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SURFACE STUDIES OF ABSORBENTS FOR THE REMOVAL OF SO_x AND NO_x

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SUMMARY

The removal of sulfur dioxide from the flue gas is one of the major problems facing the utilization of coal for electric power generation. CuO supported on Al_2O_3 shows considerable promise as a regenerable SO_2 absorbent for flue-gas clean up. It is important to understand the processes on the CuO sorbent in order to facilitate its most efficient operation. Through a coordinated experimental and computational study we have gained detailed understanding (1) of the local environment of the copper atoms in relationship to the aluminum oxide support material and (2) how these copper atoms are involved chemically in the absorption of SO_2 . This has allowed us to assess the operating conditions and the percentage loading of CuO on the support that is optimum for the efficient operation of the sorbent. This assessment is presented in the CONCLUSIONS section of the report which follows. Detailed discussions with the technical monitors after initiation of the project resulted in a joint decision to focus our efforts on SO_2 absorption rather than nitrogen oxides, and to emphasize detailed understanding of the functioning of the CuO-based sorbents rather than emphasizing examination of transition metal oxide sorbents based on metals other than copper. However, we have devoted some effort to exploring the possibilities for zinc oxide and molybdenum oxide based sorbents. The modeling work indicated little promise for the use of zinc oxide; and this was confirmed by the experimental work that did not reveal any significant participation of ZnO in the SO_2 removal process. The possibility of using molybdenum oxide was investigated only by modeling. This did show some possible promise that could be pursued in a future detailed study.

We have used X-ray Absorption Near Edge Structure (XANES) to study the local environment around the absorbing copper atom. This has been done by comparing the XANES spectrum, before and after exposure of the sorbent to flue gas, with the "fingerprints" we established provided by well-characterized standard compounds. X-ray Absorption Fine Structure (EXAFS) was used to establish the local crystallographic environment of the copper atoms on the support material. The experimental work was coordinated with, and guided by the computational modeling work. This consisted of two stages which related to the EXAFS and XANES work, respectively. Extended surface total energy calculations, using the Film Linearized Muffin-Tin Orbital

(FLMTO) method we developed, were first used to identify the preferred site location of the copper atoms in the support material, and then an ab-initio molecular cluster method was used to model the adsorption of the SO_2 on copper atoms on the support material and the resulting modifications of the local environment of these copper atoms. This provided binding energy and local geometry information that was validated by the measurements and that provided guidance for optimal operating temperature for efficient absorption.

In the final stage of the study, we carried out x-ray absorption studies at the copper K-edge of two commercial $\text{CuO}/\text{Al}_2\text{O}_3$ sorbent samples with different metal concentrations, 5% and 7% by weight. The in-situ measurements were carried out with the samples exposed to the flue gas produced by the combustion of coal, and in the presence of nitrogen gas. Our measurements show that CuO in the samples is in the form of very small disordered clusters. The sorbent is thermally stable from room temperature to 400 C. We observed a partial transformation of Cu^{++} to Cu^+ at high temperatures (above 200° C). The formation of Cu^+ is a strong function of temperature and occurs only when the flue gases are present. The observed transformation is partially reversible if the temperature does not exceed 300 C. Copper ions in the spent sorbents are in a mixed mono- and di-valent state immediately after cooling the sample to room temperature (Cu^{++} is the dominant species). Eventually the copper ions in the sorbent become totally di-valent. The reaction products are copper sulfates. The optimum reaction conditions depend on both the copper concentration in the sorbent and the reaction temperature. Our measurements suggest that the sorbent with 7% Cu loading is more efficient in terms of Cu^+ formation. The optimum temperature for this process is around 200° C.

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1. INTRODUCTION

The removal of sulfur dioxide from the flue gas is one of the major problems facing the utilization of coal for electric power generation. CuO supported on Al_2O_3 shows considerable promise as a regenerable SO_2 absorbent for flue-gas clean up. the study of this material has attracted great attention in recent years^{1,2}. It is important to understand the ongoing processes on the CuO sorbent in order to facilitate its most efficient utilization. In-situ studies become feasible when x-rays are used as analytical probes. The chemical environment at the transition metal site can be studied using x-ray absorption techniques.

X-ray Absorption Near Edge Structure (XANES) has been employed in recent years to study the local chemistry around the absorbing atom^{3,4}. The XANES spectrum is very sensitive to the electronic structure of the absorbing atom. It is possible to use the XANES spectra of well-characterized standard compounds as fingerprints to investigate unknown materials. Previous studies^{2,5} of the $\text{CuO}/\text{Al}_2\text{O}_3$ sorbent show that the CuO unit in the sorbent is in the form of very small disordered clusters and that the sorbent is thermally stable from room temperature up to 400 C. X-ray Absorption Fine Structure (EXAFS) measurements indicate that the copper ion is surrounded by an average of 2.4-2.7 oxygens in an as-yet-unknown configuration. This low coordination number may have some relation to the good absorbing properties of the material towards SO_2 .

We have performed x-ray absorption studies at the copper K-edge of $\text{CuO}/\text{Al}_2\text{O}_3$ samples with different metal concentrations. The in-situ measurements were carried out with the samples exposed to the flue gas produced by the combustion of coal, and in the presence of nitrogen gas. We also investigated in-situ the XANES and EXAFS spectra of model compounds like CuO, Cu_2O , and CuSO_4 in the presence and absence of coal flue gases to serve as a basis of comparison. These measurements, as guided by and coordinated with the computational modeling studies have allowed us to assess the operating conditions and the percentage loading of CuO on the Al_2O_3 support that is optimum for the efficient operation of the sorbent.

A. Experimental Methodology:

The experiments were performed on beam line X-18B at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. A double crystal Si(111) monochromator was used in these measurements. The

energy range covered in the measurements was 100 eV below, and 1200 eV above the Cu K-edge (8979.2 eV). We choose the maximum of the first derivative of Cu metal at the K-absorption edge as the threshold energy. This allows the background subtraction by a polynomial spline method and normalization of the edge jump. The experimental setup is schematically shown in Fig. 1. The sample chamber has two windows sealed with thin Capton films to allow the X-ray beam to pass through the chamber. The first ion chamber is 10 cm long and filled with 100 KPa of Nitrogen. It is placed before the sample to record the incident x-ray intensity. The second ion chamber is 30 cm long and filled with 33 KPa of Argon. It is placed behind the sample chamber to measure the transmitting flux intensity. The large area ionization detector is placed on the side of the sample chamber to measure the fluorescence yield. 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. The heater outside the chamber heats up the coal to 500 C to start the combustion. The coals used in these experiments were a Kentucky #11 and WV Blacksville #2 coals (3.4% total sulfur). The $\text{CuO}/\text{Al}_2\text{O}_3$ samples² with different loadings were studied in the presence and absence of flue gases. The samples were heated from room temperature to 300 C and then cooled back. The in-situ measurements were performed for several temperatures. The fresh sorbent samples are in the form of small spheres of 1-2 mm in diameter; a more detailed description of the sample preparation can be found in reference 2. These small spheres are carefully stuck onto a Capton tape as close to each other as possible. This allows maximum absorption area exposed to the flue gas and results in a good fluorescence signal. We also carried out measurements on samples that were made into powder prior to the experiments. These samples were measured from room temperature to 400 C, and were also measured in a nitrogen flow. We also measured several pure copper compounds, Cu_2O , CuO , and CuSO_4 , from room temperature to 400 C, in the presence and absence of flue gases. The raw data were analyzed using the conventional methods described in the literature^{3,4}.

B. Computational Modeling Methodology:

There are two methods generally used to study surface electronic and geometric structure theoretically. One method, using a slab geometry to get overall electronic structure of the surface through band structure calculation,

requires translational symmetry. The other method, using cluster geometry to perform quantum chemistry molecular orbital calculations, deals with local electronic structure and properties.

In this study we use both methods to approach the problem. For the first stage of adsorption we use the self-consistent Film Linearized Muffin-Tin Orbital (FLMTO) method⁶ to find the adsorption site of copper atom on the support materials and the electronic properties of the system. For the second stage of the adsorption, the adsorption of SO₂, we use a molecular cluster method⁷⁻¹⁰ to search for the possible local structures of the adsorption site and the corresponding adsorption bonding energy.

The FLMTO method employed in this calculation has been proven by a number of calculations of 3d, 4d and 5f metals¹¹⁻¹⁵ to be an efficient and an accurate way to provide high quality results. The relatively small basis employed by the FLMTO method makes it possible to deal with a system having a large number of atoms in an unit cell. The method has been described in detail in our previous work^{6,11,15} and we give only a brief outline here.

The basis functions used in FLMTO are a combination of the standard Muffin-Tin Orbitals (MTOs) and the Plane-Wave Orbitals (PWOs)¹¹. The MTOs inside the sphere consist of a linear combination of the solution of the radial Dirac equation and its energy derivative for the spherically averaged actual potential at each iteration. In the interstitial region, the MTO is a Hankel function, while in the vacuum it is modified to be a linear combination of the solution of the one-dimensional Schrodinger equation and its energy derivative for the plane averaged vacuum potential. The PWOs, employed here as independent basis functions, are two-dimensional plane waves in the direction parallel to the slab surface. Along the direction perpendicular to the surface however, they either have real exponential form or a plane-wave-like form, depending on the energy parameter and parallel reciprocal lattice vector in the interstitial region. Like the MTOs, the PWOs are augmented inside the muffin-tin spheres. All these functions are continuous and have continuous first derivatives everywhere. We do not use the Atomic Sphere Approximation (ASA)¹⁶; the full potential is used everywhere except inside the muffin-tin spheres where it is approximated by the extended interstitial Non-Muffin-Tin potential. Both valence and core electrons are treated self-consistently. The exchange-correlation potential is calculated using the Vosko-Wilk-Nusair method¹⁷. The iterative calculations were carried on until

the difference of input and output potential was of the order of a few mRy at all locations. A special set of k points in the irreducible Brillouin Zone of the two-dimensional lattice has been used to obtain a good approximation to the density of states and the charge density distribution.

For the local properties of a crystal surface, such as impurities, vacancies and adsorbents on the surface, since translational symmetry is absent, a more suitable method to obtain the local electronic structure and the bonding energy of the adsorbent is a quantum chemistry calculation of a finite cluster which is carefully designed to simulate reliably the local atomic structure. The molecular cluster method in general has been used to investigate the surface properties of catalysts¹⁸ and many attempts¹⁹ have been made to improve the technique. The ab-initio molecular orbital calculation employed here originated from Pople's work⁸. The cluster molecular orbitals and the total energy of the cluster are calculated using Hartree-Fock molecular orbital theory where the molecular orbitals are expanded as a Linear Combination of Atomic Orbitals (LCAO) which has Gaussian form⁹. The use of Gaussian form orbitals makes the multi-center integrals relatively easy and less computer time consuming. The state-of-the-art form of the ab-initio quantum chemistry calculation program we used, Gauss-88, was developed by a group of experienced workers¹⁰. The performance of the calculation with the program heavily depend upon the speed and large memory of a supercomputer. (We obtained time at the Pittsburgh Supercomputing Center at no cost to the project).

Although the use of the cluster method of ab-initio calculation restricts the calculation to rather small clusters, the method has been successfully used in point-defect²⁰ calculations and in surface adsorption²¹ calculations. Our aim here is to study the chemisorption of SO_2 at the $\text{CuO}/\text{Al}_2\text{O}_3$ surface which involves probably only 1-5 atoms at the active site. Thus, we believe that a cluster calculation to simulate the local structure of the crystal surface with 10-20 heavy atoms of the adsorbent and the atoms around it, as performed in our work discussed in this report, should give reliable results.

2. RESULTS AND DISCUSSION

A. CuO/Al₂O₃

The key experimental results for CuO/Al₂O₃ sorbents involved assessing the functioning of commercial CuO/Al₂O₃ samples with two different loadings. This assessment made use of the information and capabilities developed over the course of the study and was guided by the predictions and physical picture developed in the computational modeling studies. X-ray Absorption Edge Near Structure (XANES) and X-ray Absorption Fine Structure (EXAFS) measurements, before and after reaction with flue gases, in comparison with the "fingerprints" of standard compounds which we characterized by XANES and EXAFS measurements, were used to make this assessment.

compounds used as standards:

We used a number of organic sulfur compounds as standards, phenyldisulfide, bensylsulfide, dibenzothiophene, and thioanisole. Other sulfur compounds selected as standards were sulfur, CuS, CuSO₄, FeS₂ and FeS. Because their structures are known²², the XANES spectra are used for comparison to our sorbents and to extract the EXAFS phase shifts. The XANES spectra of the model compounds are shown in Figure 2.

The features observed in the XANES spectra are mainly due to electron transitions to empty bound states, although other processes such as shake-up and shake-down, and continuum resonances also contribute. In Figure 2 the narrow and intense features at the sulfur K-edge correspond to the dipole transition to a level possessing significant p-orbital character (e.g. $1s \rightarrow \pi^*$ or $1s \rightarrow \sigma^*$). Different electronic structure and environment will give a different XANES spectrum. The spectrum of a model compound can be used for fingerprinting XANES spectra of unknown materials. To make this clear, we will give a brief description and discussion of the measurements on the inorganic standards. Their XANES and EXAFS spectra are given in Fig. 3 and Fig. 4 respectively.

CuSO₄:

The ion SO₄²⁻ belongs to the T_d point group. It has two unoccupied valence antibonding orbitals: a_1^* of 3s character and t_2^* of 3p character. Although the S 1s to a_1^* transition is dipole forbidden, the orbital may have some mixtures of p character. In Fig. 3 the strong peak B (at 2481.74 eV) is assigned to the S 1s to t_2^* dipole transition, while the small shoulder A (at 2478.38 eV) is associated with the S 1s to a_1^* transition (see Table 1). This weak

peak was not observed in previous work^{23,24}. The two broad features C (at 2490.0 eV) and D (at 2497.72) eV) are assigned to d-type shape resonances.

Cupric sulfate is orthorhombic with four molecules in a cell of the dimensions: $a_0=8.3956$ Å, $b_0=6.6982$ Å and $c_0=4.8291$ Å (26 C). The sulfate group forms a tetrahedron with four oxygen atoms occupying the corners of the tetrahedron and the sulfur atom in the middle. The S-O distances in the sulfate tetrahedron lie between about 1.48 and 1.53 Å. The major peak A (at 1.211 Å) in Fig. 4 is due to the S-O distance of 1.48 Å. The S-O pair phase shift information can be obtained from this measurement.

FeS₂:

The first peak in Fig. 3 is associated with the transitions to both the lowest unoccupied band e_g and the antibonding band σ_u . According to recent band calculations²⁵ these are very close in energy. The e_g band has some p character, and the σ_u band has mainly p character²⁶. The asymmetric shape of the peak suggests a fit to the peak with two Gaussian functions which results in two peaks A (at 2471.25 eV) and B (at 2472.64 eV). Peak C (at 2479.25 eV), peak D (at 2485.50 eV) and peak E (at 2490.50 eV) are assigned to d-type shape resonances, see Table 1. There are some weak (but above the noise level) features that cannot be identified at the present time.

Pyrite is known to have a NaCl-like structure with the iron atoms and the S₂ pairs located at the Na and Cl sites. The crystal is cubic with a unit cell of 5.40667 Å. The adsorbing sulfur atom has a neighboring sulfur atom at a distance of 2.153 Å. These two distances are so close that they should produce a single peak A at 1.996 Å (no phase correction) in Fig. 4. However iron is a stronger backscatterer than sulfur, and iron has a larger coordination number than sulfur (3 to 1); thus the S-Fe signal must be the dominant one. Peak B at 2.553 Å is due to the second nearest neighbors of sulfur at 3.077 Å from the center sulfur atom. The phase information for the pairs S-Fe and S-S is extracted from peak A and B respectively. Peak C (at 3.011 Å) is identified as giving a S-S distance of 3.315 Å and D (at 3.436 Å) as giving a S-Fe distance of 3.432 Å.

CuS:

A tentative explanation of the XANES spectrum is given here by an extension of Terakura's theory²⁷ (as Sugiura's paper²⁶ did for FeS). Terakura has calculated the densities of 3s and 3p states at the site of Si embedded in Cu and Fe as a single impurity using a pseudo-Greenian formalism. His result

shows that the p states undergo a significant redistribution through a hybridization with the host 3d band, forming bonding and antibonding states separated by a deep valley at the top of the d band. With the transition-metal impurity (Fe), the valence electrons with p symmetry fill only the bonding orbitals, while with the noble-metal impurity (Cu), the electrons are divided into the bonding and antibonding orbitals. Therefore the peak A (at 2469.50 eV) and peak B (at 2471.25 eV) correspond to the transitions to the partially empty bonding and antibonding orbitals respectively. The broad peak C (at 2475.39 eV) and E (at 2485.20 eV) are due to a d-type resonance. The strong sharp peak D (at 2481.74 eV) and broad peak F (at 2499.60 eV) are due to the presence of sulfates in the CuS powder sample. (See the discussion about the sulfate in the FeS section below.)

Cupric sulfide is hexagonal with an elongated six-molecule cell: $a_0=3.796 \text{ \AA}$ and $c_0=16.36 \text{ \AA}$. The various sulfur and copper atoms have different interatomic distances and environments that are in some ways unexpected. The S-S distance is $2.05 \text{ \AA}$, while S-Cu have distances of $2.19 \text{ \AA}$, $2.31 \text{ \AA}$, and $2.35 \text{ \AA}$. These distances produce a broad EXAFS peak (A) in Fig. 4.

FeS:

Troilite has the NiAs structure. We use the same arguments as above in analyzing the XANES measurements. The strong peak A (at 2470.25 eV) is attributed to the S 1s to 3p antibonding bound state. The broad peaks B (at 2477.00 eV) and D (at 2488.0 eV) are identified as shape resonances. The small narrow peak C (at 2481.75 eV) and broad peak E (at 2498.25 eV) are produced by the presence of iron sulfates. There is small amount of sulfate on the surface of the FeS sample due to the oxidation. The troilite sample was powdered after this round of measurements and the measurement was repeated on the powder sample. We observed an increase in the intensities of these two peaks, as expected, since the powder has a larger surface area exposed to air.

SORBENTS:

We carried out x-ray adsorption studies at the copper K-edge of two commercial $\text{CuO}/\text{Al}_2\text{O}_3$ sorbent samples with different metal concentrations, 5% and 7% by weight. The in-situ measurements were carried out with the samples exposed to the flue gas produced by the combustion of coal, and in the presence of nitrogen gas.

The near-edge spectrum is usually divided into two regions: pre-edge and continuum. In the pre-edge region, the weak and discrete features,

usually called pre-edge peaks, are due to transitions to unoccupied orbitals; while in the continuum region the peaks are due to multiple-scattering of the photoelectron, which are sensitive to both coordination geometry and interatomic distances. The Cu K-edge spectrum primarily represents electric dipole transitions (E1) from 1s core level to final states with non-zero np components, which are governed by the electronic structure of the material. The XANES spectra for the standard copper compounds are shown in figure 5. Peak P corresponds to the 1s $\rightarrow$ 3d transition, and peak A corresponds to the 1s $\rightarrow$ 4p transition. The absence of peak P in Cu metal and Cu₂O is attributed to the absence of empty 3d states.

The normalized near edge fluorescence spectra and their first derivatives for the two sorbent samples (5% and 7% of copper respectively) are given in Figures 6 and 7. Features A and B correspond to an overlap of electric dipole transitions from the 1s state to various np final states of Cu⁺ and Cu⁺⁺ in the sorbent samples. The first derivative spectra are also shown to better visualize the different spectral features. The spectrum at the bottom of the figures is one of the fresh sample at room temperature, before the coal flue gas was introduced into the sample cell. The rest are the in-situ measurements of the sorbent sample exposed to the flue gases at various temperatures from 50 C to 300° C. The spectrum at the top of the figure was measured after the sample was cooled back to 50 C. There is a small peak P in the pre-edge region. Features A and B are shown on all spectra while peak S appears only when the flue gas is present. Peak S is identified as Cu⁺. This result is inferred from the comparison of the shape and position of the spectra to those of the standards. It is noted that the intensity of peak S varies with temperature. The copper concentration in the sorbent also plays a role in the development of peak S. This can be easily seen from the difference in temperature dependence for the two samples. For the 7% sample, peak S reaches a maximum at about 200 C while the maximum appears around 300 C for the 5% Cu sample. The amount of the phase identified with peak S for the 7% sample after cooling back to 50 C is less than that of the 5% sample. The peak positions and their intensities are summarized in Table 2 and Table 3. The counterpart of the peak is the derivative spectrum, labeled with a prime (e.g., P', S', A', and B'). The peak positions for the two samples are very close (within 0.5 eV).

Previous studies of the $\text{CuO}/\text{Al}_2\text{O}_3$ sorbent reveal that the copper species are not in the form of crystalline CuO nor CuAl_2O_4 , but in a form less well-defined, very small disordered units probably in octahedral configuration and held at the surface or near the surface of the support. Although the Cu-O bond length in the sorbent is the same as that of bulk CuO , the coordination geometry is not. Because of this difference, the sorbent spectrum is slightly different from that of the pure CuO standard compound. The peak S is a signature of Cu^+ . The appearance of peak S indicates that part of the Cu^{++} in the sorbent turns into Cu^+ during reaction with SO_2 . There is a charge transfer to the copper ion when the SO_2 molecules are adsorbed on the surface of the sorbent. It also indicates that the reaction process occurs mainly at the copper oxide sites. Copper in the sorbent is in a mixture of states, Cu^+ and Cu^{++} in the presence of the coal flue gases. The amount of the Cu^+ in this intermediate stage can be estimated by mixing the spectra of properly selected standards to best-fit the experimental spectrum. We select pure Cu_2O and the fresh sorbent as standards. One of the reasons for doing so is that Cu_2O has only Cu^+ and the fresh sorbent has only Cu^{++} . Their normalized spectra are added together with weights R1 and R2 respectively, giving an artificial spectrum:

$$Y[\text{Fit}] = R1x Y[\text{Cu}_2\text{O}] + R2x Y[\text{Fresh Sorbent}]. \quad (1)$$

By adjusting R1 and R2, $Y[\text{Fit}]$ is then fitted to $Y[\text{Sorbent}]$, the measured spectrum of the sorbent containing both Cu^+ and Cu^{++} . The Marquardt-Levenberg algorithm is used in the fitting process. The fitted and measured spectra for the 5% sample at 200 C are plotted together in Fig. 8. It is a good example of the goodness of the fit. They match very well in the pre-edge and the threshold region. The match is not as good in the continuum region where the multiple-scattering and EXAFS features begin to play a role. The mismatch also can mean that the Cu^+ in the sorbent is not exactly in the same crystallographic form as in bulk Cu_2O . It has to be in a highly dispersed form since the Cu^{++} before the adsorption is not crystalline. The results of the fit using Eq. 1 are summarized in Table 4. The transformation rates of the Cu^{++} into Cu^+ in the presence of the flue gases are plotted as a function of temperature in Fig. 9. For the 5% sample, the Cu^+ to Cu^{++} ratio increases as the temperature raises from 50 C to 300 C. About 48% of copper in this sample becomes monovalent at 300 C. About 37% of the copper remains as Cu^+ after the temperature drops back to 50 C. The Cu^+ to Cu^{++} ratio increases until the

temperature reaches 200 C; above this temperature the amount of Cu^+ is reduced. The maximum amount of Cu^+ at 200 C is 52%. There is 28% of Cu^+ left when the temperature returns to 50 C.

We carried out similar measurements using a powder sorbent with 7.2% loading obtaining very similar results. We measured the XANES spectrum up to 400 C; and using flue gases produced by the combustion of a WV Backsville #2 coal, we observed the formation of Cu^+ . We carried out the same in-situ measurements using nitrogen gas instead of flue gases. In the latter case we did not observe the formation of Cu^+ in the sample.

We performed similar measurements using model compounds instead of the supported sorbents. We did not detect any appreciable change in the XANES spectra of the standards in the presence of flue gases, and as a function of temperature. However, we must point out that the reactions will take place at the surface of the CuO which is a very small fraction of the sample, as compared to the bulk.

The appearance of Cu^+ during the removal process is indicative of the formation of intermediate species. The XANES spectrum of CuSO_4 is significantly different from those observed in the in situ measurements at high temperatures. It is possible that an intermediate process occurs with the formation of species like

The SO_2 molecules react with the CuO on the surface of the alumina. At high temperatures the Cu is in a mixed state of $\text{Cu}^+/\text{Cu}^{++}$. Eventually when the sample is at room temperature the dominant species found on the sorbent is CuSO_4 . From the Cu^+ formation point of view, the sorbent with 7% metal loading is more efficient in removing SO_2 from the flue gases. More copper atoms involved in the charge transfer process is suggestive of a more active participation in SO_2 removal.

Model Design and Results

$\gamma\text{-Al}_2\text{O}_3$ used as carrier or support material has a distorted spinel structure, in which a cubic close-packed (ccp) lattice of oxygen is fairly ordered, while the aluminum tetrahedral sublattice is strongly distorted. One unit cell of $\gamma\text{-Al}_2\text{O}_3$ consists of 32 ccp oxygen atoms, which provides 16 octahedral sites and 8 tetrahedral sites for $21 \frac{1}{3}$ Al atoms distributed randomly and leaves some octahedral and tetrahedral vacancies. The material itself in the $\text{CuO}/\text{Al}_2\text{O}_3$ system probably acts only as a frame with vacancies where the

copper atom moves in and becomes an active center. In other words, as a carrier of the catalyst, the chemical components of the support material are not very important, but the vacancies at or near the surface are important in a sense that copper atoms could be fit in. While the detailed surface structure of a small particle of $\gamma\text{-Al}_2\text{O}_3$ is not known, an experimental study²⁸ indicates that for $\gamma\text{-Al}_2\text{O}_3$ the (100) plane of the spinal structure is preferentially exposed. The material used as carrier is often in porous form with average pore diameter of less than 100 Å.

Based on the information above, models are carefully designed to simulate the system. As mentioned earlier, the real surface of the material is very complicated, and since the unit cell of alumina is very large, including probably more than 60 atoms with an adsorbed SO_2 molecule, we have to choose the size of a unit cell of a slab and size of a cluster properly to simulate the system and also to make the calculation practical. For this reason our models are limited to simulate only part of the surface in the FLMTO calculation and to simulate only few possible configurations of adsorption in the cluster calculations. In our calculations the size of a slab unit cell is chosen to have 5-12 atoms for FLMTO method and the size of clusters to be 19-25 heavy atoms (not including the terminating hydrogen atoms). As a first step, two models, Model 10a for the adsorption at an octahedral site and Model 10b for the adsorption at a tetrahedral site shown in Fig. 10 are constructed to determine the adsorption site of the Cu atom on the surface. A three layer slab for both Model 10a and 10b has three oxygen atoms and two copper atoms in a unit cell. The highly symmetric form of the structures makes it possible to obtain very accurate total energy. The volume difference of the two models in the interstitial region of a unit cell is normalized to give the final energy difference. Both models use the exact local atomic arrangement as that of $\gamma\text{-Al}_2\text{O}_3$.

In order to find the electronic properties of the Cu surface, we build three slab models shown in Fig. 11 a, b and c in which we take the copper atoms to be at octahedral sites of the (100) surface after knowing that the site is energetically favorable for copper atom adsorption. All three models have 3 layers with 4 atoms in each layer of a unit cell. The positions for the center layer atoms and oxygen atoms at the surface are the same for all three models. While model 11a (which is designed to study the properties of the copper-and-aluminum-mixed surface); has one copper and one aluminum atom on each

surface models 11b and 11c have two copper or two aluminum atoms, respectively, in order to represent the copper or aluminum covered portion of the surface. Three models therefore are designed for studying the entire (100) surface by breaking the surface into purely aluminum covered, purely copper covered and mixed regions.

We then go on to design a set of models for SO_2 adsorption on the $\text{CuO}/\text{Al}_2\text{O}_3$ surface. The structural chemistry of complexes involving a direct metal- SO_2 interaction has shown that the structure of the systems has mainly the following forms: (1) co-planar S-M bonded, (2) pyramidal S-M bonded, (3) (S+O)-M bonded, (4) O-M bonded²⁹. In case of SO_2 adsorption on the $\text{CuO}/\text{Al}_2\text{O}_3$ surface the four configurations could probably all be formed on the surface, but considering that the copper atom is surrounded by four oxygen atoms on the surface, two of the four configurations, namely co-planar and O-M bounded configurations, seem to have larger chance. Placing the Cu atom at the octahedral position on the surface, we constructed several models, including the co-planar and the O-M bonded configurations shown in Fig. 12a and 12b. Taking the porous structure of the material into account, which provides chances for SO_2 molecule being adsorbed "across" two metal atoms via O-M bonding, we also built three "bridge" configuration models, shown in Fig. 12c, 12d, and 12e. The three "bridge" models are constructed for the SO_2 molecule sitting (12c) between the Cu atom and a neighboring octahedral vacancy hole, (12d) between the Cu atom and a neighboring Al atom with the S atom of the SO_2 molecule bent nearer to the surface or, (12e) with the S atom bent away from the surface. Although the results for model (a) (c) and (d) rule out the possibility of the adsorption for these three configurations, the calculations for model (b) and (e) do give a minimum bonding energy of about 2 eV, ((b) 1.98 eV and (e) 1.66 eV) which is a weak chemical bonding. For the "bridge" configurations we went on to substitute the copper and aluminum atoms on the surface with two copper atoms or two aluminum atoms to calculate the bonding energy at different portions of the surface and obtained much higher bonding energy.

The total energy calculations for model 10a and model 10b show that the energy of the copper atom at the surface octahedral vacancy is lower than that of the copper atom at the tetrahedral vacancy by 0.2 Ryd. per copper atom. The calculated energy difference of 0.2 Ryd between these two sites seems to be large, which we think is caused by the very short bond length of 1.7 Å for the

tetrahedral configuration. Most existing compounds of copper and oxygen have longer bond lengths. For example, copper monoxide, CuO has a bond length of 1.95 Å, and copper dioxide, CuO₂ has a bond length of 1.9-2.0 Å. In this calculation we simply squeeze the copper atom into the tetrahedral position which probably makes the energy high. The ideal octahedral position for copper atom gives a copper-oxygen bond length of 1.975 Å, which is very close to the CuO bond length and agrees well with the EXAFS experiments^{2,30}. For a quite small particle of γ -Al₂O₃ however, the oxygen atoms around the tetrahedral copper atom could be moved to give a longer bond length between the copper and the oxygen atoms, which might make the total energy associated with the tetrahedral site lower than the result we obtained here. This could very likely happen near the surface at high temperature. The experimental results³⁰ for samples calcinated at high temperature seem to point to this possibility.

The calculations for model 11a, 11b and 11c provide us with the electronic properties of the surface. The sphere projected density of states, shown in Fig. 13a, b and c, show a general characteristic of γ -Al₂O₃ for the center aluminum and oxygen atoms, in which there is a low lying single peak, coming from the 2s band of oxygen atoms, located at about 25 eV below the Fermi level. The 2p bands of the oxygen atoms however, are spread widely in an energy range from the Fermi level to about 10 eV below it. All s, p and d bands of the aluminum atoms are located in this energy region. This indicates a very strong hybridization between oxygen and aluminum orbitals. The position and the shape of the DOS for these aluminum and oxygen atoms agree well with experimental observation³¹ for pure γ -Al₂O₃.

The DOS of the surface copper and aluminum atoms together with the surface oxygen atoms reveals information on the copper species adsorbed at the octahedral site. The location of the 2p bands of the surface oxygen atoms and the d bands of the copper atoms shows that these orbitals are strongly hybridized. Considering that the main part of the 3d orbitals are not as extended as the 3p orbitals, however, we believe that the bonding between copper and oxygen atoms is not as strong as between aluminum and oxygen atoms. This is clear when we plot the charge distribution contour maps given in Fig. 14a, b and c. From the maps, it is clear that the charge of the copper atoms is more spherically distributed compared to the charge distribution of the aluminum atoms; which suggests that the bonding between the copper and

oxygen atoms is not as strong as the bonding between the aluminum and oxygen atoms. Moreover the non-spherical charge distribution of the aluminum atom makes the surface charge distribution near the aluminum atom not as smooth as that near the copper atoms. The surface charge distribution near copper atoms shows flat behavior; while the charge distribution near the aluminum atoms has pronounced P_x orbital shape, showing a typical P_x dangling bond.

The unevenly distributed charge density near the surface aluminum atom provides more charge in the vacuum region near the aluminum atom which increases the surface dipole moment nearby. This is consistent with the results we obtained for the potential difference calculations. Then calculated potential difference from the energy level of the highest occupied state to the vacuum level is 11.33 eV for the copper-atom-covered surface, 12.0 eV for the mixed surface and 12.21 eV for the aluminum-atom-covered surface.

In the cluster calculations we focused our attention on different configurations and the corresponding bonding energies. For each configuration we calculated the total energy with and without the SO_2 molecule, the difference between the total energies then being compared with the energy of the isolated SO_2 molecule to find the bonding energy between the adsorbent and the SO_2 molecule. For the SO_2 adsorbed on the copper atom with S-Cu bonding, our calculations of the minimum total energy with optimization of the bond length indicates that this configuration is not energetically favorable for adsorption. For the O-Cu bonding however, the calculation gives a minimum (without optimization of the bond length) bonding energy of about 2 eV. The bonding energies of the "bridge" models constructed for the SO_2 molecule adsorbed on the surface are given in Table 5.

The results of the bonding energy calculation seems to suggest that the most possible adsorption site for the SO_2 molecule is the Al-Al site on the surface, which probably is true for high temperature adsorption³². The large bonding energy associated with the site makes the SO_2 molecule adsorbed on the surface difficult to be removed. This could be related to the fact that there is a small amount of SO_2 molecule remaining on the system² even after the regeneration procedure.

The carrier material alumina is not pure but contains water³⁰ from a few tenths percent to about 5percent, depending upon temperature and water vapor pressure. The water is adsorbed at the aluminum atom on the surface in

either hydroxyl ions form or water molecule form. During drying of the sample the water molecule could be removed totally at about 300 C. Above this temperature the hydroxyl ions are gradually expelled; but even at very high temperatures a small amount of the hydroxyl ions are still adsorbed on the surface. This could be a reason why the SO_2 molecule is not adsorbed at the surface aluminum site rather than the Cu site, i.e. because the aluminum sites are covered by the hydroxyl ions. This could be especially true for the low temperature adsorption.

It is significant that, according to our calculation, the adsorption occurs through O-Cu bonding but not through S-Cu bonding; because first, the interactions of complexes involving SO_2 -metal are less likely through O-M bonding, and secondly the S-M bonding of co-planar form is hardly reversible²⁷ which makes the disabsorption difficult. The geometrical parameters of the $\text{CuO}/\text{Al}_2\text{O}_3$ surface play a key role for the "bridge" SO_2 adsorption. The distance between the two nearest metal atoms on the smooth surface is 2.7945 Å, which is very close to the O-O distance 2.505 Å of SO_2 . A curved surface, such as in porous material, provides more chance to match the O-O distance with metal-metal atom distance on the surface. In this calculation we let the angle of SO_2 increase by about 15 degrees and the bond length of SO_2 by about 0.1 Å to make the matching, and it is not optimized.

A charge transfer between the substrate and the adsorbed SO_2 molecule shows that there is indeed chemical bonding between them. The amounts of the charge transfer seem to be related to the strength of the bonds. The configuration of SO_2 adsorbed on two Al atoms has about one electron charge transferred from the metal atoms to the SO_2 molecule, while for the two Cu atom configuration this is only 0.75 electron. As for the Cu-Al "bridge", charge is transferred from the Al atom to the SO_2 molecule, then it is transferred back to the Cu atom, resulting in the SO_2 molecule losing about 0.15 electrons. For the O-Cu bonded model the charge transfer is 0.22 electrons from SO_2 to the adsorbent.

In summary, we have used both band structure calculations and cluster calculations to investigate the process of SO_2 adsorption on $\text{CuO}/\text{Al}_2\text{O}_3$ surface theoretically. The band calculations using the FLMT0 method reveal that the copper atoms are adsorbed at the surface octahedral sites of $\text{CuO}/\text{Al}_2\text{O}_3$ surface and that the Cu-O bonding is not as strong as the Al-O bonding. The calculated local potential difference between the highest occupied state and vacuum

shows that the adsorption of the copper atoms on the surface moves the energy level of the highest occupied state up by about 1 eV. The calculations for carefully designed clusters show that the SO_2 is adsorbed on the surface via "on-top" O-Cu bonding or in the form of "bridge" with the two oxygen atoms of SO_2 sitting above two surface metal atoms. We argue that even if the configuration with the two metal atoms being aluminum atoms gives the highest bonding energy in the three possible combinations, the configurations with the two atoms being Cu-Cu or Cu-Al are probably the best candidates for the adsorption, with Cu-Al providing low bonding energy probably necessary for regeneration.

Thus our results suggest that low-temperature adsorption is desirable to make the adsorbent reusable because of the lower bonding energy of the O-Cu "on-top" configuration or the bridging of Cu-Al.

B. Possibility of Zinc Oxide or Molybdenum Oxide Sorbent Systems

We devoted a moderate amount of time to exploring the possibility of using either zinc oxide or molybdenum oxide as the basis of a sorbent system rather than copper oxide.

Experimental Work:

The in-situ x-ray studies of ZnO sorbents reacting with coal flue gases were performed on beam line X-18B at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. A double crystal Si(220) monochromator was used in these measurements. The energy range covered in the measurements was 100 eV below, and 1200 eV above the Zn K-edge (9659 eV). We chose the maximum of the first derivative of Zn metal at the K-absorption edge as the threshold energy. This allows the background subtraction by a polynomial spline method and normalization of the edge jump. We employed the same experimental setup used for the CuO studies. The sample chamber has two windows sealed with thin Capton films to allow the x-ray beam to pass through the chamber. The first ion chamber is 10 cm long and filled with nitrogen. It is placed before the sample to record the incident x-ray intensity. The second ion chamber is 30 cm long and filled with argon. It is placed behind the sample chamber to measure the transmitting flux intensity. The large area ionization detector is placed on the side of the sample chamber to measure the fluorescence yield. 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. The heater outside the chamber heats up the coal to 500 C to start the combustion. The coal used in these experiments was a Pawhatan #5 coal. The samples were heated from room temperature to 500 C and then cooled back. The in-situ measurements were performed for several temperatures. The fresh samples were in powder form.

The XANES and EXAFS measurements on the powder ZnO sample are shown in figures 15 and 16. The results of our measurements indicate that no noticeable structural or electronic change occurs at the ZnO during reaction with the flue gases. Our results indicate that ZnO is quite stable to the temperature variations and inactive towards coal flue gases. This result is in marked contrast to our measurements on CuO. In a mixed sorbent containing ZnO and CuO, the zinc oxide plays only a role as an inactive support and also promotes the physical dispersion of the CuO. We find no evidence from the x-ray adsorption measurements of an active role for ZnO in the SO₂ removal process.

Theoretical/Computational Modeling Work:

We performed a modeling survey of the possibility of using zinc oxide rather than copper oxide as a sorbent dispersed on alumina. From the results of our survey, this does not look promising. We found that for the zinc system, the "on-top" and "side-on" models for the adsorption of SO₂ do not show any chemisorption binding, while the "bridge" site model shows only a weak chemisorption. We then performed a similar modeling survey for the use of molybdenum oxide. This did show some possible promise that could be pursued in a future, more detailed study. We found that for the molybdenum system the "side-on" and the "on-top" models both show the possibility of chemisorption, but the "bridge site model" was not favorable for chemisorption.

3. CONCLUSIONS

The modeling study indicated that successful use of a CuO-based sorbent supported on Al_2O_3 would probably depend on taking advantage of the O-Cu bonding energy being lower than the O-Al bonding energy. This indicates that for regeneration of the absorbent it is desirable to operate at relatively low temperature where the hydroxyl ions render the Al sites ineffective. Furthermore, the bridging of SO_2 across two copper atoms gives a very much higher bonding energy than oxygen bonding on-top of a copper atom or SO_2 bridging across copper and an aluminum atom, and gives lower energy than SO_2 bridging across two aluminum atoms. This indicates some sensitivity to copper loading, with a value of copper loading that is neither too low nor overly high being most effective. The desirability of relatively low temperature operation and the sensitivity to copper loading have been borne out experimentally.

Our measurements show that CuO in the samples is in the form of very small disordered clusters. The sorbent is thermally stable from room temperature to 400 C. We observed a partial transformation of Cu^{++} to Cu^+ at high temperatures (above 200 C). The formation of Cu^+ is a strong function of temperature and occurs only when the flue gases are present. The observed transformation is partially reversible if the temperature does not exceed 300 C. Copper ions in the spent sorbents are in a mixed mono- and di-valent state immediately after cooling the sample to room temperature (Cu^{++} is the dominant species). Eventually the copper ions in the sorbent become totally di-valent. The reaction products are copper sulfates. *The optimum reaction conditions depend on both the copper concentration in the sorbent and the reaction temperature. Our measurements suggest that the sorbent with 7% Cu loading is more efficient than that with 5% loading in terms of Cu^+ formation. The optimum temperature for this process is around 200 C.*

The modeling survey indicated little promise for the use of zinc oxide, and this was confirmed by the experimental work that did not reveal any significant participation of ZnO in the SO_2 removal process. Due to lack of further time, the possibility of using molybdenum oxide was investigated only by modeling. This did show some possible promise that could be pursued in a future detailed study.

4. Listing of Publications and Papers Prepared for Publication.

1. Modeling of Chemisorption of Copper Oxides Supported on Alumina, Y.H. Hao and B.R. Cooper, Journal of Vacuum Science and Technology A, Vol. 9, 1898 (1991).
2. In-Situ X-Ray Studies of $\text{CuO}/\text{Al}_2\text{O}_3$ Sorbents Reacting with Coal Flue Gases, Y. Cao and P.A. Montano, to be published.
3. Sulfur K-Edge XANES and EXAFS Studies of $\text{CuO}/\text{Al}_2\text{O}_3$ after Reaction with Coal Flue Gases, Y. Cao and P.A. Montano, to be published.
4. Modeling and Calculation of Chemisorption of Copper Oxide Supported on Alumina, Y.G. Hao and B.R. Cooper, to be published in Surface Science.
5. In-Situ X-Ray Studies of ZnO Sorbents Reacting with Coal Flue Gases, Y. Cao and P.A. Montano, to be published.

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REFERENCES

1. D.H. McCrea, A.J. Forney, J.G. Myers, J. Air Pollut. Control Assoc. 20, 819 (1970).
2. S.S. Pollack, W.P. Chisholm, R.T. Obermyer, S.W. Hedges, M. Ramanathan, and P.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, ed. D.C. Koningsberger and R. Prins, Chemical Analysis, Vol. 92, (1988).
5. Y. Cao and P.A. Montano, Preprints of the Fuel Division of the ACS, Vol. 35, 1409 (1990).
6. H. Krakauer and B.R. Cooper, Phys. Rev., B 16, 605 (1977).
7. N. Sahoo, S.K. Mishra, K.C. Mishra, A. Coker, T.P. Das, C.K. Mitra, L.C. Snyder, A. Glodeanu, Phys. Rev. Lett., 50, 913 (1983).
8. J.A. Pople, D.L. Beveridge, in Approximate Molecular Orbital Theory, (McGraw-Hill, New York, 1970).
9. W.J. Hehre, R.F. Stewart, and J.A. Pople, J. Chem. Phys., 51, 2657 (1969).
10. M.J. Frisch, M. Head-Gordon, H.B. Schlegel, K. Raghavachari, J.S. Binkley, C. Gonzalez, D.J. Defrees, D.J. Fox, R.A. Whiteside, R. Seeger, C.F. Melius, J. Baker, R. Martin, L.R. Kohn, J.J. Stewart, E.M. Fluder, S. Topiol, and J.A. Pople, Gaussian Inc., Pittsburgh, PA.
11. G.W. Fernando, B.R. Cooper, M.V. Ramana, H. Krakauer, and C.Q. Ma, Phys. Rev. Lett., 56, 2299 (1986).
12. C.Q. Ma, M.V. Ramana, and B.R. Cooper, J. Vac. Sci. Technol., A1, 1095 (1983).
13. C.Q. Ma, J. Krakauer, and B.R. Cooper, J. Vac. Sci. Technol., 18, 581 (1981).

14. C.Q. Ma, M.V. Ramana, B.R. Cooper, and H. Krakauer, Phys. Rev., B 34, 3854 (1986).
15. You Gong Hao, G.W. Fernando, B.R. Cooper, J. Vac. Sci. Technol., A7, 2065 (1989).
16. O.K. Anderson, Phys. Rev., B 12, 3060 (1975).
17. S.H. Vosko, L. Wilk, and N. Nusair, Can. J. Phys., 58, 1200 (1980).
18. E.A. Carter and W.A. Goddard III, J. of Catal, 112, 80 (1988); A.B. Anderson, Ch. Ravimohan and S.P. Mehandru, Surf. Sci., 183, 438 (1987).
19. C.H. Patterson, R.P. Messmer, J. Am. Chem. Soc., 111, 8059 (1989); D.R. Salahub, M.C. Zerner, ACS Symp. Ser. 394 (1989).
20. V.J. Singh, J.W. Corbett, C. Weigel, L.M. Roth, Phys. Lett., 65 A, 261 (1978); G.D. Watkins, Phys. Rev., 29, 3193 (1984); D.E. Cabell, A.H. Cowley, M.J.S. Dewar, J. Am. Chem. Soc., 103, 3290 (1981).
21. B.N. Dev. K.C. Mishra, W.M. Gibson, and T.P. Das, Phys. Rev., B 29, 1101 (1984); N. Sahoo, K.C. Mishra, and T.P. Das, Phys. Rev. Lett., 55, 1506 (1985).
22. R.W.G. Wychoff, Crystal Structures Vol. 1, (1963).
23. H. Sekiyama, N. Kosugi, H. Kuroda and T. Ohta, Bull. Chem. Soc. Japan, 59, 575-579 (1986).
24. T.A. Tyson, A.L. Roe, P. Frank and K.O. Hodgson, "Polarized Experimental and Theoretical K-edge X-ray Absorption Studies of SO₄²⁻, ClO₃²⁻, S₂O₃²⁻ and S₂O₆²⁻", to be published.
25. M.A. Khan, J. Phys. C 9, 81 (1976).
26. C. Sugiura, J. Chem. Phys. 74(1), 215 (1981).
27. K. Terakura, J. Phys. Soc. Japan, 40, 450 (1976).
28. B.C. Lippens, Structure and Texture of Aluminas, Thesis Delft, Netherlands, 1961.

29. S. Sakaki, H. Sato, Y. Imai, K. Morokuma, and K. Ohkubo, *Inorg. Chem.*, 24, 4538 (1985); D.A. Johnson and V.C. Dew, *Inorg. Chem.*, 18, 3273 (1979); G.J. Kubas, R.R. Ryan, V. McCarty, *Inorg. Chem.*, 19, 3003 (1980); G.J. Kubas, *Inorg. Chem.*, 18, 182 (1979).
30. R.M. Friedman, J.J. Freeman, F.W. Lytle, *J. Catal.*, 55, 10 (1978).
31. J. Olivier and R. Poirier, *Surf. Sci.*, 105, 347 (1981).
32. Charles C. Chang, *J. Catal.*, 53, 374 (1978).

Table 1. Characteristic energies of the XANES spectra at S K-edge of some sulfur compounds.

Sample		Energy (eV)	Transition
CuSO ₄	A	2478.38	S 1s --> a ₁ * (weak)
	B	2481.74	S 1s --> a ₂ * (strong)
	K-edge	2483.50	
	C	2490.00	d-type shape resonance
	D	2497.72	d-type shape resonance
CuS	A	2469.50	S 1s --> 3p bonding
	K-edge	2470.73	
	B	2471.25	S 1s --> 3p antibonding
	C	2475.39	shape resonance
	D	2481.74	sulfate
	E	2485.20	shape resonance
	F	2499.60	sulfate
FeS ₂	A	2471.25	S 1s --> e _g
	B	2472.64	S 1s --> S _u antibonding
	K-edge	2476.19	
	C	2479.25	shape resonance
	D	2485.50	shape resonance
	E	2490.50	shape resonance
FeS	A	2470.31	S 1s --> 3p antibonding
	K-edge	2472.54	
	B	2476.63	shape resonance
	C	2481.75	sulfate
	D	2488.00	shape resonance
	E	2498.50	sulfate

Table 2. Observed peak positions and intensities in the Cu K-edge XANES spectra of the Sorbent (5%) sample at various temperatures.

Sorbent (5% Cu)				
Temperatures (Degree C)	Peak P 8978.0eV	Peak S 8982.0eV	Peak A 8989.3eV	Peak B 8997.5eV
R.T. (Fresh)	0.0442	0.0783	0.6487	1.3518
50	0.0464	0.1477	0.6852	1.3278
120	0.0517	0.2559	0.6909	1.2882
200	0.0548	0.3356	0.7085	1.2706
300	0.0563	0.3640	0.7256	1.2588
50 (Used)	0.0520	0.2956	0.7134	1.2735

Table 3. Observed peak positions and intensities in the Cu K-edge XANES spectra of the Sorbent (7%) sample at various temperatures.

Sorbent (7% Cu)				
Temperatures (Degree C)	Peak P 8979.0eV	Peak S 8982.0eV	Peak A 8989.3eV	Peak B 8998.0eV
R.T. (Fresh)	0.0463	0.0590	0.6670	1.3260
50	0.0562	0.0826	0.7279	1.2880
100	0.0632	0.3975	0.7214	1.2416
200	0.0635	0.3986	0.7363	1.2464
300	0.0593	0.3226	0.7320	1.2556
50 (Used)	0.0543	0.2411	0.7380	1.2766

Table 4. The fitting results for the Sorbent samples at various temperatures. R1 and R2 are the fraction of Cu^+ and Cu^{++} in the sample, respectively. Norm is the χ^2 of the fit.

Sorbent (5% Cu)					
Temperatures (Degree C)	R1 (Cu_2O)	R2 (F.SB.)	Norm	Cu^+ Copper	Cu^+ Tot. Wt.
50	0.140	0.867	0.15	13.9%	0.70%
120	0.311	0.695	0.16	30.9%	1.55%
200	0.440	0.570	0.22	43.6%	2.18%
300	0.485	0.531	0.32	47.7%	2.39%
50	0.377	0.632	0.24	37.4%	1.87%

Sorbent (7% Cu)					
Temperatures (Degree C)	R1 (Cu_2O)	R2 (F.SB.)	Norm	Cu^+ Copper	Cu^+ Tot. Wt.
50	0.342	0.671	0.15	33.8%	2.37%
100	0.521	0.487	0.24	51.7%	3.62%
200	0.530	0.484	0.25	52.3%	3.66%
300	0.393	0.620	0.22	33.8%	2.72%
50	0.283	0.727	0.17	28.0%	1.96%

Table 5

Bonding Energy of "Bridge" Configurations	
Cu-hole	no bonding
Cu-Al (S bent in)	no bonding
Cu-Al (S bent away)	1.66 eV
Cu-Cu (S bent away)	8.16 eV
Al-Al (S bent away)	13.52 eV

Figure 1. Experimental set up for the sulfur K-edge measurements.

Figure 2

XANES spectra of a select number of model compounds.

Figure 3
XANES spectra of CuSO_4 , CuS , FeS , and FeS_2 .

Figure 4

EXAFS spectra of CuSO₄, CuS, FeS, and FeS₂.

Figure 5

Normalized XANES and the derivative spectra of Cu metal, pure Cu_2O , CuO , and CuSO_4 compounds.

Figure 6

Normalized XANES and the derivative spectra of the Sorbent (5%)
exposed to flue gas at various temperatures.

Figure 7

Normalized XANES and the derivative spectra of the Sorbent (7%)
exposed to flue gas at various temperatures.

Figure 8

Combination of Cu₂O and a fresh Sorbent sample spectra used to simulate the in-situ spectrum of the Sorbents exposed to flue gas.

Figure 9

Transformation rates of Cu^{++} to Cu^+ in the Sorbent samples in the presence of flue gas as functions of temperature.

Figure 10. Geometry of the models for the copper atoms located at (a) octahedral position and (b) tetrahedral position.

Figure 11. Geometry of the models for (a) the mixed surface, (b) the copper atoms covered surface and (c) the aluminum atoms covered surface.

Figure 12. Geometry of the models for the SO_2 molecule "on top of" the Cu atom (a) S-Cu bonded, (b) O-Cu bonded; (c) the SO molecule across a "bridge" of Cu-hole, (d) the SO_2 molecule across a "bridge" of Cu-Al with the sulfur atom being bent toward the surface and (e) the SO_2 molecule across a "bridge" of Cu-Al with the sulfur atom being bent away from the surface.

Figure 13. Density of the state plots of (a) the mixed surface, (b) the copper atoms covered surface and (c) the aluminum atoms covered surface.

Figure 14. Charge distribution maps of (a) the mixed surface, (b) the copper atoms covered surface and (c) the aluminum atoms covered surface.

Figure 15

Figure 16

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