继续升高温度, $4\text{V}/\text{TiO}_2$ 和 $4\text{V}6\text{Mo}/\text{TiO}_2$ 催化剂活性均明显下降, 而 $4\text{V}/\text{TiO}_2$ -PILC 催化剂的活性则未出现明显下降. 原位漫反射红外光谱结果显示, SO_2 在三种催化剂表面的吸附以表面硫酸盐或亚硫酸盐物种以及离子态 SO_4^{2-} 物种形式存在, 而在 $4\text{V}/\text{TiO}_2$ -PILC 催化剂表面离子态 SO_4^{2-} 物种的量最少. X 射线光电子能谱及 O_2 程序升温脱附结果显示, 在 $4\text{V}/\text{TiO}_2$ -PILC 催化剂上, 表面吸附氧 (O_{ads}) 的量最少. 综合上述分析可以得出, 在 SO_2 气氛下, 离子态 SO_4^{2-} 物种在 SCR 催化剂表面的累积可能是导致其失活的主要原因, 而离子态 SO_4^{2-} 物种的形成可能与催化剂表面吸附氧的量有关.

关键词: 选择性催化还原; 二氧化钛柱撑黏土; 氮氧化物; 钒基催化剂; 原位漫反射红外光谱

收稿日期: 2016-01-29. 接受日期: 2016-03-05. 出版日期: 2016-06-05.

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基金来源: 国家自然科学基金 (21277009, 21577005).

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