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Orientation of CH_3O on Cu(110) as examined by near-edge x-ray-absorption fine-structure spectroscopy

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The orientation of the methoxy species (CH_3O) found as an intermediate in the catalytic dehydrogenation of methanol on Cu(110) has been determined by analysis of the near-edge x-ray-absorption fine structure at the oxygen K edge in the azimuths [001] and $[1\bar{1}0]$. In both azimuths the C-O axis is tilted by 36° ± 5° with respect to the surface normal.

During the last few years the analysis of polarization-dependent near-edge x-ray-absorption fine-structure (NEXAFS) has become a powerful and straightforward technique for the determination of the orientation of low-Z molecules adsorbed on single-crystal surfaces.[1,2] The precision is limited by normalization and background-subtraction problems,[3] the latter being less important for π-bonded systems where sharp π resonances occur. Even in unfavorable cases, however, orientational angles can be determined with an accuracy of $\leqslant 10°$ which compares well with that obtained in photoelectron diffraction studies at high kinetic energy.[4-6]

The oxidation of methanol to formaldehyde on a copper surface has been widely investigated. The reaction proceeds via the formation of a surface methoxy intermediate, CH_3O,[7] which is bonded to the surface through the oxygen atom.[8] For methoxy on Cu(100) there is conflicting evidence from different spectroscopies regarding the orientation of the C—O bond relative to the surface.[8-11] A recent NEXAFS study[11] has shown that on Cu(100) the C-O axis of CH_3O is tilted by $\alpha = 32° \pm 10°$ with respect to the surface normal. For CH_3O on Cu(110) high-kinetic-energy photoelectron diffraction studies indicated the existence of two different tilted CH_3O species, one tilted by 18° ± 3° in $[1\bar{1}0]$, the other tilted 40° ± 5° in [001].[6] It is the purpose of this Rapid Communication to show that within experimental errors NEXAFS of CH_3O on Cu(110) measures a tilt angle of $\alpha = 36° \pm 5°$ in both azimuths.

The experiments were conducted using the light from the electron storage ring BESSY. The spectra were taken by using the plane-grating grazing incidence monochromator SX-700 (Ref. 12) with a 1200-1/mm grating. The oxygen K-edge NEXAFS of methoxy was monitored in the azimuths [001] and $[1\bar{1}0]$ using the partial electron yield mode of detection excluding secondary electrons below 400 eV. The photon energy was calibrated in this region to an accuracy of ±0.5 eV. The x-ray incident angle on the sample could be varied from near grazing incidence ($\theta = 20°$), with the **E** vector close to the surface normal, to normal incidence ($\theta = 90°$) with the **E** vector parallel to the surface. The spectra shown are the ratio of covered/clean.

The Cu crysal was prepared in the usual way by orienting and cutting a slice, polishing and *in situ* ion bombarding, and annealing at approximately 600 K. The methoxy intermediate was prepared by predosing the surface with 0.2 L O_2 (where $L = 10^{-6}$ Torr sec) followed by a 5-L dose of methanol, both at 150 K. The sample was then momentarily heated to 300 K to remove molecular methanol and water.[7] The measurements were performed at 200 K in order to minimize thermal decomposition of the methoxy and background methanol adsorption. Care was taken to avoid excessive predoses of oxygen which lead to an adlayer consisting of methoxy and chemisorbed oxygen, thus disturbing the normalization procedure (see below). Excessive predoses of oxygen showed up in the spectra as a characteristic absorption step at the oxygen K edge different from the smooth atomiclike background of the methoxy absorption. To avoid contamination the surface was always recleaned and predosed with oxygen after having measured the NEXAFS at two different x-ray incident angles. Cleaning prior to exposure was achieved by heating the surface to > 500 K. A carbon buildup could not be detected after this procedure.

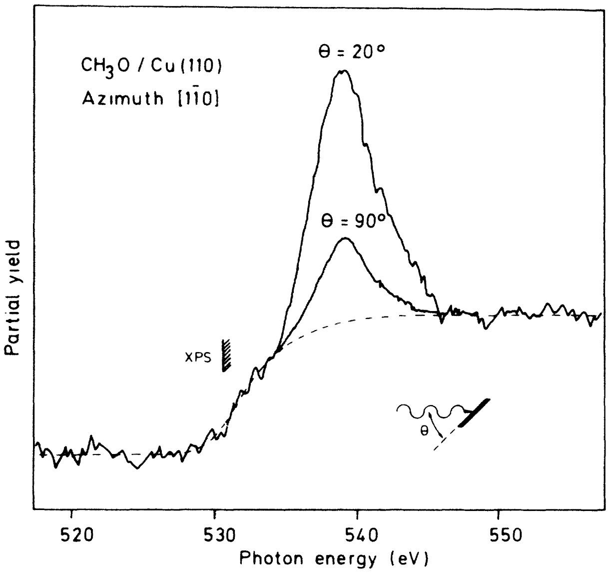

FIG. 1. Oxygen K-edge NEXAFS spectra of methoxy on Cu(110) in the azimuth $[1\bar{1}0]$ for normal ($\theta = 90°$) and near grazing ($\theta = 20°$) incidence. The spectrum for $\theta = 90°$ is drawn only in that energy region where it deviates from the spectrum taken at $\theta = 20°$. An atomiclike background was approximated as shown by the dashed line. The O 1s binding energy (referenced to the Fermi level) is labeled "XPS" (Ref. 14).

Characteristic NEXAFS spectra for the methoxy on Cu(110) are shown in Fig. 1. No π resonance is observed according to the C—O single-bond nature. A σ shape reso-

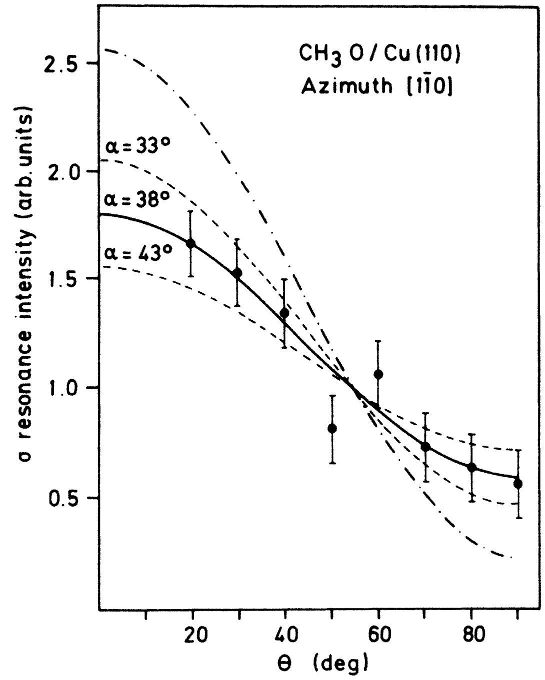

FIG. 2. Normalized σ resonance intensity as a function of the polar angle θ in the azimuth [1$\bar{1}$0]. The full line corredsponds to a least-squares fit according to Eq. (1) which yields a tilt angle of $\alpha = 38°$ between the C-O axis and the surface normal. Fits with $\alpha = 33°$ and 43° are shown as dashed lines. The dashed-dotted line is the calculated σ resonance intensity variation for an adsorption model with two different tilted CH_3 species, one tilted by 18° in [1$\bar{1}$0], the other tilted by 40° in [001].

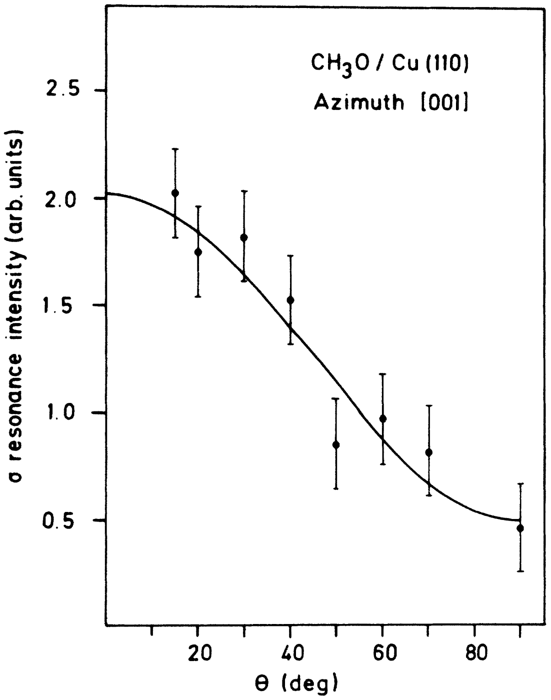

FIG. 3. Normalized σ resonance intensity as a function of the polar angle θ in the azimuth [001]. The full line corresponds to a least-squares fit according to Eq. (1) and yields $\alpha = 34°$.

nance appears at (539.0 ± 0.5) eV, which has maximum intensity near grazing incidence ($\theta = 20°$) and decreases in intensity for normal incidence ($\theta = 90°$). As the intensity of this resonance has its maximum value when the **E** vector points along the C-O axis,[1,2] Fig. 1 indicates that the methoxy C-O axis is tilted by less than 54.7° (magic angle) from the surface normal. For a quantitative intensity analysis peak, areas have to be determined. For this purpose a smooth atomiclike background (cf. dashed line in Fig. 1) was assumed. As the line shape and the linewidth proved to be independent of θ, peak heights instead of peak areas were determined. To correct for experimental changes by varying the incidence conditions, exposure, and photon flux the intensity was divided by the height of the underlying atomic adsorption step which must scale with these changes in the same way as the resonance. The normalized intensity (peak height) of the σ shape resonance as a function of the polar angle θ for the azimuths [1$\bar{1}$0] and [001] is shown in Figs. 2 and 3, respectively. Within experimental errors the $I(\theta)$ values in both azimuths coincide (without scaling).

Assuming rotational symmetry the following expression holds for the σ resonance intensity, I_σ, as a function of the polar angle θ and of the tilt angle α between the surface normal and the C-O axis for radiation with a degree of linear polarization, P,[13]

$$I_\sigma \propto [P(\sin^2\alpha \sin^2\theta + 2\cos^2\alpha \cos^2\theta) + (1-P)\sin^2\alpha] \; . \qquad (1)$$

Least-squares fits (full lines in Figs. 2 and 3) according to Eq. (1) with $P = 0.87$ (Ref. 3) yield tilt angles of $\alpha = (38 \pm 5)°$ for the azimuth [1$\bar{1}$0] and $\alpha = (34 \pm 5)°$ for the azimuth [001]. The error bars include the uncertainty in approximating the background.

The measured average tilt angle of $\alpha = 36°$ is in good agreement with that found recently by NEXAFS for methoxy on Cu(100).[11] However, it is at variance with the high-kinetic-energy photoelectron results on the Cu(110) surface, which suggest two different tilted CH_3O species, one tilted by 18° in the [1$\bar{1}$0] azimuth, and the other by 40° in the [001] azimuth.[6] Within experimental errors the latter model would fit our results for the [001] azimuth, but it cannot explain our results for the [1$\bar{1}$0] azimuth (cf. Fig. 2). It is true that in NEXAFS the quantitative analysis of σ resonance intensities is more difficult than that of π resonance intensities because of possible underlying surface extended x-ray-absorption fine-structure (SEXAFS) and multiple scattering features. However, for the investigated system large SEXAFS contributions were not observed; a further study will be necessary to show whether SEXAFS is measureable. To explain the above discrepancies underlying multiple scattering features should differ markedly in the azimuths [001] and [1$\bar{1}$0], which is not observed. Approximating the background in both azimuths in the same way, as shown in Fig. 1, line shapes and linewidths are the same for both azimuths and for all polar angles θ.

The different results of NEXAFS and high-kinetic-energy photoelectron diffraction remain thus unexplained. From SEXAFS studies of methoxy on Cu(100) (Ref. 11) the adsorption site could not completely be determined. Only atop sites were ruled out. A planned SEXAFS study of CH_3O on Cu(110) will cast some more light on the bonding geometry of methoxy on this surface and on the origin of the measured tilt of the C-O axis.

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