Synthesis, Characterization and Catalytic Activities of MnOx/TiO2 in NO Selective Catalytic Reduction with NH3

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The removal of nitrogen oxides has received much interest because of its environmental importance recently. Highly active nanorod selective catalytic reduction (SCR) deNOx catalysts composed of amorphous manganese oxides on crystalline anatase TiO_2 have been prepared by template method. The sample was characterized by BET, XRD, HRTEM and EDS. The results showed that the catalyst had superior low temperature activity and the NO_x conversion was nearly 100 % at 200 ℃. From the microstructure characterization, it could be known that the shape of nanorod was contributed to the dispersion of the manganese oxides. Due to better distributing of the manganese oxides, the catalyst performed catalytic activity very well.

Key Words: Selective catalytic reduction, MnOx/TiO2, Low temperature activity.

INTRODUCTION

Nitrogen oxides (N_2O, NO and NO_2) remain a major source for air pollution. Much effort has been focused on the development of more efficient technology[1] to remove NO_x. Selective catalytic reduction (SCR) technique has been proven to be one of the most effective methods for abatement of NO from plant exhaust gases[2,3]. The general reaction is shown below:

$$4NO + 4NH_3 + O_2 \longrightarrow 4N_2 + 6H_2O$$
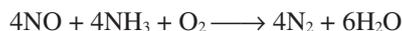
Some catalysts were reported to be active for this reaction, V_2O_5/TiO_2 system was the famous and effective commercial catalysts among them[4-6]. Although the V_2O_5/TiO_2 have many advantages but their shortcomings are also obvious. One of the disadvantages is the high operating temperature (> 300 ℃) which does not match the plant condition[7-9].

Hence, there have been strong interests to develop highly active catalysts with low pollution for low-temperature selective catalytic reduction[10]. Manganese oxides have been reported to be the most efficient transition metal oxide catalysts, because manganese oxides, containing various types of labile oxygen which are necessary to complete the catalytic cycle, have relatively high activity[11].

To enhance the catalytic activity, manganese oxides were usually supported on several carriers, like zeolite, AC, TiO_2 and Al_2O_3, NaY, which possessed profound surface acid base properties and provided high surface area, high thermal stability and strong mechanical strength[12]. At present, such manganese oxides catalysts for low-temperature selective catalytic reduction were mainly prepared by solution impregnation method, co-precipitation method and sol-gel method[13]. Many studies indicated that these methods caused the low dispersion of manganese oxide due to that the impetus of transmitting mass was rather small in the process of preparation[14].

In this study, the template synthesis method was introduced to prepare the MnOx/TiO2 catalysts for low-temperature selective catalytic reduction. The catalysts were characterized by various physico-chemical techniques such as BET surface measurement, X-ray diffraction, high-resolution transmission electron microscope and energy dispersive spectroscopy to understand the structure. The catalyst's characterization and catalytic activities were also discussed.

EXPERIMENTAL

Catalyst preparation: In a typical experiment, 2.45 g $Mn(OAc)_2 \cdot 4H_2O$ and 2.0 g cetrimonium bromide (CTAB) were added to 45 mL deionized water under stirring. After stirring about 10 min, 8.5 mL of tetrabutyl titanate (TBT) soluted in the 48 mL ethonal was added under continuous stirring to form a homogeneous solution. After 2 h, the yellow products were placed for 12 h and then dried in air at 110 ℃. Finally, the prepared products were heated to 500 ℃ at the rate of 5 ℃ min^{-1} and then maintained at 500 ℃ for 6 h. The brown powder was obtained, which was used for further analysis and characterization.

Catalytic activity text: The selective catalytic reduction activity measurement was carried out in a fixed-bed quartz reactor (2 cm i.d.). The reaction conditions were as follows: 2 g sample(pressed into small pellets), 800 ppm NO, 1000 ppm NH_3, 3 % O_2, balance N_2 1000 mL/min, the gas hourly space velocities (GHSV) = 50,000 h^{-1}. The reaction temperature was measured by a thermocouple inserted directly into the catalyst bed. The reactants and products were analyzed on-line using a flue gas analysis apparatus (made by Wuhan Cubic Optoelectronics Co., Ltd). The NO conversion was explained based on the difference of in-let and out-let concentration of NO divided by in-let NO concentration:

$$NO\ conversion\ (\%) = 100 \times \frac{(NO_{in} - NO_{out})}{NO_{in}}$$

Catalyst structure characterization: Powder sample was identified using XRD with CuKα radiation at 20 KV and 40 mA and in 2θ range from 10-80º at the rate of 4º min^{-1} (Philips XD-98). TEM images of Catalysts were acquired on a JEM 2100F transmission electron microscope. The BET surface area of catalysts was determined by N_2 adsorption at 77 K over the relative pressure range 0.002-0.15. An adsorption apparatus Coulter Omnisorb 100 CX was used for these experiments. The composition of the sample was confirmed by energy dispersive spectroscopy (EDS) equipped on above transmission electron microscope.

RESULTS AND DISCUSSION

Crystalline phase analysis: XRD was conducted to determine crystalline structure of the MnO_x/TiO_2 catalysts. The result revealed that anatase TiO_2 represented the main crystalline phase which was shown in Fig. 1. There were no peaks corresponding to MnO_x in it, maybe the manganese oxides existed as amorphous phase, or the manganese oxide particles were dispersed well in the sample[15].
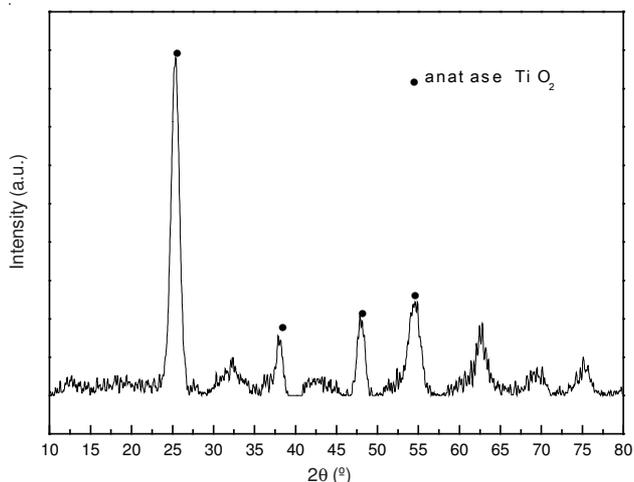

Fig. 1. XRD patterns of the MnO_x/TiO_2 catalyst sample

The energy dispersive spectroscopy (Fig. 2) confirmed that element ratio in the obtained sample was well accorded with originally added concentrations. In MnO_x/TiO_2 catalyst the atomic ratio of Mn/Ti was approximately 0.4 and the impurity elements come from the sample holder.
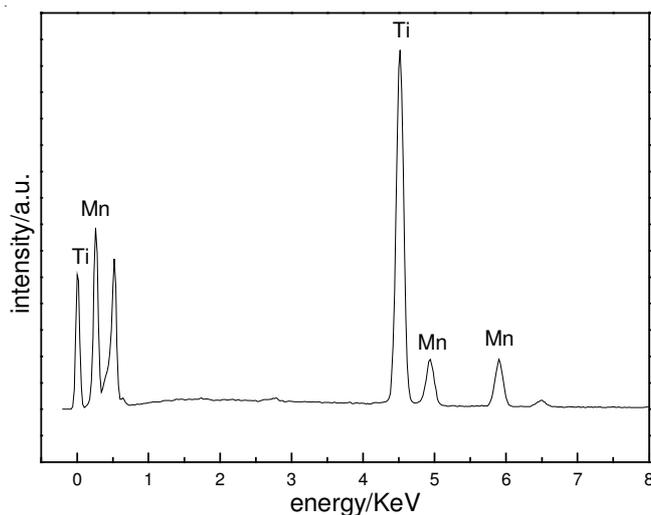

Fig. 2. Energy dispersive spectroscopy of the MnO_x/TiO_2 catalyst sample

Textural properties of the catalyst: To study the changes on the surface area of different MnO_x/TiO_2 catalysts, N_2-adsorption experiment was conducted. Fig. 3 shows the nitrogen adsorption-desorption isotherms of the catalyst sample. The BET surface area and pore size of the catalyst was 127.4 m^2 g^{-1} and 5.28 nm, respectively which was better than the tradition methods, like solution impregnation method and co-precipitation method.
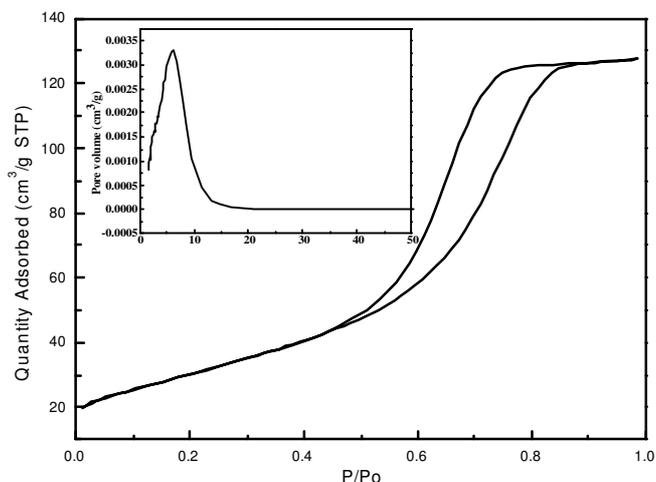

Fig. 3. Nitrogen adsorption-desorption isotherms and the pore size distribution curve of the catalyst sample

At the same time, it can be seen that the isotherm is of type IV with a H_1 hysteresis loop (according to IUPAC classification), which was a typical adsorption for mesoporous materials with one-dimensional cylindrical channels. Furthermore, a well-defined step occured at relative pressure of 0.5-0.85, indicating the filling of the uniform mesopores.

Fig. 4 showed the high-resolution transmission electron microscope images of catalyst. In Fig. 4 the particles were well dispersed and the size was about 70 nm, by calculating the lattice fringes: (a) 0.351 nm and (b) 0.260 nm, which matched anatase TiO_2 and Mn_2O_3, respectively. Furthermore the lattice fringes (a) were a little smaller than that of anatase phase plane and fringes (b) a little smaller than that of
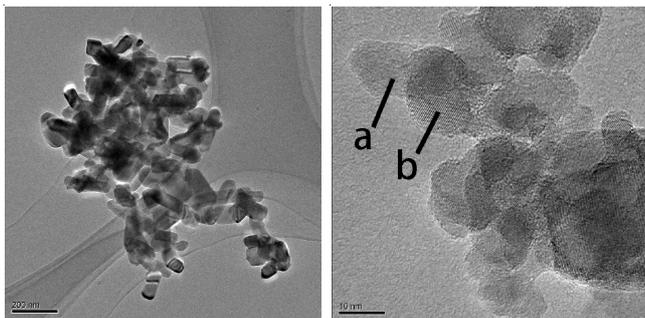
Fig. 4. HRTEM images of the catalyst sample

manganese oxides (0.272 nm). These indicated that Mn_2O_3 were well dispersed on the surface of TiO_2 and also interacted with TiO_2, which could cause the decrease in the crystallinity of TiO_2.

Catalytic activity characterization: Fig. 5 showed the catalytic activities in the reduction in NO by NH_3 over the catalyst with the variation of temperature. The sample performed efficiently with nearly 100 % NO conversion at 200 ℃, more than 80 % NO_x conversion could be achieved at 160 ℃ over the MnO_x/TiO_2 catalysts. Moreover, the catalytic properties of the catalyst increased with temperature from 100-200 ℃.
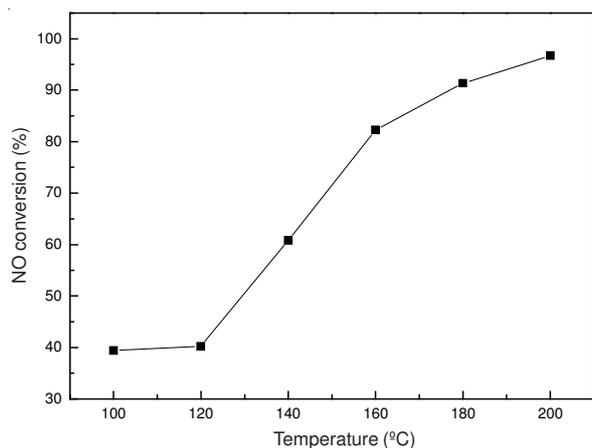

Fig. 5. NO_x conversion of the MnO_x/TiO_2 catalyst at different temperature

Conclusion

The MnO_x/TiO_2 catalyst was prepared by template method. With this catalyst more than 95 % NO conversion

could be removed. The shape of nanorod was contributed to the dispersion of the manganese oxides. All the parameters including catalyst's surface area, TiO_2 phase and the dispersion state of the MnO_x in the catalyst composites can influence the performance of the catalyst.

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