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Thermal Desorption of Ethanol from Polycrystalline Cu Surface

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It is known that low temperature adsorption gives rather an amorphous and porous than polycrystalline layer. Such a layer during heating up undergoes some ordering and phase changes before reaching the temperature of desorption. In the case of ethanol two phase changes may occur [1]. In a bulk material solidified from the liquid within an appropriate temperature regime, the phase change from amorphous (glassy state) to so-called crystal II phase occurs at about 115 K. Crystal II phase melts during heating at 127 K (± 0.5 K) producing the stable phase crystal I, finally. The triple point temperature for ethanol was determined to be about 159 K [1]. When the amorphous layer changes into a more ordered one some energy can be released. This energy may cause a partial desorption of the layer contributing to the measured TPD spectra. Additional peaks may appear when desorption from different states takes place in the course of sample heating up as it was shown by Jenniskens et al. [2] recently. Jenniskens et al. [2] have measured three different peaks for methanol on Ag(111) and assigned them to: molecules desorbing from the first monolayer, the crystallised multilayer and the layer which is located between the two other phases. The aim of this work was to measure desorption spectra and to calculate desorption energies for ethanol on polycrystalline Cu.

The experiments were performed in a stainless steel UHV system with a base pressure below 5×10^{-10} mbar. For TPD a quadrupole mass spectrometer (Balzers type QMS 421) was used. The mass spectrometer was set to monitor mass 31, since that is the most abundant fragment of ethanol produced in the QMS ionizer. Before experiments the ethanol (99.8% pure) was freeze-pump-thawed for several times to remove volatile contaminants. A thick-walled copper vessel was designed as the condensation substrate. Before the adsorption of ethanol the copper vessel was filled with LN₂ through a thin-walled stainless steel tube. Before heating up and TPD measurement each time the stainless-steel tube was preheated to clean its outer surface and prevent a generation of spurious peaks. This we found to be very important from our preliminary experiments with a monocrystal, as a substrate, fixed on the XYZ manipulator where we detected unwanted additional peaks due to desorption from sample holder parts. The thermocouple and the heater were installed inside the copper vessel. To have the substrate clean before measurements we heated the Cu vessel at about 750 K for about 10 hours. To minimise the temperature gradients on the substrate and to keep the thermocouple temperature same as that of substrate the TPD spectra were measured with a temperature rate as low as 0.1 K s⁻¹. The copper vessel working as a substrate was placed far from the axes of the needle valve through which ethanol entered the system. This precaution guaranteed us that the prepared layers were uniform in thickness.

Fig. 1 shows the TPD spectra for coverages from 0.7 L to 80 L (1 Langmuir = 1.3×10^{-6} mbar s). As is seen for all coverages only one maximum can be detected. There is no detectable desorption during exothermic transition in the region of 115 and 127 K. It means that this transitions are not accompanied by partial desorption of the sample. The layer desorbs completely at significantly higher temperature. The peak position T_p shifts to lower temperature values with increase of coverage up to a few monolayers and saturates at 155 K for higher coverages (1 ML corresponds to exposure of about 8 L [4]). This shift may indicate second order kinetics. In our opinion this is rather a demonstration of adsorbate-substrate interaction being at play just up to a few monolayers. Starting from the exposure of 30 L, for all thicker layers studied, the desorption follows first

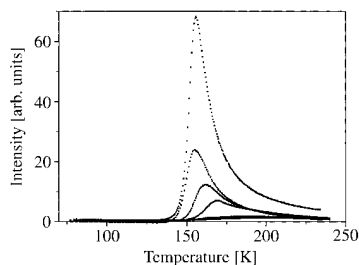


Fig. 1. Selected TPD spectra of ethanol on polycrystalline Cu

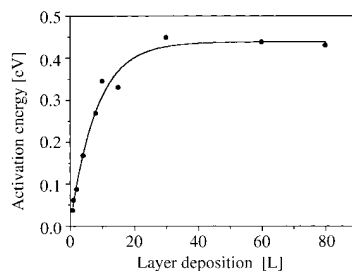


Fig. 2. Activation energy estimated by the initial rise method as a function of layer thickness

order kinetics with an activation energy of 0.45 eV. This value was obtained using the Arrhenius equation for maximum desorption rate at $T = T_p$, for the first-order kinetics:

$$Ed/(RT_p^2) = m(dt/dT) \exp(-Ed/RT_p^2), \quad (1)$$

where ν was assumed to be 10^{13} s^{-1} [3].

Very close activation energy of 0.44 eV was estimated by initial rise method for layers thicker than 3 to 4 monolayers. Fig. 2 shows the activation energy, estimated by an initial rise method, versus layer thickness within the 0.1 to 10 ML range. Only for higher coverages, starting from about 3 ML, one can obtain values that nicely approach the activation energy estimated by the peak position method. For thin layers the initial rise method gives unrealistically low values. It seems that in the system of first monolayer and polycrystalline substrate we have to do with a wide spread of bonding energies that makes this method not reliable for low coverages.

It is noteworthy that other authors [4] have observed four peaks on TPD spectra for ethanol molecules adsorbed at $T \approx 108 \text{ K}$ on polycrystalline silver substrate. They interpreted these peaks as due to ethanol molecules adsorbed on different crystal planes or different surface sites on a single plane arising from defects. Our data are in contradiction to those presented in [4] despite the fact that our data were obtained under slightly different conditions (different substrate and different adsorption temperature). We never observed more than one peak for slowly and uniformly heated samples uniform in thickness.

In conclusion: We present an evidence that pure ethanol, when adsorbed at $T \approx 78 \text{ K}$ on polycrystalline Cu as a layer uniform in thickness, generate only one peak on the TPD spectrum. Thick layer spectra do not exhibit any additional structures, which one could expect due to the phase changes occurring for bulk material during thermal stimulation. The observed peak should be interpreted as the desorption connected with solid–vapour phase change. The peak temperature $T_p \approx 155 \text{ K}$ for thicker layers ($>4 \text{ ML}$) is quite close to the temperature of the triple point of ethanol. For thin layers, up to $\approx 1 \text{ ML}$ the temperature of the maximum desorption rate strongly depends on the layer thickness. T_p shifts towards higher temperature with decrease of the sample thickness (Fig.1). This indicates that the adsorbate–substrate interaction is much stronger than the interaction between molecules in the layer.

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