

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

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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 NH₃ over a temperature range of 150–250 °C. The amount of NH₃ adsorbed on the catalyst surface was greater than that of NO or NO + O₂ 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

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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 MnO₂/Al₂O₃, CuO/activated carbon (AC) and Fe₂O₃/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 CeO₂, 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 NH₃, which contributes to understanding the catalytic nature of carbon-based catalysts.

2 Experimental

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/TiO₂ (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 O₂ and pure Ar, SO₂ (When used) in Ar and NH₃ in Ar was used as reductive gas. All the gases were controlled by mass flow controllers. Concentration of NO, N₂O, NO₂, SO₂ and O₂ at the inlet and the outlet of the reactor were simultaneously monitored by an online combustion gas analyzer (Testo-pro 350, Germany) equipped with NO, NO₂, SO₂, O₂ and analyzer (PGD-100, Austria) equipped with N₂O.

2.3 The Catalyst Characterization

The CuO/CNT catalysts were characterized by X-ray diffraction (XRD) patterns, scanning electron microscopy (SEM, JEOL JSM-6700F), and transmission electron microscopy (TEM, JEOL JEM 3010) equipped with energy dispersive X-ray spectroscopy (EDS).

The temperature-programmed desorption of NH₃ (NH₃-TPD) and NO or NO + O₂ was performed in a fixed-bed quartz reactor. A typical experiment used at a 200 mg sample and a gas flow rate of 100 ml/min. The catalyst was pre-treated under Ar at 300 °C for 2 h before being subjected to the adsorption of 1,000 ppm of a sample gas for 1 h at 30 °C, and TPD was measured at 10 °C/min under Ar from 30 to 960 °C.

3 Results and Discussion

Figure 1 illustrates the SEM, TEM and XRD patterns of the 10 wt% CuO/CNT catalyst. It is obvious that the

diffraction peaks ($2\theta = 26.0, 42.8$) can be indexed to CNT [20], and the diffraction peaks ($2\theta = 36.3$) were attributed to hexagonal phase of CuO (JCPDS Card No. 45-0937) [26]. The average size of CuO particles on the catalysts surface was approximately 6–10 nm, which was obtained by analysis of the appropriate XRD data and agreed with the TEM results.

Figure 2a summarizes the changes in the SCR activity at different CuO loading relative to the weight of CuO/CNT catalyst at 200 °C. The catalytic activity of CuO/CNT catalyst increased when the CuO loading was increased within the range of 1–10 wt%. NO conversion reached 88.5 % when the CuO loading was 10 wt%. However, NO conversion decreased when CuO loading was greater than 10 wt%. The decrease in the catalytic activity might be due to aggregation of the copper oxide particles on the CNT surface. N₂O has not been observed in this reaction process and only a small amount of NO₂ (less than 10 ppm) was observed. To further exhibit the excellent catalytic properties of CuO/CNT catalysts, SCR activity of a commercial titanium dioxide-supported CuO catalysts (CuO/TiO₂) was investigated and shown in Fig. 2b. It is obvious that the SCR activity of the CuO/CNT catalyst is much higher than that of the CuO/TiO₂ catalyst.

Figure 3 reveals the performance of the 10 wt% CuO/CNT catalyst during the reduction of NO_x with a reaction temperature between 120 and 250 °C. These results demonstrated that the NO conversion over the 10 wt% CuO/CNTs catalyst increased when the reaction temperature was increased. NO conversion reached approximately 88.5 % when the reaction temperature was increased to 200 °C. However, when the reaction temperature was increased to 250 °C, NO conversion declined to approximately 70.5 % because the oxidation of ammonia was more favorable at increased reaction temperatures which led to decreased reduction of NO by ammonia. The appearance of a small amount of N₂O and NO₂ in the reaction mixture confirmed this process.

The effect of the flue gas space-velocity on NO conversion with 10 wt% CuO/CNT catalyst under the reaction temperature of 200 °C is shown in Fig. 4. The NO conversion reached 97.3 % when the flue gas space velocity was 10,000 h⁻¹. The NO conversion also exhibited a negative trend when the flue gas space velocity was increased. Using a small space velocity can increase the amount of the flue gas adsorbed on the surface and provides a long interval for the flue gas to react with an active component. However, NO conversions can high reached 88.5 % when the space velocity was 30,000 h⁻¹.

From a theoretical and technical point of view, the stability of the CuO/CNT catalysts must be studied. Figure 5 shows the stability of the 10 wt% CuO/CNT catalyst at 200 °C. The CuO/CNT catalyst demonstrates excellent

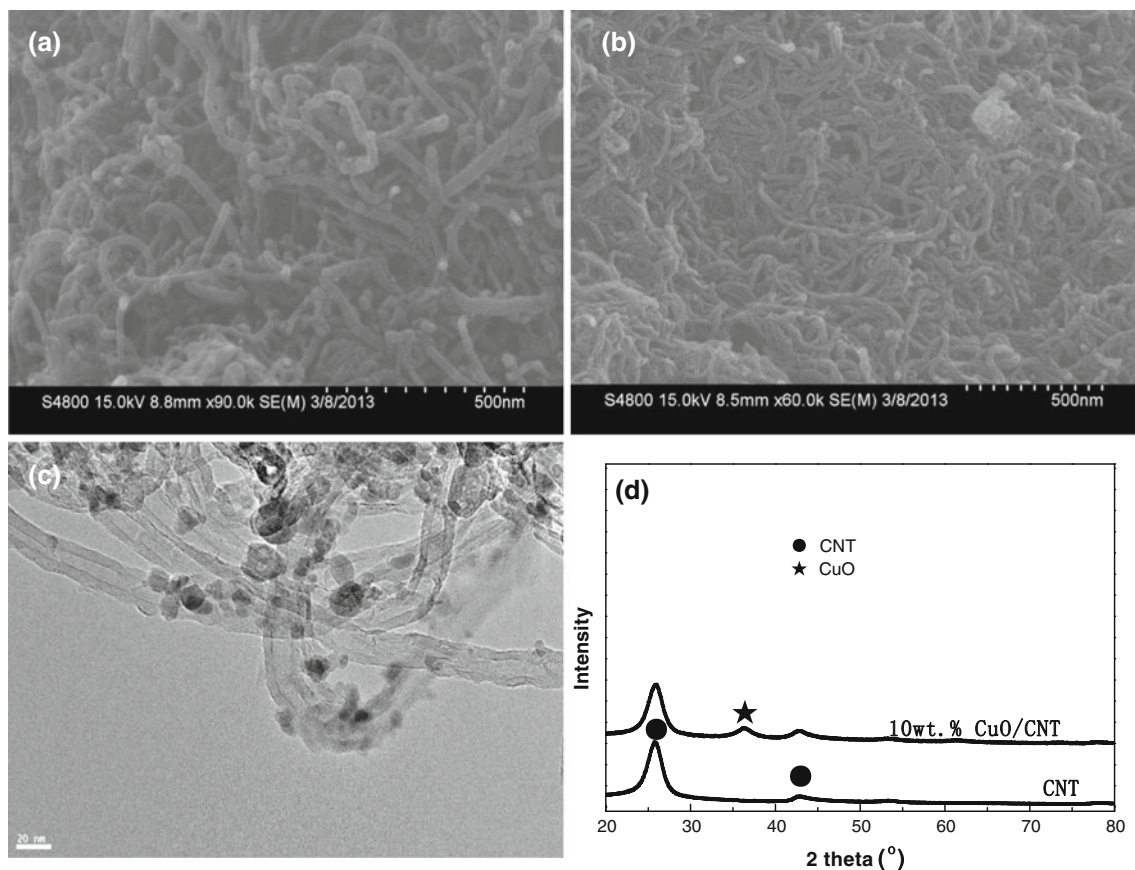


Fig. 1 SEM (a, b) and TEM (c) of the 10 wt% CuO/CNT catalysts and X-ray diffraction of copper oxide catalysts support on carbon nanotubes (d)

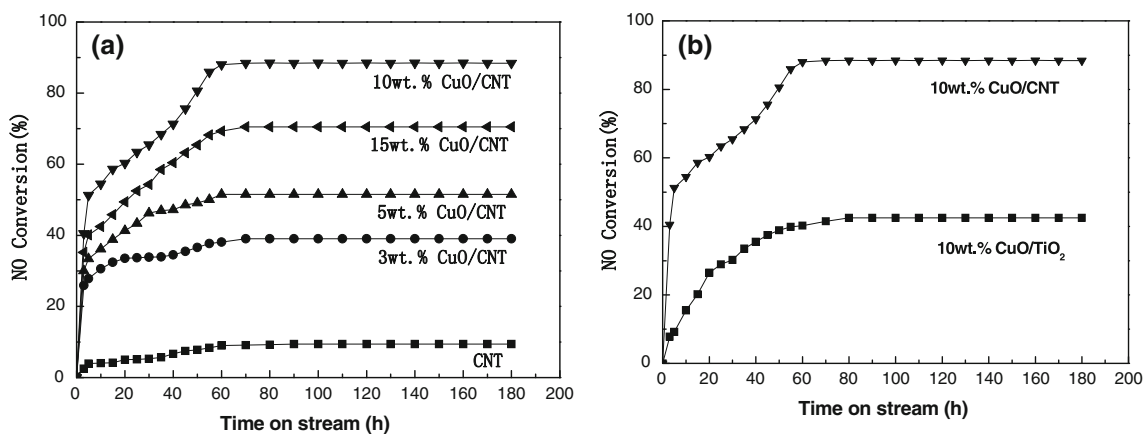


Fig. 2 a Effect of CuO loading on the activity of CuO/CNTs catalysts at 200 °C; b NO conversion of CuO/CNT catalysts and CuO/TiO₂ at 200 °C. Reaction conditions: 450 ppm NO, 500 ppm NH₃, 5 vol% O₂, WHSV, 30,000 h⁻¹, Catalyst weight: 200 mg

catalytic activity and NO conversion efficiency keeps 88.5 % over a 72 h of use. These results indicate that the CuO/CNT catalysts have a moderately good stability.

To understand the influence of SO₂ on the CuO/CNT catalyst, SO₂ transient response experiments consisting of five consecutive parts (Fig. 6) were carried out at 200 °C

using the 10 wt% CuO/CNT catalyst. The concentrations of NO and SO₂ were monitored at the outlet during the experiments. In part I, NO conversion was approximately 88.5 % in the absence of SO₂; however, this value decreased to 9 % after introducing SO₂ into the system in part II, and further increases in the SO₂ concentration

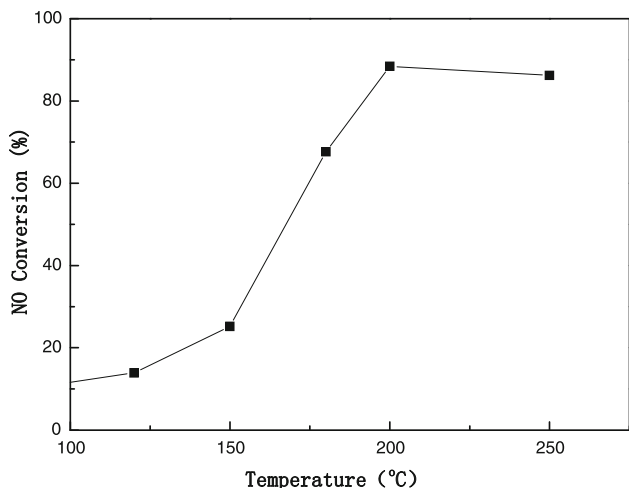


Fig. 3 Effect of reaction temperature on the activity of the 10 wt% CuO/CNTs catalysts. Reaction conditions: 450 ppm NO, 500 ppm NH₃, 5 vol% O₂, WHSV, 30,000 h⁻¹, Catalyst weight: 200 mg

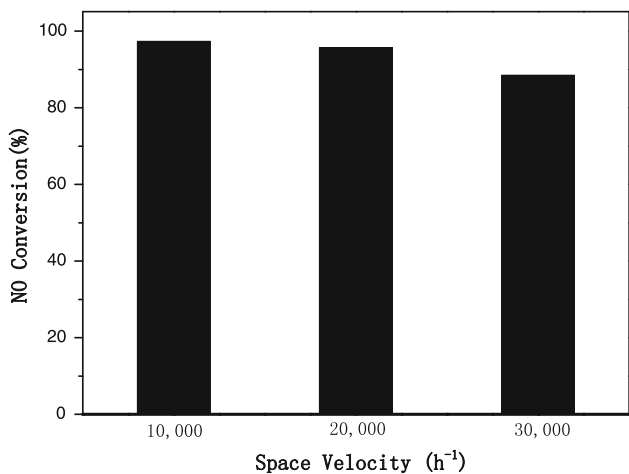


Fig. 4 Effect of space velocity on the activity of the 10 wt% CuO/CNTs catalysts. Reaction conditions: 450 ppm NO, 500 ppm NH₃, 5 vol% O₂, Reaction temperature: 200 °C

exhibit similar results. When SO₂ 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 H₂O on the SCR activity over CuO/CNT catalyst was investigated and is shown in Fig. 6b. In the absence of H₂O, the NO conversion over the 10 wt% CuO/CNT catalyst was 88.5 %, and a slight decrease after introducing

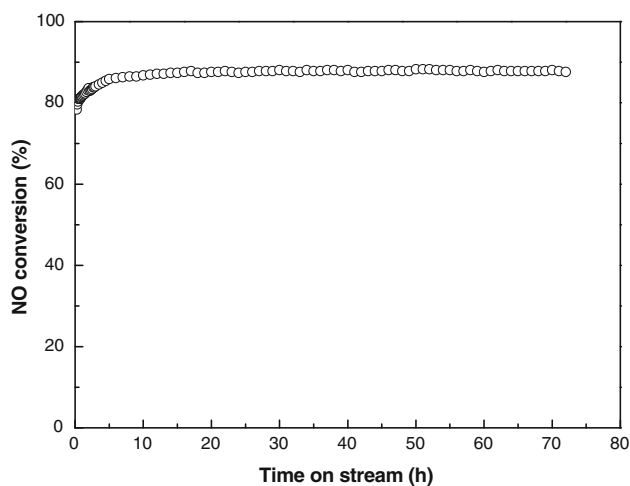


Fig. 5 A test of the stability of the 10 wt% CuO/CNTs catalysts for SCR reaction. Reaction conditions: 450 ppm NO, 500 ppm NH₃, 5 vol% O₂, WHSV, 30,000 h⁻¹, Catalyst weight: 200 mg, Reaction temperature: 200 °C

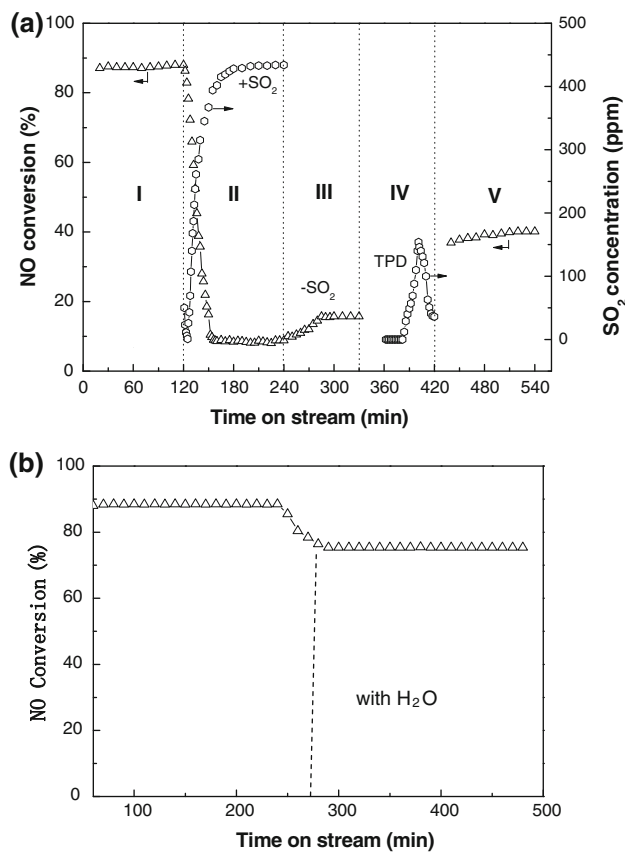


Fig. 6 Effect of SO₂ (a) and H₂O (b) on the activity of the 10 wt% CuO/CNTs catalysts. Reaction conditions: 450 ppm NO, 500 ppm NH₃, 5 vol% O₂, 400 ppm SO₂ (when used), 7.0 vol% H₂O (when used), WHSV, 30,000 h⁻¹, Catalyst weight: 200 mg, reaction temperature, 200 °C

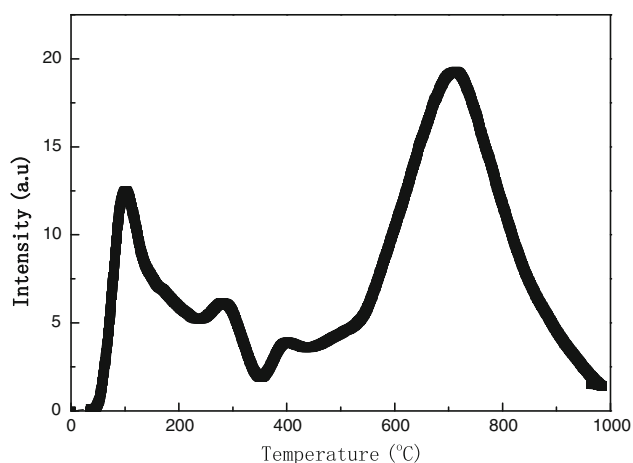


Fig. 7 NH_3 -TPD profiles of the 10 wt% CuO/CNT catalyst

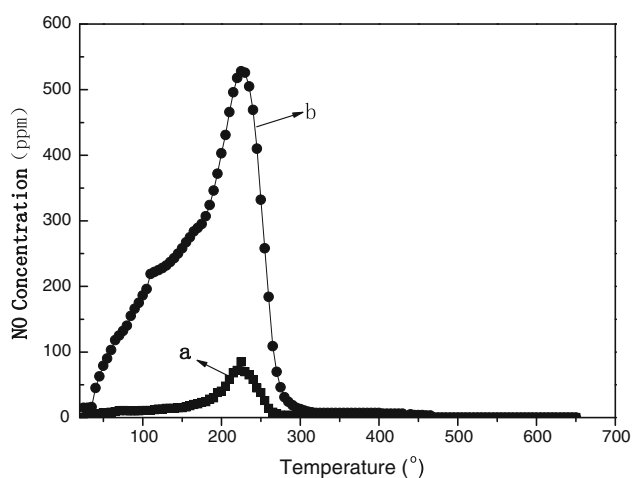


Fig. 8 $\text{NO} + \text{O}_2$ -TPD profiles of the CNT (a) and 10 wt% CuO/CNT catalyst (b)

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 Brønsted 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.

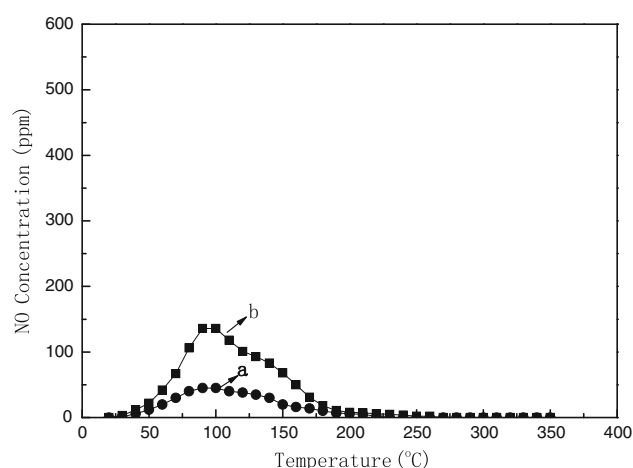


Fig. 9 NO TPD profiles of the CNT (a) and 10 wt% CuO/CNT catalyst (b)

NO and $\text{NO} + \text{O}_2$ TPD curves over CNT and CuO/CNT catalysts are summarized in Figs. 8 and 9. The amount of desorbed NO on the CNT surface was small in the presence and in the absence of O_2 . The amount of NO desorbed over the CuO/CNT catalysts was larger when O_2 was present. However, the amount of NH_3 desorbed over the CuO/CNT catalysts was larger than the amount of desorbed NO in the presence or absence of O_2 . These results suggest that the SCR reaction proceeds on the CuO/CNT catalysts between the adsorbed ammonia and NO from the gas phase or weakly adsorbed NO.

4 Conclusions

Copper oxide supported on carbon nanotube developed for the SCR of NO with ammonia demonstrates excellent catalytic activity over the temperature range of 150–250 °C. The catalysts exhibit good stability. The SCR reaction proceeds between adsorbed ammonia and NO that exists in the gas phase or weakly adsorbed NO. The best NO conversion of 88.5 % was obtained with the 10 wt% CuO/CNT at 200 °C and a GHSV of 30,000 h^{-1} .

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