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Chemistry of SO₂ and NO₂ on ZnO(0001)-Zn and ZnO powders: changes in reactivity with surface structure and composition

José A. Rodríguez*, Tomas Jirsak, Sanjay Chaturvedi, Joseph Dvorak

Department of Chemistry, Brookhaven National Laboratory, Upton, NY 11973, USA

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Abstract

Synchrotron-based high-resolution photoemission and X-ray absorption near-edge spectroscopy (XANES) have been used to study the interaction of SO₂ and NO₂ with ZnO(0001)-Zn and polycrystalline surfaces of zinc oxide (films and powders). Important differences are observed when comparing the chemical behavior of the adsorbates on these oxide surfaces. These differences are in part a consequence of changes in structural properties (flat versus rough surfaces), but in some cases they clearly originate in variations in surface composition (zinc ↔ adsorbate versus oxygen ↔ adsorbate interactions). For example, the Zn-terminated (0001) crystal face of ZnO is much less reactive towards SO₂ than polycrystalline ZnO. On ZnO(0001)-Zn and polycrystalline ZnO, the Zn ↔ SO₂ bonding interactions are weak. Adsorption of SO₂ on Zn sites was seen only at temperatures below 200 K. In contrast, the SO₂ molecules react readily with O sites of Ar⁺ sputtered ZnO(0001)-Zn or polycrystalline ZnO forming very stable SO₃ species. Due to its radical nature, adsorbed NO₂ is more chemically active than SO₂. After dosing nitrogen dioxide to ZnO(0001)-Zn at 100 K, chemisorbed NO₂ and NO₃ coexists on the surface. A partial NO_{2, ads} → NO_{3, ads} transformation is observed from 150 to 300 K. The data for the NO₂/ZnO(0001)-Zn system clearly prove that large quantities of NO₃ can be formed on metal sites of an oxide surface as a consequence of partial decomposition or disproportionation of NO₂. The routes for the formation of SO₃ and NO₃ on ZnO can be different, but these species have in common a high stability and decompose at temperatures well above 500 K. Thus, ZnO powders can be useful as sorbents in DeSO_x and DeNO_x operations. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Nowadays, a large effort in environmental catalysis is focused on reducing the content of sulfur and nitrogen oxides in the atmosphere [1]. NO₂ and SO₂ are common air pollutants produced during the combustion of fuels in automotive engines, factories and

power plants [2]. SO₂ results from the burning of sulfur-containing impurities present in all oil and coal derived fuels. On the other hand, NO₂ is produced by the thermal fixation and oxidation of nitrogen in combustion operations that use air as an oxidant. In our industrial society, there is a clear need to develop methods with a high efficiency for the removal or destruction of SO₂ (DeSO_x processes) and NO₂ (DeNO_x processes) [1–3]. Metal oxides can be useful in this respect [1,3–5]. In several chemical and petrochemical processes, sulfur-containing molecules are removed

* Corresponding author. Tel.: +1-631-3442246;

fax: +1-631-3445815.

E-mail address: rodriguez@bnl.gov (J.A. Rodriguez).

from the feedstream by adsorption on a bed of ZnO [3,4]. Zinc oxide is able to catalyze the reduction of nitrogen dioxide by alkanes [5].

In this article, we use synchrotron-based high-resolution photoemission to study the chemistry of SO₂ and NO₂ on a well-defined ZnO(0001)-Zn single crystal and compare it to results for adsorption on polycrystalline surfaces of zinc oxide (films and powders). Our main objective here is to examine possible changes in chemical reactivity with surface structure and composition. A priori, reactive molecules like sulfur and nitrogen dioxide can interact with the metal (i.e. chemisorbed SO₂ and NO₂) or oxygen centers (i.e. SO_{2, gas} + nO_{lattice} → SO₃/SO_{4, ads} or NO_{2, gas} + O_{lattice} → NO_{3, ads}) of an oxide surface. Previous studies have examined the adsorption of these molecules on well-defined oxide surfaces which expose either oxygen centers or a combination of oxygen and metal centers: ZnO(0001)-O [6], TiO₂(110) [7,8], TiO₂(100) [9], Ti₂O₃(1012) [10], Fe₂O₃(0001) [11], V₂O₃(1012) [12], V₂O₅(001) [13], NiO(100) [14] and MgO(100) [15,16]. An study of the interaction of SO₂ with ZnO(0001)-Zn is interesting because this surface exposes only coordinatively unsaturated metal centers (see Fig. 1), making it difficult the formation of SO₃ and NO₃ by direct interaction with oxygen from the ZnO lattice. This facilitates a detailed study of the chemistry of SO₂ and NO₂ on the Zn²⁺ cations, and by comparison to reported results for other systems one can establish the relative importance of metal ↔ adsorbate and oxygen ↔ adsorbate interactions on an oxide substrate. It is known that the ZnO(0001)-Zn surface is chemically active for the dissociation of H₂S

[17,18] and the adsorption of many small molecules (CO, NH₃, H₂O, HCOO, ethylene, benzene, etc.) [19,20].

2. Experimental methods

2.1. Work with ZnO(0001)-Zn and ZnO films

The photoemission experiments for the adsorption of SO₂ and NO₂ on ZnO(0001)-Zn and polycrystalline surfaces of ZnO were carried out in a conventional ultrahigh vacuum (UHV) chamber at the U7A beamline of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory [6]. The UHV chamber is fitted with a hemispherical electron energy analyzer with multichannel detection, instrumentation for low-energy electron diffraction (LEED), and a quadruple mass spectrometer. The S 2p spectra were recorded using a photon energy of 260 eV, whereas the deeper N 1s core level was taken with a photon energy of 480 eV. During the photoemission experiments we did not observe charging of the oxide samples, in agreement with the behavior found in previous works for ZnO [21–23].

The mounting of the ZnO(0001)-Zn crystal in the UHV chamber was done following the procedure described in [23]. The ZnO(0001)-Zn sample was mechanically attached to a flat Ta plate using four 0.25 mm Ta wires [23]. The Ta plate could be resistively heated to 950 K and liquid-nitrogen cooled to 100 K. Temperatures were measured by using a type C thermocouple located in one edge of the Ta plate and ZnO crystal. Small errors in the temperature measurements were corrected by comparing to the known desorption temperatures for multilayers of formic acid (~195 K) and formate decomposition (~575 K) [23]. To allow thermal equilibration between the ZnO(0001)-Zn crystal and the Ta support, heating was done at a rate of ~1 K/s and the sample was hold at the final temperatures for a period of ~1 min. The Zn-terminated (0001) surface was distinguished from the O-terminated (0001) surface by etching in 5% HCl [22] and chemisorption tests [19]. The cleaning of the ZnO(0001)-Zn sample involved cycles of argon ion-bombardment (700 eV) and annealing in vacuum to 850 K [23]. This cleaning procedure resulted in a contamination level below

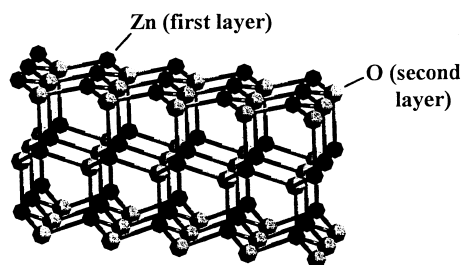


Fig. 1. Representation of the (0001) Zn-terminated face of zinc oxide. A first layer of zinc atoms (dark spheres) is followed by a second layer of oxygen atoms (grey spheres).

the level of detection of photoemission and produced surfaces with a good (1×1) LEED pattern.

In this work, films of ZnO (greater than 10 layers in thickness) were grown on clean Pt(1 1 1) or Rh(1 1 1) substrates using procedures described elsewhere [24,25]. In short, Zn was vapor-deposited (resistive heating of a W wire wrapped with an ultrapure Zn wire) under an O_2 atmosphere (1×10^{-6} Torr) on the Pt or Rh support at 100 K. This was followed by heating of the sample (~ 1 K/s) to 700 K in the presence of 1×10^{-5} Torr of O_2 . Following this methodology one gets quasi-layer-by-layer growth, and the ZnO films are polycrystalline with electronic properties and a phonon structure that are identical to those of bulk zinc oxide [26,27]. The Pt(1 1 1) or Rh(1 1 1) substrate was mounted in a manipulator that allowed resistive heating to 1300 K and liquid-nitrogen cooling to 100 K. A W-5%Re/W-26%Re thermocouple attached to the back of the crystals was used to measure the temperature.

SO_2 and NO_2 were dosed to ZnO(0001)-Zn and the polycrystalline films of ZnO through glass capillary array dosers. The gas exposures are based on the ion gauge reading and were not corrected for the capillary array enhancement.

2.2. Work with ZnO powders

The experiments for the adsorption of SO_2 or NO_2 on bulk powders of zinc oxide (Aldrich, 99.9% purity) were carried out in a RXM-100 instrument from Advanced Scientific Designs. Before exposure to the adsorbates, the ZnO powders were heated at 650 K under vacuum for 20 min to induce the desorption of any OH groups that could be present on the surface. This was followed by “oxidation” of the samples under a 30%- O_2 /70%- N_2 mixture (500 Torr, 15 min) at 500 K. Such a procedure led to powders that exhibited the typical O 1s XPS [6,28], Zn LMM Auger [28], and O K-edge XANES [29] spectra of ZnO. The ZnO powders were exposed to SO_2 or NO_2 in a reaction cell (“batch-reactor mode”) at 323 K for 15 min with constant gas pressures of 400–500 Torr. The S K-edge XANES spectra were recorded at the NSLS on beamline X19A in the “fluorescence-yield mode” using a Stern–Heald–Lytle detector [30,31]. The energy resolution was better than 0.5 eV. Beamline U7A of the NSLS was used to collect the N K-edge data for the

NO_2 /ZnO systems. These spectra were taken in the “electron-yield mode” by using a channeltron multiplier located near the sample surface and the energy resolution was close to 0.3 eV.

3. Results

3.1. Sulfur dioxide adsorption

Fig. 2 shows S 2p photoemission spectra acquired after dosing SO_2 to a ZnO(0001)-Zn surface at 100 K. A dose of 0.11 produces a doublet in the S 2p region (168–166 eV) that indicates the presence of a small amount of SO_3 on the oxide surface [6,15]. Since there is no sulfur deposition, the SO_3 must be formed by

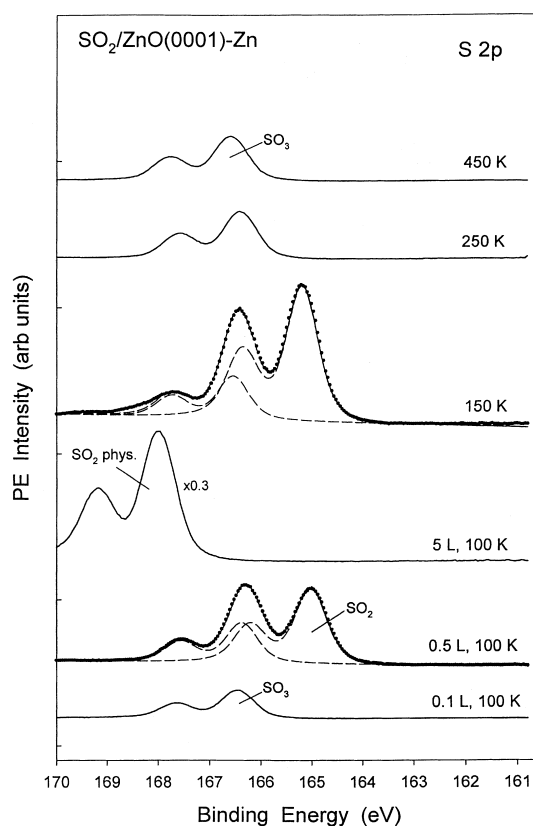


Fig. 2. S 2p photoemission data for the adsorption of SO_2 on ZnO(0001)-Zn at 100 K. Upon dosing SO_2 (0.1, 0.5 and 5 L), the sample was heated to 150, 250 and 450 K. All the spectra were acquired using a photon energy of 260 eV.

reaction of SO_2 with O centers that are near defect sites of the surface:

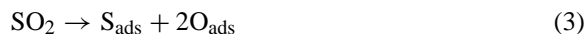


Other possible source is the disproportionation of SO_2 :



on Zn sites around the steps. Reaction (2) is known to occur on metallic Zn at very low temperatures [32], but it requires a significant coverage of SO_2 on the surface and this is not seen in Fig. 2 before the production of SO_3 . In Fig. 2, upon additional dosing of SO_2 (0.5 L), extra features appear between 166.5 and 164 eV which correspond to chemisorbed SO_2 [33]. This SO_2 is probably bonded to metal centers on the (0001)-Zn terraces. A large SO_2 dose of 5 L produces a thick multilayer of physisorbed SO_2 and the features for chemisorbed SO_3 and SO_2 are completely attenuated. Heating from 100 to 150 K induces desorption of the physisorbed SO_2 [6,15] leaving a surface on which the dominant species by far is chemisorbed SO_2 . The SO_2 is weakly bound and disappears upon further heating to 250 K. At this point, SO_3 is the only species present on the surface. By comparing the area under the S 2p features to areas observed after adsorbing SO_2 on $\text{ZnO}(000\bar{1})\text{-O}$ [6], we estimate that the amount of SO_3 formed on $\text{ZnO}(0001)\text{-Zn}$ was in the order of 0.10–0.15 mL. This small coverage of SO_3 was probably associated with defect sites on the surface and the adsorbate decomposed at temperatures well above 500 K.

Previously, we have found that the O-terminated (000 $\bar{1}$) face of ZnO exhibits a good reactivity towards SO_2 with an SO_3 saturation coverage of ~ 0.4 mL [6]. The results in Fig. 2 indicate that a (1 \times 1) $\text{ZnO}(0001)\text{-Zn}$ surface is not very reactive towards SO_2 . We were able to activate this surface by bombardment with Ar^+ ions. Fig. 3 displays S 2p spectra for the adsorption of SO_2 on a defect rich $\text{ZnO}(0001)\text{-Zn}$ surface produced by ion sputtering. The adsorption process led mainly to SO_3 formation with a tiny amount of atomic sulfur as a result of the decomposition of SO_2 :



In a (1 \times 1) $\text{ZnO}(0001)\text{-Zn}$ surface, the Zn centers are tri-coordinated and interact weakly with SO_2 . Zn

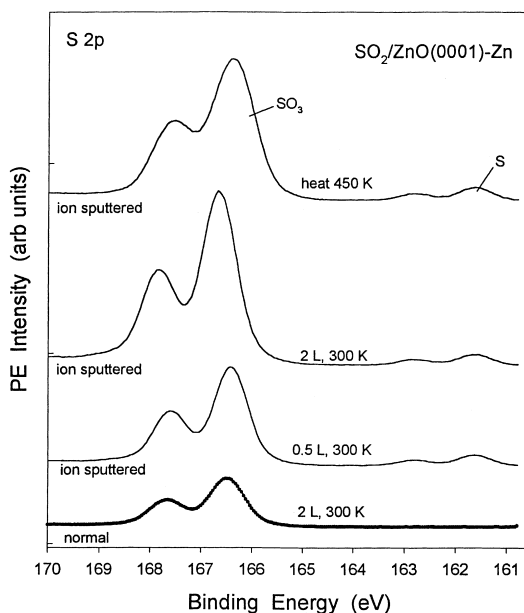


Fig. 3. S 2p photoemission data for adsorption of SO_2 on well-defined (normal, dots) and ion-sputtered (solid traces) $\text{ZnO}(0001)\text{-Zn}$ surfaces at 300 K. The electrons were excited using a photon energy of 260 eV.

centers with a lower coordination number (less than 3) can be expected on rough surfaces of polycrystalline ZnO. To examine the strength of the $\text{Zn} \leftrightarrow \text{SO}_2$ interactions on polycrystalline ZnO we studied the adsorption of sulfur dioxide on films of ZnO. The surfaces of these films exposed approximately a 50:50 mixture of Zn and O sites [24,25,34,35]. Our previous studies have shown that the zinc sites of these surfaces are very active for bonding sulfur-containing molecules (S_2 [34], H_2S [35], thiophene [24], CH_3SH [25]). For example, species like S, SH and CH_3S mainly adsorb on the Zn sites, and some of them completely ignore the O sites. In addition, when working with polycrystalline ZnO films, one is dealing with surfaces that are rich in O atoms which have a lower coordination number (less than 3) and a higher mobility than the O atoms in a $\text{ZnO}(000\bar{1})\text{-O}$ surface or the O atoms near the step sites or imperfections in a $\text{ZnO}(0001)\text{-Zn}$ surface.

Fig. 4 displays S 2p spectra for the adsorption of SO_2 on a polycrystalline ZnO film at 100 K. The spectrum obtained after a 0.45 L exposure can be curve fitted by a set of three doublets. These can be assigned

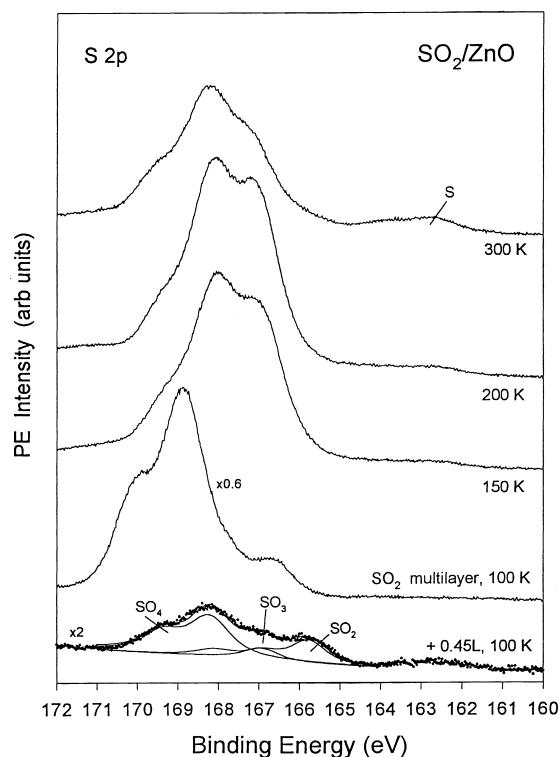


Fig. 4. S 2p spectra for a SO_2 multilayer deposited on a polycrystalline film of ZnO at 100 K and subsequently annealed to the temperatures indicated in the figure. All the spectra were acquired using a photon energy of 260 eV.

to SO_2 ($2p_{3/2}$ component at ~ 165.6 eV [6,33]), SO_3 ($2p_{3/2}$ component at ~ 166.8 eV, see above), and perhaps SO_4 ($2p_{3/2}$ component at ~ 168.0 eV [6,15]). Upon saturation of the surface with a SO_2 multilayer and heating to 150 K, one sees very strong features ($\theta_{\text{SO}_x} > \text{ML}$) between 170 and 166 eV that correspond to SO_3/SO_4 species. No features for adsorbed S are seen between 163 and 161 eV, which indicates that there is no dissociation of SO_x on Zn sites of the surface at 150 K. Upon heating to 300 K a trace of atomic sulfur is observed. In Fig. 4, the peaks for SO_3/SO_4 , which result from the reaction of SO_2 with O centers, are much more intense than the peak for SO_2 , which is a product of the chemisorption of the molecule on Zn centers. *Therefore, we can conclude that SO_2 preferentially interacts with the O centers of ZnO even when dealing with very rough surfaces.* This is corroborated by XANES data for the adsorption of SO_2 on bulk powders of zinc oxide.

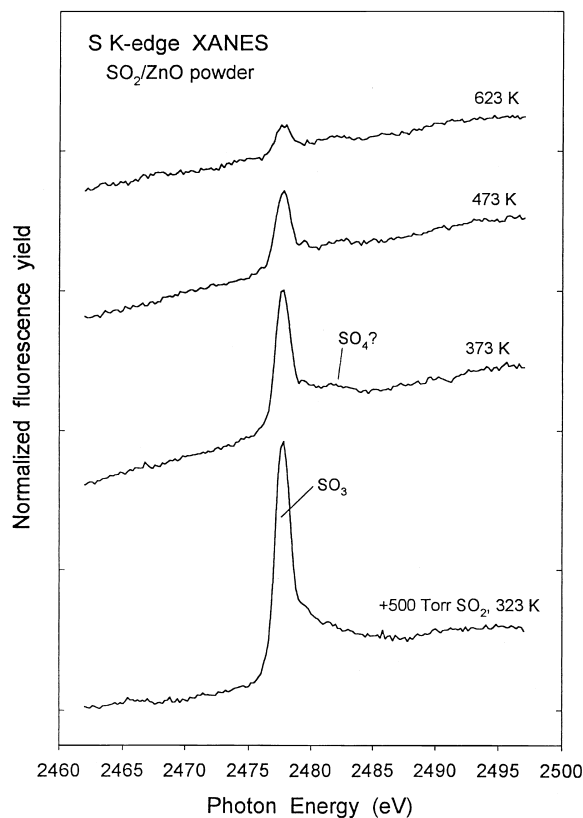


Fig. 5. S K-edge X-ray absorption spectra for a ZnO powder exposed to 500 Torr of sulfur dioxide. After dosing SO_2 at 323 K, the gas was evacuated and the sample was then heated to the indicated temperatures in vacuum.

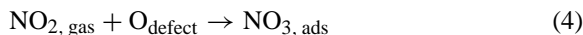
Fig. 5 shows XANES spectra at the S K-edge for a ZnO powder exposed to 500 Torr of SO_2 at 323 K. For this and smaller doses (5, 10, 50 Torr) of sulfur dioxide, there was only one clear peak in the spectrum with the maximum at a photon energy of ~ 2478 eV. This peak position matches very well that expected for SO_3 [8,9,15,31], is bigger than those reported for chemisorbed SO_2 (~ 2473.5 eV [8,9]) or S bonded to Zn (~ 2470 eV [31]), and smaller than the position for SO_4 (~ 2482 eV [8,9,15,31]). In Fig. 6, there is no clear feature which will indicate the presence of a sulfate species on the oxide powder. Upon heating from 323 to 373 K, the intensity of the signal for SO_3 decreases and a weak feature appears between 2481 and 2483 eV that could be attributed to a small amount of SO_4 [8,9,31]. This weak feature is still visible after heating to 623 K.

On the basis of the results in Figs. 2–5, we can conclude that the $\text{Zn} \leftrightarrow \text{SO}_2$ bonding interactions in SO_2/ZnO are weak and do not compete favorably with $\text{O} \leftrightarrow \text{SO}_2$ bonding interactions. Adsorption of SO_2 on zinc sites of the oxide surface was observed only at temperatures below 200 K.

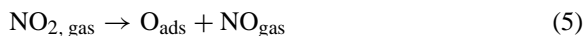
3.2. Nitrogen dioxide adsorption

We found that NO_2 is able to interact strongly with the zinc centers of ZnO . Fig. 6 displays N 1s photoemission spectra for the adsorption of nitrogen dioxide on $\text{ZnO}(0001)\text{-Zn}$. A large dose of NO_2 at 100 K leads to the deposition of a physisorbed multilayer of the N_2O_4 dimer [36,37] on the oxide substrate. Heating to 150 K induces desorption of the physisorbed N_2O_4 and leaves a N 1s spectrum with two clear peaks that indicate the presence of adsorbed NO_3 (~ 406.9 eV [16,38,39]) and NO_2 (~ 403.6 eV [16,38,39]). As in the case of the SO_3 on ZnO , the NO_3 may be formed by interaction of the adsorbate

with O sites near imperfections of the $\text{ZnO}(0001)\text{-Zn}$ surface:



Other possible routes for NO_3 formation involve partial decomposition of the NO_2 molecule:



Or disproportionation on the surface:



The amount of NO_3 formed is too large to be attributed only to reaction (4). Reaction (5) is an attractive possibility since it deposits O atoms on the surface with a low coordination number and is known to be a very efficient way for depositing oxygen on metal surfaces [27,36,37,40–42]. Evidence in support of reaction (7) is provided by the data in Fig. 6: as the temperature

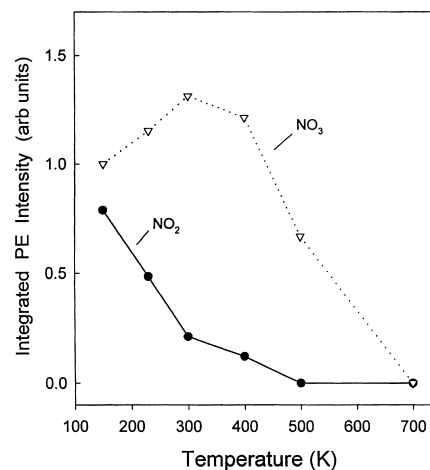
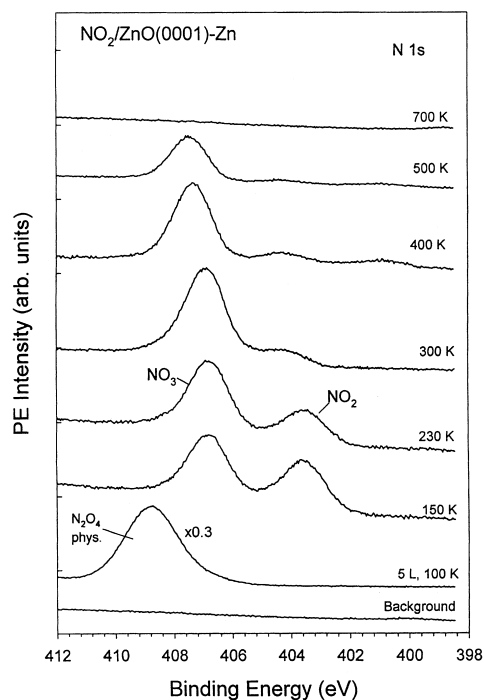


Fig. 6. N 1s photoemission spectra for the adsorption of NO_2 on $\text{ZnO}(0001)\text{-Zn}$ at 100 K with subsequent heating to elevated temperatures (100 K \rightarrow 700 K). The electrons were excited using a photon energy of 480 eV. The right-side panel shows the variation of the signal for chemisorbed NO_2 and NO_3 as a function of temperature.

is raised from 150 to 300 K there is a simultaneous increase in the NO_3 signal and a decrease in the NO_2 signal that point to a $\text{NO}_2 \rightarrow \text{NO}_3$ transformation. When similar experiments were done in front of a mass spectrometer we detected an increase in the NO signal (mass 30) that could not be attributed to the cracking of desorbing NO_2 (mass 46). All this is consistent with reaction (7).

In Fig. 6, there is a substantial amount of Zn-bonded NO_2 at temperatures below 250 K. A small fraction of the adsorbed NO_2 is stable up to temperatures around 400 K. The coverage of NO_3 reaches a maximum near 300 K and then decreases as the temperature is increased. By 700 K the decomposition of NO_3 was complete. This decomposition led to desorption of NO_2 and NO into gas phase. During the experiments of Fig. 6, no N 1s signal was detected between 396 and 400 eV. Therefore, the NO_x adsorbates did not undergo full decomposition to atomic nitrogen on the oxide surface [37,38].

Bombardment with Ar^+ ions enhanced the activity of the $\text{ZnO}(0001)\text{-Zn}$ surface. Fig. 7 displays N 1s spectra acquired after dosing NO_2 to (1×1) and ion-sputtered $\text{ZnO}(0001)\text{-Zn}$ surfaces. For the well-ordered (normal) surface, adsorption of NO_2 at room temperature produces mainly NO_3 and some

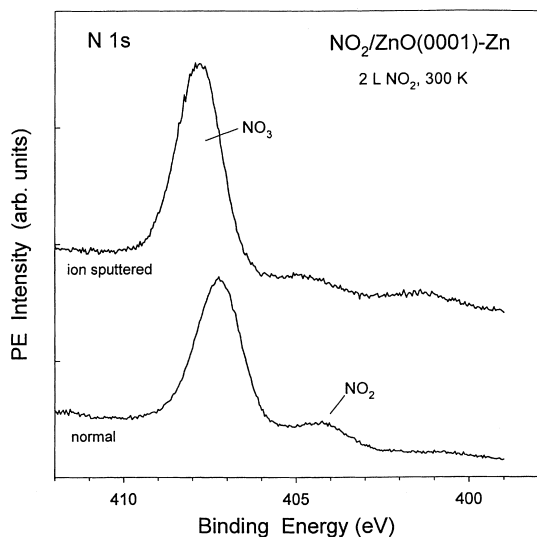


Fig. 7. N 1s spectra ($h\nu = 480$ eV) for the adsorption of NO_2 on well-defined (normal) and ion-sputtered $\text{ZnO}(0001)\text{-Zn}$ surfaces at 300 K.

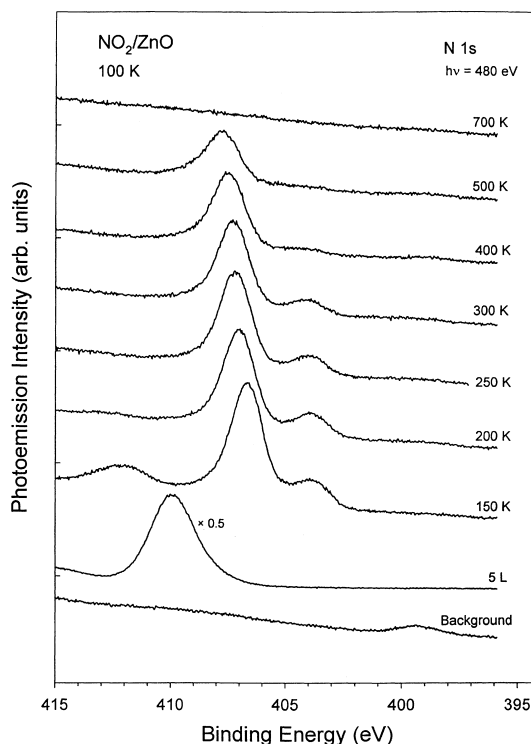


Fig. 8. N 1s photoemission data for adsorption of NO_2 on a polycrystalline film of ZnO at 100 K. After dosing 5 L of the molecule the sample was heated to the indicated temperatures. The electrons were excited using a photon energy of 480 eV.

chemisorbed NO_2 . In the case of the ion-sputtered surface, the peak for NO_3 is very intense and there are weak features at ~ 404 and 401 eV that probably originate from very small coverages of NO_2 and NO [16,38].

Fig. 8 shows photoemission spectra for the adsorption of NO_2 on a thick polycrystalline film of zinc oxide. The N 1s spectrum at the bottom shows that the ZnO surface is essentially nitrogen free before beginning the dosing of NO_2 . A trace of N at ~ 399 eV comes from the presence of residual NO_2 and NO gases in the UHV chamber during the preparation of the ZnO film [24–26]. This is not a problem since upon interaction with NO_2 the atomic N was oxidized to NO_x species. In Fig. 8, the dosing of NO_2 at 100 K produces multilayers of the N_2O_4 dimer on the oxide substrate. By 200 K a peak for NO_3 at ~ 407 eV [39] dominates the N 1s region, with a small peak for NO_2 at ~ 404 eV [39]. The NO_2 features disappear upon

annealing to 400 K. Further heating to 700 K leads to complete decomposition of the NO_3 leaving pure ZnO. The general trends in Figs. 6 and 8 are similar at temperatures above 300 K. On the other hand at low temperatures, the NO_3/NO_2 ratio is clearly larger on the polycrystalline surface. This can be expected since this surface exposes a much larger number of O centers than $\text{ZnO}(0001)\text{-Zn}$, which substantially favors reaction (4). In addition, Zn sites in the rough ZnO film are probably more reactive than the adsorption sites in $\text{ZnO}(0001)\text{-Zn}$ facilitating the transformation of NO_2 following reactions (5)–(7).

In a set of experiments, bulk powders of ZnO were exposed to moderate pressures of NO_2 (450–500 Torr)

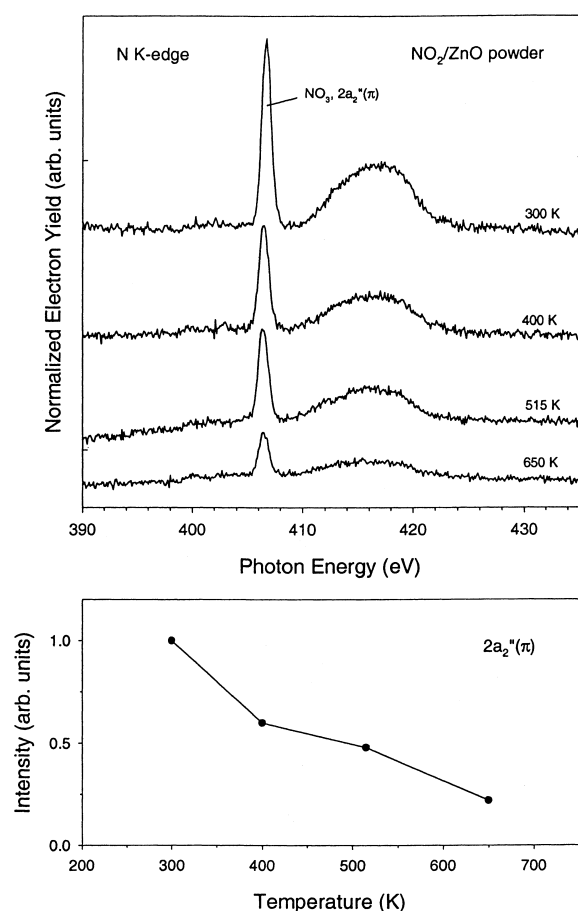


Fig. 9. Top: N K-edge XANES spectra taken after exposing a bulk powder of ZnO to NO_2 (450 Torr) at 300 K and subsequent heating to 400, 515 and 650 K. Bottom: intensity of the $2a_2''(\pi)$ resonance of NO_3 on ZnO as a function of annealing temperature.

at 100 and 300 K. Fig. 9 displays XANES data at the N K-edge for one of these systems. The line shape of the spectra matches well that observed for pure nitrates (KNO_3 , $\text{Mg}(\text{NO}_3)_2$, $\text{Ce}(\text{NO}_3)_3$ [16,38]) which exhibit the typical electronic transitions within the NO_3 group. The intense resonance at ~ 407 eV corresponds to $1s \rightarrow 2a_2''(\pi)$ electronic transitions, whereas the broad features between 410 and 420 eV probably come from excitations into the $5a_1'$ and $5e'$ empty σ orbitals of NO_3 [43]. After exposing bulk powders of ZnO to NO_2 at 100 K and warming to 300 K, in the N K-edge region we saw a strong resonance at ~ 407 eV (NO_3) and weak peaks between 400 and 402 eV that could be attributed to a small amount of chemisorbed NO_2 or NO [16,38]. These weak features disappeared upon heating to 350–400 K.

In Fig. 9, when the temperature is raised from 300 to 650 K, one sees a continuous decrease in the intensity of the NO_3 resonances in the N K-edge. This agrees qualitatively with trends found in the photoemission experiments of Figs. 6 and 8 which indicate that the nitrate is not stable at temperatures near 700 K.

4. Discussion

Important differences are observed when comparing the chemical behavior of SO_2 and NO_2 on $\text{ZnO}(0001)\text{-Zn}$ and polycrystalline zinc oxide. These differences are in part a consequence of changes in structural properties (flat versus rough surfaces), but in some situations they clearly originate in variations in surface composition (zinc \leftrightarrow adsorbate versus oxygen \leftrightarrow adsorbate interactions). For example, the Zn-terminated (0001) face of zinc oxide bonds weakly SO_2 . In contrast, $\text{ZnO}(000\bar{1})\text{-O}$ [6] and polycrystalline ZnO exhibit strong O \leftrightarrow SO_2 bonding interactions that lead to formation of large amounts of SO_3 . On $\text{ZnO}(0001)\text{-Zn}$ and polycrystalline ZnO, evidence for bonding of Zn to SO_2 was found only at low temperatures (< 200 K). This is consistent with trends found in ab initio self-consistent-field (SCF) calculations for the energetics of SO_2 chemisorption on ZnO clusters [32]. On O sites of the clusters, the adsorption energy of SO_2 was 15–20 kcal/mol larger than on Zn sites [32]. The Zn–O bonds reduce the electron density on zinc, making very difficult the donation of electrons from the metal into the LUMO of

SO₂ (the so-called “ π -back-donation” [44,45]) [32]. This electron transfer plays a very important role in the bonding interactions between SO₂ and metals [15,45,46].

Experimental studies for the adsorption of SO₂ on TiO₂(1 1 0) [8], TiO₂(1 0 0) [9], α -Fe₂O₃(0 0 0 1) [11] and MgO(1 0 0) [15] show adsorbed SO₃ or SO₄ as the final product. These oxide surfaces expose a mixture of metal and oxygen sites, but the SO₂ molecule prefers to interact with the oxygen centers. On the TiO₂ systems, SO₂ bonded to Ti sites is observed at very low temperatures (100–150 K) but eventually the adsorbate migrates to the O sites and forms stable SO₃ or SO₄ species [8,9]. No chemisorbed SO₂ has been observed after exposing bulk powders of several oxides (ZnO, MgO [15,47], TiO₂ [47], Fe₂O₃,¹ V₂O₅, ZrO₂ [47], CeO₂ [48], CoMoO₄ [49], NiMoO₄ [49]) to SO₂ at room temperature. In these systems, SO₃ and SO₄ are the only adsorption products. Theoretical studies show that the metal cations of ZnO [32], MgO [15,46] and MoO₂ [50] interact weakly with the LUMO of sulfur dioxide (S–O antibonding). This leads to small adsorption energies on these sites and makes very difficult the dissociation of the molecule.

Thus, it appears that in general SO₂ interacts weakly with metal centers of oxides. In the case of NO₂ on ZnO(0 0 0 1)-Zn, the photoemission results show substantial bonding interactions between the adsorbate and Zn cations. The adsorbed NO₂ undergoes a disproportionation to form NO₃ on the metal centers. Results of DFT and INDO/S calculations for the NO₂/ZnO(0 0 0 1)-Zn system show strong Zn \leftrightarrow NO₂ interactions and suggest that the zinc sites should get oxidized or nitrated as a result of them [38]. For SO₂ and NO₂ on MgO(1 0 0), one also finds weak Mg \leftrightarrow SO₂ and strong Mg–NO₂ bonding interactions [15,16,46]. The differences in the behavior of SO₂ and NO₂ probably arise from the radical nature of the NO₂ molecule. Fig. 10 compares the molecular orbital energies of NO₂ [38] and SO₂ [51] plus the band energies of ZnO [20,51]. As mentioned above, the interactions between the LUMO of SO₂ (3b₁ orbital) and the occupied orbitals of a metal play a predominant role in the energetics of the metal–SO₂ bond [45,46]. In Fig. 10 the LUMO of SO₂ appears at much higher energy than the occupied Zn 4s band in

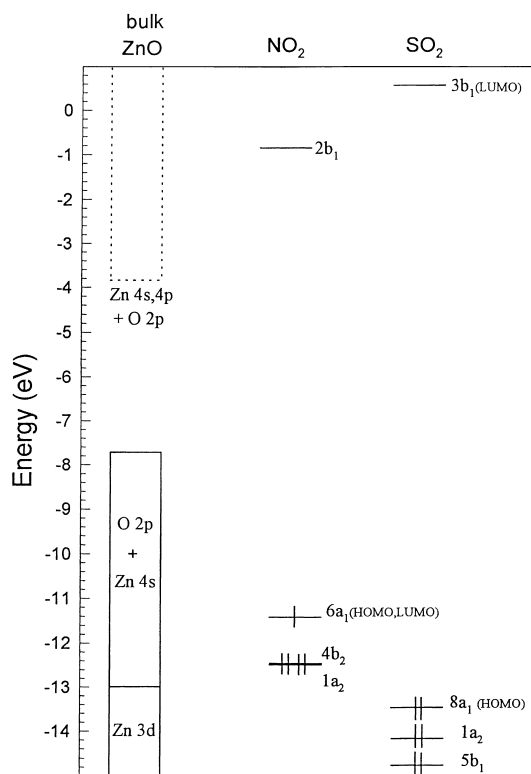


Fig. 10. Energy range covered by the bands of ZnO [20,51] plus the MO's of NO₂ [38] and SO₂ [51]. The empty and occupied states of ZnO are indicated by dotted and solid lines, respectively. All the energies are reported with respect to the vacuum level.

ZnO, making Zn(4s)–SO₂(3b₁) bonding interactions very difficult. On the other hand, in the case of NO₂, the 6a₁ orbital is only half occupied and its energy position is ideal for electron donor–electron acceptor interactions with occupied and empty states of Zn centers. These differences lead to weak Zn \leftrightarrow SO₂ and strong Zn \leftrightarrow NO₂ bonding interactions on zinc oxide.

The photoemission results for NO₂/ZnO(0 0 0 1)-Zn are interesting because they clearly prove that large quantities of NO₃ can be formed on metal sites of an oxide surface as a consequence of partial decomposition or disproportionation of NO₂, reactions (5)–(7). It must be pointed out that after exposing pure metallic zinc to NO₂ at 150 K a mixture of NO₃ and NO₂ coexists on the surface of the metal [38]. In general studies that deal with the chemistry of NO₂ on metals indicate that partial decomposition of the molecule is a very efficient reaction pathway for depositing large co-

¹ To be published.

verages of oxygen on metal atoms [27,36–38,40–42]. In fact, NO₂ is a much better oxidizing agent than molecular oxygen [27,36,40–42]. This reflects the difference in the strength of the N–O (NO_{2, gas} → NO_{gas} + O_{gas}, Δ*H* = 73 kcal/mol) and O–O bonds (O_{2, gas} → 2O_{gas}, Δ*H* = 119 kcal/mol) [52].² The partial decomposition of NO₂ on the cations of an oxide surface, reaction (5), generates oxygen adatoms that have a relatively low coordination number and, therefore, a high reactivity towards NO₂ and the formation of NO₃. After exposing polycrystalline powders of several oxides (ZnO, CuO [53], MgO [16], CeO₂ [16], TiO₂, Fe₂O₃ [16], Al₂O₃) to NO₂ at 300 K, XANES shows NO₃ as the main species on the surface with very minor amounts of chemisorbed NO₂.

In environmental catalysis the destruction or removal of SO_x and NO_x compounds is receiving a lot of attention [1]. The data presented above indicate that ZnO can be useful as a sorbent for removing the SO₂ and NO₂ molecules generated as side products in many chemical processes and the burning of fuels. The routes for the formation of SO₃ and NO₃ on the oxide can be different, but these species have in common a high stability and decompose at temperatures well above 500 K. Zinc oxide is able to catalyze the reduction of nitrogen dioxide by alkanes [5]. Our results suggest that pure ZnO will not be good as a catalyst for the destruction of SO₂ in reactions such as: 2CO + SO₂ → 2CO₂ + S_{solid}; or H₂S + SO₂ → 2H₂O + 3S_{solid} (Claus process). The metal centers of ZnO(0001)-Zn and polycrystalline ZnO are not efficient at breaking S–O bonds.

5. Conclusions

The Zn-terminated (0001) crystal face of ZnO is much less reactive towards SO₂ than polycrystalline ZnO. This difference in reactivity arises from variations in surface composition. On ZnO(0001)-Zn and polycrystalline ZnO, the Zn ↔ SO₂ bonding interactions are weak. Adsorption of SO₂ on Zn cations was seen only at temperatures below 200 K. In contrast, the SO₂ molecules react readily with O sites of

Ar⁺ sputtered ZnO(0001)-Zn or polycrystalline ZnO forming very stable SO₃ species. Due to its radical nature, adsorbed NO₂ is more chemically active than SO₂. After dosing nitrogen dioxide to ZnO(0001)-Zn at 100 K, chemisorbed NO₂ and NO₃ coexists on the surface. A partial NO_{2, ads} → NO_{3, ads} transformation is observed from 150 to 300 K. The data for the NO₂/ZnO(0001)-Zn system clearly prove that large quantities of NO₃ can be formed on metal sites of an oxide surface as a consequence of partial decomposition or disproportionation of NO₂. The routes for the formation of SO₃ and NO₃ on ZnO can be different, but these species have in common a high stability and decompose at temperatures well above 500 K.

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² The Δ*H* associated with the SO_{2, gas} → SO_{gas} + O_{gas} reaction is 132 kcal/mol. Therefore, NO₂ should be a better oxidizing agent than O₂ or SO₂.

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