Catalysis Communications 83 (2016) 18–21

Contents lists available at ScienceDirect

Catalysis Communications

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

Short communication

Application of MnO_x/HNTs catalysts in low-temperature NO reduction with NH_3

Xianlong Zhang *, Peimeng Wang, Xuepingw Wu, Shuangshuang Lv, Jianjian Dai

School of Chemistry and Chemical Engineering, Hefei University of Technology, Hefei 230009, PR China

ARTICLE INFO

Article history:
Received 6 January 2016
Received in revised form 28 April 2016
Accepted 10 May 2016
Available online 11 May 2016

Keywords:
Halloysite
Manganese oxides
In-situ deposition
Low-temperature SCR

ABSTRACT

Halloysite (HNTs) was firstly adopted as a carrier to develop manganese based SCR catalysts. Supporting of manganese oxides (MnO_x) on halloysite was carried out via a simple in-situ reaction of $Mn(AC)_2$ and $KMnO_4$ on the surface of halloysite. The obtained MnO_x/HNTs catalyst was estimated for selected reduction of NO by NH_3. It was found that the SCR activity of the catalyst is perfectly high with a nearly 100% NO conversion at temperatures from 60 to 250 °C. Results showed that the adoption of Halloysite as carrier and the in-situ preparation method jointly play key function for the performance of the catalyst.

1. Introduction

Selective catalytic reduction of NO_x with NH_3 had proved to be a cost-effective, reliable, and fuel-efficient way to control NO_x emission, especially for stationary sources such as power boilers and combustion furnaces [1,2]. V_2O_5-WO_3(MoO_3)/TiO_2 as a kind of commercial catalyst had high activity and selectivity in SCR of NO with NH_3 at 300–400 °C, but, there were some inevitable problem that remained in this catalyst, such as the toxicity of vanadium, SO_2 oxidation to SO_3, and the need to operate at high temperature [3,4]. Therefore , the development of novel catalysts for the low-temperature NH_3-SCR remained as an important challenging task for many researchers due to their potential application in downstream of the desulfurizer and electrostatic precipitator, where the flue gas temperature was usually bellow 200 °C or ever lower [5–7]. In recent researches, Manganese based catalysts had been applied and exhibited excellent activity in low-temperature SCR reactions, such as MnO_x/Al_2O_3 [8,9], MnO_x/active carbon [10,11], but the actually low-temperature SCR activity (especially below 100 °C) for most catalysts remained unsatisfactory.

Recently, an accumulating number of researchers focused on the attempt of the nanocrystallization of catalyst carriers. Owing to the unique structure property and chemical stability, titania nanotubes and carbon nanotubes (CNTs) were widely applied as carrier materials to prepare catalysts such as MnO_x/TiO_2 [12–14], MnO_x/CNTs [15–17], Mn-CeO_x/TiO_2 [18,19], Mn-CeO_x/CNTs [20,21], which were found to be active for SCR at lower temperatures. Besides, in our previous report, we had successfully developed a manganese based SCR catalysts adopting an fibrillar aluminosilicate caly material (palygorskite) as carrier to obtain an perfect lower temperature NO removal and indicated that the traditional aluminosilicate might be more suitable for catalyst carrier [22]. But, the use of HNTs ($Al_2(OH)_4Si_2O_5 \cdot nH_2O$) which is also characterized for a hollow nanotube structure similar with CNTs and titania nanotubes as the support for manganese oxides has not yet been investigated.

In this paper, a mild in-situ deposition method operated at room temperature was introduced to prepare a novel nano-sized MnO_x/HNTs catalysts. The catalysts thus obtained exhibited ultra-high low temperature catalytic activity for cleaning NO with NH_3 from 60 to 300 °C.

2. Experimental

2.1. Catalyst preparation

Halloysite (HNTs) from golden sun ceramics Co. Ltd. (Zhengzhou, China) was used as support of the catalysts in this work. Chemical composition and Textural property of HNTs were listed in Table 1.

MnO_x/HNTs catalysts were prepared by in-situ deposition method (SP) at room temperature as illustrated in Fig. 1. Catalyst with MnO_x as active component was prepared by impregnating HNTs with $MnAC \cdot 4H_2O$ solution (1 mL/g HNTs), after 24 h of impregnation, the $KMnO_4$ solution was gradually added with thorough stirring. The mixtures were placed at room temperature for 8 h and then filtered and washed with de-ionized water 3–4 times. The resulting solid products were dried at 70 °C for 6 h and 110 °C for 12 h, respectively. For comparison, the palygorskite (PG) supported MnO_x catalysts were also prepared by in-situ deposition method. The reaction equations of $KMnO_4$

---

* Corresponding author.
E-mail address: zhangxianlong78@126.com (X. Zhang).

http://dx.doi.org/10.1016/j.catcom.2016.05.003
1566-7367/

Table 1
Physical properties of HNTs.

Chemical composition (wt%)							Textural property	
Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	Fe_2O_3	$S_{BET}(m^2/g)$	$V_{total}/(cm^3/g)$
0.8	0.2	36.47	42.92	0.91	0.61	1.24	86.362	0.291

and $MnAC \cdot 4H_2O$ as follow:

$$2KMnO_4 + 3Mn(CH_3COO)_2 + 2H_2O \rightarrow 5MnO_2 + 4CH_3COOH + 2CH_3COOK$$

For the comparison of preparation method of in-situ deposition and traditional wet-impregnation followed by calcination, MnO_x catalyst was also prepared by incipient-wetness impregnation method (DP). Carrier of HNTs was firstly impregnated with $MnAC \cdot 4H_2O$ solution (1 mL/g HNTs), and then placed at room temperature for 8 h. The impregnated catalyst was dried at 70 °C for 6 h and 110 °C for 12 h, finally, calcined in air flow at 300 °C for 2 h.

In this work, a series of MnO_x-supported catalysts based on those two support materials with 8 wt% MnO_x loading were prepared by two preparation routines. Catalysts prepared with different supports and methods were designated as MnO_x/HNTs-SP, MnO_x/PG-SP and MnO_x/HNTs-DP, and MnO_x/PG-DP as reported previously by Zhang [23]. All samples were crushed and sieved to a 20–40 mesh size for activity measurement.

2.2. Catalytic activity measurements

The SCR activity tests were conducted in a fixed-bed quartz reactor (i. d. 14 mm). The simulated flue gas consisted of 600 ppm NH_3, 600 ppm NO, 3 vol% O_2 and Ar gas as the balance. The total flow rate of 350 mL/min was maintained for all tests. Different gas hourly space velocities (GHSV) from 9000 h^{-1} to 36,000 h^{-1} were achieved by changing the volume of catalyst. The gas concentrations of NO were measured online by a flue gas analyser (Testo350-XL). All the dates were collected after 40 min when the SCR reaction reached a steady state.

2.3. Catalyst characterization

The chemical composition was analyzed by X-ray fluorescence (XRF-1800). Brunauer-Emmett-Teller (BET) analysis was conducted with a specific area and pore analyser (NOVA 2200e, Quantachrome, USA). Transmission electron microscopy (TEM) images of the samples were obtained by a JEM-2100F (Hitachi, Japan) analyser. Energy-dispersive X-ray spectroscopy (EDX) was used to determine the element content on the sample surface. The powder X-ray diffraction (XRD) measurement was carried out on a Rigaku D/MAx2500V system with Cu Kα radiation.

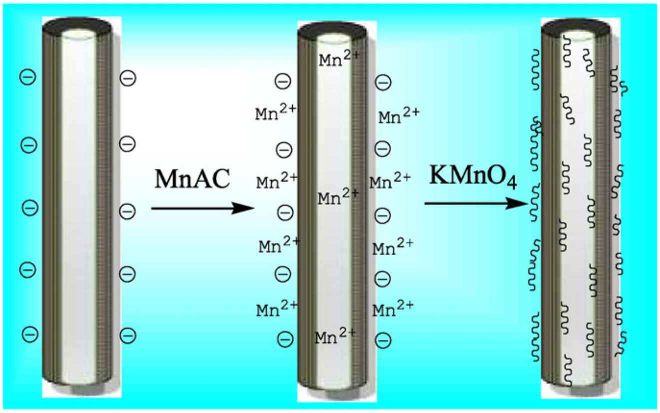

Fig. 1. Schematic illustration of the synthesis process of in-situ deposition method.

3. Results and discussion

3.1. Catalytic activity

In order to investigate the effect of different experiment method and carrier material on catalyst's SCR activities, the activities tests of four different catalysts with 8 wt% MnO_x loading were given at the same space

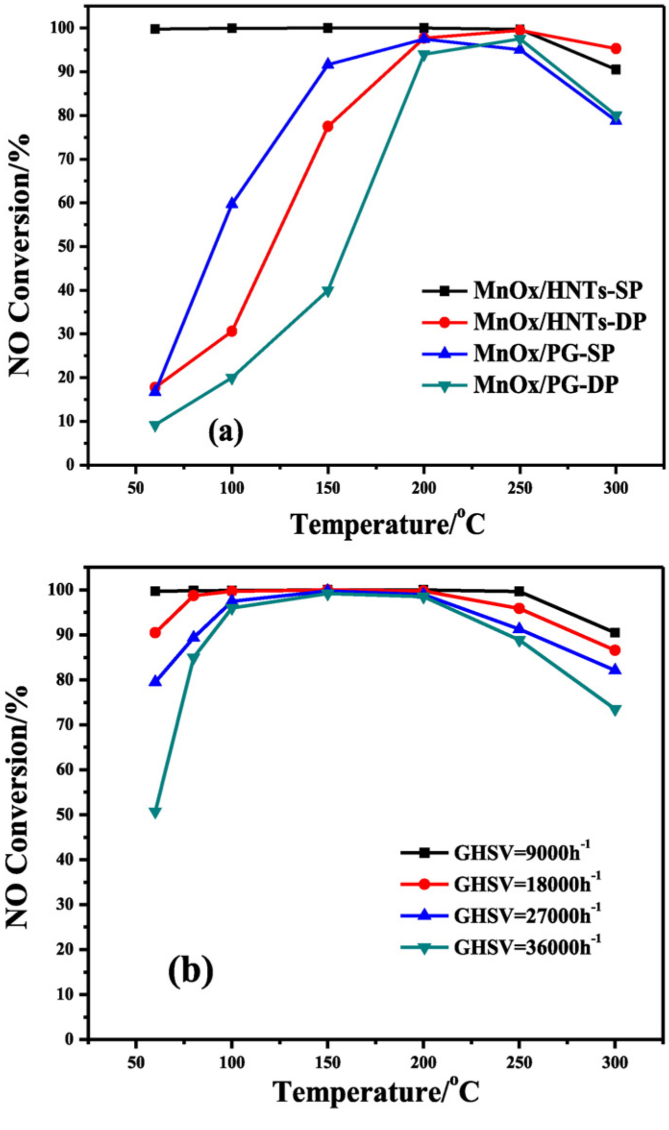

Fig. 2. (a) NO conversions for MnO_x catalysts prepared by different methods and carriers at the space velocity of 9000 h^{-1} and (b) NO conversion over MnO_x/HNTs-SP with different GHSV. Reaction conditions: [NO] = [NH_3] = 600 ppm, [O_2] = 3 vol.%, N_2 as the balance gas, total flow rate = 350 mL/min.