

# Speciation of copper in ZSM-48 during NO reduction

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## Abstract

Speciation of copper in ZSM-48 and MCM-41 was studied by in situ extended X-ray absorption fine structural (EXAFS) and X-ray absorption near edge structural (XANES) spectroscopies to reveal the abrupt changes in yields of N<sub>2</sub>O, NO<sub>2</sub> and CO<sub>2</sub> from the catalytic reduction of NO with CO at 673 K. Component fitted XANES spectra showed that oxygen was inserted into the metallic copper (Cu(0)) in ZSM-48 and MCM-41 during NO reduction. In the confined channels of ZSM-48, about 91% of total copper was Cu(I) that involved in the catalytic reduction of NO with CO at 673 K. By in situ EXAFS, we found that during the NO reduction process, the oxygen-inserted copper possessed Cu–O, Cu–Cu, and Cu–(O)–Cu bond distances of 1.88, 2.61 and 2.95 Å, respectively, suggesting the possible existence of a linear type cluster with an averaged structure of Cu<sub>2</sub>O in ZSM-48. Furthermore, in the channels of ZSM-48, due to the restricted diffusion, NO reduction as well as CO oxidation might primarily occur at the head or end of the clusters. Note that NO could penetrate into ZSM-48 containing the clusters. On the contrary, in the parallel experiment, mainly CuO was observed in the mesopores (~32 Å) of MCM-41.

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## 1. Introduction

Reduction of NO<sub>x</sub> is of great importance and interest in air pollution control especially in the high temperature combustion processes. The major NO<sub>x</sub> emission sources are fuel combustion in automobile engines and coal fired power plants. Emissions of nitrous oxide (N<sub>2</sub>O) have also received much attention because of its global warming effects. Generally, NO is much abundant than other nitrogen oxides in the NO<sub>x</sub> pollutants.

CO is also found in ineffective combustion processes. Catalytic reduction of NO in the presence of CO has been widely studied in the emission control of automobile exhausts [1–3]. Generally, reduction of NO with CO can be catalyzed by precious metals (Rh, Pt, or Pd) dispersed on Al<sub>2</sub>O<sub>3</sub> or other supports [4–8]. However, due to the scarcity and high cost of these precious metals, copper/zeolite catalysts are of increasing importance in catalytic reduction of NO [9–15].

Since the discovery of the remarkable NO decomposition activities of Cu/ZSM-5 catalysts by Iwamoto et al. [16] in 1986, many efforts have been made to reveal the main reasons of the peculiarity on the Cu/ZSM-5 in comparison to other copper containing systems or transition metal ions exchanged ZSM-5 [16–18]. Zeolite ZSM-48 has an unidimensional channel structure based on the ferrierite sheet with linear

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non-interpenetrating 10-membered ring channels (ideal dimensions of 5.3–5.6 Å) [19]. Mainly due to the microporous channel structures, ZSM-48 exhibits unique catalytic and shape selective characteristics in the methanol to hydrocarbons and alkene isomerization processes [19–21]. MCM-41, first synthesized in 1992 [22,23], on the other hand, has a hexagonal arrangement of unidimensional mesopores with diameters of 20–100 Å. MCM-41 is thermally stable at 1300 K with very high surface areas of >900 m<sup>2</sup>/g [24]. MCM-41, in fact, bridges the gap between microporous zeolites and macroporous amorphous aluminosilicates in chemical and catalysis applications.

Copper/zeolite catalysts have been extensively studied by ESR, XPS, and IR spectroscopies [25–27]. However, speciation of copper in zeolites in the catalysis processes has not been well studied [28–31]. EXAFS and XANES spectroscopies are very useful in identification of elements with a different environment, degree of aggregation or location [32–34]. By EXAFS, we found that copper oxides involved in the catalytic decomposition of NO [28,29] and supercritical water oxidation of chlorophenols in ZSM-5 [30,31]. The molecular-scale data were very useful in revealing the nature of active species in the catalysis processes. Since ZSM-48 and MCM-41 possess an unidimensional pore structure with micro- and mesopore systems, respectively, it is of great interest to study the speciation of copper involved in catalytic NO reduction in those zeolite channels. Thus, the main objective of the present work was to study the chemical structure of copper during the catalytic reduction of NO in the channels of ZSM-48 and MCM-41 by in situ EXAFS and XANES spectroscopies. Specifically, we examined the speciation of active copper species and reveal the possible reaction pathway in the NO reaction process.

## 2. Experimental

Zeolite MCM-41 was prepared in a mixture containing sodium silicate (Fisher Scientific Co.), fumed silica (Sigma), cetyltrimethylammonium bromide (CTAB), (TCI-EP) and tetramethylammonium hydroxide (TMAOH; Lancaster). The mixture was stirred well at room temperature for 2 h. A diluted sulfuric acid solution was used to adjust the pH

value of the mixture at 11–12. The molar composition of the solution was 1 SiO<sub>2</sub>:0.27 TMAOH:0.58 CTAB:86 H<sub>2</sub>O. The mixture gel was heated at 423 K in a teflon-lined autoclave (100 ml) for 48 h. Zeolite ZSM-48 with a Si/Al ratio of about 300 was synthesized from a reaction mixture containing rice husk ash (>95% amorphous silica), 1,6-diamino-hexane (C<sub>6</sub>DN), NaBr, and water. The mixture was heated at 423 K for 48 h in a stainless-steel autoclave until crystals of ZSM-48 were formed. The as-synthesis solid materials (MCM-41 and ZSM-48) were filtered, washed with distilled water, dried at 373 K for 16 h, and calcined at 823 K for 8 h to decompose the templating materials.

Cu/MCM-41 and Cu/ZSM-48 (5 wt.% Cu) catalysts were prepared by impregnation of the Cu(NO<sub>3</sub>)<sub>2</sub> solution (Merck) onto MCM-41 and ZSM-48, respectively. About 1.0 g of the catalyst was reduced in a flowing 10% H<sub>2</sub>/He (30 ml/min) gas at 573 K for 1 h prior to the in situ EXAFS/XANES studies. Composition of the off gas from the catalytic reduction of NO (2% NO and 2% CO balanced by He) at 303–873 K was monitored by on-line FT-IR spectroscopy and gas chromatography (GC; with a column of molecular sieve 5 Å). 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 cm<sup>-1</sup>. Yields of N<sub>2</sub>, NO<sub>2</sub>, N<sub>2</sub>O and CO<sub>2</sub> were expressed as 2[N<sub>2</sub>]/[NO]<sub>i</sub>, [NO<sub>2</sub>]/[NO]<sub>i</sub>, [N<sub>2</sub>O]/[NO]<sub>i</sub>, [CO<sub>2</sub>]/[CO]<sub>i</sub>, respectively (where [NO]<sub>i</sub> and [CO]<sub>i</sub> denote concentrations of NO and CO in reactants and [N<sub>2</sub>], [NO<sub>2</sub>], [N<sub>2</sub>O] and [CO<sub>2</sub>] denote concentrations of N<sub>2</sub>, NO<sub>2</sub>, N<sub>2</sub>O and CO<sub>2</sub> in gas products), in the catalytic reduction of NO with CO.

Structure of the catalysts was characterized by X-ray powder diffraction (XRD) spectroscopy (RIGAKU Model D/MAX III-V). In order to study the speciation of copper in zeolites under reaction conditions, a home-made in situ EXAFS cell (see Fig. 1) was used in the transmission mode for X-ray absorption spectroscopic measurements. XANES and EXAFS spectra of the catalysts were recorded on the Wiggler beamline of the Taiwan Synchrotron Radiation Research Center (SRRC). The electron storage ring was operated at energy of 1.5 GeV and current of 120–200 mA. A Si(1 1 1) double-crystal monochromator was used for selection of energy with an energy

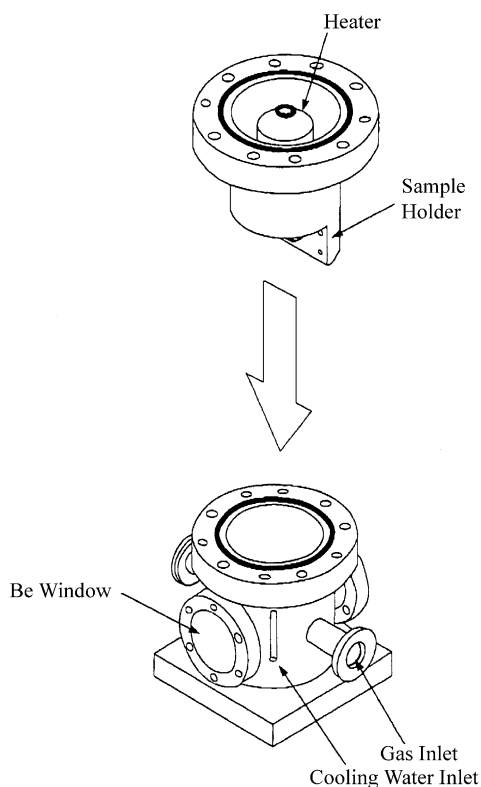


Fig. 1. A schematic diagram of the in situ EXAFS cell.

resolution of  $1.9 \times 10^{-4}$  (eV/eV). Photon energy was calibrated by characteristic pre-edge peaks in the absorption spectrum of Cu foil (8979 eV).

The EXAFS data were analyzed using the UWXAFS 3.0 and FEFF 8.0 programs [35]. The raw absorption data in the region of 50–200 eV were fitted to a straight line using the least-square algorithms. The fitted pre-edge background was extrapolated throughout the whole data range and subtracted and normalized to reduce effects of the sample thickness. The Fourier transform was performed on  $k^3$ -weighted EXAFS oscillations in the range of 2.8–14  $\text{\AA}^{-1}$ . Multiple shell fitting of the EXAFS data was conducted in the R-space.

XANES spectra of model compounds such as CuO, Cu<sub>2</sub>O, and Cu foil were also measured on the Wiggler beamline. The principal component (factor) analysis (PCA) method was used in the data treatment to optimize the quantitative extraction of relative concentrations. Semi-quantitative analyses of the edge

spectra were conducted by the least-square fitting of linear combinations of model compound spectra to the spectrum of each sample. The height and area of the near-edge band in a copper spectrum were quantitatively proportional to the amount of copper species. We fitted the near-edge 3d–4p mixing peaks from the experimental absorption edge. A calibration curve could, therefore, be obtained. On the average, an uncertainty limit of 5% corresponds to an error of ca. 2.0% in the fit results.

### 3. Results and discussion

Fig. 2 shows the temperature dependence for the yields of N<sub>2</sub>, NO<sub>2</sub>, CO<sub>2</sub> and N<sub>2</sub>O in the catalytic reduction of NO with CO at 473–873 K. Generally, NO is dissociatively adsorbed on copper ( $\text{NO}_{(\text{g})} \rightleftharpoons \text{NO}_{(\text{ad})} \rightleftharpoons \text{N}_{(\text{ad})} + \text{O}_{(\text{ad})}$ ) [28]. N<sub>2</sub>O is formed via a reaction between NO and nitrogen ( $\text{N}_{(\text{ad})}$ ) ( $\text{NO}_{(\text{ad})} + \text{N}_{(\text{ad})} \rightleftharpoons \text{N}_2\text{O}_{(\text{g})}$ ). Note that the yield of N<sub>2</sub>O was abruptly decreased at 673 K. NO<sub>(ad)</sub> can also be oxidized with oxygen ( $\text{O}_{(\text{ad})}$ ) to yield NO<sub>2</sub>. N<sub>2</sub> was formed via a recombination of adsorbed nitrogen ( $2\text{N}_{(\text{ad})} \rightleftharpoons \text{N}_{2(\text{g})}$ ). The molar fraction for N<sub>2</sub> on Cu/ZSM-48 was about 0.13 which was greater than that on Cu/MCM-41 (0.05) in the NO reduction process at 673 K. The yield of N<sub>2</sub> highly depended on the availability of the adsorbed nitrogen atoms that were also consumed in the formation of N<sub>2</sub>O. However, thermodynamically, N<sub>2</sub>O is not stable at high temperatures.

CO played an important role in the NO reduction process. At 673 K, in MCM-41, the yield of CO<sub>2</sub> was increased with a decrease in the formation of NO<sub>2</sub> (a competitive reaction) as the reaction temperature increasing. On the contrary, in the confined channels of ZSM-48, the yield of NO<sub>2</sub> was increased at 573–773 K while the yield of CO<sub>2</sub> was decreased at 673 K and then increased at higher temperatures. NO and CO molecules with kinetic diameters of 3.2 and 3.8  $\text{\AA}$ , respectively, can diffuse freely in the channels of ZSM-48 (ideal dimensions of 5.3–5.6  $\text{\AA}$ ) and MCM-41 (about 32  $\text{\AA}$ ). However, the minimum cross section of copper oxide in the channels of ZSM-48 is about 1.9  $\text{\AA}$ . Thus, the most possible interactions of CO or NO molecules with active centers might occur on both sides of copper oxide formed

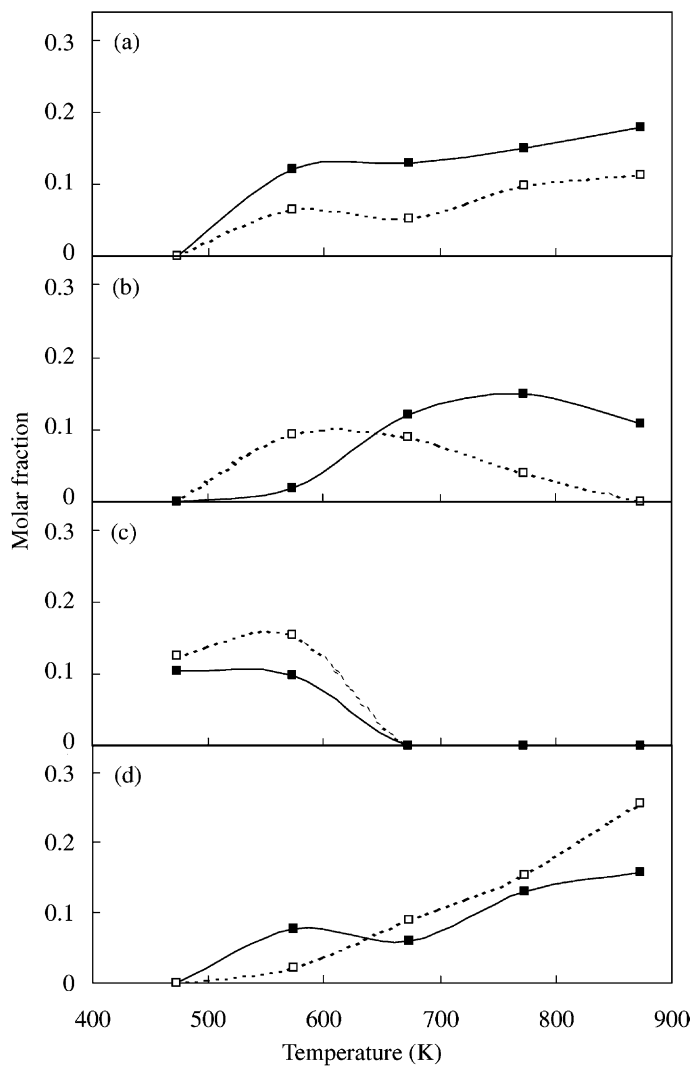
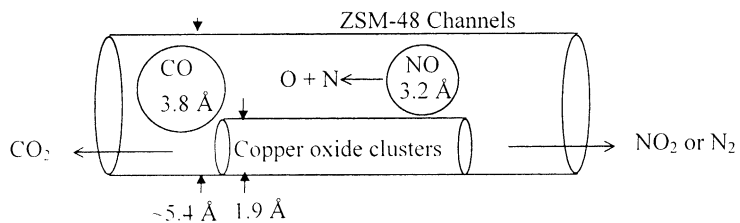


Fig. 2. Temperature dependence for molar fraction of product gases (a) N<sub>2</sub>, (b) NO<sub>2</sub>, (c) N<sub>2</sub>O, and (d) CO<sub>2</sub> in the catalytic reduction of NO with CO on Cu/ZSM-48 (solid line) and Cu/MCM-41 (dashed line).



Scheme 1.

in the channels of ZSM-48 (shown in Scheme 1). Note that NO molecules could penetrate into channels containing copper oxide. On the contrary, in the mesopores of MCM-41, NO and CO molecules can diffuse freely.

The abrupt changes for yields of NO<sub>2</sub>, N<sub>2</sub>O and CO<sub>2</sub> at 673 K during NO reduction in the meso- and micropore zeolites were very unique and of great interest in revealing the speciation of the active copper species involved in the catalysis process. Fig. 3 show the experimental and fitted EXAFS data of copper in MCM-41 and ZSM-48. The bond distances of Cu–O,

Cu–Cu and Cu–(O)–Cu in ZSM-48 were 1.88, 2.61 and 2.95 Å, respectively (if compared with model compounds (Cu, Cu<sub>2</sub>O and CuO); Table 1), suggesting an insertion of oxygen atoms into the metallic copper matrix during NO reduction.

The in situ XANES spectrum (see Fig. 4(a)) determined during the catalytic reduction of NO with CO on Cu/ZSM-48 at 673 K shows that the pre-edge feature at 8981–8984 eV may be attributed to the dipole-allowed 1s–4p transition of Cu(I) that was formed via the oxidation of metallic copper (Cu(0)) with NO. The component fits of XANES spectra suggested the Cu(0)

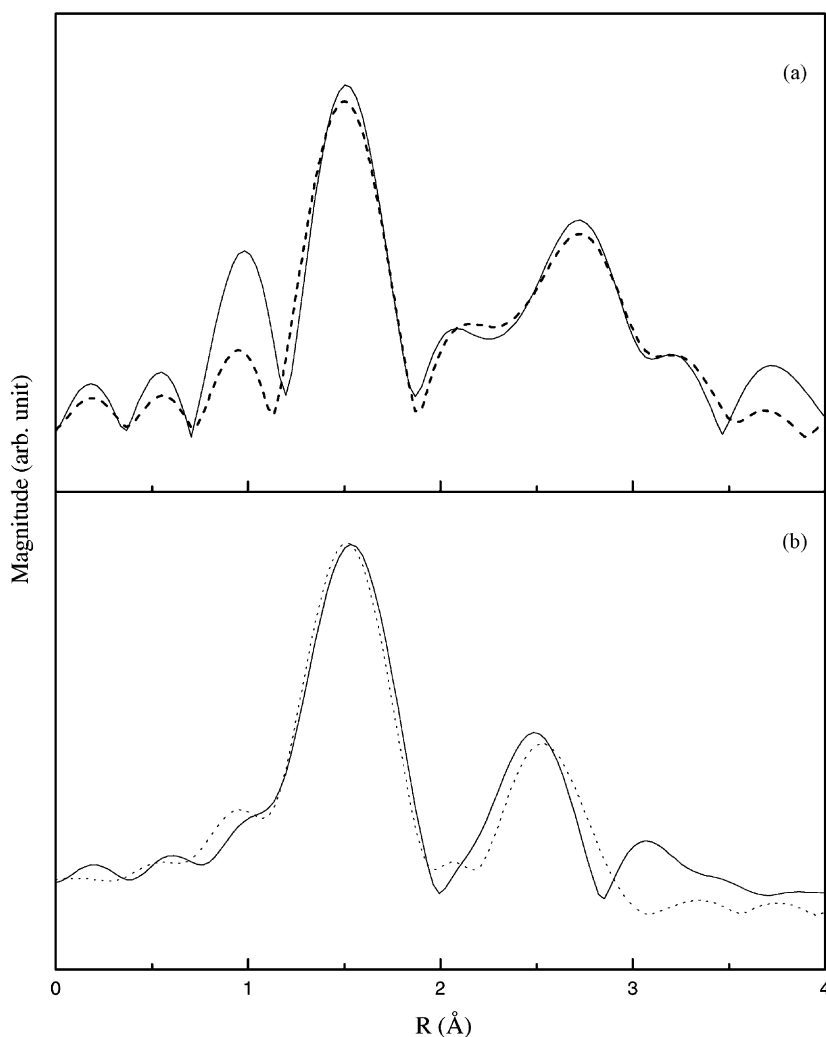


Fig. 3. The Fourier transformed Cu K edge EXAFS of (a) Cu/ZSM-48 and (b) Cu/MCM-41 during NO reduction with CO at 673 K. The dotted curves denote the best fitting of the EXAFS spectra.

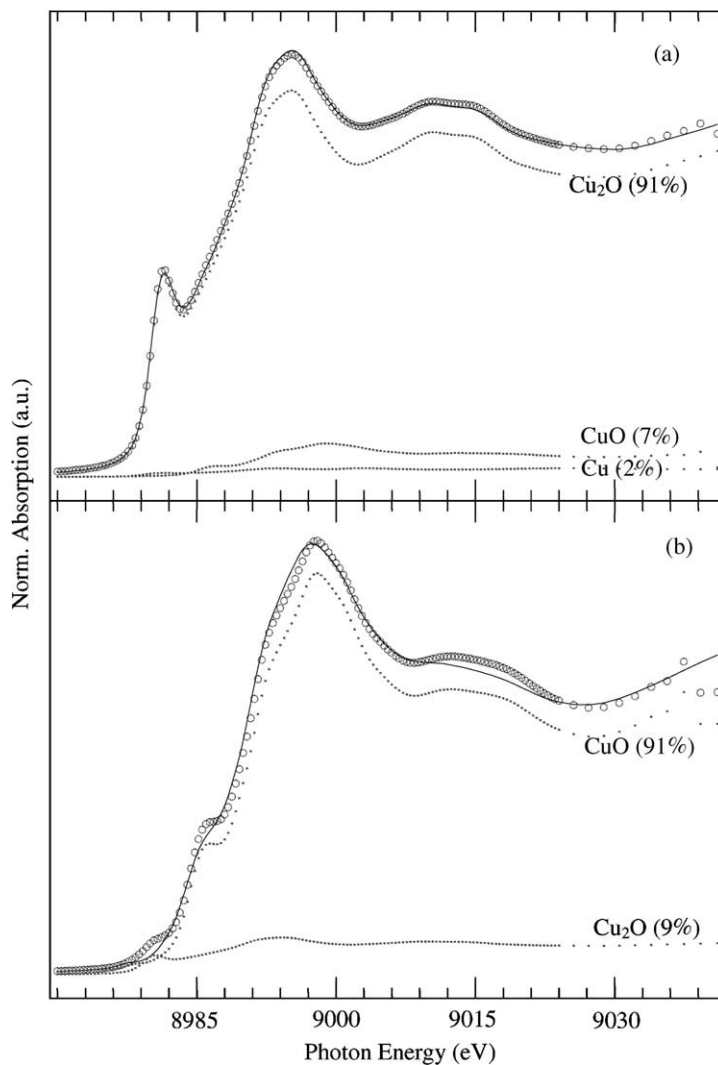


Fig. 4. In situ XANES spectra (and component fits) of (a) Cu/ZSM-48 and (b) Cu/MCM-41 during catalytic reduction of NO with CO at 673 K. The dotted line denotes the best fits of the XANES spectra.

was oxidized to Cu(I) (91%) and Cu(II) (7%) during the NO reduction process. Combined EXAFS and XANES results suggest that an averaged structure of Cu<sub>2</sub>O might be formed in the confined channels of ZSM-48 (see Scheme 1).

Interestingly, in Fig. 4(b), the in situ XANES spectrum shows that the main copper species involved in the catalytic reduction of NO with CO in the channels of MCM-41 at 673 K is Cu(II). Dissociative adsorption of NO on Cu/MCM-41 may cause an oxidation

of the metallic copper (Cu(0)) to mainly Cu(II) (91%) and a small amount of Cu(I) (about 9%). The EXAFS data of copper indicated that about 3.4 oxygen atoms were coordinated to copper atoms. By contrast, in the microporous zeolite ZSM-48, due to a confined channel structure, the CN of Cu–O was about 1.3.

Generally, Cu(I) possesses a higher activity than Cu(II) in catalytic reduction of NO [28,29,36]. We found that the relatively lower catalytic activity of NO reduction with CO (at 673 K) might be due to the less

Table 1

Speciation (studied by in situ EXAFS) of copper in unidimensional channel zeolites (ZSM-48 and MCM-41) during catalytic reduction of NO with CO at 673 K

Catalyst	Shell	Bond distance (Å)	Coordination number	$\sigma^2$ (Å <sup>2</sup> )
Cu foil	Cu–Cu	2.53	11.4	0.008
Cu <sub>2</sub> O	Cu–O	1.79	2.5	0.003
	Cu–(O)–Cu	3.00	12.2	0.020
CuO	Cu–O	1.95	6.0	0.004
	Cu–(O)–Cu	2.82	1.4	0.004
Cu/ZSM-48	Cu–O	1.88	1.3	0.003
	Cu–Cu	2.61	0.7	0.009
	Cu–(O)–Cu	2.95	4.3	0.022
Cu/MCM-41	Cu–O	1.94	3.4	0.002
	Cu–(O)–Cu	2.85	3.2	0.012

$\sigma$ : Debye–Waller factor.

active sites (Cu(I)) in MCM-41. Note that the abstraction of oxygen from copper oxides by CO to form CO<sub>2</sub> also caused a reduction of Cu(II) to active species Cu(I) during NO reduction process. CO molecules with a size of 3.8 Å might have a high collision frequency with copper oxides in the confined channels of ZSM-48. Cu/ZSM-48, therefore, possessed a higher N<sub>2</sub> yield from NO reduction than Cu/MCM-41.

#### 4. Conclusions

The in situ XANES spectrum suggested that metallic copper (Cu(0)) in ZSM-48 was oxidized to mainly Cu(I) (91%) during the catalytic reduction of NO with CO at 673 K. On the contrary, mainly Cu(II) (91%) and a small amount of Cu(I) (about 9%) were found in MCM-41. Since Cu/ZSM-48 possessed more active species (Cu(I)), yield of N<sub>2</sub> on Cu/ZSM-48 was greater than that on MCM-41 by at least 8% in the catalytic NO reduction process. By in situ EXAFS, we found that during the NO reduction process, with the insertion of oxygen into the matrix of Cu(0), Cu–O, Cu–Cu, and Cu–(O)–Cu in ZSM-48 possessing bond distances of 1.88, 2.61 and 2.95 Å, respectively, suggesting the possible existence of a linear-type copper oxide cluster (an averaged structure of Cu<sub>2</sub>O) in ZSM-48. Due to the confined channel structure of ZSM-48, NO reduction as well as CO oxidation might

primarily occur at the head or end of the clusters. On the contrary, in the mesopores (~40 Å) of MCM-41, mainly CuO was observed during in the NO reduction process, that might account for the less NO reduction activity on copper/MCM-41.

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