Methanol adsorption on Cu(110) and the angular distribution of the reaction products

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Integral and angle resolved thermal desorption spectroscopies were used to study methanol adsorption and oxidation on clean and oxygen covered Cu(110) surfaces. Special emphasis was put on the Cu–CuO stripe phase, which forms when the Cu(110) surface is covered with 0.25 ML of oxygen. In the temperature regime between 200 and 300 K associative desorption of methanol and water takes place, showing a normal desorption character with peaks shifting to lower temperature with increasing coverage and with a nearly cosine angular desorption distribution. In the temperature range of about 350 K formaldehyde, hydrogen, and again methanol desorb nearly concomitantly in the form of a very narrow peak (full width at half maximum=10 K), with peaks shifting to higher temperature with increasing methanol coverage. The angular distribution of these peaks is strongly forward focused, indicating activation barriers being involved. In the case of the Cu–CuO stripe phase the angular distribution of the desorption products is clearly different in the [110] and [001] azimuthal directions, demonstrating the influence of the border lines between the copper and the copper oxide stripes on the desorption process. © 2007 American Institute of Physics. [DOI: 10.1063/1.2730788]

I. INTRODUCTION

The interaction of methanol with copper surfaces has been studied intensively in the past, because copper plays an important role in the catalytic synthesis and oxidation of methanol.1,2 In particular, the influence of oxygen on a Cu(110) surface on the methanol adsorption and reaction rate has attained considerable interest.3–10 The sticking coefficient for methanol can be increased by more than an order of magnitude due to oxygen.11 Oxygen on Cu(110) forms a special surface oxide by nucleation and aggregation of Cu–O added rows, resulting in a (2 × 1) superstructure.12,13 At 0.25 ML of oxygen the so called Cu–CuO stripe phase forms, which consists of well ordered stripes of equidistant copper oxide and clean copper areas, separated by about 6 nm.14 This self-assembled surface has attained considerable interest recently as a template for nanostructured thin films.15 Here we investigate the role of this particular stripe phase for methanol adsorption and oxidation.

Thermal desorption spectroscopy is a well established method to follow the reactions taking place on a surface. Methanol adsorbed on a Cu(110) surface at low temperature (100 K) forms a condensed multilayer which desorbs around 145 K.16 The monolayer dissociates partially into methoxy and hydrogen. Upon further heating recombination of methoxy and hydrogen takes place leading to desorption of methanol between 200 and 300 K. In the case of an oxygen covered surface this is accompanied by water desorption, due to recombination of hydrogen and hydroxyl. At about 360 K an additional methanol peak shows up which is accompanied by hydrogen and formaldehyde desorption.3 Finally, at about 460 K CO2 desorption takes place, which was interpreted to be indicative of the decomposition of formate on the surface. There was some dispute concerning the formation of formate,4,9,17 however, in a recent work using high resolution x-ray photoelectron spectroscopy (XPS) the existence of a formate species was clearly verified.10 Despite the large number of available literature in this context, quite a bit of qualitative and quantitative disagreement still exists. The reason for many discrepancies in the literature can be attributed to the strong adsorption temperature dependence of the subsequent reaction/desorption processes and to the enormous influence of small amounts of oxygen on the adsorption and reaction behavior of methanol. Additional microscopic information on the methanol interaction with Cu(110)+O surfaces has been obtained from scanning tunneling microscopy (STM) investigations of Silva et al.9 and Leibsle et al.18,19 They observed that the elongated (2 × 1) oxygen islands are shrinking at the small side of the islands, along the [001] direction, during desorption of the reaction products. Unfortunately, their experiments have been done only at or slightly above room temperature, a temperature where the methanol layer is already very unstable.

Although the basic features of methanol oxidation on the oxygen covered Cu(110) were described in the paper by Wachs and Madix 25 years ago,3 this topic has regained interest recently, in particular, from the theoretical point of view. Density functional theory (DFT) calculations and kinetic Monte Carlo (MC) simulations have been performed to reveal the microscopic details of the oxidation kinetics.20–22 Comparisons between the calculations and the thermal desorption spectra by Wachs and Madix yield reasonable qualitative agreement after proper adjustments of the activation