

Experimental Investigations of the Interaction of SO₂ with MgO

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Abstract

High resolution adsorption isotherms, temperature programmed desorption (TPD), x-ray diffraction (XRD) and x-ray absorption near edge spectroscopy (XANES) methods were used to investigate the interaction of SO₂ with high quality MgO powders. The results of these investigations indicate that when SO₂ is deposited on MgO in monolayer quantities at temperatures near 100K both SO₃ and SO₄ species form that are not removed by simply pumping on the pre-dosed samples at room temperature. TPD and XANES studies indicate that heating of pre-dosed MgO samples to temperatures above 350 °C is required for full removal of the SO₃/SO₄ species. XANES measurements made as a function of film thickness indicate for coverages near monolayer completion that the SO₄ species form first.

Introduction

Sulfur dioxide is one of the main pollutants released into the atmosphere as a result of volcanic activity, and the burning of sulfur bearing fossil fuels in automobile engines, industrial complexes, power plants and households. The subsequent interaction of the sulfur dioxide with air and atmospheric moisture results in the formation of "acid rain" leading to the corrosion of metals and degradation of stone buildings and statuary [1]. To diminish the environmental effects of sulfur dioxide emissions one must either dissociate or remove the SO₂ from the effluent. MgO and CaO are two materials that are widely used as commercial scrubbers in industry[2]. We describe our recent investigations using adsorption isotherms, TPD, XANES and XRD investigations of the interaction of SO₂ with MgO.

Experimental Results

A novel process recently developed in our laboratory [3] was used to produce the MgO powders used in the present experiments. Transmission electron microscopy (TEM) indicates that the MgO consists of uniform cubic particles, approximately 2000Å on a side with predominantly the (100) surface exposed(see fig.1). The quality of the substrates was judged using a methane adsorption isotherm performed volumetrically at 77 K, a typical example of which is shown in Fig.2. The isotherms are performed using an automated isotherm apparatus which has been described elsewhere[4]. Typical adsorption areas of about 10 m²/gm are obtained.

In order to quantify the adsorption characteristics of sulfur dioxide with the

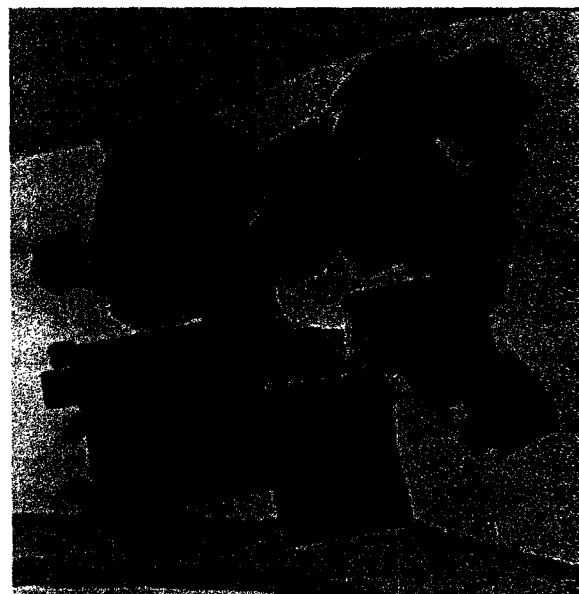


Fig. 1 TEM image of MgO Powder. Largest cube is about 2000Å on an edge.

MgO(100) surfaces we performed adsorption isotherms. Before use the MgO powder was heat-treated in a quartz oven *in vacuo* at about 950°C for about 36 hours and subsequently transferred in an inert-gas filled glove box into a sample cell that was mounted on a closed-cycle refrigerator. Fig.3 shows the typical adsorption behavior of SO₂ on MgO at 200 K when two successive isotherms are performed. The second SO₂ isotherm was performed after the sample was warmed to room temperature and simultaneously evacuating the adsorption cell with a turbo pumped based pumping station (base pressure ~10⁻⁷ torr). Notice that during the second adsorption isotherm there is nearly a fifty percent reduction in the apparent amount of SO₂ adsorbed.

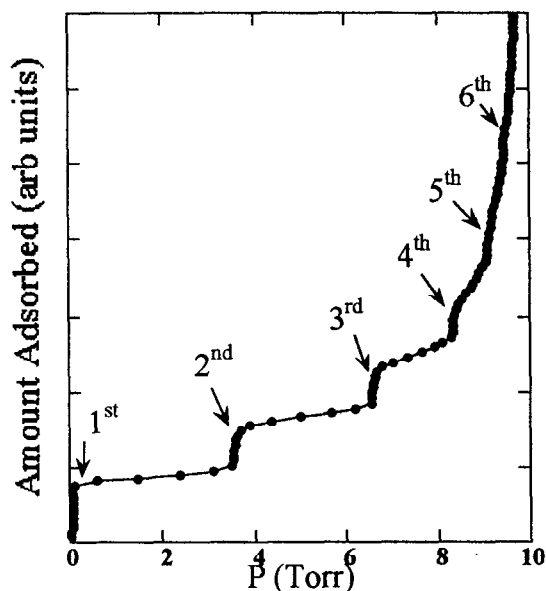


Fig. 2 CH₄ on MgO isotherm at 77K.

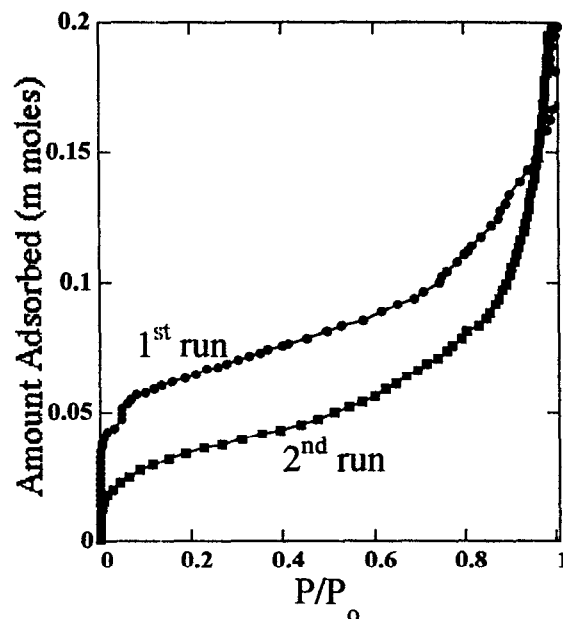


Fig. 3 SO₂ on MgO isotherm at 200K.

In order to understand the isotherm results shown in fig. 3 temperature programmed desorption of the SO₂ was performed. A MgO sample predosed with about 2 layers of SO₂ near 77K was warmed to room temperature and then transferred in an argon filled glove bag to a quartz sample cell. The quartz cell containing the SO₂ loaded MgO was then placed inside of a furnace. The evolution of mass products from the cell was monitored using a quadrupole mass spectrometer while a linear temperature ramp was applied. Fig. 4 illustrates the SO₂ signal (64 amu) as a function of time (temperature noted). It is quite clear that an increase in the SO₂ evolution starts at temperatures above of 100°C that decreases above about 350°C. This clearly establishes that significant quantities of SO₂ are still adsorbed on the MgO (100) surface until well above 100°C reconciling the observed decrease in the adsorption capacity shown in fig. 3 above.

To determine the chemical nature of the adsorbed SO₂ species XANES at the sulfur K-edge was performed on MgO samples loaded at 77K with about two monolayers of SO₂. The samples were handled in the following way. First, the SO₂ loaded MgO was warmed to room temperature and evacuated (similar to the way the isotherm samples were handled). A small aliquot of the dosed sample was removed from the quartz cell in an argon filled glove bag and set aside for XANES analysis. The quartz cell containing the remaining sample was then heated to 100°C while being evacuated. Once the sample reached 100°C it was quenched to room temperature and another aliquot was removed in a glove bag and set aside for analysis. This process was repeated at 100°C increments up to 400°C. The five aliquots were examined using XANES on the X19-A beamline at the NSLS in the "fluorescence yield mode" with a Stern-Heald-Lytle de-

tection scheme. Spectral locations of the S, SO₃ and SO₄ species were calibrated using standards ZnS, NaSO₃ and MgSO₄. The results are plotted in fig. 5. It is clear that both SO₃ and SO₄ species are present on the MgO (100) surface with the SO₄ species being the most stable (i.e. present

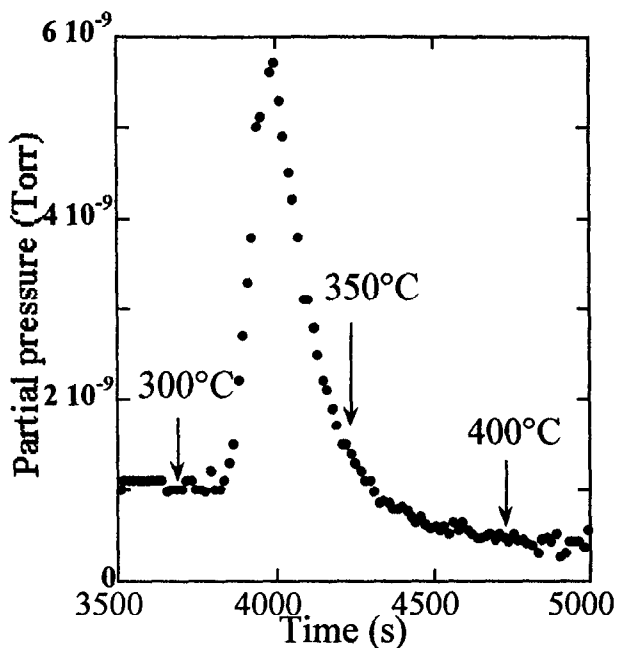


Fig. 4 TPD of monolayer SO₂ on MgO. Approximate temperature indicate arrows.

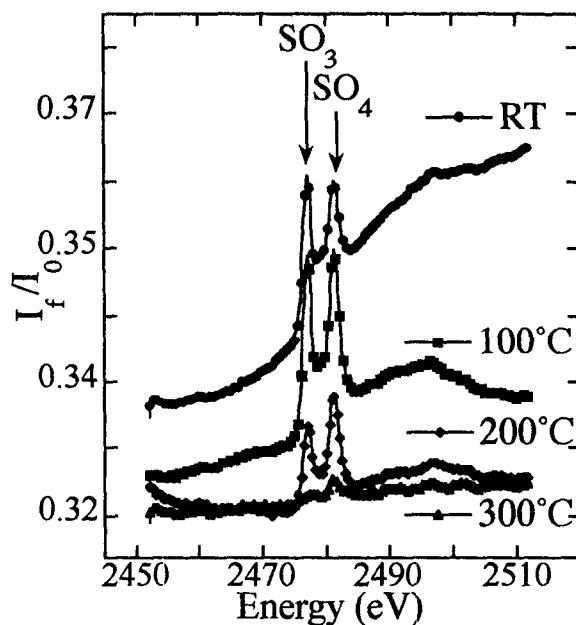


Fig. 5 Temperature dependence of Sulfur K-edge XANES for ~2 monolayer SO₂ on MgO.

until the highest temperatures). Furthermore, the temperature dependence of the XANES signals is consistent with the TPD results shown in fig. 4. The experiment described above monitors the relative concentration of SO₃/SO₄ species on the MgO as a function of temperature but, it is also important to determine the coverage dependence. Hence, another set of SO₂ dosed MgO samples were prepared by depositing one, two and three layers of SO₂ on the MgO at 77K. The SO₂ loaded samples were warmed to room temperature and evacuated as before. Fig. 6 shows the

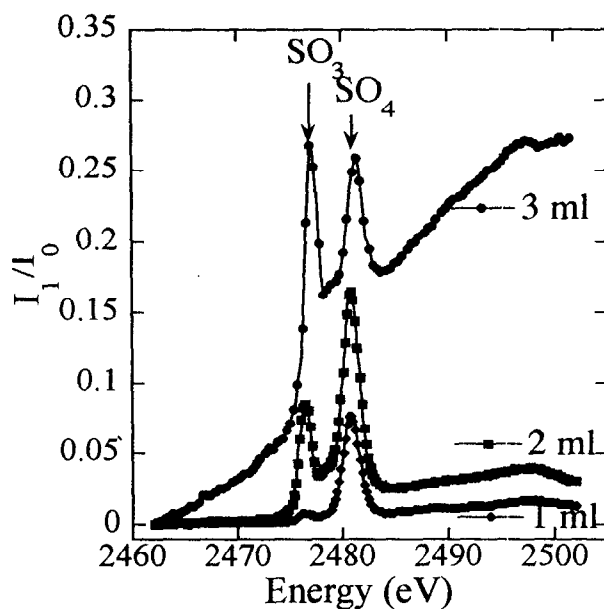


Fig. 6 Coverage dependence of Sulfur K-edge XANES at Room Temperature for SO₂ on MgO

resulting XANES spectra. Once again, these results establish the presence of both SO_3 and SO_4 on $\text{MgO}(100)$ and furthermore, that the SO_4 species are the first to form.

Powder x-ray diffraction (XRD) has also been used to study the adsorption of SO_2 on MgO . These measurements were performed on the Chemistry Dept. beamline X7B at the NSLS. These measurements were performed using a highly collimated x-ray beam and a MAR 345 image plate detector. Fig. 7 shows the general experimental arrangement. Difference patterns (gener

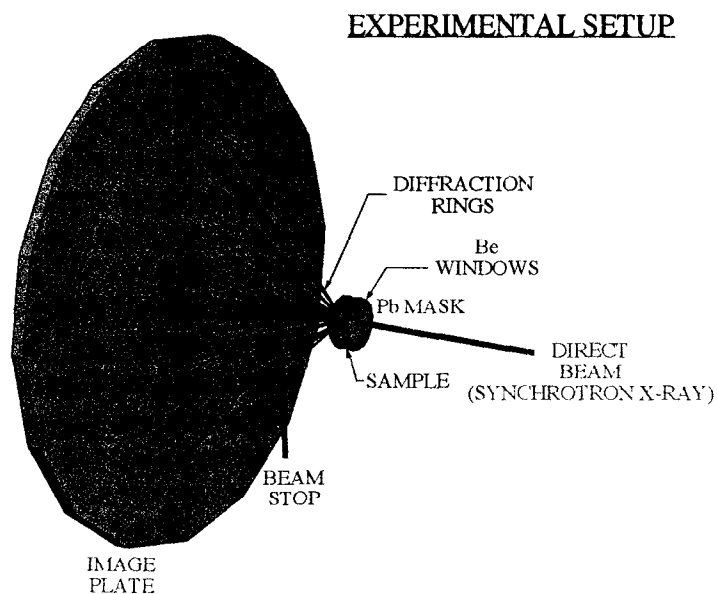


Fig. 7 Schematic diagram of X-ray Diffraction Setup for SO_2/MgO studies on X7b at NSLS.

ated by subtracting a diffraction pattern of a clean MgO powder from one of the same sample after SO_2 is adsorbed) are presented in fig. 8 for two different SO_2 coverages indicated by the arrows labelled "A" and "B" inset from fig. 3 above. Several comments can be made concerning

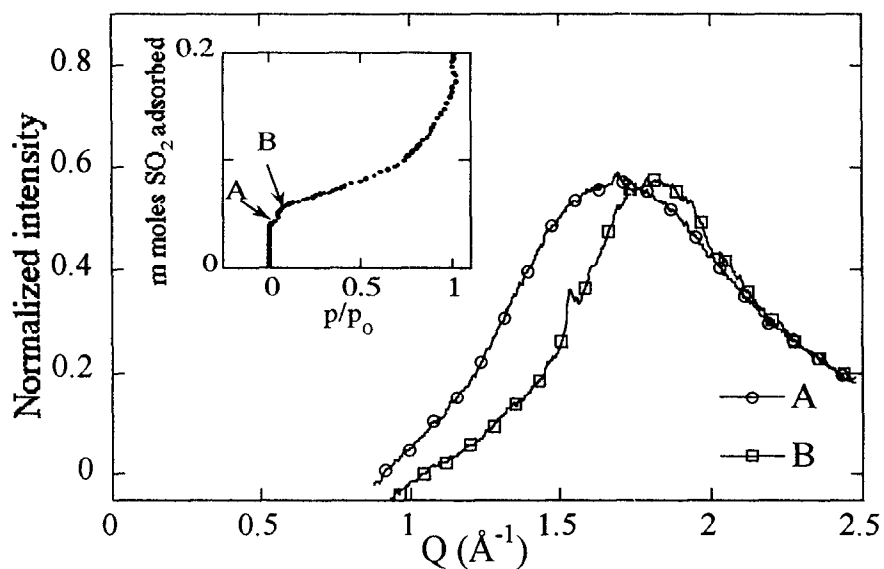


Fig. 8 X-ray diffraction profile from SO_2 film adsorbed on MgO at two different coverages near monolayer completion (inset identifies location on adsorption isotherm).

the diffraction measurements. First the broad diffraction feature recorded between $1.25\text{-}2.35 \text{ \AA}^{-1}$ in Q indicates that no long range ordered appears in the SO_2 films. Second, the movement of the peak of the diffraction pattern to higher Q values with increasing SO_2 coverage indicates that the mean density of the adsorbed species increases. Third, no evidence for the formation of magnesium sulphate or another sulfur based magnesium compounds is recorded. These diffraction data are still in the preliminary state and future studies will be aimed at obtaining a more comprehensive set of data as a function of temperature and SO_2 coverage.

Discussion

Numerous experimental studies of the interaction of SO_2 with MgO have been performed. The EPR work of Lin and Lunsford [5] found that SO_2 is photochemically oxidized to SO_3^- on the surface of MgO in the presence of water vapor while infrared work by Bensitel *et al* [6] found that bulk-like sulfate (SO_4^-) surface species were formed on a high surface area MgO . Waqif *et al.* [7] have also examined the interaction of SO_2 with MgO and find that sulfite, SO_3 , species are formed and Schoonheydt and Lunsford [8] reported that sulfate (SO_4) species form upon heating. The interaction of SO_2 with acid and basic sites of clean, fully dehydroxylated MgO have been investigated by Pacchioni, Clotet and Ricart [9] using *ab initio* cluster model calculations. They find that SO_2 adsorbs molecularly at five-coordinated Mg^{2+} sites and evidence for SO_3 formation at basic O^{2-} ions. However, they rule out the possibility of the formation of SO_4 formation at an unreconstructed MgO surface.

Fig. 9 schematically illustrates how the formation of both SO_3 and SO_4 can take place on the MgO (100) surface. Note that the SO_4 species formation requires that the sulfur sits in a bridging location between adjacent surface oxygen atoms (i.e. with the C_{2v} axis parallel to the surface normal). However, the SO_4 formation requires either the oxygen-oxygen distance at the surface of the MgO be less than that found in the bulk lattice or that a distorted sulfate species forms such that the sulfur-oxygen bond length is greater than that found in the isolated molecule.

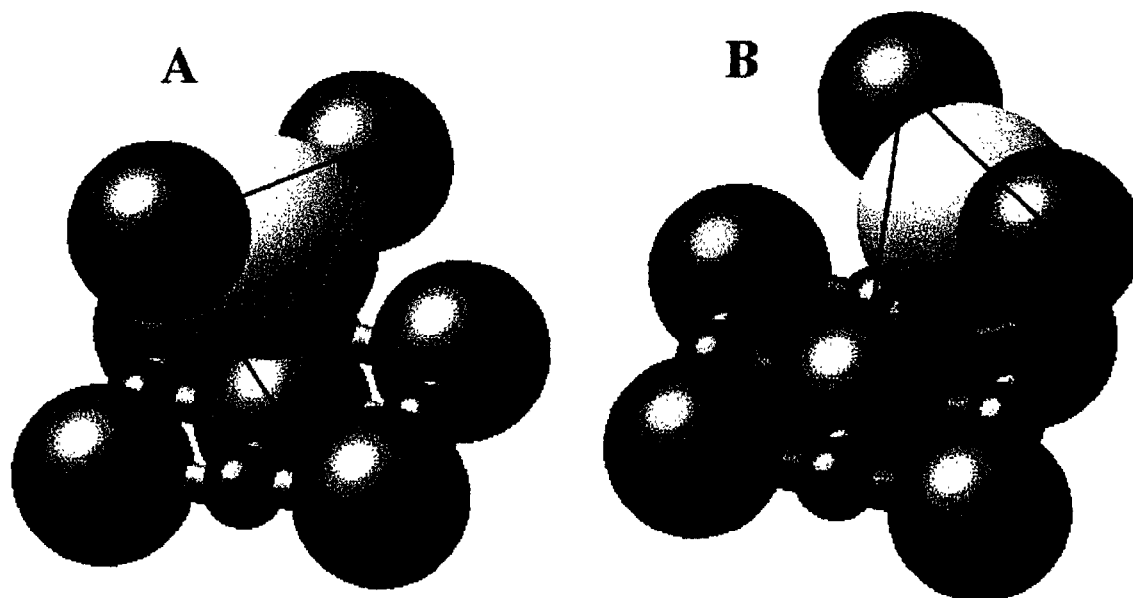


Fig. 9 Schematic view of possible configurations for SO_2 on MgO for SO_3 (A) and SO_4 (B) species. Sulfur, Oxygen and Magnesium atoms in order of size from largest to smallest.

Conclusion

As we have indicated above understanding the interaction of SO₂ with MgO is an important step in identifying better ways to remediate its environmental impact. We have demonstrated that exposure of monolayer quantities of SO₂ to MgO results in the formation of surface adsorbed SO₃ and SO₄ species that are stable to temperatures in excess of 300°C. No evidence of atomic sulfur deposition on the MgO surface is recorded during the sulfite/sulfate decomposition process. Future work will be aimed at understanding what effects coadsorption of other simple molecules like water and carbon monoxide and the addition of controlled amounts of dopants to the MgO powders have on the adsorption and dissociation properties of SO₂.

Acknowledgement

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