available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article

Highly dispersed V_2O_5/TiO_2 modified with transition metals (Cu, Fe, Mn, Co) as efficient catalysts for the selective reduction of NO with NH_3

Xin Zhao^a, Lei Huang^{a,#}, Hongrui Li^a, Hang Hu^a, Jin Han^a, Liyi Shi^{b,\$}, Dongsong Zhang^{a,*}^a Research Center of Nano Science and Technology, Shanghai University, Shanghai 200444, China^b Department of Chemistry, Shanghai University, Shanghai 200444, China

ARTICLE INFO

Article history:

Received 18 June 2015

Accepted 25 July 2015

Published 20 November 2015

Keywords:

deNO_x

Selective catalytic reduction

Vanadate

Transition metal

ABSTRACT

Different transition metals were used to modify V_2O_5 -based catalysts (M-V, M = Cu, Fe, Mn, Co) on TiO_2 via impregnation, for the selective reduction of NO with NH_3 . The introduced metals induced high dispersion in the vanadium species and the formation of vanadates on the TiO_2 support, and increased the amount of surface acid sites and the strength of these acids. The strong acid sites might be responsible for the high N_2 selectivity at higher temperatures. Among these catalysts, Cu-V/ TiO_2 showed the highest activity and N_2 selectivity at 225–375 °C. The results of X-ray photoelectron spectroscopy, NH_3 -temperature-programmed desorption, and *in-situ* diffuse reflectance infrared Fourier transform spectroscopy suggested that the improved performance was probably due to more active surface oxygen species and increased strong surface acid sites. The outstanding activity, stability, and SO_2/H_2O durability of Cu-V/ TiO_2 make it a candidate to be a NO_x removal catalyst for stationary flue gas.

© 2015, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Selective catalytic reduction (SCR) has proved to be the most effective technology in the control of NO_x emissions from both stationary and mobile sources, such as coal-fired power plants and heavy duty diesel engines [1–6]. The most widely used SCR catalyst is a V_2O_5 -based catalyst, which is very active when operating at 300–400 °C and highly tolerant to sulfur [7,8]. However, the V_2O_5 -based catalyst still suffers from a low N_2 selectivity, narrow temperature window, and sublimation of V_2O_5 at high temperatures even after modification with mo-

lybdenum and tungsten species [9–15]. The prices of tungsten and molybdenum resources have also increased recently. Therefore, improving the V_2O_5 -based catalyst with a low cost composition is still of great importance in industrial applications [16–18].

In recent years, many non-noble metals (Cu, Fe, Mn, Co, Ce, Zr, Nb, Sn, La, etc.) have been explored to promote the selectivity, operational temperature window, and stability of the V_2O_5 -based catalyst [7,19–23]. Normally, the introduced metals are in the form of oxides or vanadates, which have many effects on the active V species [13,17,24,25]. The redox properties and

* Corresponding author. Tel: +86-21-66136079; E-mail: dszhang@shu.edu.cn

Corresponding author. Tel: +86-21-66136079; E-mail: leihuang@shu.edu.cn

\$ Corresponding author. E-mail: shiliyi@shu.edu.cn

This work was supported by the National Natural Science Foundation of China (21303099), the National Basic Research Program of China (973 Program, 2014CB660803), the Shanghai Municipal Education Commission (14ZZ097, B.3704713001), and the Research Fund for Innovation Program of Shanghai University (K.10040713003).

DOI: 10.1016/S1872-2067(15)60958-5 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 36, No. 11, November 2015

dispersion of the vanadium species, the surface acid sites, and the inhibition of phase transfer from anatase to rutile are those most commonly targeted for improvement by introducing the metals. For example, the introduction of Fe_2O_3 improves the adsorption and activation of NH_3 [26], or the oxidation of NO to NO_2 [19]. Liu and co-workers [27] studied the effect of Mn on $\text{V}_2\text{O}_5/\text{TiO}_2$ for NH_3 -SCR. They found that adding Mn significantly enhanced the activity, redox cycle, and the reactive intermediates, thus promoting the NH_3 -SCR performance. Recently, some studies have shown that introducing the metals as vanadates can significantly improve the activity and N_2 selectivity, and especially the stability [28–30]. He and co-workers [29] have reported iron vanadates on TiO_2 , which showed high activity, N_2 selectivity, and $\text{H}_2\text{O}/\text{SO}_2$ durability in NH_3 -SCR reactions, which was due to the electronic inductive effect between the Fe^{3+} and V^{5+} species. Therefore, modifying the V_2O_5 -based catalysts with low cost metals is possible and could be of great importance in industrial applications.

In this work, we introduced abundant, low cost transition metals (Cu, Fe, Mn, Co) into $\text{V}_2\text{O}_5/\text{TiO}_2$, forming highly dispersed M-V/ TiO_2 catalysts for SCR reactions. The activity, N_2 selectivity, and $\text{SO}_2/\text{H}_2\text{O}$ resistance of the different M-V/ TiO_2 catalysts were studied. Both Cu-V/ TiO_2 and Fe-V/ TiO_2 performed excellently. The crystal structures and morphologies were characterised by X-ray diffraction (XRD), Raman spectroscopy, transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and energy-dispersive X-ray analysis and element mapping (EDX mapping). Redox properties, surface active oxygen species and acid sites were studied by hydrogen temperature-programmed reduction (H_2 -TPR), X-ray photoelectron spectroscopy (XPS), ammonia temperature-programmed desorption (NH_3 -TPD), and *in-situ* diffuse reflectance infrared Fourier transform spectroscopy (*in-situ* DRIFTS). The relationship between the catalytic performance and the physical and chemical properties of the catalysts was studied.

2. Experimental

2.1. Catalyst preparation

Titanium (IV) oxide (99.8%, anatase) with a particle size of about 25 nm was purchased from Aladdin. All other chemicals were purchased from Sinopharm Chemical Reagent Company and all were used without further purification.

The M-V/ TiO_2 catalysts were prepared by a co-impregnation method. In a typical process, the desired amounts of the nitrates of the different metals (Cu, Fe, Mn, Co) were first dissolved in deionised water. The amounts of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2$ (50 wt% aq.), and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were 0.23 g, 0.05 g, 0.28 g, and 0.23 g, respectively. The desired amount of ammonium metavanadate (NH_4VO_3) was dissolved in an aqueous solution of HNO_3 . These amounts were 0.16 g, 0.25 g, 0.18 g, and 0.18 g, respectively. The total amount of all the M-V oxides was kept at 10% (mass fraction) of TiO_2 to achieve approximately monolayer coverage [29]. These two solutions were then mixed by magnetic stirring. TiO_2 (2.0 g) was then added to the mixed solution and

dispersed with ultrasound and stirred for 1 h before being dried in a rotary evaporator at 48 °C with the help of a vacuum pump. These mixtures gave molar ratios of the metal to vanadium of 1:1.5, 1:17, 1:2, and 1:2, respectively, which were designed to favour the formation of vanadates, namely $\text{CuV}_2\text{O}_6/\text{Cu}_2\text{V}_2\text{O}_7$, $\text{Fe}_{0.12}\text{V}_2\text{O}_5$, MnV_2O_6 , and CoV_2O_6 . Finally, the so obtained samples were dried at 80 °C for 12 h and calcined at 400 °C for 6 h in air. For comparison, the $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst was also prepared by the same impregnation method without the addition of a nitrate.

For the comparative studies on the structure and the physical and chemical properties, the pure metal (Cu, Fe, Mn, Co) vanadates and corresponding metal (Cu, Fe, Mn, Co) oxides, namely 10% MO_x/TiO_2 , were also prepared by the same impregnation method. The TiO_2 support and the ammonium metavanadate (NH_4VO_3) was absent from the preparation of these catalysts.

2.2. Characterisation

XRD was performed on a Rigaku D/MAX-RB X-ray diffractometer using $\text{Cu K}\alpha$ (40 kV, 40 mA) radiation and a secondary beam graphite monochromator. Nitrogen adsorption-desorption isotherms of the samples were measured at –196 °C using a Micromeritics ASAP 2010 instrument, and the corresponding pore size distribution curves were calculated from desorption branches by the BJH method. The specific surface areas of the samples were calculated by the Brunauer-Emmett-Teller (BET) method. TEM and HRTEM were recorded on a JEM-200CX and JEM-2100F microscope, respectively. EDX mapping was obtained using an Inca Energy 200 TEM system from Oxford Instruments. To prepare the (HR)TEM and EDX-mapping samples, the M-V/ TiO_2 samples were first dispersed in ethanol by ultrasonication for 30 min and a Cu grid was dipped into the solution (a Mo grid was used instead of a Cu grid to avoid disturbing the copper in the Cu-V/ TiO_2 catalyst) and dried under the irradiation of infrared lamp before analysis. XPS of all the elements was recorded on a Perkin-Elmer PHI 5000C ESCA system equipped with a dual X-ray source, using a $\text{Mg-K}\alpha$ (1253.6 eV) anode and a hemispherical energy analyser. The background pressure during data acquisition was kept below 10^{-6} Pa. All the binding energies were calibrated using contaminant carbon ($\text{C } 1s = 284.6$ eV) as a reference. The visible Raman spectra were recorded on an inVia-reflex Renishaw spectrometer equipped with a holographic notch filter, a CCD detector, and irradiated with a laser at 514 nm. The UV Raman spectra were recorded on a home-assembled UV Raman system equipped with a Jobin-Yvon T64000 triple-stage spectrograph. A He-Cd laser at 325 nm was used as the excitation source.

H_2 -TPR and NH_3 -TPD were conducted on a TianjinXQ TP-5080 auto-adsorption apparatus, and NH_3 and H_2 were monitored by a TCD. Each sample (80 mg) was pre-treated with high-purity N_2 (99.999%, 30 mL/min) at 300 °C for 30 min before either test. For H_2 -TPR, after cooling to room temperature, the flowing gas was switched to 10% H_2 -90% N_2 and the reactor temperature was raised to 800 or 900 °C at a rate of 10 °C/min. For NH_3 -TPD, after cooling to 100 °C, the samples were

exposed to a flow of NH_3 at the same temperature for 1 h. Finally, the temperature was raised to 500 °C at a heating rate of 10 °C/min.

In-situ DRIFTS experiments were conducted from 1100 to 1900 cm^{-1} at a spectral resolution of 4 cm^{-1} (number of scans, 64) on an FTIR spectrometer (Nicolet 6700) equipped with a Harrick DRIFTS cell and an MCT/A detector. The catalysts were pre-treated at 400 °C in a flow of N_2 (50 mL/min) for 0.5 h to remove physisorbed water and other impurities, then cooled to the target temperature under a N_2 flow before each experiment. Background spectra were recorded in the N_2 flow and automatically subtracted from the corresponding spectra.

2.3. Activity measurements

The SCR reactions were carried out in a fixed-bed quartz micro-reactor (i.d. 8 mm) operating in steady state flow mode. The reaction conditions were as follows: 0.4 g catalysts, 550 ppm NO, 550 ppm NH_3 , 5 vol% O_2 , 8 vol% H_2O (when used), 200 ppm SO_2 (when used), and the balance N_2 . The total flow rate was 250 mL/min, and thus a gas hourly space velocity (GHSV) of 26000 h^{-1} . The temperature was increased from 150 to 400 °C. At each temperature step the concentrations of NO, NH_3 , and N_2O were recorded. The concentrations of NO in the inlet and outlet gases were measured by a 4000VM NO_x analyser. The concentrations of N_2O and NH_3 were measured by a transmission IR N_2O analyser and IQ 350 ammonia analyser. NO conversion and N_2 selectivity were calculated according to the following expressions:

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

$$\text{N}_2 \text{ selectivity} = (1 - 2[\text{N}_2\text{O}] / ([\text{NO}_x]_{\text{in}} + [\text{NH}_3]_{\text{in}} - [\text{NO}_x]_{\text{out}} - [\text{NH}_3]_{\text{out}})) \times 100\%$$

The $[\text{NO}]_{\text{in}}$, $[\text{NO}]_{\text{out}}$, $[\text{NO}_x]_{\text{in}}$, $[\text{NO}_x]_{\text{out}}$, $[\text{NH}_3]_{\text{in}}$, $[\text{NH}_3]_{\text{out}}$, and $[\text{N}_2\text{O}]_{\text{out}}$ correspond to the inlet and outlet concentration of a steady-state, respectively. NO_x means the total concentration of NO and NO_2 .

3. Results and discussion

3.1. NH_3 -SCR activity

Figure 1(a) shows the NO conversion over the different M-V/TiO₂ and V₂O₅/TiO₂ catalysts as the temperature increased from 150 to 400 °C. All the samples had an operational temperature window (the temperature range at which the conversion of NO is higher than 90%) within this range. Of these, Cu-V/TiO₂ showed the widest temperature window (225–375 °C), followed by Fe-V/TiO₂ (225–350 °C) and Mn-V/TiO₂ (275–375 °C). No obvious temperature window existed for Co-V/TiO₂. The V₂O₅/TiO₂ sample also showed a temperature window of 200–325 °C, which is a similar width to Cu-V/TiO₂ and Fe-V/TiO₂, but at lower temperatures. It should be noticed that while the loading of M-V and V were the same, the actual amount of vanadium species for V₂O₅/TiO₂ (10% V) was higher than for Cu-V/TiO₂ (6% V). It is widely accepted that the vanadium species is one of the most active components in the SCR reaction. Therefore, the high performance of

Fig. 1. (a) NO conversion and (b) N_2 selectivity for NH_3 -SCR over M-V/TiO₂ as a function of temperature at a total feed gas rate of 250 mL/min. Reaction conditions: $[\text{NO}] = [\text{NH}_3] = 550$ ppm, $[\text{O}_2] = 5\%$, GHSV = 26000 h^{-1} .

V₂O₅/TiO₂ was simply due to the increased amount of V compared with Cu-V/TiO₂ and Fe-V/TiO₂. When the amount of the vanadium pentoxide was decreased to 6% (denoted as 6% V₂O₅/TiO₂), giving an equal molar amount of vanadium species as in Cu-V/TiO₂, the temperature window moved to 225–300 °C. This range is significantly more narrow than Cu-V/TiO₂.

The N_2 selectivity over the samples for the NH_3 -SCR reactions was also studied, as shown in Fig. 1(b). It was found that the selectivity decreased for all samples as the reaction temperature increased. Among them, Cu-V/TiO₂ showed the highest selectivity, which remained above 94.9% for the temperature range of 150–400 °C. The next better ones were Fe-V/TiO₂ and Mn-V/TiO₂, where the selectivity for both remained above 89.6% over the same temperature range. In contrast, both Co-V/TiO₂ and V₂O₅/TiO₂ showed unstable selectivity, which rapidly decreased above 350 °C. The selectivity for V₂O₅/TiO₂ was below 90.0% for the entire temperature window of 200–325 °C and decreased to below 40% at 400 °C. Furthermore, the N_2 selectivity of 6% V₂O₅/TiO₂ decreased rapidly above 300 °C and was below 50% at 400 °C.

N_2O can be generated by the nonselective oxidation of NH_3 , which is usually characterised by N_2 selectivity and has a significant influence on the NH_3 -SCR performance [31]. For example, the N_2 selectivity of both the Co-V/TiO₂ and V₂O₅/TiO₂ catalysts decreased rapidly above 350 °C, and the NO conversion of the two catalysts decreased simultaneously, indicating that

the decrease in activity was probably due to the nonselective oxidation of NH_3 . The Cu-V/TiO_2 catalyst showed the highest N_2 selectivity over the temperature region of interest, indicating that the Cu-V/TiO_2 catalyst was efficient in reducing the unselective oxidation of NH_3 .

State-of-the-art V-W- TiO_2 catalysts are (1–2)% $\text{V}_2\text{O}_5/\text{TiO}_2$ and (8–10)% WO_3/TiO_2 . Therefore, we decided to study the influence of Cu and Fe on $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts with 1% V_2O_5 . Fig. 2(a) shows that both $\text{Cu-1\%V/TiO}_2$ and $\text{1\%V-10\%W/TiO}_2$ have similar operational temperature windows of about 300–475 °C, which is considerably higher than Cu-V/TiO_2 and 6% $\text{V}_2\text{O}_5/\text{TiO}_2$. $\text{Fe-1\%V/TiO}_2$ showed a more narrow temperature window of 375–475 °C. Fig. 2(b) shows that both $\text{Cu-1\%V/TiO}_2$ and $\text{Fe-1\%V/TiO}_2$ had much better selectivity than $\text{1\%V-10\%W/TiO}_2$. Specifically, the selectivity of $\text{1\%V-10\%W/TiO}_2$ decreased to below 90.0% between 400–475 °C, which was still within the operational temperature window.

From these results, the introduction of Cu and Fe simultaneously improved both the NO conversion and N_2 selectivity over $\text{V}_2\text{O}_5/\text{TiO}_2$, whereas Mn and Co did not. The addition of Cu achieved similar NO conversion and better N_2 selectivity compared with the state-of-the-art V-W- TiO_2 catalysts, implying that a copper-modified V_2O_5 -based catalyst might be a potential NH_3 -SCR catalyst.

3.2. Stability and $\text{SO}_2/\text{H}_2\text{O}$ durability

As both Cu-V/TiO_2 and Fe-V/TiO_2 catalysts showed high NO conversion and N_2 selectivity, they were chosen for further study into their stability and $\text{SO}_2/\text{H}_2\text{O}$ durability. First, the stabilities of the Cu-V/TiO_2 and Fe-V/TiO_2 catalysts were tested at 175 and 275 °C. The feed gases were the same as in the activity measurements. Fig. 3(a) shows that both Cu-V/TiO_2 and Fe-V/TiO_2 were stable for 20 h operation in the SCR reaction.

2–15 vol% H_2O and 30–2000 ppm SO_2 are usually present in exhaust flows and have a strong effect on the performance of the catalysts. The $\text{SO}_2/\text{H}_2\text{O}$ durability then was further investigated by introducing 8 vol% H_2O and 200 ppm SO_2 in the feed stream at 175 and 275 °C (Fig. 3(b)). The NO conversion over

Fig. 2. (a) NO conversion and (b) N_2 selectivity in NH_3 -SCR reaction as a function of temperature in the feed gas of 250 mL/min total rate over the $\text{Cu-1\%V/TiO}_2$, $\text{Fe-1\%V/TiO}_2$, and $\text{1\%V-10\%W/TiO}_2$. Reaction conditions: $[\text{NO}] = [\text{NH}_3] = 550$ ppm, $[\text{O}_2] = 5\%$, $\text{GHSV} = 26000$ h^{-1} .

Cu-V/TiO_2 at 175 °C showed a small decrease from 46.4% to 44.1% after the introduction of H_2O and SO_2 , but returned to 45.0% after the contaminants were turned off. The introduction of H_2O and SO_2 did not cause obvious effect on the performance of the catalyst. With the Fe-V/TiO_2 catalyst, the NO conversion decreased from 49.4% to 44.5%. When the temperature was increased to 275 °C, the combined impact of H_2O and SO_2 induced a 2.0% decrease in the NO conversion over

Fig. 3. (a) Stability test at 175 and 275 °C for 20 h and (b) $\text{SO}_2/\text{H}_2\text{O}$ durability test of the Cu-V/TiO_2 and Fe-V/TiO_2 catalysts. Reaction conditions: $[\text{NO}] = [\text{NH}_3] = 550$ ppm, $[\text{O}_2] = 5\%$, $[\text{H}_2\text{O}] = 8$ vol%, $[\text{SO}_2] = 200$ ppm, $\text{GHSV} = 26000$ h^{-1} .

Cu-V/TiO₂, but the NO conversion was recovered when the supply of H₂O and SO₂ was stopped. The NO conversion over the Fe-V/TiO₂ catalyst was not affected by the introduction of H₂O and SO₂ at this temperature, which agrees with other reports [28,29]. In summation, both the Cu-V/TiO₂ and Fe-V/TiO₂ catalysts were highly sulfur-tolerant and water-resistant.

3.3. N₂ sorption analysis

Table 1 shows the textural parameters of M-V/TiO₂ catalysts. The BET surface area of the TiO₂ support was about 89.2 m²/g. However, this decreased to 62.6–65.8 m²/g after the M-V loading, which was probably due to the impregnated species blocking the pores of the TiO₂ support or by aggregation of the TiO₂ support. The V₂O₅/TiO₂ catalyst showed the lowest surface area at 56.3 m²/g, indicating that the TiO₂ particles agglomerate more easily after loading with V₂O₅. Although the BET surface areas of the catalysts showed variation, there was no direct relationship with the activity of catalysts. For example, the NO conversion over the Cu-V/TiO₂ catalyst was the highest, but its BET surface area was relatively small (62.6 m²/g). In addition to the BET surface area, the textural parameters of the M-V/TiO₂ catalysts after the reaction test were also studied. The surface areas of some of the used catalysts were slightly increased, but this was within the error of the instrument. The decrease in activity at higher temperature was not due to the decrease of surface area, but more likely because of the nonselective oxidation of NH₃ as illustrated in Fig. 1(b). Based on these results, it appears that the textural parameters do not play an important role in the SCR reaction.

3.4. XRD analysis

XRD patterns of the catalysts were recorded to study the crystal structure of M-V/TiO₂ catalysts, after being calcined at 400 °C for 6 h. As shown in Fig. 4, only the diffraction peaks of anatase (JCPDS Card No. 21–1272) were observed in all the samples. No other peaks belonging to the metal (Cu, Fe, Mn, Co), vanadates, metal oxides, or vanadium species were detected. This indicates that the vanadium species and the introduced transition metals were amorphous or in a highly dis-

Fig. 4. XRD patterns of the M-V/TiO₂ catalysts.

persed crystallite state on the TiO₂ surface.

We further prepared the M-V oxides by the same process, but leaving out the TiO₂. The corresponding XRD patterns are shown in Fig. 5. Interestingly, vanadates were found in the M-V oxides. For Cu-V, the diffraction peaks could be assigned to the Cu₂V₂O₇, CuV₂O₆, and CuO. For Fe-V, the diffraction peaks of Fe_{0.12}V₂O₅ and Fe₂O₃ were observed. For Mn-V, the diffraction peaks of MnV₂O₆ and V₂O₅ were observed. For Co-V, the diffraction peaks of CoV₂O₆ and V₂O₅ were observed. This indicates that the metal vanadates might be formed over the M-V/TiO₂ obtained through similar processes.

3.5. Visible and UV Raman spectroscopy

Raman spectroscopy was used to study the structure of these surface metal oxide species. Visible Raman spectra (Fig. 6(a)) indicated that the M-V/TiO₂ catalysts only displayed the typical Raman shifts of anatase TiO₂ (*E_g* at 145 and 636 cm⁻¹, *B_{1g}* at 396 cm⁻¹ and *A_{1g}* at 517 cm⁻¹) [29]. No other Raman shifts that could be ascribed to metal, vanadates, or metal oxides were observed.

It has been well demonstrated that UV-Raman spectroscopy is more surface-sensitive for TiO₂-containing samples because TiO₂ has a strong absorption in the UV region [32,33]. UV-Raman spectroscopy was therefore recorded with 325 nm excitation. Fig. 6(b) shows that new bands were observed in the 700–1100 cm⁻¹ region from species other than anatase TiO₂. In this region, the band at 915–950 cm⁻¹ was assigned to a polymerised V–O–V stretching mode. In particular, the bands within 930–960 cm⁻¹ were assigned to the bridging V–O–V stretching modes of a polymeric surface vanadate species, such as VO₄ units [14,34]. The band at ~990 cm⁻¹ corresponds to terminal V=O groups in bulk V₂O₅ and indicates crystalline V₂O₅ is present on the surface of TiO₂ [34,35,36]. The V₂O₅/TiO₂ sample had two bands at 917 and 990 cm⁻¹, indicating that the vanadium species had agglomerated. For the M-V/TiO₂ samples, the 917 and 990 cm⁻¹ bands were absent (except in Fe-V/TiO₂), indicating that the introduced metals increased the dispersion of the vanadium species. Furthermore, the appear-

Table 1

Textural parameters of the M-V/TiO₂ catalysts, obtained from N₂ sorption results.

Sample	<i>S</i> _{BET} ^a (m ² /g)	<i>V</i> _{BH} ^b (cm ³ /g)	<i>D</i> _{BH} ^c (nm)
TiO ₂	89.2	0.36	15.4
Cu-V/TiO ₂	62.6	0.26	16.4
Fe-V/TiO ₂	64.7	0.27	14.8
Mn-V/TiO ₂	65.8	0.25	17.0
Co-V/TiO ₂	63.9	0.28	15.6
V ₂ O ₅ /TiO ₂	56.3	0.24	18.9
Cu-V/TiO ₂ (used) ^d	67.3	0.32	15.6
Fe-V/TiO ₂ (used) ^d	62.6	0.28	15.6
Mn-V/TiO ₂ (used) ^d	63.1	0.29	15.5
Co-V/TiO ₂ (used) ^d	65.8	0.30	15.6
V ₂ O ₅ /TiO ₂ (used) ^d	57.9	0.25	15.8

^a BET surface area. ^b BJH desorption pore volume.

^c Average pore diameter. ^d The catalysts after the activity test.

Fig. 5. XRD patterns of the M-V oxides without TiO_2 support. (a) Cu-V; (b) Fe-V; (c) Mn-V; (d) Co-V.

Fig. 6. (a) Vis-Raman and (b) UV-Raman spectra of the M-V/ TiO_2 catalysts.

ance of bands at around 940 cm^{-1} showed that vanadates are present on the TiO_2 . The presence of these bands in Fe-V/ TiO_2 was probably due to the small amount of iron in the iron vanadates ($\text{Fe}_{0.12}\text{V}_2\text{O}_5$) as seen in the XRD results.

Combining the XRD and Raman results, we proposed that the dispersal of the vanadium species on the surface of the TiO_2 was improved by the introduced transition metals. Furthermore, vanadates were formed and might be beneficial for the SCR reaction as has been demonstrated previously [28,29,37].

3.6. TEM and EDX-mapping analysis

The morphology of Cu-V/ TiO_2 was investigated by TEM as shown in Fig. 7(a). The catalyst particles were about 30–80 nm in diameter, which is significantly larger than the purchased TiO_2 (~25 nm). This might be caused by the aggregation of the TiO_2 support after loading the metal vanadates. This may also have caused the decrease in the BET surface area.

Fig. 7. (a) TEM image, (b) HRTEM image, and (c–f) EDX mapping images of the Cu-V/TiO₂ catalyst.

The morphology of the Cu-V/TiO₂ catalyst was further studied by HRTEM. Fig. 7(b) indicates that the TiO₂ support was mainly anatase, as indicated by the (101) lattice fringes at 0.346 nm. No vanadium-containing phases were observed, indicating that the Cu-V was highly dispersed. The distributions of different elements were further studied by EDX mapping as shown in Fig. 7(c–f). The distributions of V and Ti were quite similar, indicating that the V species were uniformly dispersed on the TiO₂ support. The distributions of O and Cu were similar to each other but there was evidence they extended beyond the presence of V and Ti, which was probably due to the formation of CuO that was dispersed on the TiO₂ during sample preparation. The presence of CuO was observed in the XRD patterns in Fig. 5.

3.7. H₂-TPR analysis

The redox properties of the M-V/TiO₂ catalysts were investigated by H₂-TPR. For comparison, the corresponding transition metal oxides over TiO₂ (MO_x/TiO₂) and V₂O₅/TiO₂ were

also studied as shown in Fig. 8. The assignment of the peak positions to the corresponding chemical processes of MO_x/TiO₂ and V₂O₅/TiO₂ are summarised in Table 2 [1,38–46]. It was widely accepted that the particle size has a significant influence on the reduction temperatures. Normally, the oxides with smaller particles are more easily reduced. For example, the isolated V species on a support are reduced at about 550 °C, while polymeric species are reduced above 700 °C [47–49]. However, the interaction between different oxides can cause co-reduction, which means that one component becomes easier to reduce when the nearby components are already reduced. For example, the copper species in copper vanadates were reduced at higher temperatures when compared with copper oxide, whereas the vanadium species in copper vanadates were reduced at lower temperature when compared with vanadium oxides [47]. Similar phenomena have been reported for different vanadates and were observed in this work [50,51].

Fig. 8(a) shows that the V₂O₅/TiO₂ catalyst had a reduction band at 534 °C, which was assigned to the reduction of an isolated V species from V⁵⁺ to V⁴⁺ [40,41]. The small peak at 680 °C

Fig. 8. H₂-TPR profiles of the catalysts. (a) MO_x/TiO₂; (b) M-V/TiO₂.

Table 2Temperature dependent reduction results for the MO_x catalysts.

MO _x	Peak position (°C)	Chemical process	Ref.
V ₂ O ₅	500–760	V ₂ O ₅ + H ₂ → V ₂ O ₄ + H ₂ O	[40,41]
CuO	200–220	2CuO + H ₂ → Cu ₂ O + H ₂ O	[38,39]
	250–300	Cu ₂ O + H ₂ → Cu + H ₂ O	
	400–520	3Fe ₂ O ₃ + H ₂ → 2Fe ₃ O ₄ + H ₂ O	
Fe ₂ O ₃	450–620	Fe ₃ O ₄ + H ₂ → 3FeO + H ₂ O	[42,43]
	>700	FeO + H ₂ → Fe + H ₂ O	
	320–350	2MnO ₂ + H ₂ → Mn ₂ O ₃ + H ₂ O	[1,44]
MnO ₂	350–420	3Mn ₂ O ₃ + H ₂ → 2Mn ₃ O ₄ + H ₂ O	
	460–530	Mn ₃ O ₄ + H ₂ → 3MnO + H ₂ O	
Co ₃ O ₄	300–380	Co ₃ O ₄ + H ₂ → 3CoO + H ₂ O	[45,46]
	400–480	CoO + H ₂ → Co + H ₂ O	

was attributed to a V⁴⁺ to V³⁺ reduction [40,41]. The profile of CuO/TiO₂ has two peaks at 184 and 274 °C, which were attributed to a Cu²⁺ to Cu⁺ and a Cu⁺ to Cu⁰ reduction, respectively [38,39]. For the Cu-V/TiO₂ catalyst (Fig. 8(b)), the main reduction band was at 212 °C. According to the literature and the H₂-TPR profiles of CuO/TiO₂ and V₂O₅/TiO₂, this peak could be assigned to the reduction of a copper species that has been affected by the vanadium species. The small band at 372 °C was probably due to the reduction of a highly dispersed vanadium species. Therefore, the present H₂-TPR results suggest the presence of copper vanadates on Cu-V/TiO₂ [29]. A small band at about 862 °C was due to the reduction of a polymeric vanadium species [47–49].

Fig. 8(b) also shows the H₂-TPR profiles of the Fe-V/TiO₂, Mn-V/TiO₂, and Co-V/TiO₂ catalysts. There are main reduction peaks at 451, 522, and 438 °C for the Fe-V/TiO₂, Mn-V/TiO₂, and Co-V/TiO₂ catalysts, respectively. Combined with the reported reduction processes of different metal oxides from Table 2 and the H₂-TPR results of the transition metal oxides in Fig. 8(a), these reduction bands could be attributed to the co-reduction of the transition metal and an isolated vanadium species due to the formation of vanadates. The small bands at above 700 °C were attributed to the reduction of vanadium species.

The main outcome of these experiments is that there is only one main reduction band for the M-V/TiO₂ catalysts. The formation of vanadates resulted in the reduction of vanadium species at lower temperatures whereas the reduction of the transition metals moved to higher temperatures.

3.8. XPS analysis

XPS was used to investigate the surface compositions and chemical states of the elements. The surface atomic concentrations, as estimated from the survey scan of the XPS data, are summarised in Table 3. It was clear that the ratios of transition metals to vanadium were close to the ratios of the precursor materials except for Fe-V/TiO₂, indicating that the transition metals and vanadium species were highly dispersed on the TiO₂ supports.

The O 1s bands of the different catalysts in Fig. 9(a) were deconvoluted using a curve-fitting procedure. The sub-bands at lower binding energy (530.2–530.5 eV) belong to the lattice

Table 3Binding energies, active oxygen species, and the ratios of M to V in the V₂O₅/TiO₂ and M-V/TiO₂ catalysts.

Catalyst	Binding energy (eV)		O _α /(O _α +O _β)	M/V
	O _α	O _β		
V ₂ O ₅ /TiO ₂	531.25	529.74	56.09%	—
Cu-V/TiO ₂	531.60	530.20	65.97%	1/2.7
Fe-V/TiO ₂	531.60	530.20	59.32%	1/3.8
Mn-V/TiO ₂	531.60	530.20	58.43%	1/1.7
Co-V/TiO ₂	531.60	530.20	55.05%	1/2.3

oxygen O²⁻ (denoted O_β), and the sub-bands at higher binding energy (531.6–532.1 eV) correspond to surface adsorbed oxygens (denoted O_α), such as O₂²⁻ (or O⁻) from defect oxides or hydroxyl-like groups [19,52–56]. The corresponding peak-fitting results of O 1s and the relative concentration ratios of O_α/(O_α+O_β) for these catalysts are summarised in Table 3. The O_α/(O_α+O_β) ratio for Cu-V/TiO₂ was much higher than for other M-V/TiO₂ and V₂O₅/TiO₂. Surface oxygen O_α has been shown to have higher mobility than the lattice oxygen O_β, and O_α is therefore more active in the oxidation of NO to NO₂. The presence of NO₂ is beneficial to the so called “fast SCR” reaction and is helpful in the NH₃-SCR process [57–62]. Thus, the improved SCR performance of Cu-V/TiO₂ was partially due to the presence of more surface oxygen O_α. For V₂O₅/TiO₂ and the other M-V/TiO₂ samples, the relative concentration ratios of O_α/(O_α+O_β) were quite similar, implying that the different activities were because of other factors, such as the surface acids sites and the redox properties.

The XPS results from the different transition metals are shown in Fig. 9(c). The metals were present in more than one valence state, indicating that they had complicated coordination spheres due to the formation of metal oxides and vanadates, as demonstrated in the XRD and Raman results, and the formation of new surface states. Cu 2p_{3/2} and the corresponding satellite peak confirmed that the copper species were present mainly as Cu²⁺ in CuV₂O₆, Cu₂V₂O₇, or CuO. The Fe species were present as Fe³⁺, which was doped into the crystal lattice of V₂O₅ or as amorphous Fe₂O₃. For both the Mn and Co species, the more highly oxidised Mn⁴⁺ and Co³⁺ species were observed as well as Mn³⁺ and Co²⁺, indicating that other metal oxides were formed as well as the MnV₂O₆ and CoV₂O₇ vanadates. The XPS, XRD, and Raman results indicated that the M-V oxides on TiO₂ were a mixture of vanadates, metal oxides, and/or V₂O₅.

The V 2p and Ti 2p XPS results for V₂O₅/TiO₂ and M-V/TiO₂ are shown in Fig. 9(b) and (d), respectively. The binding energies of V 2p_{3/2} and Ti 2p_{3/2} are at 517.2 and 458.9 eV, respectively, indicating that the vanadium was mainly present as V⁵⁺ and the titanium as Ti⁴⁺. Fig. 9(b) indicates that both the V 2p of Cu-V/TiO₂ and Mn-V/TiO₂ had shifted to higher binding energies. Fig. 9(d) also indicates that the Ti 2p_{3/2} peaks had shifted to higher binding energies, which was probably due to the electric effect between the vanadates and the TiO₂ support.

3.9. NH₃-TPD analysis

NH₃-TPD was performed to study the adsorption and acti-

Fig. 9. XPS spectra for (a) O 1s, (b) V 2p, (c) M (Cu, Fe, Mn, Co), and (d) Ti 2p of the catalysts.

vation of NH_3 on the active sites of the catalyst surface, as this is a crucial process in the NH_3 -SCR reaction. Normally, the NH_3 desorption peaks at 120–240 °C corresponded to partially ionic NH_4^+ bound to weak Brönsted acid sites. The peaks at 250–450 °C were assigned to the desorption of NH_4^+ bound to strong Brönsted acid sites or coordinated NH_3 bounded to Lewis acid sites.

Fig. 10(a) shows that all the NH_3 -TPD profiles of the

M-V/TiO₂ catalysts can be deconvoluted into three peaks. According to the above assignments, the peaks below 240 °C (198 °C for Cu-V/TiO₂, 190 °C for Fe-V/TiO₂, 185 °C for Mn-V/TiO₂, 184 and 238 °C for Co-V/TiO₂, 176 and 230 °C for V₂O₅/TiO₂) belong to the desorption of partially ionic NH_4^+ bound to weak Brönsted acid sites [63–65]. The peaks from 250 to 450 °C (266 and 353 °C for Cu-V/TiO₂, 250 and 340 °C for Fe-V/TiO₂, 252 and 335 °C for Mn-V/TiO₂, 332 °C for Co-V/TiO₂, 305 °C for V₂O₅/TiO₂) belong to the desorption of coordinated NH_3 bounded to Lewis acid sites.

Fig. 10. (a) NH_3 -TPD profiles, (b) the ratios of strong acid sites to weak acid sites of the catalysts, and (c) the normalised peak intensity of the total acid sites (strong acid sites + weak acid sites) for M-V/TiO₂ and V₂O₅/TiO₂.

$\text{V}_2\text{O}_5/\text{TiO}_2$) can then be assigned to the desorption of ionic NH_4^+ bound to strong Brönsted acid sites or a coordinated NH_3 bound to Lewis acid sites [20,66,67].

Because the strong Brönsted acid sites and Lewis acid sites located at 250–450 °C are difficult to identify based on the NH_3 -TPD profiles, both acid sites were assigned as strong acid sites as distinct from the weak acid sites at 120–240 °C. The ratios of the strong acid sites to the weak acid sites are summarised in Fig. 10(b), whereas the total amount of surface acids sites is summarised in Fig. 10(c). Both results indicate that the

introduction of transition metals significantly increased the total amount of acid sites and the strong acid sites, especially for $\text{Cu-V}/\text{TiO}_2$.

3.10. In-situ DRIFTS studies

NH_3 adsorption *in-situ* DRIFTS was used to investigate the surface acidity of these catalysts, and the corresponding results are presented in Fig. 11. Normally, the bands at 1430–1440 and 1650–1680 cm^{-1} are assigned to the asymmetric bending vi-

Fig. 11. *In-situ* DRIFTS of NH_3 adsorption on the catalysts. (a) $\text{V}_2\text{O}_5/\text{TiO}_2$; (b) $\text{Cu-V}/\text{TiO}_2$; (c) $\text{Fe-V}/\text{TiO}_2$; (d) $\text{Mn-V}/\text{TiO}_2$; (e) $\text{Co-V}/\text{TiO}_2$; (f) The ratios of $I_{L\text{-acid}}/I_{B\text{-acid}}$ for different catalysts. The inset in (b) zooms in on the 1400–1500 cm^{-1} region.

bration of N–H bonds in NH_4^+ chemisorbed on Brönsted acid sites [58,68–72]. The bands at 1195–1200, 1220–1225, and 1595–1610 cm^{-1} were assigned to the asymmetric and symmetric bending vibrations of N–H bonds in NH_3 coordinated to Lewis acid sites [69,72–74]. For $\text{V}_2\text{O}_5/\text{TiO}_2$ (Fig. 11(a)); the intensity of bands associated with the Brönsted acid sites was much stronger than that with the Lewis acid sites. With the introduction of transition metals, the band intensities due to the Lewis acid sites were significantly increased (except for $\text{Fe-V}/\text{TiO}_2$). For $\text{Cu-V}/\text{TiO}_2$ (Fig. 11(b)), the intensities of the Brönsted acid sites became very weak and could only be observed by zooming in on the region of interest. For $\text{Mn-V}/\text{TiO}_2$ and $\text{Co-V}/\text{TiO}_2$ (Fig. 11(d) and (e)), both Lewis acid sites and Brönsted acid sites were observed. The only exception was $\text{Fe-V}/\text{TiO}_2$, which had Lewis acid sites and Brönsted acid sites similar to $\text{V}_2\text{O}_5/\text{TiO}_2$. This was probably due to the small amount of iron in the vanadates.

Fig. 11(f) further summarises the ratios of $I_{\text{L-acid}}/I_{\text{B-acid}}$. Here, $I_{\text{L-acid}}$ and $I_{\text{B-acid}}$ corresponded to the band intensities of Lewis acid sites at 1595–1610 cm^{-1} and Brönsted acid sites at 1430–1440 cm^{-1} , respectively. The introduction of metals increased the amount of Lewis acid sites, especially for the $\text{Cu-V}/\text{TiO}_2$ catalyst. Combining the *in-situ* DRIFTS and NH_3 -TPD results, it appears that the strong acid sites on $\text{Cu-V}/\text{TiO}_2$ are mainly Lewis acid sites, while the strong acid sites on $\text{V}_2\text{O}_5/\text{TiO}_2$ and $\text{Fe-V}/\text{TiO}_2$ are mainly Brönsted acid sites. It has been widely reported that both Lewis acid and Brönsted acid improve the SCR reaction but they followed different mechanisms [75–77]. The SCR reaction mechanism at Brönsted acid sites is as follows:

At Lewis acid sites, the coordinated NH_3 and NO react another way:

Therefore, the amount and the strength of the acid sites are important for the NO conversion and N_2 selectivity.

Fig. 12 shows the normalised peak intensities due to the Brönsted acid sites and Lewis acid sites for each catalyst as the temperature increases. Fig. 12(a) shows that the intensities due to the Brönsted acid sites for $\text{M-V}/\text{TiO}_2$ ($\text{M} = \text{Mn}, \text{Co}$) and $\text{V}_2\text{O}_5/\text{TiO}_2$ decreased with increasing temperature and finally tended to zero at about 250 °C. For $\text{Cu-V}/\text{TiO}_2$, the amount of Brönsted acid sites decreased rapidly although this was from a small starting amount. In contrast, the Brönsted acid sites on $\text{Fe-V}/\text{TiO}_2$ were much more stable than the other $\text{M-V}/\text{TiO}_2$ and $\text{V}_2\text{O}_5/\text{TiO}_2$ and were stable to 350 °C, due to the increased prevalence of stronger Brönsted acid sites, as seen in the NH_3 -TPD profiles.

Fig. 12. The normalised peak intensity of the (a) Brönsted acid sites and (b) Lewis acid sites on different catalysts.

Fig. 12(b) indicated that the intensity due to the Lewis acid sites also decreased as the temperature increased. All the Lewis acid sites on the $\text{M-V}/\text{TiO}_2$ had not disappeared by 400 °C, indicating that they were more stable than the Brönsted acid sites. Remarkably, the Lewis acid sites on $\text{V}_2\text{O}_5/\text{TiO}_2$ were not nearly as stable and completely disappeared by 350 °C, which means that NH_3 will be effectively not adsorbed on $\text{V}_2\text{O}_5/\text{TiO}_2$ above 350 °C. It has been reported that the strong adsorption of NH_3 on a surface could determine the upper temperature limit for NO_x -reduction, and might account for the oxidation of NH_3 at higher temperatures [78]. Coincidentally, an obvious decrease in NO_x conversion and N_2 selectivity also occurred at 350 °C. We then proposed that the strength of the acids sites is very important in the N_2 selectivity at higher temperature [79–81].

4. Conclusions

Different transition metals ($\text{Cu}, \text{Fe}, \text{Mn}, \text{Co}$) were successfully introduced to modify V_2O_5 -based catalysts ($\text{M-V}/\text{TiO}_2$) for the SCR of NO with NH_3 . The introduced metals induced the formation of vanadates, which helped disperse the V species as seen in the XRD, Raman, and (HR)TEM results. The introduced metals also significantly increased the amount of surface acid sites and the strength of these acid sites. The strong acid sites might be responsible for the high N_2 selectivity at higher tem-

peratures. Among these catalysts, Cu-V/TiO₂ showed a much higher activity and selectivity than the other M-V/TiO₂ and V₂O₅/TiO₂. XPS, NH₃-TPD, and *in-situ* DRIFTS results suggested that the improved performance was probably due to more active surface oxygen species and more strong surface acid sites. The Cu-V/TiO₂ might be as a potential SCR catalyst for stationary flue gas.

References

- [1] Zhang L, Shi L Y, Huang L, Zhang J P, Gao R H, Zhang D S. *ACS Catal*, 2014, 4: 1753
- [2] Kamolphop U, Taylor S F R, Breen J P, Burch R, Delgado J J, Chansai S, Hardacre C, Hengrasmee S, James S L. *ACS Catal*, 2011, 1: 1257
- [3] Deka U, Lezcano-Gonzalez I, Weckhuysen B M, Beale A M. *ACS Catal*, 2013, 3: 413
- [4] Maitarad P, Zhang D S, Gao R H, Shi L Y, Li H R, Huang L, Rungrotmongkol T, Zhang J P. *J Phys Chem C*, 2013, 117: 9999
- [5] Chen L, Li J H, Ge M F. *J Phys Chem C*, 2009, 113: 21177
- [6] Ettireddy P R, Ettireddy N, Boningari T, Pardemann R, Smirniotis P G. *J Catal*, 2012, 292: 53
- [7] Phil H H, Reddy M P, Kumar P A, Ju L K, Hyo J S. *Appl Catal B*, 2008, 78: 301
- [8] Bai S L, Zhao J H, Wang L, Zhu Z P. *Catal Today*, 2010, 158: 393
- [9] Kompio P G W A, Brückner A, Hippler F, Auer G, Löffler E, Grünert W. *J Catal*, 2012, 286: 237
- [10] Putluru S S R, Schill L, Gardini D, Mossin S, Wagner J B, Jensen A D, Fehrmann R. *J Mater Sci*, 2014, 49: 2705
- [11] Camposeco R, Castillo S, Mugica V, Mejía-Centeno I, Marín J. *Chem Eng J*, 2014, 242: 313
- [12] Koh H L, Park H K. *J Ind Eng Chem*, 2013, 19: 73
- [13] Centeno M A, Malet P, Carrizosa I, Odriozola J A. *J Phys Chem B*, 2000, 104: 3310
- [14] Lietti L, Nova I, Forzatti P. *Top Catal*, 2000, 11–12: 111
- [15] Lietti L, Nova I, Ramis G, Dall'Acqua L, Busca G, Giamello E, Forzatti P, Bregani F. *J Catal*, 1999, 187: 419
- [16] Du X S, Gao X, Fu Y C, Gao F, Luo Z Y, Cen K F. *J Colloid Interface Sci*, 2012, 368: 406
- [17] Li Q, Yang H S, Nie A M, Fan X Y, Zhang X B. *Catal Lett*, 2011, 141: 1237
- [18] Putluru S S R, Riisager A, Fehrmann R. *Catal Lett*, 2009, 133: 370
- [19] Gao R H, Zhang D S, Liu X G, Shi L Y, Maitarad P, Li H R, Zhang J P, Cao W G. *Catal Sci Technol*, 2013, 3: 191
- [20] Lee K J, Kumar P A, Maqbool M S, Rao K N, Song K H, Ha H P. *Appl Catal B*, 2013, 142–143: 705
- [21] Lee K J, Maqbool M S, Kumar P A, Song K H, Ha H P. *Catal Lett*, 2013, 143: 988
- [22] Ettireddy P R, Ettireddy N, Mamedov S, Boolchand P, Smirniotis P G. *Appl Catal B*, 2007, 76: 123
- [23] Vargas M A L, Casanova M, Trovarelli A, Busca G. *Appl Catal B*, 2007, 75: 303
- [24] Boningari T, Koirala R, Smirniotis P G. *Appl Catal B*, 2012, 127: 255
- [25] Sagar A, Trovarelli A, Casanova M, Scherрманz K. *SAE Int J Engines*, 2011, 4: 1839
- [26] Yang S J, Wang C Z, Ma L, Peng Y, Qu Z, Yan N Q, Chen J H, Chang H Z, Li J H. *Catal Sci Technol*, 2013, 3: 161
- [27] Liu Z M, Li Y, Zhu T L, Su H, Zhu J Z. *Ind Eng Chem Res*, 2014, 53: 12964
- [28] Huang L, Shi L Y, Zhao X, Xu J, Li H R, Zhang J P, Zhang D S. *CrystEngComm*, 2014, 16: 5128
- [29] Liu F D, He H, Lian Z H, Shan W P, Xie L J, Asakura K, Yang W W, Deng H. *J Catal*, 2013, 307: 340
- [30] Casanova M, Scherрманz K, Llorca J, Trovarelli A. *Catal Today*, 2012, 184: 227
- [31] Park E, Kim M, Jung H, Chin S, Jurng J. *ACS Catal*, 2013, 3: 1518
- [32] Zhang J, Xu Q, Li M J, Feng Z C, Li C. *J Phys Chem C*, 2009, 113: 1698
- [33] Zhang J, Xu Q, Feng Z C, Li M J, Li C. *Angew Chem Int Ed*, 2008, 47: 1766
- [34] Gao X T, Jehng J M, Wachs I E. *J Catal*, 2002, 209: 43
- [35] Giakoumelou I, Fountzoula C, Kordulis C, Boghosian S. *J Catal*, 2006, 239: 1
- [36] Besselmann S, Löffler E, Muhler M. *J Mol Catal A*, 2000, 162: 401
- [37] Huang L, Zhao X, Zhang L, Shi L Y, Zhang J P, Zhang D S. *Nanoscale*, 2015, 7: 2743
- [38] Li K R, Wang Y J, Wang S R, Zhu B L, Zhang S M, Huang W P, Wu S H. *J Nat Gas Chem*, 2009, 18: 449
- [39] Huo C L, Ouyang J, Yang H M. *Sci Rep*, 2014, 4: 3682
- [40] Zhao W, Zhong Q, Pan Y X, Zhang R. *Chem Eng J*, 2013, 228: 815
- [41] Zhao Y B, Qin Z F, Wang G F, Dong M, Huang L C, Wu Z W, Fan W B, Wang J G. *Fuel*, 2013, 104: 22
- [42] Chen S, Chu W, Liu X, Tong D G. *J Nat Gas Chem*, 2011, 20: 553
- [43] Liu F D, He H, Zhang C B, Feng Z C, Zheng L R, Xie Y N, Hu T D. *Appl Catal B*, 2010, 96: 408
- [44] Trawczyński J, Bielak B, Miśta W. *Appl Catal B*, 2005, 55: 277
- [45] Zheng J, Chu W, Zhang H, Jiang C F, Dai X Y. *J Nat Gas Chem*, 2010, 19: 583
- [46] Li C M, Zhou J Y, Gao W, Zhao J W, Liu J, Zhao Y F, Wei M, Evans D G, Duan X. *J Mater Chem A*, 2013, 1: 5370
- [47] Palacio L A, Silva J M, Ribeiro F R, Ribeiro M F. *Catal Today*, 2008, 133–135: 502
- [48] Nguyen L D, Lorient S, Launay H, Pigamo A, Dubois J L, Millet J M. *J Catal*, 2006, 237: 38
- [49] Chary K V R, Kumar C P, Rajiah T, Srikanth C S. *J Mol Catal A*, 2006, 258: 313
- [50] Palacio L A, Silva E R, Catalão R, Silva J M, Hoyos D A, Ribeiro F R, Ribeiro M F. *J Hazard Mater*, 2008, 153: 628
- [51] Casanova M, Scherрманz K, Llorca J, Trovarelli A. *Catal Today*, 2012, 184: 227
- [52] Cai S X, Zhang D S, Zhang L, Huang L, Li H R, Gao R H, Shi L Y, Zhang J P. *Catal Sci Technol*, 2014, 4: 93
- [53] Fang C, Zhang D S, Shi L Y, Gao R H, Li H R, Ye L P, Zhang J P. *Catal Sci Technol*, 2013, 3: 803
- [54] Zhang D S, Zhang L, Shi L Y, Fang C, Li H R, Gao R H, Huang L, Zhang J P. *Nanoscale*, 2013, 5: 1127
- [55] Zhang L, Zhang D S, Zhang J P, Cai S X, Fang C, Huang L, Li H R, Gao R H, Shi L Y. *Nanoscale*, 2013, 5: 9821
- [56] Fang C, Zhang D S, Cai S X, Zhang L, Huang L, Li H R, Maitarad P, Shi L Y, Gao R H, Zhang J P. *Nanoscale*, 2013, 5: 9199
- [57] Shan W P, Liu F D, He H, Shi X Y, Zhang C B. *Catal Today*, 2012, 184: 160
- [58] Shan W P, Liu F D, He H, Shi X Y, Zhang C B. *Appl Catal B*, 2012, 115–116: 100
- [59] Tronconi E, Nova I, Ciardelli C, Chatterjee D, Weibel M. *J Catal*, 2007, 245: 1
- [60] Koebel M, Madia G, Raimondi F, Wokaun A. *J Catal*, 2002, 209: 159
- [61] Schwidder M, Heikens S, De Toni A, Geisler S, Berndt M, Brückner A, Grünert W. *J Catal*, 2008, 259: 96
- [62] Shi X Y, Liu F D, Xie L J, Shan W P, He H. *Environ Sci Technol*, 2013, 47: 3293
- [63] Liu F D, Asakura K, He H, Liu Y C, Shan W P, Shi X Y, Zhang C B. *Catal Today*, 2011, 164: 520
- [64] Long R Q, Yang R T. *J Catal*, 2002, 207: 158
- [65] Cheng L S, Yang R T, Chen N. *J Catal*, 1996, 164: 70

Graphical Abstract

Chin. J. Catal., 2015, 36: 1886–1899 doi: 10.1016/S1872-2067(15)60958-5

Highly dispersed V_2O_5/TiO_2 modified with transition metals (Cu, Fe, Mn, Co) as efficient catalysts for the selective reduction of NO with NH_3

Xin Zhao, Lei Huang*, Hongrui Li, Hang Hu, Jin Han, Liyi Shi*, Dengsong Zhang*
Shanghai University

Highly dispersed V_2O_5/TiO_2 modified with transition-metal copper shows high activity, N_2 selectivity, high stability and H_2O/SO_2 durability for the SCR of NO with NH_3 .

- [66] Liu F D, He H. *J Phys Chem C*, 2010, 114: 16929
 [67] Chmielarz L, Dziembaj R, Grzybek T, Klinik J, Łojewski T, Olszewska D, Węgrzyn A. *Catal Lett*, 2000, 70: 51
 [68] Wu Z B, Jiang B Q, Liu Y, Wang H Q, Jin R B. *Environ Sci Technol*, 2007, 41: 5812
 [69] Chen L, Li J H, Ge M F. *Environ Sci Technol*, 2010, 44: 9590
 [70] Peng Y, Wang C Z, Li J H. *Appl Catal B*, 2014, 144: 538
 [71] Zhu J, Gao F, Dong L H, Yu W J, Qi L, Wang Z, Dong L, Chen Y. *Appl Catal B*, 2010, 95: 144
 [72] Gu T T, Jin R B, Liu Y, Liu H F, Weng X L, Wu Z B. *Appl Catal B*, 2013, 129: 30
 [73] Liu F D, He H, Ding Y, Zhang C B. *Appl Catal B*, 2009, 93: 194
 [74] Larrubia M A, Ramis G, Busca G. *Appl Catal B*, 2001, 30: 101
 [75] Qi G, Yang R T, Chang R. *Appl Catal B*, 2004, 51: 93
 [76] Long R Q, Yang R T. *J Catal*, 2002, 207: 224
 [77] Zhou G Y, Zhong B C, Wang W H, Guan X J, Huang B C, Ye D Q, Wu H J. *Catal Today*, 2011, 175: 157
 [78] Foo R, Vazhnova T, Lukyanov D B, Millington P, Collier J, Rajaram R, Golunski S. *Appl Catal B*, 2015, 162: 174
 [79] Burkardt A, Weisweiler W, van den Tillaart J A A, Schäfer-Sindlinger A, Lox E S. *Top Catal*, 2001, 16–17: 369
 [80] Si Z C, Weng D, Wu X D, Li J, Li G. *J Catal*, 2010, 271: 43
 [81] Zhang Q L, Song Z X, Ning P, Liu X, Li H, Gu J J. *Catal Commun*, 2015, 59: 170

过渡金属(Cu, Fe, Mn, Co)改性高分散 V_2O_5/TiO_2 作为高效 NH_3 -SCR脱硝催化剂

赵欣^a, 黄垒^{a, #}, 李红蕊^a, 扈航^a, 韩瑾^a, 施利毅^{b, \$}, 张登松^{a, *}

^a上海大学纳米科学与技术研究中心, 上海 200444

^b上海大学化学系, 上海 200444

摘要: 选择性催化还原(SCR)是目前固定源及移动源中控制 NO_x 排放最为有效的技术手段之一。工业上应用最广泛的商业SCR催化剂是钒基催化剂。钒基催化剂经钨(钼)改性后具有较好的活性、稳定性和抗水抗硫性能,但在应用过程中仍存在 N_2 选择性较低、活性温度窗口(300–400 °C)较窄及高温下 V_2O_5 极易流失等不足,且钨(钼)的价格十分昂贵。因此,用廉价组分提高钒基催化剂的催化性能在实际工业应用中仍具有重要意义。研究发现,很多非贵金属(如Cu, Fe, Mn, Co, Ce, Zr, Nb, Sn, La等)都可以代替钨(钼)用来提高钒基催化剂的选择性、活性温度窗口和(热)稳定性等。引入的金属通常以氧化物或钒酸盐形式存在,并与活性组分钒物种有很强的相互作用,从而提高钒物种的氧化还原性能及分散度,同时增大表面酸性位数量,抑制锐钛矿向金红石相转变。近年来很多研究发现,经金属改性的钒基催化剂以钒酸盐形式存在时可有效提高催化剂活性和 N_2 选择性,尤其可显著提高催化剂的(热)稳定性。

本文采用浸渍法以廉价易得、储量丰富的过渡金属改性钒基催化剂,得到高度分散的M-V/ TiO_2 (M = Cu, Fe, Mn, Co)脱硝催化剂。结果发现, Cu-V/ TiO_2 和Fe-V/ TiO_2 催化剂表现出较好的催化活性和 N_2 选择性以及优异的稳定性和抗 H_2O/SO_2 性能,其中Cu-V/ TiO_2 的工作温度窗口扩展到225–375 °C。X射线衍射、拉曼光谱和EDX-mapping表征结果证明,钒物种及引入的金属高度分散在 TiO_2 载体表面,并生成了钒酸盐。氢气程序升温还原结果表明,钒酸盐的形成导致钒物种的还原峰向低温区移动,有利于催

化剂氧化还原性能的提升. X射线光电子能谱结果表明, Cu-V/TiO₂催化剂表面具有更多的活性氧物种(O_w), 且具有较强的电子间相互作用, 是SCR活性提高的关键原因之一. NH₃程序升温脱附和原位红外光谱实验结果表明, 金属的引入可以提高酸量和酸强度; Cu-V/TiO₂催化剂表面主要为Lewis酸性位, 而Fe-V/TiO₂催化剂表面主要为Brønsted酸性位, 两者可能导致不同的SCR反应机理, 但均可以提高催化剂在高温下的N₂选择性.

综上所述, 过渡金属改性的钒基催化剂中Cu-V/TiO₂具有最好的活性和N₂选择性以及较强的稳定性和抗H₂O/SO₂性能, 可能得益于其表面更多的活性氧物种和更多更强的酸性位.

关键词: 脱硝; 选择性催化还原; 钒酸盐; 过渡金属

收稿日期: 2015-06-18. 接受日期: 2015-07-25. 出版日期: 2015-11-20.

*通讯联系人. 电话: (021)66136079; 电子信箱: dszhang@shu.edu.cn

#通讯联系人. 电话: (021)66136079; 电子信箱: leihuang@shu.edu.cn

\$通讯联系人. 电子信箱: shiliyi@shu.edu.cn

基金来源: 国家自然科学基金(21303099); 国家重点基础研究发展计划(973计划, 2014CB660803); 上海市教委项目(14ZZ097, B.3704713001); 上海大学创新基金(K.10040713003).

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).