Site requirements for the reactions of CH_3SH and $(CH_3)_2S_2$ on ZnO(10(1)Overbar 0)

B. Halevi
University of Pennsylvania

John M. Vohs
University of Pennsylvania, vohs@seas.upenn.edu

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Keywords

thermal desorption spectroscopy, surface chemical reaction, zinc oxide, low index single crystal surfaces

Comments

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Site Requirements for the Reactions of CH_3SH and $(CH_3)_2S_2$ on ZnO$(10\bar{1}0)$

B. Halevi and John M. Vohs*.

Department of Chemical and Biomolecular Engineering
University of Pennsylvania
Philadelphia, PA 19104-6393

Abstract

Temperature programmed desorption (TPD) was used to investigate the adsorption and reaction of CH_3SH and $(CH_3)_2S_2$ on the nonpolar $(10\bar{1}0)$ surface of ZnO. Methanethiol was found to dissociate on the $(10\bar{1}0)$ surface to produce adsorbed methylthiolates. The primary reaction pathways for the methylthiolates were methyl group transfer between adjacent thiolates to produce $(CH_3)_2S$ at 510 K, and transfer of methyl groups to surface lattice oxygen to produce adsorbed methoxides which were oxidized to CH_2O at 525 K and adsorbed formate. Dimethyldisulfide was found to dissociate via cleavage of the S-S bond to form adsorbed methylthiolates. The reaction pathways for thiolates produced in this manner were similar to those produced from CH_3SH except for an additional low-temperature pathway for the production of CH_2O. Comparison of the results obtained in this study to our previous study of the reaction of CH_3SH and $(CH_3)_2S_2$ on ZnO(0001) and published STM studies of ZnO$(10\bar{1}0)$ and ZnO(0001) indicates that step edges are the active sites for the reaction of thiols and disulfides on these surfaces

*corresponding author

vohs@seas.upenn.edu

Introduction

The reaction of thiols, disulfides and other organosulfur compounds on catalytically active metal oxides is of technological interest for the removal of these compounds from hydrocarbon feedstocks and fuels, and the synthesis of fertilizers and pharmaceutical precursors. While this area of catalytic chemistry is of increasing importance there have been relatively few fundamental studies of structure-activity relationships for the reaction of organosulfur compounds on metal oxides compared to other classes of molecules such as oxygenates. In order to provide fundamental insight into the active sites, intermediates, and pathways involved in the reaction of organosulfur compounds on metal oxides we have been studying the adsorption and reaction of thiols and dialkyldisulfides on model catalysts consisting of the surfaces of metal oxide single crystals [1, 2]. To date the bulk of our work has focused on reactions of these molecules on ZnO(0001) and $ZnO(000\bar{1})$. In the work reported here we have extended these studies to include the reactions of CH_3SH and $(CH_3)_2S_2$ on $ZnO(10\bar{1}0)$.

In our previous study of the reaction of thiols and disulfides on ZnO(0001) [1, 2], temperature programmed desorption (TPD) experiments revealed that CH_3SH, like other Brønsted acids [3-5], adsorbs dissociatively on this surface to form methylthiolates (CH_3S). The primary reaction pathways for these thiolate intermediates during TPD is recombinative desorption as CH_3SH at 440 K and coupling to produce $(CH_3)_2S$ and adsorbed sulfur atoms at 520 K. Methyl group transfer to surface oxygen anions to form methoxide species that undergo dehydrogenation at 580 K producing gaseous CH_2O was also observed as a minor pathway.

The conventional picture for the dissociative adsorption of Brønsted acids on ZnO(0001) is that the reaction occurs on exposed cation-anion site pairs forming a surface hydroxyl group and the conjugate base anion of the acid which is bound to the surface Zn^{2+} cation [6-11]. Figure

1 displays a model of the ZnO(0001) surface. Note that this surface is terminated by Zn^{2+} cations that have a single dangling bond (i.e. coordination vacancy) that is directed perpendicular to the surface. The second layer O^{2-} anions are also exposed on this surface. This model illustrates one problem with the cation-anion site pair model for dissociative adsorption of Brønsted acids, which is that while the Zn^{2+} cations each have one dangling bond, the O^{2-} anions are fully coordinated and, therefore, would not be expected to be very reactive.

Based on detailed STM studies of the structure of vacuum-annealed ZnO(0001) surfaces Dulub et al. [12] proposed an alternative model for the active sites on ZnO(0001). In this model dissociative adsorption of Brønsted acids occurs at step edges which contain under-coordinated O^{2-} anions. This conclusion was based on the observation that UHV-prepared ZnO(0001) is covered with single layer, high, triangularly shaped islands, and that these features produce a high concentration of oxygen-terminated single layer high steps [12, 13]. The model of the ZnO(0001) surface in Figure 1 contains an example of a triangular island and shows the structure of the step edge. Dulub et al. also proposed that the formation of the islands decreases the surface Zn^{2+} concentration and this helps stabilize the polar surface [14]. This proposed model of the active sites is consistent with our TPD studies of alcohols and thiols [1, 2] and helps to explain why the saturation coverage of thiolates and alkoxides on ZnO(0001) are substantially less than what would be expected if all of the Zn^{2+}-O^{-2} sites exposed on the (0001) terraces were active.

Our TPD studies of the reaction of $(CH_3)_2S_2$ on ZnO(0001) are also consistent with the step-edge model for the location of Zn^{2+}-O^{2-} sites which are active for the dissociative adsorption of Brønsted acids [2]. Dissociative adsorption of $(CH_3)_2S_2$ via cleavage of the S-S bond to form methylthiolates bonded to Zn^{2+} cations on ZnO(0001) does not require exposed, unsaturated O^{2-} sites and could occur across two adjacent Zn^{2+} cations on this surface. This model predicts that the (0001) terraces would be active for dissociative adsorption of $(CH_3)_2S_2$ and that you should obtain higher coverages of methylthiolates by exposing the surface to $(CH_3)_2S_2$ relative to CH_3SH which only adsorbs at the step edges. Our TPD results show that this is indeed the case.

In contrast to the (0001) terraces on the ZnO(0001) surface in which only the Zn^{2+} cations have a dangling bond, on the $(10\bar{1}0)$ surface both the exposed the O^{2-} and Zn^{2+} ions each have a single dangling bond. A model of this surface is shown in Figure 2. Note that the dangling bonds on Zn and O ions are directed towards each other and are at angle of ~60º relative to the plane of the surface. Dulub et al. have also used STM to characterize the structure of UHV-prepared ZnO$(10\bar{1}0)$ surfaces [12]. They observed that this non-polar surface was relatively stable and composed of large rectangular $(10\bar{1}0)$ terraces that were separated by single unit high steps oriented along the $[1\bar{2}10]$, and [0001] directions. The structures of these steps are illustrated in Figure 2. In light of the model presented above for the dissociative adsorption of Brønsted acids on ZnO(0001) one would expect the ZnO$(10\bar{1}0)$ surface to be more active for this type of reaction since all the surface Zn and O ions each have a dangling bond. A previous study of the reaction of methanol on the $(10\bar{1}0)$ surface suggests, however, that this is not the case. Cheng et al. [4] used TPD to study the reaction of CH_3OD on the $(10\bar{1}0)$, $(50\bar{5}1)$, $(40\bar{4}1)$ surfaces on ZnO. The $(50\bar{5}1)$, $(40\bar{4}1)$ surfaces are stepped surfaces which contain $(10\bar{1}0)$ terraces with [0001] oriented steps. They observed that the reactivity of these surfaces increased in the following order $(10\bar{1}0) < (50\bar{5}1) < (40\bar{4}1)$ and concluded that step edges or defects were the active sites for methanol decomposition. In addition to illustrating the pathways for the reaction of CH_3SH and $(CH_3)_2S_2$ on ZnO$(10\bar{1}0)$ and ZnO(0001), the results of the present study provide further insight into the active sites for reaction on the $(10\bar{1}0)$ surface and support the model that dissociative adsorption of Brønsted acids on this surface occurs primarily at step edges.

Experimental Methods

Studies of the reactivity of ZnO $(10\bar{1}0)$ surfaces were conducted using an ion-pumped, ultrahigh vacuum (UHV) surface analysis system. The system had a base pressure of $2x10^{-10}$ torr and was equipped with a sputter ion gun (Physical Electronics), a mass spectrometer (UTI), and an electron energy analyzer (Leybold-Heraeus) and an X-ray source (VGMicrotech), which were used for X-ray photoelectron spectroscopy (XPS). The single-crystal ZnO $(10\bar{1}0)$ substrate was 7x7x0.5mm in size and 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 ZnO crystal using a ceramic adhesive (Aremco). The sample was heated via conduction from the resistively heated tantalum foil holder. The $(10\bar{1}0)$ surface was 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. To insure that the surface was fully oxidized the sample was then annealed in 10^{-8} torr of O_2 at 875 K for 60 min.

The quadrupole detector of the mass spectrometer was enclosed in a quartz glass shroud with 5-mm diameter aperture which the sample was placed in front of during TPD experiments. A heating rate of 2 K/s was used in all of the TPD runs. The liquid $(CH_3)_2S$ (Aldrich, 99%), and $(CH_3)_2S_2$ (Aldrich, 99%) reactants were purified using repeated freeze-pump-thaw cycles prior to use, and the gaseous CH_3SH (Aldrich, 99.5+%) reactant was used as received from the manufacturer. The reactants were administered into the vacuum systems using variable leak valves, and saturation exposures (10 L) were used in all of the TPD experiments. The TPD data presented below have been corrected for overlapping cracking patterns and scaled to account for the mass spectrometer sensitivity factors for each product. The TPD spectra for each product were based on the following m/z values: 18-H_2O, 26-CH_2CH_2, 30-CH_2O, 44-CO_2, 48-CH_3SH, 62-$(CH_2)_2S$, 64-SO_2.

Results and Discussion

TPD data for the reaction of CH_3SH on ZnO$(10\bar{1}0)$ are displayed in Figure 3A. In this experiment the sample was exposed to a 10 L dose of CH_3SH at 300 K which was sufficient to saturate the surface with chemisorbed species. The primary gaseous specie produced during TPD was the parent molecule, CH_3SH, which desorbed in a broad peak centered at 400 K. It is likely that this peak corresponds to recombinative desorption of surface thiolates and hydroxyl groups. In addition to the parent molecule, peaks for a variety of reaction products are present in the TPD data including H_2O at 400 K, $(CH_3)_2S$ at 510 K, CH_2O at 525 K, CO_2 at 560 K, and a small peak for C_2H_4 at 570 K. Peaks for Zn metal (not shown in the figure) and SO_2 are also present centered at 825 K. The relative product yields for the various carbon-containing products are listed in Table 1. The data in this table show that only 20% of the adsorbed thiolates produced by dissociative adsorption of CH_3SH react further to products other than the parent molecule.

The most likely pathway for the production of $(CH_3)_2S$ at 510 K is the transfer of a methyl group between two adjacent surface methylthiolates. This leaves a sulfur atom on the surface which is ultimately oxidized to SO_2 at 825 K. The CH_2O product occurs at a temperature that is close to CH_2O production via the dehydrogenation of methoxide intermediates produced by dissociative adsorption of CH_3OH on this surface [3]. This similarity suggests that in the case of the CH_3SH-dosed ZnO$(10\bar{1}0)$, the pathway for the production of CH_2O also proceeds through a methoxide intermediate. Such species could be produced by transfer of the methyl group in an adsorbed methylthiolate to an adjacent surface O^{2-} site. Likewise, the CO_2 peak temperature corresponds to that reported for the decomposition of formate intermediates on the $(10\bar{1}0)$ surface [3], again suggesting the formation of oxygenate intermediates on the CH_3SH-dosed $(10\bar{1}0)$ surface. The reactions producing CH_2O and CO_2 also leave sulfur atoms on the surface which are oxidized to SO_2 at 825 K.

Comparison to the reaction of CH_3SH on ZnO(0001) provides useful insight into the possible reaction sites for thiolates on the $(10\bar{1}0)$ surface. TPD data for ZnO(0001) exposed to a 10 L saturation dose of CH_3SH are displayed in Figure 1B and the relative product yields of the carbon-containing products are listed in Table 1. A detailed analysis of this data has been reported previously [2]. Like the $(10\bar{1}0)$ surface, the primary reaction pathways for methylthiolates on ZnO(0001) are recombinative desorption as CH_3SH at 440 K, methyl transfer to produce $(CH_3)_2S$ at 510 K, and oxydesulfurization to produce CH_2O at 560 K. The latter pathway again most likely proceeds through a methoxide intermediate. Production of carbon dioxide was not observed on the (0001) surface.

In addition to the difference in the relative product yields, the data in Figure 3 show a large difference in the saturation coverage of methylthiolates produced by exposure of each surface to CH_3SH. Note that in this study the ZnO$(10\bar{1}0)$ and ZnO(1000) samples were of roughly the same size, mounted in the same sample holder and the TPD data were collected using the same mass spectrometer settings and heating rate; thereby, facilitating a quantitative comparison of the TPD results for the two surfaces. As the scale factors in the figure imply, the saturation coverage of thiolate species on the $(10\bar{1}0)$ surface was significantly less than that on the (0001) surface. Quantitative analysis of the TPD data shows that the saturation thiolate coverage on the $(10\bar{1}0)$ surface was only 25% of that on the (0001) surface. This result is somewhat surprising in light of the accepted model for the reaction of Brønsted acids on ZnO where dissociative adsorption is thought to occur on exposed surface cation-anion site pairs.

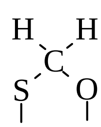
As noted in the introduction and shown in Figure 2, all the Zn and O ions on the $(10\bar{1}0)$ surface have a single dangling bond and according to the site-pair model the entire $(10\bar{1}0)$ surface should be active for dissociative adsorption of Brønsted acids. The low coverage of thiolates on the $(10\bar{1}0)$ surface relative to the (0001) surface is consistent, however, with previous studies of the reaction of alcohols and carboxylic acids on these two surfaces. For example, Akhter et al. report that the saturation coverages of methoxides and formates produced by exposure to CH_3OH and HCOOH, respectively, are much smaller on the $(10\bar{1}0)$ surface relative to the (0001) surface [3]. We have also observed this trend for methanol in our own studies [2, 15]. One possible explanation for this result is that the cation-anion site pairs on the $(10\bar{1}0)$ surface are passivated by adsorbed H and OH species which are formed by adsorption of water from the background gas in the UHV chamber. Previous studies of the interaction of H_2O with the $(10\bar{1}0)$ surface have shown that adsorbed water and hydroxyl groups are removed by heating above 550 K [16] which is substantially lower that the annealing temperature used in the current study. This coupled with the fact that background pressure of water in the UHV chamber was less than 10^{-10} torr suggests that complete passivation of the $(10\bar{1}0)$ surface by adsorbed water is unlikely. Nonetheless, since there is a small H_2O peak in the TPD spectra the possibility that adsorbed water played a role can not be completely ruled out. A more likely explanation, however, for the low saturation coverage of thiolates on the $(10\bar{1}0)$ surface is that dissociation of CH_3SH proceeds at defect sites. As will be shown below, the TPD results for the reaction of $(CH_3)_2S_2$ on the $(10\bar{1}0)$ and (0001) surfaces are consistent with the conclusion that defect chemistry dominates on $(10\bar{1}0)$ surface.

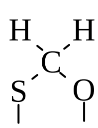
Figure 4 displays TPD data obtained from $ZnO(10\bar{1}0)$ dosed to saturation with 10 L of $(CH_3)_2S_2$. Since dissociative adsorption of $(CH_3)_2S_2$ via cleavage of the S-S bond would produce adsorbed CH_3S species, one might expect the TPD results for CH_3SH- and $(CH_3)_2S_2$-dosed $ZnO(10\bar{1}0)$ to be similar. Comparison of the TPD data in Figure 3 for CH_3SH with that in Figure 4 for $(CH_3)_2S_2$ reveals that while there are some similarities there are also some significant differences. For the $(CH_3)_2S_2$-dosed $(10\bar{1}0)$ surface only a small amount of the parent molecule desorbs at 400 K and the primary reaction product is CH_3SH which desorbs in a broad peak centered at 420 K. This peak temperature is similar to that for recombinative desorption of CH_3SH from the (0001) surface and confirms that $(CH_3)_2S_2$ adsorbs dissociatively on $ZnO(10\bar{1}0)$ via cleavage of the S-S bond. While it is not completely clear where the hydrogen required for this reaction comes from, as discussed above, it is possible that it is provided by water that may have adsorbed from the background as suggested by the small water peak centered at 400 K.

Other similarities in the TPD results for the reaction of CH_3SH and $(CH_3)_2S_2$ on the $(10\bar{1}0)$ surface are the production of a small amount of C_2H_4 between 500 and 600 K and the $(CH_3)_2S$ product at 510 K. On both surfaces CO_2 was also produced at 560 K, and SO_2 and Zn (not shown in the figure) desorbed above 800 K. As noted above, the CO_2 product and desorption temperature are indicative of the decomposition of formate intermediates on this surface [3, 8, 9, 17]. The biggest difference in the TPD results for the CH_3SH and $(CH_3)_2S_2$-dosed $(10\bar{1}0)$ surfaces are in the CH_2O desorption spectra. For the CH_3SH-dosed surface, CH_2O was produced in a single peak centered at 525 K, which can again be attributed to the dehydrogenation of a methoxide intermediate. While a CH_2O desorption feature between 500 and 600 K is also observed for the $(CH_3)_2S_2$-dosed surface, an additional much larger CH_2O peak appears at 420 K. Note that this low-temperature pathway to CH_2O may also be a source for the hydrogen required for the production of CH_3SH at 420 K. The saturation coverage of methylthiolate species produced by dissociative adsorption of $(CH_3)_2S_2$ on the $(10\bar{1}0)$ surface was also found to be roughly half of that produced by dissociative adsorption of CH_3SH.

Comparison of the TPD results for $(CH_3)_2S_2$ on the $(10\bar{1}0)$ and (0001) surfaces again provides some insight into the reactions of thiolates on these surfaces. TPD results obtained from a (0001) surface dosed with 10 L of $(CH_3)_2S_2$ at 300 K are displayed in Figure 4B. This data has been described in detail previously [2]. As was the case for CH_3SH, the data for the two surfaces shows that the saturation coverage of methylthiolates produced from $(CH_3)_2S_2$ on the $(10\bar{1}0)$ surface is less that 10% of that on the (0001) surface. The saturation coverage of methylthiolates produced from $(CH_3)_2S_2$ on the $(10\bar{1}0)$ surface is also roughly half that produced by dissociative adsorption of CH_3SH on this surface. These observations lead to the conclusion that the majority of the $(10\bar{1}0)$ surface is not active for the dissociative adsorption of $(CH_3)_2S_2$ and that reaction must occur primarily at step edges or other defect sites. This result is in contrast to that obtained for the (0001) surface where relatively high coverages of methylthiolates are produced upon exposure to $(CH_3)_2S_2$. We have previously proposed that $(CH_3)_2S_2$ adsorbs dissociatively across adjacent Zn^{2+} cations on the (0001) surface [2]. Each Zn cation on this surface has a single dangling bond that is directed perpendicular to the surface. As shown in Figure 2, the Zn ions on the $(10\bar{1}0)$ surface also have a single dangling bond and the distance between adjacent Zn sites on the $(10\bar{1}0)$ and (0001) surfaces are identical. Nevertheless, the $(10\bar{1}0)$ surface is not very reactive towards $(CH_3)_2S_2$. Since the dangling bonds on the Zn ions on ZnO(1010) are at a 60º angle from the surface rather than perpendicular to the surface as on ZnO(0001), it is possible that steric interactions between the methyl groups and the $(10\bar{1}0)$ surface results in a large barrier for dissociative adsorption of $(CH_3)_2S_2$.

Finally, another interesting aspect of the data in Figure 4 is that the shapes CH_2O desorption curves from the $(CH_3)_2S_2$-dosed $(10\bar{1}0)$ and (0001) surfaces are nearly identical, containing overlapping peaks of the same relative intensities centered at 410 and 570 K. Comparison to studies of the reaction of methanol on these surfaces allows the high-temperature peak to be assigned to dehydrogenation of adsorbed methoxide intermediates. For the (0001) surface we have previously argued that the low-temperature CH_2O product is produced via the following pathway involving a thio-oxymethylene ($SOCH_2$) intermediate [2]

$CH_3S(ad)$ + 2 O(lattice) →  + OH(ad) (1)

 → $CH_2O(g)$ + S(ad) (2).

While spectroscopic identification of the thio-oxymethylene is needed to verify this pathway, the similarity of the CH_2O desorption signals for the reaction of $(CH_3)_2S_2$ on the ZnO$(10\bar{1}0)$ and ZnO(0001) indicates that the pathways and the active sites are similar on both surfaces. The step edges on these surfaces again seem to be the most likely location of the active sites. On ZnO(0001) the steps are predominantly perpendicular to the $[\bar{1}100]$, $[01\bar{1}0]$, and $[10\bar{1}0]$

directions (see Figure 1). Since these directions are crystallographicaly equivalent, the exposed corners at the steps all have the same structure and consist of zigzag rows of Zn^{2+} and O^{2-} ions each having a single coordination vacancy. On the $(10\bar{1}0)$ surface, the steps run along the [0001] and $[1\bar{2}10]$ directions. The step edges that are perpendicular to the $[1\bar{2}10]$ direction expose sites that are essentially identical to those on the $(10\bar{1}0)$ terraces. In contrast, the step edges that are perpendicular to the [0001] direction consist of zigzag rows of Zn^{2+} and O^{2-} ions which each have a single coordination vacancy. Thus, these step edge sites on the $(10\bar{1}0)$ surface are similar to those on the step edges on the (0001) surface. Given the similarity in the CH_2O desorption spectra from both surfaces and the observation that these step edge sites are the feature shared by both surfaces, we postulate that these step edges contain the active sites for the reactions that produce CH_2O. The fact that much less CH_2O is produced on the $(10\bar{1}0)$ surface relative to the (0001) surface is also consistent with this model of the active sites since the step edge density on the $(10\bar{1}0)$ surface is significantly less than that on the (0001) surface.

Conclusions

The results of this study show that methane thiol adsorbs dissociatively on the $ZnO(10\bar{1}0)$ surface to form adsorbed thiolate species. The saturation coverage of thiolates produced in this manner is substantially less than one monolayer indicating that the active sites for dissociative adsorption are step edges or other surface defects. The primary reaction pathways for adsorbed methylthiolates produced from CH_3SH are recombinative desorption as the parent molecule at 400 K, transfer of a methyl group between adjacent thiolates producing gaseous $(CH_3)_2S$ at 510 K, and transfer of methyl group to a surface lattice oxygen. The methoxide species produced by the latter reaction either undergo dehydrogenation to CH_2O at 525 K, or oxidation to surface formate which decomposes to produce CO_2 at 560 K.

Dimethyldisulfide was found to dissociate via cleavage of the S-S bond to form adsorbed methylthiolate species on the ZnO$(10\bar{1}0)$ surface. While higher than that for CH_3SH, the saturation coverage of CH_3S produced from $(CH_3)_2S_2$ was substantially less that a monolayer again suggesting that step edges or other defects are the active sites for the dissociative adsorption of this molecule. The pathways for the reaction of methylthiolates produced from $(CH_3)_2S_2$ were similar to those from CH_3SH except an additional low-temperature pathway for the production of CH_2O at 420 K.

The similarity in the CH_2O desorption spectra from $(CH_3)_2S_2$- and CH_3SH-dosed ZnO$(10\bar{1}0)$ and ZnO(0001) indicates that the surface reactions occur at similar sites on these two surfaces. Furthermore, based on comparison to STM studies of the local atomic structure of these surfaces we postulate that $[1\bar{2}10]$ and $[12\bar{1}0]$ oriented step edges on the $(10\bar{1}0)$ surface and $[\bar{1}100]$, $[01\bar{1}0]$, and $[10\bar{1}0]$ oriented step edges on the (0001) surface, which have similar structures, are the location of these active sites.

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Figure captions

Figure 1. Model of the ZnO(0001) surface showing triangular island and step structure.

Figure 2. Model of the ZnO$(10\bar{1}0)$ surface showing rectangular terrace and step structure.

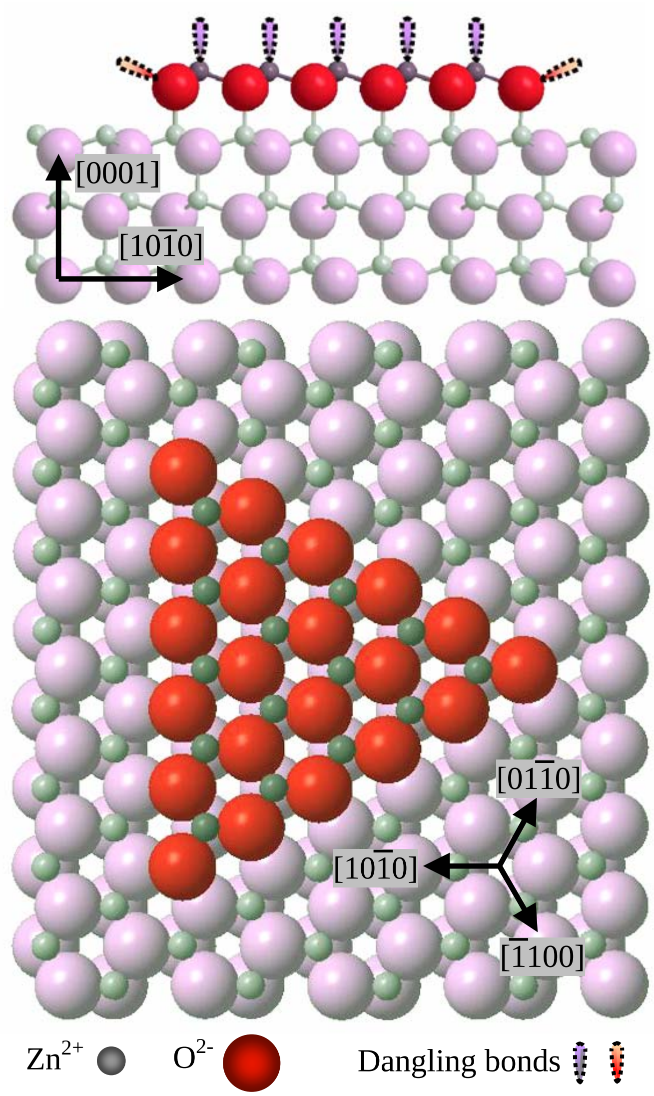
Figure 3. TPD data for the reaction of CH_3SH on (A) ZnO$(10\bar{1}0)$ and (B) ZnO(0001).

Figure 4. TPD data for the reaction of $(CH_3)_2S_2$ on (A) ZnO$(10\bar{1}0)$ and (B) ZnO(0001).

Table 1. Relative product yields

	Surface and Reactant			
	$(10\bar{1}0)$	$(10\bar{1}0)$	(0001)	(0001)
Product	CH_3SH	$(CH_3)_2S_2$	CH_3SH	$(CH_3)_2S_2$
CH_2CH_2	2%	0%	0%	0%
CH_2O	10%	21%	14%	25%
CO_2	3%	5%	0%	19%
CH_3SH	81%	64%	65%	0%
$(CH_3)_2S$	4%	4%	21%	35%
$(CH_3)_2S_2$	0%	6%	0%	0%
CO	0%	0%	0%	21%

Figure 1



[0001]
[10$\bar{1}$0]
[01$\bar{1}$0]
[10$\bar{1}$0]
[$\bar{1}$100]
Zn2+
O2-
Dangling bonds

Figure 2

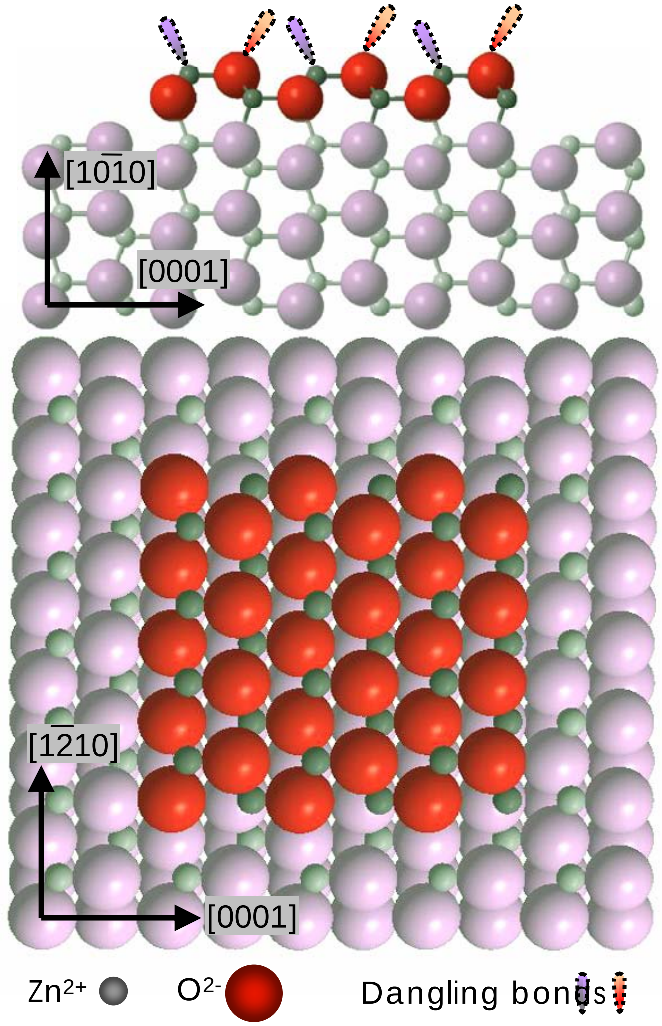
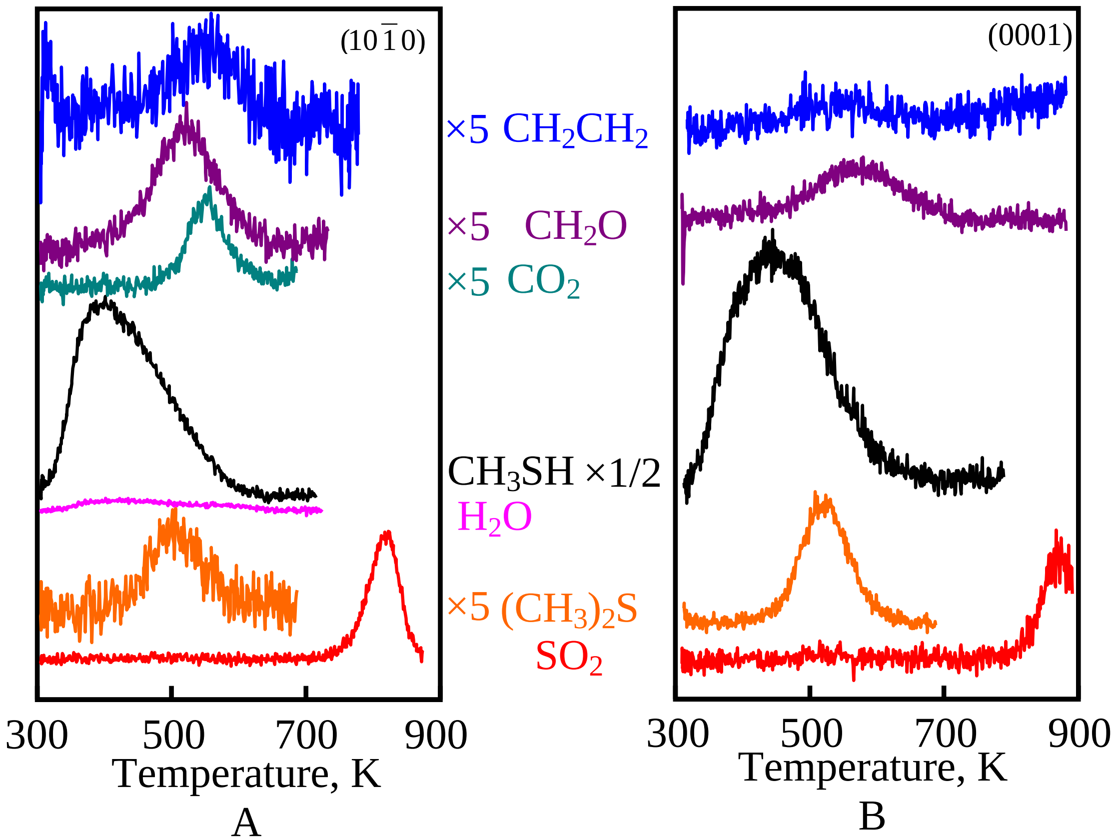
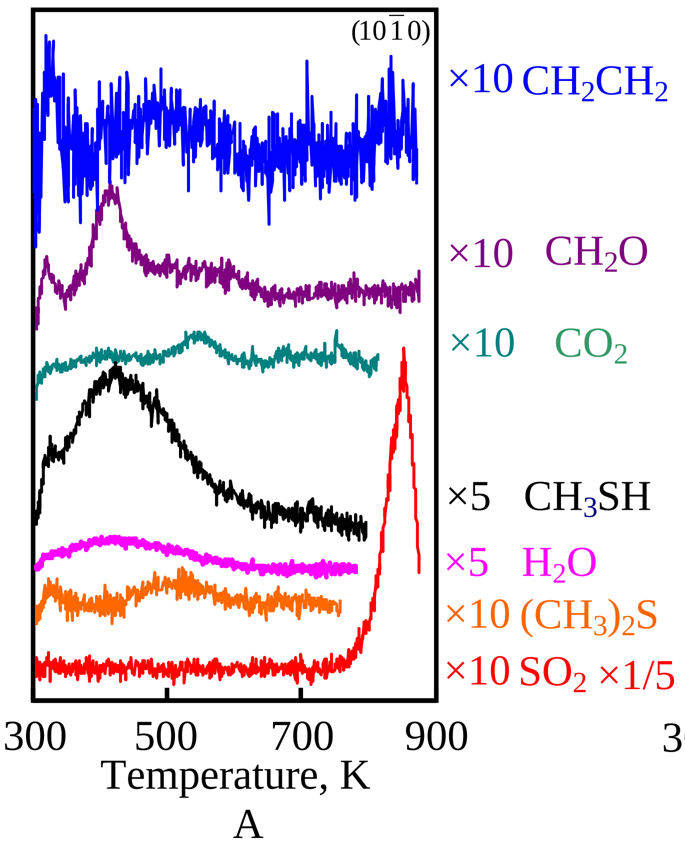


Figure 3



(10$\bar{1}$0)
×5 CH2CH2
×5 CH2O
×5 CO2
CH3SH ×1/2
H2O
×5 (CH3)2S
SO2
300
500
700
900
Temperature, K
A
(0001)
300
500
700
900
Temperature, K
B

Figure 4



(10$\bar{1}$0)
×10 CH2CH2
×10 CH2O
×10 CO2
×5 CH3SH
×5 H2O
×10 (CH3)2S
×10 SO2 ×1/5
300
500
700
900
Temperature, K
A
(0001)
300
500
700
900
Temperature, K
B