INTERACTIONS OF COPPER AND ZINC IN MCM-41

HSIN-LIANG HUANG* † and H. PAUL WANG* † §
* Department of Environmental Engineering
† Sustainable Environment Research Center
National Cheng Kung University
Tainan City, 701, Taiwan
‡ hlhuang@mail.ncku.edu.tw
§ wanghp@mail.ncku.edu.tw

H. C. WANG
Division of Chest Medicine, Department of Medicine
Veterans General Hospital-Kaoshiung, Kaoshiung, Taiwan
hcwang@isca.vghks.gov.tw

YU-LING WEI
Department of Environmental Science and Engineering
Tunghai University, Taichung City, 407, Taiwan
yulin@mail.thu.edu.tw

Speciation of copper and zinc (1:1) in MCM-41 has been studied by X-ray absorption near edge structural (XANES) and X-ray absorption fine structural (EXAFS) spectroscopies in the present work. The least-square fitted XANES spectra show that Cu(II) and Zn(II) are the major copper and zinc species, respectively in the channels of MCM-41 during calcination at 573–1173 K. The EXAFS data indicate that copper in MCM-41 possesses a Cu–O bond distance of 1.97 Å with a coordination number (CN) of 3.4. During calcination at 573–1173 K, about 3.8–4.2 nearest oxygen atoms are bonded to the central copper atoms with Cu–O bond distances of 1.95–1.96 Å in MCM-41. A small amount of Cu–Zn alloy may be formed during calcination. Existence of Zn–(O)–Si (3.05–3.11 Å) with CNs of 1.7–2.3 is also observed by EXAFS, suggesting an interaction between zinc and the framework SiO\(_2\) of MCM-41 during calcination.

Keywords: XANES; EXAFS; MCM-41; nanowires; Cu–Zn alloys.

1. Introduction

Mesopore molecular sieves (such as MCM-41) have a hexagonal structure with an array of tubular channels of a uniform diameter (15–200 Å).\(^1\)\(^,\)\(^2\) MCM-41 has a high thermal stability (up to 1300 K). Surface areas of MCM-41 are generally 500–1500 m\(^2\)/g.\(^3\) Therefore, MCM-41 is desirable as catalysts, catalyst supports and potential adsorbents for large molecules. In the separated experimental work, by extended X-ray absorption fine structural (EXAFS) spectroscopy, we found that...
copper oxide clusters (in ZSM-5, ZSM-48 or MCM-41) are involved in the catalytic decomposition of NO and oxidation of chlorophenols in supercritical water.\textsuperscript{4–6} The EXAFS and XANES (X-ray absorption near edge structural) spectroscopies are very useful in determination of elements with a different environment and degree of aggregation or location. Synthesis of nanowires in the 4 nm channels of molecular sieve is of increasing importance and interest, for instance, in the applications of nanosize heating elements. Thus, the main objective of the present work was to study speciation of copper and zinc calcined at elevated temperatures to yield nanowires in the channels of MCM-41 by EXAFS and XANES spectroscopies.

2. Experimental

In the MCM-41 synthesis procedure, sodium silicate (27\% SiO$_2$ and 14\% NaOH (Aldrich)) was stirred with C$_{16}$TMAB (cetyltrimethylammonium bromide (99\%) (Merck)) at 303 K for 10–20 min until the gel solution was formed. A total of 1.20 M of H$_2$SO$_4$ was used to adjust the pH value of the gel solution at 9.0. The molar ratio of main compounds in the mixture was C$_{16}$TMAB:SiO$_2$:Na$_2$O:H$_2$SO$_4$:H$_2$O = 1:1:0.39:0.29:(50–400). The gel mixture was heated at 373 K for 48 h in an autoclave. After filtration, the as-synthesized MCM-41 was washed with deionized water and calcined in air at 853 K for 6 h to decompose the templating organics. The CuO–ZnO/MCM-41 was prepared by impregnation of an aqueous solution of 0.6 M Cu(NO$_3$)$_2$ (99\%, Hanawa Guaranted Reagent) and 0.6 M of Zn(NO$_3$)$_2$ (99\%, Hanawa Guaranted Reagent) onto the MCM-41. CuO–ZnO/MCM-41 was calcined at 573, 923, and 1173 K for 2 h.

The structure of CuO–ZnO/MCM-41 was determined by X-ray powder diffraction (XRD) (D8 advance, Bruker) with a CuK$_\alpha$ (1.542 Å) radiation. Samples were scanned from 10 to 50° (2θ) with a scan rate 5°/min. The Cu K-edge XANES and EXAFS spectra of CuO–ZnO/MCM-41 and model compounds were collected on the Wiggler beamline at the Taiwan National Synchrotron Radiation Research Center (NSRRC). Nanosize CuO (99.3\%, Kanto Chemical Co. Inc.), CuO (99\%, Merck), Cu(II)$_{\text{ads}}$ (prepared by impregnation of 0.6 M of Cu(NO$_3$)$_2$ (99\%, Hanawa Guaranted Reagent) onto MCM-41), nanosize ZnO (99.5\%, Kanto Chemical Co. Inc.), ZnO (99\%, Fluka), and Zn(II)$_{\text{ads}}$ (prepared by impregnation of 0.6 M of Zn(NO$_3$)$_2$ (99\%, Hanawa Guaranted Reagent) onto MCM-41) were measured as the model compounds for the least-square fitting of linear combinations of standard spectra to the spectra of the samples. The electron storage ring was operated at energy of 1.5 GeV with ring current = 120–200 mA. A Si(111) double-crystal monochromator was used for selection of energy with an energy resolution of $(\Delta E/E)1.9 \times 10^{-4}$ (eV/eV). The absorption spectra were collected by means of ion chambers filled with helium gas. Beam energy was calibrated by the adsorption edge of copper and zinc foils at energy of 8979 and 9659 eV, respectively. The standard deviation calculated from the averaged spectra was used to estimate the statistical noise and error associated with each structural parameter.
The EXAFS data of samples were analyzed with the UWXAFS 3.0 and FEFF 8.0 programs. The background of all the data was justified by the AUTOBK program. To reduce the number of fitted variables, the many-body factor ($S_0^2$) were fixed at 0.9. It is generally accepted that the empirical fits of model compounds have an error of ±0.01 Å in radius and of ±10% in coordinations (CNs) for the first shell atoms, and of ±0.02 Å and ±25% for the second shell atoms. In all EXAFS data analyses, the Debye–Waller factors ($\sigma^2$) were less than 0.01.

3. Results and Discussion

The XRD patterns of the CuO–ZnO/MCM-41 are shown in Fig. 1. As the CuO–ZnO/MCM-41 was calcined at 573–923 K, mainly CuO is found in the channels of MCM-41. Further calcination at 1173 K, CuO and Zn$_2$SiO$_4$ are observed as the framework of MCM-41 was collapsed and crystalline SiO$_2$ was formed.

XANES and EXAFS spectra of copper and zinc in the CuO–ZnO/MCM-41 were also determined. In the pre-edge XANES spectra (Fig. 2), the existence of the Cu(II) species is evident because of the 1s-to-4p$_z$ and 1s-to-4p$_{x,y}$ transitions at 8985–8988 eV and 8994–9002 eV, respectively. The component fitted XANES spectra show that Cu(II)$_{(ads)}$ (83%) and nanosize CuO (17%) are the main copper species in the channels of MCM-41 (see Fig. 2(a)). At 573 K, formation of nanosize CuO is significantly increased by 46%. At 1173 K, the framework of MCM-41 is collapsed and forms crystalline SiO$_2$ that enclose the nanosize CuO.

In Fig. 3, a shoulder at 9668 eV can be attributed to the 1s-to-3d transition indicating the existence of Zn(II). In the channels of MCM-41, the major zinc species are Zn(II)$_{(ads)}$ (88%) and nanosize ZnO (12%) (see Fig. 3(a)). At $T > 573$ K, interactions between ZnO and amorphous SiO$_2$ (wall of MCM-41) are found and lead

![Figure 1](image_url)

Fig. 1. XRD patterns of (a) dried (at 333 K for 16 h) and calcined CuO–ZnO/MCM-41 at (b) 573, (c) 923, and (d) 1173 K for 2 h (1, SiO$_2$; 2, Zn$_2$SiO$_4$; 3, CuO).
Fig. 2. Experimental data (solid line) and the least-squares fits (circles) of XANES spectra of copper in (a) dried and calcined CuO–ZnO/MCM-41 at (b) 573, (c) 923, and (d) 1173 K.

to formation of Zn$_2$SiO$_4$ from EXAFS (Fig. 4). The $k^3$-weighted EXAFS spectra of copper and zinc in MCM-41 during calcination were Fourier transformed to yield the structural parameters for the copper and zinc species, as shown in Table 1. In all EXAFS data analyzed the errors in Debye–Waller factors ($\Delta\sigma^2$) are $< 0.01\,\text{Å}^2$.

Fig. 3. Experimental data of XANES spectra of zinc in (a) dried and calcined CuO–ZnO/MCM-41 at (b) 573, (c) 923, and (d) 1173 K for 2 h.
Figure 4 shows Fourier transformed weighted EXAFS data for copper and for zinc. CuO–ZnO/MCM-41 at 573 K has Cu–O and Zn–O bond distances of 1.95 and 1.98 Å with coordination numbers (CNs) of 4.2 and 5.7, respectively. At 923–1173 K, the bond distances of second shell Cu–(O)–Cu and Zn–(O)–Si correlations evident in Fig. 4 are, respectively, 2.85–2.86 Å (CNs = 2.4–2.5) and 3.05 Å (CNs = 2.3–2.7).

Table 1. Structural parameters of copper and zinc in MCM-41 during calcination at 573–1173 K for 2 h.

<table>
<thead>
<tr>
<th>Calcinated temperature (K)</th>
<th>Shell</th>
<th>Bond distance (Å)</th>
<th>Coordination number</th>
<th>$\sigma^2$ (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>573</td>
<td>Cu–O</td>
<td>1.97</td>
<td>3.4</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td>Zn–O</td>
<td>2.07</td>
<td>6.7</td>
<td>0.010</td>
</tr>
<tr>
<td></td>
<td>Cu–O</td>
<td>1.95</td>
<td>4.2</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>Zn–O</td>
<td>1.98</td>
<td>5.7</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>Zn–(O)–Si</td>
<td>3.11</td>
<td>1.7</td>
<td>0.009</td>
</tr>
<tr>
<td>923</td>
<td>Cu–O</td>
<td>1.96</td>
<td>3.8</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>Cu–(O)–Cu</td>
<td>2.85</td>
<td>2.4</td>
<td>0.010</td>
</tr>
<tr>
<td></td>
<td>Zn–O</td>
<td>1.93</td>
<td>5.4</td>
<td>0.010</td>
</tr>
<tr>
<td></td>
<td>Zn–(O)–Si</td>
<td>3.11</td>
<td>2.7</td>
<td>0.007</td>
</tr>
<tr>
<td>1173</td>
<td>Cu–O</td>
<td>1.96</td>
<td>3.9</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>Cu–(O)–Cu</td>
<td>2.86</td>
<td>2.5</td>
<td>0.010</td>
</tr>
<tr>
<td></td>
<td>Zn–O</td>
<td>1.94</td>
<td>4.4</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>Zn–(O)–Si</td>
<td>3.05</td>
<td>2.3</td>
<td>0.006</td>
</tr>
</tbody>
</table>

$\sigma^2$, Debye–Waller factor.
4. Conclusions

The least-square fits of XANES spectra show that the main copper and zinc species in the channels of MCM-41 are mainly impregnated Cu(II) and Zn(II) with some nanosize CuO and ZnO, respectively. By combined XRD, XANES, and EXAFS observations, nano copper–zinc alloy wires in the 4 nm channels of MCM-41 may be formed during calcination at 573 K. Copper in the channels of MCM-41 are identified from Cu–(O)–Cu correlations, whereas zinc appears to interact with the amorphous SiO$_2$ walls of MCM-41 between 873 and 1173 K as evidenced from second shell Zn–(O)–Si correlations. This work is therefore an example of the utilization of XANES and EXAFS spectroscopies in revealing the chemical structure of nano alloy wires in the channels of molecular sieves.

Acknowledgments

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References