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TPD study of the reaction of CH_3CH_2SH and $(CH_3CH_2)_2S_2$ on ZnO(0001) and ZnO

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Temperature programmed desorption (TPD) was used to study the reaction of CH_3CH_2SH and $(CH_3CH_2)_2S_2$ on the (0001) and surface of ZnO. The interaction of these molecules with ZnO was found to be structure-sensitive. Both the thiol and disulfide adsorbed dissociatively on ZnO(0001) forming adsorbed ethylthiolate intermediates, while only molecularly on ZnO . This result indicates that exposed cation-anion site pairs and exposed cations are the active sites for dissociative adsorption of CH_3CH_2SH and $(CH_3CH_2)_2S_2$, respectively. Decomposition to produce ethylene and adsorbed sulfur atoms was the only reaction pathway observed for adsorbed ethylthiolates on the (0001) surface. This is in contrast to adsorbed methylthiolates which undergo coupling to produce dimethylsulfide and oxydesulfurization to produce aldehydes and adsorbed carboxylates.

KEY WORDS: ethanethiol; diethyldisulfide; ZnO; catalysis; desulfurization.

1. Introduction

Thiols and other organosulfur compounds are present in most hydrocarbon feedstocks. They are well-known catalyst poisons and their byproducts upon combustion are environmental pollutants. Oxide-catalyzed reactions are important in industrial processes that are used to remove sulfur compounds from hydrocarbons, such as the Claus process, and for the synthesis of organosulfur compounds such as alkyl sulfides. In light of these examples, it is surprising that relatively few fundamental studies of the adsorption and reaction of these molecules on oxide catalysts can be found in the literature [1–4]. Due to this lack of study, insight into the reaction mechanisms is limited. In an effort to provide fundamental insight into structure-activity relationships for the reaction of thiols on metal oxides we have recently started studying the adsorption and reaction of thiols and alkyldisulfides on single crystal, metal oxide surfaces. In a recent paper we reported on the pathways and intermediates for the reaction of methanethiol (CH_3SH) and dimethyldisulfide (CH_3S–SCH_3) on the (0001) and (000$\bar{1}$) surfaces of ZnO [5]. In this letter we present temperature programmed desorption (TPD) results for the reaction of ethanethiol (CH_3CH_2SH) and diethyldisulfide ($(CH_3CH_2S)_2$) on the (0001) and (000$\bar{1}$)surfaces of ZnO and compare them to our previous results for the C_1 analogs and to the reaction of ethanol.

2. Experimental

Experiments were performed in two ion-pumped, ultra-high vacuum (UHV) surface analysis systems with base pressures of 2×10^{-10} torr. Both systems were equipped with a sputter ion gun (Physical Electronics) for sample cleaning, a mass spectrometer (UTI), and leak valves for introduction of gaseous reactants. One of the systems contained a cylindrical mirror electron energy analyzer (Omicron) and an electron gun that were used for Auger electron spectroscopy (AES), and the other contained a hemispherical electron energy analyzer (Leybold–Heraeus) and an X-ray source (VGMicrotech) which were used for X-ray photoelectron spectroscopy (XPS).

ZnO(0001) and ZnO oriented single crystals approximately 6 mm × 6 mm × 1 mm in size were used in this study. The crystals were mounted in a tantalum foil holder that was attached to the sample manipulator on the UHV chamber. The sample temperature was monitored using a chromel-alumel thermocouple that was attached to the back surface of the crystal using a ceramic adhesive (Aremco). The samples were heated via conduction from the resistively heated tantalum foil holder. The Zn-terminated (0001) and O-terminated surfaces were cleaned using repeated cycles of sputtering with 2 kV Ar^+ ions followed by annealing at 875 K. The sputter/anneal cycles were repeated until the surface was free from carbon and other impurities as determined by XPS or AES. To insure that each surface was fully oxidized they were then annealed in 10^{-8} torr of O_2 at 875 K for 60 min. Surfaces prepared in this manner exhibited sharp 1 × 1 hexagonal LEED patterns.

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The ionizer of the mass spectrometer on each system was enclosed in a quartz glass tube which had a 5 mm diameter aperture at one end. The ZnO sample was placed in front of this aperture during TPD experiments. A heating rate of 2 K/s was used in all TPD experiments. The liquid CH_3CH_2OH (Aldrich, 99+%), CH_3CH_2SH (Across, 99+%), and $(CH_3CH_2)_2S_2$ (Aldrich, 99.0%) reactants were purified using repeated freeze-pump-thaw cycles prior to use and their purity was checked by mass spectrometry. The reactants were administered into the vacuum systems using variable leak valves and saturation exposures (~3 L) were used in all of the TPD experiments. Except where noted otherwise, all of the TPD data presented below have been corrected for overlapping cracking patterns and the sensitivity factors of the various products.

3. Results and discussion

For comparison purposes it is useful to initially consider the reaction of CH_3CH_2OH on ZnO(0001) and ZnO $(000\bar{1})$. Previous studies have shown that alcohols adsorb dissociatively on exposed cation–anion site pairs on the (0001) surface and only molecularly on the $(000\bar{1})$ surface which lacks such sites [5–11]. TPD data obtained for the reaction of ethanol on ZnO(0001) are displayed in figure 1. Consistent with previous studies [6,7,10–12], these TPD results show that ethanol adsorbs dissociatively at room temperature on the (0001) surface to form adsorbed ethoxides. The primary reaction pathways for the ethoxides are recombination and desorption as ethanol at 380 K and dehydrogenation which produces gaseous acetaldehyde at 460 K. Dehydration competes with dehydrogenation and a small amount of ethylene is also produced at this temperature. Some CO and CO_2 is produced at 700 K which is also consistent with previous studies where these products have been attributed to decomposition of carboxylates formed via reaction of ethoxides with surface lattice oxygen [10]. The reactions that remove lattice oxygen from the surface are accompanied by reduction of a portion of the surface Zn cations and the resulting Zn metal desorbs at 820 K.

Based on the reaction of ethanol one would expect ethanethiol to adsorb only molecularly on the $(000\bar{1})$ surface and dissociatively on the (0001) surface at room temperature. This was indeed found to be the case and indicates that for thiols, like alcohols, exposed cation-anion pairs are the active sites for dissociative adsorption. Extending the analogy with the reaction of ethanol, one might expect adsorbed ethylthiolates on the (0001) surface to react upon heating to produce ethylene and thioacetaldehyde (CH_3CHS). TPD results obtained from the ZnO(0001) surface following exposure to 3 L of CH_3CH_2SH at room temperature are displayed in figure 2. This exposure was found to be sufficient to saturate the surface and similar results were obtained for lower coverages of the thiol. The data in figure 2 show that while there are some similarities between the reaction of ethanol and ethanethiol there are also some

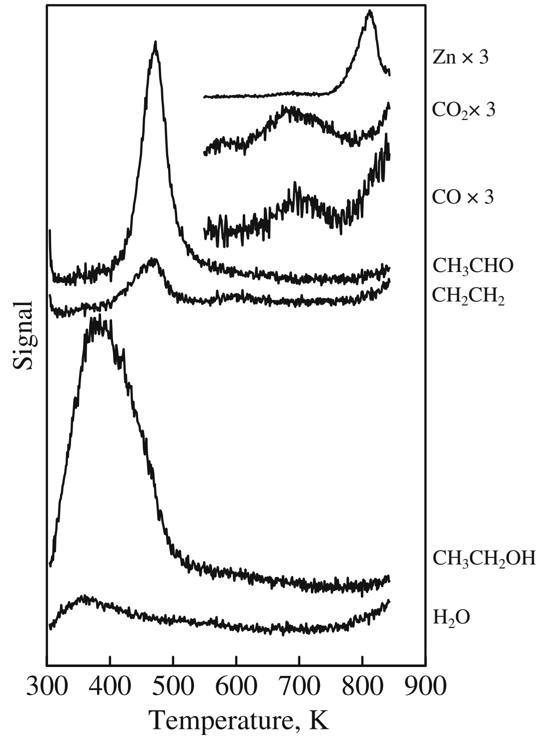

Figure 1. TPD data obtained from ZnO(0001) dosed with 3 L of CH_3CH_2OH at 300 K.

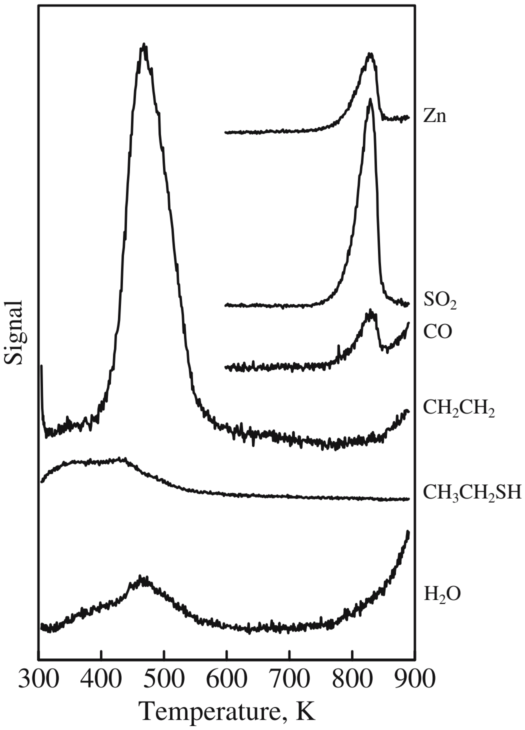

Figure 2. TPD data obtained from ZnO(0001) dosed with 3 L of CH_3CH_2SH at 300 K.

differences. The production of water between and 300 and 400 K indicates that ethanethiol adsorbs dissociatively at room temperature. In contrast to ethoxides, however, recombinative desorption of ethylthiolates and hydrogen to produce the parent, ethanethiol, is only a minor reaction pathway and occurs in two overlapping peaks centered at 360 and 440 K.

The primary reaction pathway for adsorbed ethylthiolates produced ethylene and water at 460 K. As shown in figure 1, decomposition of adsorbed ethoxides also produces some C_2H_4 at this temperature, although only as a minor product. The rate limiting step for the production of ethylene from both the thiolate and the alkoxide is almost certainly C–H bond cleavage. The fact that this reaction occurs at nearly the same temperature for both intermediates indicates that the C–H bond energies in the ethoxide and ethylthiolate are similar. While the C–H bond energies in ethanethiol have yet to be reported in the literature, this conclusion is consistent with those reported for the C_1 analogs, methanol and methanethiol [13]. In the case of the ethoxide, following C–H bond cleavage, direct desorption of acetaldehyde competes favorably with further reaction to produce ethylene and the product selectivity strongly favors acetaldehyde. In contrast, for ethylthiolate the corresponding thioaldehdye, CH_3CHS, was not observed as a product and only ethylene was produced. This difference in selectivity for the decomposition of the thiolate and alkoxide is most likely due to the difference in the C–S and C–O bond energies in the two intermediates. Based on the reported values for the C_1 analogs, the C–S bond in CH_3CH_2SH is approximately 70 kJ/mol less stable than the C–O bond in CH_3CH_2SH [14]. Thus, C–S bond cleavage in the ethylthiolate would be more facile than C–O bond cleavage in the ethoxide.

The decomposition of the ethylthiolate to produce gaseous ethylene at 460 K leaves sulfur atoms on the surface which are oxidized to SO_2 at 830 K. The sulfur oxidation reaction results in the reduction of a portion of the surface Zn cations to Zn metal which also desorbs at this temperature. A small amount of CO is also produced at 830 K which is likely to be due to the oxidation of surface carbon atoms formed by nonspecific decomposition of a small fraction of the adsorbed ethylthiolates at lower temperatures.

It is also useful to compare the reaction of ethanethiol on ZnO(0001) to the reaction of methanethiol on this surface. We have previously shown that the primary reaction pathways for methylthiolates produced via dissociative adsorption of CH_3SH on ZnO(0001) are recombinative desorption as the parent thiol and methyl group transfer between two adsorbed methylthiolates to produce gaseous dimethylsulfide ($(CH_3)_2S$) which occurs at 510 K during TPD [5]. As Shown in figure 2, this coupling pathway to the dialkylsulfide was not observed for adsorbed ethylthiolates. Note that the TPD results show that the reaction of ethylthiolate to produce ethylene occurs 50 K lower in temperature than the reaction of methylthiolate to produce dimethylsulfide and therefore has a lower activation energy. This lower energy pathway apparently precludes the production of the dialkylsulfide in the case of adsorbed ethylthiolates.

Another difference between the reaction of methane- and ethanethiol on ZnO(0001) is the absence of oxydesulfurization pathways for the latter. The reaction of methanethiol on this surface produces a small amount of formaldehyde at 560 K in addition to the main product dialkylsulfide which desorbs at 510 K [5]. Based on comparison to the reaction of methanol on this surface, it has been proposed that production of formaldehyde on the CH_3SH-dosed surface proceeds through a methoxide intermediate formed by transfer of the methyl group in the methylthiolate to a surface oxygen. Higher coverages of methylthiolates can be produced via exposure of ZnO(0001) to dimethyldisulfide relative to methanethiol and additional reaction pathways are observed for dimethyldisulfide-dosed surface. During TPD from dimethyldisulfide-dosed ZnO(0001), formaldehyde was produced at both 395 and 560 K. The high-temperature peak can again be attributed to reaction of methoxide species. The origin of the low-temperature peak was not clear, although it has been suggested that it may involve thio-oxymethylene intermediates ($SOCH_2$) adsorbed at step edge sites [5]. For dimethyldisulfide-dosed ZnO(0001), CO and CO_2 peaks were also observed at 585 K which are characteristic of formate decomposition.

In our previous study it was proposed that methanethiol adsorbs dissociatively at exposed cation-anion site pairs at step edge sites which are prevalent on sputter and annealed ZnO(0001) surfaces [5,15], while dimethyldisulfide adsorbs dissociatively on exposed Zn cation sites on (0001) terraces. This difference in adsorption site can explain the higher coverages of methylthiolates produced by exposure to the disulfide relative to the thiol. The additional pathways for oxydesulfurization of methylthiolates produced from dimethyldisulfide compared to methanethiol were thought to be related to these differences in coverage. In the present study TPD data were also collected from diethyldisulfide-dosed ZnO(0001). These data are displayed in figure 3. Note that with the exception of the production of a small amount of ethanethiol between 300 and 500 K, the TPD results from the diethyldisulfide-dosed surface are nearly identical to those from the ethanethiol-dosed surface with ethylene at 470 K and SO_2 at 830 K being the primary gaseous products. Oxydesulfurization pathways leading to oxygenated products were not observed. Quantitative analysis of the TPD results for the ethanethiol and diethyldisulfide dosed surfaces did show, however, that a higher saturation coverage of ethylthiolates was produced from the diethyldisulfide reactant consistent with our previous results for the C_1 analogs.

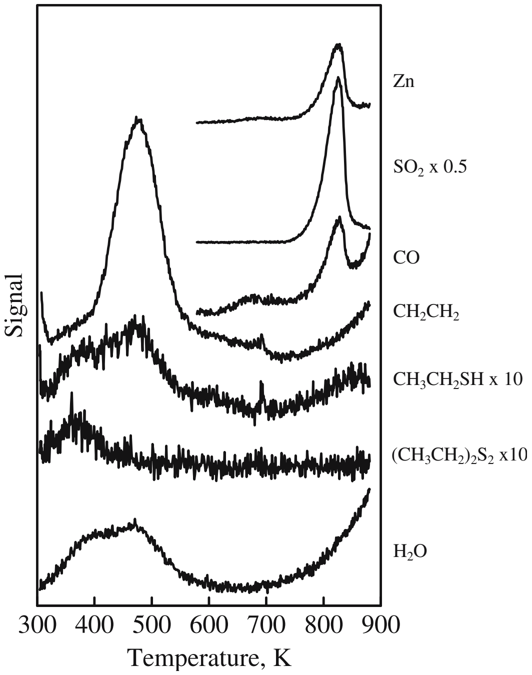

Figure 3. TPD data obtained from ZnO(0001) dosed with 3 L of $(CH_3CH_2)_2S_2$ at 300 K.

4. Summary

TPD was used to study the reaction of CH_3CH_2SH and $(CH_3CH_2)_2$ on the (0001) and $(000\bar{1})$ surface of ZnO. The adsorption of these molecules was found to be structure sensitive. Dissociative adsorption produces ethylthiolates on the (0001) surface, while only molecular adsorption occurs on the $(000\bar{1})$ surface. For ethanethiol this result is consistent with previous studies of the interaction of both alcohols and thiols with ZnO and indicates that exposed cation-anion site pairs on ZnO(0001) are the active sites for dissociative adsorption of Brønsted acids. The observation that higher coverages of ethylthiolates on the (0001) surface could be obtained via dissociative adsorption of $(CH_3CH_2)_2$ relative to CH_3CH_2SH supports the notion that only cation–anion site pairs at step edges are active for dissociative adsorption of the thiol while the disulfide can adsorb dissociatively on adjacent Zn cation sites on the (0001) surface.

The primary reaction pathway for adsorbed ethylthiolate on ZnO(0001) produced by dissociative adsorption of either ethanethiol or diethyldisulfide was hydride elimination followed by C–S bond cleavage to produce gaseous ethylene and adsorbed sulfur atoms which occurred at 460 K during TPD. The observation of only a single reaction pathway for adsorbed ethylthiolate is in contrast to the more complex chemistry reported previously for methylthiolates on this surface which included coupling to diethylsulfide and oxydesulfurization to aldehydes.

Acknowledgments

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