

Reaction Intermediates of HSCH₂CH₂OH on Cu(111)

Beamline

24A1 Wide Range SGM beamline

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The surface intermediates from thermal decomposition of HSCH₂CH₂OH on Cu(111) have been identified by X-ray photoelectron spectroscopy. Based on the variations in the core-level binding energies of carbon, oxygen, and sulfur atoms as a function of temperature, it is found that HSCH₂CH₂OH decomposes to form the surface intermediates of –SCH₂CH₂OH and –SCH₂CH₂O– sequentially. –SCH₂CH₂OH is present on Cu(111) near 100K and is transformed into –SCH₂CH₂O– at a temperature higher than 200K. Both the surface intermediates decompose at elevated temperature (>350K). Theoretical calculations based on density functional theory suggest that –SCH₂CH₂OH is preferentially bonded at a 3-fold hollow site and –SCH₂CH₂O– is most probably adsorbed with its S and O bonded at hollow and bridging sites, respectively.

Alkanethiols are commonly employed in forming self-assembled monolayers (SAMs) on noble metals. The chemical structure of the SAMs that binds to the surfaces is alkanethiolates, evidenced by the H–S bond scission taking place after adsorption. A chemical modification of the outer terminal groups of the SAM alters the surface properties and effects novel applications in electrochemistry, molecular electronics, lubrication, corrosion, wetting, and etching.

Figures 1-3 show the temperature-dependent C 1s, O 1s, and S 2p photoelectron spectra for the Cu(111) exposed to 1.6 L HSCH₂CH₂OH at 100 K, followed by brief heating of the surface to the temperatures indicated. All the spectra were measured at 100 K. In the 123 K spectrum

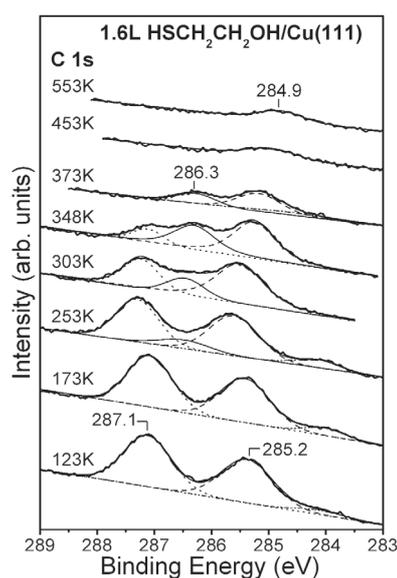


Fig. 1: Variation of C 1s X-ray photoelectron spectra with annealing temperature (J. Phys. Chem. B **109**, 5055, (2005)).

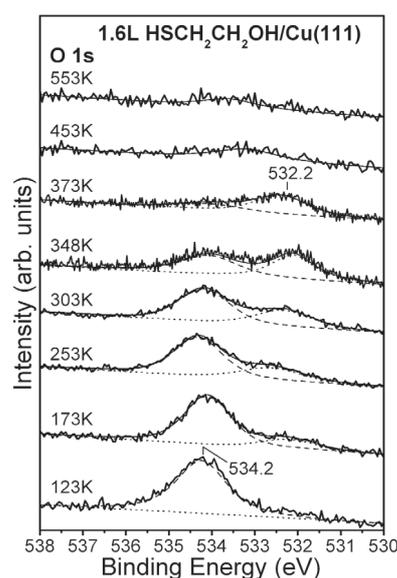


Fig. 2: Change of O 1s X-ray photoelectron spectra with annealing temperature (J. Phys. Chem. B **109**, 5055, (2005)).

of Fig. 1, the C 1s peaks appear at 285.2 and 287.1 eV, which indicate two different chemical bonding environments of carbon atoms. The 285.2 and 287.1 eV peaks are attributed to the carbon atoms bonded to the sulfur and oxygen, respectively, based on previous studies of C_2H_5SH and $HOCH_2CH_2OH$. In the 123 K spectrum of Fig. 2, the O 1s signal appears at 534.2 eV and is attributed to $-COH$. Apparently, the O–H bond of $HSCH_2CH_2OH$ does not dissociate on Cu(111) at this temperature. In the case of S shown in the 123 K spectrum of Fig. 3, two peaks at 162.6 and 163.8 eV are observed. The 1.2 eV difference and the 2:1 ratio of the integrated area of the 162.6 eV peak to that of 163.8 eV indicate that the 162.6 and 163.8 eV peaks are S $2p_{3/2}$ and S $2p_{1/2}$ signals, respectively, from the same surface species. The S $2p_{3/2}$ signal peaked at 162.6 eV is attributed to the S atoms of thiolate groups with the support of the XPS studies of C_2H_5SH on Mo(110) and Cu(110), because it is close to the 162.4 eV peak of $C_2H_5S^-$. Taking together the binding energies of C 1s, O 1s, and S $2p_{3/2}$ at 123 K and their related chemical bonding environments into account, it is concluded that $HSCH_2CH_2OH$ decomposes via S–H bond scission, forming $-SCH_2CH_2OH$ on Cu(111) at this temperature. CH_3SH and C_2H_5SH have been reported to dissociate on Cu(110) by S–H scission at 100 K. In terms of the previously reported intensities of S $2p_{3/2}$ and Cu $2p_{3/2}$ of the ordered CH_3S layers ((2×2) and $c(6 \times 2)$) on Cu(100), it is estimated that, in the present case of 1.6

L $HSCH_2CH_2OH$ adsorbed on Cu(111), the $-SCH_2CH_2OH$ coverage is 0.31, which is close to one adsorbed $-SCH_2CH_2OH$ molecule for every three surface copper atoms.

The C 1s peak at 287.1 eV, characteristic of the carbon atom in a C–OH group, decreases in intensity above 173 K and vanishes at 373 K. This is a result of desorption of reaction products or chemical transformation of the C–OH moiety on the surface. For the latter case, it may be due to C–O or O–H bond scission. As a contrast, a new peak at a binding energy of 286.3 eV appears at a temperature >173 K. This signal is attributed to the C 1s of C–O of alkoxide species. Furthermore, the intensity of the 285.3 eV peak, representing the carbon of C–S, remains approximately the same between 123 and 303 K. This result indicates that $-SCH_2CH_2OH$ molecules decompose at a temperature higher than 173 K by O–H bond breakage, forming adsorbed $-SCH_2CH_2O^-$. The chemical transformation of $-SCH_2CH_2OH$ into $-SCH_2CH_2O^-$ does not change the binding energy and intensity of the C 1s of the SCH_2 moiety, but the C 1s of the CH_2O moiety decreases by 0.8 eV after O–H bond scission. Both the C 1s signals of $-SCH_2CH_2O^-$ gradually decrease in intensity at a temperature higher than 323 K. Parallel to the reaction pathway from $-SCH_2CH_2OH$ to $-SCH_2CH_2O^-$, identified by the variation of the binding energies of C 1s with temperature, the oxygen signal of $-COH$ at 534.2 eV decreases in intensity and that of $-CO^-$ formed grows at 532.2 eV. In the change from $-COH$ to $-CO^-$, the O 1s binding energy is shifted by 2 eV on Cu(111) in the present study, as compared to 1.2 eV in the case of $HOCH_2CH_2OH$ on Mo(110). The change of sulfur signal with temperature is more complicated than those for C 1s and O 1s. In the temperature range of 173–253 K, the observation of the gradual decrease of S $2p_{3/2}$ peak at 162.6 eV, characteristic of $-SCH_2CH_2OH$, and the simultaneous growth of the peak at 163.3 eV seem to relate to the chemical transformation from $-SCH_2CH_2OH$ into $-SCH_2CH_2O^-$. Because the SCH_2CH_2 moiety remains intact in this transformation process, the S $2p_{3/2}$ binding energy is not expected to change, instead of the 0.7 eV shift observed here. The intensity changes of the 162.6 and 163.3 eV signals between 173 and 253 K in Fig. 3 are due to other temperature-dependent surface effects. It has been found that the S $2p_{3/2}$ binding energy of CH_3S^- depends on the local bonding of sulfur atoms, possibly altered by surface coverage

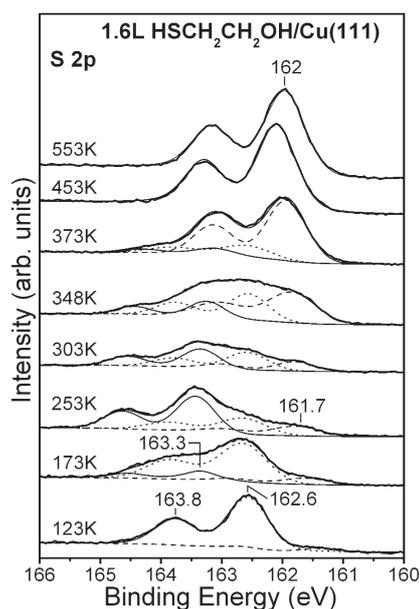


Fig. 3: Change of S 2p X-ray photoelectron spectra with annealing temperature (J. Phys. Chem. B **109**, 5055, (2005)).

and by local surface reconstruction. The S $2p_{3/2}$ of methyl thiolate (CH_3S) on Ni(111), suggested to be adsorbed at a bridging site below 150 K, has a binding energy between 162.3 and 162.7 eV, depending on the surface coverage. In the temperature range of 150–250 K, a fraction of bridging CH_3S is relocated to hollow sites with the S $2p_{3/2}$ energy increased by 0.6–1.0 eV. In the case of Cu(111), the temperature-dependent S $2p$ binding energy of CH_3S is attributed to surface reconstruction induced by the thiolate adsorption at higher temperatures. It is suggested that CH_3S is adsorbed on reconstructed Cu(111) at room temperature and its S $2p_{3/2}$ binding energy was larger than that of CH_3S on unreconstructed Cu(111) at lower temperatures by ~ 0.9 eV.

Figure 4 shows the change of each fitted and the

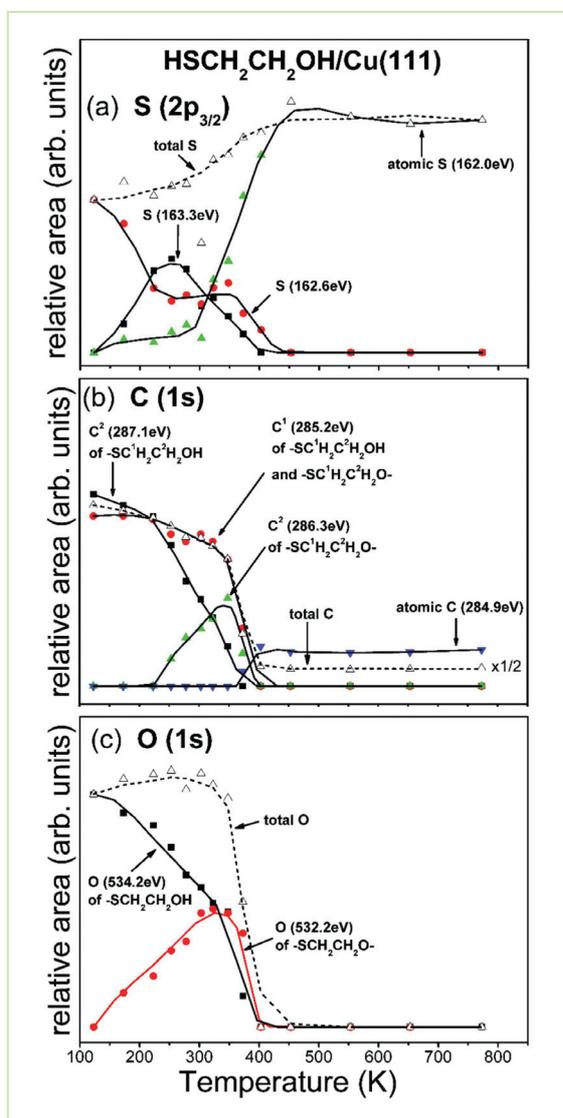


Fig. 4: Change of the peak areas of S $2p_{3/2}$, C $1s$, and O $1s$ with surface temperature (J. Phys. Chem. B **109**, 5055 (2005)).

total areas of the S $2p_{3/2}$, C $1s$, and O $1s$ peaks with temperature after 1.6 L $\text{HSCH}_2\text{CH}_2\text{OH}$ adsorption on Cu(111) at 100 K. The C $1s$ curves suggest that $-\text{SCH}_2\text{CH}_2\text{OH}$ is the surface predominant species below 223 K, consistent with the variation of O $1s$ signals with temperature, although the latter already shows the formation of some $-\text{SCH}_2\text{CH}_2\text{O}-$ molecules. The reaction from $-\text{SCH}_2\text{CH}_2\text{OH}$ to $-\text{SCH}_2\text{CH}_2\text{O}-$ proceeds at a temperature >223 K. At higher temperatures (>350 K), the amounts of $-\text{SCH}_2\text{CH}_2\text{OH}$ and $-\text{SCH}_2\text{CH}_2\text{O}-$ decrease substantially, in contrast to the rapid increase of atomic sulfur at 162.0 eV. Both $-\text{SCH}_2\text{CH}_2\text{O}-$ and $-\text{SCH}_2\text{CH}_2\text{OH}$ react on the surface, with desorption products containing C and O, but leaving sulfur atoms on the surface. The measured intensity of atomic sulfur is higher than the total sulfur intensity of $-\text{SCH}_2\text{CH}_2\text{OH}$ and $-\text{SCH}_2\text{CH}_2\text{O}-$, because the S signals for the latter two species can be attenuated by C and O.

Experimental Station

Surface Science Station III-Interface Structure

Publication

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