

Reduction of NO with CH₄ Effected by Copper Oxide Clusters in the Channels of ZSM-5

Y.-J. Huang and H. Paul Wang*

Department of Environmental Engineering, National Cheng Kung University, Tainan, Taiwan

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Fine structures of the copper oxide clusters involved in catalytic reduction of NO were studied by X-ray absorption spectroscopy. The Extended X-ray absorption fine structural (EXAFS) spectra indicate that about 2.89 nearest oxygen atoms bond to the Cu central atoms with a Cu–O bond distance of 1.96 Å for the oxidized Cu–ZSM-5 catalyst. Reduction of the catalyst in hydrogen at 573 K led to the formation of mainly Cu–Cu (2.54 Å) species with the coordination number (CN) of 2.91. The Cu₄O₂ clusters in the channels of ZSM-5 observed by EXAFS were formed in the NO reduction process via incorporation of oxygen into the metallic copper matrix with desorption of N₂. Due to the restricted channel structure of ZSM-5, the Cu₄O₂ clusters were reduced promptly by CH₄.

Introduction

Nitrogen oxides (NO_x) are the main air pollutants that cause photochemical smog formation, acid rain, and general atmospheric visibility degradation. Worldwide, over 3×10^7 tons of nitrogen oxides are vented to the atmosphere each year.¹ Reduction of NO_x emission has become one of the major problems to be solved for environmental protection. Many methods for reduction of NO_x emissions such as reduction absorption, chelation absorption, catalytic decomposition, and catalytic reduction have been widely studied.^{2–7} Selective catalytic reduction with ammonia (NH₃–SCR) has been put to practical uses; however, the system is expensive in terms of handling the toxic ammonia. It has been recognized that the selective catalytic reduction of NO with hydrocarbons (HC–SCR) using copper-exchanged ZSM-5 (Cu–ZSM-5) catalysts is very effective.^{6,7}

The active species of the Cu–ZSM-5 catalysts involved in the NO reduction have been studied spectroscopically.^{8–10} It is generally recognized that the selective reduction of NO on Cu–ZSM-5 occurs via a copper cation–dinitrogen intermediate. The Cu-dimer species (Cu–O–Cu)²⁺ also plays an important role in the reduction of NO with hydrocarbons.¹¹ However, the reaction mechanism of the catalytic NO reduction process is still not well-understood.¹²

X-ray absorption spectroscopy (extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES)) are very useful in identification of the environment, degree of aggregation, or location of specific elements.^{13–15} Thus, the main objective of the present work was to study the fine structure of the active copper species in the channels of ZSM-5 in the NO reduction process by X-ray absorption spectroscopy.

Experimental Section

Zeolite ZSM-5 was prepared from a mixture of rice husk ash (approximately comprised of over 95% amorphous silica), tetrapropylammonium bromide ((TPA)Br), NaOH, and water (detailed procedures were described in ref 16). The as-synthesized ZSM-5 was dried and calcined at 873 K for 24 h. Crystallinity of the zeolite ZSM-5 was 99+ % if compared with

the Mobil ZSM-5. A 0.02 M Cu(NO₃)₂ solution was used in preparing copper-exchanged ZSM-5. The Cu–ZSM-5 catalyst has a molar ratio of Cu/Al = 0.31, Si/Al = 5.52, and Ca/Al = 0.087 (determined by SEM/EDX (JSM-35)).

The Cu–ZSM-5 catalyst was reduced in flowing 10% H₂/He at 573 K for 1 h. About 0.9–1.2 g of the Cu–ZSM-5 catalyst were used in catalytic reduction of NO with CH₄ (4% NO and 4% methane balanced by helium) in a fixed-bed reactor at 473–873 K. Off gas was monitored by on-line FTIR spectroscopy. Infrared spectra were recorded on a Digilab FTIR 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⁻¹.

X-ray absorption spectra (XANES and EXAFS) were recorded at the Wiggler beam line SL-3B 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 ($\Delta E/E$) of $\pm 1.9 \times 10^{-4}$ (eV/eV). Adsorption and reduction of NO with CH₄ on reduced Cu–ZSM-5 catalyst was conducted in a grease-free vacuum system (10^{-5} – 10^{-6} Torr). Samples were sealed in the EXAFS cell in a nitrogen-purged glovebag and measured in the fluorescence mode. Photon energy was calibrated by characteristic preedge peaks in the absorption spectrum of a Cu foil (8979 eV).

The EXAFS data were analyzed using the UWXAFS 3.0 program.¹⁷ The raw absorption data in the region of 50–200 eV below the edge position were fit to a straight line using the least-squares algorithms. The fitted preedge 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 Å⁻¹. Multiple shell fitting of the EXAFS data was conducted in R-space.

Results and Discussion

Zeolite ZSM-5 is a microporous crystalline solid. NO and CH₄ molecules with kinetic diameters of 3.2 and 3.8 Å, respectively, can diffuse freely in the channels of ZSM-5. Reduction of NO with CH₄ on the reduced Cu–ZSM-5 catalyst

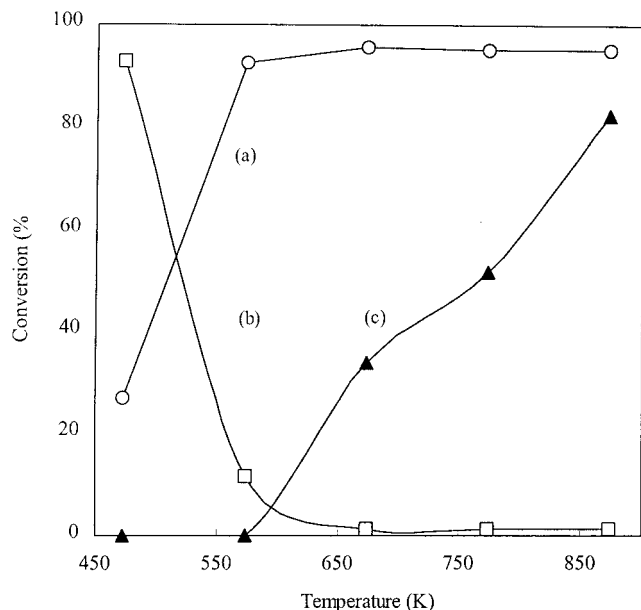


Figure 1. Reduction of (a) NO with (b) CH₄ and formation of (c) CO₂ on the reduced Cu-ZSM-5 at a GHSV of 1000 h⁻¹.

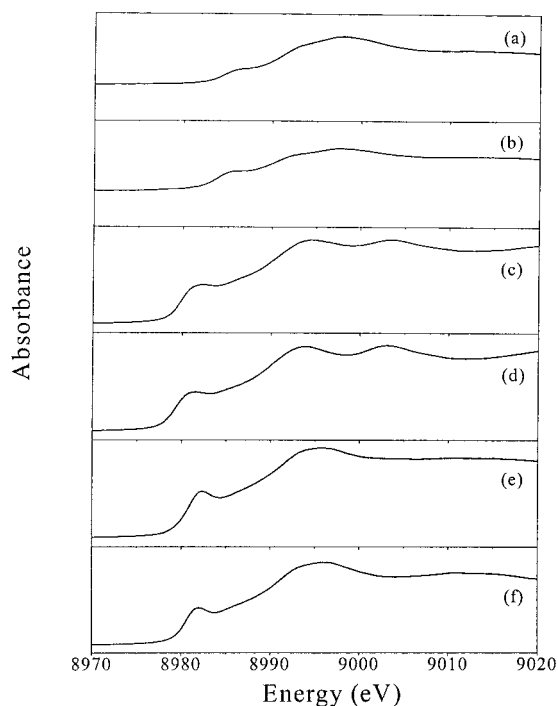


Figure 2. XANES spectra of (a) oxidized Cu-ZSM-5, (b) CuO powder, (c) reduced Cu-ZSM-5, (d) Cu foil, (e) NO adsorbed on the Cu-ZSM-5 at 573 K, and (f) Cu₂O powder.

was investigated in a fixed-bed reactor at 473–873 K with a gas hourly space velocity (GHSV) of ~1000 h⁻¹. Figure 1 shows that over 90% of NO molecules were catalytically reduced at 573–873 K. In the NO reduction process, CH₄ was oxidized to form CO₂ and H₂O. In the very restricted environment of the ZSM-5 channels, CH₄ molecules may spend less time in free flight and more time in collision with, for instance, the active oxygen on the copper catalyst and are eventually oxidized.

Representative XANES spectra showing the comparison of the Cu-ZSM-5 catalysts, Cu foil, Cu₂O, and CuO are shown in Figure 2. The pre-edge XANES spectra of the oxidized Cu-ZSM-5 catalyst exhibit a very weak 1s → 3d transition (8975–

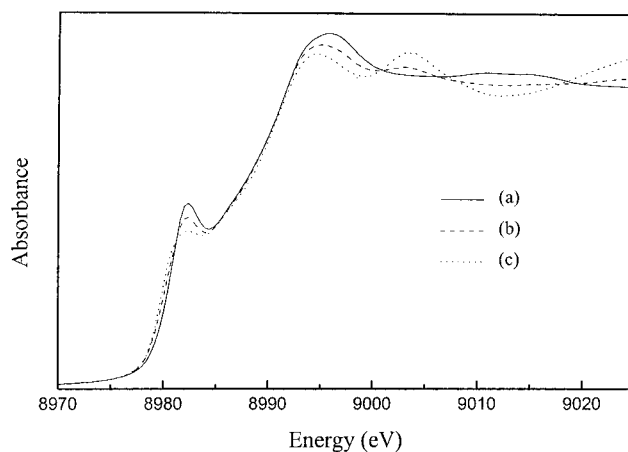


Figure 3. XANES spectra of Cu-ZSM-5 in the catalytic reduction of NO with CH₄ at (a) 573, (b) 673, and (c) 773 K.

8980 eV) which is forbidden by the selection rule in the case of perfect octahedral symmetry. A shoulder at 8984–8988 eV and an intense band at 8995–9002 eV are attributed to the 1s → 4p transition that indicates the existence of the Cu(II) species. The XANES spectrum of the reduced Cu-ZSM-5 catalyst is very similar to that of the Cu foil. The metallic copper has a very low activity in NO reduction, generally.¹⁸ The bands at 8981–8984 eV are due to the dipole-allowed 1s → 4p transition of Cu(I). The Cu(I) sites are very active in reduction of NO.^{19,20} In Figure 2, the pre-edge band of Cu(I) appears as NO and CH₄ were adsorbed on the reduced Cu-ZSM-5 catalyst at 573 K.

The EXAFS spectra of the Cu-ZSM-5 catalysts were recorded and analyzed in the *k* range of 2.5–11 Å⁻¹. Figure 3 shows the XANES spectra of the Cu-ZSM-5 catalyst that was used in the reduction of NO with CH₄ at 573–773 K. By comparison of the relative absorbance of the absorption edge at 8981–8984 eV and 8992–9001 eV, it is apparent that the amount of Cu(I) species decreases as NO was reduced at higher temperatures. Consistently, the absorbance of the metallic Cu species at 9001–9008 eV also increases with temperature. NO molecules were dissociated into nitrogen and oxygen molecules in the reduction process. However, part of the oxygen atoms may interact with copper species in the channels of ZSM-5. The presence of the Cu-O-Cu species in the channels of ZSM-5 in the catalytic reduction of NO is confirmed by EXAFS.

It seems that Cu(I) plays a major role in catalytic reduction of NO in the channels of ZSM-5. However, it is of great importance to reveal the active species involved in the very restricted channel system of ZSM-5. The straight channels of ZSM-5 have an elliptical cross-section of 5.7–5.8 Å by 5.1–5.2 Å that are interconnected by zigzag channels with a nearly circular cross-section and diameter of 5.5 Å, and the channel length is 4.5–6.6 Å.^{21,22} The EXAFS data indicate that about 2.89 oxygen atoms lie near central copper atoms (see Table 1 and Figure 4). Interactions of the copper species with the ≡Si-O-Al≡ sites of ZSM-5 are insignificant. In addition, the coordination number of Cu-(O)-Cu is about 1.80 in the second shell. Due to the confined environment in the channels of ZSM-5, it is possible that Cu-O atoms may be formed as clusters in the channels of ZSM-5. The postulated structure of the copper oxide clusters involved in the NO reduction in the channels of ZSM-5 is Cu₄O₂.

The reduced catalyst has a Cu-Cu bonding distance of 2.54 Å. Interaction of NO with the reduced copper generated a Cu₄O₂ cluster with desorption of N₂ molecules in the channels of ZSM-

TABLE 1: Fine Structural Parameters of the Cu–ZSM-5 Catalysts and Cu Foil, CuO, and Cu₂O

catalyst	shell	bond distance (Å)	coord. no.	σ^2 (Å ²) ^d
oxidized Cu–ZSM-5	Cu–O	1.96	2.89	0.0031
	Cu–(O)–Cu	2.94	1.80	0.0077
reduced Cu–ZSM-5	Cu–Cu	2.54	2.91	0.0031
	Cu–O	1.88	1.19	0.0015
Cu–ZSM-5 ^a	Cu–Cu	2.59	2.46	0.0085
	Cu–O	1.88	0.96	0.0001
Cu–ZSM-5 ^b	Cu–Cu	2.56	2.85	0.0054
	Cu–O	1.88	0.91	0.0007
Cu–ZSM-5 ^c	Cu–Cu	2.56	2.88	0.0059
	Cu–O	1.95	2.14	0.0035
CuO	Cu–Cu	2.91	1.07	0.0044
	Cu–Cu	2.55	10.25	0.0086
Cu foil	Cu–O	1.86	2.05	0.0065
	Cu–Cu	3.04	12.99	0.0277

^a Reduction of NO with CH₄ on Cu–ZSM-5 at 573 K. ^b Reduction of NO with CH₄ on Cu–ZSM-5 at 673 K. ^c Reduction of NO with CH₄ on Cu–ZSM-5 at 773 K. ^d Debye-Waller factor.

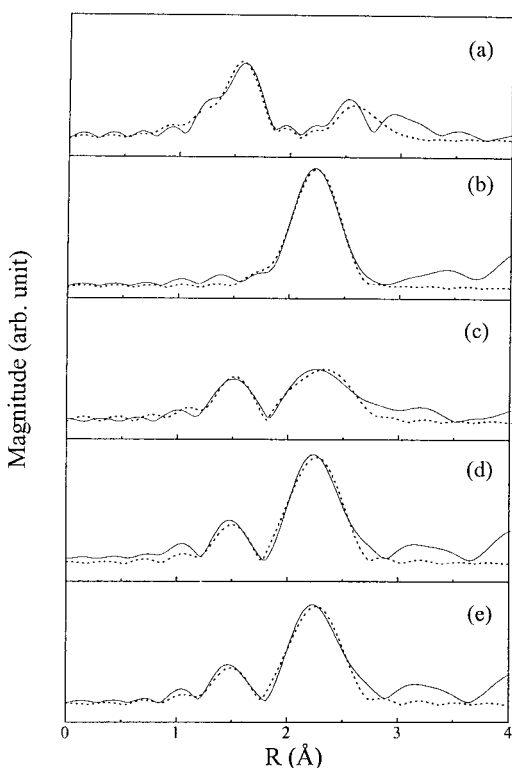
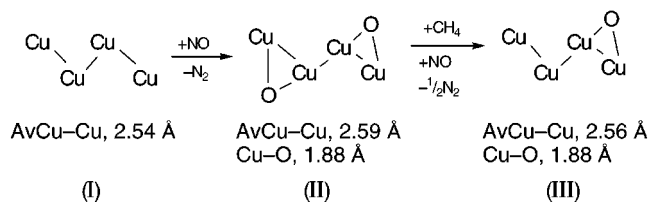


Figure 4. Fourier transformed Cu K edge EXAFS of (a) oxidized, (b) reduced, and reacted Cu–ZSM-5 catalysts in reduction of NO with CH₄ at (c) 573, (d) 673, and (e) 773 K. The dotted curves denote the best fitting of the EXAFS spectra.

5. The Cu₄O₂ cluster was reduced to Cu₄O by oxidation of CH₄. Since the kinetic diameter of NO (3.2 Å) or CH₄ (3.8 Å) is less than the effective channel openings of ZSM-5, NO and CH₄ molecules can diffuse freely in its channels. In a separate experiment, we found that the channels of ZSM-5 were very flexible in accepting large molecules diffused into the channels.²³ Insertion of oxygen into the reduced Cu cluster (Cu–Cu bond distance, 2.54 Å) in the channels in the NO reduction process may cause the Cu–Cu bond distance of the cluster (Cu₄O₂) to be slightly increased by 0.05 Å. In reduction of the Cu₄O₂ cluster by CH₄ (see Figure 1), the Cu–Cu bond distance is decreased by 0.03 Å with the CN of Cu–O decreasing slightly. The reduction–oxidation process of the copper oxide cluster is described as follows. It is possible, although there is little direct

evidence at present, that these clusters may migrate in the channels of ZSM-5 in the NO reduction process.



Conclusions

Over 90% of NO can be reduced to N₂ catalyzed by Cu–ZSM-5 catalyst at 573 K. EXAFS data indicate that the oxidized Cu–ZSM-5 has a Cu–O bonding of 1.96 Å with the coordination number (CN) of 2.89. Reduction of the catalyst in hydrogen at 573 K led to the formation of mainly Cu–Cu (2.54 Å) species with the CN of 2.91. Adsorption of NO on the reduced Cu–ZSM-5 catalyst causes an increase in CN of Cu with oxygen with the Cu–O bond distance of 1.88 Å. Due to the confined environment in the channels of ZSM-5, interaction of NO with the reduced copper generated a Cu₄O₂ cluster which was reduced to Cu₄O by CH₄.

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