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Registry No. *trans*-[Co([14]aneN$_4$)(OH)$_2$]$^+$, 128900-14-1; *cis*-[Co([14]aneN$_4$)(OH)$_2$]$^+$, 128900-16-3; Au, 7440-57-5; NaOH, 1310-73-2; *trans*-[Co([14]aneN$_4$)Cl$_2$]Cl, 90529-42-3; *cis*-[Co([14]aneN$_4$)Cl$_2$]Cl, 90580-83-9; *trans*-[Co([14]aneN$_4$)(H$_2$O)$_2$]$^{3+}$, 130466-94-3; *cis*-[Co([14]aneN$_4$)(H$_2$O)$_2$]$^{3+}$, 130466-95-4; *trans*-[Co([14]aneN$_4$)(OH)$_2$], 128835-34-7; *cis*-[Co([14]aneN$_4$)(OH)$_2$], 128900-18-5.

Structure Sensitivity, Selectivity, and Adsorbed Intermediates in the Reactions of Acetone and 2-Propanol on the Polar Surfaces of Zinc Oxide

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The reactions of 2-propanol and acetone on the (0001)-Zn and (000$\bar{1}$)-O polar surfaces of zinc oxide were investigated by using temperature-programmed desorption and X-ray photoelectron spectroscopy. 2-Propanol adsorbed dissociatively on the (0001)-Zn surface to form surface isopropoxide ((CH$_3$)$_2$HCO) species. These alkoxide intermediates underwent both dehydration and dehydrogenation reactions to produce propylene and acetone. Acetone dissociated on the (0001)-Zn surface to form enolate intermediates, fingerprinted by a broad envelope in the C(1s) spectrum. These enolates decomposed unselectively above 600 K to deposit carbon, which was oxidized to CO and CO$_2$ at higher temperatures. Neither acetone nor 2-propanol reacted on the oxygen polar surface, and both were adsorbed molecularly and desorbed intact from this surface below 300 K.

Introduction

The reaction of 2-propanol is one of the most common probes of the behavior of metal oxide catalysts. The focus of such experiments is generally on the dehydration (to propylene) vs dehydrogenation (to acetone) selectivity as a measure of surface acid–base properties.[1-4] Other side reactions are less important for this secondary alcohol than for primary alcohols, although such reactions reported for 2-propanol include both oxidation and formation of higher molecular weight products.[5,6]

In considering the behavior of 2-propanol and its dehydrogenation product, acetone, on a single oxide, zinc oxide, it is apparent that a wide variety of observations have been reported in previous studies. Temperature-programmed desorption studies of 2-propanol decomposition on ZnO powders by Bowker, Waugh, and Petts[7-9] indicated that roughly equal amounts of acetone and propylene, the principal products, were produced. These workers concluded that stable isopropoxide species were formed upon 2-propanol adsorption; these decomposed to acetone (peak temperature = 468 K) and propylene (480 K). It was suggested that the two principal products might arise from alkoxides bound on different types of sites; these in turn might be located on different crystallographic planes. These workers reported minimal side reactions; no oxidation to CO or CO$_2$ was observed, and it was further noted that acetone desorbed intact below 450 K in acetone adsorption/TPD experiments. Similar 2-propanol TPD experiments on ZnO powders by Chadwick and O'Malley[10] yielded results differing in several notable respects from those above. First, the dehydration/dehydrogenation selectivity was approximately 9:1 rather than 1:1. Second, they detected oxidation products such as CO$_2$, H$_2$O, and CH$_4$ at high temperatures ($>$700 K) in addition to the C$_3$ products appearing at 400–600 K. They concluded that different crystallographic planes could account for the different product states observed, with propylene produced on both polar and nonpolar planes and acetone evolved only from the nonpolar surface.[10]

As we have noted previously,[11,12] the structural dependence of alcohol decomposition has been the subject of a number of conflicting reports. In contrast to the above powder studies which proposed structural effects on product distribution, Djega-Mariadassou et al.[13] have concluded that 2-propanol decomposition on ZnO is a structure-insensitive reaction. TPD and steady-state reaction studies on ZnO single crystals by Kung and co-workers[14-16] have found evidence for 2-propanol conversion to acetone plus lesser amounts of propylene on the (0001)-Zn and (000$\bar{1}$)-O polar and (50$\bar{5}$1) nonpolar surfaces. The zinc polar surface was the most active in both steady-state and temperature-programmed experiments.[16] In contrast, Zwicker et al.[17] found that activity for the decomposition of 2-propanol was confined to the (0001)-Zn face. Previous results from this laboratory for primary alcohols and other Brønsted acids have also detected activity for dissociation and decomposition only on the zinc polar surface.[11,12,18-20]

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(1) Tanabe, K. *Solid Acids and Bases*; *Academic*: New York, 1970.
(2) Krylov, O. V. *Catalysis by Nonmetals*; Academic: New York, 1970.
(3) Ai, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1328.
(4) Winterbottom, J. M. *Catalysis*; Royal Society of Chemistry: London, 1981, Vol. 4, p 141.
(5) Volta, J. C.; Turlier, P.; Trambouze, Y. *J. Catal.* **1974**, *34*, 329.
(6) Wheeler, D. J.; Darby, P. W.; Kemball, C. *J. Chem. Soc.* **1960**, 332.
(7) Bowker, M.; Petts, W.; Waugh, K. C. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 3073.
(8) Waugh, K. C.; Bowker, M.; Petts, R. W.; Vandervill, H. D.; O'Malley, P. J. R. *J. Appl. Catal.* **1986**, *25*, 121.
(9) Bowker, M.; Petts, R. W.; Waugh, K. C. *J. Catal.* **1986**, *99*, 53.
(10) Chadwick, D.; O'Malley, P. J. R. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 2227.
(11) Vohs, J. M.; Barteau, M. A. *Surf. Sci.* **1986**, *176*, 91.
(12) Vohs, J. M.; Barteau, M. A. *Surf. Sci.* **1989**, *221*, 590.
(13) Djêga-Mariadassou, G.; Davignon, L.; Marques, A. R. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 2447.
(14) Akhter, S.; Lui, K.; Kung, H. H. *J. Phys. Chem.* **1985**, *89*, 1958.
(15) Lui, K.; Vest, M.; Berlowitz, P.; Akhter, S.; Kung, H. H. *J. Phys. Chem.* **1986**, *90*, 3138.
(16) Berlowitz, P.; Kung, H. H. *J. Am. Chem. Soc.* **1986**, *108*, 3532.
(17) Zwicker, G.; Jacobi, K.; Cunningham, J. *Int. J. Mass Spectrosc. Ion Phys.* **1984**, *60*, 213.
(18) Vohs, J. M.; Barteau, M. A. *J. Phys. Chem.* **1987**, *91*, 4766.
(19) Vohs, J. M.; Barteau, M. A. *Surf. Sci.* **1988**, *201*, 481.

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While structure sensitivity and dehydration/dehydrogenation selectivity have been the principal focus of the TPD studies noted above, more conventional experiments with zinc oxide catalysts have suggested that the chemistry of 2-propanol and acetone may be even richer. For example, zinc oxide is known to be active for the aldol condensation of aldehydes and ketones.[21] Somewhat curiously, no evidence for such chemistry has been reported in the TPD studies of ZnO of which we are aware. The base-catalyzed aldol condensation of acetone to products such as $(CH_3)_2C(OH)CH_2C(O)CH_3$ and $(CH_3)_2C{=}CHC(O)CH_3$ is initiated by proton abstraction from one of the methyl groups of acetone to form an enolate anion.[22] Evidence for the formation of stable enolate and enol species on ZnO surfaces has been provided by infrared spectroscopy in studies by Miyata et al.[23,24] and Koga et al.[25] These species have been reported to undergo further oxidation to adsorbed carboxylates and also represent potential intermediates in the total oxidation of acetone and 2-propanol.

The present study is an examination by TPD and XPS of the reactions of 2-propanol and acetone on the two polar planes of ZnO. Although it is clear that all of the previous observations cannot be reconciled in their entirety, many of them can be confirmed. We consider here aspects of the structure sensitivity, selectivity, and the identity of adsorbed intermediates on well-defined surfaces which provide insights into this important family of reactions.

Experimental Section

All experiments were conduced in a stainless steel ultra-high-vacuum chamber (Physical Electronics 550) that was equipped with a cylindrical mirror analyzer and electron and photon sources for collecting Auger and photoelectron spectra (both XPS and UPS). Temperature-programmed desorption spectra were collected with a UTI-100C quadrupole mass spectrometer. The mass spectrometer was multiplexed with an IBM Personal Computer allowing up to eight masses to be monitored simultaneously. The computer was also used to control the sample heating rate (3.3 K/s) during TPD experiments.

The zinc oxide single crystal was obtained from Litton Airtron and was approximately 6 mm × 6 mm × 2 mm in size. The sample was polished with diamond paste until the surface was smooth as viewed through an optical microscope. After polishing, the sample was mounted on a manipulator and loaded into the vacuum chamber. The sample was attached to a four-pin electrical feedthrough at the end of the manipulator by a small tantalum wire which was wrapped in a groove cut around the edges of the crystal. Heating of the sample was achieved by resistive heating of the tantalum wires, and the sample could be cooled to ca. 150 K by immersing the atmospheric side of the four-pin feedthrough in liquid nitrogen. The sample temperature was monitored with a chromel–alumel thermocouple pressed against the back side of the crystal. The mounting hardware was spring-loaded to provide good thermal contact between the sample and the thermocouple and to ensure accurate temperature measurements.

The reactants, 2-propanol (Aldrich, 99+%) and acetone (Aldrich, 99.5%), were contained in glass sample tubes connected to a stainless steel dosing line and were purified by repeated freeze–pump–thaw cycles prior to use. The reactants were admitted into the vacuum chamber through a needle valve equipped with a 1/16-in. stainless steel dosing needle. The ZnO sample was positioned in front of the dosing needle while gases were admitted into the vacuum chamber. Saturation exposures were used in all experiments described below; no significant variations in reaction behavior were noted for lower exposures. With the assumption that the dosing needle increased the reactant flux to the front of the crystal by a factor of 100, a 60-langmuir (1 langmuir = 10^{-6} Torr·s) dose was sufficient to saturate the surface with either acetone or 2-propanol. Although it is difficult to determine absolute coverages of these species in the absence of a calibration standard (e.g., ordered CO layers on most metal surfaces), we estimate the extent of alcohol dissociation on the ZnO(0001) surface to be of order 0.1–0.5 monolayers on the basis of adsorption stoichiometries on polycrystalline materials and the comparable times required for C(1s) signal resolution in XPS studies on metal and oxide surfaces with the spectrometer described above.

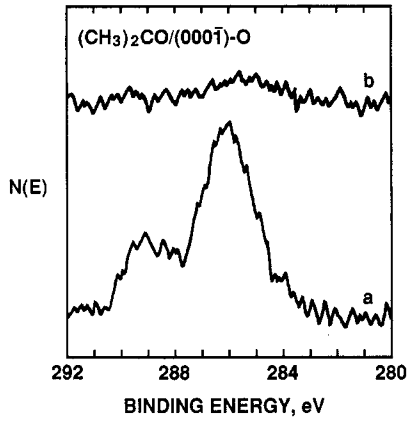

Figure 1. C(1s) spectra of the acetone-dosed $(000\bar{1})$-O surface: (a) acetone adsorbed on the $(000\bar{1})$-O surface at 150 K; (b) sample in (a) heated to 300 K.

All XPS spectra were collected by using Al Kα X-rays ($h\nu$ = 1486.6 eV). In order to account for small band-bending shifts (less than 0.4 eV) which occurred following adsorption of the reactants on the polar surfaces, XPS spectra were referenced to the $Zn(2p_{3/2})$ peak which appears at 1021.7 eV on the clean surface.

Results

$(000\bar{1})$-O Polar Surface. We have previously shown that the $(000\bar{1})$ oxygen polar surface of zinc oxide is inactive for dissociation of Brønsted acids over a range of acidities which includes alcohols, and is inactive for nucleophilic oxidation of aldehydes and esters to carboxylates as well.[11,12,18-20] Zwicker et al.[17] have also demonstrated that 2-propanol does not dissociate or decompose on the oxygen polar surface. This observation was confirmed in the present study; following exposure of the $(000\bar{1})$-O surface to 2-propanol at temperatures from 150 to 300 K, only the parent molecule was detected in TPD experiments. There was also no evidence for reaction in similar experiments in which the surface was exposed to acetone. The $(000\bar{1})$-O surface thus provides an excellent medium for obtaining photoelectron spectra of the unreacted parent molecules adsorbed on zinc oxide. Previous studies[11,12,19,27] have shown little difference between XPS spectra of weakly bound molecular speices on either of the polar surfaces.

C(1s) spectra for both acetone and 2-propanol on the O-polar surface were consistent with gas-phase spectra of these molecules. As shown in Figure 1, the spectrum for acetone adsorbed at 150 K consisted of two peaks centered at 289.0 and 286.1 eV. The separation of these peaks, 2.9 eV, was slightly greater than the 2.6-eV separation which has been reported for the gaseous reactant.[28-30] It is possible that this difference is due to changes

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(20) Barteau, M. A.; Vohs, J. M. In *Successful Design of Catalysts*; Inui, T., Ed.; Elsevier: Amsterdam, 1988; p 89.

(21) Hassouni, R.; Cressely, J.; Idriss, H.; Kiennemann, A. In *Heterogeneous Catalysis and Fine Chemicals*; Guisnet, M., Ed.; Elsevier: Amsterdam, 1988; p 307.

(22) March, J. *Advanced Organic Chemistry*; McGraw-Hill: New York, 1985; p 830.

(23) Miyata, H.; Hata, K.; Kubokawa, Y. *J. Catal.* **1981**, *49*, 8.

(24) Miyata, H.; Nakajima, T.; Kubokawa, Y. *J. Catal.* **1981**, *69*, 292.

(25) Koga, O.; Onishi, T.; Tamaru, K. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 19.

(26) Vohs, J. M.; Barteau, M. A. *Surf. Sci.* **1988**, *197*, 109.

(27) Vohs, J. M.; Barteau, M. A. *J. Electron Spectrosc. Relat. Phenom.* **1989**, *49*, 87.

(28) Bakke, A. A.; Chen, H. W.; Jolly, W. L. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *20*, 333.

(29) Jolly, W. L.; Schaaf, T. F. *J. Am. Chem. Soc.* **1976**, *98*, 98.

(30) Gelius, V.; Heden, P. F.; Hedman, J.; Lundberg, B. J.; Manne, R.; Nordberg, R.; Nordling, C.; Siegbahn, K. *Phys. Scr.* **1970**, *2*, 70.

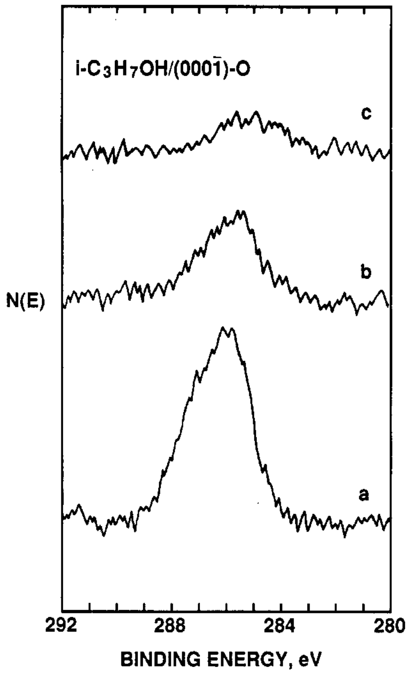

Figure 2. C(1s) spectra for 2-propanol adsorbed on the O-polar surface: (a) 2-propanol-dosed O-polar surface at 180 K; (b) sample in (a) heated to 300 K; (c) sample (b) heated to 450 K.

TABLE I: Relative Product Yields for Acetone Decomposition on the (0001)-Zn Surface

product	peak temp, K	rel yield
CO	745	0.56
CO_2	745	1.00
Zn	745	1.62

in the relaxation process between gaseous and adsorbed species. Alternatively, as has been suggested for aldehydes,[31-33] acetone may be coordinated to the surface oxygen anions in part via the carbonyl carbon. In either case the surface–adsorbate interaction is relatively weak and reversible; the molecule desorbs from the surface intact at temperatures below 300 K, as shown by its disappearance from the spectrum in Figure 1 upon warming the surface to this temperature.

The trend in the C(1s) intensity of 2-propanol adsorbed on the $(000\bar{1})$ surface was the same as that of acetone, as well as of the primary alcohols.[11,12] The C(1s) envelope for 2-propanol adsorbed at 180 K was broad (fwhm = 2.7 eV) and asymmetric, with greater intensity on the low binding energy side of the envelope center, as shown in Figure 2. The shape of the envelope is consistent with the structure of 2-propanol: the two methyl groups give rise to the peak at lower binding energy, and the central carbon, bearing the hydroxyl group, is responsible for the shoulder on the higher binding energy side of this peak. The characteristic fwhm obtained with this instrument for a single type of carbon on ZnO was 1.7; thus, the width of the C(1s) envelope suggests that the binding energy separation of the two types of carbons in 2-propanol is approximately 1 eV, consistent with gas-phase data for aliphatic alcohols.[34] Upon warming the surface, the C(1s) envelope simply decreased in intensity, finally disappearing between 400 and 500 K with no evidence for the presence of other adsorbates in the interim.

(0001)-Zn Polar Surface. Temperature programmed desorption was used to monitor the reactions of acetone and 2-propanol on the polar surfaces of zinc oxide. TPD spectra following the adsorption of acetone on the (0001)-Zn surface at 300 K are displayed in Figure 3 and the relative product yields are listed in Table I. The primary decomposition products were CO, CO_2, and Zn which desorbed coincidentally at 745 K. The high-temperature carbon oxide peaks are characteristic of the oxidation of atomic carbon on this surface; similar peaks have been observed following the adsorption of aldehydes,[31,32] carboxylic acids,[19] and alkynes.[18] In the case of the aldehydes and carboxylic acids, surface carbon is produced during the decomposition of surface carboxylate species at lower temperatures.

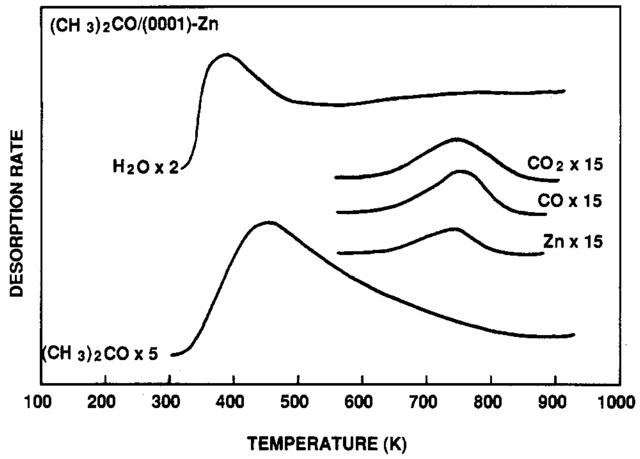

Figure 3. Temperature-programmed desorption spectra following acetone adsorption on the (0001)-Zn surface at 300 K. (Note: spectra have not been corrected for mass spectrometer sensitivities.)

During the high-temperature carbon oxidation reactions, lattice oxygen is removed from the surface. Consequently, in order to maintain charge neutrality, some of the surface zinc ions are reduced to zinc metal. Previous studies[11,26] have shown that this metallic species is weakly bound with a heat of adsorption approaching the heat of sublimation of zinc metal; it therefore desorbs coincidentally with the carbon oxide peaks which signal the lattice reduction. Zinc metal desorption peaks are characteristic of reactions which remove oxygen from the lattice and have been observed following the reaction of a variety of hydrocarbons and oxygenates on the (0001)-Zn surface.[11,12,15,18,19,26,31,32,35]

TPD experiments were also conducted following acetone adsorption at 170 K. No changes in the decomposition behavior of acetone were observed as the adsorption temperature was lowered; with the exception of a slight decrease in the total amount of decomposition products, the TPD results following adsorption at 170 K were nearly identical with those following adsorption at room temperature. This is in contrast to the reaction of aldehydes on this surface for which the adsorption temperature was found to have a profound effect on the selectivity of surface oxidation reactions.[31,32] For acetaldehyde and propionaldehyde, lowering the adsorption temperature below approximately 250 K resulted in the appearance of peaks at 575 K characteristic of the decomposition of surface formate species. In the case of the aldehydes, surface reaction proceeds via the nucleophilic attack of latice oxygen at the carbonyl carbon to form dioxyalkylidene species ($RHCO_2$). At room temperature this is followed by hydride elimination to form higher carboxylates, while at lower temperatures alkyl elimination competes with hydride elimination, producing formate and alkyl species in addition to the higher carboxylates. The surface dioxyalkylidene intermediate that would be produced by the analogous nucleophilic attack of acetone would not contain any α-hydrogens; subsequent alkyl elimination would be expected to produce surface acetate and methyl species.

There is little evidence for the formation of surface carboxylates, however, in the photoelectron spectra of the adsorbed species derived from acetone. C(1s) spectra of the surface species formed following the adsorption of acetone on the (0001)-Zn surface at 300 K are displayed in Figure 4. The C(1s) spectra were quite complex and for surface temperatures less than 650 K numerous

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(31) Vohs, J. M.; Barteau, M. A. *J. Catal.* **1988**, *113*, 497.

(32) Vohs, J. M.; Barteau, M. A. *Langmuir* **1989**, *5*, 965.

(33) Vohs, J. M. Ph.D. Dissertation, University of Delaware, 1988.

(34) Siegbahn, K.; Nordling, C.; Johansson, G.; Hedman, J.; Heden, P. F.; Hamrin, K.; Gelius, V.; Bergmark, T.; Werme, L. O.: Manne, R.; Baer, Y. *ESCA Applied to Free Molecules*, North Holland: Amsterdam, 1969.

(35) Vohs, J. M.; Barteau, M. A. *J. Phys. Chem.* **1989**, *93*, 8343.

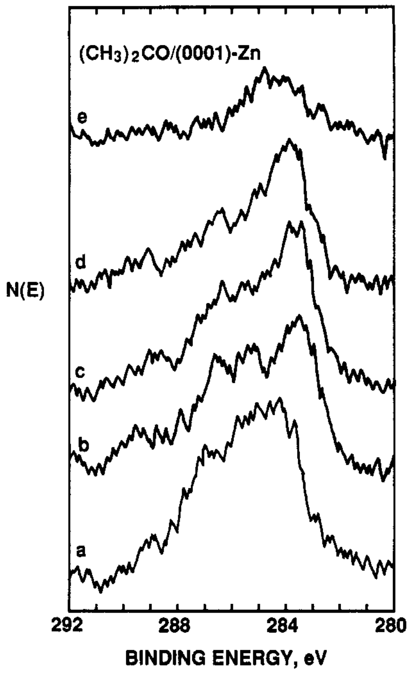

Figure 4. C(1s) spectra of the acetone-dosed (0001)-Zn surface as a function of temperature: (a) acetone adsorbed on the (0001)-Zn surface at 300 K; (b) sample in (a) heated to 400 K; (c) sample in (b) heated to 550 K; (d) sample in (c) heated to 650 K; (e) sample in (d) heated to 750 K.

overlapping peaks were observed. For sample temperatures between 400 and 650 K four separate C(1s) peaks were resolvable at ca. 289.2, 286.4, 285.5, and 283.6 eV. As the temperature was increased from 400 K, the first and third of these peaks were most strongly attenuated; the peaks at 286.4 and 283.6 eV became increasingly prominent. Conversely, the 300 K spectrum contained greater contributions from peaks in the vicinity of 289 and 286 eV. The 300 K spectrum for acetone on the (0001) surface can be decomposed into a linear combination of the 550 K spectrum in Figure 4 and the spectrum in Figure 1 of molecularly bound acetone on the $(000\bar{1})$ surface. Thus the spectrum of the acetone-derived adlayer on the (0001) surface is consistent with the presence of molecular acetone plus a more strongly bound species. As the surface is heated, the molecular acetone contribution at ca. 286 and 289 eV decreases; the more strongly bound species which gives rise to peaks at ca. 284 and 286.5 eV persists to temperatures greater than 650 K. There is also significant intensity in the C(1s) spectrum in between these two peaks, which remains at elevated temperatures.

Although the positions of these C(1s) peaks are consistent with the formation of adsorbed acetates and methyl groups from acetone, the relative intensities are not. As shown in previous studies on the ZnO(0001) surface,[12,19,20,31,32] acetates give rise to two peaks, at 285.5 and 289.1 eV, characteristic of their methyl and carboxyl carbons, respectively. C(1s) binding energies for adsorbed alkyl groups are typically less than 284 eV.[27,32] While there is significant intensity in the 300–550 K spectra of Figure 4 at 285.5 and 284.0 eV, the signal at ca. 289 eV which could correspond to carboxyl groups is quite weak. The intensity in this region of the spectrum can also be accounted for by the carbonyl group of molecularly adsorbed acetone (observed at 289.0 eV on the $(000\bar{1})$ surface). Even if all of the peak at ca. 289 eV in the 400 K spectrum of Figure 4 were attributed to acetates, this peak represents only 6–8% of the total C(1s) area, suggesting that no more than 20–25% of the adlayer reacts via nucleophilic attack of lattice oxygen at the carbonyl carbon. Again, given the contribution of molecular acetone to the C(1s) signal at 289 eV, the fraction of the total acetone reacted to acetate plus methyl species is likely below this upper bound. Further, the acetone TPD spectrum in Figure 1 shows little indication of the CO_2 peak at 640 K characteristic of acetate decomposition; this peak has been observed previously in experiments with CH_3COOH, CH_3CHO, and CH_3CH_2OH, all of which form acetates on this surface.[12,19,31,32]

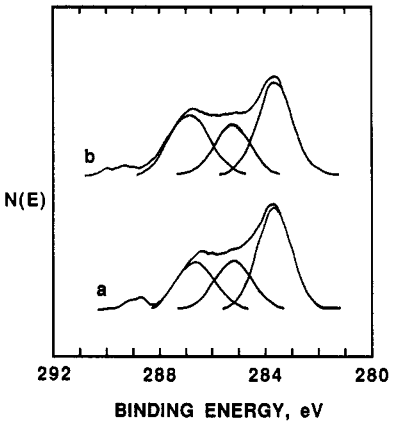

Figure 5. Comparison of C(1s) spectra of surface intermediates derived from (a) acetone and (b) 2-propanol adlayers, heated to 550 and 520 K, respectively. The spectra correspond to those of Figures 4 and 8, smoothed and curve-fit with the data analysis package supplied with the spectrometer.

The principal channel for acetone decomposition must involve the species characterized by the C(1s) peaks in the 550 K spectrum of Figure 4, which are present in all of the lower temperature spectra illustrated. This same species (or collection of species) can also be derived from 2-propanol. As shown in Figure 5, the C(1s) spectra of the acetone and 2-propanol-derived adsorbate layers at 520–550 K are quite similar. Both spectra consist of a broad envelope spanning the range from 283 to 288 eV which must include contributions from at least three types of carbon atoms. Deconvolution of such broad envelopes is rather inexact, but given the typical fwhm value of 1.7 eV for a single type of carbon, one can define three peaks centered at approximately 286.7, 285.2, and 283.7 eV. If one allows for the potential contribution of adsorbed methyl groups (formed by the minor acetone oxidation pathway) to the peak at 283.7 eV, the remainder of the three peaks are of approximately equal intensity. Since the original reactants, acetone and 2-propanol, each contain three carbon atoms, it is reasonable to consider potential surface intermediates in which the three carbons of the original framework become inequivalent.

We have previously examined a variety of carboxylic acids, aldehydes, and primary alcohols on the ZnO(0001) surface and have observed that common functional groups give quite well-defined and consistent C(1s) binding energies among the adsorbates which contain them. For example, the α-carbon of surface alkoxides typically gives rise to a peak at 286.4–286.8 eV.[11,12] Pendant alkyl groups in alkoxides and carboxylates are ca. 1 eV lower in energy, at 285.4 ± 0.2 eV.[12,19] The only species observed to date which produce C(1s) peaks below 284.0 eV are surface-bound alkyls, formed either by elimination from aldehydes[31,32] or by adsorption of diethyl zinc.[27] These species are easily distinguished from atomic carbon, which has a characteristic binding energy of 284.3 eV[18] (as in the 750 K spectrum of Figure 4).

The ca. 500 K spectra of the acetone and 2-propanol-derived adlayers appear to consist of peaks attributable to each of the organic functions above: a surface-bound alkyl carbon at 283.7 eV, a surface-bound (through the oxygen) alkoxide carbon at 286.7 eV, and a pendant methyl group at 285.2 eV. An adsorbed intermediate containing each of these functions can be constructed by removal of a single hydrogen atom from acetone: $-CH_2-C(CH_3)-O-$. The central carbon of this enolate species is, of course, unsaturated. This difficulty can be resolved by assuming either that the C–C–O backbone is π-bonded to the surface (as in the case of the analogous, isoelectronic π-allyl) or that the central carbon contains an additional hydrogen (i.e., $-CH_2-(H)C-(CH_3)-O$). Both of these alternatives have some drawbacks. C(1s) binding energies for π-bonded moieties are higher than for σ-bonded alkyls; for example, π-propargyl species ($CH_2{=}C{=}CH$) give a characteristic peak at 285.0 eV on ZnO.[18] However, it

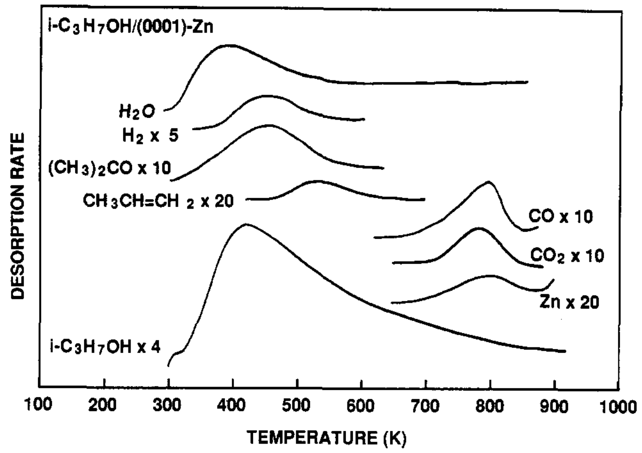

Figure 6. Temperature-programmed desorption spectra following 2-propanol adsorption on the (0001)-Zn surface at 300 K.

should be noted that the acetylide ligand of the propargyl is considerably more electron-withdrawing than the acetyl ligand of the enolate (electron affinity = 2.94 eV (CCH)[36] vs 0.423 eV $(COCH_3)$[37]). Thus the C(1s) binding energy of the methylene carbon of the enolate should be substantially less than that of the propargyl, as observed. The alternative saturated surface intermediate, formed by isomerization rather than deprotonation of acetone, is not consistent with the observation that the bulk of the water formed by acetone decomposition appears below 400 K in TPD experiments (Figure 3) and this molecule must therefore supply hydrogen atoms to the surface below this temperature. Other acetone isomers, such as the enol, $CH_2{=}C(CH_3){-}OH$, would appear to be less likely. There is little evidence for rehybridization of carbon–carbon double bonds on zinc oxide, and the C(1s) values for α-carbons in molecular alcohols are typically greater than 287.2 eV on ZnO, outside the binding energy range of the peaks in Figure 5.

Previous studies by infrared spectroscopy have produced evidence for the formation of stable intermediates similar to those postulated above in reactions of ketones and secondary alcohols on polycrystalline oxides, including zinc oxide. Miyata, Kubokawa, and co-workers[23,24,38,39] have reported the formation of stable enolate intermediates of the form $CH_2{\cdots}C(CH_3){\cdots}O$ from acetone and 2-propanol on ZnO, NiO, and MgO. Homologous enolates observed on ZnO include $CH_2{\cdots}C(C_2H_5){\cdots}O$ and $CH_3CH{\cdots}C(CH_3){\cdots}O$ from 2-butanone and $CH_3CH{\cdots}CH{\cdots}O$ from 2-methyloxirane. Supporting evidence from other laboratories for enolate formation on NiO[40] and ZnO[41] has been cited by Koga et al.,[25] although they assign acetone-derived infrared bands on zinc oxide to enol molecules ($CH_2{=}C(CH_3){-}OH$) coordinated to surface cations. Kinetic studies[6] have also found evidence for a strongly bound acetone state (present at temperatures up to 573 K) on polycrystalline zinc oxide. Although not unambiguous, the XPS results of the present study are most consistent with the assigment of this state to the enolate species proposed by Miyata and Kubokawa.[23,24]

While the formation of such species from acetone could be as simple as cleavage of a single C–H bond, the route to enolates from 2-propanol must involve additional reaction steps. These are somewhat more straightforward than those of acetone in TPD and XPS studies. Temperature-programmed desorption of 2-propanol on the (0001)-Zn surface resulted in the evolution of dehydrogenation, dehydration, and complete oxidation products. TPD spectra following 2-propanol adsorption on the (0001)-Zn surface at 300 K are displayed in Figure 6 and the relative product yields are listed in Table II. The principal decomposition products were acetone, propylene, and carbon oxides, which desorbed at 455, 530, and 785 K, respectively. These results are similar to those observed for temperature-programmed desorption of ethanol from this surface.[12] During temperature programming of an ethanol-dosed (0001)-Zn surface, acetaldehyde and ethylene desorbed simultaneously at 480 K and carbon oxides were observed at 740 K. In the case of primary alcohols the low-temperature dehydration and dehydrogenation products were due to reaction of surface alkoxide species; by analogy, the low-temperature products from the 2-propanol-dosed surface can be assigned to the decomposition of surface isopropoxide species. The high-temperature (>550 K) products can be attributed to the decomposition of the surface enolate species discussed above.

TABLE II: Relative Product Yields for 2-Propanol Decomposition on the (0001)-Zn Surface

product	peak temp, K	rel yield T_{ads} = 180 K	rel yield T_{ads} = 300 K
H_2	455	1.02	0.37
$(CH_3)_2CO$	455	1.00	1.05
C_3H_6	530	1.15	0.44
CO	785	0.25	0.39
CO_2	785	0.36	0.38
Zn	785	0.55	0.48

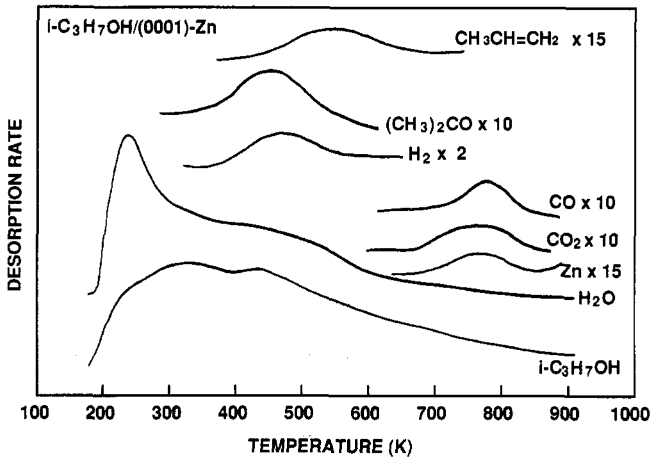

Figure 7. Temperature-programmed desorption spectra following 2-propanol adsorption on the (0001)-Zn surface at 180 K.

Decreasing the 2-propanol adsorption temperature did not result in the appearance of peaks characteristic of the decomposition of surface carboxylate species in contrast to the behavior of the primary alcohols, ethanol and 1-propanol.[12] This result is not surprising, given the absence of these species from the reaction network for acetone on this surface, discussed above. TPD spectra following 2-propanol adsorption at 180 K are displayed in Figure 7 and the relative product yields are listed in Table II. Comparison of the relative product yields for the two adsorption temperatures reveals that the decrease in the adsorption temperature was accompanied by a shift in the selectivity; for adsorption at 300 K the ratio of dehydrogenation products to dehydration products was 2.4, while for adsorption at 180 K this ratio was only 0.9.

C(1s) spectra of the surface species produced via the reaction of 2-propanol on the (0001)-Zn surface at 300 K are displayed in Figure 8; spectra obtained for reaction at 170 K were qualitatively similar. Following adsorption at 300 K, the C(1s) signal could be resolved into two peaks in roughly a 1:2 area ratio centered at 286.4 and 285.4 eV. These peaks can be assigned to the central carbon and the methyl carbons of adsorbed isopropoxide species, respectively. The central carbon is at a slightly higher binding energy relative to the methyl carbons due to the electron-withdrawing effect of the oxygen attached to it.

Heating to 400 K then 520 K produced dramatic changes in the C(1s) spectrum. The most noticeable of these was a marked

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[36] Janousek, B. K.; Brauman, J. I.; Simons, J. *J. Chem. Phys.* **1979**, *71*, 2057.

[37] Nimlos, M. R.; Soderquist, J. A.; Ellison, G. B. *J. Am. Chem. Soc.* **1989**, *111*, 7675.

[38] Miyata, H.; Toda, Y.; Kubokawa, Y. *J. Catal.* **1974**, *32*, 155.

[39] Miyata, H.; Wakamiya, M.; Kubokawa, Y. *J. Catal.* **1974**, *34*, 117.

[40] Rufov, Y. N.; Kadushin, A. A.; Roginsky, S. Z. *Proc. IVth Int. Congr. Catal. Moscow* **1968**; *3*.

[41] Nagai, K.; Miyahara, K. *J. Res. Inst. Catal., Hokkaido Univ.* **1975**, *23*, 110.

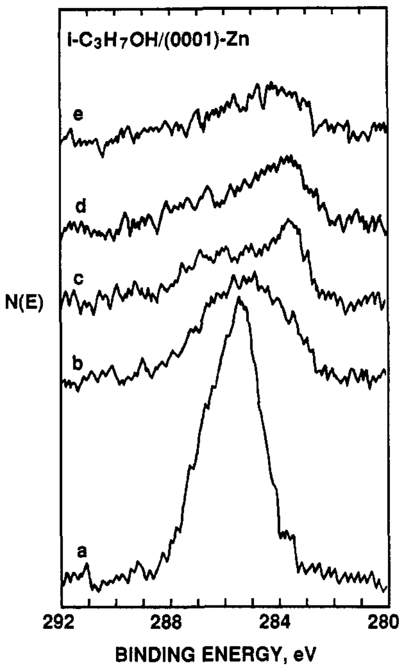

Figure 8. C(1s) spectra of the 2-propanol-dosed (0001)-Zn surface: (a) 2-propanol adsorbed on the (0001)-Zn surface at 300 K; (b) sample in (a) heated to 400 K; (c) sample in (b) heated to 520 K; (d) sample in (c) heated to 657 K; (e) sample in (d) heated to 775 K.

decrease in the overall area of the C(1s) peaks, indicative of the desorption of carbon-containing species. This is consistent with the TPD results in which acetone and propylene desorption was observed in this temperature range and demonstrates that these products are produced by direct decomposition of the surface alkoxide species. The spectrum for a sample temperature of 520 K was indistinguishable from that of the enolate species derived from acetone, as demonstrated above. These species decompose unselectively above 650 K to release carbon which is combusted to CO and CO_2 at ca. 750 K, as illustrated in Figures 3 and 6.

Discussion

The above results are consistent with a number of the observations previously reported for reactions of 2-propanol and acetone on both single-crystal and polycrystalline surfaces. As suggested previously by Kung et al.[14-16] and by Zwicker et al.,[17] the decomposition of 2-propanol on zinc oxide is a structure-sensitive reaction. We concur with the latter workers that the activity difference between the two polar planes is an absolute one rather than a matter of degrees. As discussed in previous publications,[11,12,18-20] dissociation and reaction of Brønsted acids appears to require an accessible Zn–O site pair, provided by the zinc-polar surface but not by the oxygen-polar surface of the wurtzite structure.

The adsorbed isopropoxides formed by dissociation of 2-propanol on the zinc-polar surface can react to liberate both acetone and propylene. It is not necessary to invoke different crystallographic planes to explain the formation of both products. The dehydrogenation/dehydration selectivity was of order unity, in agreement with the previous observation of Bowker et al.[7-9] It was also observed, consistent with that report, that propylene formation was more highly activated than acetone formation; indeed the separation of the peak temperatures in TPD experiments was even larger than in the previous powder study. The fraction of isopropoxides reacted unselectively to combustion products (CO + CO_2) was of the order of 10–15%, in agreement with the value from the powder study of Chadwick and O'Malley.[10] Alcohol dehydrogenation/dehydration selectivities are clearly influenced by a number of variables, including at the least alcohol structure, the extent of reduction and the redox properties of the oxide, and temperature. Such selectivities vary widely among this and previous studies of pure oxides containing no Brønsted acid sites; thus dehydration/dehydrogenation selectivities are a hazardous measure of catalyst acid–base properties.

The XPS results of this study provide evidence for the formation of stable enolates from 2-propanol and acetone, previously detected only by infrared spectroscopy on oxide powders. By comparison with results on other oxides, we conclude that the enolate species are formed from 2-propanol by dissociation of the acetone produced by isopropoxide dehydrogenation, rather than by direct reaction of isopropoxides. Results from this laboratory for 2-propanol decomposition on the {011}-faceted $TiO_2(001)$ surface provide an example in which no acetone was produced in TPD experiments and there was correspondingly no evidence for enolate formation in XPS.[42]

Enolate formation by proton transfer from acetone appears to be the preferred reaction channel on ZnO, in contrast to the preferred nucleophilic attack of the oxygen at the carbonyl carbon observed for aldehydes. The greater difficulty of ketone vs aldehyde oxidation is surprising only in that we have previously observed that nucleophilic oxidation of aldehydes can lead to alkyl elimination on ZnO. Proton abstraction from acetone is to be expected; indeed acetone is a stronger acid than 2-propanol in the gas phase.[43] The enolate intermediates do not appear to give rise to any reactions other than complete decomposition under the conditions of this study. Their stability on ZnO at temperatures of 550–650 K, demonstrated by the XPS spectra of Figure 4, exceeds that of surface formates[11,26] and acetates,[19] precluding the isolation of these intermediate oxidation products. No evidence for aldol condensation was observed in the present study, either. This reaction would involve the coupling of acetone with enolates, but as shown in Figure 3, molecular acetone is weakly bound on the ZnO(0001) surface. In the absence of gas phase acetone in these UHV TPD experiments, the apparently higher barrier for aldol condensation than for acetone desorption may prevent significant aldolization.

Conclusions

The reactions of 2-propanol and acetone on the polar surfaces of zinc oxide are structure sensitive. These molecules react on the (0001)-Zn surface to produce dehydrogenation, dehydration, and oxidation products. In contrast, these molecules adsorb only molecularly on the $(000\bar{1})$-O surface and desorb intact at temperatures less than 300 K. These results provide further examples of the role of surface cation–anion site pairs as active sites for the reaction of oxygenates on zinc oxide surfaces.

2-Propanol adsorbed dissociatively on the active (0001)-Zn surface to form surface isopropoxide intermediates. These alkoxides underwent net dehydration and dehydrogenation reactions to produce propylene and acetone. Acetone dissociated on this surface to form enolate intermediates stable to temperatures above 600 K. These enolates, characterized by a broad envelope of peaks in the C(1s) spectrum, decomposed unselectively, depositing carbon on the surface and forming CO and CO_2 at higher temperatures.

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(42) Kim, K. S.; Barteau, M. A. *J. Mol. Catal.* **1990**, *63*, 103.

(43) Bartmess, J. I.; McIver, R. T., Jr. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1979; Vol. 2, p 87.