Journal of Molecular Catalysis A: Chemical 371 (2013) 86–93

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Catalysis A: Chemical

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

Low-temperature selective catalytic reduction of NO with NH_3 using perovskite-type oxides as the novel catalysts

Runduo Zhang, Na Luo, Wei Yang, Ning Liu, Biaohua Chen*

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China

ARTICLE INFO

Article history:
Received 14 October 2012
Received in revised form 22 January 2013
Accepted 23 January 2013
Available online 30 January 2013

Keywords:
In situ DRIFTS
Low temperature
Manganese
Perovskites
SCR of NO with NH_3

ABSTRACT

In order to investigate the activities of perovskite-type mixed oxides for selective catalytic reduction (SCR) of NO with NH_3, a series of $LaBO_3$ or La_2BO_4 perovskite-based catalysts with different B-site ions (B = Cu, Co, Mn, and Fe) was prepared by citrate complexation procedure and characterized by XRD, BET, TPD of NO + O_2 and NH_3. It was found that Mn-based perovskite exhibited the best catalytic activity, yielding 78% NO conversion at 250 °C. The NH_3 adsorption ability of the perovskites is the key factor for the SCR performance. In situ DRIFTS investigation was further carried out over $LaMnO_3$ to explore the reaction mechanism. It is revealed that the SCR reaction starts with NH_3 chemical adsorption, being thought as the rate-determining step. The mechanism essentially involves a Langmuir–Hinshelwood mechanism mainly depending on an interaction between NH_4^+ ionic species and nitrite species in the low-temperature range.

1. Introduction

Selective catalytic reduction with NH_3 as a reductant (NH_3-SCR) has been applied to reduce NO_x emissions from the stationary sources for several decades [1]. Generally, in order to avoid the catalyst deactivation caused by the high concentration of ash and SO_2 poison, the SCR unit is suggested to be located at the downstream of the electrostatic precipitator and desulfurizer [2]. As a result, the flue gas temperatures are commonly below 200 °C or even lower [3]. The commercial catalyst used for this process, V_2O_5–WO_3 (MoO_3)/TiO_2, shows a satisfactory performance, however, the reaction temperature is limited in a narrow and relatively higher range (300–400 °C) [4]. Therefore, the development of the SCR catalysts with superior activities at lower temperatures for avoiding the high cost of reheating the flue gas has attracted lots of attention from the scientific academy.

In recent years, the hotspots of the catalyst researches for SCR of NO with NH_3 are mainly focused on the metal oxides and zeolites [5]. Tang et al. studied single MnO_x oxides prepared by three kinds of methods [6], and Liu et al. also reported $FeTiO_x$ catalysts achieved good SCR performance [7]. Additionally, MnO_x–CeO_2 [8,9], Fe–Mn [10], Ce–Ti [11], and Ce–P–O [12] catalysts were investigated by many researchers. Moreover, a variety of supports such as TiO_2 [3,13–15], Al_2O_3 [16], and AC (active carbon) catalysts [1,2,17,18] was proposed to load Mn-, Ce- and Fe-based oxides for the better SCR activities. As for the zeolite catalysts, copper ion-exchanged zeolites used for SCR have been reported by Yahiro and Iwamoto [19]. Generally speaking, ZSM-5 zeolites were commonly used to support the Fe-, Cu-, and Mn-containing oxides for selective catalytic NO reduction [20–22].

Perovskites, the promising catalysts for air pollutants purification due to the excellent thermal stability, superior redox properties, great versatility and low cost [23], seem to be the ideal candidates for the SCR of NO with NH_3 at low-temperature region. Perovskite-type mixed oxides with a general ABO_3 formula are well known that their physicochemical properties can be effectively modified by partial substitution of A- and/or B-site cations. Although lots of work for the low-temperature NH_3-SCR process has been done, none was related to use perovskites as catalytic materials according to our knowledge.

In this study, a series of perovskite catalysts with different B-site cations (B = Cu, Co, Mn, and Fe) was synthesized by the citrate complexation procedure and further characterized by N_2 physisorption, temperature programmed desorption (TPD) of NH_3 (or NO + O_2). Based on the best-performing (the highest NO conversion) $LaMnO_3$, in situ DRIFTS was performed for a better understanding of reaction mechanism for the low-temperature SCR of NO by NH_3 occurring over perovskites.

2. Experimental

2.1. Catalyst preparation

The preparation of all perovskite catalysts including $LaBO_3$ (B-Mn, Fe, Co) and La_2BO_4 (B-Cu) was carried out by complexation method using citric acid as a complexation agent [24]. The

---

* Corresponding author. Tel.: +86 10 64412054; fax: +86 10 64419619.
E-mail address: chenbh@mail.buct.edu.cn (B. Chen).

1381-1169/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.molcata.2013.01.018

individual metal nitrates were used as the precursors for A-site or B-site cations. The molar ratio of total metallic ions to citric acid was 1:1. The mixture of different required metal nitrates in stoichiometric amounts was initially dissolved in the distilled water. Thereafter, a solution containing citric acid in water was slowly added into the precursor solution under gentle stirring at 80 °C until a gel was obtained. This gel was finally transferred to oven for drying at 110 °C for 24 h. Self-combustion was caused by setting fire to the dry gel in order to get the spongy residues. After a calcination of these residues at 600 °C, all the obtained solids were crushed and sieved to 40–60 mesh for the following characterization and activity evaluation.

2.2. Catalyst characterization

X-ray diffraction (XRD) measurements were carried out using X-ray diffractometer equipped with Cu-Kα ($\lambda = 0.15406$ nm) (Rigaku, D/max 2500VB2) in the range of 20–80° at a scan rate of 0.05° per second. The crystal phase and symmetry were confirmed through JCPDS reference.

A static nitrogen adsorption equipment JW-RB24 was used to measure the specific surface area of the samples at liquid N_2 temperature (−196 °C) with outgas pretreatment at 200 °C under vacuum.

Before the NO + O_2-TPD and NH_3-TPD experiments, the samples (50 mg) were pretreated in a flow of 1000 ppm NO/He + 6% O_2 or 1000 ppm NH_3/He at 200 °C for 1 h. After the samples were cooled down to room temperature (30 °C) under the same atmosphere, the stream was switched to the He flow (20 mL/min) for another hour to remove the physically adsorbed species. Then, the temperature was raised linearly to 500 °C at a rate of 5 °C/min. NO, NO_2 and N_2O desorbed during NO + O_2-TPD experiments were simultaneously detected and on-line recorded using a quadrupole mass spectrometer (OmniStar, MS200) with $m/z = 30$, 46 and 44, respectively. Moreover, during NH_3-TPD experiments the signals of $m/z = 16$, 30, 44 and 46 were monitored for NH_2, NO, N_2O and NO_2 fragments.

In situ DRIFTS experiments were conducted on a FTIR spectrometer (TENSOR 27, Bruker) equipped with a MCT detector cooled by liquid nitrogen and a diffuse reflection accessory (Praying Mantis, Harrick) which carries a high temperature reaction chamber. This accessory is attached to an automatic temperature controller (Harrick) which controls precisely the temperature of reaction chamber. After the sample was placed into the reaction chamber under He flow (20 mL/min), the temperature was raised to 200 °C. As the background spectrum was collected and the baseline of spectrum was stabilized, the He flow was cut off and the feeding gases were introduced into the chamber. IR spectra were recorded by accumulating 64 scans at a spectrum resolution of 4 cm^{-1}.

2.3. Catalytic activity measurement

The NH_3-SCR of NO was carried out in a fixed-bed quartz reactor in the temperature range of 100–400 °C by a step of 50 °C. The reaction was performed in a flow of 100 mL/min (given a GHSV of 30,000 h^{-1}), composed of 1000 ppm NO, 1000 ppm NH_3, 6% O_2, and balanced with He, over 200 mg of each sample. The contents of the gas components (NO, NH_3, N_2O, and NO_2) were analyzed by an infrared gas analyzer (Nicolet Nexus 470). N_2 was determined using a gas chromatograph (GC, HP 5890) fitted with TCD and columns of 5A and TDX-01.

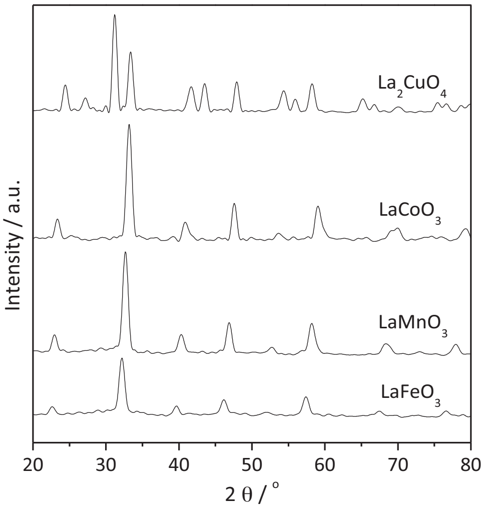

Fig. 1. XRD patterns of $LaBO_3$ or La_2BO_4 (B-Cu, Co, Mn and Fe) perovskite catalysts.

3. Results and discussion

3.1. Crystal structure and specific surface area

The XRD patterns of perovskites with the diverse B-site cations are shown in Fig. 1. A comparison of these spectra with JCPDS charts indicated that this series of $LaBO_3$ (B = Fe, Mn and Co) samples was nearly pure perovskite-type structure. $LaCoO_3$ presented a rhombohedral symmetry (JCPDS card 86-1662). Similarly, pure cubic $LaFeO_3$ (JCPDS card 75-0541) and rhombohedral $LaMnO_{3.15}$ (JCPDS card 50-0298) perovskite-type structure were also confirmed by XRD patterns. Since the preparation of $LaCuO_3$ was found to be difficult, in our present work La_2CuO_4, having a special structure of A_2BO_4, was synthesized successfully at 600 °C, and performed an orthorhombic symmetry of perovskite structure (JCPDS card 82-2142). The physical properties of prepared samples are summarized in Table 1. It can be seen that Mn-based perovskite showed a relatively higher surface area than those of other perovskites, resulting a decreasing order of $LaMnO_3$ (36.5 $m^2 g^{-1}$) > $LaFeO_3$ (32.7 $m^2 g^{-1}$) > $LaCoO_3$ (24.3 $m^2 g^{-1}$) > La_2CuO_4 (23.3 $m^2 g^{-1}$). It is common knowledge that an increase in surface areas of heterogeneous catalysts is beneficial for an enhancement in their reactivities. Considering the latter activity data, the contribution from the enhancement in surface areas on NO conversion was thought to be rather limited in comparison with the chemical properties of perovskites.

3.2. NO_x and NH_3 adsorption abilities

Fig. 2a illustrates the desorption signals of NO ($m/z = 30$) and NO_2 ($m/z = 46$) as a function of temperature during the NO + O_2-TPD process over all the perovskite samples. A quantitative analysis based on the deconvolution and integration of these desorption peaks is listed in Table 2. It can be seen that in the low-temperature region of 50–200 °C, NO desorption could be detected only over $LaMnO_3$ and $LaCoO_3$. Two medium NO peaks centered at about 200 °C and 317 °C over $LaCoO_3$ were observed, as well as a weak peak at >400 °C. Surprisingly, NO desorption could be always monitored over $LaMnO_3$ throughout the whole temperature range (70–500 °C), particularly at about 380 °C, where a board and strong desorption peak presented. While NO desorptions over La_2CuO_4 and $LaFeO_3$ initially started at around 225 °C and 200 °C, respectively, and each of them performed several obvious and broad peaks within the high-temperature range (>250 °C), especially for La_2CuO_4. The