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ARTICLES

Interaction of Sulfur with Well-Defined Metal and Oxide Surfaces: Unraveling the Mysteries behind Catalyst Poisoning and Desulfurization

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Introduction

Sulfur-containing molecules are common impurities in fuels and oil-derived feedstocks.¹ Today, these impurities constitute a major problem in our industrial society.¹⁻⁷ When fuels are burned, the S-containing impurities react with oxygen, forming sulfur oxides (SO_x). In the atmosphere, the SO_x species undergo further oxidation and interact with water, producing acid rain that kills vegetation and corrodes buildings and monuments.² In addition,

sulfur oxides poison catalysts that are used for the removal of CO and NO from automobile exhaust.³ Sulfur poisoning can have very negative effects on the performance of catalytic processes.⁴⁻⁶ Metal/oxide catalysts play an important role in the chemical and petrochemical industries.⁵ In general, these catalysts are deactivated by the S-containing impurities present in oil-derived feedstocks.⁴⁻⁶ Millions of dollars are lost every year in the chemical and oil industries as a consequence of sulfur poisoning.^{4,5}

To minimize the negative effects of sulfur in environmental pollution and industrial operations, one can follow two different approaches. The first involves removing sulfur from crude oil and designing catalysts with a high efficiency for hydrodesulfurization processes.^{1,4,5} It is unlikely that all the S-containing molecules can be removed from the oil. Therefore, the second approach is to improve the sulfur tolerance of catalytic processes currently used in industry by working with catalysts that are less sensitive to sulfur poisoning.³⁻⁵ To accomplish any of these goals, one has to understand at a fundamental level how sulfur affects the structural, electronic, and chemical properties of metal and oxide surfaces.

Industrial catalysts are complex systems that can contain several interacting phases and only a small fraction of active sites.⁵ Part of the problem in explaining the mechanisms by which sulfur poisons industrial catalysts arises from the fact that these systems are very difficult to characterize.^{4,5} Useful knowledge on this subject can be obtained by examining the properties of organometallic sulfur compounds or well-defined surfaces of metals and oxides.^{6,7} Using these "simple" models, one can isolate and study in detail different aspects associated with sulfur poisoning or desulfurization reactions.^{6,7} In recent years, studies that use the modern techniques of surface science have shown a series of novel and important phenomena when sulfur or S-containing molecules interact with well-defined surfaces of metals and oxides. Interesting trends have been observed for the chemical reactivity of bimetallic and metal/oxide systems. In this

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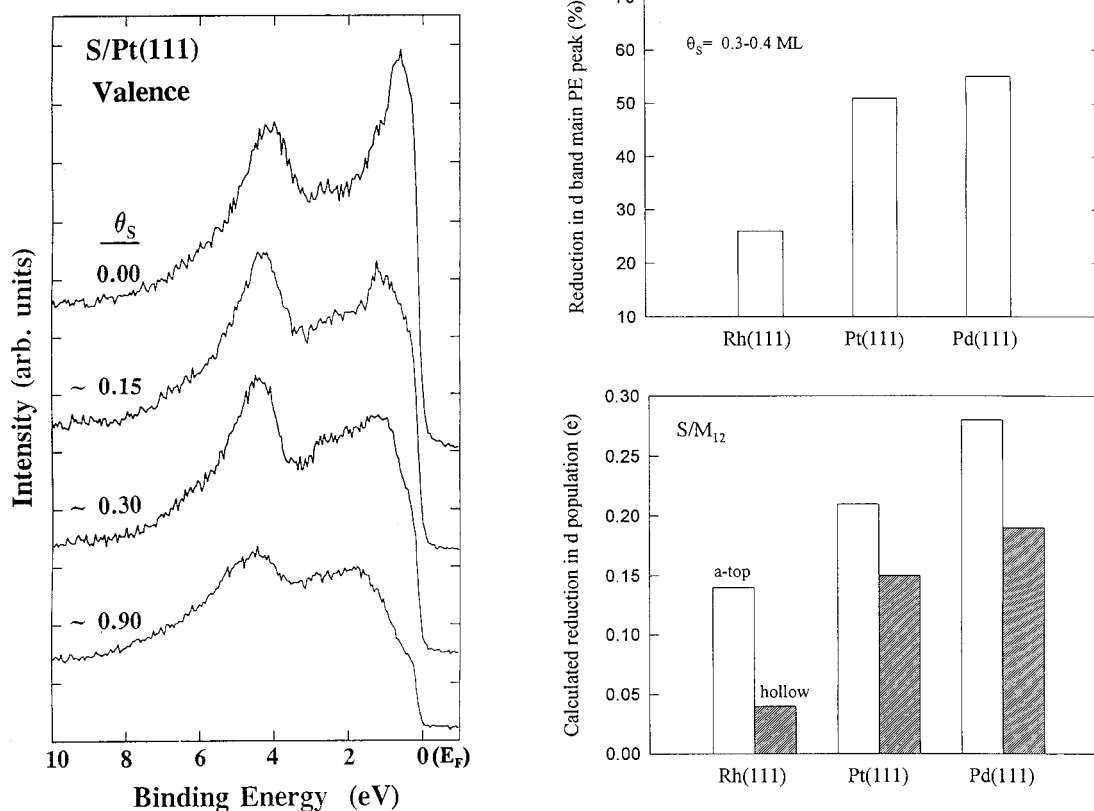


FIGURE 1. Left: Valence photoemission spectra for Pt(111) and S/Pt(111) surfaces. Right, top: Results of photoemission (PE) measurements for S/Rh(111), S/Pt(111), and S/Pd(111) surfaces with a S coverage of 0.3–0.4 ML. The graph displays the percentage decrease induced by sulfur on the intensity of the main peak (located at 0–1 eV below the Fermi level) in the Rh 4d, Pt 5d, and Pd 4d bands.⁸ Right, bottom: Calculated decrease in the valence d population for a metal atom bonded to S in S/Rh₁₂, S/Pt₁₂, and S/Pd₁₂ clusters. The 12-atom metal clusters model the (111) face of Rh, Pt or Pd. S was bonded on an a-top or a hollow site.⁸

Account, we present a short overview of this work and discuss its significance.

Interaction of Sulfur with Metals

On transition-metal surfaces, the adsorption energy of atomic sulfur varies between 80 and 140 kcal/mol. In several cases, a substantial decrease in the adsorption energy with increasing S coverage has been reported. In general, the chemical bonds between S and metal surfaces are strong. The formation of these bonds induces perturbations in the electronic properties of the metals.^{8–10} Figure 1 shows valence photoelectron spectra for Pt(111) and S/Pt(111).⁸ Electron emissions from the S 3p levels appear between 4.5 and 6 eV and overlap with one of the main features of the Pt 5d band. The adsorption of sulfur induces a large reduction in the density of states (DOS) that the Pt substrate exhibits near the Fermi level (0 of binding energy, E_F). The Pt 5d features that appear at ~ 0.8 eV attenuate and shift toward higher binding energy when the S coverage is raised. The results of ab initio self-consistent field (SCF) calculations on clusters that model the S/Pt(111) system show a decrease in the valence 5d population of Pt as a result of a metal \rightarrow S charge transfer and a rehybridization of the Pt(5d,6s,6p) orbitals.^{8a}

After examining the bonding of S to surfaces of several transition metals (Pt, Pd, Ni, Rh, Mo, W),^{8–10} one finds that,

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in all the cases, sulfur withdraws charge from the metal and induces a decrease in its DOS around the Fermi level. The magnitude of these electronic perturbations depends on the nature of the metal. The right-side panels in Figure 1 compare the electronic perturbations found after adsorbing sulfur on the three metals most commonly used in automotive catalytic converters:³ Rh, Pt, and Pd. In a S/Rh(111) surface with 0.4 monolayer (ML) of S, the adsorbate produces a reduction of $\sim 25\%$ in the DOS near the Fermi level, whereas in a S/Pd(111) system the corresponding reduction is close to 55%.⁸ The results of ab initio SCF calculations for model clusters (S/Rh₁₂, S/Pt₁₂, S/Pd₁₂)⁸ indicate that the tendency of a metal to lose d electrons increases in the following order: Rh < Pt < Pd. This agrees well with the relative occupancy of the d shell in the isolated elements: Rh, d^8s^1 < Pt, d^9s^1 < Pd, $d^{10}s^0$. A clear correlation is seen between the changes in the d population of a metal and the attenuation of its DOS near the Fermi level. Pd shows the biggest drop in the d population and the largest attenuation in the DOS. The electronic perturbations in Figure 1 indicate that Pd should be more affected by sulfur than Rh. Indeed, automotive exhaust catalysts based on Pd are more sensitive to sulfur poisoning than catalysts based on Rh.³ In the chemical and petrochemical industries, Pd is notorious for its extreme sensitivity to sulfur poisoning.^{3,5,11}

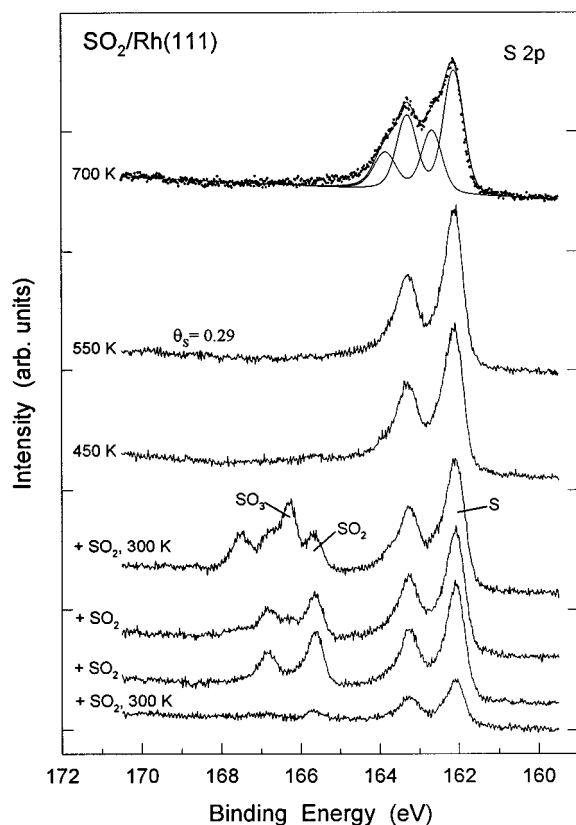


FIGURE 2. S 2p photoemission spectra for the adsorption of SO_2 on Rh(111) at 300 K and subsequent heating to 450 and 700 K.²⁵

In general, the modifications induced by sulfur to the valence bands of metals can lead to significant changes in the chemical and catalytic properties of these elements.^{8,9} For example, theoretical calculations for the S/Rh(100) and S/Pd(100) systems show that the electronic perturbations caused by S diminish the ability of these metals to adsorb CO and dissociate H_2 .⁹ The verification of this prediction at an experimental level is complicated by the fact that sulfur poisoning is a complex phenomenon which can result from combining electronic and steric effects plus morphological changes.^{4–6} *Theoretical studies predict that the electronic perturbations induced by S have a long-range character.*^{9a,12} For S/Rh(100), the Fermi level DOS is reduced by sulfur even at nonadjacent metal sites.¹² On jellium-like surfaces, the electrostatic repulsion between S and another adsorbate remains significant at next-nearest neighbor metal sites (distances of 3–3.5 Å).¹² The long-range character predicted for the S effects is consistent with experimental results,^{6,13} which show that small coverages of S almost completely poison the chemisorption of CO and dissociation of H_2 on Ni(100), plus the methanation of CO on Ni(100), Ru(001) and Rh(111). *On these systems, the initial attenuation of catalytic activity by sulfur suggests that 10 or more equivalent metal sites are deactivated by one sulfur atom.*¹³ This behavior cannot be explained by invoking steric effects or morphological changes.

From studies using single-crystal metal surfaces, it is well established now that sulfur inhibits the chemisorption of small molecules (H_2 , CO, NO, C_2H_4 , etc.),^{13–15} CO

methanation,^{6,13} alkane hydrogenolysis,⁶ olefin hydrogenation,⁶ and the water–gas shift reaction.¹⁶ In general, a combination of electronic and ensemble or steric effects has been proposed to explain sulfur poisoning. On Ni(100), the experimental data for CO methanation ($\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$)¹³ and ethane hydrogenolysis ($\text{C}_2\text{H}_6 + \text{H}_2 \rightarrow 2\text{CH}_4$)⁶ suggest that electronic effects, rather than ensemble requirements, dominate the poisoning mechanism. On the other hand, for the water–gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$) on Cu(111), the decay of the reaction rate with sulfur coverage can be easily understood in terms of a simple site-blocking model, where S adatoms sterically prevent the dissociation of water.¹⁶

The coadsorption of CO and S on metal surfaces has been the subject of many experimental and theoretical studies.^{6,9,13–15,17} The properties of the CO/S/Pt(111) system have been studied in detail using several techniques for surface characterization.^{15,17} Sulfur decreases the adsorption energy of CO by ~ 8 kcal/mol.¹⁵ This probably reflects a S-induced weakening in the metal–CO($2\pi^*$) bonding interactions.¹⁵ The repulsive S \leftrightarrow CO interactions reduce the rates of adsorption and diffusion of CO in the Pt surface.^{15,17} Results of scanning tunneling microscopy (STM) indicate that S adatoms have a large mobility on metal surfaces.¹⁷ When CO adsorbs on S/Pt(111), there is a reordering of the S overlayer, and the repulsive S \leftrightarrow CO interactions force the S adatoms into domains of high local coverage, eventually leading to the formation of molecular S_n species.¹⁷ The morphology of the CO/S/Pt(111) system has a *dynamic character*, in which the structures of the Pt substrate and {CO + S} overlayer change depending on composition and temperature.¹⁷

A large number of studies deal with the surface chemistry of H_2S , thiophene, and thiols (RSH) on metals.^{6,18} This very interesting area has been reviewed recently.¹⁸ When dealing with sulfur poisoning or hydrodesulfurization processes, it is important to know the mechanisms for the cleavage of S–H and S–C bonds on metals. In general, it has been found that the S–H bonds in H_2S and thiols break below 200 K, whereas the S–C bonds in thiols and thiophene usually cleave at temperatures between 250 and 400 K.¹⁸ During the dissociation of organosulfur molecules on metals, S and C atoms are left on the surface while H_2 and hydrocarbon species desorb into gas phase. The exact chemistry depends on the metal and on the complexity of the organosulfur molecule.¹⁸

In recent years, the behavior of SO_2 on metals has received a lot of attention,^{19–25} mainly due to the negative effects of this molecule in air pollution, the corrosion of materials, and the poisoning of catalysts.^{2,3} Sulfur dioxide decomposes either spontaneously or by thermal activation on all the metal substrates studied so far (Fe, Ni, Cu, Mo, Ru, Rh, Pt, Zn, Sn, Cs) except Ag.^{19–25} A comparison of the data for SO_2 on Cs/Mo(110), Mo(110), Ru(001), Rh(111), and Pt(111) shows that the reactivity of the metals toward the molecule increases following the sequence: Pt \approx Rh < Ru < Mo < Cs/Mo < Cs.^{23a,24,25} In experiments performed using synchrotron-based high-resolution photo-

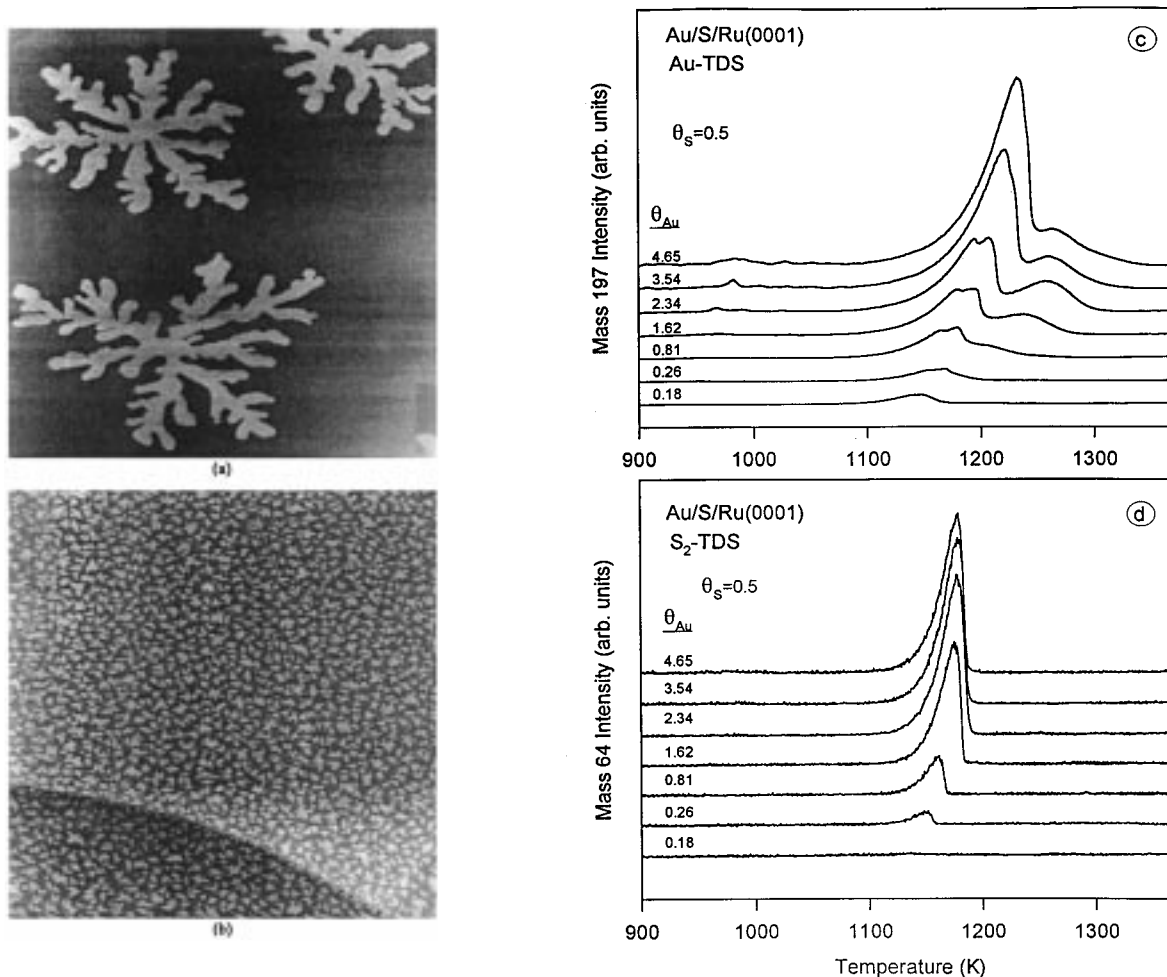


FIGURE 3. Left: STM images ($1 \mu\text{m}^2$) for the deposition of Au on clean Ru(001), top, and a S/Ru(001) surface with 0.05 ML of S, bottom. The white areas correspond to the islands of gold, whereas the dark background denotes the S and Ru atoms. Au was vapor-deposited at room temperature.^{27a} Right: Au and S₂ thermal desorption spectra for a series of Au/S/Ru(001) surfaces. Heating rate, 5 K/s.^{27b}

emission, several sulfur species with distinct electronic properties have been identified.^{19,21,23–25} A typical result is shown in Figure 2. Rhodium-based automotive catalysts are deactivated by SO₂.³ At temperatures below 250 K, SO₂ chemisorbs intact on Rh(111).²⁵ At room temperature, the molecule reacts, depositing atomic S ($\text{SO}_{2,\text{gas}} \rightarrow \text{S}_a + 2\text{O}_a$) and forming SO₃ and SO₄ species ($\text{SO}_{2,\text{gas}} + n\text{O}_a \rightarrow \text{SO}_{2+n,a}$, $n = 1$ or 2) on the metal surface. The molecular SO_x species dissociate upon heating to 450 K, leaving S adatoms, which penetrate into the Rh substrate at temperatures above 600 K.²⁵ Again, one finds results that reinforce the idea that S poisoning is a complex phenomenon that probably involves changes in the electronic properties (Figure 1) and morphology of the metal catalyst.

Interaction of Sulfur with Bimetallic Systems

In industrial applications, catalysts that combine two metals are common.^{5,6} These bimetallic systems exhibit superior performance (activity and/or selectivity) with respect to their individual counterparts. This can be a result of electronic perturbations produced by metal–metal bonding (“ligand” effect) or a consequence of changes in the number of active sites present on the

surface (“ensemble” or “cooperative” effects).^{5,6} In the last 10 years, the interaction between sulfur or S-containing molecules and well-defined bimetallic surfaces has been the subject of a large series of studies.^{10b,18,23,26–31} In principle, on the basis of the evidence presented in the previous section, one can expect that sulfur will induce substantial changes in the physical and chemical properties of bimetallic systems. *This already complex picture is further complicated by the fact that bimetallic bonding can modify the chemical reactivity of a metal toward S-containing molecules.*^{23,25,26,29} In this section, we examine different situations that can occur when sulfur interacts with bimetallic surfaces.

Catalytic reforming is one of the basic petroleum refining processes yielding a large variety of liquid fuels.^{1,5} Due to their low chemical activity, the noble metals (Au, Ag, Cu) are ideal masking agents (or site blockers) frequently added to transition-metal catalysts to reduce the number of active sites and improve selectivity toward hydrocarbon isomerization (avoiding C–C hydrogenolysis and coke formation) in catalytic reforming.^{5,10b} In these systems, the “wetting” of the surface of the transition metal by the noble metal (Au, Ag, or Cu) is a critical factor

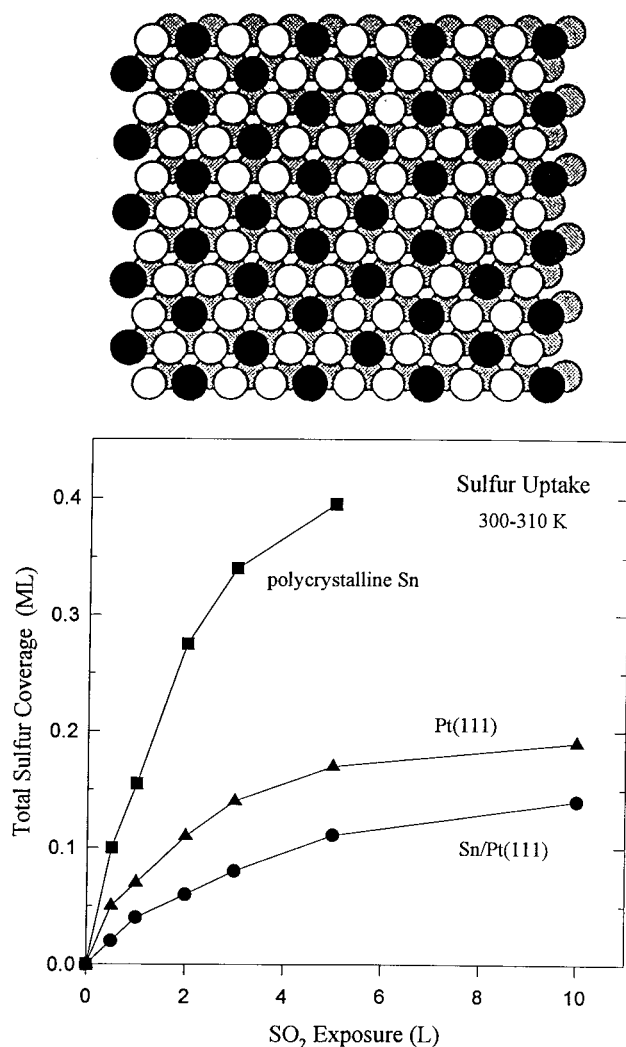
$(\sqrt{3} \times \sqrt{3})R30^\circ\text{-Sn/Pt(111)} \quad \theta_{\text{Sn}} = 0.33 \text{ ML}$


FIGURE 4. Top: Structural geometry for a $(\sqrt{3} \times \sqrt{3})\text{-R}30^\circ\text{-Sn/Pt(111)}$ surface alloy. The dark and white circles represent Sn and Pt atoms, respectively. The Sn atoms are present only in the top layer and protrude 0.22 Å from the plane of Pt atoms.³³ Bottom: Total sulfur uptake for the adsorption of SO_2 on polycrystalline Sn, Pt(111), and a $(\sqrt{3} \times \sqrt{3})\text{-R}30^\circ\text{-Sn/Pt(111)}$ alloy.^{23a}

for good performance of the catalysts. Recent studies have examined the coadsorption of Au and S on Pt(111), Rh(111), Ru(001), Mo(110), and Mo(100).^{10b,27,28,31} On atomically flat Ru(001), Au grows, forming large two-dimensional islands that have dendritic shape (Figure 3a).^{27a} A small precoverage of sulfur, $\sim 0.05 \text{ ML}$, dramatically alters the morphology of the Au overlayer on the Ru substrate (Figure 3b).^{27a} Repulsive interactions between Au and S impose severe limitations in the mobility of Au. As the sulfur coverage raises, Au forms three-dimensional clusters or islands instead of “wetting” the Ru(001) surface. At the same time, Au compresses S into domains of high local coverage that favor S–S coupling, producing drastic changes in the kinetics of S_2 desorption (Figure 3c,d).^{27b} This type of behavior seems to be more general, since it

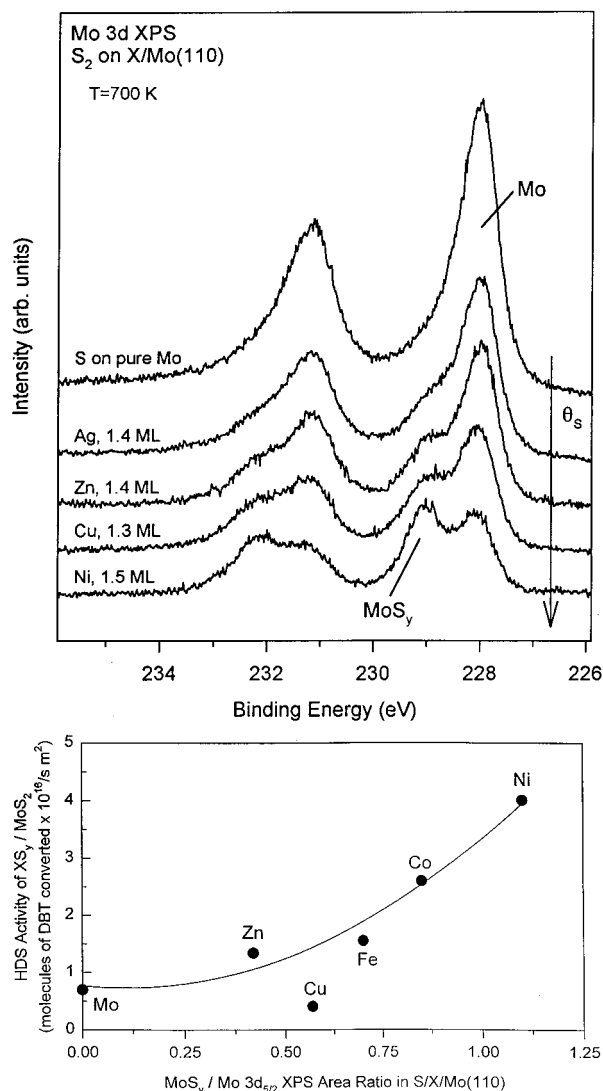


FIGURE 5. Top: Mo 3d core-level photoemission spectra acquired after dosing S_2 to Mo(110) and X/Mo(110) surfaces. X = Ag, Zn, Cu, Fe, Co, or Ni.²⁹ Bottom: Activity of a series of XS_y/MoS_2 catalysts for the hydrodesulfurization of dibenzothiophene³⁴ versus amount of MoS_y formed in each $\text{S}_2/\text{X}/\text{Mo(110)}$ system.²⁹

has been also observed on Pt(111), Rh(111), Mo(110), and Mo(100).^{10b,28,31}

Results of STM indicate that small amounts of sulfur cause big changes in the morphology of the Ag/Ru(001) and Cu/Ru(001) systems.^{27a,30} For S/Ag/Pt(111) and S/Cu/Pt(111), the situation is even worse because, in addition to the morphological changes caused by S, Cu and Ag promote Pt ↔ S interactions and the formation of platinum sulfides.^{23b,31} Thus, in Ag/Pt and Cu/Pt reforming catalysts, the “inert” site blocker probably accelerates the poisoning of the active phase (Pt).^{23b,31}

In many cases, the formation of a metal–metal bond induces important perturbations in the electronic properties of the bonded metals.^{31,32} These perturbations can modify the chemical affinity of a metal for sulfur.^{23,25,26,29} For the S/Ag/Pt(111) and S/Cu/Pt(111) systems, the effects of bimetallic bonding are negative since there is an enhancement in the rate of sulfidation.^{23b,31} When trying to minimize the effects of S poisoning in the reforming

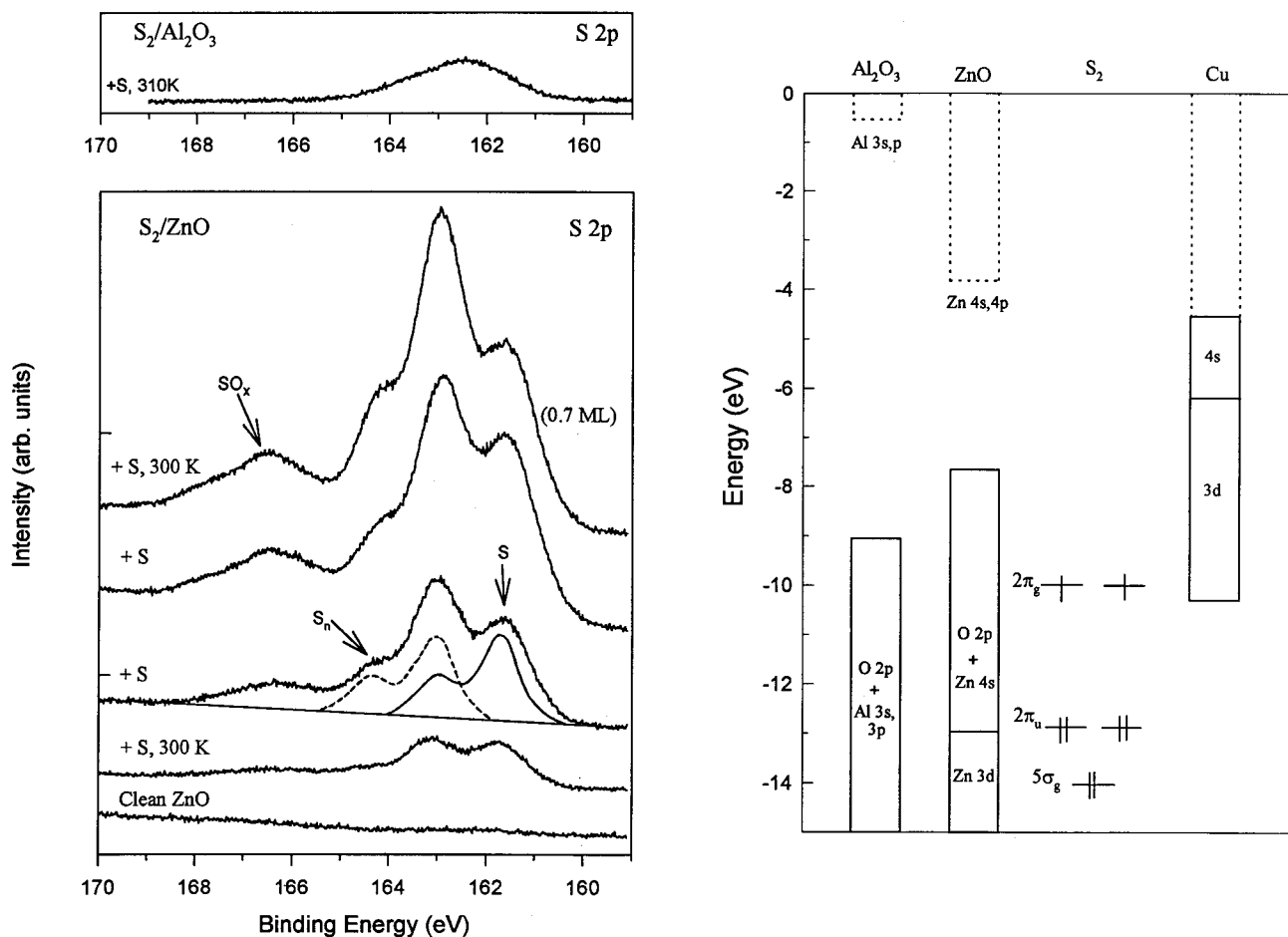


FIGURE 6. Left: S 2p spectra for the adsorption of S₂ on Al₂O₃ and ZnO at 300–310 K. The spectrum for S₂/Al₂O₃, $\theta_S \approx 0.1$ ML, and the last spectrum for S₂/ZnO, $\theta_S \approx 0.7$ ML, were acquired after dosing the same amount of S₂ to both oxides.³⁶ Right: Energy positions for the bands of bulk alumina, zinc oxide, and metallic copper. The empty and occupied states are indicated by dotted and solid lines, respectively. For comparison, we also include the energies for the MOs of S₂.³⁶

process, one seeks bimetallic systems that have catalytic activity and are not very reactive toward S-containing molecules. Tin, also added as a site blocker to platinum reforming catalysts,⁵ forms well-defined alloys with Pt(111) (see top of Figure 4) that are very stable.³³ When compared to pure Sn or Pt, these alloys exhibit a lower chemical reactivity toward SO₂ (see Figure 4), S₂, H₂S, and thiophene.²³ Among the common site blockers (Cu, Ag, Au, Al, Zn, Sn), tin is the best choice for reducing the sensitivity of Pt reforming catalysts to sulfur poisoning.^{23b} *The electronic perturbations associated with the Pt–Sn bond²³ produce a system that has a remarkably low reactivity toward S-containing molecules.* Bimetallic bonding also offers a useful route for increasing the sulfur tolerance of Pd-based catalysts. *Metal ↔ metal interactions reduce the electron donor capabilities of Pd³² and set limits on its ability to form strong bonds with molecules such as SO₂ and thiophene.²⁵* A bimetallic system (Pd/Rh,²⁵ PdNi,¹¹ or PdMn,¹¹ for example) can have a good catalytic activity and be less sensitive to the presence of S-containing molecules in the feedstream than pure Pd.

In hydrodesulfurization (HDS) processes, there is a clear need to enhance the reactivity of metals (Mo or W) toward S-containing molecules.⁵ Bimetallic bonding can be useful in this respect. Figure 5 shows Mo 3d XPS spectra

acquired after dosing S₂ to clean Mo(110) and Mo(110) surfaces with similar coverages (~ 1.5 ML) of Ni, Cu, Zn, and Ag.²⁹ Adsorption on clean Mo(110) produces only a chemisorbed layer of sulfur, and no molybdenum sulfide (MoS_y) is formed. *The admetals promote Mo ↔ S interactions and the formation of molybdenum sulfide.²⁹* The amount of MoS_y formed depends strongly on the nature of the admetal: Ag \approx Zn < Cu < Fe < Co < Ni. The bottom panel in Figure 5 compares trends observed in the activity of a series of XS_y/MoS₂ catalysts (X = Zn, Cu, Fe, Co, or Ni) during the desulfurization of dibenzothiophene³⁴ with trends found for the sulfidation of molybdenum in X/Mo(110) surfaces. In general, a good correlation is observed between the changes in the two properties. The presence of Ni leads to a significant enhancement in the Mo ↔ S interactions and a very large HDS activity. In contrast, the effects of Zn, Cu, and Fe on the Mo ↔ S interactions and HDS activity are less pronounced. *The Ni ↔ Mo and Ni ↔ S ↔ Mo interactions increase the electron density on Mo.³⁵* This makes Mo more chemically active in two key steps for HDS reactions: the adsorption of S-containing molecules and the dissociation of H₂.³⁵

In summary, we have seen that, depending on the nature of the sulfur ↔ metal and metal ↔ metal interac-

tions, several phenomena can occur when sulfur reacts with a bimetallic surface. In some cases, the interaction between sulfur and one of the metals is repulsive, with sulfur and the metal showing a tendency to segregate into separate domains or regions. This produces big morphological changes and reduces the degree of "mixing" of the metals. In other cases, bimetallic bonding can cause an unexpected increase in the rate of poisoning by modifying the chemical affinity of one of the metals for sulfur. When properly "controlled", the effects of metal-metal bonding can be useful for making some types of catalysts less sensitive to sulfur poisoning, or for improving the performance of a metal in hydrodesulfurization processes.

Interaction of Sulfur with Oxides and Metal/Oxide Systems

Metal/oxide catalysts are widely used in the chemical and petrochemical industries.⁵ In these systems, the oxide may behave as an inert support or may actually form part of the "active phase" of the catalyst.⁵ Oxides are also themselves catalysts for a large variety of commercial processes.⁵ To design metal/oxide catalysts that have a high tolerance to sulfur poisoning, one must have a fundamental understanding of the chemistry of S-containing molecules on oxide and metal/oxide surfaces. On the surface of a metal oxide, sulfur can interact with the metal or oxygen sites, producing species that have very different electronic properties ("sulfide" versus "sulfate" formation). Experiments for the adsorption of S₂, H₂S, CH₃SH, and thiophene on a series of oxides (Al₂O₃, ZnO, Cu₂O, MoO₂, Cr₂O₃, CeO₂) show that the S atoms produced by the dissociation of these molecules mainly interact with the metal centers of the surface.³⁶⁻⁴¹ On the other hand, SO₂ preferentially reacts with O centers, readily forming SO₃ and SO₄ species.²⁴

It is important to establish what type of oxides are very reactive toward S-containing molecules. Figure 6 shows S 2p spectra for the adsorption of S₂ on polycrystalline surfaces of Al₂O₃ and ZnO.³⁶ The spectrum for S₂/Al₂O₃ and the top spectrum for S₂/ZnO were acquired after dosing the same amount of S₂ to both oxide surfaces. On alumina, one finds a small coverage of S, ~0.1 ML, bonded to Al sites, and no signal is seen for SO_x species. In contrast, the S₂/ZnO system shows a large sulfur coverage, ~0.7 ML, with S and S_n bonded to Zn and a minor amount of SO_x species. *It is clear that the metal and oxygen sites in ZnO are more reactive than the corresponding sites in alumina.* The right-side panel in Figure 6 compares the molecular orbital energies of S₂ and the band energies of bulk Al₂O₃ and ZnO.³⁶ S₂ is an open-shell system with only two electrons in the 2π_g orbitals. These orbitals interact mostly with the occupied bands of the oxide, and a simple model based on orbital mixing and perturbation theory^{36,39} predicts the following dependence for the adsorption energy (*Q*) of S₂:

$$Q \propto (E_{\text{TVB}} - E_{2\pi}) \quad (1)$$

where *E*_{TVB} is the energy for the top of the valence band

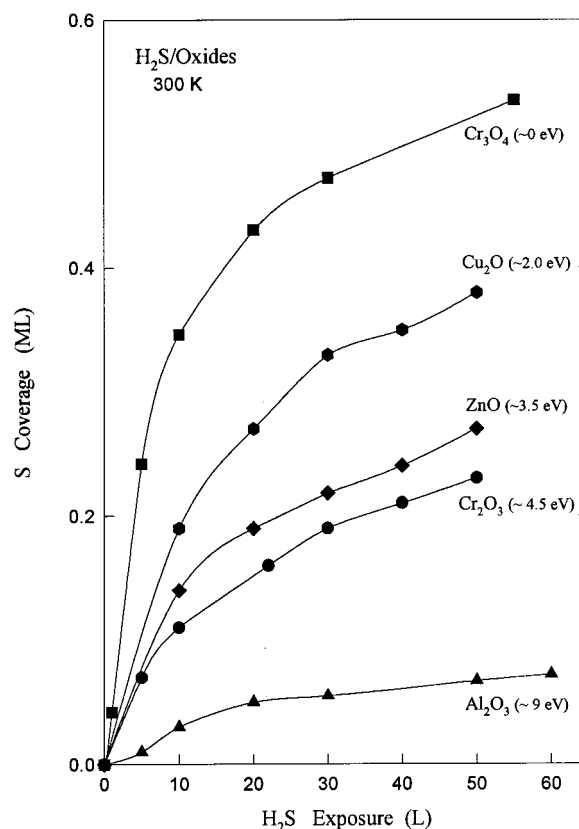


FIGURE 7. Sulfur uptake for the dissociative adsorption of H₂S on several oxides at 300 K. In parentheses is shown the band gap of each oxide.^{36,43}

of the oxide and *E*_{2π} is the energy for the S₂(2π_g) orbitals. Thus, the interaction of S₂ with ZnO is predicted to be stronger than that with Al₂O₃, in agreement with the experimental results.

For adsorbates such as S, SH, and RS groups, perturbation theory gives an equation similar to (1) for the bonding energy on an oxide.³⁶ In simple terms, when the band gap in an oxide decreases, the stability of the valence band of the oxide also decreases, and eq 1 predicts an increase in the reactivity of the oxide toward S-containing molecules. This prediction was tested by examining the adsorption of S₂ and H₂S on a series of oxides.^{36,40,43} Figure 7 displays the results for the sulfur uptake after dosing H₂S.^{36,43} In parentheses is reported the band gap for each oxide. *There is a qualitative correlation: the smaller the band gap in an oxide, the bigger its reactivity toward H₂S.* An identical behavior was observed for the adsorption of S₂.^{36,40} The results of ab initio SCF calculations indicate that the trends seen for the adsorption of H₂S and S₂ reflect variations in the intrinsic or individual reactivity of the metal centers in the oxides.^{36,40,43} *The ability of a metal center to move its electrons and respond to the presence of a S-containing molecule depends on the stability of the valence band in which these electrons are located.* The larger the band gap in the oxide, the more stable the valence band and the more difficult to move the valence electrons. In general, the correlation between the band-gap size and reactivity works well when comparing the reactivity of oxides that exhibit a substantial difference in the size of their band

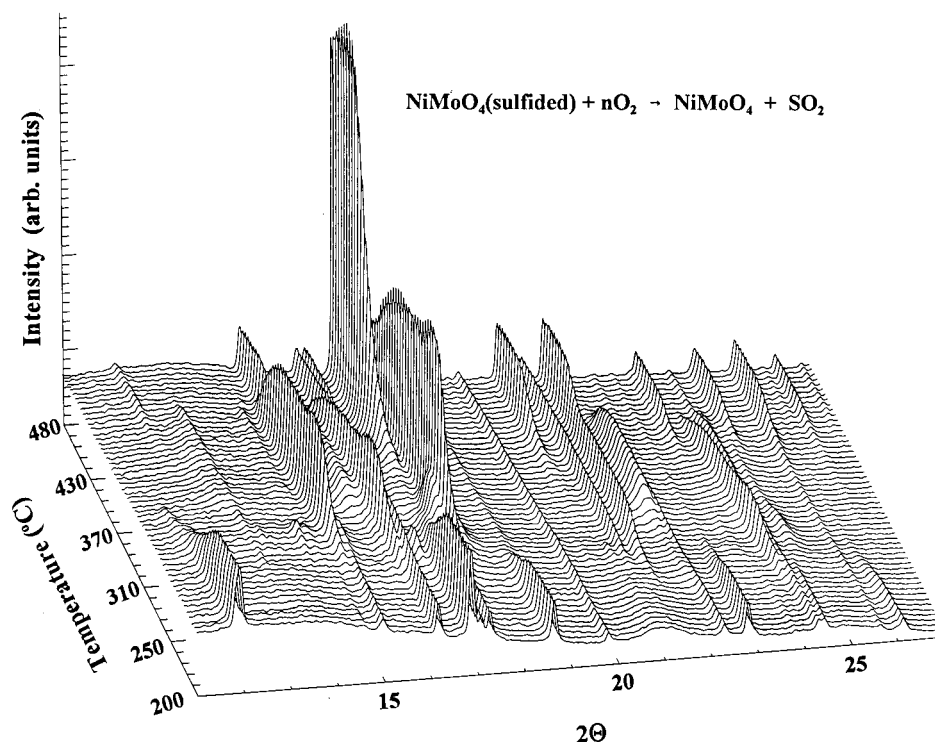


FIGURE 8. Time-resolved X-ray powder diffraction patterns for the regeneration of sulfided NiMoO_4 . The sample was set in an open capillary exposed to air and heated from 25 to 650 °C. Heating rate, 1.2 °C/min.⁴⁵

gaps. This is the case with Al_2O_3 versus ZnO or Cu_2O . For oxides that have band gaps of similar size, other factors (morphology of the surface, number of metal centers, presence and type of oxygen vacancies, etc.) can determine their relative reactivities for the adsorption and dissociation of S-containing molecules.

During the poisoning of metal/oxide catalysts, does sulfur prefer to bond to the metal or to the oxide support? In Figure 6, the bands of metallic Cu (a typical metal) offer a better match in energy for the frontier orbitals of S_2 (or organosulfur molecules)³⁶ than the bands of alumina or zinc oxide. This is also valid for other metals.³⁶ Now, metal particles supported on an oxide can show electronic perturbations with respect to the corresponding bulk metals,^{41,42} but in general these perturbations are not large enough to compensate for the differences in energy seen in Figure 6 for the metal and oxides. *Studies for a large series of metal/oxide systems that contain different types of metals (Ru, Ni, Pd, Pt, Cu, Ag, Au, Cs) on several oxide substrates (Al_2O_3 , ZnO , Cu_2O , Cr_2O_3 , MoO_2) show that S_2 , H_2S , and organosulfur molecules always prefer to interact with the supported metals.*^{24,36,40,43,44} In addition, while alumina is practically ignored by the adsorbed molecules, supports such as ZnO and Cr_2O_3 get sulfided.^{36,44}

The so-called “metal ↔ support interactions”⁵ can play an important role in sulfur poisoning.⁴⁰ *Metal particles supported on oxides that have a small band gap (“interacting supports”)⁵ in many cases exhibit unique electronic properties that lead to chemical behavior different from that seen for bulk metals.*^{41,42} The Cu/ ZnO system is a good example for an extreme situation in which metal ↔ support interactions make a metal less sensitive to the presence of S-containing molecules (i.e., sulfur poison-

ing).⁴⁰ The opposite case is the Au/ Cr_2O_3 system, where metal ↔ support interactions make the Au adatoms much more reactive toward H_2S than pure metallic gold.⁴⁰

Regeneration of Poisoned Catalysts

Since most poisoned catalysts are expensive, there is a need to reactivate or regenerate them. One can attempt to remove sulfur from the surface of a catalyst by reaction with pure hydrogen ($\text{S}_{\text{solid}} + \text{H}_{2,\text{gas}} \rightarrow \text{H}_2\text{S}_{\text{gas}}$) or oxygen ($\text{S}_{\text{solid}} + \text{O}_{2,\text{gas}} \rightarrow \text{SO}_{2,\text{gas}}$) at high temperatures. In some situations, this procedure is useful for the regeneration of poisoned metal/oxide catalysts.^{4,5a} But in many cases there are problems associated with this methodology, since hydrogen may reduce the oxide support and oxygen may oxidize the metal component.^{3,4} Reaction with oxygen is a promising route for regenerating pure oxide catalysts.^{4,5a} The process is carried out under pressures of oxygen (0.2–2 atm) that are not compatible with most of the techniques currently used in surface science. One can study it using X-ray absorption near-edge spectroscopy (XANES) and X-ray diffraction (XRD).^{38,45} Investigations at Brookhaven National Laboratory have established the feasibility of conducting subminute, time-resolved XRD experiments under a wide variety of temperatures and pressure conditions ($-190 < T < 900$ °C; $P \leq 45$ atm).⁴⁶ This important advance results from combining the high intensity of synchrotron radiation and new data-collection devices.⁴⁶ This unique approach has been used to study the regeneration of poisoned oxide catalysts. A typical case is shown in Figure 8. After exposing a nickel molybdate (NiMoO_4) to H_2S , one sees the formation of metal sulfides and sulfates that change the X-ray diffraction pattern of the

system.⁴⁵ In the presence of O₂, this "mixture" is stable up to ~250 °C, when reaction begins.⁴⁵ As the temperature is raised, several intermediates are observed, and at ~400 °C the diffraction lines for pure NiMoO₄ appear. At 480 °C, only the XRD pattern of NiMoO₄ is seen.⁴⁵ Results of time-resolved XRD and XANES indicate that reaction with oxygen at high temperature is effective for removing sulfur from poisoned NiMoO₄, ZnO, NiO, and MoO₃ catalysts.

Concluding Remarks

Studies examining the interaction of sulfur with well-defined metal and oxide surfaces have helped to explain or unravel many of the mysteries behind catalyst poisoning. These studies provide a clear and conclusive proof that sulfur poisoning is a complex issue that can involve large changes in the structural, morphological, and electronic properties of a catalyst. Using well-defined surfaces in combination with the modern techniques of surface science, one can get a *fundamental understanding* of the behavior of S-containing molecules on metals and oxides. Following this approach, a series of phenomena have been discovered that are interesting from the viewpoint of surface chemistry in general. It has been shown that the chemical activity of a metal can be changed by metal ↔ metal and metal ↔ oxide interactions. Knowledge is being gained on what type of systems are reactive and which are not. This is *the first necessary step* for a scientific design of catalysts that have a low sensitivity to sulfur poisoning, or a high activity for hydrodesulfurization and DeSO_x processes.

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