



Short Communication

Novel promoting effects of tungsten on the selective catalytic reduction of NO by NH₃ over MnO_x-CeO₂ monolith catalyst

Qiulin Zhang, Chuntian Qiu, Haidi Xu, Tao Lin*, Maochu Gong, Yaoqiang Chen

Key Laboratory of Green Chemistry and Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, PR China

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ABSTRACT

A series of tungsten modified MnO_x-CeO₂ monolith catalysts were prepared and used for selective catalytic reduction (SCR) of NO by NH₃ in the presence of O₂. The experimental results showed that the SCR performance and SO₂-resistant ability of MnO_x-CeO₂ were greatly enhanced by the introduction of tungsten. The catalyst containing 10% WO₃ showed the highest NO conversion in a wide temperature range of 162–374 °C. The highly dispersed or amorphous tungsten oxide and the strong interaction between tungsten and MnO_x-CeO₂ should be the reasons for the excellent performance of the catalyst containing 10% WO₃.

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1. Introduction

Nitrogen oxides (NO_x) from the burning of fossil fuels have caused serious environmental problems such as photochemical smog, acid rains, ozone depletion and greenhouse effect. The selective catalytic reduction (SCR) of NO_x by NH₃ (or urea) is recognized as the most effective technology for the abatement of NO_x [1]. Although the commercial V₂O₅/TiO₂ (promoted by WO₃ or MoO₃) catalyst has been widely used for NO_x removal in the past few decades, problems still remain [2,3]. These problems involve narrow activity temperature window, toxicity, potential volatility, formation of N₂O at high temperatures and high activity for oxidation of SO₂ to SO₃. Consequently, many efforts have been made in developing superior non-vanadium catalysts with high activities in a wide temperature range for SCR of NO_x with NH₃.

Many kinds of transition metal oxides have been extensively studied and found to be active for SCR of NO with NH₃ [4–16]. In these studies, manganese-based catalysts have been reported as promising candidates for low temperature SCR [4–8], ceria-based oxides with advantages of unique oxygen storage capacity and excellent redox properties have been attracting more attention for SCR of NO [7–12]. More recently, further studies were performed by Yang et al. [8,11] and Wu et al. [7,12], and it was found that cerium could well promote the SCR performance of manganese-based catalyst. Simultaneously, the use of tungsten oxide as an additive in commercial V₂O₅/TiO₂ catalyst has generated great interest in the study of the

properties for this oxide. The wide application of tungsten oxide either as a promoter or as an active catalyst for SCR of NO is due to its unique acidity [2,3,13–16], however, few reports have focused on the reduction of NO by NH₃ over tungsten modified manganese based catalyst.

It is well-known that the monolith catalyst is more representative in industrial application of NO reduction due to its low pressure drop, short diffusion distances and large geometric surface area [17]. In this study, a series of tungsten modified MnO_x-CeO₂ monolith catalysts were prepared. The N₂ adsorption, XRD, XPS and SEM were performed for these catalysts. The influence of H₂O and SO₂ was also studied.

2. Experimental

2.1. Catalyst preparation

MnO_x-CeO₂ (MC) compound oxide catalyst was prepared by a co-precipitation method. Ce(NO₃)₃·6H₂O (AR) and Mn(NO₃)₂ (AR) were dissolved in distilled water with a molar ratio of 1:1, then the mixed solution was precipitated by adding the excessive mixture solution of ammonia and (NH₄)₂CO₃ with continuous stirring. The above mixture was aged for 5 h and filtered, the resulting precipitate was filtered, washed, and dried at 110 °C overnight, and then it was calcined at 550 °C for 4 h in air. The tungsten promoted MnO_x-CeO₂ catalysts were prepared by impregnating the MnO_x-CeO₂ powder with (NH₄)₆H₂W₁₂O₄₀·xH₂O aqueous solution. The prepared samples were first dried at 110 °C overnight and then calcined at 550 °C for 4 h in air. The resulting powders and MC were coated on cylindrical honeycomb cordierites of the size 2.63 cm (length) × 0.55 cm (radius)

* Corresponding author. Tel./fax: +86 28 85418451.

E-mail address: nic7501@scu.edu.cn (T. Lin).

with a cell density of 400 cpsi by Jiang Su Yixing (2.5 cm^3) and then calcined at $550 \text{ }^\circ\text{C}$ for 4 h in air.

The washcoat loading was about 180 g/L. These catalysts containing 5%, 10%, 15% and 20% WO_3 are denoted as 5% W–MC, 10% W–MC, 15% W–MC and 20% W–MC, respectively. The WO_3 was prepared by calcination of $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$ at $550 \text{ }^\circ\text{C}$ for 4 h in air. The commercial V-based monolith catalyst was supplied by Dongfeng automobile Inc. The compositions of the commercial V-based catalyst as determined by EDS are 49.76% O, 38.63% Ti, 1.24% V and 10.37% W.

2.2. Activity test

The catalytic activity measurements were carried out in a fixed-bed quartz flow reactor at atmospheric pressure. About 2.5 cm^3 of monolith catalyst was used in all the experiments. Reactant gases were regulated by means of mass-flow controllers before entering reactor. The concentrations of simulated gases were as follows: 1000 ppm NO, 1000 ppm NH_3 , 5% O_2 , 100 ppm SO_2 (when used), 10% H_2O (when used), and balance by Ar. The total flow rate of 416 ml/min was maintained for all the measurement runs with a gas hourly space velocity (GHSV) of $10,000 \text{ h}^{-1}$, the $\text{GHSV} = \text{Total flow rate of mixed gases/Volume of catalyst}$. The water vapor was generated by passing Ar flow through a gas-wash device containing de-ionized water. The concentrations of NO_x in inlet and outlet gases were continually analyzed by a chemiluminescent NO/NO_x analyzer (Model 42i, Thermo Inc). The durability reaction for the catalyst was continuously carried out for 200 h at $250 \text{ }^\circ\text{C}$ under the above reaction conditions.

2.3. Catalyst characterization

The N_2 adsorption tests of samples were tested on a QUADRASORB SI automatic surface analyzer (Quantachrome Inc) at liquid nitrogen temperature (77 K). Powder X-ray diffraction (XRD) measurements were carried out on a Rigaku D/MAX-rA X-ray diffractometer with Cu radiation. The X-ray photoelectron spectroscopy (XPS) analysis results were acquired using a XSAM-800 (KRATOS Co.) with Al $K\alpha$ radiation. The scanning electron microscope (SEM) patterns of catalysts were observed by JSM 5900 LV scanning electron microscope.

3. Results and discussion

3.1. Characterization of catalysts

The surface area, pore volume and average pore size of MC and W–MC catalysts are listed in Table 1. It is clear that the addition of tungsten decreased the specific surface area, pore volume and average pore size. The MC catalyst presented the maximal surface area ($98.2 \text{ m}^2 \text{ g}^{-1}$), pore volume ($0.20 \text{ cm}^3 \text{ g}^{-1}$) and average pore size (8.2 nm). From Table 1, it also can be seen that as the tungsten content increased, the surface area and pore volume decreased, that is: $\text{MC} > 5\% \text{ W-MC} > 10\% \text{ W-MC} > 15\% \text{ W-MC} > 20\% \text{ W-MC}$. This can be easily understood by the fact that the free pore of MC was partially occupied by the tungsten oxide. The average pore size of all catalysts was located in typical mesopore range. Moreover, as shown in Table 1,

Table 1
Physical property of catalysts with different tungsten contents.

Samples	BET surface area (m^2/g)	Pore volume (ml/g)	Average pore size (nm)
MC	98	0.20	8.2
5% W–MC	88	0.17	7.6
10% W–MC	80	0.15	6.8
15% W–MC	79	0.14	7.4
20% W–MC	67	0.12	7.4

the surface area and pore volume of 10% W–MC and 15% W–MC was very close to each other, but for the 20% W–MC, the surface area and pore volume rapidly decreased. This implied that more free pores were occupied by the tungsten for 20% W–MC, and the surface of MC was partially covered by tungsten oxide. Thus it is obvious that the excessive tungsten oxide restrained its dispersal on the surface of MC and reduced the exposed active sites of MC.

The XRD patterns are shown in Fig. 1. It can be seen that MC and all the W–MC catalysts showed typical diffraction patterns for cubic fluorite structure of CeO_2 . MC presented here did not provide other diffraction patterns except for cubic CeO_2 structure. This indicated the fine distribution of manganese in the cubic CeO_2 , and it was in good consistent with the results of literatures [8,11,18]. For W–MC catalysts, no visible diffraction pattern of tungsten species was observed at low tungsten loadings ($\leq 10\%$). This demonstrated that tungsten existed as a highly dispersed or amorphous surface species. At high tungsten loadings ($\geq 10\%$), the weak diffraction peaks of MnO_2 were detected, which suggested that the addition of high tungsten contents ($\geq 10\%$) induced the crystallization of MnO_2 . When the tungsten loadings achieved 15%, the weak diffraction patterns of MnWO_4 were found. After further increase of the tungsten loadings, the diffraction peaks of MnWO_4 became apparent and grew sharper. These results suggested that tungsten oxide was not well dispersed on the surface of catalyst at high tungsten loadings ($\geq 15\%$). It is clear that the exposed surface active sites were reduced by the appearance of MnWO_4 crystalline phase, thus the catalytic activity for SCR of NO by NH_3 was negatively influenced.

3.2. NH_3 -SCR activity test

The catalytic activities at various temperatures for the SCR of NO by NH_3 over different monolith catalysts are shown in Fig. 2(a). The activities were very low for the MC monolith catalyst, the activity temperature window was narrow, and the maximum NO conversion was lower than 85%. It should be noted that the catalytic activity for NO reduction was greatly enhanced with the addition of tungsten within a wide temperature range. Increasing tungsten loading further increased NO conversion in a wide temperature range until the tungsten loading reached 10%, and the maximum NO conversion shifted towards higher temperatures. For 10% W–MC, the maximum NO conversion was 96%. NO conversion was greater than 80% in a wide temperature range of $162\text{--}374 \text{ }^\circ\text{C}$. After this level, a further increase of the tungsten loading from 10% to 20% decreased the NO conversion at

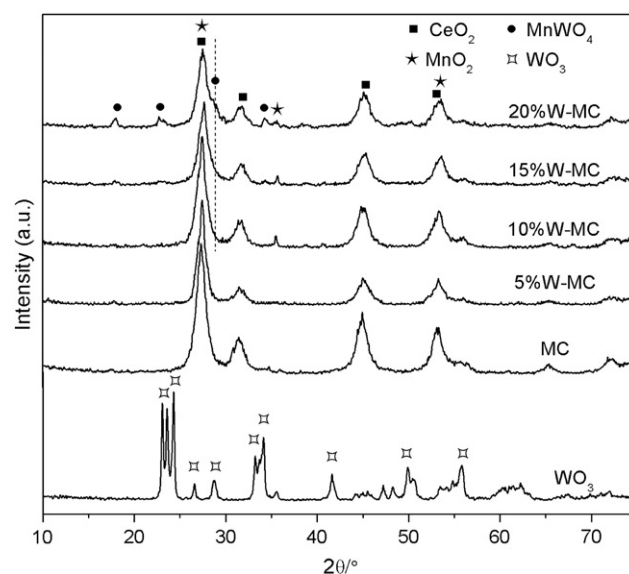


Fig. 1. Powder X-ray diffraction results of samples.

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