SPECTROSCOPIC INVESTIGATIONS OF
SMALL-MOLECULE INTERACTIONS
ON METAL OXIDE SURFACES

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ABSTRACT

Angle integrated and angle resolved ultraviolet photoelectron spectroscopy (UPS and ARPES) and high resolution electron energy loss spectroscopy (HREELS) have been performed on the low index single crystal surfaces of zinc oxide in order to probe the interaction of this methanol synthesis catalyst with a variety of catalytically important small molecules. A detailed study of the CO/ZnO system has determined that the mode of binding is dominated by 5σ donation from the carbon end of the molecule to the unsaturated surface zinc ion with little π backbonding to the $\text{CO}2\pi^*$ orbital, thus providing an explanation for the increased CO stretching frequency, which is observed upon CO chemisorption to ZnO powders. This electronic structure description is further verified by our HREELS study where a normal coordinate analysis of the experimentally observed Zn-C-O surface complex is performed. The geometry of CO binding (as determined by ARPES) has been shown to be completely consistent with the results of low energy electron diffraction (LEED) studies where no symmetry changing reconstructions are observed to occur, and where the CO molecule forms an approximately linear Zn-C-O surface complex along the coordinatively unsaturated directions of the surface zinc ions. The implications of these studies to the mechanism of methanol synthesis is described. These UPS studies have also provided insight into the bonding interaction between small molecules such as NH_3 and CO_2 (as well as preliminary information on H_2O , C_2H_4 , CH_3OH , H_2S and CH_3SH) and the ZnO single crystal surfaces.

INTRODUCTION

During the past three years this research program has made significant progress towards gaining an understanding of the electronic and geometric structure of the interaction of ZnO with a variety of catalytically important small molecules. Our approach has been to study structurally well defined (as determined by low energy electron diffraction (LEED) single crystal surfaces in ultra high vacuum (UHV) using angle integrated ultraviolet photoelectron spectroscopy (UPS), angle resolved photoelectron spectroscopy (ARPES), and high resolution electron energy loss spectroscopy, (HREELS).

Interaction of CO with ZnO

The adsorption of CO on ZnO is an important problem in relation to methanol synthesis (1). The CO-ZnO bond is unusual because of the observation of a $\sim 70 \text{ cm}^{-1}$ increase in the CO stretching frequency upon chemisorption of CO on ZnO powders (2). This is in contrast to the decrease in the stretching frequency relative to the gas phase value of 2143 cm^{-1} which is normally observed upon chemisorption to metals and in organometallic complexes. In an effort to gain a detailed microscopic understanding of the nature of the CO/ZnO interaction, we have performed a variety of He(I) 21.2eV and He(II) 40.8eV UPS studies on the four chemically different surfaces of ZnO. The (0001) contains only coordinatively unsaturated zinc sites, the (10 $\bar{1}$ 0) and (11 $\bar{2}$ 0) contain both zinc and oxide ions with coordinatively unsaturated positions, and the (000 $\bar{1}$) nominally contains only oxide ions with open coordination positions directed normal to the surface. (See Figure 1)

Figure 1. Surface geometry of the four low-index surfaces of ZnO. Large circles represent oxide ions, small circles represent zinc ions, shaded circles represent the surface layer, and open circles represent the second layer.

Our initial He(I) and He(II) angle integrated UPS measurements are discussed in Gay, et al. (Ref. 3). The He(II) photoemission peak associated with the 4σ molecular orbital of the CO molecule serves as a probe of the amount of adsorbed CO on the ZnO surface. (See Figure 2)

Figure 2. (a) 40.8-eV UPS spectrum of the (10 $\bar{1}$ 0) surface at 90 K before and after exposure to a 10^{-6} torr ambient of CO (the clean spectrum has been attenuated and shifted to maximize overlap in the oxygen valence region). (b) Difference curve between exposed and clean spectrum in a (—) showing the effect of a +100-meV (---) and -100-meV (---) shift of the clean spectrum. (c) 35-eV UPS spectrum^{27,27} of gas-phase CO.

Three dominant features are observed in the UPS spectrum of ZnO. The first peak from 3 to 6 eV is due to O2p nonbonding electrons; the peak from 6 to 8.5 eV is due to the bonding combination of Zn4s and 4p with O2p electrons; and the intense peak from 8.5 to 12 eV is due to the Zn 3d band.

After CO adsorption, new features are observed: the peak at 14-15 eV is attributed to emission from the 4σ orbital of CO while emission from the 1π and 5σ strongly overlap the Zn 3d band.

The adsorption of CO was found to be reversible and the measurements of the equilibrium coverage as a function of temperature and pressure demonstrated that the bonding interactions are very similar on all four faces with an initial heat of adsorption of $12.0 \pm .4$ kcal/mole which decreases approximately linearly with coverage due to repulsive adsorbate-adsorbate interactions. Ligand competition experiments were also performed where it was found that the Lewis base NH_3 readily displaces chemisorbed CO indicating the involvement of Lewis acid Zn ions in the binding of CO to the surface. (See Figure 3)

CO difference spectrum

NH_3 difference spectrum

The bonding of CO to ZnO was described by a dominant σ donor interaction between the carbon end of the CO molecule and the zinc ion as determined by the observed decrease in the $4\sigma - 5\sigma$ splitting relative to gas phase value. The lack of significant π back bonding is supported by the increase of the dipole moment of the coordinated CO molecule to approximately .6D (negative side toward the surface) as determined by He(I) work function measurements. This mode of binding of CO to ZnO is consistent with the observed increase in CO stretch which is normally observed.

Following this initial work, we proceeded to perform a series of detailed angle resolved UPS (ARPES) experiments on the $(10\bar{1}0)$, (0001) and $(000\bar{1})$ faces of ZnO in the hope of further clarifying the geometric description of the CO/ZnO interaction.

The combined results for the angle resolved experiments on the $(10\bar{1}0)$ (K. L. D'Amico, Ref. 4, M. J. Sayers, Ref. 5); (0001) (M.R. McClellan, Ref. 6) and $(000\bar{1})$ (K. L. D'Amico, Ref. 7) are shown in Figure 4.

Figure 4. Photoelectron angular distribution for the CO 4σ intensity in the plane of incidence for (a) $(10\bar{1}0)$, (b) (0001) , (c) $(000\bar{1})$ surfaces. In each case the light is incident of 60° away from surface normal and in the p polarized configuration.

This figure clearly illustrates the dramatic differences between p polarized in plane sweeps for the three surfaces of ZnO. The maximum intensity on the $(10\bar{1}0)$ is observed at 30° off normal in the $(000\bar{1})$ direction. This coincides with the CO molecule binding to the coordinatively unsaturated Zn sites on the $(10\bar{1}0)$ terrace. On the $(000\bar{1})$ face, the maximum CO 4σ intensity occurs at approximately normal emission indicating that the Zn-C-O complex is along the coordinatively unsaturated Zn sites normal to the surface. Both of these observed binding geometries are consistent with the ideal terrace structures of the unreconstructed single crystal surfaces.

One of the puzzling aspects of our CO/ZnO studies, however, was the observation (3) of a small but nonzero amount of CO 4σ photoelectron intensity indicative of CO binding to the $(000\bar{1})$ surface, which ideally contains only oxide ions. The temperature and pressure dependence of this 4σ intensity further indicated that the CO binds with the same heat of adsorption at zero coverage to $(000\bar{1})$ as to the other three surfaces. This originally led to the proposal by Gay, et al., (Ref. 3), that CO binds to zinc containing step defect sites on this surface. LEED studies (8) on $(000\bar{1})$ indicate a significant density of $(10\bar{1}0)$ steps which expose zinc sites with coordinatively unsaturated positions $\sim 70^\circ$ off the surface normal.

The results of the $(000\bar{1})$ ARPES study (Ref. 7) (as illustrated in Fig. 4C) indicate that the CO molecule does not bind the oxide normal to the surface (the 4σ intensity distribution does not

show the expected pattern for such a binding geometry), but rather that the CO molecule binds roughly along the coordinatively unsaturated positions of the Zn ion on the $(10\bar{1}0)$ step sites in confirmation of our earlier proposal (3).

Thus, the angular behavior of the Zn-C-O surface complexes on the three low index single crystal surfaces of ZnO have been shown to be completely consistent with the results of LEED studies where in all cases no symmetry changing reconstructions are observed and where the polar surfaces are known to form a high density of $(10\bar{1}0)$ defect sites.

This geometric pictures of the CO/ZnO interaction is shown in Figure 5.

Figure 5. On the (0001) the CO molecule is normal to the surface while on the $(10\bar{1}0)$ the CO is bound 30° off the surface normal. On the $(000\bar{1})$ surface, where we would ideally expect no CO chemisorption, the small yet significant CO intensity was determined to be on the $(10\bar{1}0)$ defect step sites which are known (from streaking the LEED patterns) to exist on the polar faces.

We have also recently performed high resolution electron energy loss spectroscopy (HREELS) (9) studies on the $(10\bar{1}0)$ surface which verified that the CO molecule binds to this surface

with a CO stretching frequency of 2200 cm^{-1} and a metal ligand Zn-CO stretch of 250 cm^{-1} . A normal coordinate analysis has indicated that only 10 cm^{-1} of the increased CO stretch could be attributed to coordination to the surface. The remaining 60 cm^{-1} increase results from changes in bonding.

In summary, these combined UPS, ARPES and HREELS studies have clearly demonstrated that CO binds carbon end down to the coordinatively unsaturated terrace zinc site on the (0001) and (10 $\bar{1}$ 0) surfaces, and to the coordinatively unsaturated Zn sites on the defect (10 $\bar{1}$ 0) steps of the (0001) surface, forming approximately linear Zn-C-O complexes. Here CO acts as a 5σ donor by transferring electron density from this weakly anti-bonding orbital, with little π back bonding to the CO $2\pi^*$ orbital, resulting in a net donation of charge to the surface zinc ion. Hence, the CO bond order is increased, and the CO molecule is polarized with some positive charge at the carbon.

This geometric and electronic structure picture of CO on ZnO has implications regarding its reactivity, in particular with respect to the synthesis of methanol. The polarized molecule has a strengthened CO bond initially making CO bond rupture less probable, but making the molecule susceptible to heterolytic attack by dissociated H_2 which is known to adsorb as Zn-H^- and OH^+ .

Interaction of Zinc Oxide with other Catalytically Important Small Molecules

Utilizing this detailed understanding of the CO-ZnO interaction, as a starting point, we expanded to a study of the interaction of ZnO with a variety of other catalytically important small molecules. The main theme of this research was to apply our knowledge of the differing chemical properties of the three ZnO surfaces to aid in characterizing the mode of small molecule binding (specifically, H_2O , NH_3 , CO_2 , C_2H_4 , CH_3OH , H_2S , CH_3SH and O_2) via the technique of angle integrated UPS

Ammonia was found to adsorb nondissociatively on the surface zinc sites with a heat of adsorption of $5.9 \pm .2$ kcal/mole for the physisorbed form and 27.5 ± 3.5 kcal/mole for the chemisorbed form.

He(II) UPS of Clean and NH_3 Covered ZnO

Difference curve for $NH_3/ZnO \rightarrow$

Upon chemisorption the $3a_1$ lone pair is stabilized by approximately 2eV and the work function change is negative indicative of a bonding interaction through the N lone pair via electron donation to the surface zinc.

CO_2 also adsorbs in a physisorbed and chemisorbed form. The physisorbed form resembles gas phase CO_2 while the chemisorbed form is quite perturbed. Work function measurements show that the CO_2 accepts electron density from the surface and ligand competition experiments show that NH_3 and CO_2 do not compete for the same surface site. From these results we infer the formation of a carbonate type species with CO_2 binding to coordinatively unsaturated oxide sites.

Since much of the chemistry of ZnO powders has been described by acid base behavior, a major goal of this work is to determine if deprotonation reactions producing surface hydroxyls do occur on the ZnO single crystal surfaces.

The three chemically different faces of ZnO provide the possibility for probing site specific chemical reactions. Since the deprotonation step requires the presence of both the Zn and O ions, the $(10\bar{1}0)$ surface would appear to be required for such chemical reactions while on the (0001) these Lewis bases would bind to the Zn^{2+} terrace sites yet be unable to deprotonate. Work in this area on CH_3OH , H_2O , NH_3 and CH_3SH has begun, however, at the present time only NH_3 has been completed. (See above.) This research, therefore, will be continued when our new UPS, surface science instrumentation arrives at Stanford University.

FOOTNOTES

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Footnotes (Cont'd)

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