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## NO REDUCTION ON CU-ZSM-5 STUDIED BY EXAFS

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### ABSTRACT

Extended x-ray absorption fine structural (EXAFS) spectroscopy was used to study the nature of the Cu species in ZSM-5 involved in catalytic reduction of NO. The EXAFS data indicate that about 2.5 nearest oxygen atoms surrounding the center atom Cu with a Cu-O bond length of 1.95 Å in the oxidized Cu-ZSM-5 catalyst. Reduction of the catalyst in hydrogen at 573 K leads to the formation of Cu-Cu (2.53 Å) bonds. The coordination number (CN) of the Cu-Cu species in the reduced catalyst is 5.7. Over 90 % of NO can be reduced to N<sub>2</sub> at 573 K effected by the Cu-ZSM-5 catalyst with the CN of the Cu-O bonding being 1.01.

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**Key words:** Cu-ZSM-5, EXAFS, NO Reduction

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### 1 INTRODUCTION

About  $3 \times 10^7$  tons per year of NO<sub>x</sub> are emitted into the earth atmosphere [1]. NO<sub>x</sub> cause many environmental problems including formation of acid rain and the resultant acidification of aquatic systems, ground-level ozone (smog), and general atmospheric visibility degradation. Reduction of NO<sub>x</sub> emission has become one of the major environmental protection issues.

Selective catalytic reduction of NO<sub>x</sub> by ammonia (NH<sub>3</sub>-SCR) has been practically used [2, 3]. However, the NH<sub>3</sub>-SCR process is suffering from the economic difficulty in terms of handling the toxic ammonia [4]. Many catalysts for selective catalytic reduction of NO<sub>x</sub> effected by hydrocarbons (HC-SCR) have been reported [4-7]. Metals (such as Cu, Co, Mn, Ni or Ru) supported on ZSM-5 (Zeolite Socony-Mobil-5) or metallosilicates (ferrosilicate and gallosilicate) have been used as HC-SCR catalysts. It is known that copper exchanged ZSM-5 (Cu-ZSM-5) is very active in selective catalytic reduction of NO<sub>x</sub> [7]. The Cu-ZSM-5 catalyst is also very effective in reduction of NO<sub>x</sub> in automobile exhausts [8, 9]. However, the nature of the catalyst used in the HC-SCR process has not been extensively studied, especially the behavior of oxygen in the matrix of CuO in the channels of ZSM-5 [10, 11]. Extended X-ray absorption fine structural (EXAFS) and X-ray absorption near edge structure (XANES) are very useful in identification of elements with a different environment, degree of aggregation or location [12-14]. Thus, the main

objective of the present work was to investigate the structure of copper species in the channels of ZSM-5 in the catalytic reduction of NO by EXAFS spectroscopy. Reduction and oxidation of the Cu-ZSM-5 catalyst were also studied by temperature programmed reduction (TPR).

## 2 EXPERIMENTAL

Zeolite ZSM-5 was prepared from a reaction mixture containing a source of silica from rice husk gasification ash. The as-synthesized ZSM-5 was dried and calcined at 873 K for 24 hours. Crystallinity of the zeolite ZSM-5 is 99% if compared with the Mobil ZSM-5. A 0.02 M  $\text{Cu}(\text{NO}_3)_2$  solution was used in preparing Cu exchanged ZSM-5 (Cu-ZSM-5) catalysts that have a molar ratio of  $\text{Cu}/\text{Al} = 0.31$ ,  $\text{Si}/\text{Al} = 5.52$ , and  $\text{Ca}/\text{Al} = 0.087$  (determined by SEM/EDX (JSM-35)).

The Cu-ZSM-5 catalyst was characterized by X-ray powder diffraction (RIGAKU Model D/MAX III-V). EXAFS spectra were recorded at the double-crystal monochromator (DCM) X-ray beamline at the SRRC (Synchrotron Radiation Research Center) of Taiwan. The electron storage ring was operated at an energy of 1.3 GeV and 80-200 mA current. A Si (111) double-crystal monochromator was used for selection of energy with an energy resolution of  $1.9 \times 10^{-4}$ . Samples were measured in fluorescence mode. Photon energy was calibrated by characteristic pre-edge peaks in the absorption spectrum of a Cu foil (8980 eV). Each EXAFS spectrum was recorded at least twice. The EXAFS data were analyzed using the UWXAFS 3.0 program [14]. The raw absorption data in the region from 200 to 50 eV below the edge position was fit to a straight line using the least-square algorithm. The fitted pre-edge background was extrapolated throughout the whole data range and then subtracted and normalized to reduce the effect of sample thickness. The Fourier transformation was performed on  $k^2$ -weighted EXAFS oscillations in the range of  $2.8\text{--}12 \text{ \AA}^{-1}$ . Multiple shell fitting of the EXAFS data was calculated in R-space.

Cu-ZSM-5 catalyst was reduced in flowing 10%  $\text{H}_2/\text{He}$  at 573 K for one hour. About 0.9–1.2 grams of Cu-ZSM-5 catalyst were used in catalytic reduction of NO (4% NO and 4% methane balanced by helium) in a fixed-bed reactor at 303–873 K. Off gas was monitored by on-line FTIR spectroscopy. Infrared spectra were recorded on a Digilab FT-IR spectrometer (FTS-40) with fully computerized data storage and data handling capability. For all spectra reported, a 64-scan data accumulation was carried out at a resolution of  $4 \text{ cm}^{-1}$ .

In the temperature programmed reduction (TPR) experiments, Cu-ZSM-5 was reduced in 10%  $\text{H}_2/\text{He}$  with a heating rate of  $10 \text{ K min}^{-1}$ . A thermogravimetry analyzer (SDT 2960 simultaneous TGA-DTA) was used to monitor the weight change of sample in the reduction process.

## 3 RESULTS AND DISCUSSION

Zeolite ZSM-5 is a microporous crystalline solid. The straight channels of ZSM-5 have an elliptical cross section of  $5.7\text{--}5.8 \text{ \AA}$  by  $5.1\text{--}5.2 \text{ \AA}$  [15]. These channels are interconnected by zigzag channels with a

nearly circular cross section and diameter of 5.4 Å. Reduction of NO with CH<sub>4</sub> and O<sub>2</sub> on the oxidized Cu-ZSM-5 catalyst at elevated temperatures was investigated in a fixed-bed reactor. In Figure 1, it seems that oxidation of NO to NO<sub>2</sub> may occur at the early stage of the temperature programmed reaction process. Reduction of NO to form N<sub>2</sub>O on the surface of the catalyst is also observed at 473-673 K. The IR data also

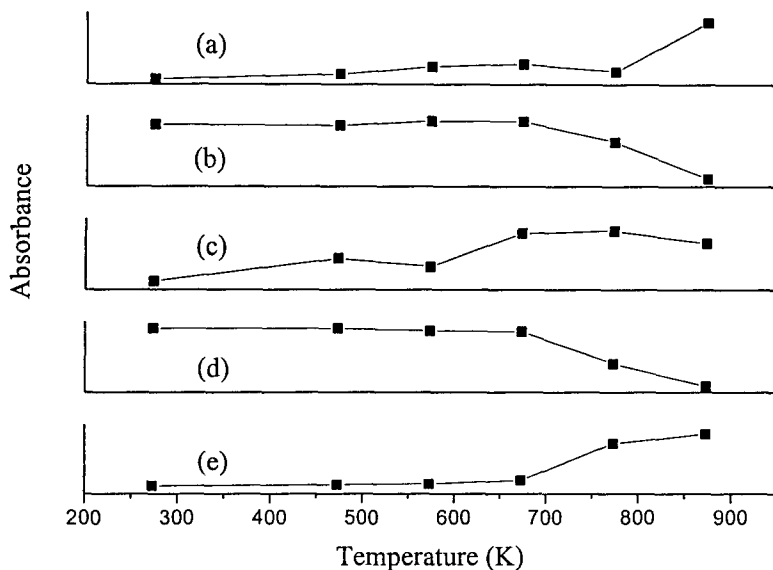


Figure 1 Infrared absorbance of (a) NO, (b) NO<sub>2</sub>, (c) N<sub>2</sub>O, (d) CH<sub>4</sub>, and (e) CO<sub>2</sub> for the off gas of temperature programmed reaction of NO with O<sub>2</sub> and CH<sub>4</sub> on the oxidized Cu-ZSM-5 catalyst.

indicate that gaseous NO<sub>2</sub> reacts directly with CH<sub>4</sub> to form N<sub>2</sub>O and CO<sub>2</sub> at 673 K. The X-ray diffraction pattern of the oxidized Cu-ZSM-5 catalyst (shown in Figure 2) suggests that the main Cu species in the

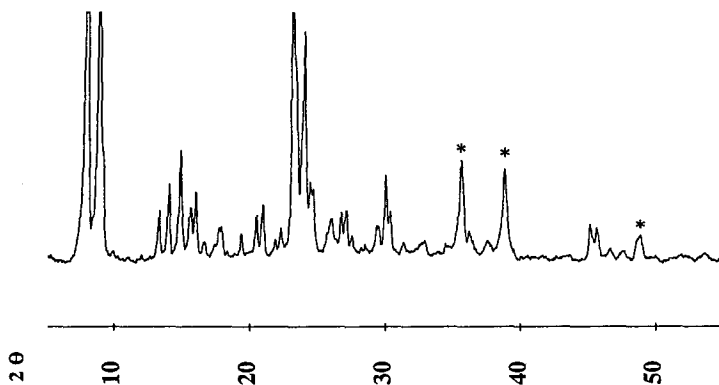


Figure 2 X-ray diffraction pattern of oxidized Cu-ZSM-5 catalyst. \* denotes the character peaks of CuO.

channels of ZSM-5 is CuO. In addition, the temperature programmed reduction of the oxidized Cu-ZSM-5 catalyst shows that the exchanged CuO species are in the channels of ZSM-5 (Figure 3(a)). However, in

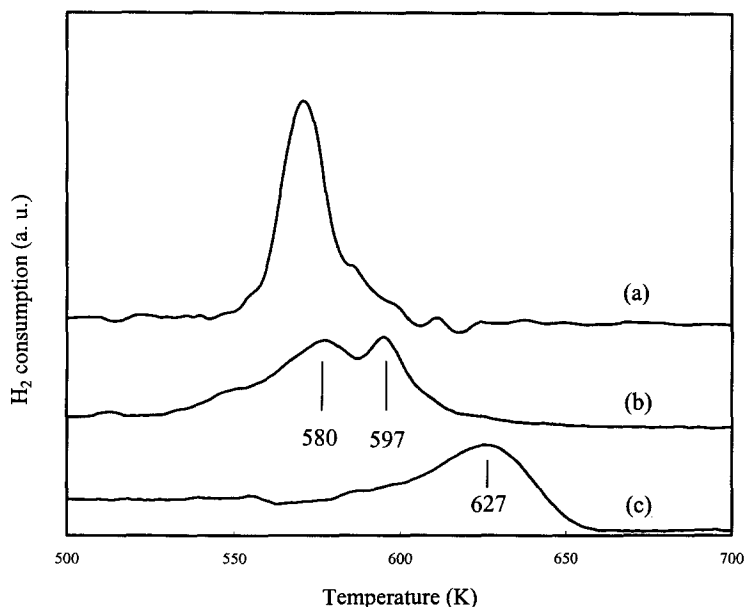


Figure 3 Temperature programmed reduction of (a) oxidized Cu-ZSM-5, (b) spent Cu-ZSM-5 (used in NO reduction) and (c) re-oxidized Cu-ZSM-5 in 10% H<sub>2</sub>/He at a heating rate of 10 K min<sup>-1</sup>.

the reducing environment, NO was reduced and oxidized to N<sub>2</sub>O and NO<sub>2</sub>, on the reduced Cu surfaces at 473 K (Figure 4). Generally, the surface species (Cu<sup>+</sup>-(NO)<sub>2</sub>) are formed via the adsorption of NO on the Cu<sup>+</sup> sites [16, 17]. At 574 K, over 90 % of NO can be catalytically reduced to N<sub>2</sub> at 573 K by the copper in the channels of ZSM-5. At 673-873 K, CH<sub>4</sub> is directly oxidized with NO to form N<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>O. Reduction of the catalyst Cu-ZSM-5 used in reduction of NO in the presence of CH<sub>4</sub> and O<sub>2</sub> shows two features at 580 and 597 K in the TPR curve. Possibly the involvement of migration of the copper species in the process of reduction or oxidation may facilitate the increasing of particle size in these very restricted channels of ZSM-5. It should be noted that the strong electric field as well as the extremely high surface area in the channels of ZSM-5 may be responsible for preservation of the copper species in the channels. However, a repeated oxidation-reduction of Cu-ZSM-5 may lead to an interaction of copper with zeolite framework (Cu<sup>i</sup>O<sub>x</sub>) (shown in Figure 3(c)). The Cu<sup>i</sup>O<sub>x</sub> species may be reduced at 627 K. Note that the Cu<sup>i</sup>O<sub>x</sub> species has a very low NO reduction activity [18].

For better understanding the nature of active copper species in ZSM-5, XAFS spectra were

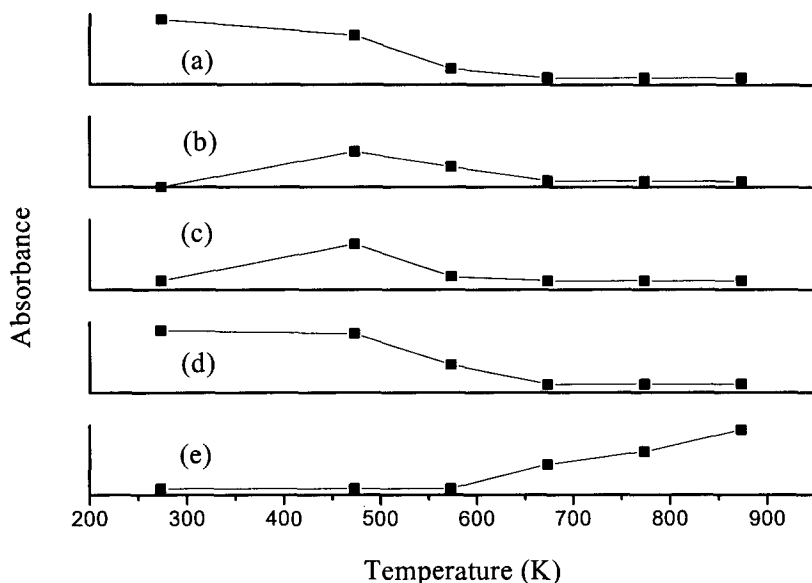


Figure 4 Infrared absorbance of (a) NO, (b) NO<sub>2</sub>, (c) N<sub>2</sub>O, (d) CH<sub>4</sub>, and (e) CO<sub>2</sub> for the off gas of the temperature programmed reaction of NO and CH<sub>4</sub> on the reduced Cu-ZSM-5 catalyst.

determined. The XANES spectra of the Cu-ZSM-5 catalyst, Cu foil, Cu<sub>2</sub>O, and CuO are shown in Figure 5. The preedge XANES spectra of the oxidized Cu-ZSM-5 exhibits only very weak absorbance band for the 1s→3d transition which is forbidden by the selection rule in the case of perfect octahedral symmetry [12, 13]. A shoulder at 8992-8995 eV and an intense band at about 9007-9010 eV are attributed to the 1s→4p transition that indicates the existence of Cu<sup>2+</sup> species in the channels of ZSM-5. These results are also consistent with the measurements of Anpo [19] and Giamello [20] on the distorted hydrated Cu<sup>2+</sup> ions in the Cu/zeolite samples. The observed XANES spectra on the reduced Cu-ZSM-5 catalyst compared to the Cu foil are consistent with a different type of Cu<sup>2+</sup> in the two samples. However, due to the fact that metallic copper has a very low activity in NO reduction [21], complete reduction to form metallic copper is not desirable. The Cu<sup>+</sup> sites are, in general, very active for NO reduction [22, 23]. In Figure 5, the preedge band for Cu<sup>+</sup> appears when NO is adsorbed on the reduced Cu-ZSM-5 catalyst at 573 K. The feature at 8983-8984 eV, due to the dipole-allowed of 1s→4p electronic transition, indicates the existence of Cu<sup>+</sup> [24-26]. It is apparent that the metallic copper in ZSM-5 becomes activated via adsorption NO. Lei and his coworkers [27] indicated that the Cu<sup>+</sup> species is formed via decomposition of the intermediate Cu<sup>2+</sup>-O<sup>2</sup>-Cu<sup>2+</sup> while adsorbed NO is converted to N<sub>2</sub> and O<sub>2</sub> on the catalyst surfaces.

The EXAFS spectra were recorded and analyzed in the k range of 2.5-11 Å<sup>-1</sup>. Figure 6 shows the

curve-fitting analyses of the EXAFS spectra of the Cu-ZSM-5 catalysts. In Table 1, the oxidized Cu-ZSM-5 has a Cu-Cu bonding of 1.95 Å with a coordination number (CN) of 2.47. Reduction of the

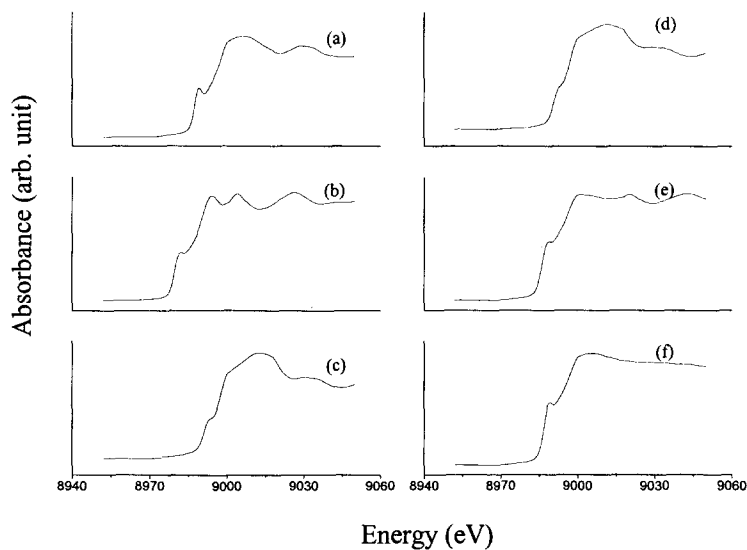


Figure 5 XANES spectra of (a) CuO, (b) Cu foil, (c) Cu<sub>2</sub>O, (d) oxidized, (e) reduced, (f) NO adsorbed on Cu-ZSM-5 catalyst.

catalyst in hydrogen at 573 K for one hour, the EXAFS spectra indicate that the Cu-Cu bonding are predominant for central Cu atoms in the channels of ZSM-5. In the NO reduction process, coordination of

Table 1 EXAFS data of Cu-ZSM-5 catalyst

Samples	Shell	R <sup>a</sup> (Å)	CN <sup>b</sup>	σ <sup>2c</sup> (Å <sup>2</sup> )
Oxidized Cu-ZSM-5	Cu-O	1.95	2.47	0.003
	Cu-(O)-Cu	2.90	8.87	0.029
Reduced Cu-ZSM-5	Cu-Cu	2.53	5.71	0.008
	Cu-Cu	3.57	7.10	0.020
NO/Cu-ZSM-5 <sup>d</sup>	Cu-O	1.87	1.01	0.003
	Cu-Cu	2.58	3.12	0.009

<sup>a</sup> Bond distance; <sup>b</sup> Coordination number; <sup>c</sup> Debye-Waller factor;

<sup>d</sup> NO adsorbed on reduced Cu-ZSM-5 at 573 K.

copper with oxygen or nitrogen in the Cu-ZSM-5 may take place. Experimentally, the bond distance of Cu-O in the Cu-ZSM-5 is 1.87 Å which is similar to that of Cu<sub>2</sub>O. Moreover, the CN of the Cu-O bond for

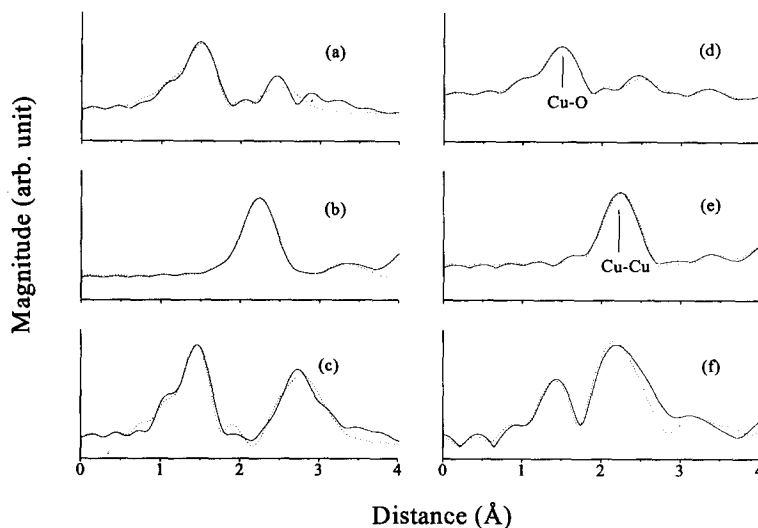


Figure 6 Fourier transformed Cu K edge EXAFS of (a) CuO, (b) Cu foil, (c) Cu<sub>2</sub>O, (d) oxidized, (e) reduced, (f) NO adsorbed on the Cu-ZSM-5 catalyst. The dotted curves denote the best fitting of the EXAFS spectra.

the NO adsorbed on reduced Cu-ZSM-5 is determined as 1.01. Both the XANES and EXAFS data indicate that copper may be oxidized to form Cu<sup>+</sup> in the NO adsorption and reduction process. Note that about 45.3 % of copper species in the channels of ZSM-5 are oxidized to form the active site Cu<sup>+</sup> in the NO adsorption process.

#### 4 CONCLUSIONS

Over 90 % of NO can be catalytically reduced to N<sub>2</sub> at 573 K by the copper in the channels of ZSM-5 synthesized from rice husk ashes. EXAFS data indicate that copper in the oxidized Cu-ZSM-5 catalyst has about 2.5 nearest oxygen atoms surrounding with a Cu-O bond length of 1.95 Å. Reduction of the catalyst in hydrogen at 573 K leads to the formation of Cu-Cu bonds (2.53 Å). The coordination number (CN) of Cu-Cu species for copper in ZSM-5 is 5.7, approximately. Essentially, no Cu-O bonding was observed in the reduced Cu-ZSM-5 catalyst. About 45.3 % of copper species in the channels of ZSM-5 are oxidized to form the active site Cu<sup>+</sup> in the NO adsorption process. In NO reduction process, copper was partially oxidized to the active Cu<sup>+</sup> state in which the CN of Cu-O is 1.01.

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