Methanol synthesis on Cu(100) from a binary gas mixture of CO_2 and H_2

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The rate of methanol synthesis over a Cu(100) single crystal from a 1 : 1 mixture of CO_2 and H_2 has been measured at a total pressure of 2 bar and a temperature range of 483–563 K. At these conditions the apparent activation energy is determined to be 69 kJ mol^{-1}, and at 543 K the turnover rate is 2.7×10^{-4} (site $s)^{-1}$. A kinetic model for the methanol synthesis is presented. Predictions from this model are in good agreement with the rates of methanol synthesis observed on real catalysts at industrial conditions.

Keywords: methanol; synthesis; Cu(100); hydrogenation

1. Introduction

The synthesis of methanol has achieved much attention in the literature [1]. Still, several of the most important questions remain unanswered or controversial. Methanol is synthesized commercially from a gas mixture of CO, CO_2, and H_2 at 220–240°C and 50–100 bar over a catalyst containing Cu, ZnO, and Al_2O_3 [1]. There is now good evidence, from ^{14}C labeling [2–4] that CO_2 is the main source of the carbon in the methanol. Other investigations show that methanol cannot be synthesized from a CO, H_2 mixture over Cu on SiO_2 catalysts [5] consistent with the labeling experiments [2–4].

Concerning the role of the Cu and the ZnO, there is strong disagreement. Some authors suggest that copper in the valence state Cu^+ stabilized by the ZnO plays an important role [6]. X-ray photoelectron spectroscopy (XPS) investigations of a catalyst, transferred from working conditions to the spectrometer under high

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vacuum, show, however, that the copper within the limits of detectability is exclusively in the metallic phase [7]. In situ surface X-ray diffraction (XRD) and extended X-ray absorption fine structure (EXAFS) investigations on a working catalyst confirm this [8,9].

It has been shown that the methanol synthesis rate scales almost linearly with the area of metallic copper in the catalyst [10], and that the turnover rates of $Cu/ZnO/Al_2O_3$ catalysts are about the same as those where Cu is supported on other materials [10] suggesting strongly that metallic Cu is the active material.

A very interesting experiment is the synthesis of methanol over a single crystal of copper in connection with an UHV system, so that the surface is well defined and can be characterized before and after the synthesis. It should then be possible to answer the question whether metallic copper is active in the synthesis. This experiment was recently performed by Szanyi et al. [11], who showed that methanol was synthesized. However, in that work it was concluded that the observed rate was far too low compared to what would be required, if it should explain the activity of the commercial catalyst.

In the present paper we also investigate the synthesis of methanol over a Cu single crystal. Contrary to Szanyi et al. [11] we find a turnover rate that can explain the rates observed on real catalysts. Furthermore, the only species found on the surface after reaction is carbon and oxygen exclusively in the form of formate and hydrogen.

2. Experimental details and results

The experiments were performed in a custom designed UHV chamber equipped with facilities for XPS, high resolution electron energy loss spectroscopy (HREELS), low energy electron diffraction (LEED), and a quadrupole mass spectrometer (QMS) for temperature programmed desorption (TPD). Furthermore the chamber is also equipped with a high pressure cell (HPC) which allows the crystal to be exposed to gases at pressures up to 10 bar and subsequent analyses in UHV without exposure to contaminating atmospheres. For further details of the system, see ref. [12].

The crystal was prepared and cleaned as described in ref. [12]. As a new feature, however, the crystal was mounted on a gold wire, so it could be resistively heated. Gold was selected in order to minimize undesired reactions on the surfaces of the hot wires. The temperature was measured by a chromel–alumel thermocouple pressed into a hole in the crystal.

In this study, the experiments were performed at a constant pressure of 2 bar and a fixed gas composition of $H_2 : CO_2 = 1 : 1$. A synthesis experiment was done as follows: (1) The exposure to the synthesis gas was performed as described in ref. [13]. (2) At the end of an exposure, the crystal was cooled to room temperature and simultaneously, the contents of the high pressure cell was expanded to a Cu coil cooled in liquid nitrogen. (3) The hydrogen was then slowly pumped away through the cell. Thereafter the coil was thawed to room temperature and then cooled in a MeOH(s)/MeOH(ℓ) slurry (178 K). Then the CO_2 was pumped away. (4) The coil was again isolated and heated to 323 K and the species remaining in the coil were admitted into the QMS where these were analyzed. Details of the above procedure will be given elsewhere [14].

Methanol was identified as a reaction product by the mass spectrometer cracking patterns ($m/e = 31$, 32 and 30) which were identical to those obtained by expanding known amounts of methanol into the high pressure cell, mixing with synthesis gas and then distilling as described above. Furthermore, by performing a synthesis experiment with a $D_2 : CO_2$ mixture a shift in the dominating m/e values was observed: 31 to 34, 32 to 36 and 30 to 32 indicating the synthesis of CD_3OD. The quantitative determining of methanol was obtained from the integral of the $m/e = 31(34)$ peak [14].

After each synthesis experiment, the crystal was checked by XPS and the only species detected was carbon and oxygen in a stoichiometric ratio of 1 : 2, which by use of HREELS and TPD was identified as formate as in ref. [12]. Carbon in the form of graphite and sulfur was found to be common contaminants, when the system had been opened to air, but extensive bakeout in the high pressure cell for several days in H_2 limited these contaminations to below detection limit.

In order to estimate an absolute turnover frequency for the methanol synthesis, it was necessary to perform a calibration. A fixed volume of 1 cm^3 was filled with methanol to a known pressure in the range of 0.1–1 mbar, which then was admitted to the high pressure cell. Synthesis gas to a pressure of 2 bar was then let into the high pressure cell, and the distillation and detection procedure (4)–(10) was performed. In this way a linear dependency of the QMS signal and known amounts of methanol was established [14]. A similar procedure was attempted for CH_2O without success as most of the formaldehyde disappeared in the high pressure cell.

Blind experiments showed that methanol was only produced if the crystal was heated. Thus formation of methanol during detection or distillation could be eliminated. In order to check whether the produced methanol originated from the crystal or from somewhere else in the high pressure cell, synthesis experiments were also performed with the crystal substituted by a gold plated Cu crystal of the same dimensions as the clean crystal. In this case, it was found that the background contribution to the synthesized methanol was 5–10% of the amount measured on a clean Cu(100) surface. The background scaled almost with the crystal temperature in the same manner as the signal originating from the crystal, which suggested that the background originated from the power feedthroughs (consisting of Cu) on which the Au-wires for the crystal heating were mounted or from the chromel–alumel thermocouple. XPS investigations showed, that the Au surface was clean after each synthesis experiment.

In fig. 1, the measured amounts of methanol are plotted as function of the time of exposure at a pressure of 2 bar, and a gas composition of $CO_2 : H_2 = 1 : 1$ at dif-

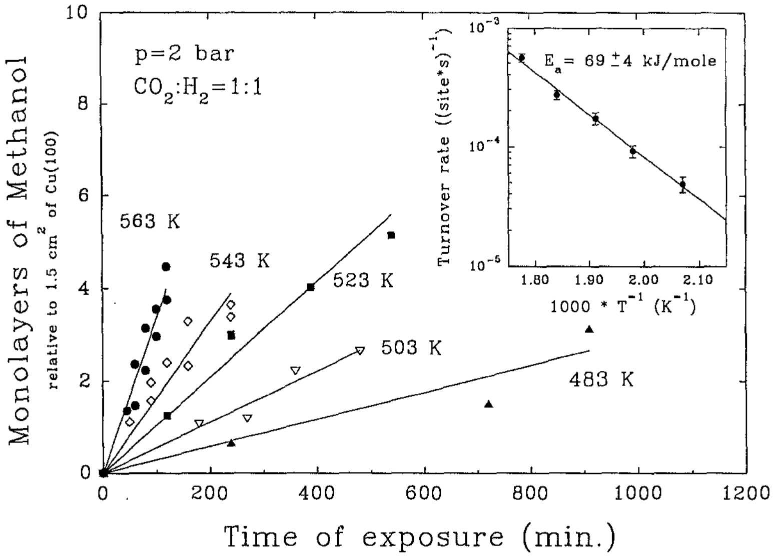

Fig. 1. The amounts of synthesized methanol as function of time at different temperatures and a pressure of 2 bar. In the inset, the turnover rates are plotted in an Arrhenius plot, yielding an apparent activation energy of 69 kJ mol^{-1}.

ferent temperatures. In the inset, the turnover rates are plotted in an Arrhenius plot. The apparent activation energy is 69 ± 4 kJ mol^{-1} and at 543 K, the absolute turnover rate is 2.7×10^{-4} $(site\,s)^{-1}$.

3. Kinetic modelling and discussion

We have to consider the two following reactions in constructing a model of the methanol synthesis:

$$CO + H_2O \rightleftharpoons CO_2 + H_2\,, \qquad (1)$$

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O\,. \qquad (2)$$

The proposed reaction mechanism is shown in table 1. Here * symbolizes a free surface site and X* symbolizes the adsorbed atom or molecule X. The first eight elementary steps describe the kinetics of the redox mechanism for the water–gas shift reaction (WGS), which has been analyzed in great detail [15]. The WGS model [15] successfully reproduced results measured on industrial catalysts over a wide range of temperatures, pressures and gas compositions. The next seven steps complete our proposed kinetic model for the methanol synthesis.

The rate limiting step in our model is unknown, and we have to consider steps 10, 11 and 12 as possible candidates. If step 11, the hydrogenation of dioxomethylene, is taken as the rate limiting step, then we get the following set of rate and equilibrium equations:

Table 1
Elementary steps in the kinetic model

Step	Surface reactions
1	$H_2O(g) + * \rightleftharpoons H_2O*$
2	$H_2O* + * \rightleftharpoons OH* + H*$
3	$2OH* \rightleftharpoons H_2O* + O*$
4	$OH* + * \rightleftharpoons O* + H*$
5	$2H* \rightleftharpoons H_2(g) + 2*$
6	$CO(g) + * \rightleftharpoons CO*$
7	$CO* + O* \rightleftharpoons CO_2* + *$
8	$CO_2* \rightleftharpoons CO_2(g) + *$
9	$CO_2* + H* \rightleftharpoons HCOO* + *$
10	$HCOO* + H* \rightleftharpoons H_2COO* + *$
11	$H_2COO* + H* \rightleftharpoons H_3CO* + O*$
12	$H_3CO* + H* \rightleftharpoons CH_3OH* + *$
13	$CH_3OH* \rightleftharpoons CH_3OH(g) + *$

$$K_1 \frac{p_{\mathrm{H_2O}}}{p_0} \theta_* = \theta_{\mathrm{H_2O}*} , \tag{3}$$

$$r_2 = k_2 \theta_{\mathrm{H_2O}*} \theta_* - \frac{k_2}{K_2} \theta_{\mathrm{OH}*} \theta_{\mathrm{H}*} , \tag{4}$$

$$K_3 \theta^2_{\mathrm{OH}*} = \theta_{\mathrm{H_2O}*} \theta_{\mathrm{O}*} , \tag{5}$$

$$r_4 = k_4 \theta_{\mathrm{OH}*} \theta_* - \frac{k_4}{K_4} \theta_{\mathrm{O}*} \theta_{\mathrm{H}*} , \tag{6}$$

$$K_5 \theta^2_{\mathrm{H}*} = \frac{p_{\mathrm{H_2}}}{p_0} \theta^2_* , \tag{7}$$

$$K_6 \frac{p_{\mathrm{CO}}}{p_0} \theta_* = \theta_{\mathrm{CO}*} , \tag{8}$$

$$r_7 = k_7 \theta_{\mathrm{CO}*} \theta_{\mathrm{O}*} - \frac{k_7}{K_7} \theta_{\mathrm{CO_2}*} \theta_* , \tag{9}$$

$$K_8 \theta_{\mathrm{CO_2}*} = \frac{p_{\mathrm{CO_2}}}{p_0} \theta_* , \tag{10}$$

$$K_9 \theta_{\mathrm{H}*} \theta_{\mathrm{CO_2}*} = \theta_{\mathrm{HCOO}*} \theta_* , \tag{11}$$

$$K_{10} \theta_{\mathrm{HCOO}*} \theta_{\mathrm{H}*} = \theta_{\mathrm{H_2COO}*} \theta_* , \tag{12}$$

$$r_{11} = k_{11} \theta_{\mathrm{H_2COO}*} \theta_{\mathrm{H}*} - \frac{k_{11}}{K_{11}} \theta_{\mathrm{H_3CO}*} \theta_{\mathrm{O}*} , \tag{13}$$

$$K_{12}\theta_{\mathrm{H_3CO*}}\theta_{\mathrm{H*}} = \theta_{\mathrm{CH_3OH*}}\theta_{*}\,, \tag{14}$$

$$K_{13}\theta_{\mathrm{CH_3OH*}} = \frac{p_{\mathrm{CH_3OH}}}{p_0}\theta_{*}\,. \tag{15}$$

K_i are the equilibrium constants calculated from the partition functions of the intermediates, k_i are the rate constants assumed to be of the Arrhenius form and p_0 is the thermodynamic reference pressure. The coverage $\theta_{\mathrm{X*}}$ of the intermediates can be found from the conservation law $\sum_i \theta_i = 1$, the equations (3)–(17) and the requirement of mass balances of OH* and O*. In the present model, one active site is defined as two Cu sites with c(2 × 2) the highest possible coverage.

The net rate of the water and methanol productions will then be

$$r_{\mathrm{CH_3OH}} = k_{11}K_{10}\frac{\theta_{\mathrm{HCOO*}}\theta^2_{\mathrm{H*}}}{\theta_*} - \frac{k_{11}}{K_{11}}\theta_{\mathrm{H_3CO*}}\theta_{\mathrm{O*}}\,, \tag{16}$$

$$r_{\mathrm{H_2O}} = k_{11}K_{10}\frac{\theta_{\mathrm{HCOO*}}\theta^2_{\mathrm{H*}}}{\theta_*} - \frac{k_{11}}{K_{11}}\theta_{\mathrm{H_3CO*}}\theta_{\mathrm{O*}} - k_7\theta_{\mathrm{CO*}}\theta_{\mathrm{O*}} + \frac{k_7}{K_7}\theta_{\mathrm{CO_2*}}\theta_*\,. \tag{17}$$

General techniques to determine the model parameters have been published previously [15]. A paper is in preparation with a detailed discussion of the methods used to derive all the input parameters [16]. For the purpose of this letter a short presentation will be given of the method used to determine the ground state energy of formate. TPD results of formate decomposition on Cu(100) [12] were analyzed to deduce the ground state energy E_g of chemisorbed formate. We define the rate constant of formate decomposition as $k_{-9} = k_9/K_9$. The equilibrium constant K_9 is a function of E_g, and the extraction of the ground state energy was performed by a best fit to the TPD curves. Published results of formate synthesis on Cu(100) [12] were used to determine the rate constant of formate synthesis k_9. A kinetic model was presented in ref. [12] consisting of three steps equivalent to the steps 5, 8, and 9 in our model. In the investigation of the model by the authors of ref. [12] a repulsive formate–formate interaction energy of 14 kJ mol^{-1} was introduced to explain the measured data. We have analyzed the published data using the same kinetic model with no pairwise interactions of species. Measured data were reproduced successfully without the formate–formate repulsion if the coverage of formate $\theta_{\mathrm{HCOO*}} \leqslant 0.25$ ML. The competition for free surface sites at a higher coverage of formate requires a more detailed statistical mechanical treatment. However, in this work the coverage of formate was always below $\theta_{\mathrm{HCOO*}} \leqslant 0.05$ ML. For simplicity we neglect the formate–formate interaction and only use points with $\theta_{\mathrm{HCOO*}} \leqslant 0.25$ ML in the calculation of the rate constant k_9. The value of E_g was required in the evaluation of k_9, but this problem was solved by repeating the fitting procedures of E_g and k_9, until a self-consistent solution was obtained. The complete kinetic model in this work was used to derive the rate constant of methanol synthesis k_{11} by an analysis of the presented methanol data. The results are

$A_9 = 2.2 \times 10^{10}$ (site s)$^{-1}$, $E_9^{\ddagger} = 78$ kJ mol^{-1}, $A_{11} = 4.3 \times 10^{20}$ (site s)$^{-1}$, $E_{11}^{\ddagger} = 159$ kJ mol^{-1}, $E_g = 553$ kJ mol^{-1}, $K_{10} = 0.78 \exp(-37.0 \text{ kJ mol}^{-1}/RT)$, $K_{11} = 1.80 \exp(-70.7 \text{ kJ mol}^{-1}/RT)$.

The methanol synthesis experiment on Cu(100) has been repeated with different total pressures and varying gas compositions. All results were reproduced successfully by our kinetic model [14,16]. The model prediction of the overall activation energy was 65 kJ mol^{-1} at pressure $p = 2$ bar and temperature $T = 543$ K, very close to the measured result of 69 ± 4 kJ mol^{-1}.

Graaf et al. [17,18] have measured the activity of a commercial Cu/ZnO/Al_2O_3 catalyst in a spinning basket reactor at pressures $p = 15$–50 bar, temperatures $T = 483$–518 K, and various gas mixtures of H_2, CO_2 and CO. The Cu area of the catalyst is 20 m^2 (g catalyst)$^{-1}$ [19]. The kinetic model can now be extrapolated to the conditions where the experiments [17,18] were performed. Agreement between measured rates and model predicted rates is expected, if the active phase of the catalyst is metallic copper. In fig. 2, the rates measured in Graaf's work are plotted versus the rates calculated from the kinetic model described above. The agreement is good, and in no case is the calculated rate off by more than a factor of three, except for a few data points at conditions where the measured turnover rate is very low (below 1 × 10^{-3} (site s)$^{-1}$). This accuracy is as good as can be expected from the present simple model, which is based on a mean field description of adsorbates with no interaction except the nearest neighbor repulsion determining the maximum coverage.

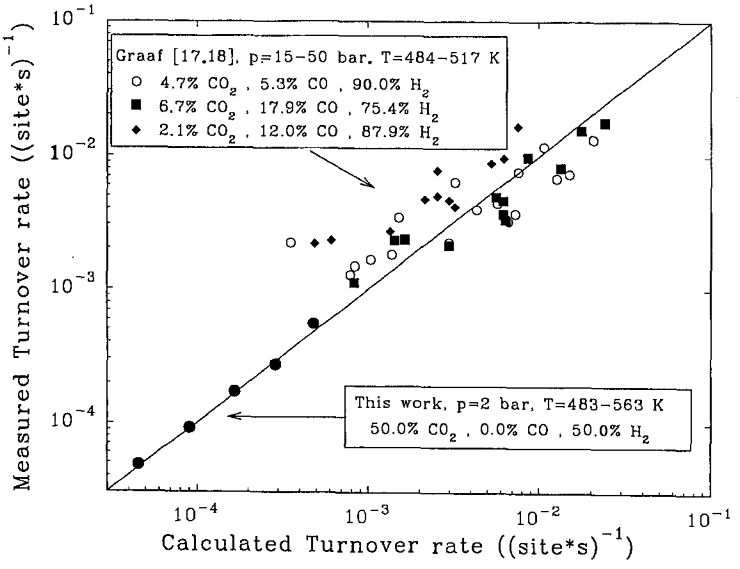

Fig. 2. Correlation between measured and calculated turnover rates of methanol synthesis for a real catalyst working under industrial conditions and the single crystal results from this work.

A systematic deviation of the data points can be observed in fig. 2. Predicted turnover rates are underestimated with a high p_{CO}/p_{CO_2} ratio and overestimated with a low p_{CO}/p_{CO_2} ratio. An explanation of this feature was given by Clausen et al. [20]. It was suggested, that the active area of the catalyst depends on the gas composition. Calculations showed a considerable increase of the Cu area with a high reduction potential of the gas. This result is in nice accordance with the systematic deviations of the turnover rates seen in fig. 2.

The observation that methanol can be synthesized on a Cu single crystal from CO_2 and H_2, is in good agreement with the conclusion from the labeling experiments [2–4] that CO_2 is the carbon source in the synthesized methanol. This result is also in agreement with a recent FTIR study by Millar and co-workers [21], who showed that methanol could be synthesized from CO_2 and H_2 on both a Cu/SiO_2 and a $Cu/ZnO/SiO_2$ catalyst but not on a ZnO/SiO_2 catalyst. Furthermore, in ref. [21] it was suggested that formate was the pivotal intermediate, since this was the only species observed on the Cu part of the catalyst. That observation is not in disagreement with the conclusion in this work, that step 11 is rate limiting, since the model from this work suggests that the coverage of CH_2O_2* always will be very low (below 10^{-4} at the conditions of ref. [21]) and therefore hardly detectable.

4. Summary

The findings of this work can be summarized as follows:

– It has been shown that methanol can be synthesized on a Cu(100) crystal from a gas mixture of CO_2 and H_2. The apparent activation energy is 69 ± 4 kJ mol^{-1}, and at 543 K the turnover rate is 2.7×10^{-4} (site s)$^{-1}$ at a pressure of 2 bar and a gas composition of $CO_2 : H_2 = 1 : 1$.

– It is possible from the presented kinetic model to give semi-quantitative predictions of the rates observed on a commercial catalyst working under industrial conditions.

– The implication is that metallic Cu is the active catalyst. The role of ZnO is then one of determining the degree of dispersion, and possibly, distribution of Cu surface planes exposed. This is in good agreement with the general linear relationship between the methanol activity and the Cu area [10]. The deviation from this may then be due to different distributions of Cu surface planes for different synthesis gas compositions [20].

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