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A thermogravimetric study of the partial oxidation of methanol for hydrogen production over a $Cu/ZnO/Al_2O_3$ catalyst

Stefan Rabe *, Frédéric Vogel

Paul Scherrer Institut, General Energy Research Department, Laboratory for Energy and Materials Cycles, CH-5232 Villigen PSI, Switzerland

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ABSTRACT

The partial oxidation of methanol for the production of hydrogen was investigated in both a fixed-bed microreactor and in a thermogravimetric analyzer (TG-FTIR) from 180 °C to 250 °C using a commercial $Cu/ZnO/Al_2O_3$ catalyst. In the microreactor, a hot spot in the undiluted catalyst bed of 4 K and 32 K was observed at 180 °C and 220 °C, respectively. Methanol conversion was strongly accelerated between 180 °C and 220 °C. In the TG-FTIR experiments, the reduced copper was completely oxidized to cuprite, Cu_2O, with increasing time-on-stream in the presence of oxygen and methanol ($O_2/MeOH = 0.5$) at 180 °C. The selectivity to formaldehyde increased in the same manner as the catalyst was oxidized to cuprite. In contrast, at 250 °C the catalyst remained completely reduced for the same $O_2/MeOH$ ratio. Two main reaction pathways are proposed explaining the influence of the copper oxidation state on the product distribution.

1. Introduction

Methanol can be used as a fuel for direct methanol fuel cells (DMFC) which are regarded as an interesting option for powering small to midsize electronic devices. However, the efficiency of the DMFC is lower compared to hydrogen driven fuel cells. An efficient reforming of methanol to produce hydrogen can increase the overall efficiency of methanol fuel cell systems [1]. Furthermore, reformed methanol fuel cells may be used in fuel cell driven vehicles since they can help to reduce greenhouse gas emissions [2]. Hydrogen can be extracted on-board from methanol by steam reforming (SR, Eq. (1)), partial oxidation (POX, Eq. (2)), or a combination of both reactions (autothermal reforming ATR, Eq. (4)). Heterogeneous copper-based catalysts exhibit an excellent selectivity to hydrogen since they do not catalyze the methanation reaction, as opposed to nickel and other metals.

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \qquad (1)$$

$$CH_3OH + 1/2O_2 \rightarrow CO_2 + 2H_2 \qquad (2)$$

$$CH_3OH + 3/2O_2 \rightarrow CO_2 + 2H_2O \qquad (3)$$

$$CH_3OH + 1/8O_2 + 3/4H_2O \rightarrow CO_2 + 11/4H_2 \qquad (4)$$

A compact fuel processor equipped with a commercially available Cu/ZnO catalyst was presented in the literature [3]. Several studies have been undertaken to investigate the properties of copper-based catalysts for the steam reforming reaction [4–12].

The dry partial oxidation reaction (POX, Eq. (2)) has received less attention [13]. The stability of copper-based catalysts is limited by sintering of the copper crystallites above ca. 300 °C. Furthermore, fully oxidized copper has no activity for POX, and only total oxidation (TOX, Eq. (3)) to carbon dioxide and water is observed [14].

The influence of oxygen on the reaction mechanism of the dry partial oxidation is still an open question. It has been shown that activity and selectivity of the Cu/ZnO catalysts strongly depend on the oxygen concentration of the feed. It was suggested that copper metal (Cu^0) is active for the partial oxidation of methanol to produce hydrogen whereas Cu^I favors the formation of water and carbon monoxide [14]. A detailed study of the copper oxidation state over Cu/ZnO/Al-catalysts using X-ray photoelectron spectroscopy revealed that at a low oxygen concentration in the feed ($O_2/MeOH = 0–0.25$) Cu^0 is the dominating species, independent of the temperature. A temperature dependence of the oxidation state was observed if a higher oxygen content ($O_2/MeOH = 0.42$) was applied: the formation of Cu^I was detected between 470 K and

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* Corresponding author. Tel.: +41 56 310 2640; fax: +41 56 310 21 99.
E-mail address: stefan.rabe@psi.ch (S. Rabe).

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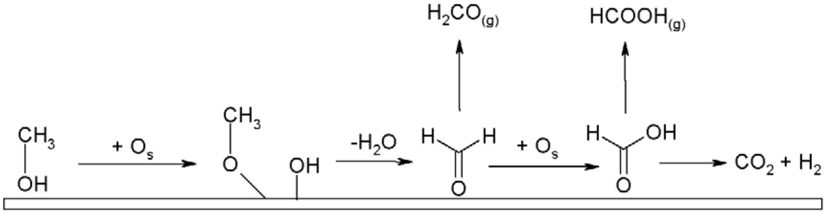

Fig. 1. Surface reaction network of the dry partial oxidation of methanol over a copper catalyst.

510 K, above 530 K only Cu^0 was detected [15]. The oxidation state of the catalyst during the methanol POX may be also affected by the support material [15,16]. The methanol POX over an unsupported copper catalyst was also investigated by in-situ X-ray absorption spectroscopy [17–20]. It was found that the activity of the catalyst was a function of the O_2/MeOH ratio in the feed. It was proposed that the active structure of the catalyst consisted of a Cu^0-lattice in which oxygen atoms are intercalated.

The oxidative steam reforming of methanol over a Cu/ZnO catalyst was also investigated by means of in-situ time-resolved X-ray absorption spectroscopy [21].

The results of this study with respect to the oxidation state of the catalyst were similar to the dry POX: the catalyst was oxidized at low temperature and reduced at higher temperature.

The formation of intermediate products (i.e. methyl formate and formaldehyde) during the partial oxidation of methanol for hydrogen production under various reaction conditions has been reported in the literature. The decomposition of methanol over $Cu/ZnO/Al_2O_3$ catalysts yields hydrogen and CO. Methyl formate, $HCOOCH_3$, is formed as an intermediate [22]. However, to our knowledge a detailed study of the conditions at which these intermediates are formed has not been published.

The mechanism of the dry partial oxidation (POX, Eq. (2)) on Cu(1 1 0) surfaces was also studied [23–26]. Formaldehyde and formate species are involved in the surface reaction network (Fig. 1).

It was found that for oxygen-rich mixtures formaldehyde is the major product but when methanol was in 5:1 excess, formate (HCOOH) was produced [24]. A combustion-reforming mechanism was proposed for Cu/ZnO catalysts prepared by a microemulsion technique in the low temperature regime [27]. Here, methanol is totally oxidized to water and carbon dioxide. In a subsequent step, steam reforming of methanol occurs.

The aim of this study was to gain a better understanding of the reactions involving both methanol and oxygen on a commercially available Cu/ZnO/alumina catalyst with a focus on the catalyst oxidation state at different reaction conditions. Furthermore, the conditions where intermediate products like methyl formate and formaldehyde are formed were investigated. Thermogravimetric analysis coupled with FTIR spectroscopy is an excellent tool to study the bulk oxidation state of a catalyst in-situ, because, in the absence of coking, this is directly related to the weight change of the catalyst.

2. Experimental

A commercial $Cu/ZnO/Al_2O_3$ catalyst obtained from Johnson Matthey was used for all experiments. The catalyst consisted of 35 wt% Cu, 37 wt% Zn and 5.4 wt% Al (ICP analysis). The active copper surface area of the catalyst was determined by N_2O decomposition experiments to be 16 m^2/g. This corresponds to a dispersion of 7.1% assuming that the number of surface atoms of copper is 1.47×10^{19} atoms/m^2 [28].

2.1. Microreactor experiments

Microreactor experiments were performed in a fixed-bed tubular reactor (6.35 mm O.D., 4 mm I.D.) made of glass-lined stainless steel, and fitted with a thermowell (1.5 mm O.D.) for measuring axial temperature profiles. The $Cu/ZnO/Al_2O_3$ catalyst was crushed and sieved to a particle size range of 125–250 μm, 750 mg of which were sandwiched in the reactor between two layers of SiC. The reactor was placed in the isothermal zone of an electrically heated oven developed at our institute. Reduction of the catalyst was performed by flowing a mixture of 20% H_2/80% N_2 at 300 °C for 2 h. Liquid methanol was fed to the reactor at a weight hourly space velocity (WHSV) of 2.2 h^{-1}. Before entering the reactor, the methanol was vaporized in a heated coil and diluted with nitrogen. The feed gas composition was $MeOH:O_2:N_2 = 5.5:1:120$. The gaseous effluent was analyzed for CO, CO_2, H_2, N_2, O_2, CH_4 and methyl formate (MF) using a gas chromatograph (Agilent 6890 plus) equipped with a two-column switching system and a thermal conductivity detector. The conversion of methanol (X_{MeOH}) and the yields (Y) of CO, CO_2, H_2 and methyl formate (MF, $HCOOCH_3$) were calculated from the molar flows:

$$X_{MeOH} = \frac{(MeOH^{in} - MeOH^{out})}{MeOH^{in}}, \quad Y_{CO} = \frac{CO}{MeOH^{in}},$$

$$Y_{CO_2} = \frac{CO_2}{MeOH^{in}}, \quad Y_{H_2} = \frac{H_2}{2MeOH^{in}}, \quad Y_{MF} = \frac{2HCOOCH_3}{MeOH^{in}}$$

2.2. Thermogravimetric experiments

The thermogravimetric experiments were conducted at atmospheric pressure on a Netzsch STA 449 thermogravimetric analyzer coupled to an FT infrared spectrometer (Bruker Tensor 27) for simultaneous gas analysis (MeOH, CO, CO_2, H_2O, H_2CO, $HCOOCH_3$). Helium was used as carrier gas in order to minimize buoyancy effects. A mass spectrometer was not available for the experiments.

The samples (100 mg) were placed in an aluminium oxide crucible (volume = 0.8 ml). The size of the catalyst particles used was 125–250 μm. Prior to each experiment, the catalyst was oxidized (12.5% O_2 in He, 80 ml/min, ca. 100 min) at the temperature applied in the experiment and subsequently reduced with hydrogen (20% H_2 in He, 100 ml/min, 20 min). Pure helium, helium saturated with methanol vapor, and oxygen were fed to the TG-FTIR according to the sequences described in Table 1.

Sequences B and C were introduced in order to probe if the adsorption of methanol was reversible. During the experiments, it turned out that the results after the turn off-and-on of methanol (sequence B and C) did not deviate significantly from those obtained after sequence A. Steps B and C were therefore left out in some experiments.

Product gases were analyzed in the FTIR spectrometer for CO, CO_2, H_2O, methanol, and methyl formate. The methanol conversion