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Methanol synthesis over Cu/SiO_2 catalysts

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The rates of CO and CO/CO_2 hydrogenation at 4.2 MPa and 523 K are reported for a series of Cu/SiO_2 catalysts containing 2 to 88 wt.% Cu. These catalysts were prepared on a variety of silica sources using several different Cu deposition techniques. In CO/CO_2 hydrogenation, the rate of methanol formation is proportional to the exposed Cu surface area of the reduced catalyst precursor, as determined by N_2O frontal chromatography. The observed rate, 4.2×10^{-3} mole CH_3OH/Cu site-sec, is within a factor of three of the rates reported by others over Cu/ZnO and $Cu/ZnO/Al_2O_3$ catalysts under comparable conditions. These results suggest that the ZnO component is only a moderate promoter in methanol synthesis. Hydrogenation of CO over these catalysts also gives methanol with high selectivity, but the synthesis rate is not proportional to the Cu surface area. This implies that another type of site, either alone or in cooperation with Cu, is involved in the synthesis of methanol from CO.

Keywords: Methanol; methanol synthesis; CO hydrogenation; copper catalysts; copper/silica catalysts

1. Introduction

The nature of the active Cu phase in low-pressure methanol synthesis catalysts remains a subject of ongoing debate. Some researchers suggest that a highly dispersed form of Cu(I) in the support matrix is the active site [1–4]. They propose that supports such as ZnO enhance the stability/dispersion of Cu(I) to provide the most active catalysts and report that Cu metal shows *no* measurable methanol synthesis activity. Others state that the methanol synthesis activity is directly proportional to the metallic Cu surface area and independent of the support [5–7]. Numerous groups concur that methanol synthesis rates are proportional to the Cu surface area for Cu on a given support [8–14]. However, several of these studies indicate that the rate depends strongly on the choice of support [10–14]. According to one proposal, the high turnover rates (molecules MeOH/Cu site-sec) obtained on ZnO-containing Cu catalysts results from a bifunctional scheme wherein hydrided ZnO promotes hydrogenation of formate

Table 1
Synthesis and properties of Cu/silica catalysts

Catalyst	Support [a]	Method [b]	wt.% Cu	Cu surface atoms (μmole/g cat.)	ppm	
					Na	Fe
A	Shell	IW	9.3	31	548	560
B	Shell	IE	9.0	91	570	610
C	Davison	UN	14.8	295	7	13
D	n.a.	co-ppt	88.1	86	n.d.	n.d.
E	Davison	UN	2.1	61	93	69
F	Davison	UN	5.2	132	68	59

[a] Shell spheres S980D, 130 m^2/g or Davison 57, 220 m^2/g.

[b] IW = Incipient Wetness; IE = Ion Exchange at pH = 12; co = ppt = coprecipitated; UN = Urea-assisted decomposition of aqueous Cu Nitrate.

intermediates adsorbed on metallic Cu surfaces [15–18]. These studies also report that the beneficial effects of the ZnO component are observed even when it is physically separated from the Cu component. Finally, a very recent proposal posits that defects in the support matrix (whose concentration depends on contact with the metal) are in fact the active sites for methanol synthesis from CO [19].

In order to gain further insight regarding the role of metallic Cu in methanol synthesis, we have studied methanol synthesis kinetics on family of Cu/SiO_2 catalysts. Silica supports have not been as extensively studied as ZnO, Al_2O_3, or ZrO_2 in methanol synthesis catalysts. However SiO_2 provides a good model system because it is widely regarded as unreducible under synthesis conditions and because it is neither strongly basic like zinc oxide nor acidic like alumina. Also, silica is less likely than the other oxides to stabilize substantial fractions of the Cu component as an unreducible surface phase [20].

2. Experimental

Table 1 summarizes the preparations and properties of the Cu/SiO_2 samples. For impregnated catalysts, the silica supports were crushed and sieved to 60–100 mesh, then calcined at 773 K in air for 16 h. Puratronic Grade copper salts (Aesar), and doubly distilled water were used in all preparations. Ion-exchange catalysts were prepared by adding a solution of $Cu(NH_3)_4^{2+}$ to silica in aqueous ammonia at pH 12. The "urea-nitrate" method refers to catalysts prepared by heating mixtures of Cu nitrate, urea, silica, and water at 363 K for two h to deposit the Cu, with subsequent filtration and drying at room temperature [21]. The coprecipitated 87% Cu/SiO_2 was prepared by adding aqueous $(NH_4)_2CO_3$ to an aqueous solution of Cu nitrate and tetraethylorthosilicate at 363 K until the pH was 7. The resulting precipitate was filtered and resuspended in water, then filtered again and dried at 363 K. All catalysts were calcined (O_2; 523 K; 4 h), reduced (H_2; 1.5 K/min to 523 K; hold at 523 K for 6 h), and passivated with 1% O_2 in He at 298 K prior to storage in air. Elemental analyses were performed by ion-coupled plasma emission spectroscopy in our Analytical Sciences Laboratories.

N_2O frontal chromatography measurements [22] were performed with a modified gas chromatograph (Hewlett-Packard Model 5880). Samples of prereduced and passivated materials were placed in 1/4″ stainless steel tubes, heated at 1.5 K/min in H_2 to 523 K, purged with He at 523 K for 15 min, and then cooled in He to 333 K for the adsorption experiments using 2% N_2O in He. The N_2 and N_2O concentrations were determined by thermal conductivity measurements. Copper surface area determinations were made on fresh and used catalyst samples, assuming an O/Cu_s stoichiometry of 0.5 [22].

Kinetic studies were performed in a single-pass, isothermal, fixed bed reactor with electronic mass flow controllers. Premixed feeds (31% CO/62% H_2/7% N_2 and 10% CO_2/10% CO/70% H_2/10% N_2; Matheson) were purified by passage through De-Oxo (Matheson) traps. Hydrocarbon and oxygenate products were separated on capillary and 1/8 inch packed columns; their concentrations were measured by flame ionization detection. CO, CO_2, and N_2 concentrations were determined by thermal conductivity detection. CO and CO_2 conversions were calculated using N_2 as an internal standard.

In a typical experiment the passivated catalyst (3 to 7 g) was charged into a 3/8″ O.D. stainless steel reactor, heated in flowing H_2 (101 kPa MPa) at 1 K/min to 523 K, and maintained at 523 K for 4 h. The H_2/CO feed was then introduced and the reactor was pressurized to 4.2 MPa. The reactor was maintained at this temperature and pressure 24 to 48 h or until a constant methanol synthesis rate was achieved. The H_2/CO feed was then replaced with $H_2/CO/CO_2$ at the same pressure, temperature and space velocity. Methanol synthesis rate measurements were again carried out until constant rates were observed (4 to 48 h). Finally, the catalysts were returned to the H_2/CO feed for 10 to 24 h. Activities measured during the first and second periods in H_2/CO were always within 10% of each other. The CO (or CO_2) conversion never exceeded 10% in order to maintain differential behavior and avoid thermodynamic limitations. In some experiments, the passivated catalyst was not pretreated with H_2. Instead, they were heated directly in synthesis gas (H_2/CO or $H_2/CO/CO_2$) in order to determine the effect of pre-reduction on the methanol synthesis rate. Activities are reported as both a mass specific rate (molecules CO_x converted/g catalyst-s) and turnover frequency (molecules CO_x converted/surface Cu atom-s). The selectivity to methanol always exceeded 95%. Blank runs with a quartz-filled reactor gave about 0.03% conversion to methane under the same reaction conditions and space velocity.

3. Results

TIME-DEPENDENT CATALYTIC BEHAVIOR

Fig. 1 shows the conversion vs. time behavior in a typical kinetic experiment (in this case, catalyst E). The synthesis rate in H_2/CO feed slowly increases to its steady-state value in 24 to 48 h. Similar activation behavior occurred when a prereduced catalyst was initially exposed to $H_2/CO/CO_2$ feed or when the reduced/passivated catalyst was heated to reaction temperature in H_2/CO without H_2 pre-reduction. Others have reported similar time-dependent activation behavior [9]. Its origins are clear, but our results exclude several possible explanations. It cannot result from changes in Cu dispersion because N_2O frontal chromatograms of fresh and used catalysts are the same within 15%. Redispersion or other structural rearrangements of Cu particles can occur in CO-containing feeds [24]. Here, however, we find that if such morphological changes do occur in synthesis gas, they are not reversed by re-exposure to high temperature H_2. Steady-state catalysts treated in H_2 at 523 K recover their previous steady-state activity within 1 hour of feed reintroduction without any transient activation behavior. On-going electron microscopy and in-situ Cu EXAFS studies in our laboratory address the contributions of Cu valence state and of structural changes to the gradual activation process.

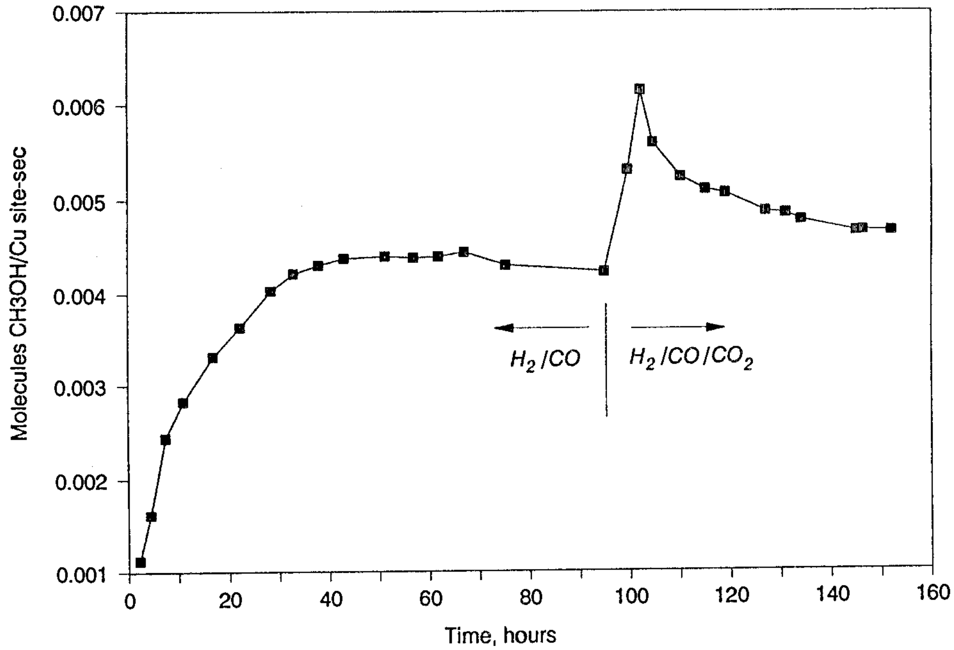

Fig. 1. Rates of CO and CO/CO_2 hydrogenation over catalyst E as a function of time at 523 K, 4.2 MPa total pressure. The vertical line indicates when the feed was shifted from H_2/CO to $H_2/CO/CO_2O$.

Table 2
Methanol synthesis activity measurements

Run number	Catalyst	Startup [a]	Activity [b]			
			$CO/CO_2/H_2$		CO/H_2	
			STY	MSR	STY	MSR
207	A	1	5.9×10^{-3}	1.8×10^{-7}	1.0×10^{-2}	3.1×10^{-7}
208	A	3	4.0×10^{-3}	1.2×10^{-7}	6.4×10^{-3}	2.0×10^{-7}
199	A	1	6.0×10^{-3}	1.8×10^{-7}	7.5×10^{-3}	2.3×10^{-7}
201	A	1	6.5×10^{-3}	2.0×10^{-7}	1.0×10^{-2}	3.1×10^{-7}
209	A	2	4.0×10^{-3}	1.2×10^{-7}	9.4×10^{-3}	2.9×10^{-3}
203	B	1	6.0×10^{-3}	5.5×10^{-7}	3.8×10^{-3}	3.5×10^{-7}
210	C	1	4.5×10^{-3}	13.3×10^{-7}	1.2×10^{-3}	3.5×10^{-7}
213	D	1	4.2×10^{-3}	3.6×10^{-7}	1.1×16^{-3}	0.9×10^{-7}
215	E	1	4.6×10^{-3}	2.8×10^{-7}	4.3×10^{-3}	2.6×10^{-7}
216	F	1	3.5×10^{-3}	4.6×10^{-7}	1.8×10^{-3}	2.4×10^{-7}

[a] Run startup procedures. 1 = prereduced catalyst re-reduced in-situ with H_2 then first exposed to H_2/CO feed. 2 = prereduced catalysts re-reduced in-situ with H_2 then first exposed to $H_2/CO/CO_2$ feed. 3 = prereduced catalyst heated to reaction temperature in H_2/CO.

[b] 250 °C; 42 bar total pressure. STY = site-time yield (molecules CH_3OH/Cu surface sites); MSR = mass specific rate (moles (H_3OH/g catalyst-s).

CO/CO_2 HYDROGENATION

Table 2 reports steady-state methanol synthesis rates on Cu/SiO_2 catalysts as both mass-specific (molecules CH_3OH/g cat.-s) and turnover rates (molecules CH_3OH/Cu site-s). In CO_2-containing feeds, turnover rates vary over a rather narrow range, (3.5 to 6.5×10^{-3} s^{-1}). The similarity of the turnover rates suggests that mass-specific rates are proportional to the Cu surface area (from N_2O frontal chromatography). Such a relationship is plotted in fig. 2. A least squares fit of these data yields a methanol turnover frequency of 4.3×10^{-3} methanol molecules/Cu site-sec at 4.2 MPa and 523 K ($R = 0.98$). The effects of start-up procedures on steady-state performance were examined for one catalyst (A). From table 2 it is apparent that pre-reduction in H_2 vs. H_2/CO or initial exposure of the catalyst to H_2/CO vs. $H_2/CO/CO_2$ feeds have at best a weak influence on the rates of CO or CO/CO_2 hydrogenation. Furthermore, there is no pronounced effect of Cu dispersion on synthesis rate for the range of dispersions examined here (0.6 to 12.7%).

Other groups have measured methanol synthesis rates from similar feeds over Cu/SiO_2 catalysts at reaction conditions close to those employed here. At 5.0 MPa in 14% CO/14% CO_2/46% H_2/26% He feeds at 513 K, Chinchen et al. determined a turnover rate of 1.1×10^{-2} s^{-1} on a Cu/SiO_2 of undefined composition [5]. On 1% Cu/SiO_2 Pan et al. measured a turnover rate of 5.7×10^{-3} s^{-1} at 523 K in 5.0 MPa 24% CO/6% CO_2/76% H_2 [7]. At somewhat lower pressure (1.4 MPa), Bell et al. found a 1×10^{-1} s^{-1} turnover

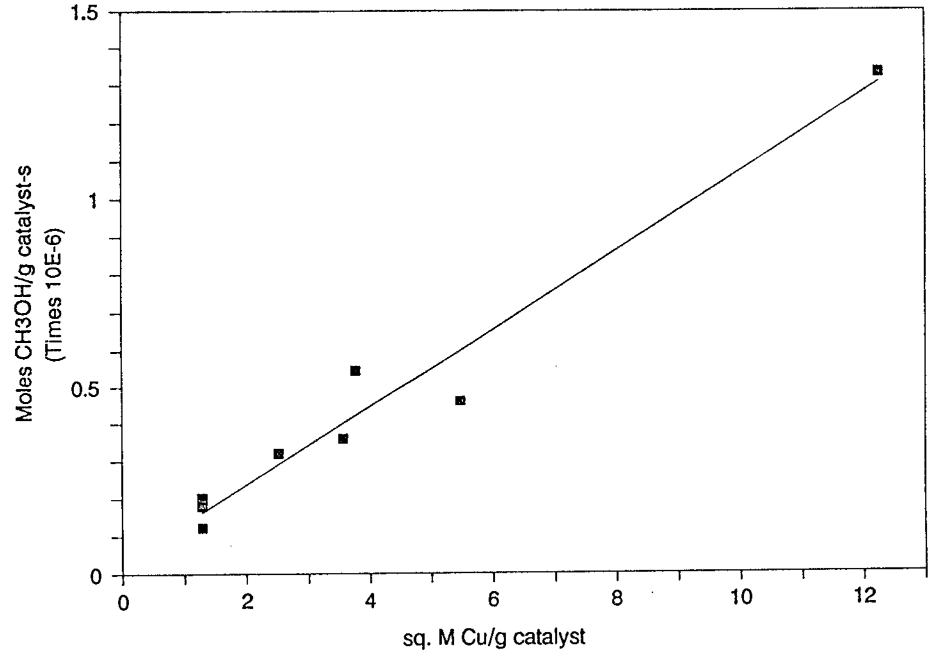

Fig. 2. Mass specific rate of methanol synthesis from $H_2/CO/CO_2$ plotted vs. Cu surface area for catalysts A-F in ten independent experiments.

rate for CO_2 hydrogenation (3:1 H_2/CO) at 523 K over 9.3% Cu/SiO_2 [25]. Burch and coworkers have measured CO/CO_2 hydrogenation rates over several series of Cu/SiO_2 catalysts with varying Cu loading [8,9]. In 10% CO/10% CO_2/18% H_2 at 4.0 MPa and 523 K, they also found that the methanol synthesis rate is proportional to the Cu surface area, but their turnover rate (5.7×10^{-4} s^{-1}) is significantly lower than we and others have determined. The possible origins of these differences will be discussed later.

CO HYDROGENATION

On a mass-specific basis, the rate of methanol formation is higher in H_2/CO than in $H_2/CO/CO_2$ for one catalyst (A), while the opposite is true for the other catalyst samples. In any case, the per-gram activity differences in CO_2-containing vs. CO_2-free feeds are usually small and it is recognized that the optimal CO_2 concentration for maximum methanol productivity is a sensitive function of catalyst composition [26,27].

In contrast to the finding for CO/CO_2 hydrogenation, there is no linear relationship between CO hydrogenation rates and exposed Cu surface area (table 2, fig. 3). Turnover rates vary by a factor of ten for this series of catalysts, while mass specific rates vary over a much narrower range. There are relatively few studies of CO hydrogenation rates over Cu/SiO_2 at comparable tempera-

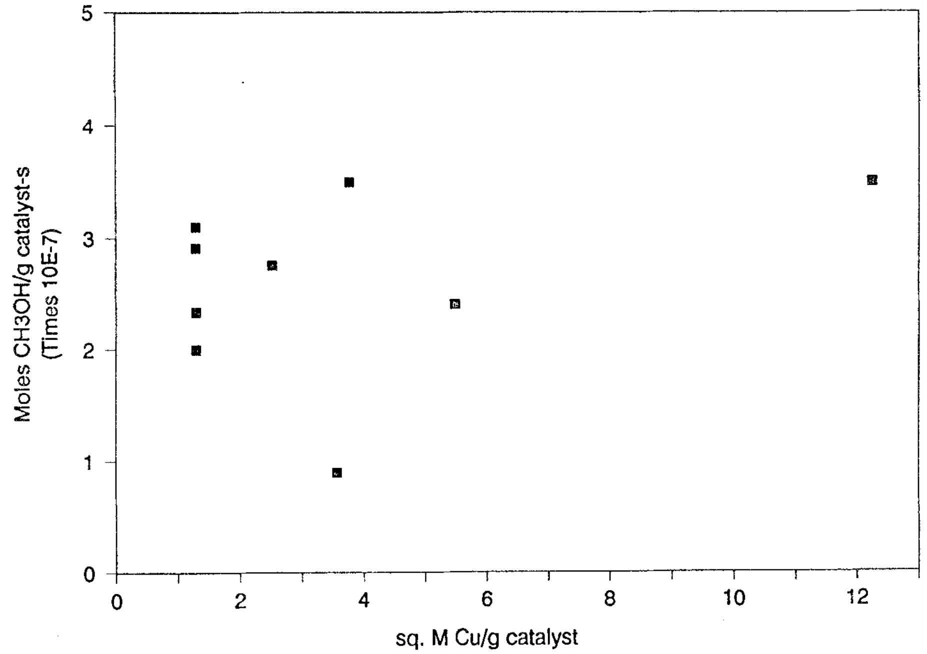

Fig. 3. Mass specific rate of methanol synthesis from H_2/CO plotted vs. Cu surface area for catalysts A-F in ten independent experiments.

tures and pressures. In 2 : 1 H_2/CO Bell et al. measured a CO turnover frequency of 7.6×10^{-3} s^{-1} on 9.3% Cu/SiO_2 at a lower pressure (1.06 MPa) and a higher temperature (573 K) than we employed. They also noted high selectivity to methane rather than methanol [28]. Burch et al. have measured CO hydrogenation rates at 4.0 MPa and 523 K over a series of Cu/SiO_2 catalysts [8,9]. Their materials showed > 95% selectivity to methanol, as we find here. However, the methanol synthesis rates they report on a mass specific basis (1.5–20×10^{-9} moles CH_3OH/g cat-s) and on a turnover rate basis (6.2–12.5×10^{-5} s^{-1}) are significantly lower than we measure on our catalysts.

4. Discussion

Fig. 2 shows that in CO_2-containing feed a linear relationship exists between methanol synthesis rate and the exposed Cu surface area, as measured by N_2O decomposition. This finding agrees with that of Burch et al. [8,9]. Under similar reaction conditions, the methanol turnover rate we observe (ca. 4×10^{-3} s^{-1}) is close to that measured by three other groups over Cu/SiO_2 [5,7,25], but nearly a factor of ten higher than that reported by Burch's group [8,9]. It seems unlikely that the higher rates reflect the presence of impurity promoters such as alkali. From tables 1 and 2 we see that essentially similar rates are found on catalysts containing 7 to 550 ppm Na and < 2 to 610 ppm Fe. It is possible that low activity Cu/SiO_2 catalysts result from the rapid heating of the precursor materials in H_2 during the initial reduction step. As Burch has suggested, these circumstances can lead to high local exotherms and concomitant annealing of Cu particles [8]. This may be a critical variable if methanol synthesis rates depend on the morphology of the Cu crystallites [8]. In any case, the data presented here establish that a variety of common catalyst preparation techniques can provide Cu/SiO_2 samples with reasonably high turnover rates for methanol synthesis from $CO/CO_2/H_2$ feeds.

The methanol turnover frequencies reported here are only a factor of three lower than those reported (1.1×10^{-2} s^{-1}) for a series of six Cu/ZnO catalysts at the same temperature in a similar $CO/CO/H_2$ feed at 5 MPa [7]. Our observations are consistent with previous suggestions that surface Cu formate, generated via the interaction of CO_2 with H on Cu, is an intermediate in the synthesis of methanol from CO_2-containing feeds [5,6,29]. Related studies in our laboratory show ZnO-modification of the Cu/SiO_2 catalysts leads to a small, but significant increase in methanol synthesis rates, both on a mass specific and turnover number basis [33]. These data and H/D kinetic isotope effect measurements in our laboratory [33] support the proposal that the rate-limiting step for methanol formation from CO_2 involves the hydrogenation of surface Cu formate [6], and that ZnO increases the hydrogenation rate by providing an additional source of H adatoms [15–18].

Different methanol synthesis pathways appear to be involved for CO/H_2 feeds [30]. No simple relationship exists between the Cu surface area and the methanol synthesis rate exists when CO_2 is absent from the feed. The methanol synthesis rates do not correlate with alkali content; catalysts B and C gave similar mass specific rates yet their alkali and iron contents differ greatly. These observations suggest that methanol synthesis from H_2/CO requires an active site, either alone or in conjunction with Cu(0) site, that is not required for the conversion of $CO_2/CO/H_2$ feeds. One possibility is that methanol synthesis occurs entirely on a unique form of silica-stabilized Cu^{+1} sites [31]. At present we feel this is unlikely. The number of such sites that remain unreduced after H_2 pretreatment should be sensitive to variables such as the Cu loading, the silica source, the copper precursor, the method of Cu deposition, and the catalyst activation procedure. Here we find that five Cu/SiO_2 catalysts with 2 to 15 wt.% Cu prepared by three different techniques exhibit very similar mass specific rates, 1.1 to 3.5×10^{-3} moles/g-sec. It would seem surprising if all these preparations all provided such a narrow range of Cu^{+1} site densities.

We propose that CO hydrogenation to methanol on supported Cu catalysts is a bifunctional reaction catalyzed by both Cu metal surfaces and by neighboring sites on the support. At reaction temperatures, CO is weakly adsorbed on Cu but not readily converted to formate in the absence of water. A likely alternative path to formate intermediates involves the reaction of CO with basic surface hydroxyl groups on either silicon ions or on silica-stabilized copper oxides. Kinnaird et al. have suggested a similar mechanism for CO adsorption on partially hydroxylated Cu surfaces [32]. Pure silica surfaces are not generally regarded as sufficiently basic to activate CO in this fashion. However, basic sites may be generated by the presence of trace alkali or by stabilized Cu oxides. In a similar vein, several groups have shown that the lowest energy pathway for CO hydrogenation over supported Pt involves intermediates which are transiently adsorbed onto the oxide support surface [34,35].

Isolated formates on ceramic oxide surfaces are fairly inert with respect to hydrogenation [29]. However those formed in the vicinity of Cu particles or with access to hydrogen adatoms generated by H_2 dissociation on Cu(0) could hydrogenate further to products by either hydrogen migration from Cu sites or by reactive migration of formate to Cu as a surface formyl. At present, these concepts remain unproven, but are consistent with the known chemistry of basic oxides and with our results. These proposals are being tested by in-situ vibrational spectroscopy and by the analysis of H/D kinetic isotope effects. The results of these studies as well as in-situ EXAFS experiments will be reported at a later date.

5. Summary

Our data establish that a variety of common catalyst preparation techniques *can* provide Cu/SiO_2 samples with good activity for methanol synthesis from CO/H_2 or $CO/CO_2/H_2$ feeds. In CO_2-containing feeds the synthesis rate scales with the Cu surface area, suggesting that metallic Cu is the active catalytic component. In CO_2-free feeds, the synthesis rate is not proportional to the Cu surface area indicating that some other type of surface site is involved catalytically. We propose that this site might be a basic surface hydroxide required for the initial conversion of CO to oxide-bound formate.

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