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On the role of adsorbed atomic oxygen and CO_2 in copper based methanol synthesis catalysts

Martin Muhler [1,2], Eric Törnqvist [1], Lars P. Nielsen [3], Bjerne S. Clausen and Henrik Topsøe

Haldor Topsøe Research Laboratories, DK-2800 Lyngby, Denmark

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The role of adsorbed atomic oxygen in methanol synthesis is investigated by a series of transient experiments of the interaction of CO and CO_2 with a ternary $Cu/ZnO/Al_2O_3$ catalyst under methanol synthesis conditions. In particular, the response of adding CO and CO_2 as *pulses* and as *steps* to the reaction gas mixture is studied. Hereby it is possible to study both the formation of CO_2 from the reaction of adsorbed atomic oxygen (O–*) with CO, and the dissociation of CO_2 in situ, i.e., while the catalyst is producing methanol. The experiments show no evidence of a significant coverage of O–* under methanol synthesis conditions. In addition, it is shown that CO_2 is the main carbon source in methanol synthesis under the given conditions.

Keywords: Cu; methanol synthesis; transient kinetics

1. Introduction

The industrial catalysts used for the low-temperature synthesis of methanol are commonly based on $Cu/ZnO/Al_2O_3$ [1]. They are typically operated at 50–100 bar and 493–513 K with a feed containing CO, CO_2, and H_2. Despite their widespread use, the nature of the active sites and the reaction mechanism are still subject to considerable controversy. It has been suggested that the predominant sites for methanol synthesis are Cu in the metallic state (e.g., refs. [2,3]), Cu^{1+}-species in close contact with ZnO (e.g., refs. [4,5]), Cu^0–Cu^{1+}-couples (e.g., refs. [6,7]), or the interface between Cu metal and the semiconducting ZnO support, the so-called Schottky junctions [8,9]. Other possible roles of ZnO have also been proposed, e.g., as being a reservoir for atomic hydrogen and promoting hydrogen spillover (e.g., ref. [10]).

[1] To whom correspondence should be addressed.
[2] Present address: Fritz-Haber-Institut der Max-Planck-Gesellschaft, D-14195 Berlin, Germany.
[3] On leave from Institute of Physics, University of Aarhus, DK-8000 Aarhus C, Denmark.

It has recently been possible to shed more light on the nature of the copper by applying in situ techniques like X-ray diffraction (XRD) and X-ray absorption fine structure measurements (XAFS) which allow studies of the catalysts under industrial synthesis conditions. Recent reports [11–13] on the results of combined XAFS and on-line activity measurements gave evidence for the presence of Cu^0 only, in agreement with several other XAFS/XRD studies [14–19], as well as an X-ray photoelectron spectroscopy (XPS) study [20]. A strong influence of ZnO on the structure of the Cu phase was observed although ZnO was not essential for the synthesis of methanol [11]. Several other studies using polycrystalline Cu samples (unsupported pure Cu or Cu dispersed at an inert support, such as SiO_2) have been carried out in attempts to clarify the question whether unpromoted Cu metal is a catalyst for the synthesis of methanol (e.g., refs. [3–5,21]). However, a clear cut interpretation of the results from these studies has been hampered by impurities typically encountered using inorganic bulk materials. Recently, the question was addressed by using Cu(100) single crystals as catalyst [22,23] and it was shown that Cu metal by itself is active in methanol synthesis. Rasmussen et al. [23] also found a rate similar to that observed in industrial catalysts.

Based on kinetic measurements it has been suggested that CO_2 is the main carbon source for methanol synthesis under industrial conditions using a feed of CO, CO_2 and H_2 [24,25]. This was confirmed by experiments using isotope labeling [26,27]. Most of the mechanisms reported in the literature assume that CO_2 adsorbed on Cu is hydrogenated to formate, which also recently was verified for Cu single crystals from studies of CO_2 and H_2 coadsorption [28]. The subsequent hydrogenation of formate adsorbed on Cu metal to methanol is generally believed to be the rate-limiting step, see e.g., ref. [1].

Adsorbed atomic oxygen on copper (O–*) has been assumed to take part in the synthesis of methanol both as reactant and as a promoter for the adsorption of CO_2, H_2O and H_2 [21]. Coverages of O–* close to saturation were inferred from a comparison of N_2O frontal chromatography measurements carried out before and after methanol synthesis [2]. The coverage of O–* was assumed to be controlled by the overall reaction:

$$CO_2 \rightleftharpoons CO + O\text{–}* \; . \tag{1}$$

In a recent report [29], we found that N_2O frontal chromatography may modify the sample irreversibly. Therefore, a different approach than the one used in refs. [2,21] is employed in the present investigation to elucidate the role of adsorbed atomic oxygen. In one set of experiments CO and CO_2 are added to the stream as *pulses* and in another set as *steps*. The CO-addition experiments are used to titrate the O–* coverage, and the experiments where CO_2 is added are used to study the dissociative adsorption of CO_2. Such transient experiments have the advantage of probing the O–* coverage in situ, i.e., while the $Cu/ZnO/Al_2O_3$ catalyst is producing methanol.

2. Experimental

The microreactor set-up used in this study has been described elsewhere [29]. The gases employed have the following purities: He 99.9999%, H_2 99.9997%, CO 99.997%, CO_2 99.998%. A mass spectrometer (Balzers) is used to analyze both the reactants and the products. The methanol catalyst contains 55% CuO, 26% ZnO, 8% Al_2O_3 and has a BET area of 100 m^2/g. 260 mg of the 300–150 μm sieve fraction is loaded into the reactor resulting in a bed volume of about 0.3 cm^3 and a bed height of about 2.5 cm . The reduction is carried out in a mixture of 0.5% CO, 4% CO_2, 4% H_2, and balance Ar with a heating ramp of 0.3 K/min from ambient to 493 K. Pulses of CO and CO_2 are injected into streams of 5% CO_2 in H_2 and 5% CO in H_2, respectively, by means of a 1 ml sample loop (Valco). The steady state flow is 42 Nml/min. The step experiments are carried out by the use of a four port valve (Valco). The slight initial fluctuations in the partial pressures following the switching of the valves are due to the related changes in the total pressure. In one experiment CO is added to the feed such that the concentration of the gas is changed in one step from 6% CO_2 in H_2 at 34 Nml/min to about 5% CO, 5% CO_2, and balance H_2 at 42 Nml/min. In another experiment CO_2 is added as a step changing the concentration of the feed from 6% CO in H_2 at 34 Nml/min to about 5% CO, 5% CO_2, and balance H_2 at 42 Nml/min. Prior to the transient experiments the catalyst has synthesized methanol at a stable level in 5% CO, 5% CO_2, and balance H_2 at 493 K for about 80 h. Measurements confirm that negligible further deactivation takes place during the transient experiments. All experiments reported here are carried out at atmospheric pressure.

3. Results and discussion

Fig. 1 displays the result of the experiment where pulses of CO are injected into the feed gas containing only 5% CO_2 in H_2. The temperature of the reactor is 473 K. Although the feed gas at steady state conditions is free of CO, about 0.3% CO is produced. This CO is formed by the reverse water–gas shift (WGS) reaction:

$$CO_2 + H_2 \rightleftharpoons CO + H_2O . \tag{2}$$

About 0.4% H_2O is also formed. The actual H_2O concentration is presumably lower (by 500–1000 ppm) since there is a background pressure of H_2O inside the mass spectrometer from previous experiments. About 300 ppm methanol, corresponding to about 0.04 μmol/s g, is also formed at steady state conditions. 0.9 Nml CO is repeatedly injected through the dosing volume into the reaction gas mixture whose flow is 42 Nml/min. It is evident that the CO addition does not increase the methanol production, rather a slight decrease is observed. The CO concentration measured at the mass spectrometer is seen to increase sharply 45 s after

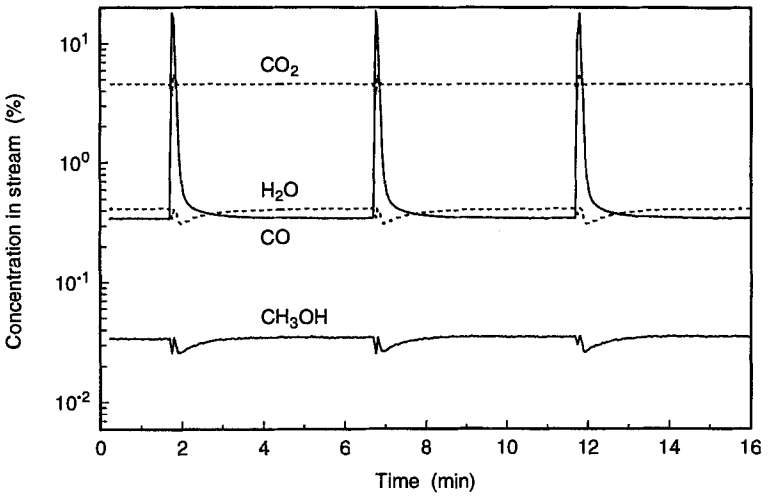

Fig. 1. Concentrations of CO_2, H_2O, CO and methanol in the reactor outlet at 473 K plotted versus time. 0.9 Nml CO was dosed repeatedly into a flow of about 5% CO_2 in H_2 (42 Nml/min).

each injection and reaches its maximum value of 18% within less than 3 s. The time delay of 45 s is simply related to the system volume (32 ml) between the dosing valve and the mass spectrometer. After reaching its peak the CO concentration decays rapidly and returns to the "steady state" value within 60 s. The broadening of the pulse and its slightly asymmetric shape are due to gas-phase diffusion in the tubings, and the finite pumping speed of the mass spectrometer chamber. The pulsing of CO is repeated several times and the same response is observed with each pulse. This demonstrates a high degree of reproducibility of the experiment as well as indicates the absence of any irreversible changes of the catalyst. By integrating the area under the CO peaks an average value of 38 μmol CO is obtained which is in good agreement with the dosed amount of 41 μmol. The amount of CO_2 formed during the CO pulses is found to be less than 1 μmol and the concentrations of methanol and water are slightly decreasing. All these observations suggest that little or no atomic oxygen is adsorbed at the catalyst surface.

Chinchen et al. studied the dependence of the oxygen coverage on the CO_2/CO-ratio in the feed gas for methanol synthesis. The oxygen coverage was deduced by applying the N_2O frontal chromatography method before and after reaction [2,30]. Using a CO_2/CO-ratio of 1.3 the authors estimated an oxygen coverage of 0.4 after high-pressure synthesis (50 bar, 523 K, 6 h) [30], which is close to the saturation coverage of 0.5. Researchers from the same group also carried out an experiment at atmospheric pressure using a CO free feed containing 10% CO_2 in H_2. In this case an oxygen coverage of 0.37 was found after reaction at 500 K [31] by means of CO frontal chromatography at 470 K. This method is based on the titration of O–* by CO when a front of CO in He is passed through the catalyst bed [32].

Using the authors' value of 0.4 for the oxygen coverage this corresponds to 70 μmol O–∗ at the surface of the present catalyst (the specific Cu metal area is about 20 m^2/g). During the CO pulse at 473 K a significant fraction of the O–∗ is expected to react with CO to form CO_2. However, only less than 1 μmol CO_2 is formed during the CO pulse. The effect would be even more noticeable in the CO pulse itself since the pulse would diminish significantly, if not be completely wiped out, when a large part of the adsorbed O–∗ reacts with it. Clearly, this is not observed. Thus, the results indicate an essentially oxygen-free Cu metal surface in contrast to the previous report [21].

The response of injecting pulses of CO_2 into a stream of approximately 5% CO in H_2 is displayed in fig. 2. The qualitative behavior is clearly very different from the CO pulse experiments shown in fig. 1. Methanol (slightly less than 1 μmol/g) is formed in parallel with the CO_2 pulses together with water (about 1.5 μmol/g). The fast rise in the concentration of methanol reaching 600 ppm and the similarity in the pulse shapes of methanol, water, and CO_2 indicate a much faster rate of methanol formation from CO_2 than from CO. At steady state prior to the pulses only 100 ppm methanol is found. This is much lower than at steady state with the CO_2/H_2 mixture above, and in accordance with the observation by many researchers (e.g., refs. [24,25]) that the rate of methanol formation from CO/H_2 mixtures is lower than from $CO/CO_2/H_2$ mixtures over Cu/ZnO based catalysts. Correspondingly, the H_2O concentration is less than 200 ppm in the CO/H_2 mixture compared to about 4000 ppm in the CO_2/H_2 feed above. The actual water concentration is probably lower than the 200 ppm since also in this case there is a significant background pressure of water inside the mass spectrometer from previous experiments. The observed CO_2 concentration of 0.1% prior and after the pulses is

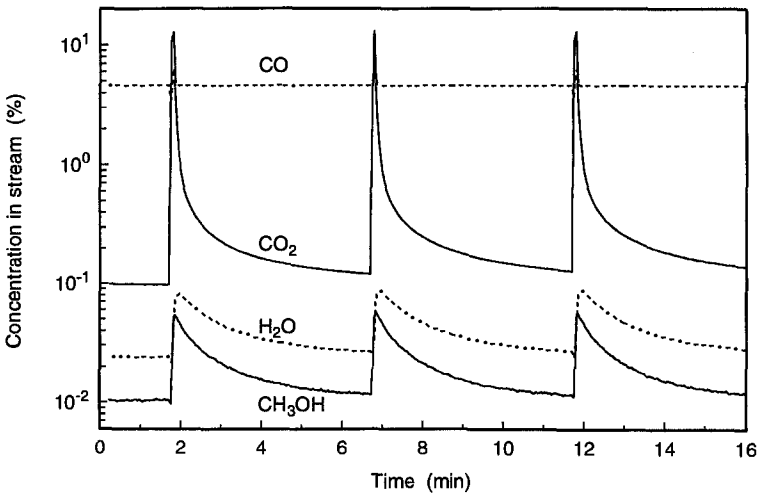

Fig. 2. Concentrations of CO_2, H_2O, CO and methanol in the reactor outlet at 473 K plotted versus time. 0.9 Nml CO_2 was dosed repeatedly into a flow of about 5% CO in H_2 (42 Nml/min).

caused by the high vapor pressure of frozen CO_2 at the liquid nitrogen cooled shroud of the mass spectrometer. The time delay between the injection and the observation of the CO_2 pulse is found to be the same as in the case of the CO pulse experiments. The CO_2 concentration at peak maximum is 13%. Integrating the peak areas yields an averaged value of 38 μmol CO_2 which is close to the dosed amount of CO_2 (41 μmol). Thus, under the pulse conditions about 2% of the CO_2 is converted to methanol, the remainder being consumed in the reversed water–gas shift reaction.

The two pulse experiments have clearly demonstrated the role of CO_2 as the main carbon containing source in methanol synthesis from $CO/CO_2/H_2$ mixtures under the present conditions. Apart from the H_2O produced during methanol synthesis there is an additional production of H_2O from the reverse WGS reaction (2) giving rise to a slightly larger concentration of H_2O than methanol. This is also in accordance with the quantitative values of the different concentrations.

Since the feed gas in the experiments of fig. 2 contains only CO and H_2, the coverage of O–∗ should be negligibly small before the CO_2 pulse enters the catalyst bed. Consequently, one might expect according to the suggestions of Chinchen et al. [21] that a considerable part of the CO_2 pulse would be converted to CO in order to establish the proposed large coverages of O–∗ according to reaction (1). Furthermore, the authors [21] observed an induction period for the formation of methanol and for the reverse WGS reaction. They attributed this to the period of time necessary to form the coverage of O–∗ controlled by the reaction (1). The above authors observed the induction period after switching to a $CO/CO_2/H_2/Ar = 10/10/80/10$ mixture at 1 bar and 503 K [21]. In several respects the present experiments are not in accordance with these observations. No considerable CO formation is observed. Instead, CO_2 is converted to methanol and H_2O without any measurable time delay between the pulse of CO_2 and the formation of methanol and H_2O. This strongly indicates that methanol and H_2O are formed on a Cu metal surface at which insignificant amounts of oxygen are present. The present result does therefore not lend support to the role of O–∗ as an essential promoter of the formation of methanol [21]. The origin of this discrepancy may be related to the possibility that the difference between N_2O surface areas used to estimate the coverages by O–∗ are also affected by other catalyst changes such as sintering [33].

In agreement with the observations in fig. 1, the catalyst in the CO step experiment (fig. 3) is producing about 500 ppm of methanol at steady state when feeding 6% CO_2 in H_2. Water and CO is produced by the reverse WGS reaction. Adding CO shifts the WGS equilibrium and reduces the amount of H_2O produced. The concentration of methanol is reduced initially but regains slowly its original value after about 30 min. If the Cu metal surface had a significant coverage of O–∗ prior to the addition of CO, then the concentration of CO_2 should increase with an amount corresponding to the amount of O–∗ titrated off the Cu surface. Instead, the experiments show that the concentration of CO_2 decreases from about 6 to 5%

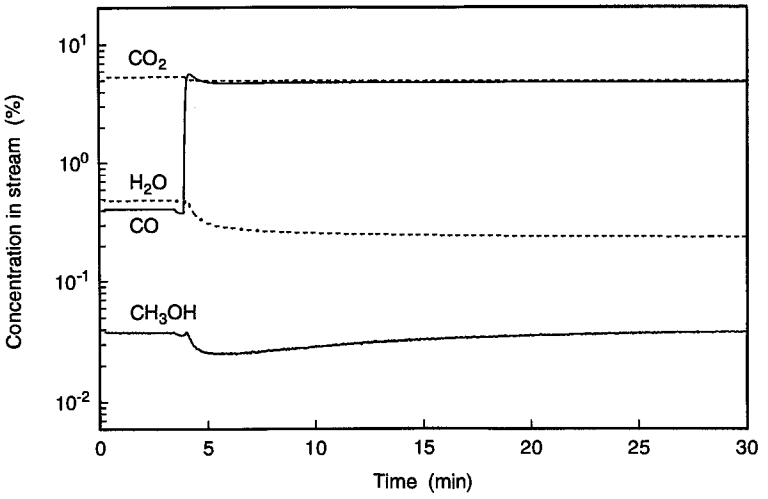

Fig. 3. Concentrations of CO_2, H_2O, CO and methanol in the reactor outlet at 473 K plotted versus time. The feed gas composition was changed from about 6% CO_2 in H_2 (36 Nml/min) in one step to about 5% CO_2, 5% CO, and balance H_2 (42 Nml/min).

in accordance with the change in gas composition upon introducing the CO and the shift in the WGS equilibrium. Thus, also this experiment is in agreement with the absence of a significant coverage of adsorbed atomic oxygen under synthesis conditions.

The results of the CO_2 step experiment are shown in fig. 4. Similar to the CO_2

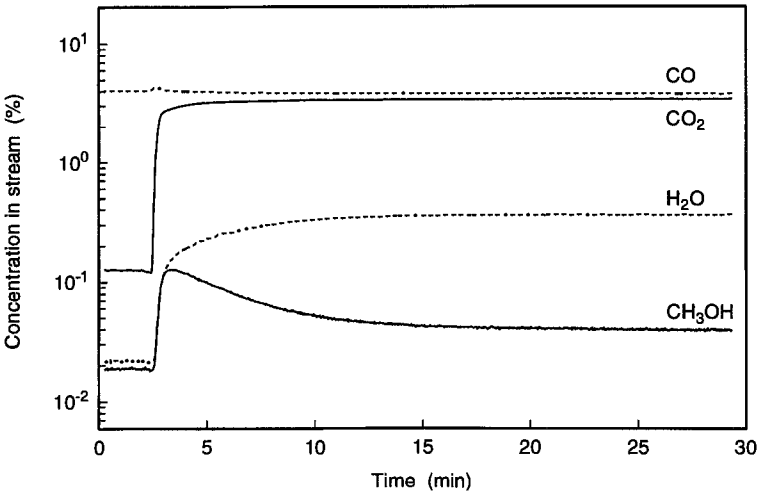

Fig. 4. Concentrations of CO_2, H_2O, CO and methanol in the reactor outlet at 493 K plotted versus time. The feed gas composition was changed from about 6% CO in H_2 (34 Nml/min) in one step to about 5% CO_2, 5% CO, and balance H_2 (42 Nml/min).

pulse experiment (fig. 2) no measurable time delay is observed between the increases in the concentration of CO_2, H_2O and methanol. Apparently, CO_2 does not dissociate to a significant extent and an upper limit on the amount of CO formed can be estimated to 1 μmol. Water and methanol reach their steady state values after about 30 min. The concentration of methanol shows an interesting transient behavior. Initially, the concentration reaches a maximum value of over 1000 ppm after which it decays slowly to a value of about 400 ppm (the same final value as in fig. 3). Apparently, the treatment with a CO_2 free feed gas has produced a very active, but not stable state of the catalyst. Similar transients were observed for the Cu/ThO_2 system [9]. Such transient behavior of methanol formation on the $Cu/ZnO/Al_2O_3$ catalyst, after the CO/H_2 exposure, could be due to a change in the catalytic properties of the proposed Cu/ZnO interface [8,9]. However, a dependence of the amount of active sites on the CO/CO_2 ratio in the feed is also possible [33].

Both the step experiments and the pulse experiments fail to provide any evidence for a significant coverage of O–* under methanol synthesis conditions indicating a much slower rate of CO_2 dissociation than previously suggested by Chinchen et al. [21]. The present findings agree with Campbell's discussion of the atomic oxygen coverage on copper during methanol synthesis [34] as well as with two recent reports on the dissociation probability of CO_2 on Cu(110) [35] and Cu(100) [36]. The Cu(110) surface is supposed to be one of the most active facets due to its microscopic roughness but Nakamura et al. [35] found a very low dissociation probability and an activation energy of dissociation of 67 kJ/mol. They further estimated that a CO_2/CO pressure ratio in excess of about 100 is necessary in order to establish a significant coverage of O–* under typical methanol synthesis conditions. In a recent report on the temperature-programmed desorption of H_2 from supported Cu catalysts [29] it was found that a sufficient dose of pure H_2 at room temperature removes half a monolayer of O–* completely. If the removal of O–* by H_2 is taken into account even higher CO_2/CO pressure ratios may be necessary. Studies of the interaction of CO_2 with Cu(100) [36], show that the dissociation probability of CO_2 at 500 K is 7.5×10^{-12} which was about three orders of magnitude lower than on Cu(110). The activation energy was found to be 93 kJ/mol. No direct CO_2 dissociation experiments are available for Cu(111) but due to the similar atom density, the reactivity of Cu(111) may be expected to be quite similar to Cu(100). In agreement with the present results the above surface science studies therefore also render it rather unlikely that there is a significant coverage of O–* on Cu metal under methanol synthesis conditions.

4. Conclusions

No support is found in the present pulse and step experiments for the previously proposed role of O–* as an important reaction intermediate and promoter of

methanol synthesis. The experiments show that methanol is formed on an essentially O–* free Cu metal surface. The results have been shown to be in accord with recent surface science experiments. In agreement with several previous studies, the present results have clearly demonstrated that CO_2 is the main carbon source leading to the formation of methanol. The transient increase and subsequent decrease in the formation of methanol after the addition of CO_2 to a feed containing only CO and H_2 indicate that the state of the catalyst depends on the reaction gas mixture. Further studies are presently being conducted to elucidate the origin of this behavior.

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