Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Catalysis 232 (2005) 295–301

JOURNAL OF CATALYSIS

www.elsevier.com/locate/jcat

Low-pressure methanol oxidation over a Cu(110) surface under stationary conditions: (II) adsorbate coverages and reactivity

L. Zhou, S. Günther, R. Imbihl [*,1]

Institut für Physikalische Chemie und Elektrochemie, Universität Hannover, Callinstrasse 3-3a, D-30167 Hannover, Germany

Received 13 October 2004; revised 25 November 2004; accepted 29 November 2004

Abstract

The kinetics of methanol oxidation on a Cu(110) surface have been followed under stationary reaction conditions in the 10^{-7} to 10^{-5} mbar range with low-energy electron diffraction, Auger electron spectroscopy, photoelectron emission microscopy, and rate measurements. A large, 300–400 K-wide hysteresis occurs with cycling of the temperature. The (5×2) and $c(2 \times 2)$ structures, attributed to intermediates of the reaction, are seen only in a T-interval from 300 to ≈ 380 K, where the reaction ignites. The surface exhibits substantial carbon coverage upon heating, but on the cooling branch the surface is largely carbon free down to ≈ 400 K, where the surface becomes covered by C-containing adsorbates again.

Keywords: Copper(110); Methanol oxidation; Formaldehyde; Hysteresis; Ordered overlayer

---

1. Introduction

Metallic copper is an important catalyst in reactions involving methanol, such as methanol synthesis from “syngas” over a Cu/ZnO catalyst, steam reforming of methanol, and partial oxidation of methanol to formaldehyde [1–4]. The Cu(110) surface has become in recent years a model catalyst for these reactions because of its high reactivity compared with other low-index planes of Cu and its tendency to form ordered adsorbate overlayers [5–16]. In particular, the fact that not only oxygen but also reaction intermediates like methoxy and formate species are arranged in ordered adsorbate phases made this system a very attractive object for scanning tunneling microscopy (STM) studies [7–15].

A general problem in relating the findings of STM studies to catalytic activities is that the highly mobile and reactive species are not imaged in STM, which means that in the extreme case, the ordered overlayers that were imaged nicely with STM may just represent a kind of spectator species with little or no relation to the catalytic activity. In this paper we combine the results of stationary measurements of the kinetics of the $CH_3OH + O_2$ reaction on a Cu(110) surface with in situ LEED, Auger electron spectroscopy (AES), and photoelectron emission microscopy (PEEM) in order to relate the presence of certain adsorbate phases to catalytic activity.

For the partial oxidation of methanol to formaldehyde, two reaction pathways can be formulated, depending on whether the hydrogen from the methanol is oxidized to water or not.

$$4CH_3OH + O_2 \rightarrow 4CH_2O + 2H_2 + 2H_2O, \tag{1}$$

$$2CH_3OH + O_2 \rightarrow 2CH_2O + 2H_2O. \tag{2}$$

It was shown that in the low-pressure regime ($p < 10^{-4}$ mbar) reaction (1) is dominant at low temperatures ($T < 750$ K), whereas (2) prevails at high temperatures ($T > 750$ K) [16]. A number of STM studies, mainly conducted by the group of Bowker, yielded detailed insights into the reaction mechanism on Cu(110) [7–15]. These researchers investigated the surface processes under non-stationary conditions by typically first adsorbing oxygen,

---

[*] Corresponding author. Fax: +49-511-762-4009.
E-mail address: imbihl@pci.uni-hannover.de (R. Imbihl).

[1] Institut für Physikalische Chemie, Universität Hannover, Germany.

0021-9517/$ – see front matter © 2005 Published by Elsevier Inc.
doi:10.1016/j.jcat.2004.11.038

followed by titration with methanol and eventual sequential heating.

Oxygen adsorbed to Cu(110) orders in a (2 × 1)-O structure with $\theta_O = 0.5$, which exhibits a reconstruction of the "added row" type. A surface fully covered with (2 × 1)-O is not reactive, but the surface is very reactive if it is only partially covered by the (2 × 1)-O [5,15]. A fully covered (2 × 1)-O thus behaves very similarly to the "oxide-like" c(6 × 2)-O ($\theta_O = 0.66$), which is also very unreactive. Exposure of the (2 × 1)-O with $\theta_O = 0.25$ at room temperature to methanol leads to a well-ordered (5 × 2)-methoxy structure [7,8]. STM shows that the conversion starts at the terminal O atoms and then propagates along the oxygen chains. The subsequent decomposition step leading to the desired reaction product formaldehyde is much slower than the methoxy-forming step, and much less is known in detail. As a competitive reaction route, the total oxidation takes place via a formate species detected after additional oxygen adsorption into a methoxy layer. One can tentatively formulate a kind of skeleton mechanism:

$$CH_3OH_{ad} + O_{ad} \to CH_3O_{ad} + OH_{ad}, \tag{3}$$

$$CH_3O_{ad} \to H_2CO + H_{ad}, \tag{4}$$

$$CH_3O_{ad} + O_{ad} \to HCOO_{ad} + H_{ad}, \tag{5}$$

$$HCOO_{ad} \to CO_2 + H_{ad}. \tag{6}$$

All hydrogen-abstracting steps can in principle be formulated as dehydrogenation or as oxidation through direct interaction with chemisorbed oxygen or an OH species. In addition to the (5 × 2)-methoxy, a c(2 × 2) has also been observed as an intermediate structure, but it is a matter of debate whether the c(2 × 2) is due to a formate species or it is a methoxy structure. Adsorption experiments with formic acid produced a c(2 × 2) and (n × 1) ($n = 3, 4$) layer on Cu(110), thus supporting the former suggestion [17,18]; however, recent STM experiments in which a c(2 × 2) was generated by co-dosing of methanol and oxygen are in favor of the methoxy interpretation [9,10].

2. Experimental

All experiments were conducted in a UHV system equipped with Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), photoelectron emission microscopy (PEEM), and differentially pumped quadrupole mass spectrometry (QMS) for temperature-programmed desorption (TPD) and temperature-programmed reaction (TPR) spectroscopy. In PEEM the sample was illuminated with UV photons from a D_2 discharge lamp (≈ 6 eV of energy). The intensity was determined from digitization of the recorded PEEM images.

The Cu(110) single crystal (1.5 mm thick, $9 \times 11\ \mathrm{mm}^2$), was held by two Ta wires, which also served for resistive heating. The temperature was monitored by means of a chromel–alumel thermocouple. The Cu(110) surface was cleaned by repeated cycles of Ar^+ ion bombardment followed by annealing to 800 K until no traces of S, C, or O were detected by AES and a sharp (1 × 1) LEED pattern was observed. In situ AES showed that no impurities other than C- and O-containing adsorbates were present under reaction conditions. The reproducibility of the hysteresis measurements without additional cleaning cycles between measurements ruled out the buildup of a significant amount of coke deposits.

Under reaction conditions the system was operated as a continuous-flow reactor in the pressure range of 10^{-7}–10^{-3} mbar. All gases were introduced via leak valves with a feedback-stabilized gas inlet system (MKS) that was also used to control the gases in pressure-ramping experiments. Oxygen of purity 5.0 and methanol of purity 2.8 were used. For kinetic measurements the sample was moved close to a cone, so that only gas molecules that were reflected from the sample could enter the cone and be detected by QMS. Heating/cooling cycles were run typically with a heating/cooling rate of 6 K/min.

3. Results

3.1. Rate measurements

Fig. 1 shows the product formation rate as the sample is held in a methanol/oxygen atmosphere in the 10^{-5} mbar range and the temperature is slowly cycled. The main product is formaldehyde. The reactivity of the surface expressed here as the reactive sticking coefficient of methanol, s_{reac}, exhibits two relative maxima, a (pressure dependent) low-temperature peak around 490 K and a high-temperature maximum around 900 K, which is already slightly outside the scanned temperature range. The rate curves display a rather pronounced and wide hysteresis between 350 and 750 K.

3.2. LEED and AES

All of the adsorbate-induced ordered structures seen before in connection with the Cu(110)/$CH_3OH + O_2$ system were obtained as sharp LEED patterns, as demonstrated by Fig. 2. The (5 × 2)-methoxy was created by sequential dosing at 300 K, starting with a surface half-filled with a (2 × 1)-O ($\theta_0 = 0.25$, 5 L O_2 exposure) followed by exposure to methanol. Co-dosing of methanol and oxygen under low pressure ($p(CH_3OH) = 1 \times 10^{-7}$ mbar, $p(O_2) = 0.5 \times 10^{-7}$ mbar) at 300 K leads also to a sharp (5 × 2) pattern in less than a minute. Co-dosing at 300 K, but with the partial pressures increased by two orders of magnitude ($p(CH_3OH) = 1 \times 10^{-5}$ mbar, $p(O_2) = 0.5 \times 10^{-5}$ mbar), causes the appearance of a c(2 × 2) pattern. Extending the co-dosing experiments to longer exposure times leads to the

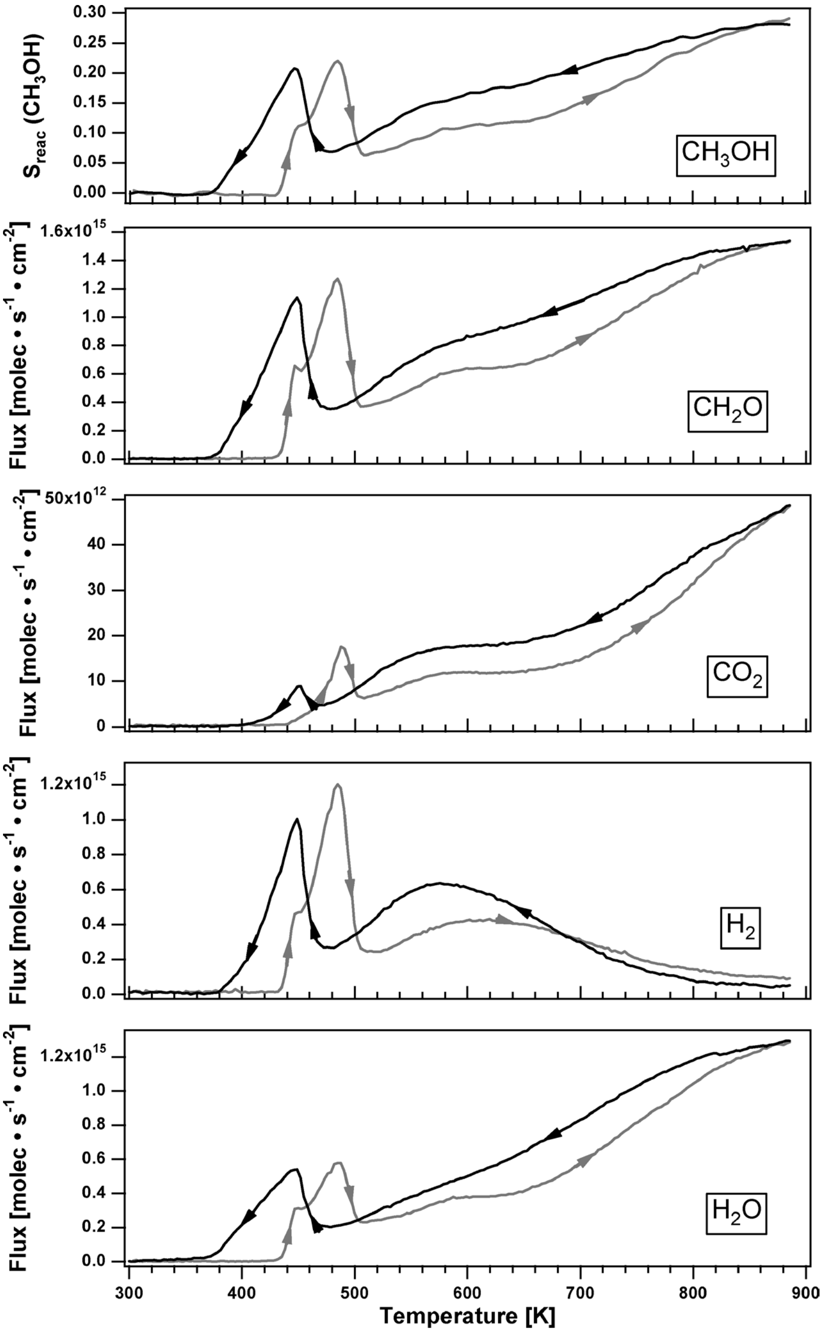

Fig. 1. Temperature programmed reaction spectroscopy in the 10^{-5} mbar range. The temperature was slowly cycled with $p(CH_3OH) = 1.0 \times 10^{-5}$ mbar and a ratio $p(CH_3OH):p(O_2) = 1:0.8$. The upper panel represents the reactive sticking coefficient of methanol, $s_{reac}(CH_3OH)$, the other panels indicate the production rates of the different products during methanol oxidation.

development of a (2 × 1) pattern that coexists with the diffuse (5 × 2) or c(2 × 2) patterns, respectively. The c(2 × 2) appears only during co-dosing in the 10^{-5} mbar range, and like to the (5 × 2)-methoxy, this structure is stable only up to ≈ 380 K.

To characterize the state of the surface under stationary reaction conditions, the Auger peaks of oxygen and carbon and the LEED pattern were monitored during temperature cycling in the 10^{-7} and 10^{-5} mbar range. The results are displayed in Fig. 3. The main observation is that during heating the surface is covered by carbon-containing species, whereas during cooling the surface is nearly carbon free but exhibits a medium oxygen coverage. At high temperatures (above 800 K), the surface exhibits a low adsorbate coverage. The (5 × 2)-methoxy and the c(2 × 2) ordered layers are observed only at low temperatures.

Clearly, the large hysteresis in the production rates is correlated with an equally large hysteresis in the adsorbate species and coverages. The amount of oxygen on the surface can be calibrated to the O_{KLL}/Cu_{KLL} ratio of 0.22 obtained

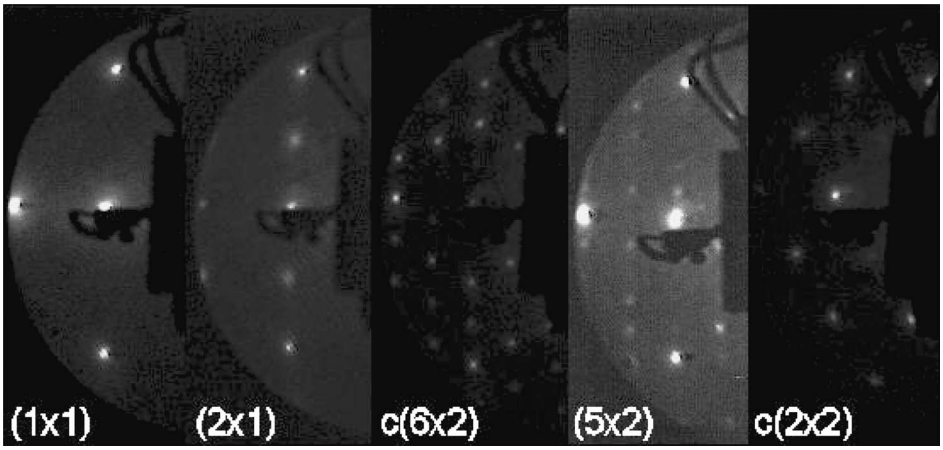

Fig. 2. LEED structures observed in methanol oxidation over Cu(110) (see text).

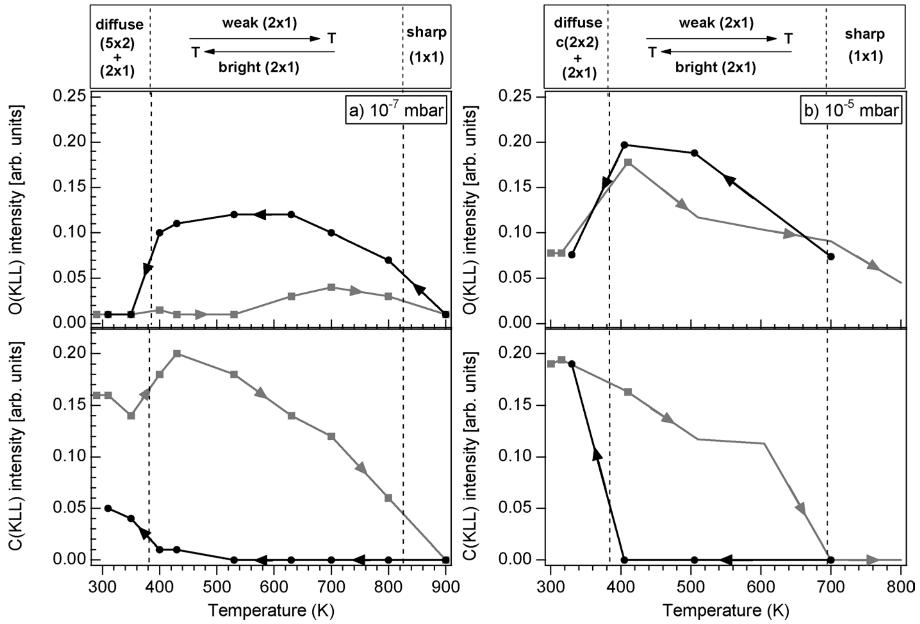

Fig. 3. In situ measured Auger data showing a hysteresis in the adsorbate coverages during temperature cycling under stationary reaction conditions. Shown are the O_{KLL}/Cu_{KLL} and C_{KLL}/Cu_{KLL} Auger intensity ratios during cycling in two different pressure ranges, at 10^{-7} and 10^{-5} mbar. Experimental conditions: (a) $p(CH_3OH) = 1 \times 10^{-7}$ mbar, $p(O_2) = 0.6 \times 10^{-7}$ mbar, (b) $p(CH_3OH) = 1 \times 10^{-5}$ mbar, $p(O_2) = 0.8 \times 10^{-5}$ mbar. The LEED structures observed in situ during the T-cycles are indicated.

from a (2 × 1) oxygen layer with 0.5 ML. Using this reference, we can estimate that in the 10^{-5} mbar experiment at high temperatures the surface is covered by ≈ 0.1 ML oxygen, whereas at about 400 K, ≈ 90% of the surface should be covered by a (2 × 1)-O adlayer.

Unfortunately, calibration of the carbon Auger signal turned out not to be feasible. Since Leibsle et al. [8] have reported the sensitivity of the methoxy layer to the electron beam of their LEED system, beam damaging effects are probably present in our measurements too. In any case, the beam damaging effect should decrease with increasing total pressure because with higher pressure the turnover frequency of the reaction will increase and with it the probability that dissociation products formed by the electron beam are removed through a clean-off reaction. This effect could be responsible for the small oxygen signal that is seen in the heating part of the 10^{-7} mbar cycle, because at 10^{-5} mbar the oxygen coverage during heating is substantial. This is what one would expect, because if the carbon is present as a methoxy or formate species, a correspondingly large oxygen signal has to be found. Thus the absence of such an oxygen signal in the 10^{-7} mbar range might well be due to beam damaging effects. We have no indication that aside from this possible effect any other results are significantly influenced by beam damaging.

3.3. PEEM

The problem of beam damaging effects can be avoided with the use of PEEM to monitor the state of the surface under reaction conditions. PEEM images primarily the local work function with a typical spatial resolution of 1 µm. The original motivation to use PEEM in this study has been the idea that the ignition and extinction phenomena that occur in the hysteresis experiments might be associated with the spreading of reaction fronts. However, in the investigated parameter range from 10^{-7} to 10^{-4} mbar, all surface changes occurred spatially uniformly on the length scales accessible to PEEM. We can nevertheless use the PEEM intensity to monitor the work function (WF) changes of the surface. The square root of the PEEM intensity was shown to follow linearly the negative work function change, that is to say, high WF areas are imaged as dark and low WF areas as bright in PEEM. Since our PEEM intensity was not calibrated against a Kelvin probe, we cannot quantitatively measure the WF. We therefore define a simple arbitrary scale of the PEEM intensity by taking the intensity of the clean Cu(110) as 1.0. With the same settings different structures were prepared and their PEEM intensity was measured. On the same scale the (2 × 1)-O yields a value of 0.4, the c(5 × 2)-methoxy a value of 1.4–1.6, and the c(2 × 2) a value of 0.67. All of these values are reproducible within 15%.

The variation in the scaled PEEM intensity during temperature cycles at 10^{-7} and 10^{-5} mbar is displayed in Fig. 4, together with the change in catalytic activity expressed here via the reactive sticking coefficient of methanol, s_{reac}. As expected, the PEEM intensity varies between two extrema, given by the intensity of the (5 × 2)-methoxy and the (2 × 1)-O, but over a wide range the intensity is much closer to the oxygen structure than to the methoxy phase.

The double-peak structure of the reactivity peak at ≈ 450 K during heating, which is hidden as a shoulder in the measurement at 10^{-5} mbar (Fig. 1), clearly shows up in the PEEM intensity. The comparison with Fig. 1 reveals that the higher-lying of the two reactivity peaks coincides with the CO_2 production maximum, which in contrast to all other products has no clearly discernible second peak, but a slowly increasing onset. The relatively low PEEM intensity is observed in the unreactive range between 300 and 400 K and is consistent with the mixture of oxygen and methoxy islands visible in LEED. The Auger data in Fig. 2 show that in the 10^{-5} mbar range the oxygen coverage grows continuously with heating from 300 K until ignition occurs at ≈ 430 K. This growth in oxygen coverage is reflected by a corresponding decrease in PEEM intensity in Fig. 4.

In an intermediate temperature range between 300 and 700 K the hysteresis effects are substantially larger in the 10^{-7} mbar range than at 10^{-5} mbar, as far as the oxygen is concerned. This is reflected by the Auger data in Fig. 3 and by the PEEM intensity in Fig. 4. The oxygen measured by Auger electron spectroscopy is the sum of chemisorbed oxygen and oxygen in organic compounds. The Auger data in the 10^{-5} mbar range show no large hysteresis effect, but since we observe in LEED only weak (2 × 1) spots with heating and sharp, bright (2 × 1) spots during cooling, we can conclude that the amount of chemisorbed oxygen has increased strongly on the cooling branch.

At high temperatures, in the range of 800–900 K, the PEEM intensity approaches the level of the clean surface, but the difference remains finite and becomes smaller with decreasing total pressure. At 10^{-5} mbar one can estimate a remaining oxygen coverage of 0.1 from a linear extrapolation of the PEEM data, which agrees with the Auger measurements in Fig. 3.

4. Discussion

We can describe the different regimes of the reaction in a temperature-programmed experiment as follows, starting with the preparation of a (5 × 2)-methoxy structure.

4.1. Transformation of the adlayer without release of reaction products (≈ 300–400 K)

The initially “perfect” (5 × 2)-methoxy slowly transforms into a mixed diffuse (5 × 2)-methoxy/(2 × 1)-O adlayer, indicating some kind of phase separation. If we assume that further decomposition of the methoxy species to formaldehyde requires vacant adsorption sites, as suggested by the STM results of Bowker [8], then the surface fully covered with oxygen or methoxy species would be quite unreactive. This explains why we do not observe any product formation in this regime, even though the methoxy decomposition is thermally activated. Nevertheless, some of the methoxy is transformed into the formate species, which, however, does not lead to the release of products into the gas phase, but to their accumulation on the surface at low T.

4.2. Ignition of the reaction at $T \approx 400$ K

The ignition of the reaction is presumably initiated by the thermal decomposition of accumulated formate to CO_2 because the immediate desorption of the CO_2 creates vacant sites where methoxy can react to formaldehyde, which is also immediately released into the gas phase as product. This process creates additional vacant sites, accelerating the reaction. In addition, formate is generated as a side product according to (5), (6), but this pathway becomes significant only at high pressure. Apparently, the thermal decomposition of formate does not require vacant sites, because otherwise an autocatalytic behavior would result, generating a steep increase in CO_2 production, which is not seen in the experiment.

4.3. Formaldehyde formation via oxidehydrogenation at $520\ \mathrm{K} < T < 750\ \mathrm{K}$ (10^{-5} mbar range)

As shown by kinetic measurements, the overall stoichiometry of the reaction in this temperature range follows at low pressure ($p < 10^{-4}$ mbar) the oxidehydrogenation

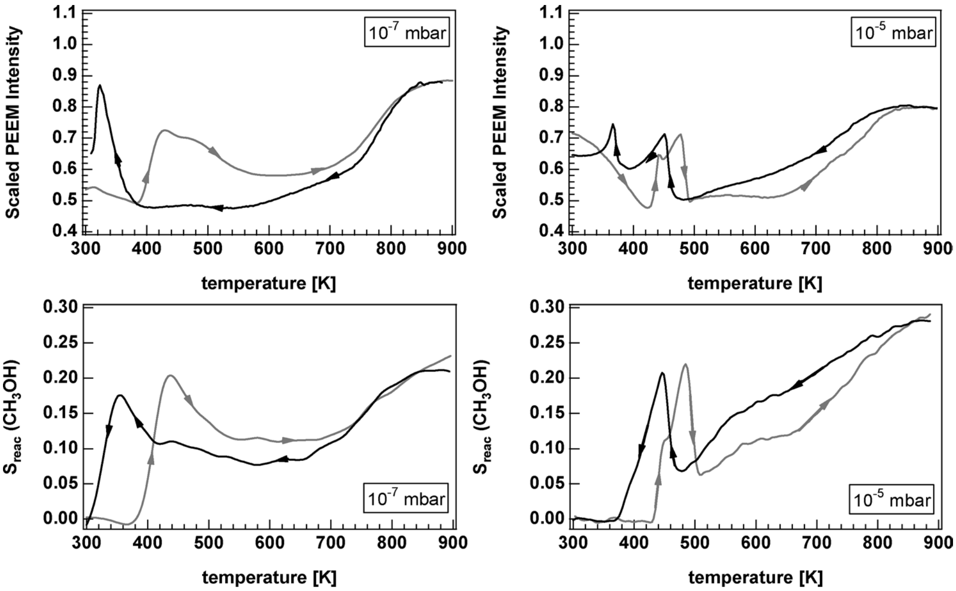

Fig. 4. PEEM intensity variations and the corresponding changes in the reactivity of the surface expressed here as reactive sticking coefficient of methanol, $s_{reac}(CH_3OH)$. Temperature cycles in two different pressure ranges, at 10^{-7} and at 10^{-5} mbar have been conducted. Experimental conditions: 10^{-7} mbar range: $p(CH_3OH) = 1.0 \times 10^{-7}$ mbar with $p(CH_3OH):p(O_2) = 1:0.6$; 10^{-5} mbar range: $p(CH_3OH) = 1.0 \times 10^{-5}$ mbar with $p(CH_3OH):p(O_2) = 1:0.8$. The PEEM data are scaled to the intensity of the clean Cu(110) surface as unity.

route (1) [16]. The fact that the generated hydrogen adatoms desorb rather than further react to H_2O indicates that the oxygen present on the surface is not reactive. This is the case when the oxygen is bound in organic molecules such as methoxy or formate species. The weak (2 × 1) spots we observe in LEED seemingly contradict this statement since they demonstrate that chemisorbed oxygen is present. Apparently these oxygen islands can occupy only a relatively small fraction of the surface. Furthermore, since only the edge atoms of the islands are reactive, only a small number of adatoms of large oxygen islands can contribute to the reactivity.

4.4. *Formaldehyde formation via oxidehydrogenation without hydrogen formation at $T > 750$ K (10^{-5} mbar range)*

In the temperature range above 750 K (10^{-5} mbar), the kinetics of the overall reaction follows the stoichiometry of (2) without hydrogen release [16]. The adsorbate coverages are small in this range, and the reactivity of the surface is high. Ordered adsorbate phases appear not to play an important role in this range, and the reaction probably proceeds through isolated adsorbate molecules or small clusters.

One other prominent feature of the reaction kinetics in this system is the presence of a very large hysteresis in temperature-dependent measurements. In surface reactions a hysteresis typically arises if one of the reactants present in large amounts on the surface inhibits the adsorption of the other reactant. The LEED/PEEM/Auger measurements conducted here clearly indicate that the hysteresis in the reaction rates is connected with a corresponding hysteresis in the adsorbate coverages. The changes in the brightness of the (2 × 1) LEED spots (Fig. 3) indicate that in addition to the total amount of oxygen, the adlayer ordering may also be different.

The kinetic measurements have shown that the low-temperature reactivity peak around 400 K undergoes a strong upward shift with increasing total pressure, which amounts roughly to a 20 K shift per decade difference in pressure. Quite generally, the increase in pressure will increase the coverage and shift processes to higher temperatures if the number of vacant sites plays an essential role. Here we can be more specific because the increase in total pressure from 10^{-7} to 10^{-5} mbar proved to be sufficient to cause a change in the structure, from a (5 × 2) at low pressure to a c(2 × 2) at high pressure. This pressure-induced structural change might be responsible for the shift in the reaction peaks. Recent X-ray photoelectron spectroscopy data indicate that the c(2 × 2) structure, whose assignment has been debated in the literature, is in fact due to a formate species [19].

5. Conclusion

The stationary kinetics of methanol oxidation over a Cu(110) surface is associated with a broad rate hysteresis upon variation of the temperature. The origin of the hysteresis can be attributed to two differently reactive surface phases connected with different carbon-containing species and different oxygen coverages. Ordered overlayers of reaction intermediates, the (5 × 2)-methoxy and the c(2 × 2)-formate, occur only in small, roughly 80 K-wide T intervals above 300 K, where the catalytic activity is negligible. Only the low-temperature reactivity peak at ≈ 400–500 K is associated with a substantial adsorbate coverage, whereas the high-temperature reactivity peak at 900 K correlates with a largely adsorbate-free surface. Apparently high adsorbate coverages have a negative effect on the reactivity of the surface. This can be traced back to a lack of vacant sites which are required for the decomposition steps to proceed and for allowing the reacting species to diffuse.

Acknowledgment

This work was supported by the DFG under the priority program 1091 “Bridging the gap between ideal and real systems in heterogeneous catalysis.”

References

[1] J. Walker, Formaldehyde, Reinhold, Amsterdam, 1964;
Ullmann, Encyclopedia of Industrial Chemistry, Chemie, Weinheim, 1982.
[2] P.L. Hansen, J.B. Wagner, S. Helveg, J.R. Rostrup-Nielsen, B.S. Clausen, H. Topsoe, Science 295 (2002) 2053.
[3] A. Knop-Gericke, M. Hävecker, T. Schedel-Niedrig, R. Schlögl, Catal. Lett. 66 (2000) 215.
[4] A. Knop-Gericke, M. Hävecker, T. Schedel-Niedrig, R. Schlögl, Top. Catal. 10 (2000) 187.
[5] I.E. Wachs, R.J. Madix, J. Catal. 53 (1978) 208.
[6] A.F. Carley, A.W. Owens, M.K. Rajumon, M.W. Roberts, Catal. Lett. 37 (1996) 79.
[7] S.M. Francis, F.M. Leibsle, S. Haq, N. Xiang, M. Bowker, Surf. Sci. 315 (1994) 284.
[8] F.M. Leibsle, S.M. Francis, S. Haq, M. Bowker, Surf. Sci. 318 (1994) 46.
[9] S.L. Silva, R.M. Lemor, F.M. Leibsle, Surf. Sci. 421 (1999) 135.
[10] S.L. Silva, R.M. Lemor, F.M. Leibsle, Surf. Sci. 421 (1999) 146.
[11] A.F. Carley, P.R. Davies, G.G. Mariotti, S. Read, Surf. Sci. 364 (1996) 525.
[12] P.R. Davies, G.G. Mariotti, J. Phys. Chem. 100 (1996) 19975.
[13] A.H. Jones, S. Poulston, R.A. Bennet, M. Bowker, Surf. Sci. 380 (1997) 31.
[14] S. Poulston, A.H. Jones, R.A. Bennet, M. Bowker, J. Phys. Condens. Mater. 8 (1996) 765.
[15] M. Bowker, Top. Catal. 3 (1996) 461.
[16] L. Zhou, S. Günther, R. Imbihl, J. Catal. 230 (2005) 166.
[17] R.A. Bennet, S. Poulston, M. Bowker, J. Chem. Phys. 108 (1998) 6916.
[18] M. Bowker, S. Poulston, R.A. Bennet, P. Stone, A.H. Jones, S. Haq, P. Hollins, J. Mol. Catal. A 131 (1998) 185.
[19] S. Günther, L. Zhou, R. Imbihl, in preparation.