Studies on the Behavior of Mixed-Metal Oxides and Desulfurization: Reaction of H_2S and SO_2 with $Cr_2O_3(0001)$, MgO(100), and $Cr_xMg_{1-x}O(100)$

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Abstract: In environmental catalysis the removal or destruction of S-containing molecules is a very important issue nowadays. The interaction of H_2S and SO_2 with $Cr_2O_3(0001)$, MgO(100) and $Cr_xMg_{1-x}O(100)$ surfaces ($x = 0.05-0.08$) was studied using synchrotron-based high-resolution photoemission. X-ray absorption near-edge spectroscopy (XANES) was used to examine the chemistry of the molecules on powders of Cr_2O_3, MgO and $Cr_xMg_{1-x}O$ catalysts. The activity toward the breaking of S−H and S−O bonds was found to increase in the sequence: MgO < Cr_2O_3 < $Cr_xMg_{1-x}O$. The mixed-metal oxide displays a unique ability for breaking S−O bonds that makes it the best catalyst for the Claus process ($2H_2S + SO_2 \rightarrow 2H_2O + 3S_{solid}$) and the reduction of SO_2 by CO ($SO_2 + 2CO \rightarrow 2CO_2 + S_{solid}$). First-principles density-functional (DF-GGA) calculations revealed that the superior catalytic properties of the mixed-metal oxide are due to the special electronic properties of Cr cations contained in a matrix of MgO. These Cr atoms have a lower oxidation state than the atoms in Cr_2O_3, and exhibit occupied 3d levels that are less stable than the valence bands of MgO. Both properties favor interactions with the LUMO of SO_2 (S−O antibonding) and the subsequent dissociation of the molecule. The behavior of the $Cr_xMg_{1-x}O$ system illustrates a fundamental principle for the design of mixed-metal oxide catalysts.

I. Introduction

Sulfur-containing compounds are present as impurities in all crude oils and coals.[1] These impurities have a very negative impact on the processing of oil-derived chemical feedstocks (catalyst poisoning[2,3] and equipment corrosion[1]) and degrade the quality of the air by forming sulfur dioxide (SO_2) during the burning of fuels.[4] In the chemical and petrochemical industries millions of dollars are lost every year due to catalyst poisoning, and the negative effects of acid rain (main product of the oxidation of SO_2 in the atmosphere) on the ecology and the corrosion of monuments or buildings are substantial. New environmental regulations call for a 90% reduction of sulfur content in automobile gasoline in the United States by the year 2004. Similar laws are being enacted around the world. They emphasize the importance of more efficient technologies for removing the sulfur from the oil and destroying the SO_2 formed during the combustion of fuels (DeSOx processes).[5−7]

In many industrial operations, oxides are used as sorbents for trapping sulfur-containing molecules or DeSOx catalysts.[6−9] The metal elements form oxides that can adopt a large diversity of crystal structures.[10,11] These oxides can behave as semiconductors or insulators, and in some cases even exhibit metallic properties,[11] leading to the possibility of large variations in chemical activity.[11−16] Previous studies[13−15,17] have compared the reactivity of different types of oxides (Cr_3O_4, Cr_2O_3, NiO, Cu_2O, CuO, ZnO, MgO, Al_2O_3) toward H_2S. Oxides that have a large degree of ionicity such as Al_2O_3 and MgO exhibited the lowest reactivity. On the other hand, oxides of chromium (no highly ionic, small band gap) were found to be the most reactive.[13,17] Recent work with high-surface area DeSOx sor-

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bents has confirmed this finding and indicates that mixed-metal oxides combining Cr and elements such as Mg, Al, Ba, Cu, or Ce are more catalytically active than pure chromia.[18] Several of these mixed-metal oxide DeSOx catalysts have the potential for industrial applications,[18] but they are rather complex systems and there is no clear understanding of what causes their good performance.

Mixed-metal oxides play a relevant role in many areas of chemistry, physics, and materials science.[11,19−20] Recently, much attention has been focused on the preparation and characterization of mixed-metal oxide catalysts.[21−23] Catalysts that consist of metal-doped MgO are a typical example.[11,18,19,24,25] In principle, the combination of two metals in an oxide matrix can produce materials with novel physical and chemical properties that can lead to a superior performance in technological applications. The two metals can behave as "isolated units" that bring their intrinsic properties to the system, or could possess properties modified by metal↔metal or metal↔oxygen↔metal interactions. In this respect, it is important to know how to choose the "right" combination of metals. Thus, an atomic-level understanding of the properties of mixed-metal oxides is crucial. The modern techniques of surface science are unique "tools" for addressing this issue.[11,12,26,27] Furthermore, these techniques have proven to be useful for studying the complex chemistry of SO_2 on metal and oxide surfaces.[11,28]

In this article, we study the interaction of H_2S and SO_2 with $Cr_2O_3(0001)$, MgO(100) and $Cr_xMg_{1-x}O(100)$ surfaces using synchrotron-based high-resolution photoemission. The chemistry of the molecules on powders of Cr_2O_3, MgO and $Cr_xMg_{1-x}O$ catalysts is investigated with X-ray absorption near-edge spectroscopy (XANES). First-principles density functional calculations and the periodic supercell approach are used to examine the bonding of H_2S and SO_2 to $Cr_xMg_{1-x}O(100)$. Our experimental and theoretical studies provide a clear explanation for the high activity of chromium-based desulfurization catalysts and illustrate how an element in a mixed-metal oxide can have special chemical properties.

II. Experimental and Theoretical Methods

II.2. Sample preparation. The experiments described in section III were performed on oriented films $\{Cr_2O_3(0001), MgO(100), Cr_xMg_{1-x}O(100)\}$, bulk MgO(100) single crystals, powders (MgO, Cr_2O_3), and unsupported catalysts ($Cr_xMg_{1-x}O$). One of the experimental techniques used in this work was synchrotron-based photoemission. Since the oxides under study were insulators or semiconductors, the effects of charging made it very difficult to carry out photoemission experiments with bulk single crystals on these materials. In particular, this is a very big problem if one is interested in obtaining reproducible absolute binding energies for the photoemission peaks. By working with ultrathin films (30−40 Å in thickness) of $Cr_2O_3(0001)$, MgO(100), and $Cr_xMg_{1-x}O(100)$ grown on metal substrates, we prevented effects of charging in our photoemission experiments. The validity of this approach is well documented.[13,17,26a,27,29−31] The MgO(100) and $Cr_xMg_{1-x}O(100)$ films were grown on a Mo(100) crystal,[29] while a Pt(111) substrate was used for growing the $Cr_2O_3(0001)$ films.[30] MgO(100) and $Cr_2O_3(0001)$ were grown following procedures described in detail in the literature.[14,29,30] In short, high-purity (99.999%) Mg or Cr was vapor deposited on the corresponding metal substrates at 500−600 K in a background O_2 pressure of $\sim 2 \times 10^{-6}$ Torr. In the case of MgO, this was followed by heating to 1200 K in 1×10^{-6} Torr of O_2.[14,29] The $Cr_2O_3(0001)$ films were annealed at 700−800 K for 5 min after deposition.[30] Core-level photoemission and low-energy electron diffraction (LEED) were used to verify the formation of MgO(100) and $Cr_2O_3(0001)$.[29,30] For preparing the $Cr_xMg_{1-x}O(100)$ systems, we followed a methodology[31] that involved simultaneous dosing of Mg and Cr to a Mo(100) crystal at ∼600 K in the presence of O_2 (5×10^{-6} Torr), with annealing at 1200 K (10 min) in the final step. The rates of deposition of Cr and Mg were controlled in such a way that the average mole fraction of Cr in the oxide films was 0.05−0.08 (metal basis). This was verified by measuring the relative intensity of the Cr and Mg core levels in photoemission. At these low concentrations the Cr was dissolved within a matrix of MgO forming a solid solution (probably occupying Mg sites in the lattice),[24,31a] and the $Cr_xMg_{1-x}O(100)$ films ($x = 0.05-0.08$) exhibited a (1 × 1) LEED pattern similar to that of pure MgO(100) films. The core-level photoemission spectra of the mixed-metal oxide films displayed peak positions characteristic of Mg^{2+} and Cr^{2+} ions.[14,29,30] In experiments of ion scattering spectroscopy (ISS) performed by the authors and another research group,[31] the $Cr_xMg_{1-x}O(100)$ films ($x = 0.05-0.08$) showed a Cr concentration at the surface (0.10−0.15, metal basis) that was somewhat larger than the average Cr concentration for the "bulk" of the sample.

Since the XANES measurements were done in the "fluorescence-yield mode", there were no problems with sample charging when working with bulk MgO(100) single crystals, powders of MgO and Cr_2O_3, or a $Cr_{0.06}Mg_{0.94}O$ catalyst. The MgO(100) crystals and powders of MgO and Cr_2O_3 were acquired from commercial sources and had a purity of at least 99.99%. The catalyst samples were prepared[18] in aqueous solution by controlled coprecipitation of Cr and Mg from inorganic salts. After being filtered and washed, the precipitate was dried in an oven, and then calcinated in an atmosphere of O_2 at 1200 K for 10 h. This produced a $Cr_{0.06}Mg_{0.94}O$ solid solution: the corresponding X-ray diffraction pattern exhibited a single phase and was similar to that of MgO.[18] Studies of EXAFS for the $Cr_{0.06}Mg_{0.94}O$ catalyst support the idea that Cr atoms were occupying Mg sites in a lattice of MgO.[18] In addition, the position and line shape of the Cr L-edge in XANES measurements indicate that the formal oxidation state of the Cr atoms in the catalyst was close to "+2".[18,26c]

II.3. Photoemission Experiments. The photoemission experiments were performed in two conventional ultrahigh-vacuum chambers (UHV) located at the U4A and U7A beamlines of the National Synchrotron Light Source (NSLS). The instrumental capabilities of these UHV chambers are described elsewhere.[14,17] The S 2p spectra reported in section III were obtained using a photon energy of 260 eV.[14] The binding energy of these spectra was calibrated by the position of the Fermi edge in the valence region. The $Cr_2O_3(0001)$, MgO(100), and $Cr_xMg_{1-x}O(100)$ films were exposed to H_2S or SO_2 at 100 and 300 K. The adsorbates were dosed through a glass-capillary array positioned

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near the sample. The gas exposures are based on the ion gauge reading and are not corrected for the capillary array enhancement.

II.3. XANES Spectra. Bulk MgO(100) single crystals, pure powders of MgO and Cr_2O_3, and $Cr_xMg_{1-x}O$ catalysts were exposed to H_2S or SO_2 in a RXM-100 unit from Advanced Scientific Designs. The dosing of the gases was done in a "batch-reactor" mode: 5 Torr, 10 min, at 300 K. Before exposure to H_2S or SO_2, the samples were heated under vacuum at elevated temperatures (650−800 K) to remove OH groups from the surface. The corresponding S K-edge XANES spectra were collected at the NSLS on beamline X19A. The spectra were recorded in the "fluorescence yield mode" with a modified Stern−Heald−Lytle detector. The energy resolution was close to 0.5 eV.

II.4. Theoretical Methods. The first-principles density functional (DF) calculations reported in section III.3. were performed using a commercial version of CASTEP (Cambridge Serial Total Energy Package)[32] available from Molecular Simulations Inc. A series of previous studies indicates that CASTEP is excellent for predicting structural geometries and energy changes associated with chemical transformations involving oxides.[23,32−36] In this code, the wave functions of valence electrons are expanded in a basis set of plane waves with kinetic energy smaller than a specified cutoff energy E_{cut}. The presence of tightly bound core electrons is represented by nonlocal ultrasoft pseudopotentials.[37] Reciprocal-space integration over the Brillouin Zone is approximated through a careful sampling at a finite number of *k*-points using the Monkhorst−Pack scheme.[38] The exchange-correlation contribution to the total electronic energy is treated in the generalized gradient corrected (GGA)[39] form of the local density approximation (LDA). In all calculations, the kinetic energy cutoff E_{cut}, and the density of the Monkhorst−Pack *k*-point mesh were chosen high enough in order to ensure convergence of the computed structures and energetics. Since the DF calculations were performed at the GGA level, one can expect good predictions for the bonding energies of the adsorbates on the oxide surfaces.[39−42] Frequently, DF-GGA calculations predict adsorption energies within an accuracy of 5 kcal/mol.[33,36d,41,42a] In any case, our main interest in this work was not in absolute bonding energies, but rather a comparison of the energetics for adsorption of S-containing species on MgO(100) and $Cr_xMg_{1-x}O(100)$.

III. Results and Discussion

III.1. Reaction of H_2S on Cr_2O_3, MgO and $Cr_xMg_{1-x}O$. We will begin by examining the adsorption of H_2S on Cr_2O_3(0001) surfaces and polycrystalline powders of Cr_2O_3. Figure 1 shows S 2p spectra for the adsorption of H_2S on Cr_2O_3(0001) at 100 K. After saturating the surface at 100 K with H_2S, one sees a clear S 2p doublet between 163.5 and 165.5 eV that corresponds to physisorbed hydrogen sulfide. In addition, there is a strong feature at ∼161.7 eV. This position is too low to be assigned to chemisorbed H_2S (S $2p_{3/2} \approx 162.3$ eV) and too high for atomic S (S $2p_{3/2} \approx 161$ eV).[43] For small doses of H_2S at 100 K, this was the dominant peak seen in the S 2p region and experiments of valence photoemission[43,44] indicate that it corresponds to HS species. Thus, the main product of the adsorption of H_2S on Cr_2O_3(0001) at 100 K is the sulfhydryl group (no H_2S or S). Heating from 100 to 200 K in Figure 1 induces desorption of the H_2S multilayer leaving a complex S 2p spectrum. To curve-fit this spectrum,[43d] one needs three doublets which indicate the presence of chemisorbed H_2S (very small coverage), HS, and S on the oxide surface. Further heating to 300 K leads to the disappearance of H_2S and HS completely decomposes into atomic sulfur.

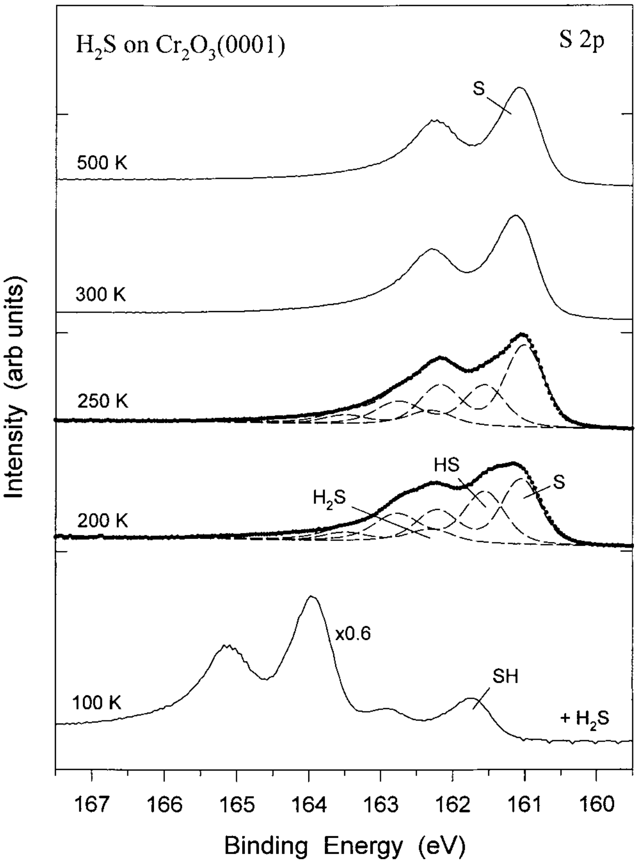

Figure 1. S 2p photoemission spectra for the adsorption and dissociation of hydrogen sulfide on a Cr_2O_3(0001) surface. The oxide substrate was saturated with H_2S at 100 K, and then the sample was heated to the indicated temperatures.

The dosing of H_2S to Cr_2O_3(0001) at 300−350 K under UHV conditions produced only S-atoms bonded to Cr sites (S $2p_{3/2}$ at 161.3−161.0 eV). When a Cr_2O_3(0001) film was exposed to 5 Torr of H_2S at 350 K in a reaction cell attached to the UHV chamber, we found a strong peak in the S 2p region for Cr-

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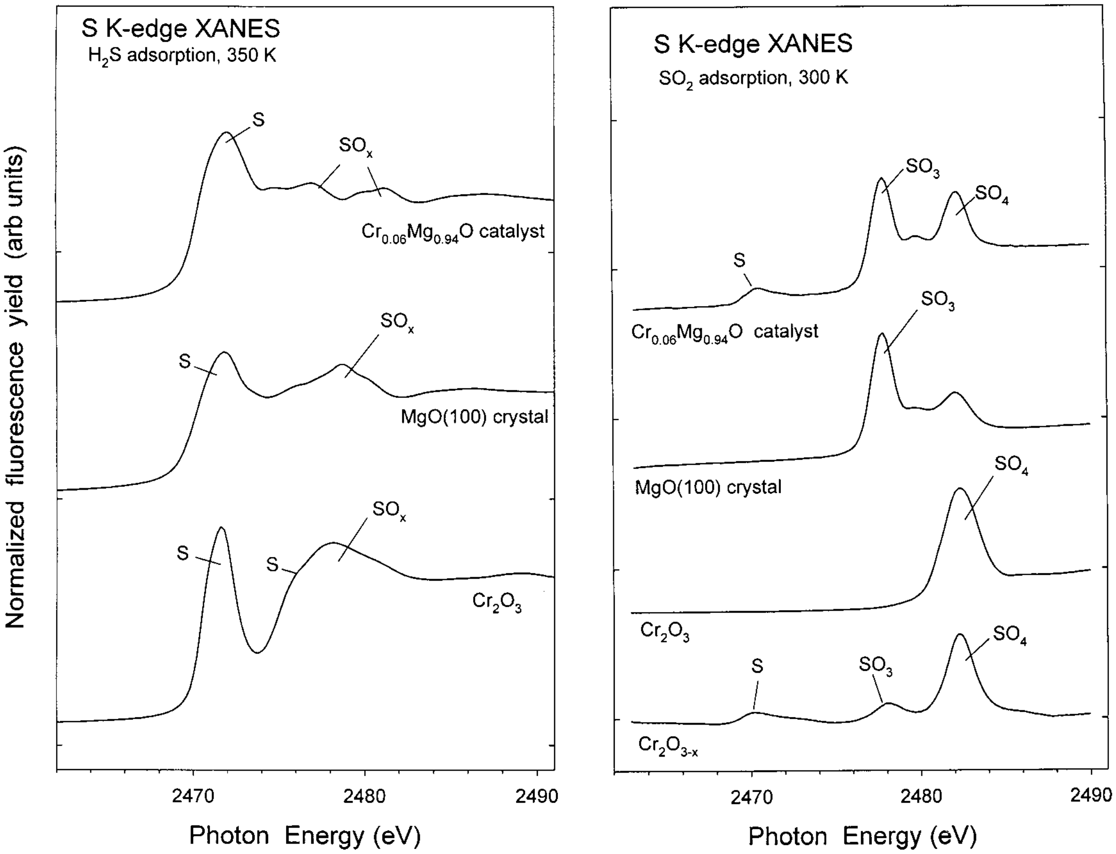

Figure 2. Left-panel: S K-edge XANES spectra for the reaction of H_2S with a Cr_2O_3 powder, a MgO(100) single crystal, and a $Cr_{0.06}Mg_{0.94}O$ powder catalyst. Before the spectra were taken, the samples were exposed to 5 Torr of H_2S at 350 K. Right-panel: S K-edge data for the adsorption of SO_2 on Cr_2O_{3-x} and Cr_2O_3 powders, a MgO(100) single crystal, and the $Cr_{0.06}Mg_{0.94}O$ powder catalyst. The samples were exposed to 5 Torr of SO_2 at 300 K, and then the spectra were collected.

bonded S and weak features between 166 and 168 eV that indicate the formation of some SO_x species.[36c,45,46] A somewhat similar result was found after exposing a Cr_2O_3 powder to H_2S at 350 K. The corresponding S K-edge spectrum (left-panel in Figure 2) showed an intense peak at ~2471.7 eV typical of metal sulfides (i.e., metal−sulfur bonds),[23b,47] plus a broad feature between 2476 and 2480 eV that probably results from a combination of sulfide and SO_x features.[47] In principle, sulfur atoms can be deposited on the metal cations (MC) of Cr_2O_3 as a result of the following reactions:

$$\mathrm{MC(surf)} + \mathrm{H_2S(gas)} \rightarrow \mathrm{MC{-}S(surf)} + \mathrm{H_2(gas)}\ (1) \qquad (1)$$

$$\mathrm{MC(surf)} + 2\mathrm{O(surf)} + \mathrm{H_2S(gas)} \rightarrow \mathrm{MC{-}S(surf)} + 2\mathrm{O{-}H(surf)} \qquad (2)$$

$$\mathrm{MC(surf)} + \mathrm{O(surf)} + \mathrm{H_2S(gas)} \rightarrow \mathrm{MC{-}S(surf)} + \mathrm{H_2O(gas)} \qquad (3)$$

Reaction 3 is frequently used for the transformation of oxides into sulfides at high temperatures.[5,9] But at temperatures near 300 K the removal of oxygen from the oxide lattice as water is difficult,[23b,27b,48] and when the H_2S molecules break apart on the surface some of the S atoms are forced to interact with O sites forming SO_x species. This reaction channel has a low probability[13,44] and is not observed under UHV conditions.

Results for the adsorption of H_2S on a bulk MgO(100) crystal and a MgO(100) film are shown in Figures 2 and 3, respectively. After exposing the MgO(100) crystal to 5 Torr of H_2S at 350 K, the S K-edge spectrum (left-panel in Figure 2) displayed an intense peak for S bonded to Mg (at ~2472 eV) and superimposed over the sulfide signal were small features for SO_x species. Mainly S and some SO_x groups were detected with photoemission after doing a similar experiment with a MgO(100) film. H_2S dosing under UHV conditions at 350 K produced only Mg-bonded S on the surface of MgO(100) films. HS was detected as an intermediate in the decomposition of hydrogen sulfide when the adsorption was carried out at temperatures below 300 K. In Figure 3, the dominant species in contact with MgO(100) are H_2S at 80 K, HS at 250−300 K, and S at 400 K,[14,49] thus revealing a $H_2S \rightarrow HS \rightarrow S$ transformation in this temperature range. Comparing the results in Figures 1 and 3, it is quite clear that Cr_2O_3 is the more active oxide for breaking H−S bonds.

Now, we turn our attention to the behavior of the $Cr_xMg_{1-x}O$ systems. Figure 4 shows S 2p data for the adsorption of H_2S on a $Cr_{0.06}Mg_{0.94}O(100)$ surface at 100 K. The spectra are complex and the most interesting feature is a peak near 160.8 eV, which indicates the presence of S atoms bonded to Cr sites (see Figure 1). The intensity of this peak saturates rapidly due

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(49) After dissociation of S_2 on MgO(100), the sulfur adatoms showed a S $2p_{3/2}$ peak centered near 162 eV. Usually the S 2p peaks for HS and H_2S are shifted ~0.7 and 1.5 eV with respect to the peak for S.[43b−d] Valence photoemission experiments for the H_2S/MgO(100) system showed mainly H_2S at 80−100 K, and HS at room temperature.

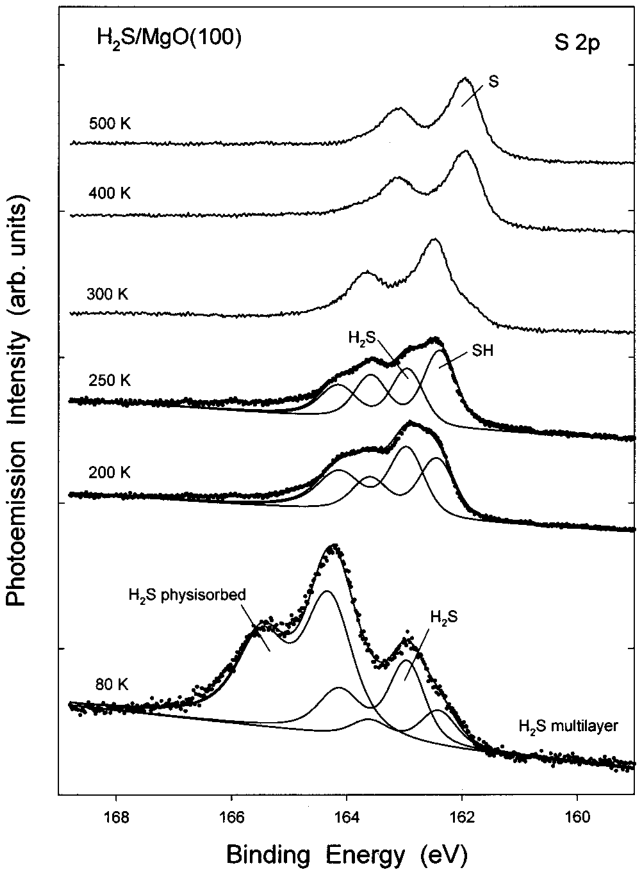

Figure 3. S 2p spectra for the interaction of H_2S with a MgO(100) surface. In the initial step, the oxide was covered with a multilayer of hydrogen sulfide at 80 K. Then, the sample was heated to higher temperatures.

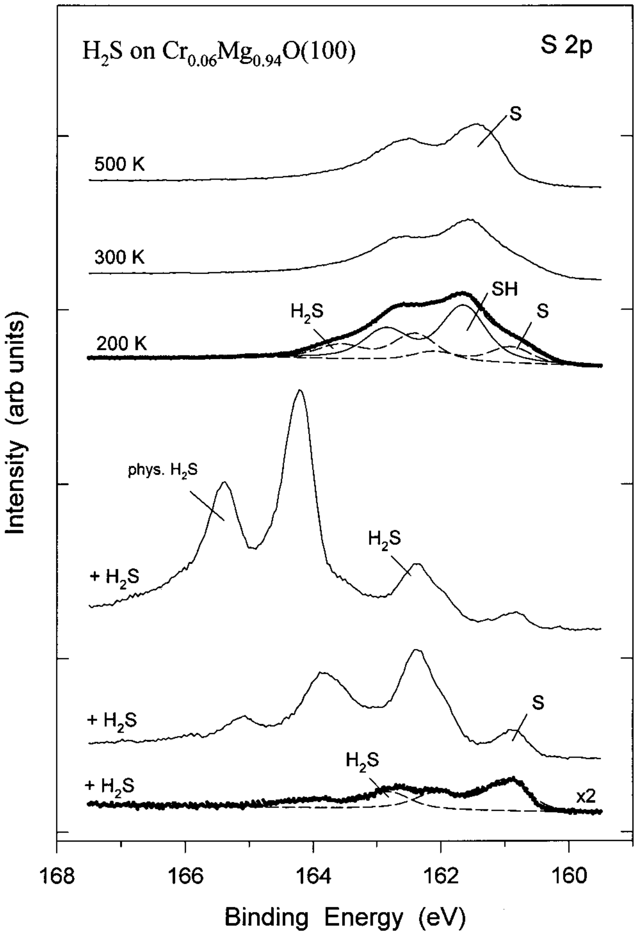

Figure 4. Photoemission data for the adsorption of hydrogen sulfide on a $Cr_{0.06}Mg_{0.94}O(100)$ surface; 0.05, 0.5, and 1.0 L of H_2S were dosed at 100 K. This was followed by heating to 200, 300, and 500 K.

to the limited concentration of Cr atoms in the oxide surface.[50] But it is clear that these Cr atoms are able to fully dissociate H_2S at 100 K, being *much more reactive* than the metal centers in pure MgO(100) or $Cr_2O_3(0001)$. In Figure 4, after saturating the surface with H_2S at 100 K and heating to 200 K, one sees a S 2p spectrum that probably results from the convolution of signals for H_2S, SH and S. By 500 K, it is likely that the morphology or structure of the surface has changed and the resulting S $2p_{3/2}$ feature is broad with a binding energy (~161.5 eV) between those expected for Mg- and Cr-bonded S.

Results of XANES showed that $Cr_{0.06}Mg_{0.94}O$ powder catalysts were very active for the full decomposition of H_2S. A typical S K-edge spectrum for the $H_2S/Cr_{0.06}Mg_{0.94}O$ system at 350 K (left-panel in Figure 2) is characterized by a strong peak for metal-bonded S and weak features for SO_x species. In this spectrum, the S/SO_x ratio is substantially larger than that seen on Cr_2O_3 and MgO powders under the same conditions, indicating that the metal sites in $Cr_{0.06}Mg_{0.94}O$ are *the most reactive for breaking S−H bonds.* Thus, according to the results for H_2S adsorption, a $Cr_xMg_{1-x}O$ mixed-metal oxide could be a better catalyst for the Claus process ($2H_2S + SO_2 \rightarrow 2H_2O + 3S_{solid}$) than pure MgO or Cr_2O_3. For the Claus reaction on oxide catalysts usually the most difficult step is the breaking of the S−O bonds in SO_2.[7,9,36c] This will be the main subject under study in the next section.

III.2. Reaction of SO_2 with Cr_2O_3, MgO, and $Cr_xMg_{1-x}O$. The chemistry of SO_2 on a metal oxide may be complex since the molecule is able to interact with metal (production of chemisorbed SO_2) and/or oxygen centers (formation of SO_3 and SO_4).[11,36c,46] In general, the (0001) face of Cr_2O_3 can expose O and Cr atoms.[11,51] Termination with a full layer of O or Cr will lead to an electrostatically unstable surface.[11,51] Figure 5 shows S 2p spectra for the adsorption of SO_2 on a $Cr_2O_3(0001)$ film at 100 K. Upon the dosing of 1 L of SO_2, one sees a set of three doublets that indicate the presence of SO_4 (S $2p_{3/2} \approx 168.2$ eV[36c,45,46]), SO_3 (S $2p_{3/2} \approx 166.3$ eV[36c,45,46]), and SO_2 (S $2p_{3/2} \approx 164.8$ eV[36c,52]). The SO_3 and SO_4 groups probably result from direct reaction of SO_2 with oxygen sites of the surface:

$$SO_2(\text{surf}) + nO(\text{surf}) \rightarrow SO_{2+n}(\text{surf}) \quad n = 1,2 \tag{4}$$

but they also could be formed by a disproportionation of SO_2 on metal sites:

$$(m+1)SO_2(\text{surf}) \rightarrow mSO(\text{gas}) + SO_{2+m}(\text{surf}) \quad m = 1,2 \tag{5}$$

[52] In Figure 5, after heating from 100 to 350 K, one sees the disappearance of the signals from SO_3 and SO_2, while the

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(50) Experiments of ISS[31] indicate that for this type of $Cr_xMg_{1-x}O(100)$ system ($x = 0.06-0.08$) the concentration of Cr in the surface was no bigger than 0.15 (metal basis) before dosing H_2S or SO_2. However, the adsorbates could induce migration of some Cr from the "bulk" of the film towards the surface due to strong Cr↔S interactions (see section III.3).

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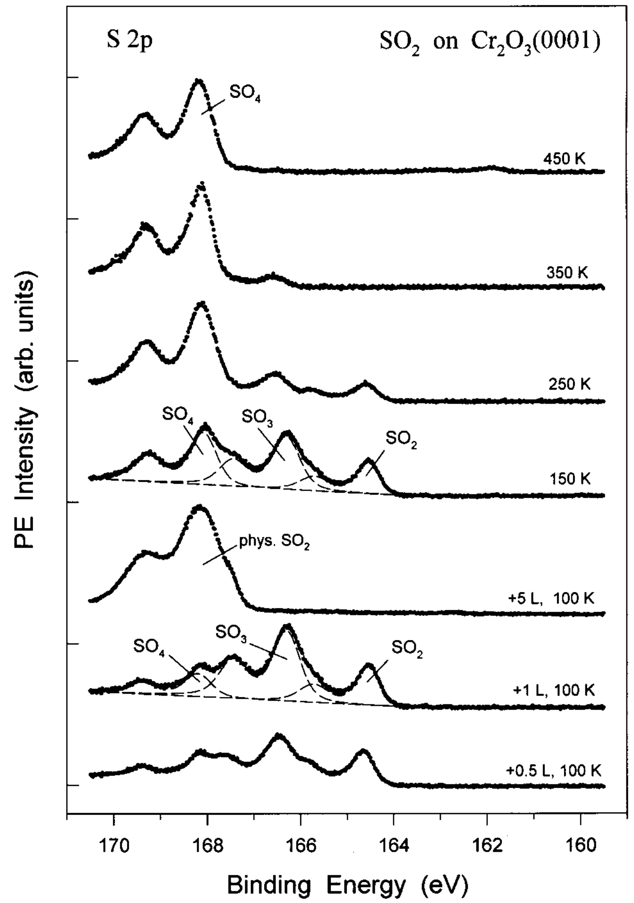

Figure 5. S 2p spectra for the adsorption of SO_2 on $Cr_2O_3(0001)$ at 100 K and subsequent heating to higher temperatures.

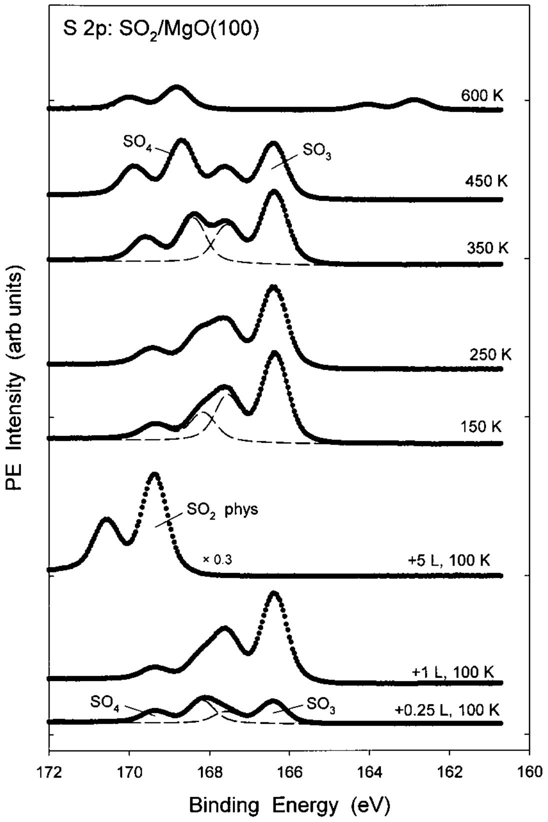

Figure 6. S 2p photoemission data for the adsorption of SO_2 on a MgO(100) surface at 100 K, followed by heating to higher temperatures.

features for SO_4 clearly grow in intensity. As the temperature of the sample is raised, the O atoms of the oxide gain mobility and the formation of SO_4 according to reaction 4 or a $SO_3 + O \rightarrow SO_4$ transformation is easier. At temperatures above 300 K, SO_4 is practically the only species present on the oxide surface. An identical result was found after exposing powders of bulk Cr_2O_3 to moderate pressures of SO_2 (1−10 Torr) at room temperature. The S K-edge XANES spectra (for an example see Figure 2) exhibited *only* the typical peak for SO_4 around 2482 eV.[36c,45,47]

The ideal (100) face of MgO exposes a 50%−50% mixture of Mg and O atoms.[11] The results in Figures 2 and 6 indicate that pure $Mg \leftrightarrow SO_2$ interactions are very weak on MgO(100) and adsorption of the molecule produces SO_3 and SO_4 species. Since there is no chemisorption or dissociation of SO_2 on metal sites, reaction 4 must be the route for the formation of SO_3 and SO_4. In Figure 6, SO_3 is the main species on the oxide surface at low temperatures. As the temperature is raised there is a $SO_3 \rightarrow SO_4$ transformation. After exposing a MgO(100) film to 5 Torr of SO_2 at 300 K in a reaction cell, adsorbed SO_3 was dominant (~80% of the total signal) in the S 2p region. XANES showed a similar result upon exposure of a MgO(100) single crystal to SO_2 at 300 K (right-panel in Figure 2). A comparison of the data for SO_2/Cr_2O_3 and SO_2/MgO shows two important differences. First, SO_4 species form more easily on Cr_2O_3.[53] Second, the metal centers in Cr_2O_3 interact stronger with SO_2 than the metal centers of MgO. Both oxides are inactive for the dissociation of SO_2, but a change in the chemical environment of the Cr atoms could lead to cleavage of S−O bonds.

Photoemission results for the adsorption of SO_2 on a $Cr_{0.08}Mg_{0.92}O(100)$ film at 100 K are shown in Figure 7. A very small dose of 0.05 L produces mainly peaks for adsorbed SO_2. Since these features are not seen on MgO(100), they can be assigned to SO_2 bonded to Cr atoms. They do not grow much with further exposure to SO_2 because the amount of Cr atoms in the oxide surface is small.[50] A 1 L dose of SO_2 leads to a spectrum dominated by the signal for SO_3 species. After depositing a SO_2 multilayer and heating to 150 K, the S 2p spectrum is characterized by intense signals for SO_4 and SO_3, but features appear at ~161 eV due to Cr-bonded S adatoms. These features grow when the sample temperature is raised from 150 to 450 K. At the same time, there is an increase in the SO_4 signal, and the signals for SO_3 and SO_2 decrease. The reaction that deposits S atoms on the surface

$$SO_n(\text{surf}) \rightarrow S(\text{surf}) + nO(\text{surf}) \tag{6}$$

also frees O atoms that can be used to transform SO_3 into SO_4. The results in Figure 7 indicate that a *$Cr_{0.08}Mg_{0.92}O(100)$ surface is much more active for the dissociation of S−O bonds than $Cr_2O_3(0001)$ or MgO(100).* An identical conclusion can be reached after analyzing XANES data for the adsorption of SO_2 on $Cr_{0.06}Mg_{0.94}O$ and pure Cr_2O_3 or MgO (see right-side panel in Figure 2). Thus, the $Cr_xMg_{1-x}O$ system should be the best catalyst for the Claus reaction ($2H_2S + SO_2 \rightarrow 2H_2O + 3S_{solid}$) or the reduction of SO_2 by carbon monoxide ($SO_2 + 2CO \rightarrow 2CO_2 + S_{solid}$). This idea agrees well with trends seen for reaction rates measured on supported DeSOx catalysts.[18]

The differences in the behavior of $Cr_xMg_{1-x}O$ and Cr_2O_3 clearly illustrate how a metal (Cr) trapped on a matrix of another

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[53] Two factors favor the formation of SO_4 on Cr_2O_3. For this oxide the content of oxygen is larger than for MgO. In addition, the O−O distances are shorter in Cr_2O_3 than in MgO.[10]

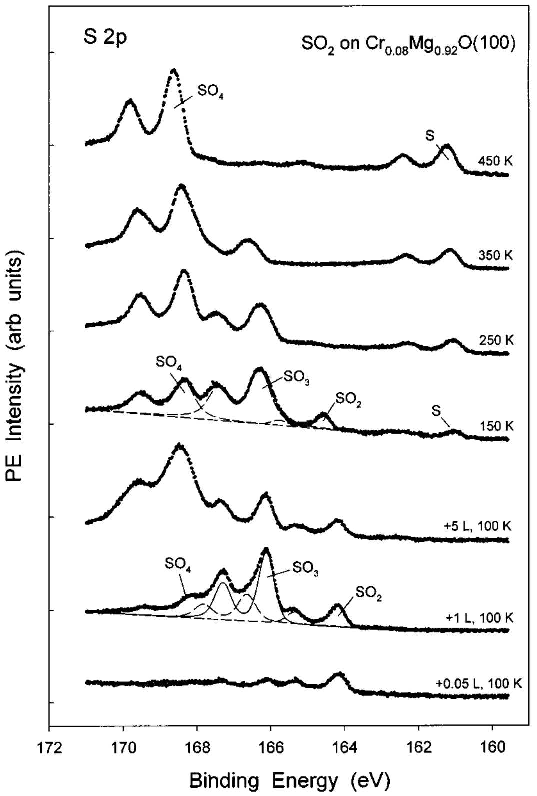

Figure 7. S 2p spectra collected after adsorbing SO_2 on a $Cr_{0.08}Mg_{0.92}O$(100) surface at 100 K and subsequent heating to 150, 250, 350, and 450 K.

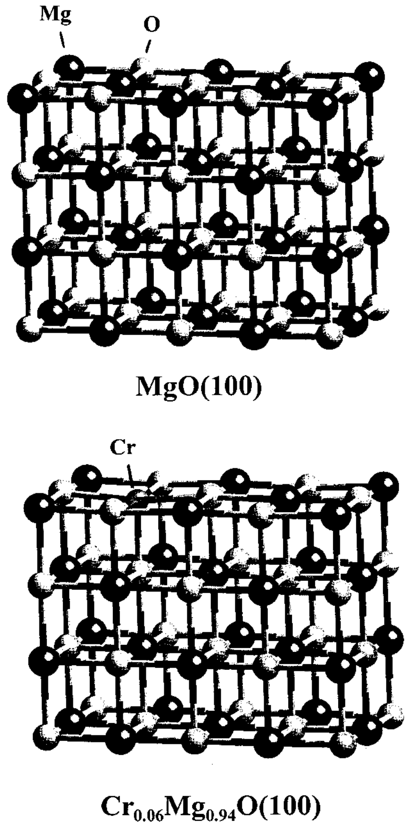

Figure 8. Schematic view of the four-layer slabs used to model MgO(100) and $Cr_{0.06}Mg_{0.94}O$(100) surfaces. The unit cell of the mixed-metal system contains only one chromium atom.

metal oxide (MgO) can have special chemical properties. Spectra of Cr core-level photoemission and Cr L-edge XANES[18] indicate that the formal oxidation state of the chromium atoms in $Cr_xMg_{1-x}O$ is closer to "+2" than to "+3" as found in Cr_2O_3. Cr^{2+} can be expected from a charge balance in a $Cr_xMg_{1-x}O$ solid solution if one assumes formal charges of "−2" and "+2" for O and Mg, respectively. Thus, the extra electron density on the chromium atoms in $Cr_xMg_{1-x}O$ may be responsible for their high activity for breaking S−O bonds. To test this hypothesis we generated Cr^{2+} sites in a Cr_2O_3 powder by reaction with a stream of H_2 at 550 K, and then exposed the Cr_2O_{3-x} system to SO_2 at 300 K. Indeed, the results of XANES (right-panel in Figure 2) showed the presence of S as a result of the dissociation of SO_2. But a key issue here is in the relative stability of the Cr_2O_{3-x} and $Cr_xMg_{1-x}O$ systems. In the presence of O_2, Cr_2O_{3-x} gets reoxidized into Cr_2O_3, whereas the chromium trapped in MgO remains stable as Cr^{2+} keeping its extra chemical activity. Cr cations with a lower oxidation state than "+3" can be present in a Cr_2O_3(0001) surface.[51] These types of cations are able to adsorb CO_2[51b] and are probably responsible for the signal for chemisorbed SO_2 in Figure 5. However, these cations are in a higher oxidation state than the Cr sites in a $Cr_xMg_{1-x}O$(100) surface and are not reactive enough for dissociating SO_2 or CO_2.[51b]

III.3. Bonding of H_2S and SO_2 to $Cr_xMg_{1-x}O$(100). First-principles density-functional (DF) calculations combined with the supercell approach[32a] were used to get a better understanding of the behavior of H_2S and SO_2 on $Cr_xMg_{1-x}O$(100) surfaces. Previously, the same methodology was successfully employed to study the interaction of the molecules with pure MgO(100).[15,36c] We did not attempt to model the interaction of S-containing molecules with Cr_2O_3(0001) due to the complex nature of this surface. This type of surface can be Cr- or O-terminated,[11,51] relaxation effects play a very important role,[51a] and more experimental/theoretical work is necessary for finding a reliable representation of such system.[54] On the other hand, it is well-known how to model MgO-based surfaces.[15,35,55,56] In our previous work, the MgO(100) system was modeled with a periodic slab containing four atomic layers as shown in Figure 8. A vacuum of 12.5 Å was placed on top of the surface to ensure negligible interactions between periodic images normal to the surface.[15,33−35] The DF calculations predicted accurate lattice constants for bulk MgO and almost no reconstruction of the MgO(100) surface, in agreement with several experimental and theoretical investigations.[15] To simulate a $Cr_xMg_{1-x}O$(100) surface, we replaced 25% percent of the Mg atoms in the first layer of the MgO(100) slab with Cr atoms. The overall concentration of Cr in the unit cell of our model, see Figure 8, was 0.0625 (metal basis). The model does not have the layer-by-layer Cr distribution expected for the $Cr_xMg_{1-x}O$(100) surfaces under study in the two previous sections (this would require very big unit cells[31,50]), but it does provide a good representation of a Cr atom contained in a matrix of MgO.

After optimizing the geometry of the bare $Cr_{0.06}Mg_{0.94}O$(100) slab, we found that the Cr atoms were relaxed downward by ~0.07 Å with respect to the plane of Mg atoms in the surface (top layer). The Mg−O distances were similar to those found

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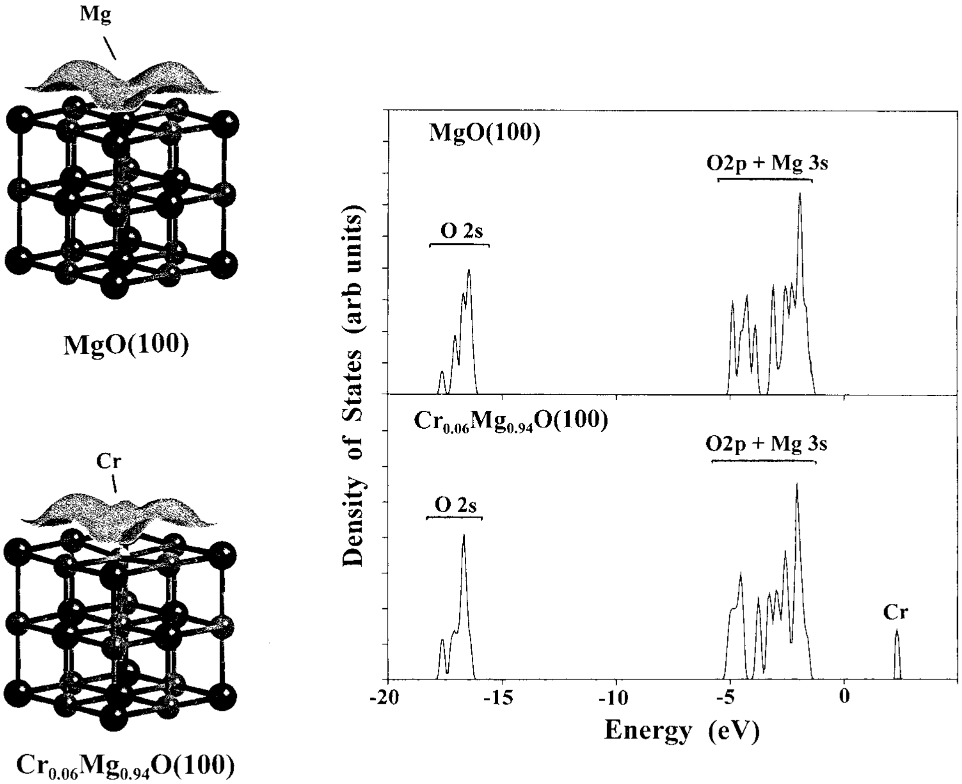

Figure 9. The left-side of the figure displays calculated (DF-GGA) electron-density plots for MgO(100), top, and $Cr_{0.06}Mg_{0.94}O(100)$, bottom, surfaces. For simplicity, only a few metal and oxygen atoms in the four-layer slabs are shown. The graph in the right-side of the figure shows the calculated DOS for the occupied bands of the MgO(100) and $Cr_{0.06}Mg_{0.94}O(100)$ systems.

in bulk MgO ($\Delta \leq 0.03$ Å). Figure 9 shows plots for the electron density around Mg and Cr surface atoms in MgO(100) and $Cr_{0.06}Mg_{0.94}O(100)$. In the case of pure MgO(100), the total electron density of the Mg atoms is small,[16,55] and the electron-density plot is characterized by maxima located on top of the oxygen atoms. On the other hand, for $Cr_{0.06}Mg_{0.94}O(100)$, one finds a substantial electron density around the Cr atoms. Figure 9 also displays calculated density-of-states (DOS) plots for MgO(100) and $Cr_{0.06}Mg_{0.94}O(100)$. These graphs include only occupied states. In the mixed-metal oxide, the occupied Cr 3d levels are less stable energetically than the levels in the occupied $\{O\ 2p + Mg\ 3s\}$ bands of MgO. Thus, from an electronic viewpoint, the Cr centers in a $Cr_{0.06}Mg_{0.94}O(100)$ surface are very well suited to respond to the presence of adsorbates.

H_2S, HS, S, and SO_2 were placed above the first layer of the $Cr_{0.06}Mg_{0.94}O(100)$ slab in the configurations shown in Figure 10. The resulting structures were optimized allowing the movement of the adsorbate and atoms in the top two layers of the slab. Tables 1 and 2 list calculated structural parameters and adsorption energies. For comparison we are also including results previously obtained for adsorption of the S-containing species on MgO(100).[15,36c] In all cases, *the bonding interactions of the adsorbates are much stronger on $Cr_{0.06}Mg_{0.94}O(100)$ than on MgO(100).* For the reaction of H_2S with MgO, the decomposition products (HS and S) interact well with the oxide but the overall rate of decomposition is small due to the relatively weak adsorption bond of H_2S.[15] This is not the case for H_2S on $Cr_{0.06}Mg_{0.94}O(100)$, where the adsorption energy of the molecule on the Cr atoms is substantial (23 kcal/mol). For SO_2 on MgO(100), the bonding interactions of the molecule with the Mg sites are very weak and, thus, the oxide cannot dissociate the molecule.[36c,57] SO_2 interacts preferentially with O sites of MgO forming SO_3 species.[36c,57] In contrast, SO_2 binds strongly to the Cr sites of $Cr_{0.06}Mg_{0.94}O(100)$, and there is an elongation of the S−O bonds that facilitates dissociation of the molecule. The Cr atoms have no problem interacting with the LUMO of the SO_2 molecule (S−O antibonding[28,52]).

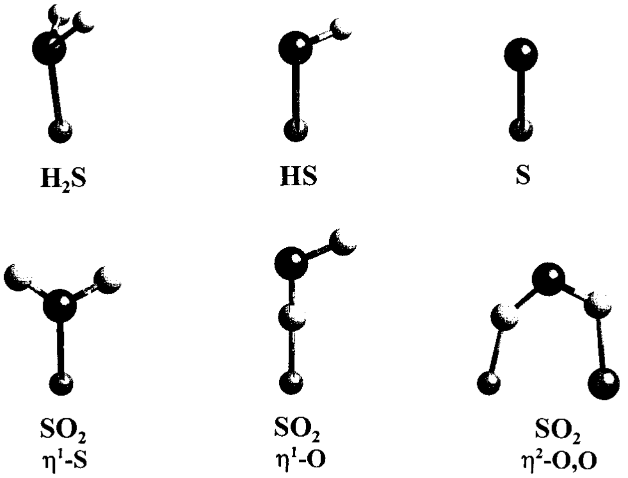

Figure 10. Adsorption geometries for H_2S, HS, S, and SO_2 on $Cr_{0.06}Mg_{0.94}O(100)$. In general, the molecules were bonded to *one* Cr atom on the surface. The η^2-O,O configuration for SO_2 is the exception, since the molecule is bridging a Cr and a Mg atom on the surface.

The theoretical results in Tables 1 and 2 are in clear agreement with the large reactivity observed for the $Cr_xMg_{1-x}O$ systems in photoemission and XANES experiments. The key to the special chemical activity of $Cr_xMg_{1-x}O$ is in the electronic properties of chromium (Figure 9). From photoemission and XANES studies,[18] it is known that the Cr atoms in $Cr_xMg_{1-x}O$ are in a lower oxidation state than the atoms in Cr_2O_3. When

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Table 1. Adsorption of H_2S on MgO(100) and $Cr_{0.06}Mg_{0.94}O(100)$: DF-GGA Results[a]

	bond lengths (Å)		ads energy
	metal−S[b]	H−S	(kcal/mol)[c]
free H_2S		1.35	
	on MgO(100)		
H_2S	2.71	1.35	9
HS	2.63	1.36	19
S	2.46		34
	on $Cr_{0.06}Mg_{0.94}O(100)$		
H_2S	2.33	1.37	23
HS	2.24	1.38	37
S	2.08		65

[a] One-quarter (0.25 monolayers) of the metal sites in the surface is covered by S-containing species. [b] Mg for MgO(100); Cr for $Cr_{0.06}Mg_{0.94}O(100)$. [c] Positive values denote an exothermic process.[15]

Table 2. Adsorption of SO_2 on MgO(100) and $Cr_{0.06}Mg_{0.94}O(100)$: DF-GGA Results[a]

	bond lengths (Å)			ads energy
	metal−O[b]	metal−S[b]	S−O	(kcal/mol)[c]
free SO_2			1.43	
	on MgO(100)			
η^1-S	not bound to this surface			
η^1-O	2.40		1.44(1.43)	5
η^2-O,O bridge	2.41		1.45	8
	on $Cr_{0.06}Mg_{0.94}O(100)$			
η^1-S		2.27	1.48	18
η^1-O	2.08		1.53(1.46)	21
η^2-O,O bridge	2.03		1.54(1.48)	27

[a] One-quarter (0.25 monolayers) of the metal sites in the surface is covered by SO_2. [b] Mg for MgO(100); Cr for $Cr_{0.06}Mg_{0.94}O(100)$. [c] Positive values denote an exothermic process.[15]

designing mixed-metal oxide catalysts, it is important to know how to choose the "right" combination of metals for obtaining a superior performance.[21,22] In this respect, previous investigations[15,23] have found a useful correlation between the electronic and chemical properties of several mixed-metal oxides: the less stable the top of the valence band in the mixed-metal oxide, the higher the chemical reactivity of the system. The same principle can be applied to MgO (Figure 9), and by adding Cr one transforms this oxide into a $Cr_xMg_{1-x}O$ catalytic material that has a very high efficiency for breaking S−H and S−O bonds. A similar effect is probably responsible for the high DeSOx activity detected for other Cr-doped oxides (BaO, CuO, NiO, CeO_2[18]).

IV. Summary and Conclusions

For the adsorption of H_2S on MgO(100), the dominant species in contact with the oxide are H_2S at 80 K, HS at 250−300 K, and S at 400 K. $Cr_2O_3(0001)$ decomposes H_2S into HS at 100 K and a HS → S transformation takes place at temperatures below 300 K. On Cr sites of $Cr_xMg_{1-x}O(100)$, H_2S fully dissociates to S at 100 K. The deposition of S and the formation of small amounts of SO_x species is observed after exposing the oxides to moderate pressures (5 Torr) of H_2S at 350 K.

Neither MgO(100) nor $Cr_2O_3(0001)$ dissociates the SO_2 molecule. The main product of the adsorption of SO_2 on MgO(100) at 100−300 K is SO_3 with some SO_4. SO_3 is also observed after dosing SO_2 to $Cr_2O_3(0001)$ at 100 K, and by 300 K a $SO_3 \rightarrow SO_4$ transformation is essentially complete. The metal centers of $Cr_2O_3(0001)$ adsorb SO_2 at 100 K, but the molecule desorbs or transform into SO_3/SO_4 species upon heating to 300 K. In contrast, the Cr sites in $Cr_xMg_{1-x}O(100)$ or a $Cr_xMg_{1-x}O$ catalyst are able to fully decompose the SO_2 molecule even at temperatures as low as 200 K.

The activity of the oxides for breaking S−H and S−O bonds increases following the sequence: $MgO < Cr_2O_3 < Cr_xMg_{1-x}O$. The behavior of the $Cr_xMg_{1-x}O$ system illustrates how an element in a mixed-metal oxide can have an enhanced chemical activity. First-principles density-functional calculations indicate that this is a consequence of the special electronic properties for Cr cations contained in a matrix of MgO. These Cr atoms have a lower oxidation state than the atoms in Cr_2O_3, and exhibit occupied 3d levels that are less stable than the valence bands of MgO. Both properties favor strong interactions with the orbitals of S-containing molecules. Thus, $Cr_xMg_{1-x}O$ is a better catalysts than MgO or Cr_2O_3 for the Claus process ($2H_2S + SO_2 \rightarrow 2H_2O + 3S_{solid}$) and the reduction of SO_2 by CO ($SO_2 + 2CO \rightarrow 2CO_2 + S_{solid}$).

Acknowledgment. We thank J.Z. Larese and H. Lee for many thought-provoking conversations on the behavior of metal-doped MgO. Special thanks to J. Evans for his help in the preparation of the $Cr_xMg_{1-x}O(100)$ films and Y. Wu for providing samples of the $Cr_xMg_{1-x}O$ catalysts. The research carried out at Brookhaven National Laboratory was supported by the Division of Chemical Sciences of the U.S. Department of Energy (Contract DE-AC02-98CH10086). M. Pérez thanks ENRI for a travel grant (99-FT026) that made possible a work-visit to BNL. J.A. Rodriguez is grateful to the American Chemical Society for supporting a trip to Venezuela that allowed the development of this research project.

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