available at www.sciencedirect.com

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

Article (Special Issue on Rare Earth Catalysis)

Tailored temperature window of $\text{MnO}_x\text{-CeO}_2$ SCR catalyst by addition of acidic metal oxides

Jiuyuan Nie^a, Xiaodong Wu^{b,c,*}, Ziran Ma^b, Tengfei Xu^a, Zhichun Si^c, Lei Chen^c, Duan Weng^{b,c}^a State Key Laboratory of New Ceramics & Fine Process, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China^b The Key Laboratory of Advanced Materials of Ministry of Education, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China^c Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, Guangdong, China

ARTICLE INFO

Article history:

Received 30 March 2014

Accepted 11 April 2014

Published 20 August 2014

Keywords:

Selective catalytic reduction

 $\text{MnO}_x\text{-CeO}_2$ mixed oxide

Acidic metal oxide

Temperature window

Redox site

Acid site

ABSTRACT

A $\text{MnO}_x\text{-CeO}_2$ catalyst was modified with various acidic metal oxides (Nb_2O_5 , WO_3 , and MoO_3) using a sol-gel method. The activities of the obtained catalysts were measured for the selective catalytic reduction (SCR) of NO_x with NH_3 to screen suitable acidic metal oxides for different temperature windows. The catalytic activities for NO and NH_3 oxidation were also evaluated. The catalysts were characterized by X-ray diffraction, N_2 adsorption, H_2 temperature-programmed reduction, NH_3/NO_x temperature-programmed desorption analyses, and infrared spectroscopic measurements of NH_3/NO_x adsorption. The $\text{MnO}_x\text{-CeO}_2$ catalyst exhibited the greatest low-temperature (100–150 °C) activity. The addition of acidic metal oxides weakened the redox properties of the catalyst, resulting in inhibition of the partial oxidation of the adsorbed NH_3 and NO_2 -assisted fast SCR reactions. Meanwhile, the oxidation of NH_3 at relatively high temperatures (250–350 °C) was suppressed, and the adsorption of NH_3 on Brönsted and Lewis acid sites was strengthened. Consequently, the temperature window of SCR reaction shifted to higher temperatures in the order $\text{Nb}_2\text{O}_5 < \text{WO}_3 < \text{MoO}_3$.

© 2014, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Nitrogen oxides (NO , NO_2 , and N_2O) from plant emissions and vehicle exhausts cause various environmental problems such as photochemical smog, acid rain, ozone depletion, and greenhouse effects. Among the methods exploited for the elimination of NO_x , selective catalytic reduction (SCR) of NO_x with NH_3 has been confirmed as the most effective approach. Two types of commercial catalysts, $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts promoted by WO_3 or MoO_3 [1–4] and transition-metal exchanged zeolites [3–6], have been applied to this process. Non-zeolitic oxides [4,7] have also been developed for the removal of NO_x at low

temperatures (100–300 °C). In recent years, CeO_2 based catalysts have attracted much attention owing to their oxygen storage and redox properties *via* the redox shift between Ce^{4+} and Ce^{3+} [8].

The low-temperature activity of $\text{MnO}_x\text{-CeO}_2$ catalyst for SCR of NO_x with NH_3 was first reported by Qi *et al.* [9–11], who initiated extensive studies in the last decade. In the catalyst, CeO_2 acts mainly as a support for dispersion of and interaction with MnO_x , leading to more facile active oxygen species. The influences of various dopants, additives, and supports, including the oxides of Nb [12,13], W [12,14,15], Ti [16], Zr [12,17], Sn [18], Ca [19], and Fe [12,20] and carbon nanotubes [21], on the

* Corresponding author. Tel: +86-10-62792375; Fax: +86-10-62772726; E-mail: wuxiaodong@tsinghua.edu.cn

This work was supported by the National Basic Research Program of China (973 Program, 2010CB732304), the National High Technology Research and Development Program of China (863 Program, 2013AA065302), and the National Natural Science Foundation of China (51202126).

DOI: 10.1016/S1872-2067(14)60106-6 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 35, No. 8, August 2014

deNO_x activity of MnO_x-CeO₂ catalysts have been widely studied. In these reports, the enhanced low-temperature SCR activities of such modified MnO_x-CeO₂ catalysts are generally ascribed to improved redox properties and increased acidity. However, controversial effects of a third component have often been obtained in different studies, depending on the Mn/Ce ratio in the catalyst and the preparation method adopted. For example, Casapu *et al.* [12] observed a drastic decrease in SCR activity when Fe₂O₃ was added to MnO_x-CeO₂ by coprecipitation. In contrast, Shen *et al.* [20] reported that Fe doping by sol-gel enhanced the catalytic activity and H₂O and SO₂ resistance of MnO_x-CeO₂/TiO₂, which is ascribed to increased specific surface area and NH₃ and NO_x adsorption capacity, as well as improved dispersion and oxidation states of Mn and Ce on the catalyst surface. Additionally, the still modest activity of MnO_x-CeO₂ catalysts at relatively high temperature and their particularly low selectivity require improvement.

High N₂ selectivity for SCR over MnO_x-CeO₂ catalysts can be obtained by adding an acidic component, but this simultaneously results in a decrease in NH₃-SCR activity at low temperatures. A comprehensive balance between redox sites and acid sites is critical to broadening the temperature window of these catalysts. Casapu *et al.* [13] achieved a good distribution of oxidizing and acidic sites in the MnNbCe catalyst structure and, through formation of MnNbO₆, diminished the oxidation ability of the Mn³⁺ species. As a consequence, the unselective oxidation of NH₃ was avoided at high temperatures. Nevertheless, an excess of Mn relative to the Nb content is needed for low-temperature SCR activity. Thus, it is important to further clarify the relationship between these two important properties of MnO_x-CeO₂ catalysts by adding different acidic components.

In this study, MMnCe (M = Nb, W, and Mo) oxide catalysts were synthesized using a sol-gel method. The temperature window of the catalysts was expected to be controllable via the redox properties of the MnO_x-CeO₂ mixed oxides and the surface acidity of MO_x. The interactions between MO_x and MnO_x-CeO₂ and the corresponding effects on the NH₃-SCR mechanisms were elucidated.

2. Experimental

2.1. Catalyst preparation

MnCe (with a molar ratio of Mn:Ce = 4:6) and MMnCe (M = Nb, W, and Mo, with a molar ratio of M:Mn:Ce = 1:4:5) catalysts were prepared by a citric acid-aided sol-gel method. Mn(NO₃)₂ (Beihua, Beijing, China), Ce(NO₃)₃·6H₂O (Yili, Beijing, China), C₁₂H₇NbO₂₄ (Alladin, Shanghai, China), (NH₄)₁₀W₁₂O₃₆·5H₂O (Beihua), and (NH₄)₆Mo₇O₂₄·4H₂O (Beihua) were used as the precursors. Citric acid was added as the complexing agent at twice the amount of the metal ions. Polyglycol was then added at 10 wt% of the citric acid. The solution was magnetically stirred and heated at 70 °C until a porous gel was formed. The obtained gel was dried at 110 °C overnight followed by decomposition at 300 °C for 1 h and calcination at 600 °C for 3 h in a muffle furnace.

2.2. Activity measurement

Measurement of the activity of the catalysts for NO_x reduction with NH₃ was carried out in a fixed-bed reactor made of a quartz glass tube. The reaction gas mixture consisted of 500 ppm NO, 500 ppm NH₃, 5% O₂, and N₂ in balance. The measurement was performed from 100 to 350 °C with a temperature interval of 50 °C. Two hundred milligrams of the catalyst was sieved to 40–80 mesh and then diluted to 1 mL with SiO₂ pellets using a gas hourly space velocity (GHSV) of 30 000 h⁻¹. The concentrations of nitrogen oxides (NO, NO₂, and N₂O) and NH₃ were measured with a Nicolet 380 FTIR spectrometer (Thermo Fisher, WI, USA) equipped with a 2 m path-length sample cell. The NO_x conversion and N₂ selectivity of the catalyst were calculated as follows:

$$\text{NO}_x \text{ conversion (\%)} = (\text{NO}_{\text{in}} - \text{NO}_{\text{out}} - \text{NO}_{2 \text{ out}}) / \text{NO}_{\text{in}} \times 100$$

$$\text{Selectivity (\%)} = (1 - (\text{NO}_{2 \text{ out}} + 2\text{N}_2\text{O}_{\text{out}}) / (\text{NO}_{\text{in}} - \text{NO}_{\text{out}} + \text{NH}_{3 \text{ in}} - \text{NH}_{3 \text{ out}})) \times 100$$

Similar reaction conditions were adopted for the NH₃ (or NO) oxidation experiments, for which NO (or NH₃) was not introduced in the gas mixture.

2.3. Catalyst characterization

X-ray diffraction (XRD) patterns of the catalysts were determined using a D/mas-RB diffractometer (Rigaku, Tokyo, Japan) employing Cu K_α radiation (λ = 0.15418 nm). The X-ray tube was operated at 40 kV and 120 mA. The XRD patterns were recorded at 0.02° intervals in the range 20° < 2θ < 80°. Identification of the phases was made with the help of JCPDS (Joint Committee on Powder Diffraction Standards) cards. The mean crystallite size of CeO₂ in the samples was calculated using the Williamson-Hall equation.

The specific surface areas of the samples were measured from their N₂ adsorption isotherms at -196 °C by the four-point Brunauer-Emmett-Teller (BET) method using an automatic surface analyzer (F-sorb 3400, Gold APP Instrument, Beijing, China). The samples were degassed in flowing N₂ at 200 °C for 2 h.

H₂ temperature-programmed reduction (H₂-TPR) was performed on an Auto Chem II (Micromeritics Instrument Corp., GA, USA). Prior to the analysis, 50 mg of sample was treated in a 50 mL/min flow of He at 500 °C for 30 min. The reactor temperature was raised to 900 °C at a heating rate of 10 °C/min in 10% H₂/He (50 mL/min).

Temperature-programmed desorption of NO_x (NO_x-TPD) was carried out in a fixed-bed reactor with the emission gases determined using a Thermo Nicolet 380 FTIR spectrometer. Powder catalyst (0.2 g) was diluted to 1 mL with silica and preheated in 5% O₂/N₂ at 500 °C for 30 min. After cooling to RT, the sample was exposed to a flow of 1000 ppm NO in 5% O₂/N₂ for 30 min and then flushed with N₂ for 30 min. The catalyst was then heated to 500 °C at a rate of 10 °C/min for NH₃ desorption.

The FTIR spectra of the catalysts and adsorbed species on the catalysts arising from contact with NH₃ were recorded in the range 4000–650 cm⁻¹ using a Thermo Nicolet 6700 FTIR

spectrometer (Thermo Fisher, WI, USA). For the NH_3 adsorption experiment, the sample was oxidized at 500 °C in a 20% O_2/N_2 flow (100 mL/min) for 30 min prior to NH_3 chemisorption. The sample was then cooled to the desired temperature and subsequently flushed with N_2 (100 mL/min) for 30 min for background collection. After that, a gas mixture containing 1000 ppm NH_3 in N_2 (100 mL/min) was passed through the sample for 30 min. The FTIR spectra were collected after purging with N_2 for 30 min.

3. Results and discussion

3.1. Catalytic activity

Figure 1 shows the NH_3 -SCR performance of the catalysts within the temperature range 100–350 °C. High NO_x conversions were achieved over the $\text{MnO}_x\text{-CeO}_2$ catalyst at low temperatures (< 200 °C) but decreased sharply with increasing temperature. Meanwhile, its N_2 selectivity was lower than 50% at 195–285 °C, accompanied by the formation of large amounts of NO_2 and especially N_2O . The operation window of the catalyst shifted to higher temperatures, and the N_2 selectivity was improved by the addition of the acidic metal oxides in the order $\text{Nb}_2\text{O}_5 < \text{WO}_3 < \text{MoO}_3$. Both NbMnCe and WMnCe reached the maximal NO_x conversion (98%) at 200 °C, but the latter catalyst exhibited a much broader temperature window with 86% NO_x conversion at 300 °C. MoMnCe achieved higher than 90% NO_x conversion at relatively higher temperatures (250–350 °C) and above 94% N_2 selectivity for the whole measured temperature range.

Fig. 2. NO oxidation activities of the catalysts.

The formation of NO_2 , which is important for the so-called fast-SCR reaction at low temperatures, was evaluated using the NO oxidation test. The results are shown in Fig. 2. The MnCe catalyst was deactivated for NO oxidation by the addition of the acidic metal oxides. The NO oxidation activities of the catalysts correlated well with their low-temperature SCR activities. In the case of the MnCe and NbMnCe catalysts, the NO conversion decreased at 350 °C owing to the limitation of equilibrium of $\text{NO} \leftrightarrow \text{NO}_2$ redox cycle in excess O_2 .

Generally, the NH_3 oxidation would be expected to lead to a lack of the reductant and thereby a decrease in SCR activity, especially at high temperatures. As shown in Fig. 3, the addition of an acidic metal oxide decreased the NH_3 oxidation activity of

Fig. 1. NH_3 -SCR activities of the catalysts. (a) NO_x conversion; (b) N_2 selectivity; (c) NO_2 concentration; (d) N_2O concentration.

Fig. 3. NH_3 oxidation activities of the catalysts.

the catalysts to different degrees. Modification with Nb_2O_5 did not obviously affect the oxidation of ammonia, while the reaction was significantly suppressed by the addition of MoO_3 . The addition of WO_3 led to a modest inhibition effect.

3.2. Structure properties

Power X-ray diffraction was used to identify the phase of the catalysts as shown in Fig. 4. All the samples exhibited typical diffraction peaks of the fluorite-like structured CeO_2 phase. No diffraction peaks of MnO_x were found in the patterns of MnCe, NbMnCe, and WMnCe. This, as well as smaller CeO_2 lattice constants than that of pure CeO_2 (around 0.5412 nm), implies the replacement of Ce^{4+} by Mn^{3+} in the fluorite structure owing to their structural similarity [10,11]. A weak characteristic peak of Mn_3O_4 was detected in MoMnCe, which may be owed to the buffering effect of MoO_3 on the formation of MnO_x - CeO_2 solid solutions. The absence of the peaks assigned to MO_x ($\text{M} = \text{Nb}$, Mo , and W) implies that these acidic metal oxides may have existed in highly dispersed or amorphous states, or were incorporated into the CeO_2 lattice. The peaks of CeO_2 were broadened on the addition of Nb_2O_5 and WO_3 compared with

Fig. 4. XRD patterns of (1) MnCe, (2) NbMnCe, (3) WMnCe, and (4) MoMnCe catalysts.

those in the binary mixture, which is consistent with the sequence of the BET surface areas of the catalysts, i.e., WMnCe ($77 \text{ m}^2/\text{g}$) > NbMnCe ($55 \text{ m}^2/\text{g}$) > MoMnCe ($36 \text{ m}^2/\text{g}$) $\approx$ MnCe ($35 \text{ m}^2/\text{g}$). The shrinkage of the crystal unit cell in the Nb- and W-modified samples may have resulted from the transition of Ce^{3+} (0.114 nm) to Ce^{4+} (0.097 nm) or the incorporation of smaller Nb^{5+} (0.064 nm) and W^{6+} (0.060 nm) cations into the CeO_2 lattice. Considering the relatively higher surface area of NbMnCe and WMnCe, the latter case, i.e., incorporation of the third metal during the sol-gel process, seems to be more plausible. The segregation of MnO_x (Mn^{4+} : 0.053 nm; Mn^{3+} : 0.065 nm; Mn^{2+} : 0.083 nm) was likely responsible for the cell expansion of CeO_2 in MoMnCe despite possible incorporation of Mo^{6+} (0.060 nm).

3.3. Redox properties

The redox properties of the catalysts were characterized by H_2 -TPR as shown in Fig. 5. Five reduction peaks were found in the H_2 -TPR curve of the MnCe catalyst. Assignment of the low-temperature (<500 °C) peaks to different MnO_x species or to specific reduction steps was not straightforward because the peaks are not only related to the oxidation state but also to the crystallinity of MnO_x . According to our previous study [22] and Delimaris *et al.*'s report [23], the first two peaks at 205 and 295 °C were related to the successive reduction of readily reducible Mn^{x+} species in the solid solutions or in the form of highly dispersed MnO_x clusters. The next two small peaks at 360 and 450 °C corresponded to the typical two-step reduction of large MnO_x crystallites. The first step involved the reduction of $\text{MnO}_2/\text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4$, and the second step was the reduction of $\text{Mn}_3\text{O}_4 \rightarrow \text{MnO}$. The oxidation state of MnO_x appeared to be a mixture of MnO_2 and Mn_2O_3 because the catalyst was calcined at 600 °C [11]. The reduction of $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$ promoted by adjacent Mn^{x+} ions could also occur at low temperatures, which contributed to the low-temperature reduction peaks. The broad reduction peak centered at 700 °C corresponded to the reduction of bulk oxygen of CeO_2 .

The H_2 -TPR curve of NbMnCe was similar to that of MnCe,

Fig. 5. H_2 -TPR profiles of (1) MnCe, (2) NbMnCe, (3) WMnCe, and (4) MoMnCe catalysts.

with the reduction peaks shifted toward higher temperatures to some extent. This implied that the addition of Nb_2O_5 retarded the reducibility of surface oxygen on $\text{MnO}_x\text{-CeO}_2$ mixed oxides, which was similar to a previous report on the weakened reducibility of $\text{CeO}_2\text{-ZrO}_2$ mixed oxides by Nb-doping [24]. Meanwhile, Nb_2O_5 was difficult to be reduced in the measured temperature range. A more pronounced depressing phenomenon of WO_3 was observed in the reduction curve of the WMnCe catalyst. The reduction peaks of different MnO_x and Ce^{4+} species overlapped each other, and a distinct peak appeared at around 385 °C. As indicated by the XRD results, the segregation and sintering of Mn_3O_4 crystallites led to the reduction peak centered at 465 °C in the MoMnCe curve. The typical reduction peaks of MoO_3 , which have been reported to be located at 680 and 860 °C [25], were not observed. Consequently, the synergistic effect between CeO_2 and MnO_x , as well as the sintering of CeO_2 -based oxides, could be affected by the addition of a third metal oxide. It has been suggested that N_2O formation in the NH_3 -SCR reaction is particularly caused by the presence of highly reactive oxygen [11,19]. This explained the low selectivity to N_2 over the MnCe catalyst. The addition of acidic metal oxides Nb_2O_5 , WO_3 , and especially MoO_3 decreased the reducibility of surface and lattice oxygen in the catalyst, resulting in worsened low-temperature SCR activity, enhanced high-temperature activity, and higher N_2 selectivity.

3.4. NH_3 adsorption

NH_3 -TPD is a basic method used to measure the amount and strength of acid sites present on NH_3 -SCR catalysts from the quantity of NH_3 desorbed and desorption temperature, respectively. The results are shown in Fig. 6. The total acid amount was estimated by integrating the peak area. The amount of NH_3 desorbed followed the order MnCe ($137 \mu\text{mol/g}_{\text{cat}}$) < MoMnCe ($412 \mu\text{mol/g}_{\text{cat}}$) < WMnCe ($455 \mu\text{mol/g}_{\text{cat}}$) < NbMnCe ($490 \mu\text{mol/g}_{\text{cat}}$). Modification with a metal oxide significantly enhanced the acidity of the $\text{MnO}_x\text{-CeO}_2$ catalyst. If we considered the amount of NH_3 desorbed per unit surface area, the order of the normalized acidity of the catalysts followed MoMnCe ($11.4 \mu\text{mol}/(\text{m}^2\cdot\text{g}_{\text{cat}})$) > NbMnCe ($8.9 \mu\text{mol}/(\text{m}^2\cdot\text{g}_{\text{cat}})$) > WMnCe (5.9

Fig. 6. NH_3 -TPD profiles of (1) MnCe, (2) NbMnCe, (3) WMnCe, and (4) MoMnCe catalysts.

Fig. 7. IR spectra of (1) MnCe, (2) NbMnCe, (3) WMnCe, and (4) MoMnCe catalysts after NH_3 adsorption at room temperature.

$\mu\text{mol}/(\text{m}^2\cdot\text{g}_{\text{cat}})$) > MnCe ($3.9 \mu\text{mol}/(\text{m}^2\cdot\text{g}_{\text{cat}})$). Thus, the high surface areas of NbMnCe and WMnCe contributed considerably to their uptake of NH_3 . Generally, there were at least two types of acid sites present on these samples, with two overlapping broad peaks at 100 (L) and 150–180 °C (H). The H/L peak area ratio was about 1.1 and 1.6–1.8 for MnCe and the modified oxides, respectively. The desorption of NH_3 ended at 250 °C for MnCe, while it persisted above 300 °C for the metal oxide-modified samples. According to the NH_3 adsorption IR spectra in Fig. 7, the NH_3 desorbed at relatively high temperatures should be mainly assigned to that coordinated on Brönsted acid sites. In this sense, a larger amount of strong acid sites were generated on the modified catalysts than the unmodified MnCe.

Figure 7 shows the IR spectra of NH_3 species adsorbed on the catalysts at room temperature for 30 min. On MnCe, bands were found at 1645 and 1290–1190 cm^{-1} , which were assigned to the asymmetric and symmetric deformations of NH_3 coordinated on Lewis acid sites on Ce^{4+} , respectively [26,27]. The band at 1540 cm^{-1} was attributed to an amide (NH_2) species (scissoring mode) [11,26]. After modification of the catalyst with the acidic metal oxides, bands were found at 1685 and 1435 cm^{-1} , which were assigned to symmetric and asymmetric deformations of ammonium ions, respectively, resulting from NH_3 adsorption on Brönsted acid sites [26, 27]. These Brönsted acid sites might have arisen from the unsaturated coordination of Ce^{3+} and acidic metal ions (Nb^{5+} , W^{6+} and Mo^{6+}) [27]. The band at 1435 cm^{-1} was extremely strong in the infrared spectrum of MoMnCe, which was consistent with the NH_3 -TPD result that MoO_3 addition could increase the amount and strength of Brönsted acid sites on the catalyst surface. Meanwhile, the Lewis acid site-associated bands at 1645 (overlapped) and 1190 cm^{-1} were also observed. Many more Brönsted acid sites were formed on MoMnCe, while a large amount of Lewis acid sites were generated on the NbMnCe catalyst. These results correlated well with the above normalized amounts of acid sites per unit surface area determined by NH_3 -TPD. A weak band was also observed at 1060 cm^{-1} , which was attributed to coordinatively adsorbed NH_3 on different Lewis acid sites asso-

Fig. 8. (a) NO_2^- and (b) NO^- -TPD profiles of (1) MnCe, (2) NbMnCe, (3) WMnCe, and (4) MoMnCe catalysts.

ciated with the impregnated metal ions [26]. The band at 933 cm^{-1} was attributed to weakly adsorbed or gas phase NH_3 , which did not appear in the spectrum of MnCe [11,19]. All these results demonstrated the larger amounts of acid sites and stronger acidities of the modified oxides.

3.5. NO_x adsorption

Figure 8 shows the NO_x desorption curves of the catalysts after pre-adsorption in $\text{NO}+\text{O}_2$. For MnCe, NbMnCe, and WMnCe, three NO_2 desorption peaks were identified in Fig. 8(a). According to the literature [28], the low-temperature peak at $95\text{ }^\circ\text{C}$ always resulted from the decomposition of nitrite species (ad-NO_2^-), while the high-temperature peaks at 185 and $275\text{ }^\circ\text{C}$ were caused by the decomposition of strongly bound nitrate species. As shown in Fig. 8(b), only a trace of NO was desorbed at low temperatures, and a small NO desorption peak appeared at around $340\text{ }^\circ\text{C}$, which was mainly attributed to the decomposition of strongly bound nitrate species [19]. The total amounts of NO_x desorbed on the different catalysts followed the sequence NbMnCe ($280\text{ }\mu\text{mol/g}_{\text{cat}}$) > WMnCe ($233\text{ }\mu\text{mol/g}_{\text{cat}}$) > MnCe ($222\text{ }\mu\text{mol/g}_{\text{cat}}$) > MoMnCe ($35\text{ }\mu\text{mol/g}_{\text{cat}}$). The amount of NO_x desorbed on NbMnCe and WMnCe was even larger than that on MnCe, attributed to their higher surface areas. In comparison, the high-temperature NO_2 desorption peak at around $275\text{ }^\circ\text{C}$ disappeared, and the total amount of NO_x desorption decreased sharply on MnMoCe. This was ascribed to the low surface area and strong acidity of the catalyst. Considering the amount of NO_x desorption per unit surface area, the normalized NO_x adsorption capacities of the catalysts were MnCe ($6.4\text{ }\mu\text{mol}/(\text{m}^2\cdot\text{g}_{\text{cat}})$) > NbMnCe ($5.1\text{ }\mu\text{mol}/(\text{m}^2\cdot\text{g}_{\text{cat}})$) > WMnCe ($3.0\text{ }\mu\text{mol}/(\text{m}^2\cdot\text{g}_{\text{cat}})$) > MoMnCe ($1.0\text{ }\mu\text{mol}/(\text{m}^2\cdot\text{g}_{\text{cat}})$). This order reflected the reduced NO_x adsorption capacity of $\text{MnO}_x\text{-CeO}_2$ after the addition of acidic metal oxides.

Figure 9 shows IR spectra of the catalysts after $\text{NO}+\text{O}_2$ co-adsorption at room temperature for 30 min. The species observed on the different catalysts were similar but had different intensities. The gaseous or weakly adsorbed NO_2 was characterized by an IR band at $1630\text{--}1620\text{ cm}^{-1}$ owing to $\nu_{\text{as}}(\text{NO}_2)$ vibration [11,27] or bridged nitrate [26]. The bands at

1545 and 1255 cm^{-1} on MnCe, NbMnCe, and WMnCe were attributed to the split ν_3 vibration of bidentate nitrate “type I” species [26]. Bidentate nitrate “type II” species, with bands at 1530 and 1295 cm^{-1} , became predominant on the MoMnCe catalyst [26]. Schraml-Marth *et al.* [29] also classified bidentate nitrates into different types on the basis of their thermal stability. It has been reported that the W addition to $\text{CeO}_2/\text{TiO}_2$ catalyst works upon not the form but the thermal stability of the adsorbed nitrate species [27].

The bands at $1450\text{--}1435$ and $1025\text{--}1020\text{ cm}^{-1}$ were assigned to the ν_3 and ν_1 stretch vibrations of a linearly coordinated nitrite [26]. The additional band at 1195 cm^{-1} was assigned to anionic nitrosyl (NO^-) species on CeO_2 , which could be readily oxidized and stored as different nitrate species in the presence of oxygen [11,19]. It was obvious that the oxidation of NO^- was much slower on MnCe than on NbMnCe and WMnCe. The NO^- band was not observed on MoMnCe. Although the amount of NO_x desorbed on MoMnCe was small, the corresponding IR band intensities were relatively strong, which might be related to adsorption of NO_x on the surface of the segregated Mn_3O_4 instead of diffusion into the bulk of the catalyst.

Fig. 9. IR spectra of (1) MnCe, (2) NbMnCe, (3) WMnCe, and (4) MoMnCe catalysts after $\text{NO}+\text{O}_2$ co-adsorption at room temperature.

3.6. Discussion

On the basis of the above structural characterizations, the incorporation of Nb₂O₅ and WO₃ into MnO_x-CeO₂ mixed oxides by sol-gel results in shrinkage of the CeO₂ unit cell and an increased surface area of the catalyst. The introduction of MoO₃ cannot inhibit the segregation of MnO_x, and so a similar BET surface area to that of MnCe is obtained. Based on the NH₃-TPD and IR spectra, the normalized NH₃ adsorption of catalyst per unit surface area follows the order MoMnCe > NbMnCe > WMnCe > MnCe. This indicates that the surface acidity of the catalyst is significantly strengthened by the addition of acidic metal oxides. Especially, the amount of Brönsted acid sites is increased on the modified catalysts. However, this does not result in any improvement of the low-temperature SCR activity of catalyst, indicating that the NH₃ adsorption is not expected to be the rate-determining step. Both Langmuir-Hinshelwood (L-H) and Eley-Rideal (E-R) pathways in the NO reduction over MnO_x-CeO₂ catalyst require the adsorption of NH₃ on acid sites and formation of NH₂ by partial oxidation [10,11]. The formation of NH₂ has been suggested as the key step in the mechanism of NO reduction over V-TiO₂ [30]. According to the NH₃ adsorption IR results, the high relative intensity of the band at 1540 cm⁻¹ in the spectrum of MnCe indicates a strong generation of amide on this catalyst. This result correlates with the superior redox properties, NH₃ oxidation activity, and low-temperature SCR activity of MnCe compared with those of the modified catalysts.

Eigenmann *et al.* [31] confirmed that after the initial step of NH₃ adsorption and partial oxidation, nitrogen formation on MnO_x-CeO₂ catalysts follows an E-R type mechanism at 100–150 °C, where adsorbed NH₃ reacts with NO_x in the gas phase, and adsorbed NO_x shows no significant reactivity. In contrast, Xu *et al.* [32] presented a simplified L-H mechanism for MnO_x/CeO₂ catalyst, in which NO molecules are adsorbed to generate NO⁻ species, which subsequently react with the activated NH₃ to form the [NH₃...NO⁻] complex as an intermediate. Some researchers have proposed the co-existence of two different reaction routes over MnO_x/Al₂O₃ [26], CeO₂-WO₃/TiO₂ [27], and Ti-Fe-Mn mixed oxides [33]. They suggested that adsorbed NH₃ species can either react with NO in the gas phase (E-R mechanism) or with nitrite species in the adsorbed phase (L-H mechanism) to form N₂. In this study, the acidic dopants increased the amount of acid sites and enhanced the surface acidity of the catalysts, which reduced the NO_x adsorption capacity and stability of nitrate species. The normalized NO_x adsorption capacity of the catalysts per unit surface area was in the sequence MnCe > NbMnCe > WMnCe > MoMnCe. In this sense, the addition of acidic metal oxides may slow the reaction through an L-H mechanism [28]. This, as well as the inhibited generation of NO₂ from NO oxidation, is likely to be another factor responsible for the decreased low-temperature activities of the modified catalysts. Both coordinated NH₃ and adsorbed NH₄⁺ participate in the E-R reaction pathway with increasing the reaction temperature. The availability of NH₃ becomes critical owing to the competitive oxidation of NH₃ by oxygen.

The maximal NO_x conversion and the selectivity to N₂ were

clearly enhanced over the modified MnO_x-CeO₂ catalysts, and their deNO_x efficiencies were improved at relatively high temperatures. It has been suggested that N₂O formation occurs especially on well-ordered MnO_x crystalline planes owing to the presence of highly reactive oxygen [11]. In our work, the redox properties of the catalyst were weakened by the addition of an acidic component, thereby increasing the selectivity for SCR. Meanwhile, the oxidation of NH₃ was also suppressed on the modified catalysts. This, as well as enhanced NH₃ adsorption on Brönsted acid sites provided by the acidic metal oxides, ensured the efficient NH₃-SCR reaction at relatively high temperatures.

4. Conclusions

The combined effects of acidity and redox properties on the NH₃-SCR activity of MnO_x-CeO₂ catalyst were investigated by introducing an acidic component using sol-gel. Incorporation of Nb₂O₅ and WO₃ into the crystal cell of CeO₂ increases the BET surface area of NbMnCe and WMnCe catalysts and does not affect the redox property severely. In contrast, failures in the incorporation of MoO₃ and formation of MnO_x-CeO₂ solid solutions result in significant losses in the reactivity and amount of surface active sites on MoMnCe catalyst. Although the NH₃ adsorption capacity is greatly increased owing to the increase in the amounts of Lewis and Brönsted acid sites, the partial oxidation of the adsorbed NH₃ to amide is limited on these modified catalysts. This is suggested to be the key step in the E-R mechanism of NO reduction on MnO_x-CeO₂ based catalysts at low temperatures (100–150 °C). The higher acidity reduces the NO_x adsorption and, with the inhibited generation of NO₂, may also slow down the so-called fast SCR reaction through an L-H mechanism. However, the stable ammonium ions on Brönsted acid sites and suppressed oxidation of NH₃ contribute to high SCR activity and high selectivity of MoMnCe catalyst at relatively high temperatures (250–350 °C). In this way, the temperature window of MnO_x-CeO₂ catalysts can be tailored by adding different acidic metal oxides to meet different specific requirements.

References

- [1] Busca G, Lietti L, Ramis G, Berti F. *Appl Catal B*, 1998, 18: 1
- [2] Heck R M. *Catal Today*, 1999, 53: 519
- [3] Liu Z M, Woo S I. *Catal Rev-Sci Eng*, 2006, 48: 43
- [4] Li J H, Chang H Z, Ma L, Hao J M, Yang R T. *Catal Today*, 2011, 175: 147
- [5] Gilot P, Guyon M, Stanmore B R. *Fuel*, 1997, 76: 507
- [6] Brandenberger S, Kröcher O, Tissler A, Althoff R. *Catal Rev-Sci Eng*, 2008, 50: 492
- [7] Burch R, Breen J P, Meunier F C. *Appl Catal B*, 2002, 39: 283
- [8] Zhang L, Pierce J, Leung V L, Wang D, Epling W S. *J Phys Chem C*, 2013, 117: 8282
- [9] Qi G S, Yang R T. *J Catal*, 2003, 217: 434
- [10] Qi G S, Yang R T. *J Phys Chem B*, 2004, 108: 15738
- [11] Qi G S, Yang R T, Chang R. *Appl Catal B*, 2004, 51: 93
- [12] Casapu M, Kröcher O, Elsener M. *Appl Catal B*, 2009, 88: 413
- [13] Casapu M, Kröcher O, Mehring M, Nachttegaal M, Borca C, Harfouche M, Grolimund D. *J Phys Chem C*, 2010, 114: 9791

Graphical Abstract

Chin. J. Catal., 2014, 35: 1281–1288 doi: 10.1016/S1872-2067(14)60106-6

Tailored temperature window of $\text{MnO}_x\text{-CeO}_2$ SCR catalyst by addition of acidic metal oxides

Jiuyuan Nie, Xiaodong Wu*, Ziran Ma, Tengfei Xu, Zhichun Si, Lei Chen, Duan Weng
Tsinghua University

NH_3 -SCR temperature window of $\text{MnO}_x\text{-CeO}_2$ mixed oxides is tailored by adding different acidic metal oxides, mainly through adjusting the redox property and surface acidity of the catalyst.

- [14] Zhang Q L, Qiu C T, Xu H D, Lin T, Gong M C, Chen Y Q. *Catal Commun*, 2011, 16: 20
- [15] Xu H D, Zhang Q L, Qiu C T, Lin T, Gong M C, Chen Y Q. *Chem Eng Sci*, 2012, 76: 120
- [16] Jin R B, Liu Y, Wu Z B, Wang H Q, Gu T T. *Chemosphere*, 2010, 78: 1160
- [17] Shen B X, Zhang X P, Ma H Q, Yao Y, Liu T. *J Environ Sci*, 2013, 25: 791
- [18] Chang H Z, Chen X Y, Li J H, Ma L, Wang C Z, Liu C X, Schwank J W, Hao J M. *Environ Sci Technol*, 2013, 47: 5294
- [19] Gu T T, Jin R B, Liu Y, Liu H F, Weng X L, Wu Z B. *Appl Catal B*, 2013, 129: 30
- [20] Shen B X, Liu T, Zhao N, Yang X Y, Deng L D. *J Environ Sci*, 2010, 22: 1447
- [21] Li L, Wang L S, Pan S W, Wei Z L, Huang B C. *Chin J Catal* (李丽, 王丽珊, 盘思伟, 韦正乐, 黄碧纯. 催化学报), 2013, 34: 1087
- [22] Wu X D, Liu S, Weng D, Lin F, Ran R. *J Hazard Mater*, 2011, 187: 283
- [23] Delimaris D, Ioannides T. *Appl Catal B*, 2008, 84: 303
- [24] Pengpanich S, Meeyoo V, Rirksomboon T, Schwank J. *J Nat Gas Chem*, 2007, 16: 227
- [25] Shi C, Zhu A M, Yang X F, Au C T. *Appl Catal A*, 2004, 276: 223
- [26] Kijlstra W S, Brands D S, Poels E K, Bliek A. *J Catal*, 1997, 171: 208
- [27] Chen L, Li J H, Ge M F. *Environ Sci Technol*, 2010, 44: 9590
- [28] Chen L, Li J H, Ge M F, Zhu R H. *Catal Today*, 2010, 153: 77
- [29] Schraml-Marth M, Wokaun A, Baiker A. *J Catal*, 1992, 138: 306
- [30] Ramis G, Busca G, Bregani F, Forzatti P. *Appl Catal*, 1990, 64: 259
- [31] Eigenmann F, Maciejewski M, Baiker A. *Appl Catal B*, 2006, 62: 311
- [32] Xu L, Li X S, Crocker M, Zhang Z S, Zhu A M, Shi C. *J Mol Catal A*, 2013, 378: 82
- [33] Chen T, Guan B, Lin H, Zhu L. *Chin J Catal* (陈婷, 管斌, 林赫, 朱霖. 催化学报), 2014, 35: 294

酸性金属氧化物对锰铈氧化物催化剂脱硝温度窗口的调控作用

聂久远^a, 吴晓东^{b,c,*}, 马子然^b, 许腾飞^a, 司知鑫^c, 陈磊^c, 翁端^{b,c}

^a清华大学材料学院新型陶瓷与精细工艺国家重点实验室, 北京100084

^b清华大学材料学院先进材料教育部重点实验室, 北京100084

^c清华大学深圳研究生院, 广东深圳518055

摘要: 利用溶胶-凝胶法, 采用三种酸性金属氧化物(氧化铌、氧化钨和氧化钼)对锰铈复合氧化物催化剂进行了改性。测试了催化剂的氮氧化物选择性催化还原(SCR)活性, 以筛选对应不同温度窗口的合适酸性氧化物改性剂。同时评价了催化剂的 NO 氧化和 NH_3 氧化活性。利用X射线衍射、BET比表面积测试、 H_2 程序升温还原、 NH_3/NO_x 程序升温脱附和 NH_3/NO_x 吸附红外光谱等手段对催化剂进行了表征。 $\text{MnO}_x\text{-CeO}_2$ 催化剂表现出良好的低温(100–150 °C)活性。酸性金属氧化物的添加削弱了催化剂的氧化还原特性, 从而抑制了 NH_3 的活化和 NO_2 辅助的快速SCR反应。与此同时, 相对高温(250–350 °C)区 NH_3 的氧化也受到了抑制, B酸和L酸上的 NH_3 吸附得以增强。因此, 催化剂的SCR脱硝温度窗口向高温移动, 改性效果 $\text{Nb}_2\text{O}_5 < \text{WO}_3 < \text{MoO}_3$ 。

关键词: 选择性催化还原; 锰铈复合氧化物; 酸性金属氧化物; 温度窗口; 氧化还原位; 酸性位

收稿日期: 2014-03-30. 接受日期: 2014-04-11. 出版日期: 2014-08-20.

*通讯联系人. 电话: (010)62792375; 传真: (010)62772726; 电子信箱: wuxiaodong@tsinghua.edu.cn

基金来源: 国家重点基础研究发展计划(973计划, 2010CB732304); 国家高技术研究发展计划(863计划, 2013AA065302); 国家自然科学基金(51202126)。

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>)。