

Thermal Decomposition and Adsorption Orientation of 2-Fluoroethanol on Clean and Oxidized Cu(100)

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Temperature-programmed reaction/desorption and reflection–absorption infrared spectroscopy have been employed to investigate the thermal reactions and adsorption geometry of $\text{FCH}_2\text{CH}_2\text{OH}$ molecules on clean and oxygen-preadsorbed Cu(100) surfaces. Molecular desorption predominates in heating $\text{FCH}_2\text{CH}_2\text{OH}$ adsorbed on clean Cu(100). However, $\sim 20\%$ adsorbed $\text{FCH}_2\text{CH}_2\text{OH}$ molecules at about half-monolayer coverage dissociate on the surface to form water, ethylene, and 1,4-dioxane. On the other hand, monolayer $\text{FCH}_2\text{CH}_2\text{OH}$ completely dissociates on oxidized Cu(100) to form 1,4-dioxane and the surface intermediate of $\text{FCH}_2\text{CH}_2\text{O}_{(\text{a})}$, which further decomposes to evolve $\text{FCH}_2\text{CHO}_{(\text{g})}$ at temperatures higher than ~ 350 K. The decomposition of $\text{FCH}_2\text{CH}_2\text{OH}$ to form $\text{FCH}_2\text{CH}_2\text{O}_{(\text{a})}$ on oxidized Cu(100) begins at ~ 160 K and is completed by 220 K. On clean Cu(100), $\text{FCH}_2\text{CH}_2\text{OH}$ molecules at ~ 0.25 monolayer coverage are adsorbed with the C–C–O skeleton approximately parallel to the surface. The C–C–O skeleton tilts away from the surface as the exposure is increased to a half-monolayer coverage. However, the parallel C–C–O orientation is not observed on the oxidized surface, even at the $\text{FCH}_2\text{CH}_2\text{OH}$ exposure for a 0.25 monolayer coverage.

Introduction

2-Fluoroethanol ($\text{FCH}_2\text{CH}_2\text{OH}$) possesses two different functional groups of C–OH and C–F. The previous study of halogenated ethanes ($\text{C}_2\text{H}_5\text{Cl}$, $\text{C}_2\text{H}_5\text{Br}$, and $\text{C}_2\text{H}_5\text{I}$) on Cu(100) has shown that $\text{C}_2\text{H}_5\text{Br}$ and $\text{C}_2\text{H}_5\text{I}$ dissociate by carbon–halogen bond dissociation to form ethyl groups on the surface and $\text{C}_2\text{H}_5\text{Cl}$ is adsorbed reversibly.¹ It is expected that $\text{C}_2\text{H}_5\text{F}$, like $\text{C}_2\text{H}_5\text{Cl}$, does not dissociate on the surface because the C–F bond is stronger than the C–Cl, C–Br, and C–I bonds. For alcohol molecules (without C–F group) there are extensive studies on metal single crystals in relation to catalysis, corrosion, and tribology. Ethanol adsorbs molecularly on Cu(111), while a small fraction decomposes to form ethoxide on Cu(100) and Cu(110) during heating.^{2,3} However, as the copper surfaces are oxidized, the transformation of ethanol to ethoxide becomes a predominant reaction pathway.^{4,5} On Cu(111), it has been reported that $\text{CF}_3\text{CH}_2\text{OH}$ is adsorbed molecularly, but on Cu(100) and Cu(110) a small fraction of the trifluoroethanol molecules forms trifluoroethoxide, which decomposes to form trifluoroaldehyde at ~ 495 K.³ On oxidized Cu(111), (100), and (110) surfaces $\text{CF}_3\text{CH}_2\text{OH}$ is predominantly transformed into trifluoroethoxide, just like ethanol. The thermal reactions of $\text{FCH}_2\text{CH}_2\text{OH}$ on metal surfaces have been studied.^{3,6,7} On Rh(111), it decomposes to evolve H_2 and CO .⁶ On oxidized Cu(111), (100), and (110), the studies are focused on the preparation, decomposition, and adsorption orientation of 2-fluoroethoxide.^{3,7} 2-Fluoroethoxide decomposes on oxidized Cu(111) to form 2-fluoroaldehyde at ~ 400 K during heating at a rate of 5 K/s.^{3,7} The activation energies for the decomposition of 2-fluoroethoxide are comparable on oxidized Cu(111), Cu(100), and Cu(110).³ Although it has been known that ethanol may decompose on clean Cu(100), via ethoxide, to form aldehyde, the thermal reaction of 2-fluoroethanol on the surface

has not been explored. This is an important and interesting question because the presence of a F atom on the β -carbon in 2-fluoroethanol may modify the reaction pathway of the α -carbon O–H group. What is the product distribution in the reaction of 2-fluoroethanol on clean Cu(100)? On oxidized Cu(100), are there other reaction channels for 2-fluoroethanol besides the formation of 2-fluoroaldehyde? Another interesting subject that has not been studied is the adsorption orientation for 2-fluoroethanol on clean and oxidized Cu(100). In the present research, temperature-programmed reaction/desorption (TPR/D) and reflection–absorption infrared spectroscopy (RAIRS) are employed to investigate the adsorption orientation and thermal reactions of 2-fluoroethanol on clean and oxidized Cu(100).

Experimental Section

All the experiments were performed in an ultrahigh-vacuum (UHV) apparatus equipped with an ion gun for sputtering, a differentially pumped mass spectrometer for temperature-programmed reaction/desorption (TPR/D), four-grid spherical retarding field optics for low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES), and an FTIR spectrometer for reflection–absorption infrared spectroscopy (RAIRS). The chamber was evacuated by a turbomolecular pump and an ion pump to a base pressure of about 2×10^{-10} Torr. The quadrupole mass spectrometer used for TPR/D study was capable of detecting ions in the 1–500 amu range and of being multiplexed to acquire up to 15 different masses simultaneously in a single desorption experiment. In TPR/D experiments, the Cu(100) surface was positioned ~ 1 mm from an aperture, 3 mm in diameter, leading to the mass spectrometer, and a heating rate of 2 K/s was used. In the RAIRS study, the IR beam was taken from a Bomem FTIR spectrometer and focused at a grazing incidence angle of 85° through a KBr window onto the Cu(100) in the UHV chamber. The reflected beam was then passed through a second KBr window and refocused on a

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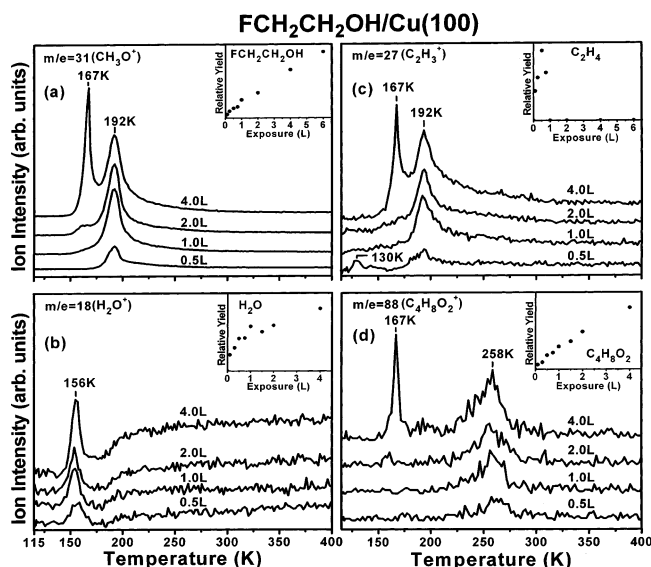


Figure 1. TPR/D spectra, collected for the ions of 18, 27, 31, and 88 amu, of 2-fluoroethanol adsorbed on clean Cu(100) at different exposures in langmuirs (1 langmuir = 10^{-6} Torr s). The insets are the relative yields of FCH₂CH₂OH, H₂O, C₂H₄, and C₄H₈O₂ as a function of exposure.

mercury–cadmium–telluride (MCT) detector. The entire beam path was purged with a Balston air scrubber for carbon dioxide and water removal. All the IR spectra were taken at temperature about 115 K with 1000 scans and 4 cm⁻¹ resolution. The presented spectra have been ratioed against the spectra of a clean Cu(100) surface recorded immediately before 2-fluoroethanol dosing. The Cu(100) single crystal (1 cm in diameter) was mounted on a resistive heating element and could be cooled with liquid nitrogen to ~110 K and heated to 1100 K. The surface temperature was measured by a chromel–alumel thermocouple inserted into a hole on the edge of the crystal. Cleaning of the surface by cycles of Ar⁺ ion sputtering and annealing was done prior to each experiment until no impurities were detected by Auger electron spectroscopy. 2-Fluoroethanol (>90%) was purchased from Fluka. Oxygen (99.998%) was obtained from Matheson. The gas manifold for 2-fluoroethanol was conditioned by backfilling with its saturated vapor pressure overnight. Prior to dosing 2-fluoroethanol into the chamber, the gas manifold and 2-fluoroethanol itself in liquid state were pumped for a while. The purity of the 2-fluoroethanol was checked by the mass spectrometer in the chamber. In the present study, the oxidized Cu(100) surface was prepared by exposing a clean Cu(100) surface at 500 K to 30 langmuirs of O₂, similar to the preparation for the oxidized Cu(100) used in Sexton's study of alcohol.⁴ Atomic oxygen was present on the surface after the O₂ treatment, as verified by Auger electron spectroscopy and electron energy loss spectroscopy. It was estimated that the oxygen coverage (θ_O) for the oxidized Cu(100) used in this study was ~0.2.⁸ The previous study showed that a long-range order started to develop at $\theta_O = 0.34$, and a $(\sqrt{2} \times \sqrt{2})R45^\circ$ structure was formed at a saturation coverage $\theta_O = 0.48$.⁸

Results and Discussion

TPR/D Study of FCH₂CH₂OH on Clean Cu(100). Figure 1 shows the TPR/D spectra, collected for the ions of 18, 27, 31, and 88 amu, of 2-fluoroethanol adsorbed on a clean Cu(100) surface at 115 K. These ions are used to represent the desorption of H₂O, C₂H₄, FCH₂CH₂OH, and C₄H₈O₂ (1,4-dioxane) which

are verified by their cracking patterns, which are similar to those measured by our mass spectrometer for FCH₂CH₂OH, H₂O, and C₄H₈O₂ or to that reported in the literature about C₂H₄.⁹ The CH₃O⁺ (31 amu) ion traces in Figure 1a correspond to 2-fluoroethanol molecular desorption. The peaks at 192 K show a first-order kinetics and are attributed to 2-fluoroethanol monolayer desorption. Assuming a 10^{13} s⁻¹ preexponential factor, the activation energy for the desorption is 11.9 kcal/mol. The 167 K peak at 4 langmuir exposure is attributed to 2-fluoroethanol multilayer desorption. The multilayer peak is observable at 2 langmuirs, but is much smaller, indicating that the monolayer coverage corresponds to an exposure slightly less than 2 langmuirs. Figure 1b shows the desorption of H₂O with the maximum rates at ~156 K. In Figure 1c, the C₂H₃⁺ (27 amu) peaks at 167 and 192 K result from 2-fluoroethanol desorption. In addition, another peak at ~130 K is observed as the exposure is smaller than 1 langmuir and is identified to be ethylene. Figure 1d shows the evolution of 1,4-dioxane. Below 2 langmuirs, the 1,4-dioxane is peaked at ~258 K. At higher exposures, another low-temperature peak appears at ~167 K, which is the same as that of 2-fluoroethanol multilayer desorption at 4 langmuirs. Previously, we have studied the adsorption of 1,4-dioxane on Cu(100);¹⁰ it is found that the amount of the 1,4-dioxane produced from 2 langmuirs of FCH₂CH₂OH is only ~4% of a monolayer 1,4-dioxane. The insets in Figure 1a–d show the relative yields of FCH₂CH₂OH, H₂O, C₂H₄, and 1,4-dioxane as a function of FCH₂CH₂OH exposure.

Comparison of Thermal Reactions of FCH₂CH₂OH and CH₃CH₂OH on Clean Cu(100). The reaction products reveal versatile FCH₂CH₂OH decomposition pathways in contrast to CH₃CH₂OH. For the formation of C₂H₄, FCH₂CH₂OH must break the C–F and C–O bonds simultaneously. The 1,4-dioxane comes from recombination of two FCH₂CH₂OH molecules after breakage of the C–F and O–H bonds. The H₂O formation is related to FCH₂CH₂OH decomposition, generating C₂H₄ to provide the O source for H₂O. The C₂H₄ signal is only detected below 1 langmuir of FCH₂CH₂OH, as shown in Figure 1c, but H₂O peaks are still observed at exposure ≥ 1 langmuir in Figure 1b. Therefore, it is believed that C₂H₄ is generated at exposure ≥ 1 langmuir as well. The reason that C₂H₄ is not detected at FCH₂CH₂OH exposure ≥ 1 langmuir is due to strong repulsive interaction between the adsorbed molecules that causes the C₂H₄ desorption temperature to be lower than our detection limit because the maximum rates for the C₂H₄ desorption appear at 141, 130, 130, and 128 K for 0.1, 0.25, 0.5, and 0.75 langmuir of FCH₂CH₂OH, respectively; i.e., the C₂H₄ desorption tends to shift to a lower temperature with increasing coverage. Previously in the study of C₂H₄ adsorption at coverage less than 1 monolayer on Cu(100), the C₂H₄ desorption peak is shifted from 185 K to a lower temperature with increasing exposure; there is even a finite desorption rate at the dosing temperature of 115 K.¹¹ It is interesting to compare the thermal reactions of CH₃CH₂OH and FCH₂CH₂OH on clean Cu(100). FCH₂CH₂OH shows the reaction routes for the formation of ethylene and 1,4-dioxane, which are not found for CH₃CH₂OH. Both of the products involve the scission of the O–H, C–O, and C–F bonds of FCH₂CH₂OH; i.e., the presence of an F atom at the β -carbon profoundly modifies the reaction route of alcohol on Cu(100).

TPR/D Study of FCH₂CH₂OH on Oxidized Cu(100). Figure 2 shows the TPR/D spectra, collected for the ions of 2, 18, 29, and 88 amu, after dosing 2-fluoroethanol on oxidized Cu(100) surface at 115 K. These ions are used to represent the evolution of H₂, H₂O, FCH₂CHO, and C₄H₈O₂ which are

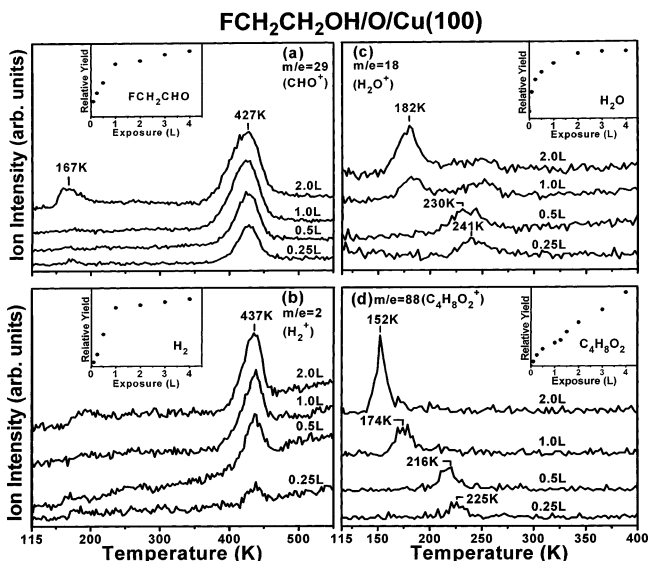


Figure 2. TPR/D spectra, collected for the ions of 2, 18, 29, and 88 amu, of 2-fluoroethanol adsorbed on oxidized Cu(100) at different exposures. The insets are the relative yields of FCH₂CHO, H₂, H₂O, and C₄H₈O₂ as a function of exposure.

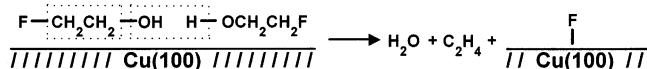
verified by their cracking patterns. In Figure 2a, the peaks at ~427 K are identified to be 2-fluoroaldehyde, and the 167 K peak at 2 langmuir exposure is due to multilayer desorption of FCH₂CH₂OH. Note that FCH₂CH₂OH monolayer desorption is not detected on oxidized Cu(100). Figure 2b shows the evolution of hydrogen which is peaked at ~437 K. Figure 2c corresponds to water desorption with maximum rates at ~240 K at exposures ≤ 0.5 langmuir, but additional peaks appear at ~180 K at higher exposures. Figure 2d shows the formation of 1,4-dioxane. The desorption peak shifts from 225 K at 0.25 langmuir to 152 K at 2 langmuirs. The insets of Figure 2 show the relative yields of FCH₂CHO, H₂, H₂O, and C₄H₈O₂ as a function of FCH₂CH₂OH exposure.

Comparison of Thermal Reactions of FCH₂CH₂OH and CH₃CH₂OH on Oxidized Cu(100). At exposures ≤ 0.5 langmuir of FCH₂CH₂OH in Figure 2, the temperatures for the maximum desorption rates of FCH₂CHO, H₂, and H₂O are similar to the thermal reactions of ethanol on oxidized Cu(100); i.e., the evolution of aldehyde and hydrogen is between 370 and 450 K and water between 200 and 300 K.⁴ At high exposures, additional new peaks appear at 182 K for H₂O. Previously, Bowker et al. proposed the following mechanistic steps for the H₂O formation in alcohol decomposition on an oxygen-preadsorbed Cu(100) surface.⁵



Ellis et al. showed that OH_(a) on Cu(100) recombined at ~220 K to form H₂O_(g).¹² Therefore, in the present study of FCH₂CH₂OH decomposition on oxidized Cu(100), the H₂O formation may originate from recombination between FCH₂CH₂OH_(a) and OH_(a) or between OH_(a) groups. On the basis of our results of RAIRS study of FCH₂CH₂OH adsorption on oxidized Cu(100) (shown later), FCH₂CH₂OH is completely dissociated by 220 K, so the H₂O evolution between 220 and 260 K in Figure 2c is not derived from eq 2 but is more likely due to recombination of OH_(a) groups. However, the lower temperature H₂O peaks at

SCHEME 1



~180 K are possibly due to eq 2. The insets of Figure 2a–c, showing the relative yields of FCH₂CHO, H₂, and H₂O as a function of FCH₂CH₂OH exposure, exhibit a similar uptake trend. This is because all three products are originally derived from FCH₂CH₂OH decomposition. The H₂O is due to the loss of hydrogen of the OH group in FCH₂CH₂OH_(a), forming FCH₂CH₂O_(a). H₂ and FCH₂CHO are due to dehydrogenation of FCH₂CH₂O_(a).

Comparison of Thermal Reactions of FCH₂CH₂OH on Clean and Oxidized Cu(100). It is interesting to compare the H₂O evolution in Figure 1b for clean Cu(100) and Figure 2c for oxidized Cu(100). On clean Cu(100), H₂O formation is originated from the breakage of the C–O bond of adsorbed FCH₂CH₂OH and is associated with C₂H₄, while on oxidized Cu(100), no C₂H₄ is detected, and H₂O formation originated from the loss of H from FCH₂CH₂OH, specifically from the OH group of adsorbed FCH₂CH₂OH. Because the mechanisms for the generation of H₂O from clean Cu(100) and oxidized Cu(100) are different, the H₂O desorption temperature responds to this difference. In Figure 1b, the H₂O evolution at 156 K on clean Cu(100) is desorption-limited, as evidenced by our separate study of H₂O adsorption, showing a maximum rate at ~160 K below 1 monolayer H₂O coverage. The H₂O desorption at 156 K is much lower than the temperature for the coupling of OH groups on Cu(100) at ~220 K.¹² Scheme 1 shows a proposed possible mechanism connecting the formation of H₂O and C₂H₄ in the decomposition of FCH₂CH₂OH on Cu(100), without resorting to surface OH groups. The formation of C₂H₄ and H₂O is resulted from reaction between two adsorbed 2-fluoroethanol molecules, but being mediated by the copper surface. Thermodynamically, the bond energy of Cu–F is substantial (~99 kcal/mol),¹³ and its formation can compensate for the energy required for the C–F bond scission in the decomposition of the adsorbed FCH₂CH₂OH. The peak area of H₂O from FCH₂CH₂OH decomposition on clean Cu(100) in Figure 1b is ~20% of that on oxidized Cu(100) in Figure 1c at 1 langmuir of FCH₂CH₂OH. Therefore, it is roughly estimated that nearly this percentage of the adsorbed FCH₂CH₂OH molecules on clean Cu(100) at 1 langmuir exposure is decomposed, without considering the formation of 1,4-dioxane. In Figure 1d, the 1,4-dioxane from thermal decomposition of FCH₂CH₂OH on Cu(100) is desorbed at ~258 K as the exposure is smaller than ~2 langmuirs, but with an additional desorption peak at ~167 K at higher exposures. The 258 K peak is desorption-limited and is associated with surface defect sites based on our previous adsorption study of 1,4-dioxane on Cu(100).¹⁰ The 167 K 1,4-dioxane peak is overlapped with the multilayer FCH₂CH₂OH desorption, implying that 1,4-dioxane molecules are formed below 167 K; they are mixed into FCH₂CH₂OH multilayer, and both are desorbed together. Furthermore, the amount of 1,4-dioxane does not get saturated at 4 langmuir FCH₂CH₂OH exposure, which approximately corresponds to two monolayer coverage. The reason for this may be (1) that the 1,4-dioxane formed on the Cu(100) surface below 167 K moves into the FCH₂CH₂OH multilayer and makes the active sites on Cu(100) for 1,4-dioxane formation still available, (2) that the presence of the multilayer changes the adsorption geometry of monolayer molecules and lowers the barrier for 1,4-dioxane formation, (3) that the 1,4-dioxane can be generated from the reaction between two FCH₂CH₂OH molecules present

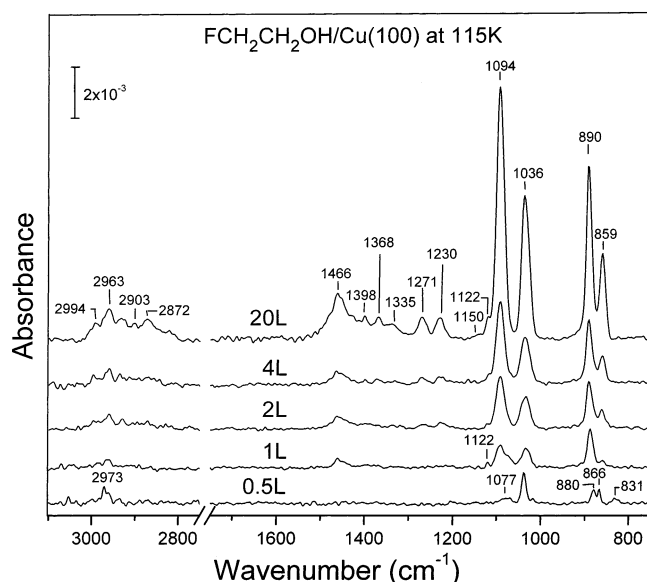


Figure 3. The 115 K RAIR spectra of 2-fluoroethanol adsorbed on clean Cu(100) as a function of exposure.

in the monolayer and multilayer respectively, or (4) that the presence of the multilayer stabilizes the activated complex for the formation of 1,4-dioxane. In the previous studies, it has been shown that dimethyl ether is only generated in the reaction of methyl iodide on TiO₂(110) at multilayer coverage,¹⁴ and cyclobutane is dissociated at multilayer coverage on Ru(001) at a temperature where the monolayer molecules do not dissociate.¹⁵ Furthermore, alkyl coupling occurs for alkyl iodides on Cu(111) near a monolayer coverage, but not at lower coverages.¹⁶ 1,4-Dioxane has been synthesized by using diethylene glycol (HOCH₂CH₂OCH₂CH₂OH) in the presence of acids,¹⁷ β,β' -dichlorodiethyl ether (ClCH₂CH₂OCH₂CH₂Cl) in the presence of OH⁻,¹⁸ ethylene glycol (HOCH₂CH₂OH) in the presence of superacidic perfluorinated resinsulfonic acid,¹⁹ or tosylated diethylene glycol monoethyl ether (TsOCH₂CH₂OCH₂CH₂OC₂H₅) through thermal decomposition.²⁰ The copper surface-catalyzed coupling of two FCH₂CH₂OH molecules to form 1,4-dioxane in the present study has never been reported before. Furthermore, an intriguing and open topic is the comparison of the reaction pathways of FCH₂CH₂OH on single copper crystal surfaces and supported copper catalysts.

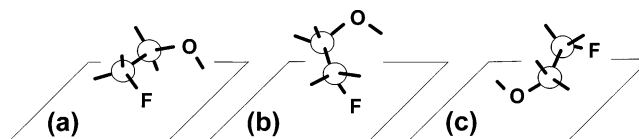
RAIRS Study of FCH₂CH₂OH on Clean Cu(100) and Analysis of FCH₂CH₂OH Adsorption Geometry. Figure 3 shows the RAIR spectra of Cu(100) taken after dosing FCH₂CH₂OH for the indicated exposures at 115 K. The IR absorption frequencies marked in the spectrum of 20 langmuirs, which is about 10 adsorption monolayers, resemble those of FCH₂CH₂OH in liquid or solid states and FCH₂CH₂OH multilayer on Cu(111).⁷ Table 1 lists the observed frequencies and their approximate modes. The gauche conformation isomer of FCH₂CH₂OH predominates on the surface, as demonstrated by the relatively strong C–F stretching band of the gauche form at 1036 cm⁻¹ with respect to the small trans band at 1150 cm⁻¹ in the 20 langmuir spectrum.^{21–23} Previous studies have shown, by spectral techniques and electron diffraction, that FCH₂CH₂OH exists predominantly (>90%) in the conformation with the OH and F gauche to one another in vapor, liquid, and solid states.^{24,25} Therefore, the following analysis of FCH₂CH₂OH adsorption orientation is based on the gauche conformation. As the exposure is reduced to 2 langmuirs, the spectral feature, including the peak frequencies and peak relative intensities, is similar to that at 20 langmuirs. Further reducing the exposure

TABLE 1: Vibrational Frequencies (cm⁻¹) and Assignments for FCH₂CH₂OH on Cu(100) and FCH₂CH₂O on Oxidized Cu(100)^a

FCH ₂ CH ₂ OH/Cu(100)		FCH ₂ CH ₂ O/O/Cu(100)	
20 langmuirs	0.5 langmuir (115 K)	2 langmuirs (220 K)	mode refs 21–23
859	831		
890	866	860	ρ (CH ₂)
1036	880	892	
1094	1036		ν (C–F),g
1122	1077	1072	ν (C–O)
1150			ν (C–C)
1230			ν (C–F),t
1271			δ_{ip} (O–H)
1335			τ or ω (CH ₂)
1368			ω (CH ₂)
1398			τ or ω (CH ₂)
1466			τ or ω (CH ₂)
2872			δ (CH ₂)
2903–2994	2973	2945, 2955	$2 \times \delta$ (CH ₂)
			ν (CH ₂)

^a ν = stretching, ρ = rocking, τ = twisting, ω = wagging, δ = scissoring, t = trans, and g = gauche.

SCHEME 2



down to 1 langmuir, an approximately half-monolayer coverage, the most striking changes are the intensities of the C–O stretching frequency (1094 cm⁻¹) and the CH₂ rocking frequency (859 cm⁻¹) are diminished to a large extent with respect to the 890 and 1036 cm⁻¹ peaks. At 0.5 langmuir, the 1094 cm⁻¹ peak either disappears or may be red-shifted to 1077 cm⁻¹ with relatively low intensity. Meanwhile, the 1036 cm⁻¹ peak becomes narrower. There are four other peaks located at 831, 866, 880, and 2973 cm⁻¹. The former three are assigned to CH₂ rocking, and the last one is assigned to CH₂ antisymmetric stretching. The weakness of the C–O stretching band in the 0.5 langmuir spectrum indicates that the adsorbed FCH₂CH₂OH adopts an orientation with the C–O bond approximately parallel to the Cu(100) surface in contrast to the strong 1094 cm⁻¹ C–O band observed for 20 langmuir exposure, likely with random FCH₂CH₂OH adsorption orientation in the multilayer.⁷ After considering also the lack of the C–C band in 0.5 langmuir spectrum, which appears at 1122 cm⁻¹ in the 20 langmuir spectrum, the FCH₂CH₂OH molecules are suggested to be adsorbed with the C–C–O skeleton parallel to the surface at 0.5 langmuir exposure, as shown in Scheme 2a. In this orientation, the dynamic moments normal to the surface for the modes of CH₂ rocking, C–F stretching, and CH₂ antisymmetric stretching are not zero; therefore, their frequencies at 831, 866, 880, 1036, and 2973 cm⁻¹ are detected in the 0.5 langmuir spectrum. The spectral feature at 1 langmuir is also unique compared to those at the lower coverage of 0.5 langmuir and at the multilayer coverage of 20 langmuirs. The major difference between the spectra of 0.5 and 1 langmuir is the presence of the bands due to the C–O stretching at 1094 cm⁻¹ and the C–C stretching at 1122 cm⁻¹ at the latter exposure, revealing that the C–C–O plane of the adsorbed FCH₂CH₂OH at 1 langmuir is not parallel to the surface. Scheme 2b,c is the suggested FCH₂CH₂OH orientation at 1 langmuir exposure with the C–C–O plane tilted away from the surface. In Scheme 2b, the F is closer to the surface, but in Scheme 2c the OH is closer to the surface.

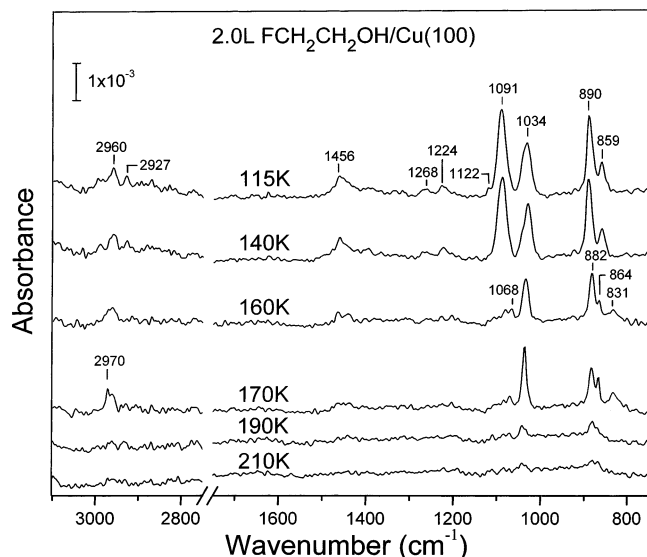


Figure 4. RAIR spectra taken after exposing 2 langmuirs of 2-fluoroethanol to a clean Cu(100) at 115 K and flashing the surface to the indicated temperatures.

For both orientations, the dynamic dipole of the rocking mode of the CH₂ bonded to the F is almost parallel to the surface in contrast to that of the CH₂ bonded to the OH. This difference is reflected in the much smaller intensity ratio of 859 cm⁻¹ to 890 cm⁻¹ in the 1 langmuir spectrum, as compared to the randomly oriented FCH₂CH₂OH at multilayer coverage of 20 langmuirs, because the 859 cm⁻¹ is mainly due to the CH₂ rocking of FCH₂ and 890 cm⁻¹ to that of CH₂OH in FCH₂CH₂OH molecule. In the previous normal-coordinate analysis of FCH₂CH₂OH, the potential energy distribution of the 859 cm⁻¹ band has 55% from the local symmetry coordinate related to the CH₂ rocking of the FCH₂ group, while the 890 cm⁻¹ only has 13% of that. The largest contribution (34%) for the 890 cm⁻¹ band comes from the local symmetry coordinate related to the CH₂ rocking of CH₂OH group.²² Briefly, at 0.5 langmuir, the FCH₂CH₂OH is adsorbed with its C–C–O plane parallel to the surface; however, as the exposure is increased to 1 langmuir, parallel orientation is changed to a tilted one, which is expected to take less surface space.

Figure 4 shows the spectra of 2 langmuirs of FCH₂CH₂OH dosed at 115 K after being flashed to the indicated temperatures. From the TPR/D study, multilayer molecules are present at this exposure. The 115 K spectrum shows randomly adsorbed FCH₂CH₂OH molecules. The spectrum at 140 K is the same as that at 115 K, showing that the adsorption orientation of FCH₂CH₂OH does not change. After brief heating to 160 K, the major changes are the significant reduction of the 1091 cm⁻¹ C–O stretching band and the appearance of the 831 cm⁻¹ CH₂ rocking band. These changes may be in part due to multilayer desorption and in part due to alteration of adsorption geometry of some monolayer FCH₂CH₂OH molecules, i.e., from tilted orientation to parallel one. As the temperature is increased to 170 K, the IR absorption feature is similar to that observed in the 0.5 langmuir spectrum at 115 K in Figure 3, apparently due to partial desorption of monolayer FCH₂CH₂OH molecules, leaving more surface space for the adsorbed FCH₂CH₂OH molecules with the C–C–O backbone parallel to the surface. After further increasing the surface temperature, the amount of FCH₂CH₂OH continues to decrease, as revealed by its reducing band intensities.

RAIRS Study of FCH₂CH₂OH on Oxidized Cu(100) and Analysis of Adsorption Geometry and Surface Intermedi-

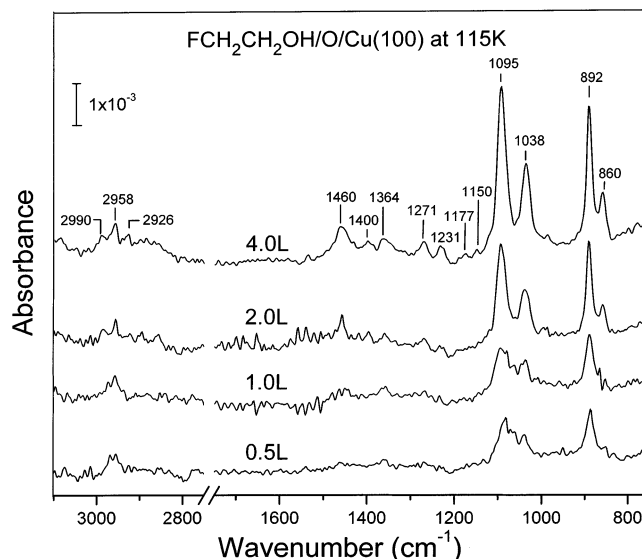


Figure 5. The 115 K RAIR spectra of 2-fluoroethanol adsorbed on oxidized Cu(100) as a function of exposure.

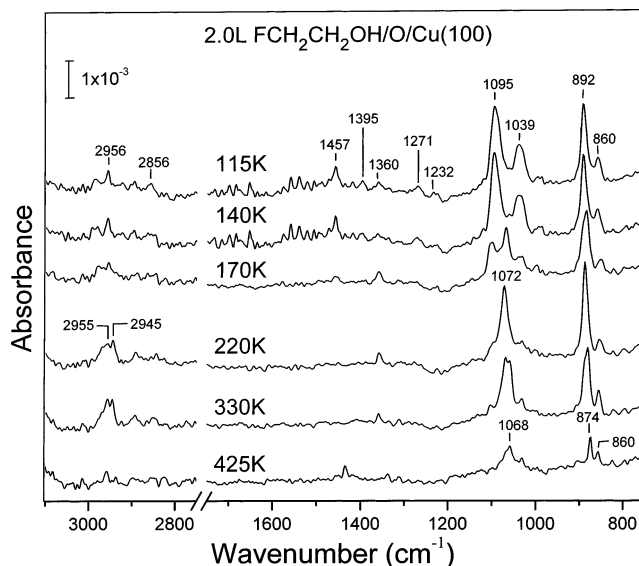


Figure 6. RAIR spectra taken after exposing 2 langmuirs of 2-fluoroethanol to an oxidized Cu(100) at 115 K and flashing the surface to the indicated temperatures.

ates. Figure 5 shows the FCH₂CH₂OH spectra on oxidized Cu(100) taken at 115 K for 0.5, 1, 2, and 4 langmuirs. The spectral feature of 4 langmuirs on the oxidized surface is similar to that on clean Cu(100). Meanwhile, this feature is not considerably altered in terms of the peak positions and relative intensities as the exposure is decreased to 0.5 langmuir. The C–O absorption band at 1095 cm⁻¹ is still relatively strong in 0.5 langmuir spectrum in Figure 5, in contrast to the absence of this band on clean Cu(100) at the same exposure, indicating that at this submonolayer coverage the FCH₂CH₂OH molecules on oxidized Cu(100) are adsorbed with tilted orientation. The change of FCH₂CH₂OH adsorption geometry in the presence of preadsorbed oxygen atoms is likely via steric and/or electronic effects. Figure 6 shows the spectra of oxidized Cu(100) after being exposed to 2 langmuirs of FCH₂CH₂OH and being flashed to the indicated temperatures. The 115 and 140 K spectra are the same, indicating that the FCH₂CH₂OH orientation on the surface does not change between this temperature range. After heating the surface to 170 K, the 1095 cm⁻¹ C–O band intensity is reduced, with a new band formed at 1072 cm⁻¹. As the

temperature is further raised to 220 K, the 1095 cm^{-1} band disappears and the 1072 cm^{-1} band continues to increase. The 220 K spectrum closely resembles the $\text{FCH}_2\text{CH}_2\text{O}_{(\text{a})}$ IR absorptions on oxidized Cu(111).⁷ Therefore, it is concluded that at $\sim 170\text{ K}$ some of the adsorbed $\text{FCH}_2\text{CH}_2\text{OH}$ have decomposed, via O–H scission, to form $\text{FCH}_2\text{CH}_2\text{O}_{(\text{a})}$, and this process is completed at 220 K. The vibrational modes for the observed frequencies of $\text{FCH}_2\text{CH}_2\text{O}_{(\text{a})}$ are listed in Table 1. Our IR measurements at other exposures show that at $\sim 160\text{ K}$ $\text{FCH}_2\text{CH}_2\text{OH}$ starts to decompose on oxidized Cu(100). The 330 K spectrum is similar to the 220 K one in Figure 6, revealing that $\text{FCH}_2\text{CH}_2\text{O}_{(\text{a})}$ is stable at 330 K, which is close to the onset temperature of $\text{FCH}_2\text{CHO}_{(\text{g})}$ evolution in Figure 2. The amount of $\text{FCH}_2\text{CH}_2\text{O}_{(\text{a})}$ decreases at temperature higher than 330 K, as shown by its reduced band intensities. The sacrifice of $\text{FCH}_2\text{CH}_2\text{O}_{(\text{a})}$ observed in the IR study leads to the $\text{FCH}_2\text{CHO}_{(\text{g})}$ formation observed in the TPD study. The mechanism for the β -hydride elimination of fluorinated ethoxide on copper surfaces to form the corresponding fluorinated aldehyde has been well investigated.⁷

Conclusion

On clean Cu(100), $\text{FCH}_2\text{CH}_2\text{OH}$ can dissociate to form water, ethylene, and 1,4-dioxane, but no fluoroaldehyde is found in the TPR/D study. For ethanol reaction on clean Cu(100), previous studies have shown that a small fraction of the adsorbed ethanol dissociate to evolve aldehyde. The present study shows that the presence of fluorine bonded to the β -carbon of ethanol profoundly modifies the alcohol reaction pathways. On clean Cu(100), $\text{FCH}_2\text{CH}_2\text{OH}$ molecules at lower surface coverages adopt a adsorption geometry with the C–C–O molecular backbone approximately parallel to the surface. At a half monolayer coverage, the geometry is changed to a tilted C–C–O skeleton with respect to the surface. However, no parallel C–C–O orientation for $\text{FCH}_2\text{CH}_2\text{OH}$ molecules on oxidized Cu(100) is observed. $\text{FCH}_2\text{CH}_2\text{OH}$ on oxidized Cu(100) begins to decompose at $\sim 160\text{ K}$ to form adsorbed

$\text{FCH}_2\text{CH}_2\text{O}$, which dissociates to evolve FCH_2CHO at a temperature higher than $\sim 350\text{ K}$. Additionally, H_2O , H_2 , and $\text{C}_4\text{H}_8\text{O}_2$ are produced as well.

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