

IN-SITU X-RAY ABSORPTION STUDIES OF A $\text{CuO}/\text{Al}_2\text{O}_3$ SORBENT DURING SO_2 REMOVAL FROM COAL FLUE GASES

Yuqun Cao¹ and Pedro A. Montano^{1,2}

1) Department of Physics, Brooklyn College of CUNY, Brooklyn, NY 11210

2) Department of Physics, West Virginia University, Morgantown, WV 26506

Keywords: X-ray absorption, copper oxide sorbent, coal cleaning

ABSTRACT

We have studied the local structure around the Cu ion in a $\text{CuO}/\text{Al}_2\text{O}_3$ sorbent using X-ray absorption (XAS). This sorbent is commercially used for the removal of sulfur dioxide from flue gases. Pure oxides of CuO and Cu_2O were also studied as a function of temperature and in the presence of flue gases. The pure oxides were used as standards. The XANES and EXAFS spectra for the sorbent in nitrogen gas at the same temperatures did not show any significant changes. By contrast, we observed the appearance of a new near edge feature in the XANES spectra of the sorbent in the presence of flue gases. A strong peak appears at an energy characteristic of monovalent copper. The amount of Cu^+ reaches a maximum at about 200C and then decreases at higher temperatures. It is noted that the EXAFS spectra do not show any significant change in the nearest neighbors distance during reaction with the flue gases.

INTRODUCTION

The removal of sulfur dioxide from the coal flue gases is one of the major tasks in the electrical power industry. The deleterious effect of the pollutants resulting from the combustion of coal is a great concern in contemporary society. A common industrial practice is the use of a sorbent for the capture of the flue gas pollutants [1,2]. Copper oxide supported on alumina is commonly used as a commercial sorbent. This sorbent is used to remove SO_2 from the coal flue gases. Our major interest in this study is to investigate the Cu local environment in the presence of the flue gases. It is important to understand the undergoing processes in order to facilitate a most efficient use of the sorbent. The chemical environment at the transition metal site can be better studied using XAS, because of the penetration capabilities of X-ray in-situ studies become possible. X-ray Absorption Fine Structure (EXAFS) and X-ray Absorption Near Edge Structure (XANES) have been used in recent years to study local structures [3,4,5]. We report here a series of in situ EXAFS and XANES measurements of a $\text{CuO}/\text{Al}_2\text{O}_3$ sorbent and model compounds. We investigated the evolution of the structure at the Cu site as a function of temperature in the presence or absence of flue gases. In the following paragraphs we describe the methodology employed and summarize the results of our measurements.

EXPERIMENTAL

The measurements were carried out at beamline X-18B at the National Synchrotron Light Source. The beamline is equipped with a double crystal monochromator. The two crystal monochromator has the advantage that the exit beam path is fixed [6]. Two ion chambers are used to measure the incident and transmitted beam intensities. They were

filled with 30 KPa of Ar. A third ion chamber is placed at the end of the second ion chamber with a thin Cu foil to obtain accurate energy calibrations. The data collecting procedure is automatic and controlled by a PDP 11/24 computer. The energy range covered in these measurements was 200 eV below and 1200 eV above the Cu K-edge ($E=8.979$ KeV). The experimental setup is schematically shown in Fig. 1. The sample chamber has two windows sealed with thin Capton films to let the X-ray beam go through. The flue gas passes through the sorbent in the chamber. A Chromel/Alumel thermocouple is attached to the sample holder for temperature monitoring. A variable transformer and a temperature controller are used for setting up the desired sorbent temperature. The coal is burned in a separate combustion chamber. It has an inlet for air and an outlet for the flue gas. A thermocouple is used here to measure the combustion temperature. We burned a West Virginia Blacksville #2 coal. This coal sample has 3.4% by weight of total sulfur (organic and inorganic). The sorbent sample used in this measurement is $\text{CuO}/\text{Al}_2\text{O}_3$. The fresh sample is in the form of small sphere of 2mm in diameter. The sample is made into powder right before the measurement and put into the sample cell. The sample cell is a 0.5mm aluminum plate with a 5mmx15mm hole in the center. The powder is sandwiched between two thin aluminum foils. On the aluminum foils a matrix of tiny pinholes are punched to allow the flue gases to go through the sorbent. Careful measurements on the effects of the aluminum foils were conducted before we began collecting data. It is found out that the aluminum foil we used here does not have side effects to the XANES. However, it contains a very small amount of zinc impurities which can be seen on the EXAFS spectrum 680 eV above the Cu K-edge. In figure 2 we show the raw EXAFS data for the sorbent at room temperature. The measurements were performed from room temperature to 400C. The sample were measured in nitrogen gas flow and in the presence of flue gases. The measurements were repeated several times in order to evaluate their reproducibility. The same set of measurements were performed using model compounds, pure copper oxides (Cu_2O and CuO) and CuSO_4 and is shown in Fig. 3. The data was analyzed using the conventional methods described in the literatures [3,4].

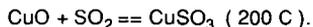
RESULTS AND DISCUSSION

We choose the maximum of the 1st derivative of Cu metal foil at the K absorption edge as E_0 . All the energy values are given with respect to this E_0 . The most prominent energy peaks of the samples are given in Table 1. The XANES of the copper compounds consists two parts: (1) the discrete part below the continuum threshold, where the weak features are usually called pre-edge peaks, due to transitions to unoccupied bound antibonding orbitals and (2) the continuum part where the peaks are due to multiple-scattering of the photoelectron, which are sensitive to both coordination geometry and interatomic distances [4,7,8,9]. The K-edge XANES of Cu primarily represents electric dipole transitions ($E1$) from the 1s core level to final states with nonzero np components, which are governed by the electronic structure of the material [8,9,10]. Peak P corresponds to the 1s \rightarrow 3d transition and peak A corresponding to the 1s \rightarrow 4p transition. The absence of peak P for Cu metal and Cu_2O is attributed absence of vacancies in the 3d orbitals.

The XANES spectra and its 1st derivative for the sorbent at various temperatures before reaction with flue gases are shown in Fig. 4. There is no noticeable change when the temperature is raised to 300C from RT and then back to RT. Comparing the peak positions

with that of the CuO standard, the first major peak A shifts from 5.0 eV to 6.0 eV, the second one, B at 12.0 eV does no change and the third peak C at 17.5 eV does not exist. The EXAFS of the sorbent is significantly different from that of the CuO standard. We identify the first shell as due to Cu-O bond. The higher order shells (2nd, 3rd and 4th) are not clearly seen in the Fourier transform of the $k^3X(k)$ (Fig. 5). This makes us believe that the CuO in the sorbent is in highly dispersed form, very small clusters. The Cu-O interatomic distance is almost the same as that in bulk CuO. The magnitude of the Fourier transform of the 1st shell decreases with temperature (Fig. 6). This is understood to be related to thermal effects on the interatomic vibrations.

The most significant change happens when the sorbent is exposed to the flue gases (Fig. 7). A peak S at 1.5 eV characteristic of Cu^+ begins to appear. It reaches a maximum at about 200C. This feature disappears when the sample is returned to RT. For temperatures in excess of 300C there is a remnant small peak at about 1.5 eV. The remaining XANES features are the same as those before reaction with the flue gases. The new peak indicates that Cu^+ is formed during the SO_2 removal process. 200C seems to be an optimal temperature for the formation of this intermediate species. At this stage the reaction product is unlikely to be $CuSO_4$. The XANES spectrum of $CuSO_4$ is different from the sorbent. We suggest that the following process is taking place,



The SO_2 molecules are chemically absorbed by the CuO clusters. The Cu is in a mixed state of Cu^{++} and Cu^+ . The EXAFS amplitudes also have a consistent change. It decreases with the increasing temperature until 200C then increases at higher temperature (Fig. 6). The magnitude also recovers at RT after the reaction. Table 2 shows the ratio of the oxygen coordination number surrounding Cu ion, $N_{CuO}/N_{Sorbent}$, and the deviation of the sorbent Debye-Waller factor from that of CuO. This gives us information on how the average oxygen coordination number around the Cu ion changes with temperature. The average oxygen coordination number for the sorbent becomes minimum at 200C. Our XANES measurements show strong evidence of mixed charge states (Cu^{++} and Cu^+).

CONCLUSIONS

We have measured XANES and EXAFS spectra of a commercial sorbent (CuO/Al_2O_3) used for the removal of SO_2 from coal flue gases. The studies shows that CuO in the sorbent is in the form of very small disordered clusters. The sorbent is thermally stable from RT to 400C in the nitrogen atmosphere. We observed a partial transformation of Cu^{++} to Cu^+ at 200C This happens only when the flue gases are present. The observed transformation is reversible if the temperature of the sorbent does not exceed 300C. Our result suggests that at 200C optimum conditions exist for the formation of this intermediate species.

ACKNOWLEDGMENT

We would like to express our appreciations to A. Bommannavar and M. Ramanathan for their help. This work was supported by the US DOE and Y. Cao acknowledge the financial support of the Division of Educational Program at Argonne National Laboratory .

REFERENCE

1. D.H. McCrea, A.J. Forney, J.G. Myers, J. Air Pollut. Control Assoc. 20, 819 (1970)
2. Sidney S. Pollack, William P. Chisholm Richard T. Obermyer, Sheila W. Hedges, Mohan Ramanathan, and Pedro A. Montano, I&EC Research, 27, 2276 (1988).
3. B.K. Teo, *EXAFS : Basic Principles and Data Analysis* (Springer, 1986).
4. *X-ray Absorption : Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES*. edited by D.C. Konigsberger and R. Prinz, Chemical Analysis, Vol. 92 (1988).
5. R.B. Greeger, F.W. Lytle, E.C. Marques, E.M. Larson, A.J. Panson, and J. Stohr in *Electronic Materials and Processes*, edited by J.T. Hoggatt, W. Jensen, M. Kushner, and S. McCollough, 2nd international Sample Electronics Conference Series, Vol 2, P.179 (June 1988).
6. M. Ramanathan, PhD thesis, *X-ray Absorption Study of the Interaction of Coal Combustion Gases with Calcium Oxide*, 1988.
7. A. Bianconi, E. Fritsch, G. Calas, and J. Petiau, Phys. Rev. B32, P.4292 (1985).
8. L.S. Kau, D.J. Spira-Solomon, J.E. Penner-Hahn, K.O. Hodgson, and E.I. Solomon, J. Am. Chem. Soc. 109, 6433 (1989).
9. F.W. Lytle, R.B. Greeger, and A.J. Panson, Phys. Rev. B37, P.1550 (1988).
10. E.E. Alp, G.K. Shenoy, D.W. Capone II, L. Soderholm, H.B. Schuttler, J. Guo, D.E. Ellis, P.A. Montano, and M. Ramanathan, Phys. Rev. B35, P.7199 (1987).

Table 1 Characteristic Energies of the XANES (Unit is in eV)

	P	A	B	C	D
Cu	—	0.0	6.0	11.0	22.0
Cu ₂ O	—	1.5	6.0	—	—
CuO	-1.5	5.0	12.0	17.5	—
CuSO ₄	-2.5	9.0	14.5	—	—
Sorbent	-3.5	6.0	12.0	—	—

Table 1. Characteristic XANES energies for the samples in this experiment.

Table 2

	Temp	N _{CuO} /N _{Sorbent}	ΔDW (Å)
Sorbent Only	RT	0.62	0.058
	100C	0.59	0.060
	200C	0.68	0.062
	300C	0.68	0.067
	RT	0.62	0.058
Sorbent Flue Gas	RT	0.72	0.063
	100C	0.82	0.065
	200C	0.89	0.064
	300C	0.77	0.064
	RT	0.70	0.061

Table 2. The ratio of the average oxygen coordination number surrounding the Cu ion, N_{CuO}/N_{Sorbent}, and the deviation of the Debye-Waller factor from that of CuO, ΔDW, obtained by the ratio method of EXAFS.

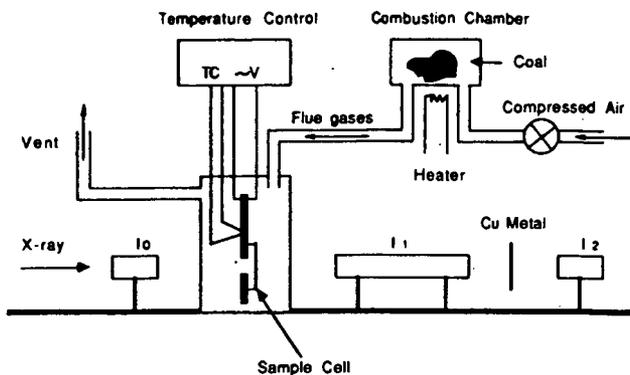


Fig. 1. Schematic drawing of the experimental setup inside the experiment hutch.

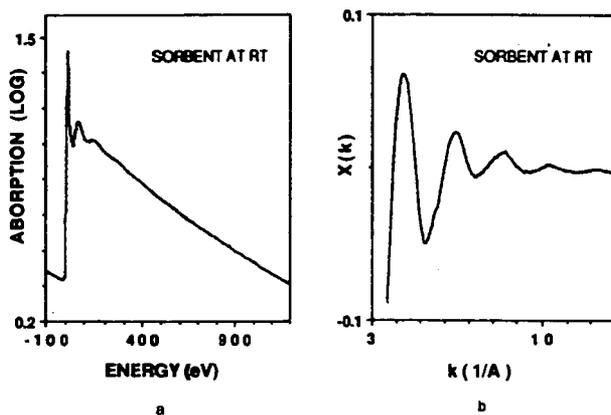


Fig. 2. a. EXAFS of the Sorbent at RT before the reaction.
 b. $X(k)$ after the EXAFS background subtraction and step height normalization.

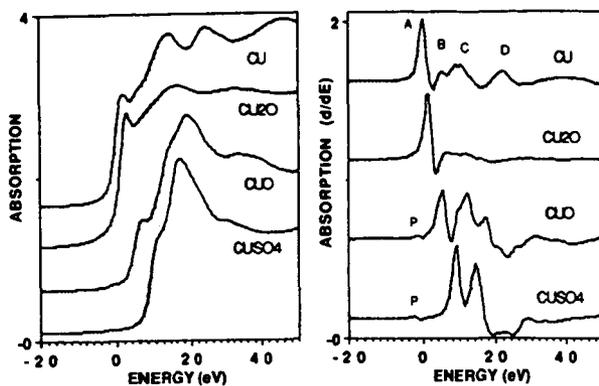


Fig. 3. XANES and 1st derivatives of pure Cu_2O , CuO and CuSO_4 .

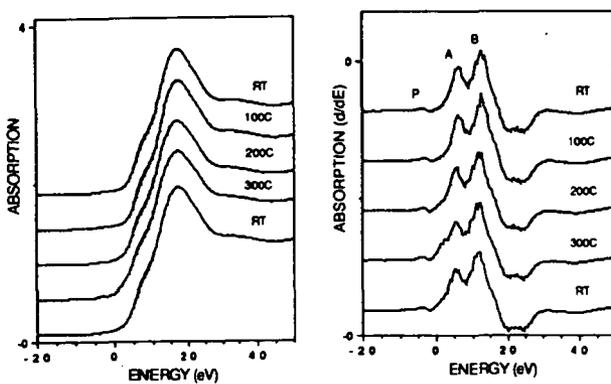


Fig. 4. XANES and 1st derivatives of the Sorbent at various temperatures under the N_2 environment.

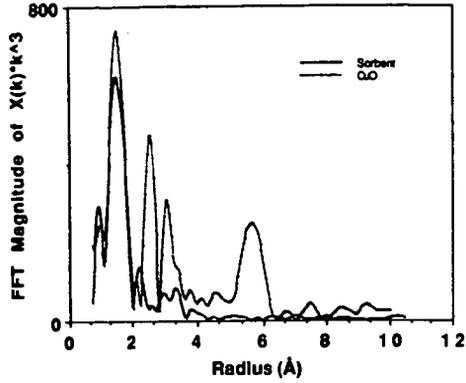


Fig. 5. Fourier transforms of the $k^3X(k)$ for the pure CuO and the sorbent at RT.

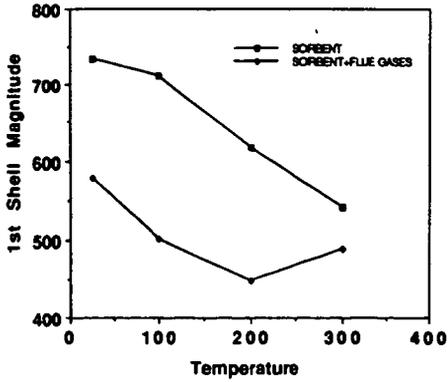


Fig. 6. Comparison of the 1st shell magnitude changes with the temperature for the sorbent with and without the flue gases.

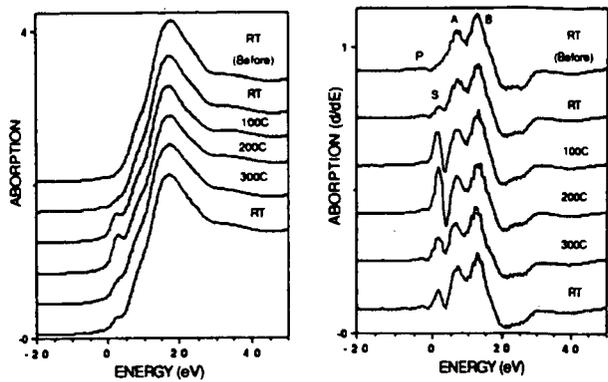


Fig. 7. XANES and 1st derivatives of the Sorbent at various temperatures in the presence of flue gases.