Mineralization of CCl₄ with CuO has been studied by in situ X-ray absorption spectroscopy (XAS) in the present work. The least-square fitted X-ray absorption near-edge structural (XANES) spectra showed that 18.9–20.1% of CuCl₂ was yielded in the mineralization of CCl₄ with CuO at 513–603 K for 20 min. By in situ extended X-ray absorption fine structural (EXAFS) spectroscopy, the structural perturbation of CuO during mineralization was observed. The perturbation may be due to an insertion of Cl species into the matrix of CuO and formation of CuCl₂. Bond distances of Cu-O (first shell) and Cu-O-Cu (2nd shell) were increased by 0.01–0.04 Å with slight decreases of their coordination numbers (CNs) in the mineralization process. CuCl₂ in the CCl₄-mineralized product solids possessed Cu-Cl bond distances of 2.10–2.12 Å, which were greater than that of the CuCl₂ model compound (2.05 Å). The in situ XAS technique exemplifies a direct observation of perturbation of CuO by Cl species during the mineralization at elevated temperatures.

© 2005 Elsevier B.V. All rights reserved.

Keywords: XANES; EXAFS; Mineralization; CCl₄; CuO

1. Introduction

CCl₄, widely used as clean solvents in dry cleaning and semiconductor industries, is one of the EPA restricted volatile organic compounds (VOCs). CCl₄ is suspected toxic and carcinogenic and known to be a hepatotoxic as well as neurotoxic to humans. In addition, CCl₄ with an estimated lifetime of 40 years may also cause ozone depletion and continuously deplete the stratospheric ozone [1].

Methods for the disposal of CCl₄ containing waste streams include catalytic incineration [2], pyrolysis [3], photodecomposition [4–6] and mineralization [7,8]. Generally, CCl₄ can be destructed in high-temperature incineration processes. However, undesired by-products such as furans and dioxins are frequently formed [2].

An effective and inexpensive method for mineralization of CFCs (e.g., CFC-11 and CFC-12) has been reported recently by Burdenius and Crabtree [7]. CFCs can be mineralized by passing the CFCs vapor through a packed bed of powdered sodium oxalate (Na₂C₂O₄) at 563 K and yield stable inorganic species such as NaF, NaCl and CO₂. Weckhuysen reported the activities for mineralization of CCl₄ with alkaline earth metal oxides decreased in the order of BaO > SrO > CaO > MgO [9]. CO₂ was the only gaseous product in the mineralization of CCl₄ with BaO and SrO at 473–573 K. However, at higher temperatures (723–823 K), CaO and MgO became active for CCl₄ mineralization and a reaction intermediate COCl₂ was formed. In a separate experiment, we found that the mineralization of CFCs was deactivated very rapidly because of the Na₂C₂O₄ surface obstruction by the mineralization products such as NaF, NaCl or carbon [8]. Regeneration of Na₂C₂O₄ with water vapor or oxygen at 473–573 K was very effective in the re-establishment of active Na₂C₂O₄ surfaces. Nevertheless, mineralization of CCl₄ with CuO could maintain a high (63–83%) mineralization efficiency at 513–603 K for at least 10–30 min [10]. However, the gas/solid reactions involved in the mineral-
X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structural (EXAFS) spectroscopies are very useful in providing the chemical structure information (<4 Å) such as oxidation state, bond distance and coordination numbers (CNs) in the complex environmental solids matrix. By EXAFS, we found copper oxides (in ZSM-5 or ZSM-48) involved in the catalytic decomposition of NO [11] and oxidation of chlorophenols in supercritical water [11,12]. These speciation data were very useful in revealing the nature of active species in the catalytic processes. Indeed, the main scientific issues concerning the chemical process ultimately depend on molecular-scale structure and properties. Basically, understanding the speciation of element embedded in complex matrices can help the development of effective methods for the disposal of hazardous substances [13,14]. However, the majority of the gas and solid reactions are generally carried out in an ex situ manner where the conditions of the solids are far from those generally present in the solids. The phase composition and the structure of the solids may change during the reaction. An in situ study has, therefore, become of increasing importance since the real structure can be revealed by approaching the real reaction conditions as much as possible. Thus, the aim of this work reported here was to investigate the speciation of CuO involved in the CCl₄ mineralization process by in situ EXAFS and XANES spectroscopies. An in situ XAS cell was used in the experiments.

2. Experimental

Mineralization of CCl₄ (Katayama Chemical) was carried out in a home-made in situ XAS cell (as shown in Fig. 1) at 513–603 K for 20 min. About two grams of CuO powder (Merck) were used in the in situ XAS experiments. The flow rate of the 10% CCl₄/N₂ gas was about 30 mL/min. The in situ EXAFS and XANES spectra were collected on the Wiggler beamline at the Taiwan Synchrotron Radiation Research Center. The electron storage ring provided an energy of 1.5 GeV and current of 80–200 mA. A SiC(1 1 1) double-crystal monochromator was used for selection of energy with an energy resolution of 1.9 × 10⁻⁴ (eV/Å). The absorption spectra were collected in ion chambers that were filled with helium gas. The photon energy was calibrated by the absorption edge of copper foil at the energy of 8979 eV.

The absorption edge was determined at the half-height (precisely determined by the derivative) of the XANES spectrum after pre-edge baseline subtraction and normalization to the maximum above-edge intensity. The standard deviation calculated from the averaged spectra was used to estimate the statistical noise and error associated with each structural parameter. Fractions of CuCl₂ and CuO in the CCl₄-mineralized product solids were determined by a least-square fit of the XANES spectra.

The EXAFS data were analyzed using the UWEXAFS 3.0 and FEFF 8.0 programs [15]. The background of all the data was justified by the AUTOBK program [15]. The isolated EXAFS data was normalized to the edge jump and converted to the wavenumber scale. The Fourier transform was performed on k³-weighted EXAFS oscillations in the range of 2.7–10.8 Å⁻¹. To reduce the number of fitted variables, the many-body factor (S²) 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 CNs for the first shell atoms, and of ±0.02 Å and ±25% for the second shell atoms [16].

Fig. 1. Schematic diagram of the in situ XAS cell.

Fig. 2. The in situ XANE spectra of the CCl₄-mineralized product solids at the mineralization temperature of (a) 513, (b) 563 and (c) 603 K.
3. Results and discussion

The in situ XANES spectra of the CCl₄-mineralized product solids at 513–603 K for 20 min are shown in Fig. 2. The weak pre-edge feature at 8977 eV is normally attributed to a dipole-forbidden electronic transition of 1s → 3d. The shoulder at 8985–8988 eV and an intense band at 8994–9000 eV are due to 1s → 4p transitions that indicate the existence of Cu(II) species. Lower oxidation state copper species such as Cu(I) and metallic copper (Cu(0)) were not observed by in situ XANES spectroscopy.

The yield of CuCl₂ in the CCl₄ mineralization process was also analyzed by the least-square fitting of the in situ XANES spectra with the linear combinations of copper oxide and copper chloride (model compounds) spectra. The fitted spectra of CuO and CuCl₂ with the corresponding experimental spectra together with the least-square fractions of the model compounds making up the fitted curve are shown in Fig. 2. Relative amounts of CuO and CuCl₂ were quantitatively proportional to the height and area of the near-edge band in a copper spectrum. The XANES spectra were expressed mathematically in a LC XANES fit vectors by fitting the absorption data within the energy of 8970–9020 eV. In Fig. 2, 18.9–20.1% of CuCl₂ was found in the CCl₄-mineralized product solids at 513–603 K for 20 min. Thermodynamically, mineralization of CCl₄ with CuO to form CuCl₂ and CO₂ (CCl₄ + 2CuO → 2CuCl₂ + CO₂) is exothermic (ΔH = −391.8 kJ/mol). A large heat released in the reaction may enhance the mineralization of CCl₄ and formation of CuCl₂.

The k³-weighted EXAFS spectra of copper during mineralization of CCl₄ are shown in Fig. 3. The normalized k³-weighted EXAFS spectra were Fourier transformed to yield radial structure functions over 2.7–10.8 Å⁻¹. The best fitted structural parameters of the copper species during mineralization are shown in Table 1. In all EXAFS data analyzed, over 99% reliability of the EXAFS data fitting for copper species were obtained and the Debye–Waller factors (Δσ²) were less than 0.015 Å². The EXAFS data showed that the bond distances of Cu=O and Cu=O–Cu (2nd shell) in CuO were increased by 0.01–0.04 Å with a slight decrease of CNs in the mineralization process. CuCl₂ in the CCl₄-mineralized product solids possessed bond distances of 2.10–2.12 Å, which were greater than that of the CuCl₂ model compound (2.05 Å). The structural perturbation of CuO during mineralization may be due to an insertion of Cl species into the matrix of CuO and a formation of CuCl₂.

4. Conclusions

By the least-square fitting of the in situ XANES spectra, 18.9–20.1% of CuCl₂ was formed in the CCl₄ mineralization with CuO at 513–603 K for 20 min. The XANES spectra also showed that Cu(II) was the main copper species during mineralization. By in situ EXAFS, we also found that the structural perturbation of CuO during mineralization may be due to an insertion of Cl species into the matrix of CuO and the formation of CuCl₂. Bond distances of Cu=O and Cu=O–Cu in CuO was increased by 0.01–0.04 Å with a slight decrease in CNs. Bond distances of Cu=Cl for mineralization product CuCl₂ were 2.10–2.12 Å, which were greater than that of a CuCl₂ model compound. The in situ EXAFS
and XANES techniques exemplify a direct observation of perturbation of CuO by Cl during mineralization at elevated temperatures.

Acknowledgements

The financial support of the National Science Council, Taiwan is gratefully acknowledged. We also thank Prof. Y.W. Yang and Dr. J.-F. Lee of the Taiwan Synchrotron Radiation Research Center for their help in the EXAFS experiments.

References