Catalysis Letters 10 (1991) 383–390

Methanol synthesis on a Cu(100) catalyst

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Received 23 May 1991, accepted 6 August 1991

The synthesis of methanol on a Cu(100) single crystal surface was studied between 500–550 K and at pressures between 44–102 kPa using a gas mixture of $CO_2/CO/H_2 = 1/2/12$. The specific reaction rates found for methanol synthesis were approximately an order of magnitude lower than those rates previously reported for silica supported, Cu-based catalysts. Furthermore the rates observed for the Cu(100) catalyst are estimated to be several orders of magnitude smaller than those rates found for ZnO supported Cu catalysts at comparable reaction conditions. The very low concentration of ionic copper species on the surface is thought to be responsible for the low activity of the Cu(100) catalyst.

Keywords: Methanol synthesis; catalysis; Cu(100)

1. Introduction

The synthesis of methanol from syngas (CO/H_2 or $CO_2/CO/H_2$) on Cu-based catalysts is one of the most extensively studied large scale industrial processes. Although considerable attention has been given to this reaction, key aspects of the process are still actively debated. Three important issues under discussion are: (1) whether the source of carbon for methanol synthesis is CO or CO_2; (2) whether there is significant metal-support interaction between Cu and the oxide supports; and (3) whether the active site for methanol synthesis is Cu^0 or Cu^{n+} ($n = 1$ or 2).

Regarding the first point, radiolabelling experiments [1–3] have suggested that the carbon source for methanol synthesis from $CO_2/CO/H_2$ mixtures is exclusively CO_2. CO is then thought to be the reducing agent responsible for the removal of adsorbed oxygen from the catalyst surface [4]. With respect to the second point, considerable work [5,6] supports the argument that there is little synergism between Cu and the oxide support, particularly for Cu/ZnO catalysts.

The third point, concerning the oxidation state of copper under reaction conditions, is currently the most actively debated aspect of methanol synthesis on Cu-based catalysts [2,7–9]. Chinchen and co-workers [5] have proposed that metallic Cu is the active form of copper for methanol synthesis. On the other hand, Sheffer and King [10] have studied the promotional effects of potassium and cesium on methanol synthesis over supported Cu catalysts using X-ray photoelectron spectroscopy (XPS). These authors concluded that metallic copper is inactive for the hydrogenation of CO, whereas the promotional effect of alkali metals was attributed to the stabilization of Cu^+ species. Recently Nonneman and Ponec [7] have provided further evidence that the active form of Cu for methanol synthesis is an ionic form. These authors studied a series of supported and unsupported Cu catalysts and found that supported Cu catalysts, free from alkali impurities, were inactive for methanol synthesis. They further demonstrated that alkali contamination present in the commercial oxide supports leach out during the catalyst preparation and effectively promote methanol production. In accordance with King [10], Nonneman and Ponec attribute this promotional effect to the stabilization of ionic copper by the alkali impurities. Characterization of model catalysts for methanol synthesis has been carried out in ultrahigh vacuum (UHV) studies [11,12]. The synthesis of methanol has also been addressed on single crystal model catalysts by using an elevated pressure reactor coupled to a UHV surface analytical system [12]. Although these studies have provided valuable structural and chemical details about the ZnO, Cu, Cu/ZnO and ZnO_x/Cu systems, no specific kinetic data have been reported for a single crystal Cu catalyst. It has been shown, however, that the turn-over-frequency (TOF, molecules/atom site/second) for methanol production on single crystal Cu catalysts is less than 2×10^{-3} at 550 K, $CO/H_2 = 1/2$, and a total pressure = 1500 Torr [12].

In this letter we report preliminary results for methanol synthesis on a Cu(100) single crystal model catalyst using a $CO_2/CO/H_2$ gas mixture. The main objective of this work concerns the oxidation state of Cu under reaction conditions.

2. Experimental

The experiments were carried out in a combined elevated pressure reactor–ultrahigh vacuum surface analytical chamber which is described in detail elsewhere [13]. The UHV chamber, with a base pressure of $< 3 \times 10^{-10}$ Torr, is equipped with Auger electron spectroscopy (AES), temperature programmed desorption (TPD), ion sputtering and gas- and metal-doser facilities. The crystal was heated resistively by a tungsten wire swaged into grooves located at the sample perimeter. The temperature of the crystal was monitored using a W/W-Re thermocouple pressed into a small well located on the edge of the sample.

Argon ion sputtering followed by annealing to 800 K were used to clean the Cu(100) sample; cleanliness was verified by AES. Following the above cleaning procedure the crystal was transferred into the reaction chamber, contiguous to the surface analytical chamber, through three doubly-differentially pumped teflon sliding seals. Pressures up to 760 Torr can be maintained in the reaction chamber with no measurable pressure increase in the UHV chamber. The reaction chamber is connected to a gas handling system and a gas chromatograph (GC) equipped with a flame ionization detector.

Upon completion of a catalytic experiment the reactant-product gas mixture was evacuated through the GC sample loop emersed in liquid nitrogen, a procedure that assured the efficient trapping of all key products. The hydrocarbons were first analyzed by warming the sample loop with a dry ice/acetone slurry; methanol was then assayed by further warming the sample loop to > 350 K. GC calibration was routinely checked for all products within the concentration range of interest. This analytical procedure provided a very sensitive and highly accurate product analysis. For example, methanol at reaction yields as low as 10^{12} molecules could be reproducibly analyzed. This analysis procedure used in conjunction with reaction times of several hours yielded a threshold TOF of $\sim 1 \times 10^{-8}$ for these studies.

Research purity (> 99.999, Matheson) gases of hydrogen, carbon monoxide, and carbon dioxide were used. CO was passed through a 142 K n-pentane/N_2 slurry trap to remove metal (Ni, Fe)-carbonyls. CO_2 was further purified by multiple distillation, while H_2 was used as received. Mixtures of $CO_2/CO/H_2$ with a ratio of 1/2/12 were prepared in situ in the reaction chamber, allowing ~ 20 minutes for mixing before commencing reaction.

3. Results and discussion

The kinetic data for methanol synthesis of a Cu(100) single crystal catalyst at $CO_2/CO/H_2 = 1/2/12$ are shown in figs. 1 and 2. The TOF for methanol production measured as a function of reaction temperature in the range 500–550 K is shown in Arrhenius form in fig. 1. The activation energy determined from these data is 73.4 ± 6.0 kJ/mole. The total pressure dependence (fig. 2), measured at 550 K, was found to be near unity (0.96 ± 0.10). This first order pressure dependency will be utilized to facilitate comparison of these data with studies carried out at higher pressures on supported Cu catalysts.

A TOF of 1.3×10^{-7} was measured at 525 K and a total pressure of 750 Torr. Burch and Chappel [14] observed a TOF of 5.6×10^{-5} for methanol production on a 5% Cu/SiO_2 catalyst at 523 K with a reactant mixture of $H_2/CO = 3$ and a total pressure of 1.0 MPa. Vannice and coworkers [15] reported a TOF of 2.3×10^{-5} at 523 K, under reaction conditions of $H_2/CO = 3$ and a total pressure of 1.5 MPa. Specific rates for ZnO supported Cu catalysts have not been reported; however, these catalysts are purported to be considerably more active per metal atom site than the corresponding silica supported Cu systems

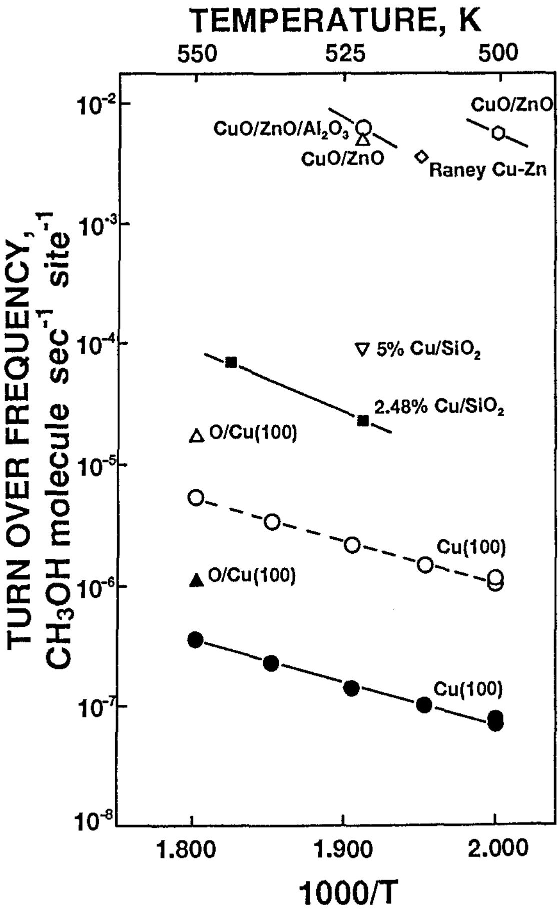

Fig. 1. The temperature dependence of methanol turnover frequencies for Cu(100) (●), oxidized Cu(100) (▲), supported Cu/SiO_2 from ref. [14] (▽), and ref. [15] (■), supported CuO/ZnO (△,) CuO/ZnO/Al_2O_3 (○) and Raney CuZn (◇) from table 1 in ref. [12]. Filled symbols represent data obtained under the actual experimental conditions. Open symbols represent data extrapolated to 1.5 MPa, the pressure used in the experiments of ref. [15].

(see fig. 1). For example, Campbell et al. [12], estimate TOF's for CuO/ZnO and CuO/ZnO/Al_2O_3 systems to be near 10^{-3} for $T = 523$ K, $CO_2/CO/H_2 = 6/24/70$ and 7.5 MPa pressure. Using the measured first order total pressure dependence of fig. 2, the reaction rates found for the Cu(100) catalyst are compared in fig. 1 with data obtained for the supported Cu catalysts acquired at higher pressures. Assuming first order behavior in total pressure, we obtain TOF's at 525 K of 1.3×10^{-6} at 1.0 MPa and 3.5×10^{-6} at 1.5 MPa for our Cu(100) catalyst. It is noteworthy that these rates represent $< 10^{-2}$ methanol molecules/Cu site/sec.

A wide range of activation energies has been reported for a variety of supported Cu catalysts. Chinchen and coworkers [16] found activation energies

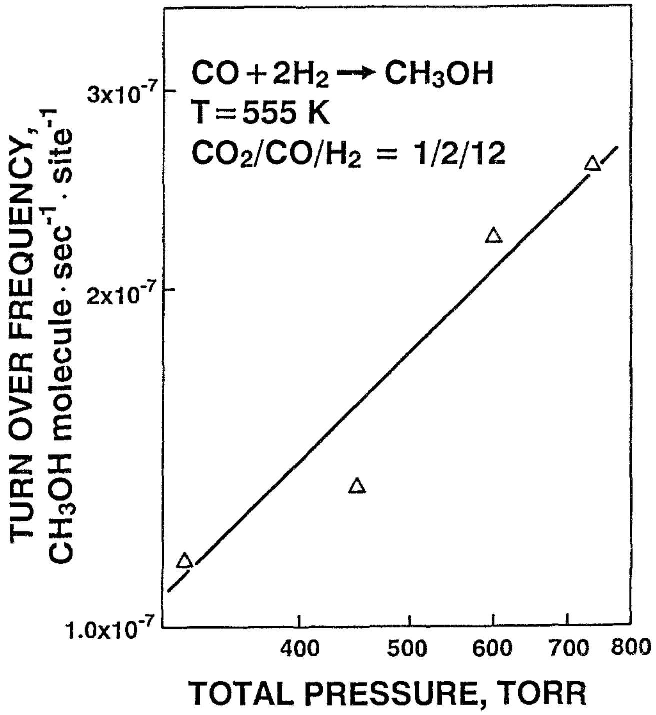

Fig. 2. The pressure dependence of the methanol turnover frequency for Cu(100). ($CO_2/CO/H_2$ = 1/2/12, T_R = 550 K, t_R = 150 minutes).

of 109 and 142 kJ/mole at temperatures of 563 and 523 K, respectively, for $Cu/ZnO/Al_2O_3$ catalysts. Klier [17] reported an activation energy of 42 kJ/mole for a Cu/ThO_2 catalyst while Leon y Leon and Vannice [15] report 52 kJ/mole for the above mentioned 2.48% Cu/SiO_2 system. Our value of 73.4 kJ/mole is in the range of these values, but closer to those values obtained for Cu/ThO_2 and Cu/SiO_2.

To monitor the change in surface composition of the Cu(100) catalyst during the reaction, Auger spectra were recorded before and after each kinetic measurement. Fig. 3 shows several Auger spectra acquired before (fig. 3a) and after (fig. 3b–c) reaction at varying conditions. Characteristic Auger features of submonolayer carbon and oxygen are seen in the spectrum (fig. 3b) taken prior to heating the sample in vacuum to the reaction temperature. A sharp decrease in the carbon peak intensities is apparent in the spectrum (fig. 3c) acquired subsequent to heating the sample to reaction temperature in vacuum. Surface oxygen was observed only after reactions which were carried out at > 540 K. These changes in the carbon and oxygen Auger peak intensities correlate with the desorption of CO and CO_2 from the Cu surface during heating. The presence of surface oxygen, even after flashing the crystal to the reaction

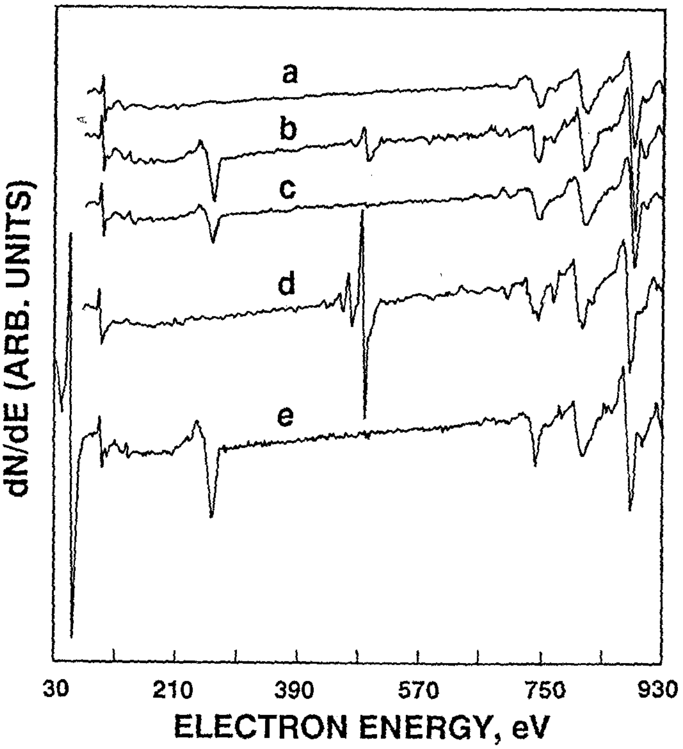

Fig. 3. Auger electron spectra of (a) the clean Cu(100) catalyst before reaction, (b) the surface of (a) after reaction prior to flashing to the reaction temperature under UHV conditions, (c) the surface of (b) flashed to reaction temperature, (d) oxidized Cu(100) (2 Torr of O_2, $T_{ox} = 555$ K, $t_{ox} = 5$ minutes), (e) the surface of (d) after reaction and subsequent to a flash to 555 K.

temperature, is consistent with the proposed promoter role of CO_2 in maintaining the Cu in a properly oxidized state for methanol synthesis [5].

The promotional effect of adsorbed oxygen, which is assumed to accelerate the adsorption of CO_2 and H_2, has been extensively investigated [5]. Ancillary experiments, therefore, were carried out to test for enhanced methanol activity for an oxidized Cu(100) surface. The Cu(100) sample was first oxidized in 2 Torr of oxygen at 555 K for 5 minutes, the surface flashed to 800 K, and the Auger spectrum then obtained (fig. 3d). The Auger spectrum of fig. 3e was measured subsequent to reaction and shows that the oxygen has virtually disappeared from the surface during the reaction. Also apparent in fig. 3e is the buildup of a significant carbon feature. The integrated catalytic activity of this oxidized surface was higher than that of the oxygen-free surface by a factor of two (see fig. 1); however, the TOF for the oxidized surface is still significantly lower than the lowest value reported for the supported, Cu-based catalysts [15].

Our experimental results are most consistent with ionic Cu sites serving as the active sites for methanol synthesis on unsupported copper. The extremely low TOF's for methanol formation found here for a Cu(100) catalyst likely is due to the very low concentration of ionic copper sites present under reaction conditions. The Auger spectra recorded before the catalytic run show that the impurity level on the Cu(100) surface is below the detection limit of the technique. However post-reaction Auger spectra indicate carbon and oxygen on the surface, consistent with the presence of some ionic Cu sites. These ionic species may result from or serve as sites for CO_x adsorption. Also the higher TOF obtained for the pre-oxidized sample is consistent with ionic Cu sites playing a key role in methanol synthesis on copper.

However, for the Cu(100) catalyst, support effects are clearly absent in contrast to the typical realistic supported, Cu-based catalysts. The support could influence the catalytic activity in two ways: first, the interaction between Cu and the support could produce sites with special coordination and activity. Although there is thought to be little synergism between Cu and ZnO in the commercial $Cu/ZnO/Al_2O_3$ methanol synthesis catalyst [5,6], a Cu-oxide support interaction could play a role in creating active sites for methanol synthesis on other supported Cu-based catalysts. A second pivotal role of the oxide support material on the activity of methanol synthesis catalyst has been discussed by Nonneman and Ponec [7]. These authors prepared a series of supported Cu catalysts using a variety of support materials, which have been acid treated to remove the alkali impurities. No activity for methanol synthesis was observed on those catalysts prepared from the acid-treated, alkali-free supports. However, the addition of trace amounts of impurities (ZnO, Cs_2CO_3 or Na_2CO_3) resulted in marked increases in methanol synthesis activity. This large improvement in the catalytic performance was attributed to the stabilization of Cu^{+n} species by these additives. It is believed that under conditions of catalyst preparation, the impurities, primarily alkali cations, are leached from the oxide support, providing sufficient Cu^{+n} species to facilitate activity. The promotional effect of alkali impurities on other supported, Cu-based catalysts likewise has been demonstrated [18].

The very wide range of TOF's found in the literature for methanol synthesis over supported Cu catalysts can be explained, in part, by the variety of oxide supports utilized and the accompanying spectrum of alkali impurities present. The absence of alkali impurities may be the essential feature giving rise to the very low methanol synthesis activity of the Cu(100) single crystal catalyst.

The dissociation of CO_2 has been shown to be an exceedingly slow process on clean Cu surfaces [12,19]. Dissociation probabilities of $< 10^{-9}$ molecules per collision have been measured for Cu(110) [19]. Sticking probabilities for the less corrugated surfaces [Cu(100) and Cu(111)] are likely to be significantly lower than those found for Cu(110). The rates then for CO_2 dissociative sticking on clean Cu(100) may well be much lower than the rate of methanol synthesis on typical Cu-based, supported methanol synthesis catalysts. Therefore the very small number of active sites created by CO_2 dissociation during the course of methanol synthesis on clean Cu may be sufficient only to produce those rates observed in this study. Upon oxidation, the activity of the Cu(100) surface for methanol production doubled with respect to the oxygen-free Cu surface. The results are consistent with an initial rapid activity which consumes the available ionic active sites, followed by an activity characteristic of the unoxidized, metallic Cu surface.

In summary our preliminary results are consistent with ionic forms of copper serving as the active sites for methanol synthesis on copper. The very low activity observed for the Cu(100) catalyst can be attributed to the absence of impurities which serve as promoters to enhance the concentration of ionic copper. Further work is in progress to unambiguously determine the role of the support and of impurities in altering methanol synthesis on copper.

Acknowledgement

We acknowledge with pleasure the support of this work by the Department of Energy, Office of Basic Energy Sciences, Division of Chemical Science.

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