Catal Lett (2014) 144:216–221
DOI 10.1007/s10562-013-1157-5

The Properties and Mechanism of CuO Modified Carbon Nanotube for NO_x Removal

Shuli Bai · Huanying Li · Li Wang · Yujiang Guan · Shengtao Jiang

Received: 18 September 2013 / Accepted: 29 October 2013 / Published online: 20 November 2013

Abstract Carbon nanotube (CNT) supported copper oxide catalysts were prepared, and the morphology and structure of the catalyst were characterized by using scanning electron microscopy, transmission electron microscopy, X-ray diffraction and temperature-programmed desorption experiments. The CuO/CNT catalysts demonstrated high catalytic activities during the selective catalytic reduction (SCR) of NO with NH_3 over a temperature range of 150–250 °C. The amount of NH_3 adsorbed on the catalyst surface was greater than that of NO or NO + O_2 adsorbed on the catalyst surface. These results suggest that the SCR reaction might proceed on the surface of the CuO/CNT catalysts and occur between the adsorbed ammonia and gas phase NO or weakly adsorbed NO. The CuO/CNT catalysts exhibited good stability at low temperatures, which makes them suitable for potential applications in industry.

Keywords Carbon nanotube · Copper oxide · NO reduction · Ammonia

S. Bai (✉) · H. Li (✉) · Y. Guan · S. Jiang
Department of Environmental Engineering, Taizhou University, Taizhou 317000, China
e-mail: baishuli@tzc.edu.cn

H. Li
e-mail: lihuanying@nimte.ac.cn

S. Bai
Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, Zhejiang Normal University, Jinhua 321004, China

L. Wang
Key Laboratory for Advanced Silicon Carbide Materials, Research Center of Functional Materials, Kaifeng University, Kaifeng 475001, Henan, China

1 Introduction

Atmospheric pollutants (sulfur dioxide, nitrogen oxides (NO_x)) are generated mainly from the burning of coal and oil. In particular, NO_x harm to the environmental because they generate acid rain, photochemical smog and cause greenhouse effects as well as destroy the ozone layer [1, 2]. Many methods have been developed to reduce the harmful effects of NO_x. The SCR of NO_x with ammonia might be the most effective methods for the reduction of NO_x. Developing a suitable catalyst for SCR reaction remains a key problem. Previous studies indicated that titanium dioxide loaded with vanadium catalysts show high efficiency for reduction nitrogen oxides above 350 °C [3, 4]. However, this catalyst has many disadvantages, including high operational temperatures and the toxicity of vanadium species [5]. Therefore, many new catalysts have been developed to avoid these shortcomings [6–8]. Many reported catalysts, such as MnO_2/Al_2O_3, CuO/activated carbon (AC) and Fe_2O_3/AC, demonstrate high activity in SCR reaction at 120–250 °C [9–12].

Recently, copper oxide catalysts have attracted considerable attention because they exhibit high low-temperature activity for catalytic removal of NO [13–18], especially activated carbon as a support. However, we could not recognize the catalytic nature for this catalyst due to the complexity of surface chemistry and pore structure of activated carbon. Carbon nanotube has pure surface and simple structure, and it is useful for us to know the catalytic nature for SCR. The CNT-supported metal oxides such as CeO_2, MnO_X, etc. have been reported for low temperature deNO_x catalysts and showed good catalytic activity [19–23]. In view of peculiar character of carbon surface on carbon nanotube for removal NO [8, 24], it is important theory for development low-temperature SCR catalysts to modify carbon nanotubes with CuO. In the present work,

the properties and mechanism of CNT-supported CuO catalysts (CuO/CNT) were studied for the low-temperature SCR of NO with NH_3, which contributes to understanding the catalytic nature of carbon-based catalysts.

2 Ex erimental

2.1 The Catalyst Preparation

The raw CNT (Tsinghua University) samples were purified by the same method as ref. mentioned [25]. The CuO/CNT catalysts were prepared by pore volume impregnation of the purified CNT with an aqueous solution of cupric nitrate solution. The catalysts were dried at 60 °C overnight and then at 110 °C for 5 h, followed by calcined in argon stream at 250 °C for 2 h. For comparison, the Cuo/TiO_2 (ISK, Japan) catalysts were obtained by the same method.

2.2 Activity Tests

The SCR activity tests were carried out in a fixed-bed glass reactor (8 mm in inner diameter and 600 mm in length). The flue gas was simulated by NO in Ar, pure O_2 and pure Ar, SO_2 (When used) in Ar and NH_3 in Ar was used as reductive gas. All the gases were controlled by mass flow controllers. Concentration of NO, N_2O, NO_2, SO_2 and O_2

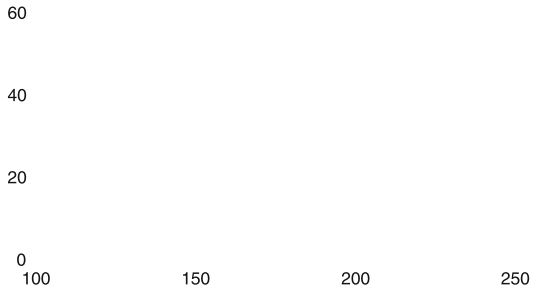

exhibit similar results. When SO_2 was removed from the feed, there was a small increase in the NO conversion (as shown in part III). After the catalyst was heated in Ar from 200 to 450 °C, which was followed by cooling to the original temperature of 200 °C (part IV). Subsequently, when the feed gas was re-subjected to the conditions in part I, the NO conversion returned to a consistent value of 40 % (part V), which was much lower than the conversion in part I. This conclusion agrees with previous observations with CuO/CNT catalysts at low temperature [11]. The influence of H_2O on the SCR activity over CuO/CNT catalyst was investigated and is shown in Fig. 6b. In the absence of H_2O, the NO conversion over the 10 wt% CuO/CNT catalyst was 88.5 %, and a slight decrease after introducing

7 vol% H_2O. This result shows that H_2O did not show obvious inhibition on the SCR activity to this SCR catalyst [19], and the inhibition of H_2O may be due to the competitive adsorption between H_2O and NH_3 on the active sites of the catalyst surface. These observations agree well with previous reports [21].

To observe the adsorption state of NH_3 on the surface of catalyst, the TPD curves were recorded after NH_3 was absorbed into the 10 wt% CuO/CNT catalysts. Figure 7 exhibits two distinct peaks, which are centered at approximately 100 and 282 °C and a very strong peak centered at 710 °C, which suggests that there are at least two NH_3 species adsorbed on the catalyst. The low-temperature (LT) peak was associated with the ammonium ions adsorbed on BrΦnsted acid sites, and the high-temperature (HT) peak might be attributed to the molecularly ammonia from Lewis acid sites [8, 25]. The HT peaks are much larger than the LH peak, which suggest that the molecular NH_3 was major form of NH_3 adsorbed on the CuO/CNT catalysts is.

NO and NO + O_2 TPD curves over CNT and CuO/CNT catalysts are summarized in Figs. 8 and 9

4. Chen L, Li J, Ge M (2010) Environ. Sci. Technol. 44:9590
5. Moura de Oliveira ML, Monteiro Silva C, Moreno-Tost R, Lopes Farias T, Jiménez L, Rodrígue C (2009) Appl. Catal. B 88:420
6. Bai SL, Zhao JH, Wang L, Zhu ZP (2009) J. Fuel Chem. Technol. 37:583
7. Zhu ZP, Liu ZY, Liu SJ, Niu HX (1999) Appl. Catal. B 23:L229
8. Huang B, Huang R, Jin D, Ye D (2007) Catal. Today 126:279
9. Singoredjo L, Korver R, Kapteijn F, Moulijn J (1992) Appl. Catal. B 1:297
10. Singoredjo L, Slagt M, Van Wees J, Kapteijn F, Moulijn J (1990) Catal. Today 7:157
11. Zhu ZP, Liu ZY, Liu SJ, Niu HX (2000) Appl. Catal. B 26:25
12. Grzybek T, Papp H (1992) Appl. Catal. B 1:271
13. Zhu J, Gao F, Dong LH, Yu WJ, Qi L, Wang Z, Dong L, Chen Y (2010) Appl. Catal. B 95:144
14. Aminna S, Tanef M (2004) J. Catal. 222:100
15. Chmielarz L, Ku-Trowski P, Pafalska-Lasocha A, Ajda D, Dziembaj R (2002) Appl. Catal. B 35:195
16. Pietrogiacomi D, Magliano A, Sannino D, Campa MC, Ciambelli P, Indovina V (2005) Appl. Catal. B 60:83
17. Xie GY, Liu ZY, Zhu ZP, Liu QY, Ge J, Huang ZG (2004) J. Catal. 224:36
18. Wan HQ, Li D, Dai Y, Hu YH, Liu B, Dong L (2010) J. Mol. Catal. A 332:32
19. Fang C, Zhang DS, Shi LY, Gao RH, Li HR, Ye LP, Zhang JP (2013) Catal. Sci. Technol. 3:803
20. Zhang DS, Zhang L, Shi LY, Fang C, Li HR, Gao RH, Huang L, Zhang JP (2013) Nanoscale 5:1127
21. Fang C, Zhang DS, Cai SX, Zhang L, Huang L, Li HR, Maitarad P, Shi LY, Gao RH, Zhang JP (2013) Nanoscale 5:9199
22. Zhang L, Zhang DS, Zhang JP, Cai SX, Fang C, Huang L, Li HR, Gao RH, Shi LY (2013) Nanoscale 5:9821
23. Zhang DS, Zhang L, Fang C, Gao RH, Qian YL, Shi LY, Zhang JP (2013) RSC Adv. 3:8811
24. Bai SL, Zhao JH, Du GX, Zheng JF, Zhu ZP (2008) Nanotechnology 19:205605
25. Bai SL, Zhao JH, Wang L, Zhu ZP (2010) Catal. Today 158:393
26. Maul J, Brito AS, de Oliveira ALM, Lima SJG, Maurera MAMA, Keyson D (2011) J.Therm. Anal. Calorim. 106:519