



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=CH₃, C₂H₅ and C₄H₉, 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, CH₄ and C₂H₆ are desorption products found after decomposition of CH₃SH on Cu(110). Fig. 1(a) shows TPD scans of CH₄ from a Cu (110) surface as a function of duration of CH₃SH exposure. The profile of TPD scans and desorption products vary with CH₃SH exposure indicating the reaction pathway is influenced by the coverage of CH₃SH 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 CH₃. Desorption states A, B and C are due to hydrogenation of the CH₃ moiety of CH₃S adsorbed at distinct adsorption sites. Four possible adsorption sites of CH₃S on a

Cu (110) surface are atop, short-bridge, long-bridge and hollow site. The CH_3S species adsorbed at various sites decompose to evolve CH_4 at distinct temperatures.

The thermal evolution of XPS serves to characterize the variation of surface composition during thermal decomposition of CH_3SH 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 CH_3SH at 100 K and warmed to the indicated temperatures. The appearance of new features and the shifts of binding energies of

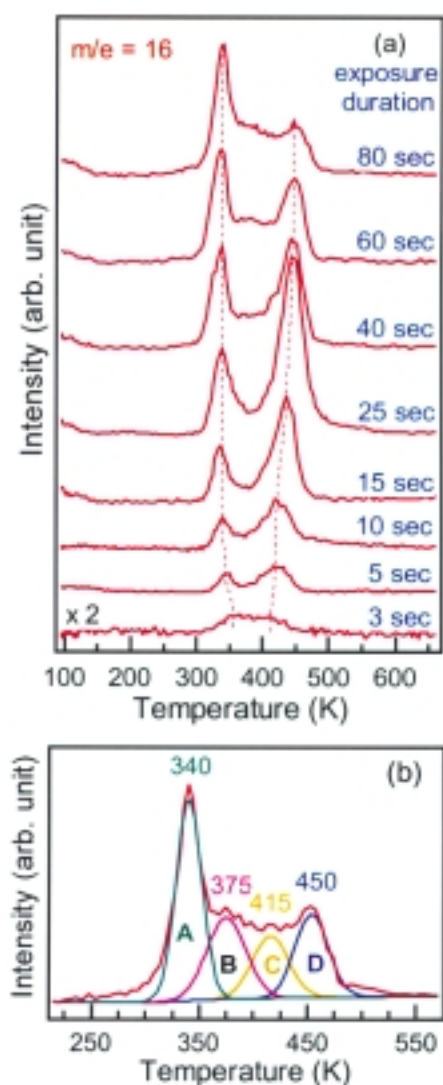


Fig. 1: (a) Temperature-programmed desorption scans of CH_4 ($m/e=16$) collected from Cu(110) as a function of duration of exposure to CH_3SH . (b) Four Gaussian peaks shown as dashed lines highlight desorption features in the TPD spectrum of CH_4 .

S 2p and C 1s are attributed to the formation of thiolate, methyl, and atomic sulfur and carbon during the thermal decomposition of CH_3SH . Based on the TPD and XPS results, a reaction mechanism of CH_3SH on Cu is illustrated in Fig. 3. We conclude that CH_4 and C_2H_6 are desorbed from the surface via hydrogenation and disproportionation, and via a coupling reaction of the CH_3 moiety of CH_3SH , respectively. Atomic sulfur and carbon left behind after thermal decomposition of CH_3SH result in the deactivation of catalysts, which might take place via site-blocking and electronic effects.

Analogous to the case of CH_3SH , features of TPD scans for $\text{C}_2\text{H}_5\text{SH}$ vary with exposure. Besides H_2 and C_2H_6 , C_2H_4 is a desorption product at large exposure of $\text{C}_2\text{H}_5\text{SH}$. The desorption features of C_2H_4 and C_2H_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 C_2H_6 and β -hydride elimination to form C_2H_4 are competing reactions in thermal decomposition of surface

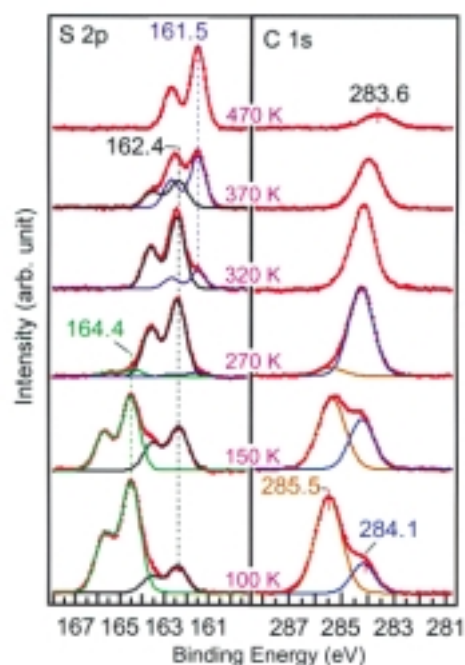


Fig. 2: XPS of S 2p for a Cu(110) surface exposed to CH_3SH at 100 K and subsequently annealed to the indicated temperatures. Dots represent data collected after background subtraction; solid lines are fitted curves, and various components are shown with dashed lines. The photon energy used to collect 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 β -hydride elimination. Increasing length of alkyl chain favors β -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

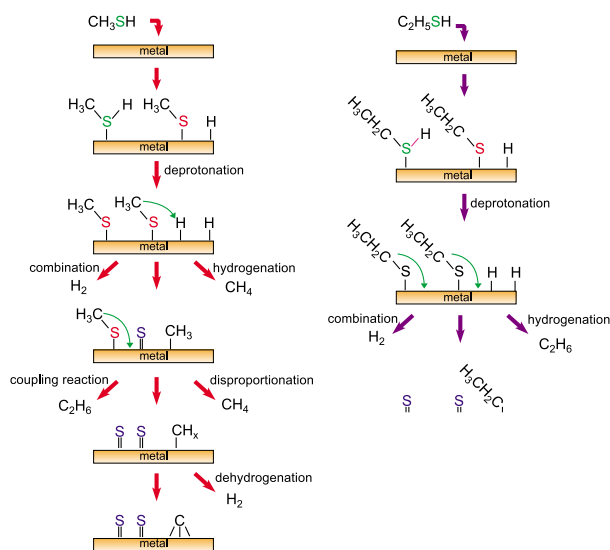


Fig. 3: A schematic diagram of a reaction mechanism for catalytic conversion of alkanethiols on a metallic surface. Methanethiol and ethanethiol here serve as prototypical examples of alkanethiols in crude oil. The reaction pathway of decomposition and desorption of alkanethiol on a metallic surface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

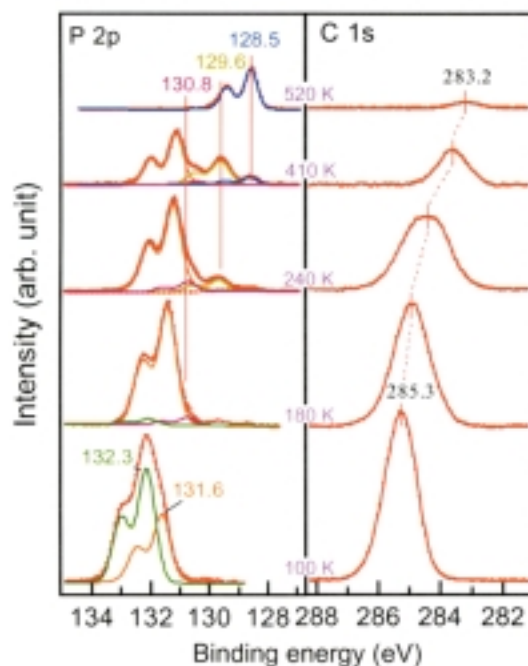


Fig. 4: XPS spectra of P 2p and C 1s for a Cu(110) surface exposed to PEt_3 at 100 K and subsequently heated to the indicated temperatures.

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 PR_3 ligands inevitably produces impurities in deposited Cu films. Comparison between thermal reactivity and reaction products of PEt_3 and PMe_3 molecules on the Cu surface provides mechanistic insight into incorporation of contaminants during CVD for Cu precursors containing PR_3 ligands.

Fig. 4 shows P 2p and C 1s spectra collected from a Cu surface exposed to PEt_3 at 100 K for 40 sec and subsequently annealed. Decomposition of 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, PMe_3 molecules decompose thermally to form surface CH_3 and phosphorus through PMe_2 as an intermediate ($\text{PMe}_3 \rightarrow \text{PMe}_2 \rightarrow \text{P}$). Surface CH_3 generated from demethylation of PMe_3 eventually disproportionates to form CH_4 and surface carbon. On the other hand, surface C_2H_5 decomposes to evolve H_2 and C_2H_4 through β -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 PEt_3 decomposition, a small proportion of surface C_2H_5 undergoes dehydrogenation to produce 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 PEt_3 is subject to decomposition into surface phosphorus relative to PMe_3 . We conclude that a choice of 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 PMe_3 .

Beamlines:

20A1 HSGM beamline
24A1 Wide Range beamline

Experimental Station:

Photoemission end station

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Publications:

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