

Chemistry of SO₂ on Model Metal and Oxide Catalysts: Photoemission and XANES Studies

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High-resolution synchrotron based photoemission and x-ray absorption spectroscopy have been used to study the interaction of SO₂ with a series of metals and oxides. The chemistry of SO₂ on metal surfaces is rich. At low coverages, the molecule fully decomposes into atomic S and O. At large coverages, the formation of SO₃ and SO₄ takes place. The following sequence was found for the reactivity of the metals towards SO₂: Pt ≈ Rh < Ru < Mo << Zn, Sn, Cs. Alloying can be useful for reducing the chemical affinity of a metal for SO₂ and controlling S poisoning. Pd atoms bonded to Rh and Pt atoms bonded to Sn interact weakly with SO₂. In general, SO₂ mainly reacts with the O centers of metal oxides. SO₄ is formed on CeO₂ and SO₃ on ZnO. On these systems there is no decomposition of SO₂. Dissociation of the molecule is observed after introducing a large amount of Ce³⁺ sites in ceria, or after depositing Cu or alkali metals on the oxide surfaces. These promote the catalytic activity of the oxides during the destruction of SO₂.

1. INTRODUCTION

Sulfur dioxide is one of the major air pollutants released to the atmosphere as a result of volcanic activity and the combustion of fuels in power plants, factories, houses and transportation [1]. After its oxidation and reaction with water in the atmosphere, it is responsible for the acid rain that leads to the corrosion of many metals. Moreover, the catalytic activity of most transition metals is drastically reduced by the presence of SO₂ or other sulfur containing compounds at an extremely low concentration in the feed.

To minimize the negative effects of SO₂, one can follow two different approaches. The first is to improve the sulfur tolerance of catalytic processes currently used in the industry by working with catalysts that are less sensitive to sulfur poisoning. The alloying of metals can be useful in this respect [2]. The second approach involves the removing or destruction of SO₂ and the design of catalysts with a high efficiency for DeSO_x reactions. Oxide-based catalysts are frequently used to accomplish this goal [1]. In an ongoing project we are investigating the surface chemistry of SO₂ on surfaces of metals and oxides using synchrotron-based high-resolution photoemission and x-ray absorption near-edge spectroscopy (XANES).

2. EXPERIMENTAL

The high-resolution photoemission experiments described in section 3 for single crystals and films of metals and oxides were carried out in a ultrahigh-vacuum (UHV) chamber that is part of the U7A beamline in the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory [3,4]. The chamber is equipped with a hemispherical electron-energy analyzer with

multichannel detection. The S 2p photoemission spectra were collected using beam photon energies of 240 and 260 eV and the overall instrumental resolution was 0.3-0.4 eV.

The experiments with bulk powders of metal oxides were performed in a RXM-100 instrument from Advanced Scientific Designs. XPS spectra for the pure and sulfided powders were obtained using a UHV chamber fitted with a Mg K α x-ray source and a hemispherical electron energy analyzer. The S K-edge XANES spectra were collected at the NSLS on beamline X19 in the "fluorescence-yield mode" using a Stern-Heald-Lytle detector [5]. The energy resolution was better than 0.5 eV.

3. RESULTS

3.1 Reaction of SO₂ with monometallic and bimetallic surfaces

The chemistry of sulfur dioxide on Pt(111) [3], Rh(111) [4], Ru(001) [6] and Mo(110) [7] was examined at temperatures between 100 and 500 K. On all these single crystal surfaces, SO₂ dissociates (SO_{2,s} → S_s + 2O_s) or transforms into SO₃ and SO₄ species (for example, see Figure 1). No evidence was found for the existence of SO as a stable product. The reactivity of the metals

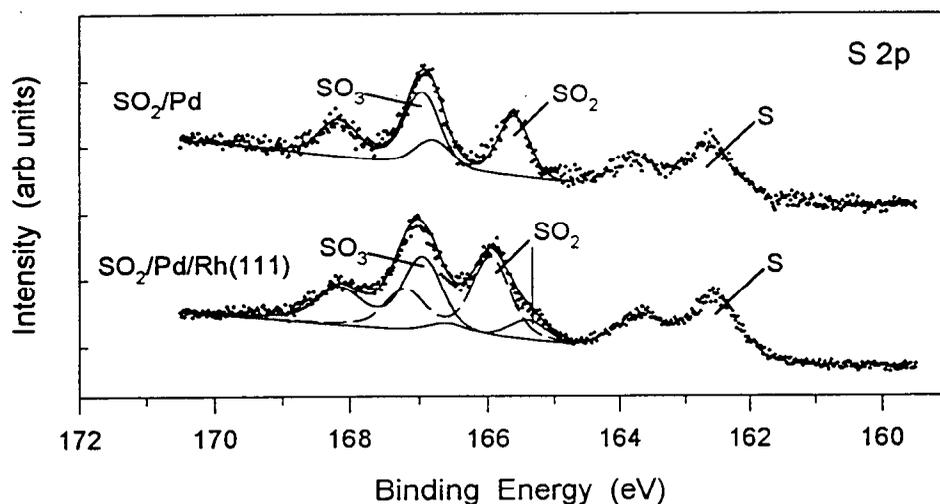


Fig 1 S 2p photoemission spectra for the adsorption of SO₂ on polycrystalline Pd and a Pd/Rh(111) surface, $\theta_{Pd} = 0.5$ ML, at 300 K. Photon energy = 260 eV.

increased following the sequence: Pt \approx Rh < Ru < Mo. Pt and Rh dissociate SO₂ at temperatures above 200 K, whereas Ru and Mo do this at 100 K. It was found that adsorption geometries in which SO₂ is di-coordinated via O,O or S,O are the most probable precursors for dissociation of the molecule.

On polycrystalline surfaces of Zn [8], Sn [3] and Cs [9], sulfur dioxide displayed an extremely high reactivity, much larger than that seen on transition metal surfaces. On the s,p metals, SO₃/SO₄ coverages well above a monolayer were relatively easy to produce with the sulfur species penetrating into the bulk of the samples. On these systems [3,8,9], SO₃ and SO₄ were formed as a result of the reaction of SO₂ with oxygen adatoms



or by disproportionation of chemisorbed SO₂



Chemisorption experiments on well-defined bimetallic surfaces reveal that metal-metal bonding can have a drastic impact on the chemical affinity of a metal for SO_2 and other sulfur-containing molecules (S_2 , H_2S and thiophene) [2,3,4,10]. A $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ\text{-Sn/Pt}(111)$ alloy is much less reactive towards SO_2 than polycrystalline tin or clean $\text{Pt}(111)$ [3]. The redistribution of charge that accompanies the formation of Pt-Sn bonds reduces the electron-donor ability of Pt and Sn, and both metals are not able to respond in an effective manner to the presence of SO_2 [3]. In a similar way, a Pd monolayer supported on $\text{Rh}(111)$ is less chemically active than pure Pd or $\text{Rh}(111)$ for the dissociation of SO_2 [4]. A very large drop in the reactivity of Pd can be expected when this metal is bonded to s,p or early-transition metals [4]. All these results together indicate that bimetallic bonding can be a useful "tool" for increasing the sulfur tolerance of Pt and Pd based catalysts [2,3,4,10].

3.2 Reaction of SO_2 with oxide surfaces

Zinc oxide and ceria can be useful in the removal (as sorbents) or destruction (as catalysts) of the SO_2 molecules generated as side products in many chemical processes and the burning of fuels [1]. In principle the chemistry of SO_2 on a metal oxide surface can be complex, since the molecule can interact with the metal and/or O centers [11]. On polycrystalline surfaces of ZnO and CeO_2 , sulfur dioxide mainly interacts with O sites of the surfaces forming SO_3 and SO_4 species [12,13]. Figure 2 compares S 2p photoemission results for the adsorption of sulfur dioxide on metallic cerium, and several ceria films. For these ceria systems, results of core and valence

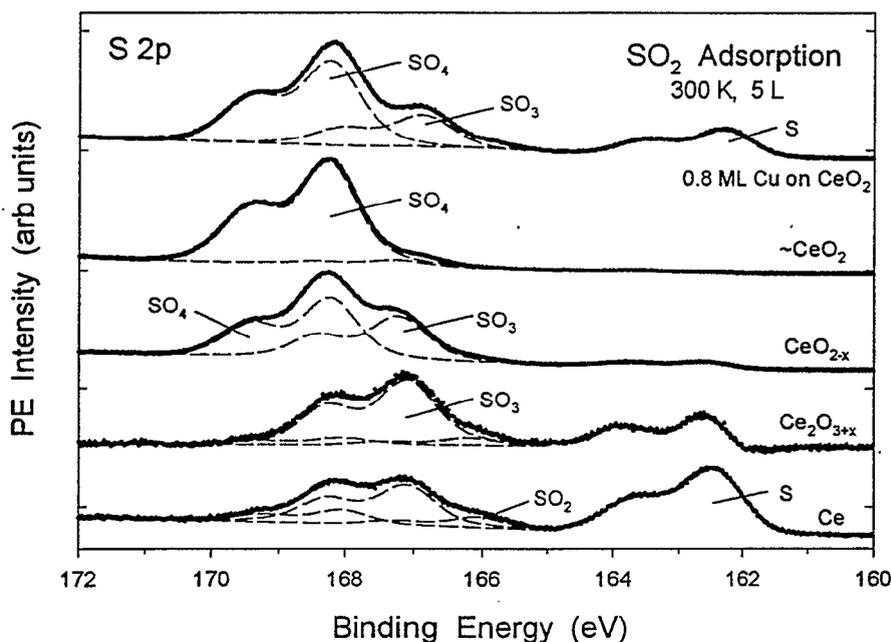


Fig 2 S 2p photoemission spectra for the adsorption of 5L of SO_2 on polycrystalline Ce, $\text{Ce}_2\text{O}_{3+x}$, CeO_{2-x} , CeO_2 and Cu/CeO_2 at 300 K. Photon energy = 260 eV.

photoemission show clear differences in the oxidation state of cerium [12]: from 0 in metallic Ce, to mainly +3 ($\text{Ce}_2\text{O}_{3+x}$) or +4 (CeO_{2-x}), and finally to only +4 in CeO_2 . From the trends in Fig 2 one can reach two important conclusions. First, as the average oxidation state of Ce increases, the ability of the system to dissociate S-O bonds clearly diminishes. Second, the introduction of O vacancies in the CeO_2 system favors the formation of SO_3 at the expense of SO_4 [12]. The second conclusion is also consistent with XANES data for the reaction of SO_2 with bulk powders. In Figure 3, the S K-edge spectrum for the SO_2/CeO_2 system exhibits a single peak at ~ 2482 eV. This peak position matches very well that expected for SO_4 [5,11], and is bigger than those reported for chemisorbed SO_2 (~ 2473.5 eV [11]) or SO_3 (~ 2478 eV [5,11]) on oxides. For adsorption of SO_2 on a ceria powder with O vacancies, CeO_{2-x} , one sees a decrease in the signal for SO_4 and the appearance of a peak for SO_3 around 2478 eV [5,11].

Ceria promoted/doped with copper is an active catalyst for the reduction of SO_2 by CO [14]



In this process the SO_2 is completely decomposed and oxygen is removed from the system by formation of CO_2 . The results in Figure 2 indicate that ceria is able to dissociate SO_2 only when Ce atoms with a low oxidation state are available. This is due to the fact that the metal needs to donate electrons into the LUMO of SO_2 (S-O anti-bonding) in order to be able to dissociate the molecule [3]. Since Ce is relatively easy to oxidize at low temperatures [12], reaction (3) can be efficient only at high temperatures (which facilitate the removal of oxygen from the system [14]) and with a CO/SO_2 ratio in the feed ≥ 2 . When Cu atoms are added to CeO_2 new active sites for the destruction of SO_2 are created, as can be seen in the top of Figure 2, and the performance of

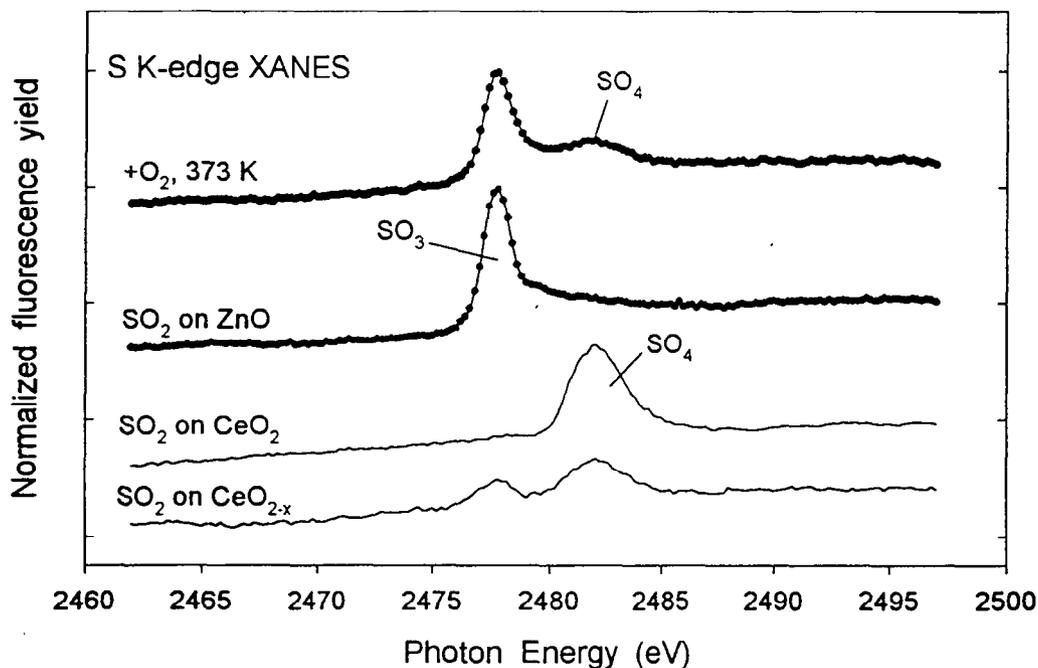


Fig 3 S K-edge XANES spectra for $\text{SO}_2/\text{CeO}_{2-x}$, SO_2/CeO_2 , SO_2/ZnO (dotted), $\text{SO}_2/\text{ZnO} + \text{O}_2$ (dotted). The oxide powders were exposed to SO_2 at 323 K.

the catalyst substantially improves [14]. From a practical viewpoint, the use of copper introduces two big advantages. First, copper does not exhibit a tendency to adopt high oxidation states as cerium does [12]. Second, it is much easier to reduce copper oxides with CO than to reduce ceria [12,14]. Thus, Cu sites eventually will remain catalytically active for a longer period of time than Ce sites [12].

For the adsorption of SO₂ on powders of ZnO (Fig 3) or a ZnO(000 $\bar{1}$)-O single crystal (Fig 4), SO₃ is the main reaction product. Formation of SO₄ was observed after exposing the SO₂/ZnO systems to a flow of O₂ (see Fig 3). On ZnO, the large O-O separation (~3.25 Å) makes difficult the formation of sulfate species using the oxygen from the lattice [8]. This is not the case on ceria (O-O separation ~ 2.70 Å), which is also an oxygen rich oxide. The adsorption of SO₂ on oxides that have an oxygen/metal ratio larger than one (TiO₂, Fe₂O₃, V₂O₃, CeO₂) mainly produces SO₄, whereas on oxides with an oxygen/metal ratio equal to one (MgO, BaO, NiO, TiO, ZnO) SO₃ dominates [13]. Our results indicate that ZnO is good as a sorbent for SO₂ but not as a catalyst for reaction (3) or the Claus process:



The addition of an alkali metal can improve the performance of ZnO as a catalyst for the removal of sulfur dioxide. The data for the adsorption of SO₂ on ($\sqrt{3}\times\sqrt{3}$)-K/ ZnO(000 $\bar{1}$)-O and ($\sqrt{3}\times\sqrt{3}$)-Cs/ ZnO(000 $\bar{1}$)-O surfaces show that the alkali adatoms promote the cleavage of S-O bonds (see Fig 4). Several sulfur species (S, SO₃, SO₄) coexist on the alkali promoted surfaces but only SO₃ is present on the pure ZnO(000 $\bar{1}$)-O system. The supported alkali atoms are in a partially ionic state (K^{δ+}, Cs^{δ+}), but they are still able to promote the performance on ZnO in desulfurization

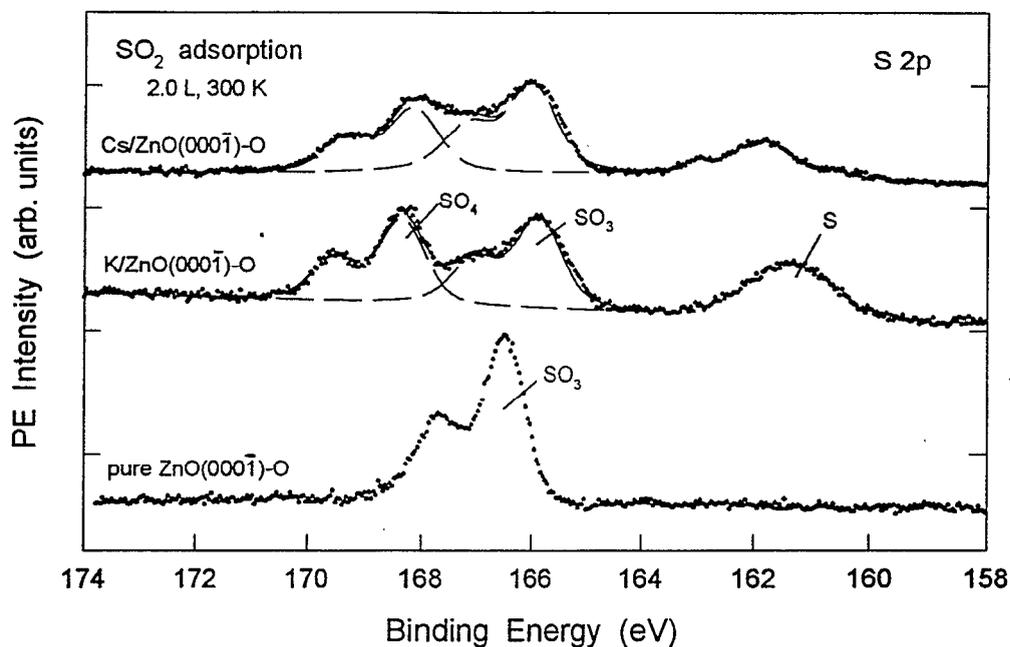


Fig 4 S 2p photoemission spectra for the adsorption of 2L of SO₂ on pure ZnO(000 $\bar{1}$)-O, ($\sqrt{3}\times\sqrt{3}$)-K/ ZnO(000 $\bar{1}$)-O and ($\sqrt{3}\times\sqrt{3}$)-K/ ZnO(000 $\bar{1}$)-O at 300 K. PE= 260 eV.

processes [15]. A simple model based on perturbation theory and orbital mixing is able to explain this behavior [15,16].

4. CONCLUSIONS

Synchrotron based photoemission and XANES are very useful for studying the reaction of SO₂ with metal and oxide surfaces. The chemistry of SO₂ on metal surfaces is rich. At low coverages, the molecule fully decomposes into atomic S and O. At large coverages, the formation of SO₃ and SO₄ takes place. The following sequence was found for the reactivity of the metals towards SO₂: Pt ≈ Rh < Ru < Mo ≪ Zn, Sn, Cs. Alloying can be useful for reducing the chemical affinity of a metal for SO₂ and controlling sulfur poisoning. Pd atoms bonded to Rh and Pt atoms bonded to Sn interact weakly with sulfur dioxide.

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Acknowledgement

Work supported by the US Department of Energy (DE-AC02-98CH10886), Office of Basic Energy Sciences, Chemical Science Division and made possible by Laboratory Directed Research and Development Funding (LDRD99-62).

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