MASTER

SPECTROSCOPIC INVESTIGATIONS OF
SMALL MOLECULE INTERACTIONS
ON METAL OXIDE SURFACES

PROGRESS REPORT
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1. Summary of Work Performed.

We have made significant advances over the past year in our goals of surveying with angle integrated UV photoelectron spectroscopy (UPS) the interactions of general classes of chemically important small molecules with metal oxide surfaces, and of elucidating in detail the geometric and electronic structures of the small molecule-surface complexes observed by angle resolved UPS. Our progress can be divided into several areas: 1) A detailed understanding of the unique active site structures associated with the interaction of CO with ZnO utilizing angle integrated and angle resolved photoemission spectroscopy. 2) Initiating survey studies into new small molecule systems with emphasis on hydrogen and ethylene. 3) Successful construction and testing of a high resolution electron energy loss spectrometer (HREELS). This progress report follows the above outline.

Angle integrated photoelectron spectroscopy has been extensively used to study the chemisorption of CO on four low-index surfaces of ZnO, an active methanol catalyst. As shown in Figure 1, these surfaces have significant differences with respect to their coordination unsaturation, thus a correlation between the absorption behavior and the surface structure enabled us to determine the geometric requirements for chemisorption. The HeII photoemission peak associated with the 4σ molecular orbital of the CO molecule (see Figure 2) serves as a probe of the amount of adsorbed CO.

The adsorption is found to be reversible, and measurements of the equilibrium coverage as a function of temperature and pressure (Figure 3) demonstrates that the bonding interactions are very similar on all four surfaces, with an initial heat of adsorption of 12.0 ± 0.4 kcal/mole, which decreases approximately linearly with coverage. In ligand competition experiments, chemisorbed CO is readily displaced by NH_3 (Figure 4), indicating the involvement of zinc ions in the bonding of CO to the surface. This is strongly supported by the relative CO coverage of the four surfaces under equivalent conditions (Figure 3) which generally correlates with the availability of unsaturated zinc sites. Angle-resolved measurements of the 4σ intensity, to be described, allowed us to determine the details of the coordination structure shown in Figure 5A.

The bonding of CO to ZnO is dominated by the sigma donor interaction of the carbon end of the molecule with the zinc ion as determined from the observed (Figure 2) decrease in the splitting of the energies of the 4σ and 5σ molecular orbitals. The lack of significant π backbonding is suggested by the increase in dipole moment of the coordinated CO molecule to ~ 0.6 debye as determined from HeI photoelectron work function measurements as outlined in Figure 6. The temperature and pressure dependence of these work function changes due to CO chemisorption on the four surfaces (Figure 7) further indicates that only the (0001) surface is significantly perturbed by the CO adsorption. This general mode of binding of CO is consistent with the observed increase in the CO stretching frequency relative to the gas phase value⁽³⁾ and suggests relevance to methanol catalysis. This polarized molecule has a strengthened CO bond, not only making C-O bond

rupture less probable, but also making the molecule more susceptible to heterolytic attack by dissociated H_2 , which likely adsorbs to ZnO as $Zn-H^-$ and $O-H^+$ (vide infra).

As indicated above, we have employed polarization dependent angle-resolved ultraviolet photoelectron spectroscopy to probe in detail the surface coordination structure of carbon monoxide on Zn-containing crystal planes of ZnO. This work consisted of two major experiments which determined the orientation (α in Figure 5A) of adsorbed carbon monoxide on the $(10\bar{1}0)$ and (0001) surfaces.⁽⁴⁾

Prior to these experiments, the angle integrated ultraviolet photoemission experiments mentioned above strongly suggested a model of CO binding that involved a dominant Zn-C interaction. In order to proceed further and develop a truly detailed picture of CO adsorption, more information was needed. In particular, while the previous work had demonstrated the existence and importance of Zn-C bonding in the adsorbed state, these experiments could not reveal whether CO required only a coordinatively unsaturated zinc ion or both a coordinatively unsaturated zinc and oxide ion to bind to the surface. The distinction is critical to an understanding of which crystal planes are active in the methanol synthesis reaction, as, if both ions are necessary for binding, only non-polar surfaces will be effective.⁽¹⁾

Our approach to answering these questions was to measure the angular distribution of photoelectrons emitted from the CO 4σ molecular orbital when irradiated on the surface by polarized HeII resonance radiation. The angular dependence of photoelectron emission intensities may be analyzed

in a straightforward fashion to determine the orientation of the CO molecular axis with respect to the surface normal. This information, coupled with the requirement that the carbon atom must bond to surface zinc ions allows us to determine the surface coordination structure.

Our first experiments were performed on the $(10\bar{1}0)$ surface, as this is the structurally simplest non-polar surface and is the most widely studied surface of ZnO. The experiments showed (Figure 8) that the CO molecule was oriented with the oxygen atom up (as expected) and directed at an angle of 30° from the surface normal in the direction of $-c$. This orientation is quite consistent with zinc-carbon bonding, and the coordinatively unsaturated position for the surface zinc ion is directed at $\sim 19^\circ$ away from the surface normal at the same azimuth. ^(4a)

The surface coordination structure in Figure 5a strongly suggests that interaction between CO and coordinatively unsaturated surface oxide ions is not important to the adsorption process. Presumably, if this interaction were rigorously absent, the orientation angle of CO would be 19° resulting in a perfectly linear Zn-C-O configuration. The distortion from 19° to $\sim 30^\circ$ is therefore probably the result of an electrostatic interaction between the oxygen end of the molecule (which has been made positive due to adsorption) and the nearby oxide ion. However, this is clearly only a mild perturbation of the (ZnO)-CO surface complex, and would not appear to be energetically important.

The surface coordination exhibited by CO on the $(10\bar{1}0)$ surface and the equivalence of the heats of adsorption for CO on $(10\bar{1}0)$ and (0001) suggested that chemisorption could occur on the ideal (0001) surface des-

pite the fact that this surface consists solely of zinc ions. However, both theory and experiment indicate that the (0001) surface is characterized by a high density of step defects which expose areas of (10 $\bar{1}$ 0) surface to which the molecules could adsorb.⁽⁵⁾ Furthermore, the non-angle-resolved UPS experiments showed substantially less CO photoemission intensity on (0001) than on (10 $\bar{1}$ 0). This could be due to a defect-only adsorption mechanism. Alternatively, the surface coverages could be comparable on the two surfaces with the excitation and collection geometries of the CMA spectra on the (0001) surface being relatively unfavorable.

The angle-resolved photoemission experiment could easily distinguish between these two possibilities as the molecular orientations for the two cases would be quite different. The results of the experiment clearly show (Figure 9) molecules oriented perpendicular to the surface and thus bound to the ideal surface planes. By comparison of the adsorbate photoelectron spectra on the (10 $\bar{1}$ 0) and (0001) faces under conditions employing similar excitation and collection geometries with respect to the (now measured) orientation of the molecular axes showed that a comparable amount of CO is adsorbed on each surface.

In summary, the addition of angle resolved photoemission spectroscopy to our previous measurements has allowed us to determine in detail the coordination structure of the CO surface complex for Zn containing surface planes. On the basis of our current understanding, we strongly believe that adsorption on the oxygen terminated (000 $\bar{1}$) face is dominated by defect adsorption (indicated in Figure 5d). Experiments to test this hypothesis are planned and are described in the section on proposed research.

Having gained a detailed understanding of the nature of CO chemisorption on ZnO, the next phase in the investigation of the methanol synthesis reaction is to probe the interaction of hydrogen and carbon monoxide on the surface. Studies of this interaction have now been initiated using a combination of angle integrated HeII photoemission and HeI work function measurements.⁽⁶⁾

Hydrogen is known to chemisorb dissociatively on ZnO surfaces, and infrared spectra of powders indicate that both Zn-H and O-H species may be formed.⁽⁷⁾ However, at temperatures at which we can adsorb CO to near-monolayer coverages (80 K) exposure of the surface to H₂ has little effect. Therefore ZnO surfaces were exposed to hydrogen atoms, directly, which were produced by H₂ dissociation on a hot tungsten filament. Experiments using submonolayer techniques have indicated that there should be no difference between surface species formed using hydrogen atoms and those generated by thermal dissociation of H₂.

The experiments performed were largely centered on the investigation of the properties of the (10 $\bar{1}$ 0) surface. Due to the low photoemission cross section of H₂ and lack of its nonbonding "fingerprint" orbitals, photoemission experiments on adsorbed hydrogen atoms are quite difficult. Therefore, two "indirect" probes of the adsorption process were employed. The first of these was work function change measurements and the second was to measure the capacity (by angle integrated UPS) of the hydrogen exposed surface to adsorb carbon monoxide (Figure 10).

(6)

These experiments revealed two distinct regimes of hydrogen atom adsorption on the (10 $\bar{1}$ 0) surface: 1) a low exposure regime which exhibits

~.5 eV downward band bending with slight attenuation of CO photoemission features, and 2) a higher exposure regime, which shows no further band bending, but continued CO attenuation with increased H atom exposure.

These results suggest the following picture for H atom adsorption on (10 $\bar{1}$ 0). On the clean n-type ZnO surface, the primary conductivity of the surface is via holes and the bands are bent up. Therefore, H $\cdot$ impinging on the surface can annihilate a hole to form H $^+$, which naturally binds to the surface oxide ions to form an OH $^-$ species. Given the hole/electron ratio at the clean (and near-clean) surface, electron capture by H $\cdot$ to form H $^-$ (bound to Zn $^{+2}$ ions as ZnH $^+$) is a highly unlikely process. Continued exposure to H $\cdot$ thus captures all the free holes at the surface until the bands are significantly bent down. At this point adsorption to form (Zn-H) $^+$ and (O-H) $^-$ are equally likely and adsorption may proceed without inducing further changes in surface charge or band bending. As hydrogen binds to surface zinc ions, CO adsorption sites are used up, and the surface can no longer adsorb CO. Thus CO and H $_2$ are site competitive in this second regime.

This mechanism of surface charge compensation may be extremely important for the ability of the surface to adsorb large amounts of hydrogen. It is known in systems exhibiting ionosorption that the resultant surface space charge can serve to turn off the adsorption process at the 10 $^{-3}$ monolayer regime (i.e., after the analog of the first regime on the (10 $\bar{1}$ 0) surface)⁽⁸⁾. In fact, our preliminary investigations of hydrogen adsorption on the Zn terminated (0001) face indicate that even relatively large exposures to H $\cdot$ do not affect the ability of the surface to adsorb CO, which may be

indicative of low surface coverage.

In addition to the hydrogen work, we have made considerable progress⁽⁹⁾ in defining the adsorption of ethylene on ZnO (1010). The 40.8 eV results clearly indicate two different forms of ethylene on the surface, one of which is found at low temperatures (~ 90 K) and the other of which is present at room temperature (~ 300 K). The low temperature form seems to be analogous to CO adsorption in that there is a weak bonding interaction (~ 10 kcal/mole). The photoelectron spectrum of the low temperature form is very similar to that of gas phase ethylene, with an ERPS shift of about -0.43 eV (Figure 11). Preliminary limited angle-resolved work on this form indicates that, unlike CO, the photoelectron distribution is essentially isotropic. In contrast, the room temperature form of ethylene is substantially different from the gas phase molecule (Figure 12). The heat of adsorption is large and there is a change in the work function upon adsorption by about 0.3 eV which is due to a change in the bandbending as measured from 21.2 eV photoelectron spectra. We have now begun to study the role of ZnO in the catalytic hydrogenation of ethylene by first adsorbing it onto the surface at low temperatures and then adding hydrogen to the chamber either with or without use of a hot tungsten filament to generate atomic hydrogen. Preliminary results indicate that neither hydrogen molecules nor hydrogen atoms interfere with the ethylene adsorption, again in contrast to what is observed for CO.

The behavior of the Lewis base NH_3 has also been investigated in some detail.⁽¹⁰⁾ NH_3 is found to physisorb in many layers on all four faces, eventually producing a spectrum in which all the features are due to the NH_3 .

with the ZnO completely obscured. It is also found to chemisorb on all four faces (Figure 13), with the smallest amount on the (000 $\bar{1}$) face. The heat of adsorption at zero coverage is substantially larger than for CO, with a value of about 27 ± 4 kcal/mole. In addition, there is an obvious sharpening of the Zn 3d band upon adsorption which may be interpreted in terms of depletion of a surface state due to interaction with the lone pair of electrons on NH₃. There is a large change in the work function when NH₃ adsorbs. The sign is the same as that for CO, but about 2-3 times the magnitude, consistent with the larger dipole moment. Quantitative treatment of the 40.8 eV spectra is rendered difficult as there is extensive overlap between the NH₃ orbitals and the bulk ZnO bands. The HREELS experiments to be described should prove of great utility in our continued study of the surface chemistry of this molecule.

The same problem arises in trying to study the adsorption behavior of H₂O. Our preliminary studies with water have shown that it exists in both a physisorbed and chemisorbed form on all four surfaces.

Survey investigations into the interactions of CO₂ and O₂ with ZnO (10 $\bar{1}$ 0) have also been performed. At low temperatures, CO₂ forms a physisorbed or weakly chemisorbed complex that correlates very well with the gas phase spectrum (Figure 14). The room temperature form of CO₂ is clearly different (Figure 15) and the dissimilarity is greater than that which would be expected for a simple change in the O-C-O bond angle. The 21.2 eV photoelectron studies at RT indicate a modest increase in the work function. Survey competition experiments have been performed between CO₂ and CO, NH₃ and H₂O producing interesting but ambiguous results which require

clarification. O_2 forms a weakly chemisorbed system with an ERPS shift of 7.8 eV (Figure 16), whereas at room temperature it has very little effect on the photoelectron spectrum.

In the research planned for the coming year a major experimental tool will be high resolution electron energy loss spectroscopy. This technique consists of impinging a highly monochromatic (~ 10 meV FWHM) low energy (~ 5 eV) electron beam on the crystal surface and measuring the loss of energy in the scattered electrons corresponding to the excitation of vibrational modes of molecules adsorbed on the surface. Accordingly, we have constructed and tested a monochromator-analyzer system for this purpose. The dispersive elements are 120° cylindrical deflectors corrected for second order image aberrations after a design by Froitzheim.⁽¹¹⁾ Figure 17 shows a test spectrum of the beam elastically scattered from a polycrystalline Cu target.

The system performance exhibited by this spectrum should prove adequate for the execution of the proposed experiments. In particular, as we are dealing with an optically active substrate, difficulties can arise due to the overlap of multi-quantum substrate features with adsorbate single quantum excitations. For the experiments we propose the only concern is the overlap of the third harmonic of the ZnO phonon frequency (~ 68 meV) with the Zn-H fundamental. However, it has been shown that the higher harmonics of the ZnO phonons may be effectively suppressed by the use of higher beam energies. This technique should allow us to study the Zn-H modes with reasonable signal to noise ratios.