Applied Catalysis A, General 545 (2017) 64–71

Contents lists available at ScienceDirect

Applied Catalysis A, General

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

Feature Article

# Nb-modified Mn/Ce/Ti catalyst for the selective catalytic reduction of NO with $NH_3$ at low temperature

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## ARTICLE INFO

*Keywords:*
Low-temperature SCR
Nb modification
Acid sites
$N_2$ selectivity
$H_2O$ and $SO_2$ resistance

## ABSTRACT

Mn/Ce/Ti and Mn/Ce/Nb/Ti catalysts were synthesized using a precipitation method and their catalytic activities for NO selective reduction with $NH_3$ at low temperatures were evaluated. Nb doping not only improved the activity of the catalyst over a wide temperature range but also restricted the generation of $NO_2$ and $N_2O$. The Mn/Ce/Nb/Ti catalyst displayed 100% NO conversion from 150 to 250 °C and > 90% $N_2$ selectivity below 250 °C. The specific surface area of the catalyst was increased and its surface acidity was strengthened after Nb doping. Moreover, Nb doping increased the NO oxidation ability and lowered the $NH_3$ oxidation activity of the catalyst. All the above factors contributed to enhancing the overall $NH_3$-SCR performance of the Mn/Ce/Nb/Ti catalyst compared with that of the Mn/Ce/Ti one. The long-term stability and resistance to $H_2O$ and $SO_2$ of the Mn/Ce/Nb/Ti catalyst were also evaluated.

## 1. Introduction

Nitrogen oxides (NO and $NO_2$) originating from the combustion process are major air pollutants that can cause ozone depletion, urban smog, and acid rain [1–4]. The selective catalytic reduction (SCR) of $NO_x$ by $NH_3$ using $V_2O_5/WO_3(MoO_3)/TiO_2$ catalysts is the most efficient method to reduce the $NO_x$ components from a stationary source developed to date. However, this kind of catalyst must be located upstream to guarantee its suitable temperature range (300–400 °C) and some problems still exist, including the volatility and harmfulness of vanadium [5], the loss of activity at high concentrations of $SO_2$, and ash in the flue gas [6,7]. Thus, there has been strong interest in developing environmentally friendly and highly active catalysts for the low-temperature (140–200 °C) SCR process. Such catalysts can be placed after the desulfurizer and electrostatic precipitator to avoid deactivation by sulfur and dust [6,8].

Compared with $V_2O_5/WO_3(MoO_3)/TiO_2$ catalysts, Mn-based catalysts, such as $MnO_x$ [9–11], $MnO_x/TiO_2$ [2,6,8,12–21], $MnO_x$-$CeO_2$ mixed oxides [1,22,23], and $MnO_x$/zeolite (NaY, USY, SBA-15, ZSM-5, etc.) [14,24–26], are more efficient in the SCR process below 300 °C. Among the various Mn-based catalysts mentioned above, the $MnO_x/TiO_2$ catalysts are the most widely studied. Smirniotis et al. [8] compared the $NH_3$-SCR activity of different metal oxides ($VO_x$, $CrO_x$, $MnO_x$, $NiO_x$, and $CuO_x$) loaded onto various supports (Hombikat-$TiO_2$, $SiO_2$, and $\gamma$-$Al_2O_3$) and found that the $MnO_x/TiO_2$ catalyst exhibited the best performance. Ettireddy et al. [13] synthesized a series of catalysts in which $MnO_x$ was supported on $TiO_2$ using a wet impregnation method to investigate the effects of $TiO_2$ supports and $MnO_x$ loadings on catalytic performance. The best catalyst in their study achieved 94% NO conversion at 175 °C with a gas hourly space velocity (GHSV) of 50,000 $h^{-1}$. $CeO_2$ is commonly used to modify $NH_3$-SCR catalysts because of its high oxygen mobility [27–29]. Boningari and co-workers [30] investigated a Ce-modified $MnO_x/TiO_2$ catalyst in the SCR reaction; they found that the distribution and concentration of the acid sites could be considerably improved by co-loading Mn and Ce onto $TiO_2$, which increased catalytic activity in the SCR reaction. Kwon et al. [19,31] used W to modify the $MnO_x/CeO_2/TiO_2$ system, increasing the number of Brønsted and Lewis acid sites, active sites, and oxygen vacancies in the catalyst. They optimized the W content to enhance the $NH_3$-SCR activity of the W-doped $MnO_x$-$CeO_2$-$TiO_2$ catalyst.

Nb is another commonly used promoter in SCR catalysts, including $MnO_x$, $FeO_x$, $Ce_xZr_{1-x}O_y$, $VO_x/TiO_2$, and $VO_x/CeO_2$ catalysts [22,32–35]. The introduction of Nb can not only improve the physicochemical properties of the catalysts, such as increasing specific surface area and tuning redox abilities, but also promote the adsorption and activation of the reactants. In our previous studies, Nb was used as

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http://dx.doi.org/10.1016/j.apcata.2017.07.024
Received 28 April 2017; Received in revised form 4 July 2017; Accepted 14 July 2017

a comparative element with W, which increased both the catalytic activity and $N_2$ selectivity of $MnO_x$-$CeO_2$ mixed oxide catalysts for $NH_3$-SCR [36]. It is possible that Nb will also have positive effects on the $MnO_x/CeO_2/TiO_2$ catalyst system. In the present study, we synthesized Mn/Ce/Ti and Mn/Ce/Nb/Ti catalysts by a precipitation method and determined their performance in the low-temperature $NH_3$-SCR reaction. The promotion effects of Nb on NO conversion and $N_2$ selectivity were investigated in detail.

## 2. Experimental

### 2.1. Catalyst synthesis

The Mn/Ce/Ti and Mn/Ce/Nb/Ti catalysts were synthesized using a precipitation method. For the Mn/Ce/Ti catalyst, 3 g of $TiO_2$ (Alfa Aesar, United States) passed through a 100-mesh sieve was added as the catalyst support into an aqueous solution of $Ce(NO_3)_3{\cdot}6H_2O$ (99.5%, Aladdin, China) and $Mn(NO_3)_2$ (50% solution, Aladdin, China); the molar ratio of Mn/Ce/Ti was 4:4:10. An excess of aqueous urea solution was then added. The solution was vigorously stirred for 4 h at 90 °C to produce a homogeneous suspension. The pH of the solution during the precipitation process was kept at ~10. Then, $H_2O_2$ solution was added to the suspension dropwise and it was stirred for another 1 h. The precipitate was filtered and washed with deionized water, dried in an oven at 110 °C overnight, and then calcined at 500 °C for 4 h in static air. To prepare the Mn/Ce/Nb/Ti catalyst with an atomic molar ratio of 4:4:1:10, $C_{10}H_5NbO_{20}$ (99.5%, Wengjiang, China) was first dissolved in $HNO_3$ solution and heated to remove the oxalic ions. Then, $Ce(NO_3)_3{\cdot}6H_2O$ and $Mn(NO_3)_2$ were added to form a homogeneous solution. The subsequent steps were the same as those followed to prepare the Mn/Ce/Ti catalyst.

### 2.2. Catalytic activity tests

The $NH_3$-SCR activities of the catalysts were evaluated using a fixed-bed reactor (i.d. 6 mm) at temperatures from 25 to 300 °C in increments of 25 °C under atmospheric pressure. Each catalyst was pressed, crushed, and passed through a 50–80-mesh sieve before 200 mg of the catalyst was put into the reactor. The reactant gas mixture consisted of 500 ppm NO, 500 ppm $NH_3$, and 5 vol% $O_2$ balanced by $N_2$ with a total flow rate of 500 mL $min^{-1}$ and a GHSV of 180,000 $h^{-1}$. Before each test, the catalyst was pretreated with 5% $O_2/N_2$ at 300 °C for 30 min. The effluent gas after the reaction, which included $NH_3$, NO, $N_2O$, and $NO_2$, was continuously detected by a Fourier transform infrared (FT-IR) spectrometer (MKS Multigas™ 2030 gas-phase, United States) with a spectral resolution of 0.5 $cm^{-1}$. The NO conversion ($NO_{conv.}$), $NH_3$ conversion ($NH_{3conv.}$), and $N_2$ selectivity ($N_{2selec.}$) after the reaction was stable for 20 min at each temperature point were calculated according to Formulas (1), (2), and (3), respectively, as follows [21,37]:

$$NO_{conv.}(\%) = \frac{[NO]_{in} - [NO]_{out}}{[NO]_{in}} \times 100\% \tag{1}$$

$$NH_{3conv.}(\%) = \frac{[NH_3]_{in} - [NH_3]_{out}}{[NH_3]_{in}} \times 100\% \tag{2}$$

$$N_{2\,selec.}(\%) = \left(1 - \frac{[NO_2]_{out} + 2[N_2O]_{out}}{[NO]_{in} + [NH_3]_{in} - out - [NH_3]_{out}}\right) \times 100\% \tag{3}$$

To investigate the long-term reaction and effects of $H_2O$ (5 vol%) and $SO_2$ (100 ppm) on the performance of the catalyst, we selected 175 °C as the reaction temperature to reflect the actual application conditions for the low-temperature SCR.

### 2.3. Catalyst characterization

The bulk compositions of the mixed oxide catalysts were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES; Vista-MPX, Varian, United States). X-ray diffraction (XRD) analysis was performed on a D8 Advance diffractometer (Bruker, Germany) using Cu $K_\alpha$ radiation ($\lambda = 0.15418$ nm) with the X-ray tube operated at 300 mA and 40 kV. Diffraction patterns were recorded between 10° and 80° at a scan rate of 6° $min^{-1}$ and interval of 0.02°.

The specific surface area and pore volume of the catalysts were determined by $N_2$ adsorption/desorption isotherms recorded at −196 °C on a JW-BK122F analyzer (Beijing JWGB, China). Prior to $N_2$ adsorption, the samples were outgassed for 2.5 h at 220 °C to desorb moisture adsorbed on their surfaces and inside their porous networks. Specific surface areas and pore volumes were calculated according to the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively.

The morphologies of the catalysts were observed using scanning electron microscopy (SEM; JSM-7001F, JEOL) with an accelerating voltage of 30 kV.

X-ray photoelectron spectroscopy (XPS) was performed under ultrahigh vacuum ($1.33 \times 10^{-8}$ Pa) conditions on an electron spectrometer (PHI-5300, ESCA) equipped with an Al Kα ($h\nu = 1486.6$ eV) radiation source. After being pretreated in 10% $O_2/N_2$ (50 mL $min^{-1}$) at 300 °C for 30 min, the catalyst was mounted onto the sample holder and the chamber was degassed to the required vacuum conditions. The binding energies (BE) of the different elements were calibrated internally using the BE of carbon C1 *s* at 284.8 eV.

Hydrogen temperature-programmed reduction ($H_2$-TPR) measurements were performed on a chemisorption system (Micromeritics Auto Chem II 2920). For each experiment, catalyst (~50 mg) was placed in a U-shaped quartz tube and pretreated in 10% $O_2/N_2$ (50 mL $min^{-1}$) at 300 °C for 30 min. The temperature was cooled to 0 °C, and then He was introduced into the reactor to purge any weakly chemisorbed oxygen species. The catalyst was then reduced in a flow of 10% $H_2$/Ar (50 mL $min^{-1}$) from 0 to 1000 °C. At the same time, the signal was recorded by a thermal conductivity detector. The $H_2$ consumption was quantitatively calculated based on calibration runs using a standard silver oxide sample (Micromeritics) in place of the catalyst.

Oxygen temperature-programmed desorption ($O_2$-TPD) measurements were conducted using the same instrument as the activity measurement and the signal was detected by a mass spectrometer (Pfeiffer Co., Ltd., Oministar 200). Catalyst (200 mg) was pretreated with 20% $O_2/N_2$ at 300 °C for 60 min and then cooled to room temperature. The residual $O_2$ was purged with pure $N_2$. The temperature was ramped from room temperature to 900 °C and the $O_2$ signal was recorded.

Ammonia temperature-programmed desorption ($NH_3$-TPD), $NH_3$ oxidation, and NO oxidation measurements were performed using the same instrument with the same amount and pretreatment procedures as employed for the $NH_3$-SCR activity tests. For $NH_3$-TPD, the pretreated catalyst was exposed to 500 ppm $NH_3$ balanced with $N_2$ for 1 h to ensure the adsorption sites were saturated with $NH_3$. $N_2$ was used to purge the catalyst for another 1 h to desorb the weakly adsorbed $NH_3$. Finally, the temperature was raised to 400 °C at a ramp rate of 10 °C $min^{-1}$ in $N_2$ flow (total flow rate of 425 mL $min^{-1}$) and the concentrations of the products were recorded. For the $NH_3$ oxidation and NO oxidation experiments, gas mixtures of 500 ppm $NH_3$ or 500 ppm NO, respectively, with 5% $O_2$ in $N_2$ (total flow rate of 500 mL $min^{-1}$) were used. The $NH_3$ and NO conversions were calculated using the formulas in Section 2.2.

## 3. Results

### 3.1. Catalyst structure and morphology

The chemical compositions of the catalysts were measured by ICP-AES and the weight percentage of each element in the catalysts is listed in Table 1. After converting the weight percentages to atomic ratios, the results are close to the nominal ratios of Mn, Ce, Nb, and Ti for the two catalysts. The XRD patterns of the catalysts are shown in Fig. 1(a). All