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CHEMISORPTION ON THIN METAL FILMS

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Abstract

The modification of the chemisorption properties of single crystal metal surfaces by thin film overlayers of a second metal has been a subject of intense investigation. In this paper, selected work from our laboratory is reviewed with particular attention being paid to the different roles played by the added metal. In the case of Ag(111), the chemisorption of CO is enhanced by added potassium even when the potassium is not detectable by AES. We propose that subsurface potassium is effective in altering the surface properties of Ag so that relatively strong CO-Ag bonding occurs. In the case of ketene on copper-covered Ru(001), new bonding modes for molecular ketene and different decomposition product distributions are found for submonolayer amounts of added Cu. For Cu coverages greater than one monolayer, there is no decomposition of ketene. For Ag on Rh(100), the chemisorption of oxygen and nitrous oxide follows a simple site blocking model.

Key Words: Chemisorption, surfaces, subsurface, silver, potassium, ketene, copper, overlayers, ruthenium, thin metal films.

Introduction

The modification of the chemisorption properties of single crystal substrates by thin metal overlayer films in the submonolayer to multilayer regime, continues to be a challenging scientific problem. From a technical materials viewpoint, these kinds of systems are important in catalysis, in electronic materials, and in high performance engineering materials.

Our research group has published a number of papers focussing on the issues surrounding the alteration of chemisorption and surface reactivity of single crystal transition metals by the addition of other metals, including alkali metals. In this paper, we briefly review three systems that illustrate a number of points and techniques that are germane to these problems.

In the first set of experiments, we have investigated how potassium alters the activity of Ag(111) for the chemisorption of CO (Roop et al., submitted). One of the main conclusions of this work is that potassium, in amounts below the detection limits of Auger electron spectroscopy (AES) and probably located beneath the Ag surface, will alter Ag(111) so that CO uptake is readily measurable during dosing at 300K and so that CO desorption occurs at temperatures above 500K. The importance of subsurface and very small amounts of potassium are thus underscored.

For ketene, CH_2CO , on Ru(001) (Henderson et al., in preparation) and Cu/Ru(001) (Henderson et al., in preparation), one of the main points is the extent to which small amounts of copper inhibit the binding of molecular ketene with both the C and O of the carbonyl both attached to Ru.

On Rh(100), we find that Ag, a group IB metal, inhibits O_2 and N_2O adsorption, and the simple site blocking models are adequate to describe their inhibition (Daniel et al., 1981).

Potassium on Ag(111)

There continues to be considerable interest in how potassium and carbon monoxide interact on transition metal surfaces (Garfunkel and Somorjai, 1982; Wesner et al., 1986; Uram et al., 1986). On group VII metals, CO adsorbs readily in the absence of K. In the presence of K the

bonding between CO and O is weakened and the possibility of dissociation is enhanced. The range and the direct or indirect character of the interaction of K and CO are continuing subjects of great interest (Luftman et al., 1984; dePaola et al., 1985; Garfunkel et al., 1982).

We have recently undertaken the study of the coadsorption of K and CO on clean well-characterized Ag(111) (Roop et al., submitted). Like copper (Lackey et al., 1985; Dubois et al. 1987), silver will not chemisorb CO at room temperature (this and Auger spectra were used as criteria for surface cleanliness). These experiments were done in an ultrahigh vacuum system equipped for AES and TPD. The potassium was dosed from a SAES getter source with the Ag at 320-330 K.

The migration of potassium into the bulk of Ag at temperatures below the K desorption temperature has been reported (Grant and Lambert, 1985) and we confirm that result by monitoring the K AES and TPD as a function of temperature. Multilayers of K do not form when dosing at 330K because K desorption competes with K adsorption for any coverage larger than 1 ML. At low coverages, the ionic character of K gives a much stronger bond and desorption does not occur until 700 - 900K (depending on the coverage). When K is on top and at sufficiently high concentrations, there is desorption of CO and K (not shown) in the 750 - 900K region (Fig. 1a) but K lags CO desorption by at least 50K. After the first flash, the remaining K is located mostly beneath the surface and the CO desorption shifts down about 100K, and there is no K desorption (Fig. 1b). In each case, the CO dose was 100L at 300K. The K(252eV)/Ag(356eV) Auger peak ratios were 0.03 and 0.015 for Figs. 1a and 1b. When additional K was dosed after completion of the experiment of Fig. 1b, raising the Auger ratio to 0.05, the CO TPD peak moved back to its original position (Fig. 1c) and, significantly, there was no evidence for a peak or shoulder at low temperatures. When a clean surface was dosed with K to give an Auger ratio of 0.014, the subsequent TPD (Fig. 1d) was broader than Fig. 1b but peaked at the same position with no evidence for a peak in the region between 750 and 900K. Other AES spectra taken as a function of temperature in the absence of CO suggest that K moves beneath the surface between 550 and 650K (there may be some incorporation even at 100K but this remains an open question). In the presence of CO, we suppose the same process is slowed and K remains near the surface to an extent depending on the initial surface and subsurface concentration distributions.

Thermal cycling of surfaces containing K slowly decreases both the amount of CO adsorbed in a 100L dose and the peak TPD temperature. Fig. 2 shows the TPD of CO from a surface that had been cycled 7 times to 900K and then exposed to 600L of CO. In this case no K AES signal was detectable before or after the CO was dosed and there was no K TPD signal.

A dose of at least 1000L is required to saturate any of these potassium-perturbed surfaces. Between 100 and 600L the sticking coefficient drops sharply from its already low initial value. Based on CO TPD from Rh(100) data taken with this instrument (Peebles et al., 1984; Kim et al., 1982), the CO coverages measured here after a 1000L dose lie

in the range 0.10 to 0.20 CO per surface Ag.

In a separate set of experiments, as much as 1000L of N₂ was dosed at 330K on a surface with K/Ag=0.025. Neither N₂ desorption nor N(KVV) AES signals were seen. In another experiment, an unannealed Ar⁺-bombarded surface was exposed to 1800L of CO at 330K. There was no CO desorbed. Other experiments show that no CO₂ is produced in this process.

Using these results we propose the following model. When K is on and/or near the surface and is present at sufficiently high concentrations, there is desorption of both CO and K in the 750-900K region but K lags CO desorption. The lack of coincidence (as observed on some other surfaces) (Luftman et al., 1984; dePaola et al., 1985; Garfunkel et al., 1982; Greenlief et al., unpublished) indicates that the breakup of surface complexes, if they exist, is accompanied by a surface process that competes with desorption -- for example, K migration into the subsurface region. If directly bound K-CO complexes do not exist, then the lag between CO and K desorption can be adequately modeled assuming an attractive interaction between CO and K adsorbed on nearest-neighbor sites (Ishi et al., 1986).

With CO adsorption/desorption cycles the K/Ag drops slowly even though no K desorption is observed unless the upper limit of the TPD temperature is above 850K where Ag and some K begin to desorb. These changes are attributed to the slow migration of the potassium further beneath the Ag surface. We have evidence that cycling without CO adsorption also reduces the K/Ag ratio. As the K/Ag ratio drops, the CO TPD peak desorption temperature drops. Even when the K is no longer detectable, a 100L dose still leads to a significant amount of adsorbed CO. These results provide striking evidence for a long range indirect interaction between K and CO.

If the adsorption process is the result of the very small number of K atoms which might still be present on the Ag(111) surface, these must perturb a very large fraction of the surface because unperturbed regions of Ag(111) would not retain CO under these conditions. This perturbation cannot be as simple as restructuring the surface to give other low index faces or to give surface defects because CO does not adsorb on other low index faces of Ag (Madix et al., 1980) and unannealed Ar⁺-bombarded Ag(111) does not chemisorb CO at 330K. We prefer an interpretation that involves a larger number of K atoms beneath the Ag(111) surface that alter the stability of surface CO.

We suggest that the underlayer K alters the surface electronic structure of the Ag by donating charge into the s- and p-bands of Ag (Heskett et al., 1985). In turn the Ag d-bands move to higher energy, that is, toward the Fermi level, and are to some extent rehybridized. Both of these effects would lead to stronger electronic coupling between Ag and CO.

Ketene on Cu/Ru(001)

Ketene (CH₂CO) has adjacent double bonds (C=C and C=O). This feature makes it an interesting candidate for chemisorption studies.

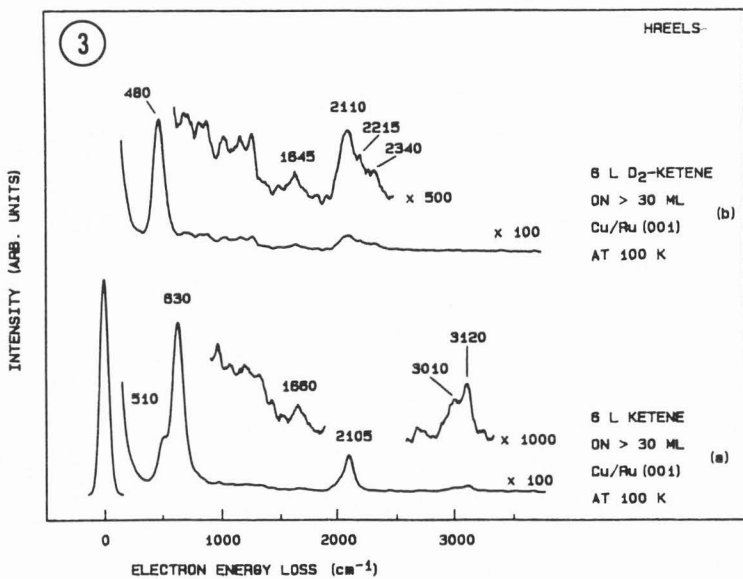
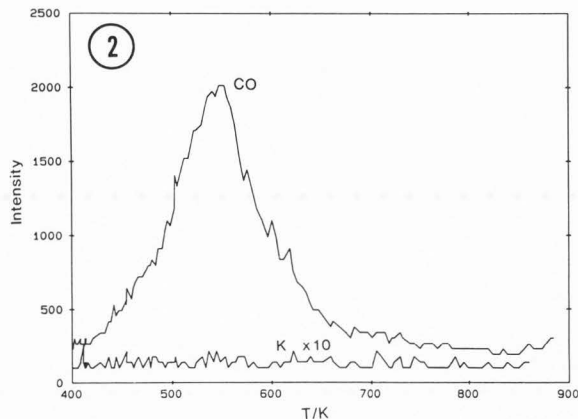
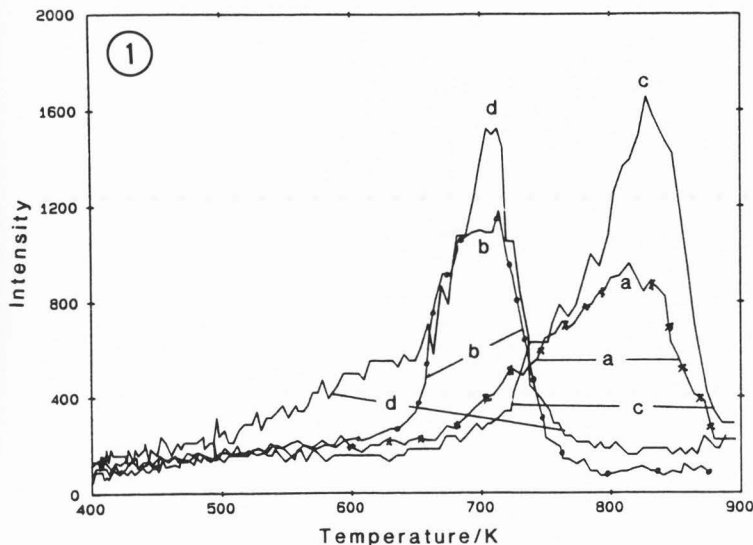


Figure 1. CO TPD from K-covered Ag(111). In each case 100L of CO was dosed at 100K and the heating rate was 15 K/s. The horizontal bars connect the left and right portions of the same TPD profile. The conditions were as follows: (a) K/Ag AES ratio = 0.03; (b) second cycle of (a) (see text); (c) K added to case (b) to give K/Ag = 0.05; and (d) clean Ag dosed with K to give K/Ag = 0.014.

Figure 2. CO and K TPD profiles after a 100L dose of CO onto a 330K Ag(111) surface for which the K level was beneath the detection limit of AES.

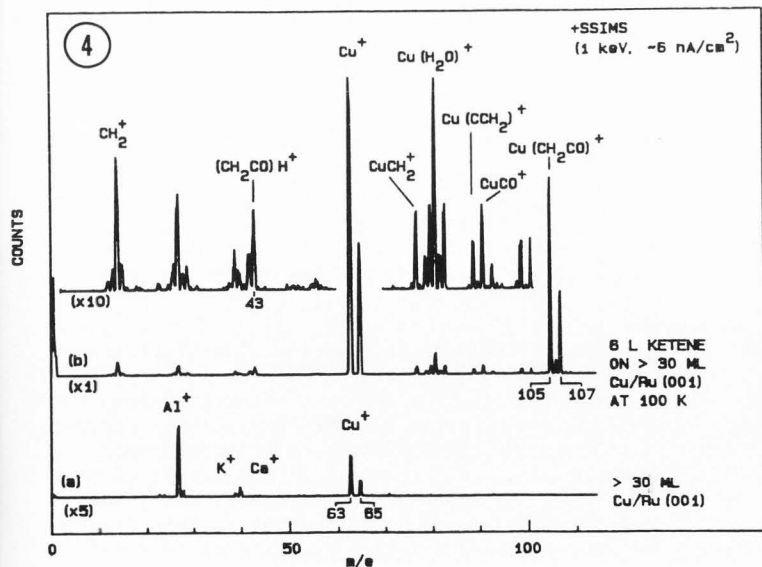


Figure 3. High resolution electron energy loss spectra for saturation molecular ketene dosed onto 30ML Cu/Ru(001) at 100K. (a) H-ketene and (b) D-ketene.

Figure 4. Secondary ion mass spectra for 30ML Cu/Ru(001) and for saturation dose of molecular ketene on 30ML Cu/Ru(001) at 100K.

From an experimental perspective, ketene is operationally troublesome; to maintain purity, we find it must be synthesized daily. In our labs this is done by the pyrolysis of acetone. If careful attention is not given to this aspect of ketene research impurities such as ethylene and dimerized ketene become significant contributors to the dosed gas.

We have investigated the adsorption and decomposition of ketene on Pt(111) (Radloff et al., 1987; Mitchell et al., 1987), on Ru(001) (Henderson, Mitchell et al., in preparation), and on Cu-covered Ru(001) (Henderson, Zhou et al., in preparation). When each surface is dosed at 100K, molecular ketene will accumulate. On Ru(001), there is some decomposition at 100K but the majority of the adsorption leads to perturbed molecular ketene bonded with the oxygen and the central carbon σ -bonded to the Ru. For Pt(111) adsorption at 100K does not produce any measurable decomposition products. The preferred bonding mode has both carbon atoms σ -bonded to the Pt. On Ru(001) covered with more than 30ML of Cu, ketene is bonded weakly with the molecular axis approximately parallel to the Cu surface. No decomposition occurs in subsequent thermal desorption but there is some evidence for the dimerization of ketene. This surface is dominated by Cu(111) unperturbed by the underlying Ru. At submonolayer coverages of Cu there are some indications of the participation of both Cu and Ru in the chemical bonding of ketene and its decomposition fragments. This leads to CO_2 production, perhaps through dimer decomposition. The point is that Cu does more than block sites.

Two examples of the kind of structural data we obtain are given here. The reader is referred to references, particularly (Radloff et al., 1987; Mitchell et al., 1987) for further details.

Figure 3 shows the high resolution electron energy loss spectrum (HREELS) of saturation doses of molecular H- and D-ketene on 30 ML of Cu. For H-ketene at lower coverages only the losses at 3120, 3010, 2105, 1350, 630 and 510 cm^{-1} are observed (i.e., the loss at 1650 cm^{-1} is absent). This and the presence of CO_2 in the thermal desorption products leads us to propose that Cu catalyzes the formation of ketene dimers.

Figure 4 shows the SIMS spectra of molecular ketene on 30ML of copper. Consistent with our picture of undissociated molecular ketene we note that the dominant ion containing carbon is the cationized parent, $\text{Cu}(\text{CH}_2\text{CO})^+$. Importantly, the C_1 region is dominated by CH_2^+ and the C_2 region by the protonated parent ion. This is just what we expect for the adsorption of molecular ketene.

Ag on Rhodium

The purpose of these experiments (Daniel et al. 1981) was to test how the dissociative chemisorption of two different molecules that deliver oxygen is altered by adding silver to a rhodium surface. Bulk silver is relatively inactive as compared to bulk rhodium. The Ag-Rh combination is particularly attractive because these two metals do not form bulk alloys. Operationally, this means it is straightforward to recover a clean Rh(100) surface by simply thermally desorbing the Ag.

Silver was dosed onto Rh(100) using a resistively heated Ag foil. The Rh surface temperature

was 300K. The silver layer grows uniformly over at least the first two monolayers as indicated by AES analysis of both the Ag and Rh transitions. Thermal desorption contains two peaks which grow sequentially and correlate with the AES data. The first peak is at 1070K and is kinetically first order. The second appears just when AES indicates the first monolayer is complete and moves from near 950K to 990K (peak temperature) as the coverage increases. This shift of peak temperature is consistent with zero order desorption kinetics and analysis gives a desorption activation energy of 66 kcal mol^{-1} , which is very close to the bulk heat of sublimation ($63.4 \text{ kcal mol}^{-1}$). When the low temperature peak begins to grow, the higher temperature peak stops growing as expected for the growth of a uniform monolayer.

Oxygen and nitrous oxide were dosed by back-filling the UHV sample chamber. The substrate temperatures were held at either 530 or 680K and the exposures were controlled by varying the dosing time at constant pressure (5×10^{-7} torr). The dose was terminated at various intervals to make AES measurements. In analyzing the oxygen uptake data we relied on earlier work (Castner et al., 1978) for the saturation coverage (0.5ML where 1ML is defined as one adsorbed oxygen atom per surface Rh atom) of oxygen atoms on Rh(100). This coupled with AES O(KVV) peak-to-peak intensities is sufficient to determine the oxygen coverage under any condition used here. After dosing N_2O , no N(KVV) AES signal appeared and in subsequent TPD (even when no AES was done so there was no e-beam effect) no N_2 desorption was detected. We concluded that nitrous oxide dissociates leaving O(a) and desorbing N_2 (g). For O_2 , the initial absolute sticking coefficient is 0.80 ± 0.15 independent of temperature. For N_2O , the initial sticking coefficient is lower than for O_2 and drops as the Rh temperature increases. In comparing O_2 and N_2O we conclude that the requirements, probably orientation with respect to the surface, are significantly more demanding for nitrous oxide than for oxygen. Activation energy requirements for dissociation of nitrous oxide are not rate-limiting; we propose that the shorter residence time at 680K coupled with rather severe orientation requirements account for the drop in the sticking coefficient with temperature.

We considered two cases when Ag was added: (1) the sticking coefficient averaged over the first 1L ($1\text{L}=10^{-6}$ torr s) of the total exposure was taken as a measure of the initial sticking coefficient and (2) the saturation oxygen coverage was determined on the basis of a 100L dose. Operationally the latter will not account for very slow uptakes that have initial sticking coefficients less than 0.001. In none of these experiments is there any evidence for significant e-beam desorption of oxygen.

Figure 5 shows the amount of oxygen accumulated in a 1L dose as a function of silver coverage for dosing at 530K. As for the case where there is no silver, the initial sticking coefficient does not depend on temperature for O_2 but certainly does for N_2O . According to this figure the nitrous oxide sticking coefficient is barely

measurable when the coverage reaches somewhere between 0.2 and 0.4 ML of Ag, depending on the dosing temperature.

Figure 6 shows the saturation coverage of O(a), determined by AES, as a function of the Ag coverage. When there is no Ag, the saturation O(KVV) signal for O₂ adsorption is twice that for N₂O. As Ag is added the saturation coverages fall linearly for both adsorbates. By extrapolation, 0.5 ML of Ag attenuates completely the uptake of N₂O whereas 1.0 ML of Ag is required to inhibit completely the uptake of O₂. The inset shows how the O(KVV) signal varies when O₂ is dosed onto a surface presaturated by adsorption from N₂O. The Ag coverage was 0.2 ML, the Rh temperature was 530K and the O₂ pressure was 5x10⁻⁷ torr.

In separate experiments, for Ag=0.7ML, N₂O adsorption (100L) led to no O(KVV) signal at 530K but a detectable signal at 680K. This is indicated as the X in Fig. 6. For a coverage of 1.3ML Ag, exposure to 100L of O₂ at 680K gave no O(KVV) signal.

That the saturation O(KVV) signal for N₂O dosed on Ag-free Rh(100) is lower by a factor of two compared to O₂ supports the idea that the steric requirements for N₂O dissociation are more severe than for O₂ dissociation. Here the considerations are somewhat different than those influencing the initial sticking coefficient. According to Fig. 6, the saturation oxygen coverage reached by N₂O dosing does not change between 530 and 680K. This removes the residence time as an important variable determining saturation coverage. Thus, we must look beyond the orientational requirements for N₂O and focus on the site requirements for N₂O dissociation. In the comparison of O₂ and N₂O, we also get some clues about the effective structure of Ag on the surface. Suppose, for example, that Ag formed islands of constant local concentration throughout most of the coverage range. Regions of low Ag concentration must accompany these and we would anticipate that the cut-off coverage for O₂ and N₂O would be much more nearly equal. That N₂O uptake is completely inhibited by an average coverage just half of that required to inhibit oxygen coverage suggests that the Ag coverage is organized uniformly over the Rh(100) surface at 0.5ML. If islands of the final density of 1ML were formed, there should be plenty of Rh areas where N₂O would still dissociate.

Summary

The three examples cited here underscore the wide-ranging effects that added metals can have on the properties of substrates. The simplest case is Ag/Rh(100) where dissociative adsorption of O₂ and N₂O can be understood in terms of simple site blocking models that are different for the two adsorbates. In the case of K/Ag(111), amounts of K that are not detectable in Auger spectroscopy have a strong influence on the ability of the surface to bind CO. We propose that subsurface K plays an important role. In the Cu/Ru(001) case the decomposition of ketene is completely inhibited by 1ML of Cu and submonolayers of Cu redirect products. We conclude that Cu blocks sites and participates in chemical bonding.

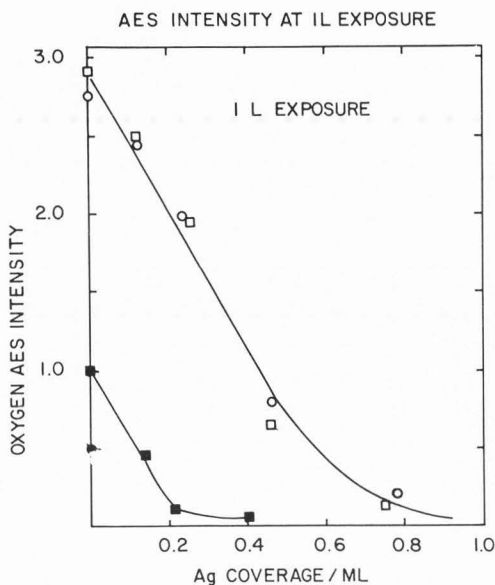


Figure 5. Oxygen (KVV) AES signals as a function of Ag coverage on Rh(100) after a 1L exposure to either O₂ (open) or N₂O (filled) at 530K.

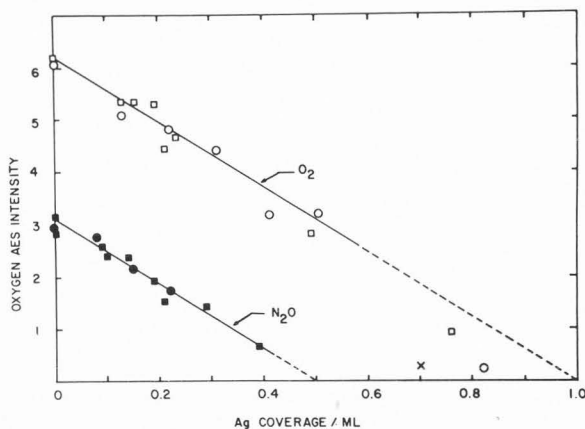


Figure 6. Saturation O(KVV) AES signals as a function of Ag coverage on Rh(100) for O₂ (open) and N₂O (filled) at 530K.

References

- Castner DG, Sexton BA, Somorjai GA (1978). LEED and Thermal Desorption Studies of Small Molecules (H_2 , O_2 , CO , CO_2 , NO , C_2H_4 , C_2H_2 and C) Chemisorbed on the Rhodium(111) and {100} Surfaces. *Surface Sci.* 71; 519.
- Daniel WM, Kim Y, Peebles HC, White JM (1981). Adsorption of Ag , O_2 and N_2O on $Ag/Rh(100)$. *Surface Sci.* 111; 189-204.
- dePaola RA, Hrbek J, Hoffmann FM (1985). Potassium Promoted C-O Bond Weakening on $Ru(001)$. I. Through-metal Interaction at Low Potassium Pre-coverage. *J. Chem. Phys.* 82; 2484-2498.
- Dubois LH, Zegarski BR, Luftman HS (1987). *J. Vac. Technol.* (in press).
- Garfunkel EL, Crowell JE, Somorjai GA (1982). The Strong Influence of Potassium on the Adsorption of CO on Pt Surfaces. A TDS and HREELS Study. *J. Phys. Chem.* 86; 310-313.
- Garfunkel EL, Somorjai GA (1982). Potassium and potassium Oxide Monolayers on the $Pt(111)$ and Stepped (755) Crystal Surfaces: A LEED, AES and TDS Study. *Surface Sci.* 115; 441-454.
- Grant RB, Lambert RM (1985). Alkali Metal Promoters and Catalysis: A Single Crystal Investigation of Ethylene Epoxidation on Cs-Doped $Ag(111)$. *Langmuir*, 1; 29-33 and references cited therein.
- Heskett D, Strathy I, Plummer EW, dePaola RA (1985). Photoemission and Electron Energy Loss Spectroscopy Investigation of $CO + K/Cu(100)$. *Phys. Rev.* B32; 6222-6237.
- Ishi S-I, Asada H, Ohno Y (1986). Cooperative Desorption of CO and Alkali Atoms from Metal Surfaces. *Surface Sci.* 171; L441-445.
- Kim Y, Peebles HC, White JM (1982). Adsorption of D_2 , CO and the Interaction of Coadsorbed D_2 and CO on $Rh(100)$. *Surface Sci.* 114; 363-380.
- Lackey D, Surman M, Jacobs S, Grider D, King DA (1985). Surface Reaction between Coadsorbed K and CO on $Cu(110)$. *Surface Sci.* 152/153; 513-521.
- Luftman HS, Sun Y-M, White JM (1984). Coadsorption of CO and K on $Ni(100)$ I. TDS Studies. *Appl. Surface Sci.* 19; 59-72.
- Madix RJ, Bowker M, Barteau MA (1980). Oxygen Induced Adsorption and Reaction of H_2 , H_2O , CO and CO_2 on Single Crystal $Ag(110)$. *Surface Sci.* 92; 528.
- Mitchell GE, Radloff PL, Greenlief CM, Henderson MA, White JM (1987). The Surface Chemistry of Ketene on $Pt(111)$: HREELS. *Surface Sci.* (in press).
- Peebles DE, Peebles HC, White, JM (1984). Electron Spectroscopic Study of the Interaction of Coadsorbed CO and D_2 on $Rh(100)$ at Low Temperature. *Surface Sci.* 136; 463-487.
- Radloff PL, Mitchell GE, Greenlief CM, White JM, Mims CA (1987). The Surface Chemistry of Ketene on $Pt(111)$. *Surface Sci.* (in press).
- Uram KJ, Ng L, Folman M, Yates Jr, JT (1986). Direct Vibrational Spectroscopic Observations of Mixed Long-range and Short-range Adsorbate Interactions - The $K + CO$ Interaction on $Ni(111)$. *J. Chem. Phys.* 84; 2891.
- Wesner DA, Coenen FP, Bonzel HP (1986). Orientation of Adsorbed CO on $Pt(111) + K$ by X-ray Photoelectric Diffraction. *Phys. Rev.* B33; 8837.

Editor's Note: All of the reviewer's concerns were appropriately addressed by text changes, hence there is no Discussion with Reviewers.