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Short Communication

Low-temperature selective catalytic reduction of NO over MnO_x/CNTs catalysts

Effect of thermal treatment condition

Xie Wang [a], Yuying Zheng [a,b,*], Zhe Xu [b], Xianbin Liu [b], Yanbing Zhang [b]

[a] College of Chemistry and Chemical Engineering, Fuzhou University, Fuzhou 350108, China
[b] College of Materials Science and Engineering, Fuzhou University, Fuzhou 350108, China

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ABSTRACT

Carbon nanotubes (CNTs) supported manganese oxide catalysts were prepared through different thermal treatment routes and used for low-temperature selective catalytic reduction of NO with NH_3. The MnO_x/CNTs catalyst prepared by calcined the precursor in air at 300 °C showed lower NO conversions than that treated at 250 °C, while it showed higher NO conversions than the one calcined in nitrogen. BET, TGA, XRD and H_2-TPR results indicated that CNTs may impose effects on the oxidation state and redox ability of the manganese oxide and hence on the catalytic activity during the calcination process at given temperatures.

1. Introduction

Nitrogen oxides (NO_x) in flue gas remain one of the most serious pollutants which can contribute to photochemical smog, acid rain, ozone depletion and greenhouse effects [1,2]. And selective catalytic reduction (SCR) of NO_x with NH_3 is considered as the most effective technology for NO_x abatement in stationary sources [3,4]. But, an inherent drawback to the commercial vanadium-based catalysts for this process is the deactivation by SO_2 and dust as well as the toxicity of vanadium species [5,6]. Therefore, it is greatly needed to develop new efficient low-temperature SCR catalysts which can place downstream of the desulfurizer and electrostatic precipitators.

Attracted by their excellent activity for low-temperature SCR process and inherently environmentally benign characteristics, Mn-based catalysts have been widely investigated in the past decades. Examples of these catalysts are MnO_x/Al_2O_3 [7,8], MnO_x/TiO_2 [9,10], MnO_x/USY [11], and MnO_x/AC [12]. The SCR activity of different pure manganese oxides was also investigated, and it was found that the preparation process could play an important role on the catalytic activity [13–15]. Recently, carbon nanotubes (CNTs) were also widely applied to be carrier materials due to their unique structure property and good chemical stability. Although a series of MnO_x/CNTs catalysts had been prepared in previous reports [16–19], the low-temperature SCR activity (below 200 °C) for these catalysts remained unsatisfactory. The low valence state of manganese oxides should be the main reason for the low activity of MnO_x/CNTs catalysts obtained in previous literature. Therefore, developing MnO_x/CNTs catalysts with high low-temperature SCR activity is highly desirable but remains challenging.

The conventional method to prepare MnO_x/CNTs catalysts was always treatment in inert gases and calcination at a high temperature. In this work, three kinds of manganese oxide catalysts supported on CNTs were prepared by calcined the precursor in different conditions, and we found that MnO_x/CNTs catalyst prepared by calcined the precursor in air at a low temperature of 250 °C showed very high NO conversions below 200 °C. Thermal gravimetric analysis (TGA), N_2 adsorption-desorption analysis, X-ray diffraction (XRD) and temperature programmed reduction by hydrogen (H_2-TPR) techniques were also used to elucidate the structure and property of the obtained catalysts.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by an incipient wetness method via different thermal treatment routes. The raw multiwall CNTs (60–100 nm in outer diameter, Shenzhen Nanoport Company) were first refluxed in concentrated nitric acid (68%, Sinopharm) at 140 °C for 4 h in order

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* Corresponding author at: College of Chemistry and Chemical Engineering, Fuzhou University, Fuzhou 350108, China. Tel./fax: +86 591 22866529.
E-mail address: yyzheng@fzu.edu.cn (Y. Zheng).

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to purify CNTs and introduce oxygenated surface groups [20]. Previous study indicated that the formed oxygenated surface groups could enhance the NO conversions of catalysts due to well dispersion of the active phase on the surface of CNTs [21]. The sample was then washed with deionized water till pH 6–7, and dried at 80 °C. After that, the acid-treated CNTs were impregnated in an aqueous solution of manganese nitrate (50 wt%, Sinopharm) at room temperature for 24 h and dried at 110 °C for 12 h to form the catalyst precursor. The precursor was calcined in air at 250 °C for 2 h and denoted as MnO_x/CNTs-A1. For comparison, the precursor was also calcined in air at 300 °C for 50 min or in N_2 at 300 °C for 2 h, denoted as MnO_x/CNTs-A2 or MnO_x/CNTs-N3, respectively. The molar ratio of Mn/C was set as 0.01 in all samples according to our previous study [22].

2.2. Catalyst characterization

The thermal stability was determined by thermal gravimetric analysis (SDT-Q600) from room temperature to 800 °C with a heating rate of 10 °C min^{-1} in air. The specific surface area of the samples calculated by the Brunauer-Emmett-Teller (BET) method was measured by a Micromeritics ASAP 2020 system at liquid nitrogen temperature (−196 °C). The samples were firstly degassed in a vacuum at 200 °C for 2 h before measurement. The XRD patterns were recorded on a Rigaku Dmax/3C X-ray diffractometer using Cu Kα radiation. The data were collected for scattering angles (2θ) ranging between 10 and 80° with a scan speed of 8°min^{-1}. H_2-TPR was carried out on a custom-made TCD setup using 50 mg catalysts. Prior to H_2-TPR experiments, samples were pretreated in N_2 at 200 °C for 1 h. H_2-TPR runs were carried out with the linear heating rate (10 °C min^{-1}) in pure N_2 containing 6% H_2 at a flow rate of 30 ml min^{-1}.

2.3. Catalytic activity tests

SCR activity measurements were performed in a fixed-bed reactor at 80–180 °C. 200 mg sample was used in each test. The gas composition was 500 ppm NO, 500 ppm NH_3, 5% O_2 and balance N_2. The total flow rate was 700 ml/min, which corresponded to a gas hourly space velocity (GHSV) of 38,000 h^{-1}. A flue gas analyzer (Kane International Limited, KM940) was employed to measure the NO and NO_2 concentrations. All the data were collected after 30 min when the SCR reaction reached a steady state.

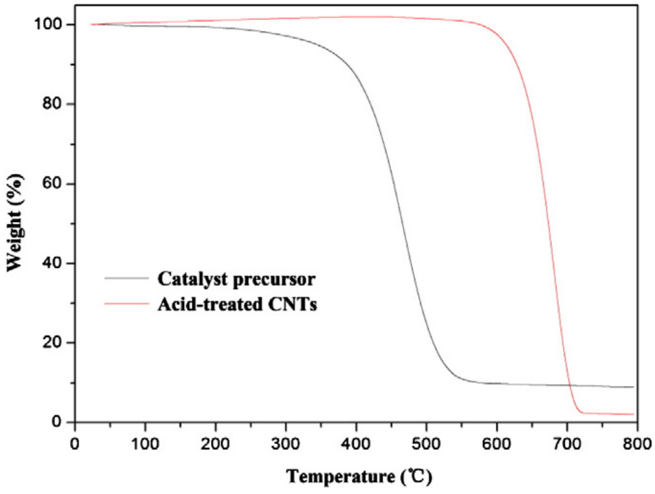

Fig. 1. TGA curves of catalyst precursor and acid-treated CNTs.

3. Results and discussion

3.1. TGA and BET

Fig. 1 shows the thermal stability of acid-treated CNTs and catalyst precursor in air. The acid-treated CNTs began to combust at about 600 °C. However, for the catalyst precursor, the oxidation started at lower temperatures (200–400 °C), indicating that the oxidation of CNTs could be catalyzed by manganese oxides and there may be an interaction between CNTs and manganese oxides during the oxidation reaction. This phenomenon could be also discovered in other metals or oxides supported CNTs, which was used to cut long CNTs into short ones or generate defects on CNTs [22–24]. In addition, it was found that the weight loss of the catalyst precursor calcined in air became fast with the gradually increasing temperature. Therefore, it was not advisable to prepare the MnO_x/CNTs catalyst by calcined in air at a high temperature or for a long time. On the other hand, the catalysts prepared by calcined in air at a low temperature (MnO_x/CNTs-A1) or at a high temperature for a short time (MnO_x/CNTs-A2) could show an ignorable weight loss in the preparation process. The BET surface area for acid-treated CNTs, MnO_x/CNTs-A1, MnO_x/CNTs-A2, and MnO_x/CNTs-N1 was 91.4, 118.5, 123.2 and 90.1, respectively. The MnO_x/CNTs catalysts prepared by calcined in air presented a significant increase in BET surface area compared with the raw CNTs, which could be owing to the additional defects on CNTs created during the calcination process [23]. While the MnO_x/CNTs catalyst prepared by treated the catalyst precursor in N_2 did not show this increase, because the CNTs could not be oxidated in lack of O_2. After calcination, the BET surface area of MnO_x/CNTs-N1 decreased due to manganese oxides dispersed on the surface of support.

3.2. Catalytic activity tests

The catalytic performance for SCR reaction over MnO_x/CNTs catalysts prepared by different methods is shown in Fig. 2. Clearly, MnO_x/CNTs-A1 catalyst showed the highest activity for the SCR reaction in the whole temperature range, more than 60% NO conversion could be obtained at even 80 °C. The SCR activity at 80–180 °C decreased in the following sequence: MnO_x/CNTs-A1 > MnO_x/CNTs-A2 > MnO_x/CNTs-N1. Besides, repetitive activity tests were also carried out on these catalysts and it found that the performance of each catalyst could be fully reproducible. This result indicated that the active phase of manganese oxide catalysts may not change during the SCR reaction. Based on the BET results, it

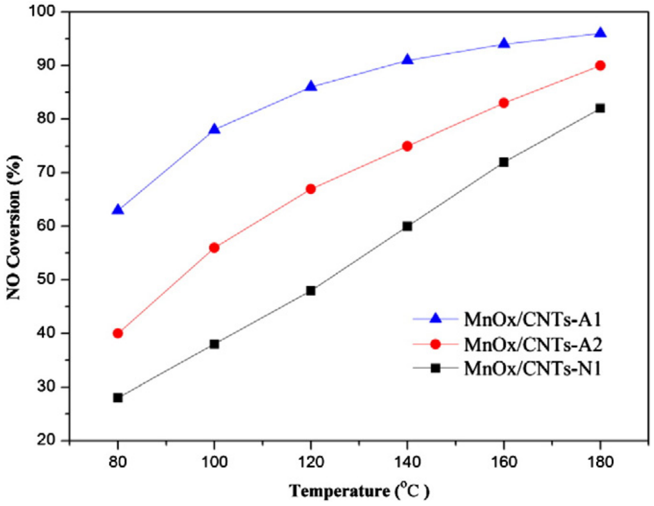

Fig. 2. NO conversions for MnO_x/CNTs catalysts prepared by different methods. Reaction conditions: $[NO] = [NH_3] = 500$ ppm, $[O_2] = 5\%$, N_2 as balance gas, GHSV = 38,000 h^{-1}, 200 mg catalyst.