The Modification of Benzene and Carbon Monoxide Adsorption on Pt(111) by the Coadsorption of Potassium or Sulfur

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Abstract: The effects of potassium and sulfur on the chemisorption of CO and benzene on the Pt(111) surface have been studied by thermal desorption spectroscopy (TDS). Potassium causes an increase in the desorption peak temperature of CO and a decrease in that of benzene. Sulfur, on the other hand, causes a decrease in the desorption peak temperatures for both benzene and CO. We interpret the effects of potassium on CO and benzene adsorption as electronic, while for sulfur, structural effects may dominate.

I. Introduction.

Submonolayer amounts of potassium and sulfur are frequently added to transition metal catalyst surfaces in order to modify (promote or poison) their catalytic properties.[1-12,30] Some have argued that the dominant effect of these and other additives is to block certain surface sites which are needed for adsorption or for the rearrangement of chemical bonds. This is sometimes called an ensemble or structural effect and can change the rate or product distribution of catalytic reactions.[7] However, changes in the heat of adsorption of CO when coadsorbed with alkali metals indicate that electronic interactions between the adsorbates and the metal atoms occur in addition to structural ones.[8] This is called a chemical, ligand, or electronic effect. Other concepts have also been employed to describe electronic effects such as surface acidity or basicity.[9]

In this continuation of earlier studies on electronic and structural effects,[11,12] we report the changes observed in the chemisorption properties of carbon monoxide and benzene when coadsorbed with potassium or sulfur on the Pt(111) surface. The main technique used in our investigation is thermal desorption spectroscopy (TDS). For potassium adsorption, it appears that an electronic effect is the dominant cause of the observed changes in the desorption behavior of CO and benzene. With sulfur coadsorption, on the other hand, structural effects might be more important than electronic ones in altering the desorption behavior of these molecules.

II. Experimental Section

A Pt(111) sample was mounted in a standard ultrahigh vacuum (UHV) chamber ($\approx 3 \times 10^{-10}$ torr base pressure), equipped with a mass spectrometer for thermal desorption spectroscopy (TDS), a low-energy electron-diffraction (LEED) system, a single-pass cylindrical-mirror analyzer (CMA) for Auger electron spectroscopy (AES), an electrochemical cell sulfur deposition gun, and a "SAES Getters" potassium source. Carbon, oxygen, silicon, and calcium impurities were removed by argon ion sputtering while heat cycling the sample between 800 and 1200 K. Final purity was checked by AES and LEED.

To achieve the desired coverages, sulfur was either (1) deposited at a constant rate for a certain time and then monitored by AES or (2) the surface was saturated with sulfur and then heated, desorbing sulfur, until a desired coverage was reached. For the CO and sulfur coadsorption system we were interested in four coverage regimes: clean Pt(111), $\theta_S = 0.25$, $\theta_S = 0.33$, and $\theta_S > 0.5$ (where θ_S is the sulfur coverage relative to the platinum monolayer atomic density). After sufficient sulfur deposition on a clean Pt(111) surface, an ordered $(\sqrt{3}\times\sqrt{3})R30°$ sulfur overlayer structure could be obtained by heating to 700–900 K. A second lower coverage, (2×2) sulfur overlayer structure was obtained by heating to 1000–1150 K. No other LEED patterns were visible at higher or lower coverages, consistent with previously reported results.[16] Since sulfur is generally believed to occupy the highest coordination site available on metal surfaces, the two overlayer LEED patterns are most likely due to the sulfur overlayers depicted in Figure 1, parts a and b. For the benzene experiments, the sulfur adlayers were not annealed: ordered sulfur overlayers would not allow strong chemisorption because of the large size of the benzene molecule.

The potassium deposition techniques and overlayer behavior on Pt(111) have been described in detail elsewhere.[17] One monolayer of potassium, defined as $\theta_K = 1$, has an atomic K/Pt surface layer density of 0.36. CO and benzene exposures were accomplished by using a needle doser in front of the sample. Heating rates for the thermal desorption spectra were ≈ 30 K s^{-1}.

III. Results

1. Chemisorbed Carbon Monoxide. a. Clean Pt(111). Carbon monoxide adsorbed on Pt(111) has been extensively studied by many researchers (see ref 18 and references therein). At low coverages, CO adsorbs on top sites on platinum, while at higher coverages bridged sites become occupied. Although there has been some debate in the literature, it was recently shown that the top and bridge sites are the only ones occupied, even at high coverages.[18,19]

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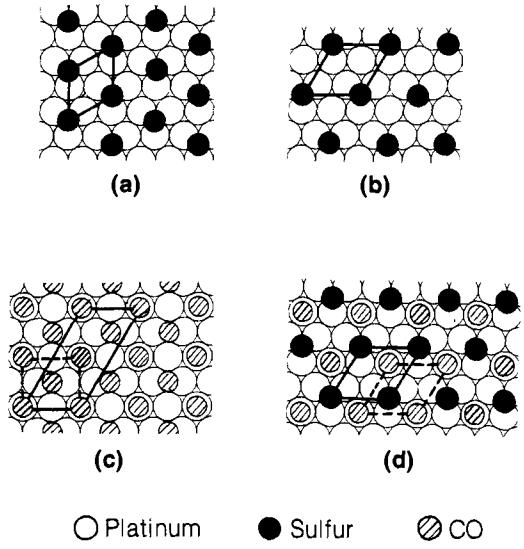

Figure 1. Real space models of sulfur and CO overlayers on Pt(111) corresponding to the following LEED patterns: (a) $(\sqrt{3}\times\sqrt{3})R30°$–S, (b) p(2×2)–S, (c) c(4×2)–CO, (d) p(2×2)–(CO plus S).

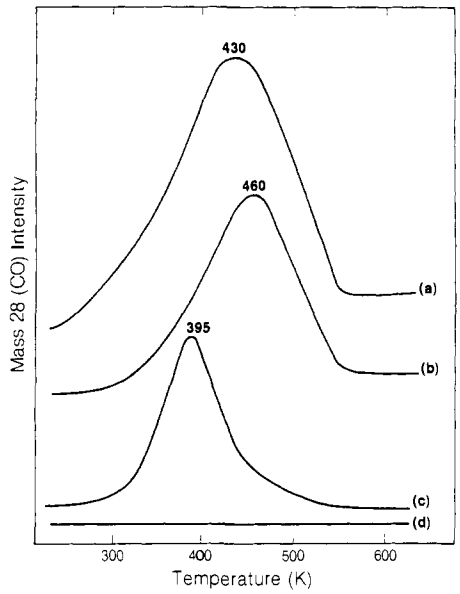

Figure 2. Carbon monoxide thermal desorption from Pt(111) after (a) 1-langmuir exposure, and (b) 0.4-langmuir exposure. CO thermal desorption from sulfided Pt(III) after (c) p(2×2)–S, 0.4-langmuir exposure, and (d) $(\sqrt{3}\times\sqrt{3})R30°$–S, 0.4-langmuir exposure. Background was substracted in all cases.

With the Pt(111) sample held at 170 K, a CO exposure of greater than 1 langmuir (1 langmuir = 1×10^{-6} torr·s) was sufficient to yield a c(4×2) overlayer LEED pattern, as observed by others.[18] Dynamical LEED intensity analyses[19] have shown this pattern to correspond to a real space representation described in Figure 1c, and a coverage of $\theta_{CO} \simeq 0.5$. In Figure 2, parts a and b, we show the CO thermal desorption spectra following 1- and 0.4-langmuir exposures. Note the increase in peak area and concomitant decrease in temperature of the peak maximum for the higher exposure. The effect is thought to be due to repulsive lateral interactions between the CO molecules.[18,19]

b. Pt(111) + Potassium. In Figure 3 is shown the saturation coverage CO thermal desorption spectra as a function of potassium coverage on the Pt(111) surface. The specifics of this system have been discussed in detail elsewhere.[11] Of importance here is to note the large increase in the CO heat of adsorption with increasing

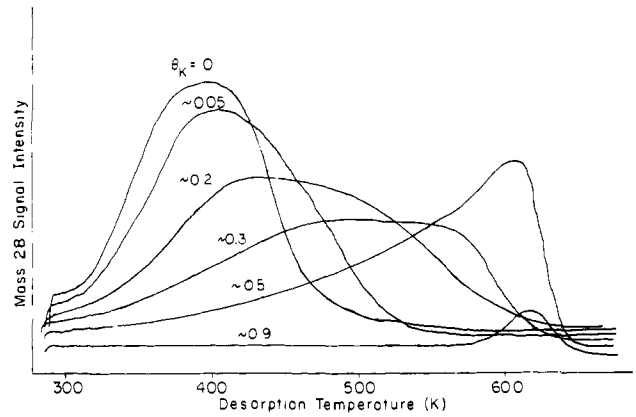

Figure 3. Carbon monoxide thermal desorption from Pt(111) after CO saturation exposures for various potassium coverages. (See ref 17 for coverage calibration.)

potassium coverage. Also, the change in heat of adsorption was a continuous function of both CO and K coverage, as shown previously.[11]

c. Pt(111) + Sulfur. The (2×2) sulfur overlayer structure on Pt(111) allowed significant CO adsorption following a 0.4-langmuir exposure as can be observed in Figure 2c. The desorption peak temperature, however, was shifted down by about 65 K from a 0.4-langmuir exposure on clean Pt(111), Figure 2b. Higher CO exposures on the p(2×2) sulfur overlayer resulted in no additional adsorption. In contrast, in Figure 2d we show the (lack of) CO thermal desorption following a 0.4-langmuir CO exposure on the Pt(111) + $(\sqrt{3}\times\sqrt{3})R30°$ sulfur surface. Similar spectra, showing little or no CO desorption, were observed for higher CO exposure as well as for higher sulfur coverages. No new, or altered, LEED patterns were observed following CO exposure. The CO thermal desorption peak area for the Pt(111) + p(2×2) sulfur + 0.4-langmuir CO overlayer (Figure 2c) was $\approx 1/2$ that of the Pt(111) + c(4×2)–CO overlayer (see Figure 2a).

In Figure 1d we show what we believe is the real space representation of a the p(2×2) overlayer structure with coadsorbed CO and S. With a p(2×2) overlayer array of sulfur atoms sitting in hollow sites, there exists another (2×2) mesh of single platinum atom sites with no coordinated sulfur atoms, where CO could be adsorbed. This model of coadsorption is consistent with the observation that the (2×2) sulfur overlayer LEED pattern was not changed when CO was adsorbed and the result that the CO thermal desorption peak area for the c(4×2)–CO structure on clean Pt(111), with a known coverage of $\theta_{CO} = 0.5$, was twice that of the p(2×2)–(S + CO) overlayer structure, with $\theta_S = 0.25$ and $\theta_{CO} = 0.25$. Assuming that this model is correct, each sulfur atom blocks three platinum substrate atoms from CO adsorption. This is also confirmed from the virtually complete blocking of CO adsorption on the $(\sqrt{3}\times\sqrt{3})R30°$ sulfur overlayer surface where $\theta_S = 0.33$, Figure 2d. A weakly chemisorbed state may exist at lower temperatures.

The p(2×2) overlayer structure with one sulfur atom and one CO molecule per unit cell is ideally suited for a dynamical LEED intensity analysis due to the small size of the unit cell. Such an analysis might yield valuable information concerning bond length distortion in coadsorption systems.

2. Chemisorbed Benzene. a. Clean Pt(111). The thermal desorption spectra of benzene on Pt(111) is shown in Figure 4. For low exposures, most of the benzene decomposed upon heating, with hydrogen being the main species monitored in the desorption spectra. For higher exposures, some of the benzene desorbed intact. Here we focus only on the molecular benzene fraction of the desorption spectra and avoid discussion of the mechanism and particulars of decomposition as discussed elsewhere.[20] The low coverage benzene thermal desorption spectra of Figure 4 resemble those previously published for adsorption near room temperature

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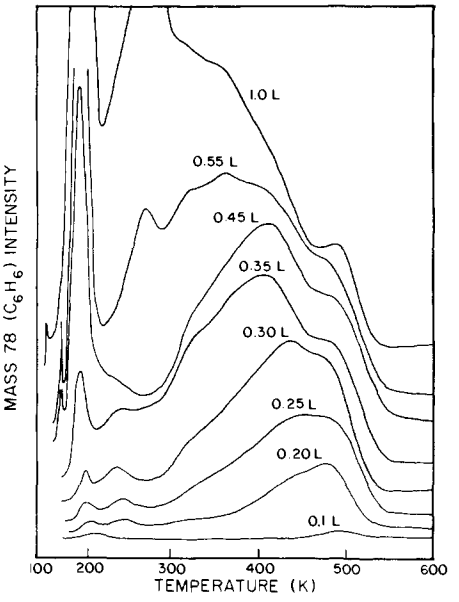

Figure 4. Benzene thermal desorption from Pt(111) after different exposures.

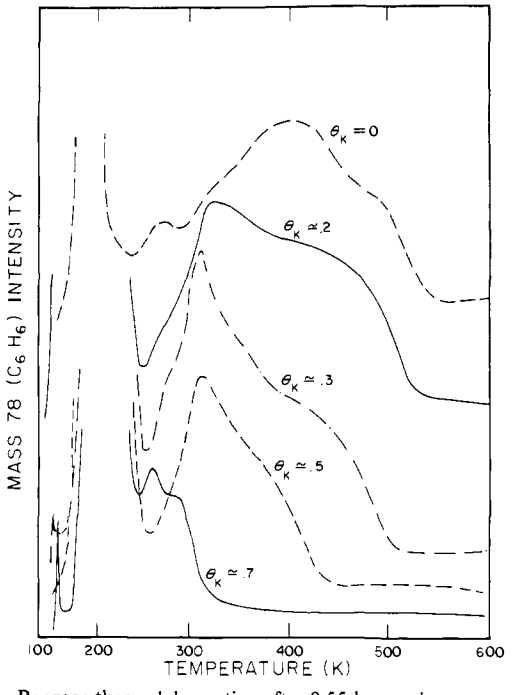

Figure 5. Benzene thermal desorption after 0.55-langmuir exposure from Pt(111) with several potassium coverages.

where two desorption peaks were observed.[12,21] Several new features arise, however, below the temperature regime previously studied. Quite noticeable is the observation that at least 2 or 3 more adsorption states exist whose adsorption energy is stronger than that of condensed-phase benzene, yet considerably less than that of the more tightly bound molecularly adsorbed benzene (where decomposition competes with desorption upon heating).

b. Pt(111) + Potassium. In Figure 5 the thermal desorption spectra are shown for benzene desorbing from Pt(111) with various coverages of potassium. The same trends are observed that were reported earlier,[12] where the experiment was carried out following room temperature adsorption. Here, with the advantage of liquid-nitrogen cooling, the decrease in benzene adsorption energy with potassium coadsorption (as evidenced by a 200 K decrease in the temperature of maximum desorption rate) is much more significant than previously observed. The same type of effect is observed at all benzene exposures; the 0.55-langmuir exposure proved most useful in understanding the effects.

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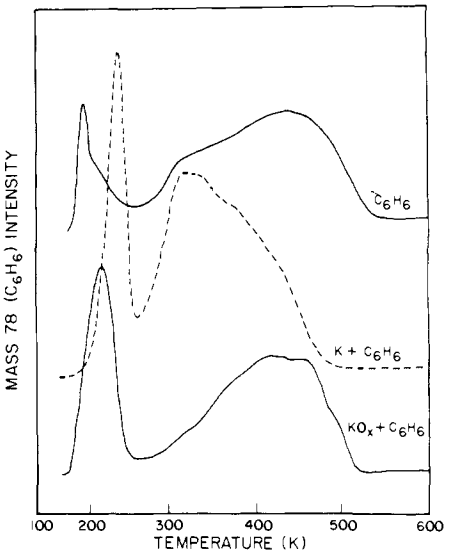

Figure 6. Benzene thermal desorption from Pt(111) clean, with potassium, and with potassium oxide.

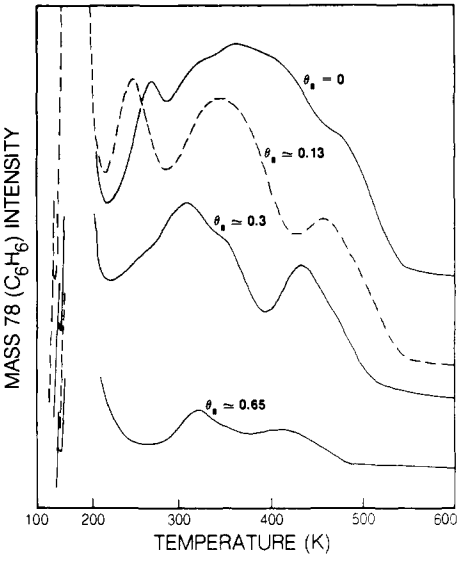

Figure 7. Benzene thermal desrotpion after 0.55-langmuir exposure from Pt(111) with several sulfur coverages.

In Figure 6 the effect that adsorbed potassium has on benzene desorption is compared with the effect that is seen with potassium oxide. In the potassium oxide case, potassium was first deposited to $\theta_K \simeq 0.3$ and then the surface was exposed to 5 langmuirs of oxygen. Oxidation of the potassium made its effect on benzene adsorption practically disappear.

c. Pt(111) + Sulfur. The effect of sulfur on the desorption of benzene is shown in Figure 7. The dominant features are (1) a slight drop in temperature of the desorption rate maximum and (2) an effective blocking of adsorption sites as indicated by a large decrease in the amount of desorbing benzene. The sulfur-covered surfaces were *not* annealed, hence they do not correspond to ordered overlayers.

IV. Discussion

The interactions of CO and benzene with sulfur and potassium (following low-temperature exposure) on Pt(111) are contrasted here because both molecules had shown large changes in their chemisorption behavior when coadsorbed with potassium in earlier studies.[11,12] Due to the different electronegativities of potassium and sulfur, an intrinsically different effect on the chemisorption of these molecules might be expected. The results show that

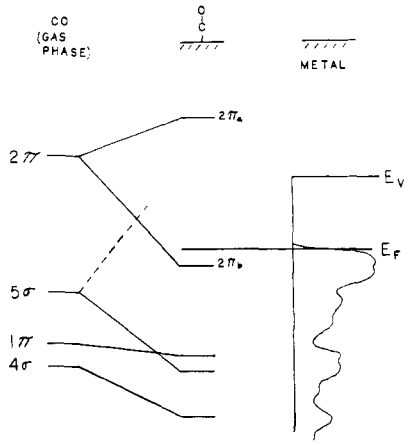

Figure 8. Molecular orbital energy diagram for CO bonding to metals.

adsorbed potassium on Pt(111) caused a 200 K increase in the peak temperature of desorption of CO and a 200 K decrease in the maximum temperature of desorption of benzene and that coadsorbed sulfur caused a decrease in the temperature of desorption of both CO and benzene.

The large potassium-induced change in desorption temperature of both CO and benzene seems to be due to a strong electronic interaction. More evidence supporting an electronic interpretation comes from the TDS, photoemission, and high-resolution electron energy loss results.[8,11,12,25] Some results also indicate that the electronic interaction is mediated by the substrate and is effective over perhaps several interatomic spacings (see ref 24 for an alternative interpretation). From the data presented in Figure 5, one can see that the CO thermal desorption peak moves up (in temperature) in a continuous manner. If direct interactions took place between CO and K, a peak would have grown in at 600 K while the 400 K peak diminished in size. Instead, the slow continuous shifts (as is more apparent elsewhere[12]) suggest a delocalized interaction. When monitored with HREELS, the stretching frequency of CO decrease substantially, implying increased electron occupancy of the 2π CO orbital.[8d,11] The increase in 2π occupancy has also recently been demonstrated by surface penning ionization spectroscopy.[23] In the absence of coadsorbed potassium, the C–metal bond energy for chemisorbed CO can be largely attributed to 5σ donation from the carbon to the metal. When potassium is coadsorbed with CO, the change in the surface dipole field allows more back-donation into the 2π level. This strengthens the metal–carbon bond but weakens the carbon–oxygen bond.

With the aid of a molecular orbital energy diagram, Figure 8, one can better imagine why coadsorbed potassium should cause the 2π CO level to increase its occupancy. The position of the levels on the surface can be monitored by various electron emission spectroscopies[8b,23,25,26] as well as being calculated by using theoretical techniques. If, by decreasing the work function, we bring the 2π gas-phase level closer to the Fermi level, then the overlap between the 2π level and the metal orbitals should increase. This would explain the larger interaction between the CO and the surface, as well as the increase in the 2π character of the conjugate metal-2π orbital. In this picture, the molecular orbitals of the adsorbate (at least the 2π level) are not "pinned" to the Fermi level: they do not follow the Fermi level exactly as one changes the work function. If all the electron energy levels moved with changes in the surface dipole field such that they remained at constant position with respect to the Fermi energy, then no changes

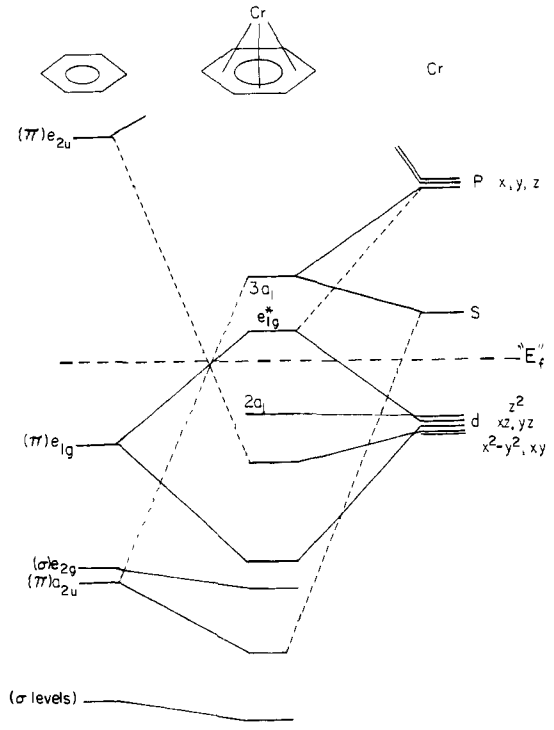

Figure 9. Molecular orbital energy diagram of a benzene–metal system. (See ref 22 and 28.)

in bonding should necessarily occur. We have also performed UPS measurements for CO and benzene coadsorbed with potassium, which are in qualitative agreement with the ideas presented here.[25]

By coadsorbing oxygen, the effect of potassium on the chemisorption of benzene almost disappeared, as we show in Figure 6. This further supports the model of an electronic effect for the potassium-induced changes. If it were structural, we would have expected the oxidation to cause an even greater change in thermal desorption peak temperature. It is also interesting to point out that K_2O is the promoter for both the ammonia synthesis[29] and CO hydrogenation reactions on iron. Our result, however, implies that electronic promotion might not take place if the potassium is oxidized to saturation (i.e., KO_2 or KO_3). In other work we found that oxygen moderated the effect of K on CO, but not to the same extent that was seen for benzene. We would suggest that under the reducing conditions of both ammonia synthesis and CO hydrogenation, the potassium is *not* oxidized to saturation, and that it is therefore able to show significant promotion effects.[22,29]

The interpretation of the effect of coadsorbed sulfur on CO and benzene is less clear than that of potassium. We observed a decrease in the temperature of CO desorption from Pt(111) when sulfur (an electronegative species) was added (Figure 2c). This might be expected (using electronic arguments) since coadsorbed potassium (electropositive) caused a large increase in the CO desorption temperature.[4] Surprisingly, analogous effects were not seen for benzene adsorption: both potassium and sulfur caused a decrease in the benzene desorption temperature.

In Figure 9 we show a molecular orbital diagram for a metal–benzene system analogous to our surface.[22,28] What is of interest here is the e_{1g}* level lying just above E_f. If by putting potassium on the surface we can lower this level enough to be populated, and it should weaken the benzene–metal interaction (as we observe).

But why then did sulfur cause a decrease in desorption temperature of benzene as well as CO? Recent work on electron

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acceptors shows that the work function of a metal does not behave in a simple manner.[27] From the point of view of adding an electron acceptor (such as sulfur) to the surface, the dipole created between the atoms and their image charge should increase the work function. But with adsorbed chlorine, for instance, sometimes a decrease in work function is observed. This can be rationalized by noting that the adsorbate-image dipole is not the only dipole component of the work function. A second dipole component comes from the bulk electron spillover into the vacuum. The changes in electron hybridization and spillover character due to adsorbates can be more complex than the adsorbate-image dipole component.[27] Recently sulfur has been shown to decrease the work function of Pt(111).[31]

To follow this argument to its logical conclusion, we would say that with sulfur, as with potassium, a decrease in work function causes the benzene e_{1g}^* level to be populated, decreasing the benzene–substrate bond energy. However, similar reasoning should lead us to predict that potassium and sulfur should have the same effect on coadsorbed CO. This was not observed: potassium and sulfur showed opposite effects on the CO desorption temperature. We are therefore led to question the electronic effect as dominating the sulfur–benzene coadsorption system.

We can, however, explain the decrease in CO and benzene desorption temperature (when sulfur is coadsorbed) as being due to a structural effect. In order to understand how a structural effect can change the rate of desorption, we briefly review the theory of rate processes. The rate of desorption, R, of an adsorbate leaving a surface may be expressed as

$$R = kf(\theta) \tag{1}$$

where $f(\theta)$ is some function of the coverage of the adsorbate. The rate constant k may be expressed from the activated complex statistical theory as

$$k = \frac{k_b T}{h} K_{eq}^{\dagger} = \frac{k_b T}{h} \frac{Q^{\dagger}}{Q_{ads}} \exp(-E_0/RT) \tag{2}$$

where $K_{eq}^{\dagger}$ is the equilibrium constant between the adsorbed and activated states, $Q^{\dagger}$ is the partition function of the activated complex, Q_{ads} is the partition function for the adsorbed species, and E_0 is the zero-point energy difference between the adsorbed and activated states.[13] For most cases, k does have some coverage dependence,[14] but we avoid this discussion here and consider the low coverage limit. Equation 2 can be expressed somewhat differently from equilibrium thermodynamics by using the equation

$$\Delta G^{\circ\dagger} = \Delta H^{\circ\dagger} - T\Delta S^{\circ\dagger} = -RT \ln K_{eq}^{\dagger}$$

then we have

$$k = \frac{k_b T}{h} \exp(-\Delta H^{\circ\dagger}/RT) \exp(\Delta S^{\circ\dagger}/R) \tag{3}$$

And since $E_a \simeq \Delta H^{\circ\dagger} - RT$ (for a condensed phase)

$$k = \frac{k_b T}{h} e^{-1} \exp(\Delta S^{\circ\dagger}/R) \exp(-E_a/RT) = A \exp(-E_a/RT) \tag{4}$$

where A is called the preexponential factor, or prefactor. The activated complex statistical theory formulism (eq 2) emphasizes the partition functions of the adsorbed and activated states, while the thermodynamic formulism (eq 4) emphasizes entropy change in the desorption process.

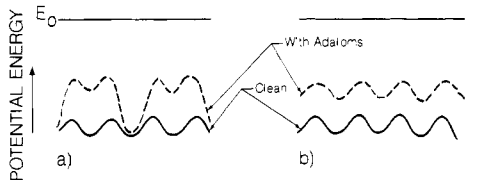

Figure 10. Potential energy contour of an adsorbate on clean and modified surfaces in which the main effect is (a) structural or (b) electronic.

If the molecule is relatively free to move along the surface then Q_{ads} should be large as in a 2-D gas. ($Q_{translation} \approx 10^{10}$ per degree of freedom (DOF) in the gas phase.) On the other hand, if the molecule is confined to a certain site on the surface Q_{ads} will be smaller: Q_{ads}(immobile) < Q_{ads}(mobile). The decrease in the translational component of the partition function will be partially compensated for by additional vibrational (and frustrated translational) DOFs. The partition functions for these DOFs, however, are many orders of magnitude less than that of a translational DOF. Since Q_{ads} is larger for the 2-D gas, the rate constant, k(mobile) from eq 2, will be smaller than k(immobile). This can be visualized graphically as follows: consider a metal surface onto which is placed sulfur adatoms, where the potential energy contour for an adsorbate along the clean and modified surfaces can be represented as in Figure 10a. It is important to note that sulfur does not bond strongly with molecules such as CO or benzene. A change in the potential energy contour for an adsorbate along the surface will cause a change in mobility of the adsorbate. A change in surface mobility will also effect the thermal desorption rate and becomes manifest in a change in the preexponential factor of the desorption equation (i.e., the surface entropy component A of eq 4 or Q_{ads} of eq 2). The temperature of the maximum rate of desorption will be lower for an immobile layer than a mobile one.

Thus, the transition from a relatively mobile to an immobile benzene or CO overlayer with the blocking of sites by sulfur (or with increasing coverage of a single species) will result in a decrease in desorption temperature. A change in the preexponential factor by three orders of magnitude would cause a change in peak temperature by about 50 K for adsorbed CO or benzene. Since this is consistent with the data, we propose that structural effects may dominate the change in desorption behavior for the sulfur coadsorption systems. (Ibach et al.[14] have reported that the coverage dependence of the preexponential factor can change the rate constant by up to four orders of magnitude. They gave a similar argument based on an equilibrium between the adsorbed species and the gas phase: transition state theory was not needed in their model.)

If, on the other hand, the surface additive affects the depth of the chemisorption potential well and not the diffusion energy along the surface then the dominant change will occur with the E_a (or ΔH_{ads}) term and not with the preexponential factor. This is depicted graphically in Figure 10b. In this extreme, the structural effects as well as changes in transition-state geometry are excluded, and the variations in desorption are due to a change in the ability of the metal substrate to bond with an adsorbate, i.e., the depth of the potential well. We believe that the dominant effect in the potassium coadsorption systems is an electronic one. Electronic effects will exist in the sulfur coadsorption systems,[30] but at least for the systems we have studied, it is possible that these effects play only a secondary role.

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