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The promotion effect of Sb on the Na resistance of Mn/TiO_2 catalyst for selective catalytic reduction of NO with NH_3

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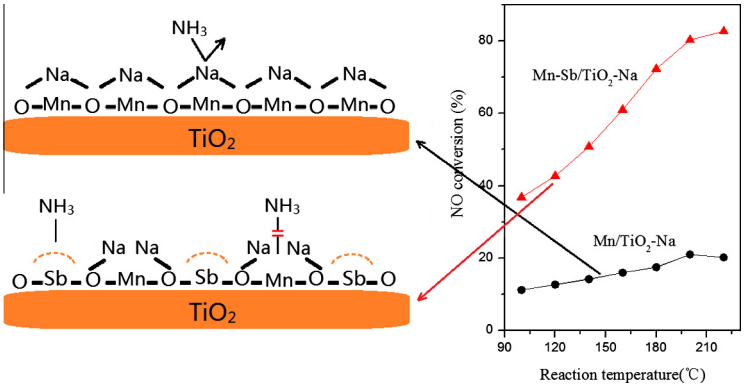
HIGHLIGHTS

- $Mn–Sb/TiO_2$ catalyst shows higher NH_3-SCR activity and wider temperature window than Mn/TiO_2 catalyst.
- $Mn–Sb/TiO_2$ catalyst has much better Na-resistance than Mn/TiO_2 catalyst.
- The addition of Sb on Mn/TiO_2 catalyst can improve its low-temperature reducibility.
- The addition of Sb on Mn/TiO_2 catalyst can generate strong Lewis acid sites for NH_3 adsorption.

GRAPHICAL ABSTRACT



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ABSTRACT

Na has a serious deactivation effect on Mn/TiO_2 catalyst for selective catalytic reduction of NO with NH_3. In this study, it was found that Sb had a promotion effect on the Na resistance of $MnOx/TiO_2$ catalyst. Then the promotion mechanism was investigated based on the characterization results of BET, XRD, H_2-TPR, NH_3-TPD, XPS and *in situ* DRIFT. The results of H_2-TPR and NH_3-TPD showed that the addition of Sb on $MnOx/TiO_2$ could enhance the redox ability and surface acidity respectively, and the results of DRIFT indicated that the addition of Sb on $MnOx/TiO_2$ could generate strong Lewis acid sites on the catalyst surface for NH_3 adsorption. Therefore, the doping of Sb has a promotion effect on the Na resistance of Mn/TiO_2 catalyst.

1. Introduction

Selective catalytic reduction (SCR) process is the state-of-the-art for NOx abatement in coal-fired power plants [1,2]. As the most widely-used catalyst, $V_2O_5–WO_3/TiO_2$ (or $V_2O_5–MoO_3/TiO_2$) exhibits high activity in the temperature range of 300–400 °C [3]. But some problems are still existed during its industrial application process, including the high activity of SO_2 oxidation to SO_3, deactivation by alkali metals in the fly ash, and the formation of N_2O at high temperature [4–6]. To avoid these problems, developing low-temperature SCR catalyst has become a research focus in recent years.

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Manganese oxides contain various types of labile oxygen, which are crucial to complete the recycle of SCR reaction [3,7]. Therefore, much effort has been devoted to studying the SCR reaction taking place on manganese-based catalyst. Jiang et al. [8] found that the $MnOx/TiO_2$ catalyst prepared by sol–gel method showed excellent SCR performance. And the study of Fang et al. [9] reported that nanoflaky MnOx supported on carbon nanotubes synthesized by a facile chemical bath deposition route exhibited high low-temperature SCR activity, wide operating temperature window and good H_2O resistance. Similar with vanadium-based catalyst, the alkali metals in the fly ash have a poisoning effect on manganese-based catalyst. Fang et al. [10] investigated the effect of precursor and preparation method on the poisoning effect of potassium on $MnOx/TiO_2$ catalyst. In our previous study [11], the different deactivation effects of sodium and potassium on $MnOx/TiO_2$ catalyst were compared and discussed based on experimental and theoretical calculation results. Recently, some efforts were made to enhance the alkali metal resistance of SCR catalyst. For example, Peng et al. [12] found that the addition of ceria could enhance the potassium resistance of $MnOx/TiO_2$ catalyst and investigated the enhancement mechanism. Du et al. [13] indicated that Sb had a promotion effect on potassium resistance of V_2O_5/TiO_2 catalyst. Thus the modification of SCR catalyst by Sb may be a feasible way to enhance its alkali metal resistance. And understanding the promotion mechanism of Sb addition on the alkali metal resistance is of great importance to direct the development of new SCR catalyst. However, the effect of Sb doping on the alkali metal resistance of low-temperature SCR catalyst is still unknown. Therefore, Mn/TiO_2 and $Mn–Sb/TiO_2$ catalysts were prepared and deactivated by Na in this study. Furthermore, the different Na-resistances of Mn/TiO_2 and $Mn–Sb/TiO_2$ catalysts were measured and compared. And the promotion mechanism of Sb addition on the Na resistance of Mn/TiO_2 catalyst would be investigated and discussed based on the characterization results.

2. Experimental

2.1. Catalyst preparation

The four catalyst samples used in this study were denoted as Mn/TiO_2, $Mn–Sb/TiO_2$, Mn/TiO_2–Na and $Mn–Sb/TiO_2$–Na respectively. Among them, the two fresh samples Mn/TiO_2 (Mn/Ti molar ratio = 0.2:1) and $Mn–Sb/TiO_2$ (Mn:Sb:Ti molar ratio = 0.16:0.04:1) were prepared by sol–gel method. When preparing Mn/TiO_2 catalyst, the mixture of butyl titanate (0.1 mol), anhydrous ethanol (2.9 mol), deionized water (1.9 mol), nitric acid (0.1 mol) and manganese nitrate (0.02 mol) were mixed under vigorous stirring at room temperature to yield a yellowish transparent sol. After dried at 80 °C for 24 h, the sol was transferred into xerogel. Then the xerogel was calcined at 500 °C for 5 h to obtain the final Mn/TiO_2 catalyst. Following a similar preparation procedure, $Mn–Sb/TiO_2$ catalyst was prepared. During this process, antimony nitrate was used as the precursor of Sb, and ethylene glycol was used as the solvent of antimony nitrate.

The two poisoned samples Mn/TiO_2–Na and $Mn–Sb/TiO_2$–Na were prepared by impregnating the two fresh catalyst samples in the solution of sodium nitrate of required concentration respectively (the molar ratio between Na/Mn or Na/(Mn + Sb) was set as 1:5). Thereafter, the mixture was stirred for 5 h, dried at 80 °C for 24 h and calcined at 500 °C in air for 5 h. All the catalyst samples used in this study were sieved to 80–100 mesh.

2.2. Characterization

The specific surface areas of the catalyst samples were measured by N_2 adsorption at 77 K on a Quantachrome Autosorb-1 instrument and calculated by the Brunauer–Emmett–Teller (BET) method. The crystal structures of the catalyst samples were determined by using XRD (BrukerD8 Advance, Cu Kα radiation). X-ray photoelectron spectroscopy (XPS) measurement was performed on a Thermal ESCALAB 250 spectrometer using Al Kα X-rays. The C1s peak (284.8 eV) was used for the calibration of binding energy values. To study the redox properties and surface acidities of the catalyst samples, the temperature-programmed reduction (H_2-TPR) analysis and the temperature-programmed desorption (NH_3-TPD) analysis were carried out on an Autosorb-iQ-C chemisorption analyzer. The *in situ* diffuse reflectance infrared transform spectroscopy (DRIFT) experiments were carried out on a Nicolet iS50 FTIR spectrometer equipped with a liquid-nitrogen cooled MCT detector. In the DRIFT cell, the catalyst sample was pretreated at 500 °C in a N_2 environment for 2 h, then cooled to 150 °C. The background spectra were collected in flowing N_2 and automatically subtracted from the sample spectrum.

2.3. Catalytic activity test

The SCR activity test was carried out on a fixed bed reactor (i.e. =8 mm) with about 0.55 cm^3 catalyst samples. The typical reactant gas contained the following components: 600 ppm NO, 600 ppm NH_3, 5% O_2, balance with Ar. And the gas hourly space velocity (GHSV) was 108,000 h^{-1}. The reaction temperature and the gas flow were controlled by intellectual temperature controller and mass flowmeter respectively. The concentrations of NO and NO_2 were monitored by a continuous flue gas analyzer (Thermo 60i). NO conversion (X_{NO}) can be calculated by:

$$\text{NO conversion} = ([\text{NO}]_{in} - [\text{NO}]_{out})/[\text{NO}]_{in} \times 100\% \quad (1)$$

where [NO] in and [NO] out are the concentrations of NO in the inlet and outlet gas stream respectively.

The reaction rate can be calculated by:

$$\text{Reaction rate} = X_{NO} * Q * C_f/(WS_{BET}) \quad (2)$$

where Q is the volumetric flow rate of simulated flue gas (L/s); C_f is the feed concentration of NO (mmol/L); W is the weight of catalyst sample used in an experimental run (g); and S_{BET} is the BET surface area of the catalyst sample (m^2/g).

3. Results and discussion

3.1. SCR activity

Fig. 1 shows the NH_3-SCR activities and the reaction rates normalized by surface areas of the four catalyst samples. It is clear that the NO conversion over Mn/TiO_2 catalyst increases with reaction temperature. And the addition of Sb on Mn/TiO_2 catalyst has a distinct promotion effect on its SCR activity and NH_3-SCR reaction rate. As shown in Fig. 1, the SCR activity and the NH_3-SCR reaction rate of $Mn–Sb/TiO_2$ are much higher than that of Mn/TiO_2 catalyst in the whole temperature range, which exhibits nearly 100% NO conversion in the temperature window of 100–220 °C. Thus the addition of Sb greatly broadens the operating temperature window of Mn/TiO_2 catalyst. A similar phenomenon was also reported by Du et al. [13]. In addition, it can be observed that the loading of Na has a great deactivation effect on the two fresh catalyst samples, and the poisoning effect of Na on Mn/TiO_2 is more serious than that on $Mn–Sb/TiO_2$. For instance, the SCR activity of $Mn–Sb/TiO_2$ decreases from 99.6% to 69.4% at 160 °C after the loading of Na, while the SCR activity of Mn/TiO_2 decreased from 61.0% to 16.0% under the same conditions. As for the NH_3-SCR reaction rates of the two fresh catalyst samples, a similar situation could also be