Methanol synthesis and reverse water–gas shift kinetics over clean polycrystalline copper

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The kinetics of simultaneous methanol synthesis and reverse water–gas shift from CO_2/H_2 mixtures have been measured at low conversions over a clean polycrystalline Cu foil at pressures of 5 bar. An absolute rate of 1.2×10^{-3} methanol molecules produced per second per Cu surface atom was observed at 510 K, with an activation energy of 77 ± 10 kJ/mol. The rate of CO production was 0.12 molecules per second per Cu surface atom at this temperature, with an activation energy of 135 ± 5 kJ/mol. The rates, normalized to the metallic Cu surface area, are equal to those measured over real, high-area Cu/ZnO catalysts. The surface after reaction was examined by XPS and TPD. It was covered by almost a full monolayer of adsorbed formate, but no other species like carbon or oxygen in measurable amounts. These results prove that a highly active site for methanol synthesis on real Cu/ZnO catalysts is metallic Cu, and suggest that the rate-determining step in methanol synthesis is one of the several steps in the further hydrogenation of adsorbed formate to methanol.

Keywords: methanol synthesis; copper catalysts; Cu–ZnO catalysts; water–gas shift; reverse water–gas shift

1. Introduction

The methanol synthesis reaction ($CO + 2H_2 \rightarrow CH_3OH$) is catalyzed commercially by Cu/ZnO catalysts. If any CO_2 or water is present, as is usually the case, this reaction occurs predominantly via the reaction

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

followed by the water–gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$) to regenerate the CO_2 [1–3]. That is, the primary source of the carbon in the methanol is CO_2, not CO, according to transient experiments with $Cu/ZnO/Al_2O_3$ catalysts [1]. The nature of the active site on the surfaces of such catalysts has been a long-standing fundamental question of some controversy. Although it is well accepted that these catalysts contain metallic Cu particles supported on a defected ZnO phase [4–32], the active site in methanol synthesis is frequently proposed to be a Cu^{1+} species in or on the ZnO phase [20,22–40]. However, some workers have been unable to identify significant amounts of Cu^{1+} [41–48] or even adsorbed oxygen [3,48] on the working catalysts using modern spectroscopic or transient techniques that should be sensitive to such species. Since it is easy to find Cu^{1+} on Cu surfaces that have not been well protected from exposure to air during transfer to an analysis chamber [47], its identification with ex situ measurements is not always unambiguous proof that it was present on the catalyst under reaction conditions. Other groups show a reasonably good linear correlation between the metallic Cu surface area and the activity of a series of Cu/ZnO or $Cu/ZnO/Al_2O_3$ catalysts [5,45,46, 49–53]. One group even reports a similar activity per Cu metallic surface area, irrespective of whether the Cu is supported on ZnO or SiO_2 [5,50], although other groups find that Cu on supports other than ZnO is very inactive [22,26–28,54–56]. Specific activities for Cu on a given support, particularly silica, vary widely from group to group [26,27,38,56,57], and depend on whether CO_2 is in the feed [2,3,57]. Frost [58] even proposes that the activity is due to minute Schottky junctions formed between Cu and ZnO interface, although this has not been supported by later studies of this effect [45,59,60]. Clearly, the nature of the active site on these catalysts is still in question.

Several groups have reported Cu site-specific rates over SiO_2-supported Cu that are orders of magnitude below those generally reported for Cu/ZnO [22,26–28,54–57]. On the other hand, Chinchen et al. [5,50] have reported quite comparable rates; other groups [38,57] have reported rates per Cu surface area over silica supported Cu that are within a factor of three of those reported over Cu/ZnO. There are well known difficulties associated with measuring the Cu area of these catalysts [3,11,61–63] and maintaining that area clean and constant during reaction [3,11,41,44,53,64]. Because of these difficulties, we have made the rate measurements on metallic Cu in a system where the integrity of the surface can be verified before and after reaction.

Szanyi et al. [28] have previously measured methanol production from $CO/CO_2/H_2$ mixtures over a Cu(100) single crystal surface. Their rates were some four orders-of-magnitude below those of high-area Cu/ZnO catalysts when compared on a per Cu surface atom basis. Taken at face value, this results proves that the active site is not metallic Cu. However, there are several factors that bring into question such an interpretation of those results. First, the surface was contaminated with carbon during the reaction. After flashing the sample to the reaction temperature in UHV (which lowered the carbon level), this carbon still gave a C(272 eV)/Cu(920 eV) AES ratio of 0.56 [28], compared to a ratio of 0.61 for the intensities of pure bulk graphite relative to pure bulk Cu [65]. Obviously, carbon was at the multilayer level on the surface of this model catalyst, since AES probes several monolayers deep into the sample [65,66]. This carbon would poison the catalyst, which would explain the low rate observed even if metallic Cu were the active phase. This carbon may be a natural consequence of the chemistry involved on pure Cu, or it might be due to impurities somehow accumulated on the surface of the model catalyst. If the former is the case, it suggests an interesting role for the

ZnO in keeping the surface clean, since such carbon is not generally reported in studies of high-area Cu/ZnO catalysts [4–32], and it was not seen when specifically probed [24]. Second, the kinetics on Cu(100) were measured at only 1 bar pressure [28], whereas the rates on the Cu/ZnO catalysts to which they compared their rates were measured at 15 bar. Since the dependence on pressure has not been measured at these low pressures, it is not clear how to extrapolate between these pressures. (Measurements down to 3.4 bar seemed to show a dependence that is greater than first order in total pressure [16], although first-order behavior is more commonly assumed [51].)

Rasmussen et al. [67] have also measured methanol synthesis rates over Cu(100), using only CO_2 and H_2 in the starting mixture, at a pressure of 2 bar. Again, they measured rates per Cu surface atom that were far below rates over real Cu/ZnO catalysts. However, their rates were only a factor of 10–100 below typical rates over real Cu/ZnO catalysts. They quantitatively attributed this to the difference in pressures used within a very reasonable microkinetic model for the reaction. Furthermore, their sample showed no carbon impurity on the surface following reaction, but instead was covered by adsorbed formate, thought to be an intermediate in the reaction, and easily removed by heating in vacuum to the reaction temperature. To the extent that their pressure extrapolation can be trusted, their results suggest that metallic Cu is the active species for methanol synthesis, completely opposite to the conclusion from the other study on Cu(100) [28].

We report here methanol synthesis kinetics over a clean polycrystalline Cu foil at pressures of 5 bar which show rates per Cu surface atom which are much higher than those measured in either study on Cu(100), but which are equal to those measured over real Cu/ZnO catalysts. We further report the accompanying reverse water–gas shift kinetics, and show that the surface after reaction is covered by adsorbed formate, but no other species like carbon or oxygen in significant amount. These results support the results of Chorkendorff's group [67], and prove that the active site for methanol synthesis on real Cu/ZnO catalysts is metallic Cu.

2. Experimental

The experiments were carried out in a batch microreactor attached to an ultrahigh vacuum (UHV) chamber for pre- and post-reaction surface analysis and sample cleaning. The sample was attached to a transfer rod for transport between these chambers, and for controlling the sample temperature. This system was similar to that described elsewhere [67,68], except that the microreactor was designed for higher pressures (up to 15 bar) and the sample repeatedly sealed into this microreactor with a teflon seat that was diffusively separated from the sample. This teflon seat is compressed by the stainless steel endplate of the sample transfer rod, through which an electrical feedthrough tube protrudes. The sample and thermocouple were mounted on these electrical connections for resistive heating and temperature monitoring. Any impurity originating at the teflon seat would have to diffuse through the reaction mixture a length of ~ 4 cm to get to the sample, along a thin annular ring between the inner diameter of the microreactor wall and the outer diameter of the electrical feedthrough tube on the end of the transfer rod. More details will be given elsewhere [69]. In addition, it was proven that the clean sample could be moved from the UHV chamber into the evacuated microreactor, sealed in it for long periods, and then returned to UHV without any significant buildup of surface species, as probed by XPS and TPD.

The sample was a 13 mm × 10 mm × 1 mm piece of high purity Cu (99.999%), mounted with two 0.25 mm diameter W wires between two 3 mm diameter molybdenum rods for resistive heating. The W wires were each spotwelded on each end to one of the rods, and the center portion was spotwelded at two points to the back of the sample. The front of the sample was cleaned by argon sputtering and annealing (800 K), as verified by highly sensitive XPS and temperature programmed desorption (TPD). The adsorption of formic acid in UHV showed TPD spectra of the expected absolute intensity and shape for a Cu sample of this size [70,71], with the simultaneous evolution of H_2 and CO_2 in a peak at 480 K due to formate decomposition. (TPD experiments were performed with a heating rate of ~ 6 K/s.)

The sample surface was initially polished to a mirror finish, but it showed some visible roughening following extended use. After use, its roughness was measured with profilometer using a 5 μm radius diamond stylus, and found to be very smooth on that scale (< 0.14 μm rms roughness), so that any extra surface area due to sample roughness should be much less than the simple geometric surface area of that sample. We base our rates here on the geometric surface area.

The microreactor had a volume of about 30 ml, and it was used in the batch reactor mode (closed volume). The reaction was initiated by rapidly heating the sample to reaction temperature after introducing it into the microreactor and pressurizing the microreactor with the reaction mixture. The reaction was terminated by stopping the sample heating current, at which time it cooled rapidly toward room temperature and the reaction was quenched. Each measurement at a different reaction time required starting the procedure completely over again from the sample cleaning step. Methanol and CO products were detected by sending several 0.8 ml aliquots of the reaction mixture from this volume to a gas chromatograph (GC), with flame ionization detection following methanation by a Ni catalyst located between the 1/8″ diameter × 6 ft long Poropak N column and the flame. (Since the reaction mixture is separated by the GC column before contacting this Ni catalyst, no other side reactions are occurring there.) The column temperature was programmed from 373 to 403 K after sample injection. The walls of the microreactor, the injection valve, and all tubing leading to the GC were maintained at ~ 330 K to prevent methanol adsorption on the walls. Since the maximum partial pressure of water produced here was ~ 40 Torr, this was also sufficient to prevent condensation of products.

Initially, we had problems with reactions on the microreactor or sample holder surfaces which slowly consumed methanol product, but these were permanently eliminated by heating the sample in ~ 100 mbar of a very dilute H_2S in Ar mixture in the microreactor. Afterwards, the catalytic activity of the sample was also poisoned by the resulting monolayer of adsorbed sulfur, as seen previously [72], but it was easily recovered by a very brief sputter cleaning that was sufficient to just barely remove most of the sulfur from the front surface. This control experiment also proved that the catalytic rates we report here are due only to the front of the Cu foil, but not due to its back or sides, or the sample holder parts.

3. Results

Fig. 1 shows the buildup versus time of product concentrations in the batch microreactor for 4.67 bar H_2 and 0.41 bar CO_2, at Cu temperatures of 510 and 570 K. The product concentrations are expressed in units of molecules produced per site, assuming 1.77×10^{15} sites per cm^2, which is the Cu surface atom density on Cu(111). As can be seen, each surface site produces many thousands of product molecules during the time of these rate measurements. The rates of both CO and methanol production are relatively linear with time at these low conversions, with perhaps some slow decay in activity as time increases at the higher temperatures.

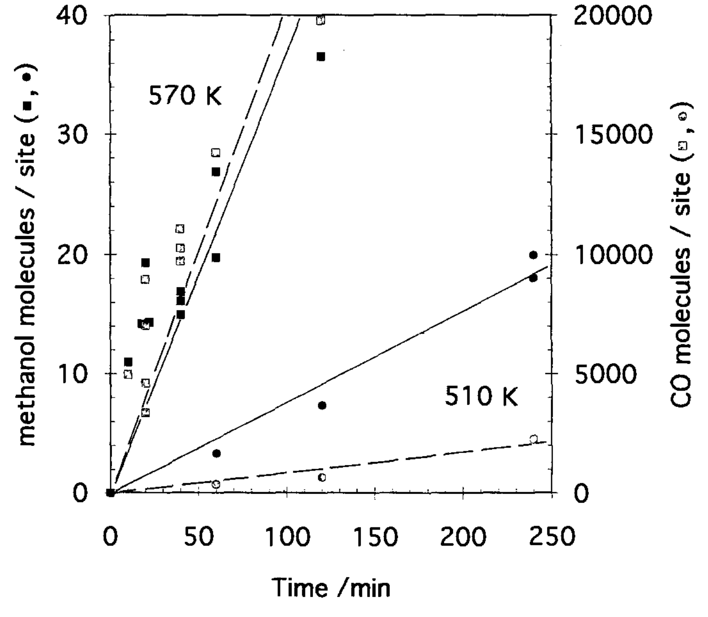

Fig. 1. Site-specific yields of methanol (filled symbols) and CO (open symbols) as a function of reaction time over a polycrystalline Cu foil at 510 and 570 K, in 4.67 bar H_2 and 0.41 bar CO_2. The CO yields are due to the reverse water–gas shift reaction. The yields are normalized to the number of Cu surface atoms assuming that there are 1.77×10^{15} Cu surface atoms (or sites) per cm^2. The solid and dashed lines represent least-squares fits of the methanol and CO data, respectively, forcing the lines to go through the origin.

Since the scatter in the data are comparable to any such curvature, we shall not discuss this effect. The straight lines through each data set represent the least-squares best fit, but forcing the lines to start at the origin.

Similar kinetic measurements were repeated at numerous temperatures between 450 and 570 K. Using best fit straight lines like those shown through the data of fig. 1 to estimate steady state reaction rates, Arrhenius plots of the rates versus temperature were constructed, as shown in fig. 2. The rates are expressed as turnover frequencies, or the number of product molecules produced per surface Cu atom per second, again assuming 1.77×10^{15} Cu surface atoms per cm^2. The activation energies for CO and methanol production were determined to be 135 ± 5 and 77 ± 10 kJ/mol, respectively. It is clear that the rate of the reverse water–gas shift reaction is much, much faster than methanol synthesis at these low conversions, even though it has a considerably higher apparent activation energy. The apparent preexponential factors in catalytic reactions are often complex combinations of rate constants and equilibrium constants, so this is not surprising.

Following the above reactions, the surface was cooled in the reaction mixture. After GC analysis, the remainder of this mixture was evacuated and the sample was transferred into UHV and analyzed with XPS. Both C(1s) and O(1s) peaks appropriate for adsorbed formate (as in ref. [70]) were seen. The surface was then analyzed using TPD, and all that desorbed was CO_2 and H_2 in nearly simultaneous

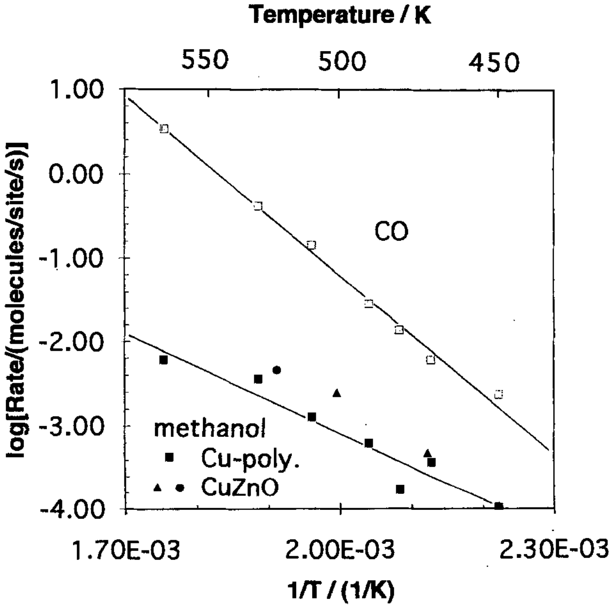

Fig. 2. Arrhenius plot of turnover frequency for methanol synthesis and reverse water–gas shift over a polycrystalline Cu foil at 4.67 bar H_2 and 0.41 bar CO_2. Methanol rates previously measured over high-area Cu/ZnO catalysts in pure $CO_2 + H_2$ feeds at total pressures from 17 to 50 bar are plotted for comparison, from refs. [2a,38].

peaks at 475 K, characteristic of the decomposition of adsorbed formate [70,71,73]. The lineshape and position of the TPD peaks were nearly identical to those after depositing formate on Cu(110) via formic acid decomposition [70], except that those from Cu(110) are sharper than seen here. (There was relatively more intensity stretching out on the low-temperature side of the peak here, so that the peak started at ~ 400 K here, compared to ~ 420 K from formic acid on Cu(110) [70].) After the removal of this formate species, the surface was again analyzed with XPS and found to be pure Cu. All carbon and oxygen had left the surface as CO_2 when the formate decomposed.

We performed control TPD experiments after dosing ~ 4 L (L = langmuir = 10^{-6} Torr s) of formic acid to this same clean polycrystalline sample, which is known to produce adsorbed formate on Cu surfaces [70,71,73]. The resulting TPD looked just like that following reaction, except that the intensities were only about 50–60% as big as seen following reaction, and there was somewhat less relative intensity along the low-temperature side of the peak. This indicated that the reaction mixture can deposit about 1.7–2 times as much formate as typically obtained from a 4 L formic acid exposure. Such an exposure deposits about 3.4×10^{14} formates per cm^2 on Cu(110) [70], so we estimate a formate coverage following reaction of about $(6-7) \times 10^{14}$ per cm^2. This is also consistent with the XPS intensities. If one assumes that each formate requires two surface Cu atoms, this coverage corresponds closely to a full monolayer of formate.

To ensure that the extraction of aliquots for GC analysis was not perturbing the surface condition after reaction, we also performed several control experiments where the GC analysis was omitted. That is, at the end of the reaction time the sample heating current was turned off and the sample was evacuated and transferred into UHV as quickly as possible. The same results were obtained: the surface was saturated in formate, but no other species were present. In control experiments where the CO_2 was omitted from the reaction mixture (i.e., pure H_2), no formate nor any other species were seen on the surface following reaction. This proves the cleanliness of our microreactor.

The presence of high coverages of formate after reaction agrees with the results of Chorkendorff's group [67,73]. As with that group, we saw no evidence for tenacious carbon on the surface following the reaction. The only carbon present on the surface was that associated with formate, which was easily removed (as CO_2) by heating to 480 K in vacuum. In contrast, only about half of the carbon reported by Szanyi et al. [28] on Cu(100) following reaction was removed by heating to >500 K in vacuum, and the amount that remained was at the multilayer level (see above).

4. Discussion

The turnover frequency of methanol synthesis reported here at 5 bar pressure and 510 K is about 1.2×10^{-3} s^{-1}. This compares favorably to values between 4×10^{-3} and 10^{-2} s^{-1} reported for the best high area Cu/ZnO catalysts at this temperature and total pressures between 32 and 50 bar, whenever both CO_2 and CO are in the feed [17,19,45,51,57]. Since the reaction rate is generally considered to be at least first order in total pressure (see above), the comparison is even better. For example, at 1 atm total pressure, a rate of only $\sim 10^{-6}$ mol m^{-2} h^{-1} was reported at 493 K for high-area $Cu/ZnO/Al_2O_3$ [40], which corresponds to a turnover frequency of only $\sim 10^{-5}$ s^{-1}. A few measurements have been reported where a turnover frequency could be determined for high area Cu/ZnO from data in pure $CO_2 + H_2$ feeds [2a,38]. These data points, which cover total pressures from 17 to 50 bar, are plotted in fig. 2 for comparison to our data. In the data from Liu et al. [2a], we have assumed that 1/3 of the total BET surface area was Cu surface area in calculating the absolute rates here. (This value of 1/3 is typical for Cu/ZnO catalysts, but is probably only accurate to within a factor of two. We know of no cases in the literature where optimum Cu/ZnO catalysts had a ratio of Cu : total surface areas that was more than a factor of two different than this value.) These data show again that the absolute rates we measure here for a clean Cu foil are within experimental error of rates on high area Cu/ZnO. Thus, the role of ZnO may be simply to maintain the surface area of the metallic Cu phase. Special Cu^{1+} sites associated with the ZnO play no measureable role, although the scatter in absolute rate data on Cu/ZnO catalysts may mask comparable contributions to the rate from sites associated with ZnO. (A recent report [74] quotes a turnover frequency of 0.17 s^{-1} for Cu/ZnO at 493 K in 30 bar of 2 : 1 H_2/CO_2. This rate is so high compared to all other literature values, with or without additional CO, that we shall assume there is some error in this reported value, and neglect it.)

The two data points from Liu et al. [2a] at different temperatures, plotted in fig. 2, are for a total pressure of 17 bar and a $H_2 : CO_2$ ratio of 2.3 : 1. Their temperature dependence is also very similar to the behavior we report here for polycrystalline Cu foil, which gives an activation energy of 77 ± 10 kJ/mol. Activation energies between 60 and 142 kJ/mol are typically reported for Cu/ZnO catalysts when CO is also present in the feed [5,51]. The activation energies reported on Cu(100) were 69 ± 4 kJ/mol in pure CO_2 and H_2 [67], and 73 kJ/mol with CO also present [28], both very close to our present value.

Rasmussen et al. [67] reported an absolute rate of methanol synthesis on Cu(100) of 2.7×10^{-4} molecules $site^{-1}$ s^{-1} at 543 K in 1 bar each of CO_2 and H_2. This is considerably lower than our rate of $\sim 4 \times 10^{-3}$ molecules $site^{-1}$ s^{-1} at this same temperature. The ~ 15-fold higher rate here may be due to the 4.7-fold higher H_2 pressure used here, which would imply that the rate is nearly second order in H_2 pressure. Usually, the rate is assumed first order in H_2 or total pressure [51]. Additionally, polycrystalline Cu may have a higher inherent activity than Cu(100) due to some structural sensitivity in this reaction. Further experiments will be required to separate these two possible effects. The rates measured by Szanyi et al. [28] on Cu(100) are a factor of 10^3–10^4 smaller than our rates, presumably due to their surface carbon mentioned above, and also due to the fact that they were operating at an H_2 pressure of only ~ 0.9 bar.

The activation energy of 135 ± 5 kJ/mol found here for the reverse water–gas shift reaction compares reasonably with a value of ~ 105 kJ/mol extracted from data for high-area Cu/ZnO [75]. A much lower activation, 70–75 kJ/mol, was found for Cu(110) [72], although Cu(110) also has a much lower activation energy for the forward water–gas shift reaction than Cu(111) [76]. The latter is the most stable plane and the one expected to dominate on our polycrystalline sample. The turnover frequency reported for the reverse water–gas shift reaction over Cu(110) [72] at 573 K, 1.2 bar H_2, and 0.2 bar CO_2 is $\sim 2\ s^{-1}$, which is close to the value found here at this temperature of $\sim 5\ s^{-1}$. Of course, the higher pressure used here can explain all of this activity difference. The lower activation energy on Cu(110) should result in its being more active than polycrystalline Cu at lower temperatures, but no rate measurements were made on Cu(110) below 573 K. In the forward water–gas shift reaction, Cu(110) is 4- to 10-fold more active than Cu(111), depending on the temperature [76].

The post-reaction surface analysis here showed only adsorbed formate, at near monolayer coverage. This does not preclude other adsorbed species being on the catalyst surface at low concentrations in the high-pressure cell during reaction. Indeed, we expect adsorbed H, OH, H_2O, CO_2, CO, H_2CO_2, H_2CO, H_3CO, H_3COH and other species to be present at very low coverages and important in the reaction. Most of these species are unstable at 300 K in vacuum, so their surface concentrations surely go down further on transfer into UHV. The high concentration of formate observed, however, suggests that one of the several elementary steps involved in its further hydrogenation to methanol must be rate limiting. Based on a very reasonable kinetic model, Rasmussen et al. [67] suggest that this step is: $H_2COO* + H* \rightarrow H_3CO* + O*$ on Cu(100).

5. Note added in proof

Another paper by Rasmussen et al. [77] has recently appeared showing that the rate of methanol synthesis in similar mixtures and at a similar temperature is 2.36 order in total pressure ($CO_2 + H_2$) below 4 bar. If we use this to extrapolate their rates on Cu(100) from [67] to our higher-pressure conditions (see above Discussion), we see that our polycrystalline Cu sample is about twice as active as Cu(100) in methanol production. (Actually, this new paper [77] explains that they define a "site" as two Cu surface atoms, whereas we define a "site" as one Cu surface atom. Thus, the specific activity of polycrystalline Cu is about four times that of Cu(100).) Our polycrystalline Cu sample surface should be mostly Cu(111) facets.

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