Optical characterization of methanol adsorption on the bare and oxygen precovered Cu(110) surface

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Abstract

We have studied the adsorption and reaction of methanol on the bare and oxygen precovered Cu(110) surface at 200 K using reflectance difference spectroscopy (RDS). On the bare and fully oxygen covered surface, the sticking coefficient is close to zero. In contrast, on the partially oxygen covered surface, a sticking coefficient close to unity is obtained. This observation suggests a high mobility of methanol on both bare and oxygen covered Cu(110) and of methoxy on Cu(110). Two reaction regimes, an oxygen supply limited and an adsorption site limited regime are identified. The transition between these two regimes occurs for an oxygen coverage of about 0.2.

1. Introduction

The oxidation of methanol on the oxygen precovered Cu(110) surface has been investigated extensively in the past. The pioneering work of Madix and co-workers [1,2] has shown that methanol transforms into methoxy by reaction with preadsorbed oxygen on Cu(110). Scanning tunneling microscopy (STM) and low energy electron diffraction (LEED) have demonstrated that the so produced methoxy forms a (5 × 2) superstructure at room temperature [3–6]. At temperatures above 300 K the methoxy species decomposes to form formaldehyde and hydrogen, both of which desorb into the gas phase at approximately 350 K [7–10].

Various experimental methods have been applied to investigate the oxidation of methanol on the Cu(110) surface, e.g., temperature-programmed desorption (TPD) [1,7–10], temperature-programmed reaction spectroscopy (TPRS) [2], X-ray photoelectron spectroscopy (XPS) [2,11,12], ultraviolet photoelectron spectroscopy (UPS) [2,7], electron energy loss spectroscopy (EELS) [7], reflection absorption infrared spectroscopy (RAIRS) [13] and scanning tunneling microscopy (STM) [3–6,14,15]. Besides, density functional theory (DFT) [16–18] and kinetic Monte Carlo (KMC) simulations [19] have been used for detailed studies of the energetics and kinetics of adsorption and reaction at the atomic level.

In this report, we present a real time reflectance difference spectroscopy (RDS) study of the adsorption and reaction of methanol on the bare Cu(110) surface and the Cu–CuO stripe phase composed of alternating Cu(110) and Cu(110)–(2 × 1)O stripes which forms after adsorption of oxygen on the Cu(110) surface [20]. The relative size of the Cu(110) and Cu(110)–(2 × 1)O stripes and the periodicity of the Cu–CuO stripe phase were varied by choosing different oxygen precoverages $\theta_0$ in the range $0 \leq \theta_0 \leq 0.5$. The advantage of RDS for the investigation of metal surfaces is its extremely high sensitivity to adsorbates [21,22], surface vacancies [23,24], and surface reconstruction [25–27]. For a partially reconstructed surface like the Cu–CuO stripe phase, the reconstructed fraction of the surface and, hence, the oxygen coverage can be determined quantitatively by RDS [28]. Besides, surface processes like adsorption or desorption as well as reactions can be monitored in real time by recording the changes of the RD signal at a selected wavelength. In this “kinetic mode” a time resolution of the order of 0.1 s has been achieved [29,30]. Furthermore, being a purely optical method, RDS can be applied to samples in any transparent environment, which would allow to bridge the pressure gap between ultra-high vacuum and the high pressure reaction regime.

2. Experiment

The experiments were carried out in a UHV chamber with a base pressure of $1 \times 10^{-10}$ mbar. The Cu(110) substrate can be