



# Nature of Surface Reaction: Dependence on Adsorption Site and Alkyl-Chain Length

The studies of organic surface reactions have a direct relevance to many research areas including heterogeneous catalysis, thin film deposition, tribology, etc. For a surface-mediated reaction to take place, organic molecules have to adsorb on the surface first and then undergo proper thermal reactions at elevated temperatures, thereby generating various desorption and decomposition products. The different reaction pathways followed by the organic molecules adsorbed on the surface could sensitively depend on their chemical structures and adsorption sites. This pathway difference manifests itself in the variation of the reaction products, or the selectivity difference as called by chemists. It is through this product selectivity derived a multitude of chemical manufacturing processes. Understanding how the reaction takes place on a given surface provides an opportunity for fine-tuning the reaction condition for a greener chemistry and for developing innovative products. Examples of the latter aspect are testified by the successful applications of the mechanistic knowledge in the chemical vapor deposition to produce artificial, novel compounds like diamond films, carbon nanotubes, etc.

Many transition metals have found wide applications as effective catalysts in organic compound synthesis. The poisonous effect of sulfur species in catalytic reactions has long been recognized and the reaching an atomic understanding of this surface process, particularly related to hydrodesulfurization, gives an impetus to surface chemistry research of sulfur-containing molecules. As alkanethiols account for main sulfur constituents in crude petroleum, their surface reactions have an important bearing on catalytic poisoning and

desulfurization effects in the petroleum industry. In the present report, we focus on how the initial binding sites and the structures of the alkanethiol adsorbates influence the ensuing reaction pathways. We also extend the thermal reactivity studies to include alkanethiols of varied chain lengths, i.e. RSH with R=CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub> and C<sub>4</sub>H<sub>9</sub>, to assess the role of hydrocarbon chain. Based on these results, we propose an adsorption configuration and a decomposition mechanism for alkanethiols on Cu(110).

Experimentally, we identify the chemisorbed hydrocarbon species via synchrotron based XPS and detect products evolved during thermal decomposition by TPD. Hydrogen, CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> are desorption products found after decomposition of CH<sub>3</sub>SH on Cu(110). Fig. 1(a) shows TPD scans of CH<sub>4</sub> from a Cu (110) surface as a function of duration of CH<sub>3</sub>SH exposure. The profile of TPD scans and desorption products vary with CH<sub>3</sub>SH exposure indicating the reaction pathway is influenced by the coverage of CH<sub>3</sub>SH on a Cu surface. The profile of TPD spectrum is determined by the reaction mechanism and kinetics processes, which are complicated by many effects, such as adsorbate-adsorbate and adsorbate-surface interactions, surface diffusion etc. As shown in Fig. 1(b), TPD spectrum can be decomposed into four peaks of Gaussian form, implying the presence four possible desorption states (labeled as A, B, C and D). State D at high temperature is attributed to a dissociative/associative process of desorption of surface CH<sub>3</sub>. Desorption states A, B and C are due to hydrogenation of the CH<sub>3</sub> moiety of CH<sub>3</sub>S adsorbed at distinct adsorption sites. Four possible adsorption sites of CH<sub>3</sub>S on a

Cu (110) surface are atop, short-bridge, long-bridge and hollow site. The  $\text{CH}_3\text{S}$  species adsorbed at various sites decompose to evolve  $\text{CH}_4$  at distinct temperatures.

The thermal evolution of XPS serves to characterize the variation of surface composition during thermal decomposition of  $\text{CH}_3\text{SH}$  on Cu and correlates with TPD results to elucidate the reaction intermediates. Fig. 2 depicts core-level spectra of S 2p and C 1s obtained from a Cu surface exposed to  $\text{CH}_3\text{SH}$  at 100 K and warmed to the indicated temperatures. The appearance of new features and the shifts of binding energies of

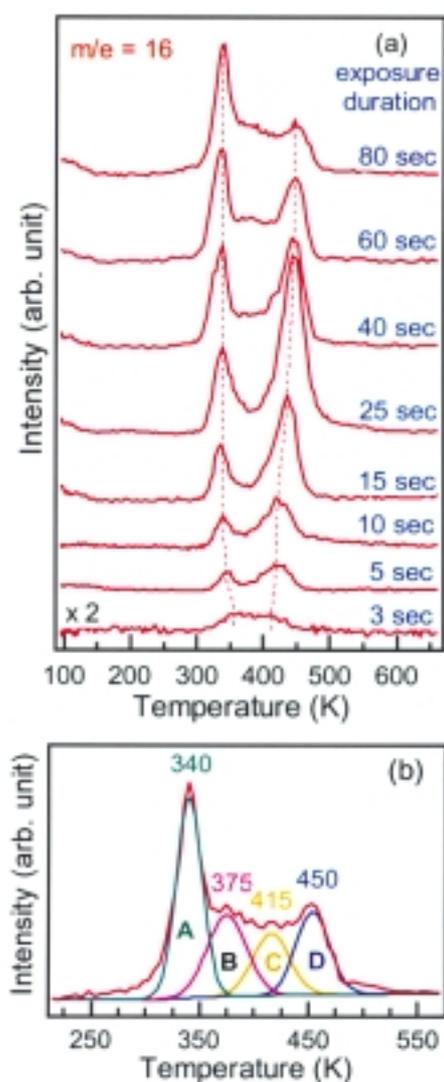


Fig. 1: (a) Temperature-programmed desorption scans of  $\text{CH}_4$  ( $m/e=16$ ) collected from Cu(110) as a function of duration of exposure to  $\text{CH}_3\text{SH}$ . (b) Four Gaussian peaks shown as dashed lines highlight desorption features in the TPD spectrum of  $\text{CH}_4$ .

S 2p and C 1s are attributed to the formation of thiolate, methyl, and atomic sulfur and carbon during the thermal decomposition of  $\text{CH}_3\text{SH}$ . Based on the TPD and XPS results, a reaction mechanism of  $\text{CH}_3\text{SH}$  on Cu is illustrated in Fig. 3. We conclude that  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  are desorbed from the surface via hydrogenation and disproportionation, and via a coupling reaction of the  $\text{CH}_3$  moiety of  $\text{CH}_3\text{SH}$ , respectively. Atomic sulfur and carbon left behind after thermal decomposition of  $\text{CH}_3\text{SH}$  result in the deactivation of catalysts, which might take place via site-blocking and electronic effects.

Analogous to the case of  $\text{CH}_3\text{SH}$ , features of TPD scans for  $\text{C}_2\text{H}_5\text{SH}$  vary with exposure. Besides  $\text{H}_2$  and  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$  is a desorption product at large exposure of  $\text{C}_2\text{H}_5\text{SH}$ . The desorption features of  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_6$  can be decomposed into two components, which originate from surface  $\text{C}_2\text{H}_5\text{S}$  adsorbed at distinct adsorption sites. Hydrogenation to form  $\text{C}_2\text{H}_6$  and  $\beta$ -hydride elimination to form  $\text{C}_2\text{H}_4$  are competing reactions in thermal decomposition of surface

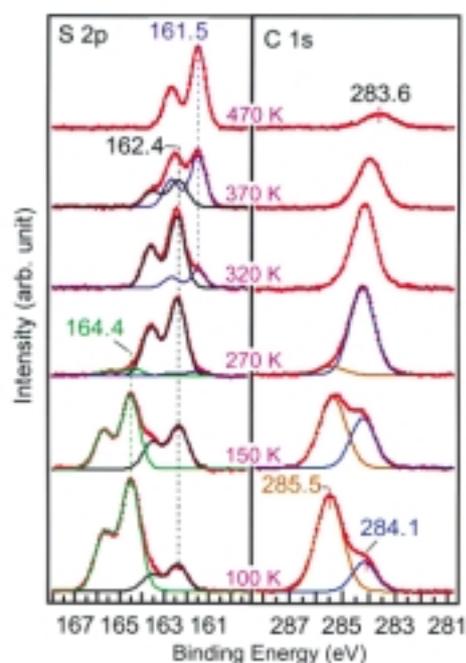


Fig. 2: XPS of S 2p for a Cu(110) surface exposed to  $\text{CH}_3\text{SH}$  at 100 K and subsequently annealed to the indicated temperatures. Dots represent data collected after background subtraction; solid lines are fitted curves, and various components are shown with dashed lines. The photon energy used to collect these spectra is 400 eV.

$C_2H_5$  generated on the cleavage of the  $C_2H_5-S$  bond, as shown in Fig. 3. The variation in the ratio of  $C_2H_4$  and  $C_2H_6$  products indicates that the reaction pathway of  $C_2H_5S$  depends on the site or configuration of adsorption. In contrast to the coupling found for  $CH_3$ , the corresponding formation of  $C_4H_{10}$  via coupling of  $C_2H_5$  is below the limit of detection at all exposures.

Thiolate species can decompose into atomic sulfur on the surface and alkyl groups by a cleavage of C-S bonds. Decomposition of  $C_2H_5S$  and  $C_4H_9S$  occurs at temperatures lower than that for  $CH_3S$ . A direct interaction between the alkyl group of thiolate and the Cu surface might be involved in the cleavage of C-S bond. The surface alkyl group is removed upon the formation of alkane via hydrogenation or alkene via  $\beta$ -hydride elimination. Increasing length of alkyl chain favors  $\beta$ -hydride elimination.  $C_4H_8$  is the only desorption product of hydrocarbon in the thermal decomposition of  $C_4H_9SH$ . Hydrogenation products  $CH_4$  and  $C_2H_6$  are observed on decomposition of  $CH_3SH$  and  $C_2H_5SH$ . An

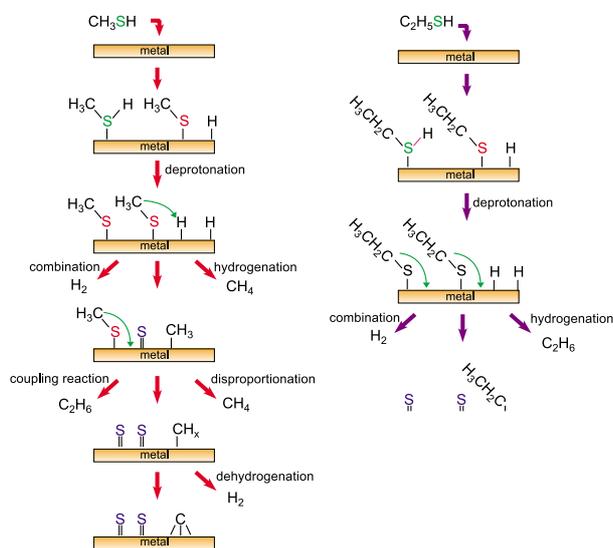


Fig. 3: A schematic diagram of a reaction mechanism for catalytic conversion of alkanethiols on a metallic surface. Methanethiol and ethanethiol here serve as prototypical examples of alkanethiols in crude oil. The reaction pathway of decomposition and desorption of alkanethiol on a metallic surface depend on the adsorption site on the surface, the presence of  $\beta$ -hydride, and the length of the carbon chain in the alkyl group.  $\beta$ -hydride elimination typically dominates the chemistry of alkyl moieties for long-chain alkanethiols.

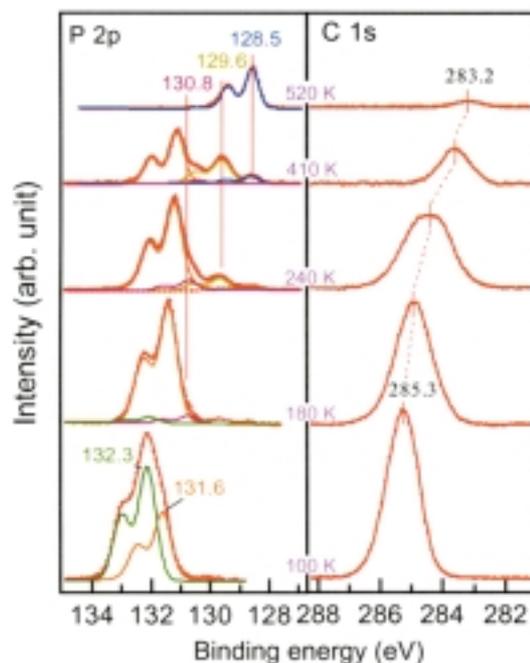


Fig. 4: XPS spectra of P 2p and C 1s for a Cu(110) surface exposed to  $PEt_3$  at 100 K and subsequently heated to the indicated temperatures.

alternative pathway for the  $CH_3$  group is a coupling that occurs at large coverage, resulting in the formation of  $C_2H_6$ . Coupling of alkyl groups is not observed for thermal decomposition of higher alkyl homologues  $C_2H_5$  and  $C_4H_9$ .

A second example demonstrating the dependence of surface reaction on the structure of adsorbate is the adsorption and thermal decomposition of trimethylphosphine ( $PMe_3$ ) and triethylphosphine ( $PEt_3$ ) on the Cu(110) surface. Various  $XCu^{(I)}L_n$  ( $n=1$  or  $2$ ) precursors have been synthesized for the Cu-MOCVD process, where X is a negative ligand and L is a neutral Lewis base (electron-pair donor). Alkylphosphines ( $PR_3$ , R=alkyl) have been used as neutral Lewis bases in Cu precursors, which can act as reducing agents in-situ to remove adventitious oxide and to form volatile phosphorous oxide. The neutral base should ideally be liberated from a precursor during deposition and completely removed through a pumping system of the reactor, but desorption products generated during deposition might re-adsorb on the surface and subsequently undergo thermal decomposition, resulting in incorporation of unwanted atoms. A choice of neutral donor ligands is thus critical in determining physical and

chemical characteristics of copper precursors and deposited films. Thermal reaction of liberated  $\text{PR}_3$  ligands inevitably produces impurities in deposited Cu films. Comparison between thermal reactivity and reaction products of  $\text{PEt}_3$  and  $\text{PMe}_3$  molecules on the Cu surface provides mechanistic insight into incorporation of contaminants during CVD for Cu precursors containing  $\text{PR}_3$  ligands.

Fig. 4 shows P 2p and C 1s spectra collected from a Cu surface exposed to  $\text{PEt}_3$  at 100 K for 40 sec and subsequently annealed. Decomposition of  $\text{PEt}_3$  into surface phosphorus takes place in a stepwise fashion ( $\text{PEt}_3 \rightarrow \text{PEt}_2 \rightarrow \text{PEt} \rightarrow \text{P}$ ). In contrast,  $\text{PMe}_3$  molecules decompose thermally to form surface  $\text{CH}_3$  and phosphorus through  $\text{PMe}_2$  as an intermediate ( $\text{PMe}_3 \rightarrow \text{PMe}_2 \rightarrow \text{P}$ ). Surface  $\text{CH}_3$  generated from demethylation of  $\text{PMe}_3$  eventually disproportionates to form  $\text{CH}_4$  and surface carbon. On the other hand, surface  $\text{C}_2\text{H}_5$  decomposes to evolve  $\text{H}_2$  and  $\text{C}_2\text{H}_4$  through  $\beta$ -hydride elimination ( $2\text{C}_2\text{H}_{5(\text{ad})} \rightarrow 2\text{C}_2\text{H}_{4(\text{g})} + \text{H}_{2(\text{g})}$ ). As there is still residual carbon on the surface after  $\text{PEt}_3$  decomposition, a small proportion of surface  $\text{C}_2\text{H}_5$  undergoes dehydrogenation to produce  $\text{H}_2$  and surface carbon ( $\text{C}_2\text{H}_{5(\text{ad})} \rightarrow 2\text{C}_{(\text{ad})} + 5/2\text{H}_{2(\text{g})}$ ). It is found that a greater fraction of chemisorbed  $\text{PEt}_3$  is subject to decomposition into surface phosphorus relative to  $\text{PMe}_3$ . We conclude that a choice of  $\text{PEt}_3$  as a Lewis base in Cu-CVD precursors might result in diminished incorporation of carbon but increased residual phosphorus in deposited films, compared to  $\text{PMe}_3$ .

#### Beamlines:

20A1 HSGM beamline  
24A1 Wide Range beamline

#### Experimental Station:

Photoemission end station

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#### Publications:

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