Applied Catalysis A: General 427–428 (2012) 43–48

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

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

Catalytic reduction of NO by NH_3 over Fe–Cu–O_X/CNTs-TiO_2 composites at low temperature

Zhaoxia Ma, Hangsheng Yang*, Qian Li, Junwei Zheng, Xiaobin Zhang

State Key Laboratory of Silicon Materials, Department of Materials Science and Engineering, Zhejiang University, Zheda Road 38, Hangzhou 310027, China

ARTICLE INFO

Article history:
Received 13 January 2012
Received in revised form 17 March 2012
Accepted 19 March 2012
Available online 28 March 2012

Keywords:
Selective catalytic reduction
Carbon nanotubes
Iron–copper oxides
NO oxidation

ABSTRACT

Activity of iron–copper oxides supported on TiO_2 and carbon nanotubes (CNTs) for low-temperature selective catalytic reduction of NO by NH_3 in the presence of oxygen was investigated. The addition of FeO_X and CNTs synergistically promoted the NO conversion through the adsorption of NO and NH_3 and the catalytic oxidation of NO to NO_2. NO_2 adsorbed on the surface of the catalysts was found to be essential for NO reduction at low temperature, and approximately 90% NO conversion could be achieved at reaction temperature as low as 150 °C. Moreover, it was found that the deactivation caused by H_2O could be recovered after H_2O was switched off, while the deactivation caused by SO_2 was dependent on the reaction temperature.

1. Introduction

Nitrogen oxides (NO_X), which induce the formation of acid rain and ground-level ozone and cause respiratory problems, are therefore harmful for the ecosystem and humanity. Selective catalytic reduction (SCR) of NO_X by NH_3 in the presence of oxygen is one of the most effective methods to decrease the NO_X levels in gaseous emissions [1]. In recent decades, a variety of SCR catalysts have been developed for possible application, which can be divided into three groups, namely, noble metals, ion-exchanged zeolites, and metal oxides. Among them, V_2O_5-WO_3/TiO_2 has been widely accepted as an industrial catalyst despite the fact that vanadium protoxide is toxic and V_2O_5-WO_3/TiO_2 is only active within a narrow and high temperature window (300–400 °C) [2–5]. So it is necessary to develop novel catalysts to reduce the vanadium loadings or replace the vanadium with other metal elements. For this reason, many researchers continue to modify current catalysts. Moreno-Tost et al. [6] investigated cobalt–iridium supported on zirconium-doped mesoporous silica as catalysts for NH_3-SCR and found out Co–Ir supported catalysts showed higher NO conversion than Co supported catalyst. Wu et al. [7] reported a MnO_X–CeO_2 catalyst which has a high NO_X conversion within a low temperature range (80–220 °C). Lu et al. [8] reported that CeO_2 supported on ACF obtained 70% NO conversion at 150 °C.

Cu and Fe are two of the typically studied transition metals in SCR catalysts. Catalytic behaviors of Cu and Fe zeolites in the NH_3-SCR of NO [9,10] as well as in the HC-SCR of NO_X have been studied systematically [11,12]. Also, copper oxides and iron oxides, supported on Al_2O_3 [13], TiO_2 [14], SiO_2 [15], ZrO_2 [16], and carbonaceous material [17,18], are found to be active in medium temperature SCR of NO. However, exhaust gases usually contain a large amount of fly ash and SO_2, which severely deactivate the catalysts. Thus, further lowering the de-NO_X temperature is necessary so that SCR systems can be installed downstream of the desulfurizer and the electrostatic precipitator.

Recently, it was reported that carbon nanotubes (CNTs) are good adsorbents of NO_2, O_2, VOCs and NH_3 [19]. We also found that the addition of CNTs was beneficial for the SCR of de-NO_X and De-VOCs over a variety of metal oxide catalysts [20–22]. Based on our foregoing research, we prepared CNTs and TiO_2-supported iron and copper oxides by sol–gel method and studied their performance for NO reduction at low temperatures in the present study.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by a sol–gel method. The purified CNTs [23] were first sonicated in ethanol for 30 min for good dispersion. Tetrabutyl titanate was then added, and the solution was sonicated for another 30 min. Copper nitrate [$Cu(NO_3)_2{\cdot}3H_2O$], ferric nitrate [$Fe(NO_3)_3{\cdot}9H_2O$], and acetic acid were dissolved in distilled water and ethanol and added into the above solution. The resulting solution was sonicated until sols were formed. The sols were aged at ambient conditions to obtain good gels, which were air-dried at 100 °C overnight and then calcined at 500 °C for 4 h in

---

* Corresponding author. Tel.: +86 571 87951404; fax: +86 571 87951404.
E-mail address: hsyang@zju.edu.cn (H. Yang).

0926-860X/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcata.2012.03.028

Table 1
Summary of the catalysts prepared via the sol–gel method.

Catalysts	Cu:Fe (wt%:wt%)[a]	CNTs (wt%)[b]	Surface atomic ratio (%)[c]		S_{BET} (m^2/g)	Catalyst label
			Cu/Ti	Fe/Ti		
$CuO_X/CNTs\text{-}TiO_2$	–	5	0.39	–	97.2	$Cu_{10}Ti_{85}C_5$
	3:1	5	0.30	0.15	80.8	$Cu_3Fe_1Ti_{85}C_5$
	2:1	5	0.25	0.23	76.9	$Cu_2Fe_1Ti_{85}C_5$
$Fe\text{–}Cu\text{–}O_X/CNTs\text{-}TiO_2$	1:1	5	0.24	0.25	76.8	$Cu_1Fe_1Ti_{85}C_5$
	1:2	5	0.22	0.27	85.1	$Cu_1Fe_2Ti_{85}C_5$
	1:3	5	0.26	0.31	50.8	$Cu_1Fe_3Ti_{85}C_5$
$FeO_X/CNTs\text{-}TiO_2$	0	5	–	0.36	56.0	$Fe_{10}Ti_{85}C_5$
$Fe\text{–}Cu\text{–}O_X/TiO_2$	1:1	0	0.31	0.26	73.0	$Cu_1Fe_1Ti_{90}$

[a] Mass ratio of the Cu and Fe atoms when added to the system.
[b] Mass ratio of CNTs when added to the system.
[c] Surface atomic ratio as determined by XPS.

a N_2 atmosphere to acquire $Fe\text{–}Cu\text{–}O_X/CNTs\text{-}TiO_2$. Seven samples were analyzed to investigate the effect of Cu:Fe ratio and CNTs on low-temperature SCR of NO by NH_3. The samples had the same 10% Cu + Fe loading with different Cu:Fe ratios and a mass fraction of 5% CNTs as shown in Table 1.

2.2. Characterization

X-ray diffraction (XRD) patterns were recorded on a Philips XD-98 X-ray diffractometer with Kα radiation (λ = 0.15406 nm). A Hitachi S-4800 scanning electron microscope (SEM) was used to characterize the morphologies of the samples. Brunauer–Emmett–Teller (BET) surface areas were measured using an ASAP2000 physical adsorber. X-ray photoelectron spectroscopy (XPS) data were obtained using a Thermo ESCALAB 250. The X-ray source was an Al Kα radiation. All binding energies were referenced to a 284.8 eV C1s.

H_2-temperature-programmed reduction (H_2-TPR) experiments were performed using 50 mg of each catalyst. The samples were pretreated under a N_2 gas flow from 40 °C to 400 °C at a temperature increment of 10 °C/min. TPR experiments were performed at a heating rate of 10 °C/min under a mixed flow of 5% H_2 in argon at a flow rate of 40 ml/min. NH_3-temperature-programmed desorption (NH_3-TPD) experiments were performed using 50 mg of each catalyst to determine their NH_3 adsorption ability. The sample was pretreated in a N_2 stream (30 ml/min) at 400 °C for 1 h, then cooled to 100 °C. The pretreated sample was exposed to a mixed flow of 4% NH_3 in argon at a flow rate of 20 ml/min for 3 h at ambient temperature, and then heated from 100 °C to 850 °C at a heating rate of 10 °C/min. The H_2-TPR and NH_3-TPD data were recorded using an on-line gas chromatograph equipped with a thermal conductivity detector.

NO oxidation experiments were performed on the catalysts using an NO-NO_2-NO_X analyzer (Testo AG testo 350) to record the NO and NO_2 signals. The catalysts were heated from 100 °C to 410 °C, and 550 ppm of NO was fed in the presence of oxygen (5%, v/v) and a N_2 balance at a total flow rate of 500 ml/min and a gas hourly space velocity (GHSV) of 36,000 h^{-1}.

NO_X-temperature-programmed desorption (NO_X-TPD) experiments were performed on the catalysts using Testo AG testo 350 to record the NO and NO_2 signals. The samples were exposed to a 550 ppm NO flow and 5 vol% O_2 for 2 h at 400 °C and cooled to 100 °C in the same gas stream, followed by a N_2 purge during sample cooling to 80 °C. Once the NO signal returned to the baseline level, the temperature was ramped from 80 °C to 420 °C in N_2 at a rate of 10 °C/min.

FT-IR experiments were performed on $Cu_3Fe_1Ti_{85}C_5$ catalyst recorded with a Nicolet 5700 Fourier Transform spectrometer (0.09 cm^{-1} resolution). $Cu_3Fe_1Ti_{85}C_5$ catalyst was pretreated under an Ar gas flow (200 ml/min) at 100 °C overnight, then the catalyst was cooled to room temperature (RT) and exposed to a mixed flow of 1000 ppm NO and 5% O_2 at RT for 12 h, followed by an Ar purge at RT, then the samples were exposed to a mixed flow of 2% NH_3 in Ar at a flow rate of 30 ml/min for 2 h at RT, 100 °C, 200 °C, 250 °C respectively, following an Ar purge when the samples were cooled down. The powder samples at every stage were compressed in KBr-supporting disks to obtain the IR spectra.

2.3. Catalytic activity measurement

SCR activity measurements were conducted in a fixed-bed flow reactor. All samples were ground and mixed with 25 wt% organoclay and pasted on 3 cm × 10 cm aluminum plates. Ten catalytic plates were placed in a reactive tank with a 5 mm interval [21,24]. The reaction conditions were as follows: 550 ppm NO, 550 ppm NH_3, 5 vol% O_2 balanced by N_2 at a total flow rate of 500 ml/min. The inlet and outlet concentrations of NO, NO_2, and O_2 were monitored using an NO-NO_2-NO_X analyzer (Testo AG testo 350). The SCR activity tests were performed at reaction temperatures between 100 °C and 300 °C at a GHSV of 36,000 h^{-1}.

3. Results

3.1. SCR activity

Catalytic performances of a series of catalysts are shown in Fig. 1. $Cu_1Fe_1Ti_{90}$ was almost inactive up to 175 °C, then, NO conversion monotonically increased with temperature, reaching 32% and 94.37% at 200 and 300 °C, respectively. The NO conversion

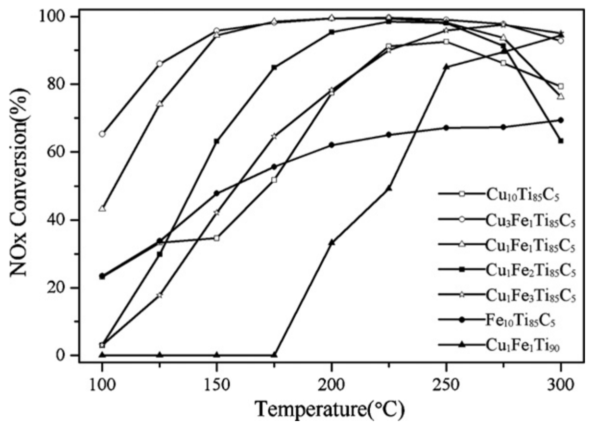

Fig. 1. NO_X conversion over the $Fe\text{–}Cu\text{–}O_X/CNTs\text{-}TiO_2$ catalysts, at 550 ppm NO, 550 ppm NH_3, 5% O_2, and 36,000 h^{-1} GHSV.