New insights into methanol synthesis catalysts from X-ray absorption spectroscopy

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Abstract

X-ray absorption spectroscopic studies from several different groups provide a consistent structural picture of methanol synthesis catalysts. Copper metal is the principal Cu species detected in all in-situ XAS studies. A small amount of Cu(II) persisted in many samples reduced below 600 K, but it appears to be catalytically irrelevant. Cu(I) was not detected in any of the in-situ XAS studies. The Zn structure did not change in response to chemical treatments in any of the ZnO-containing methanol synthesis catalysts.

We conclude that the slow approach to steady-state rate of methanol synthesis from CO/H_2 mixtures cannot result from changes in the Cu metal component of Cu/SiO_2 catalysts. By eliminating this possibility, we provide indirect evidence for the proposal that initial induction periods reflect slow changes in the surface of the SiO_2 or ZnO component in the catalysts. A bifunctional mechanism involving the formation of formate from CO on support hydroxyl groups would increase methanol synthesis rates as OH groups are formed by hydrolysis of Si–O bonds using the H_2O formed in slow methanation side reactions. The bifunctional mechanism is not required for the synthesis of methanol from CO_2-containing mixtures, because formate can form on Cu directly from CO_2 and H_2. ©1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Catalytic methanol synthesis is vastly superior to the process it replaced, the destructive distillation of wood. Early catalysts consisted of ZnO and Cr_2O_3 mixtures and produced methanol in low yields from $CO–H_2$ mixtures at high temperatures (593–673 K) and pressures (250–350 bar). Chromia was included in ZnO catalysts as a structural promoter, in preference over alumina, which catalyzes methanol dehydration to dimethyl ether. More active Cu-based catalysts were introduced commercially well after their discov-ery, because their poisoning by feed sulfur could not prevented using available purification methods [1].

Current methanol synthesis catalysts are prepared by co-precipitation of Cu, Zn, and Al as hydroxides or carbonates, which are then decomposed to mixed oxides by treatment in air and reduced in H_2 before use. Methanol synthesis feeds contain CO, H_2, and CO_2; the latter is introduced intentionally because it increases the rate of CO hydrogenation reactions. The historical evolution of methanol synthesis catalysts and processes has led to two natural issues for investigation. One is the role of Cu and its chemical state during reaction. In examining the role of Cu, it seems surprising that the active component in early methanol synthesis catalysts (ZnO) should be-
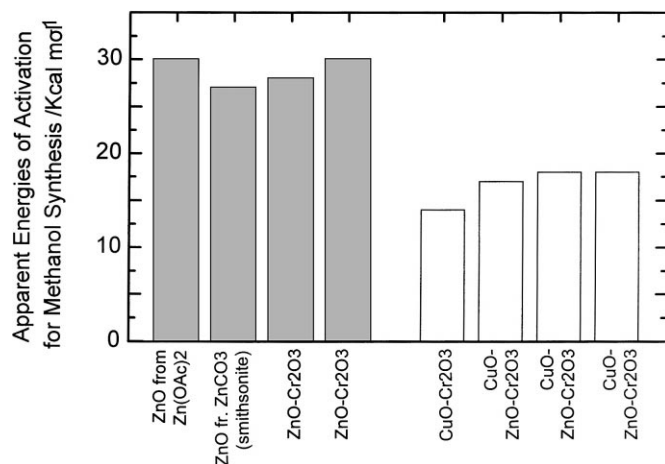
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Fig. 1. Apparent energies of activation measured over methanol synthesis catalysts containing only Zn and a Cr_2O_3 structural promoter, or including Cu [1]. Shaded bars at left refer to different preparations in which ZnO is the only active component. Bars at right refer to different preparations of catalysts that contain Cu or Cu and ZnO.

come the best promoter for Cu in the current catalysts. The other is the mechanism of CO and CO_2 hydrogenation to form methanol. Some studies conclude that methanol is formed via identical pathways on $Cu/ZnO/Al_2O_3$ and on ZnO/Cr_2O_3. In this proposal, Cu acts as an intracrystalline promoter for ZnO, and the role of CO_2 is to prevent the reduction of Cu cations to Cu metal during reaction [2–5]. Other studies conclude that the mechanism of methanol synthesis is different on Cu/ZnO and ZnO/Cr_2O_3, and that Cu is involved directly in the synthesis of methanol. Indeed, methanol synthesis activation energies are much lower on Cu-containing catalysts than on ZnO/Cr_2O_3 (Fig. 1), suggesting different pathways. These differences in activation energy, however, are not sufficient to distinguish promotion of ZnO/Cr_2O_3 from a mechanistic shift.

Recent studies agree that CO_2 rather than CO is the direct precursor to CH_3OH on Cu-containing catalysts, based on the initial appearance of $^{13}CH_3OH$ from $CO/^{13}CO_2/H_2$ mixtures [6], on infrared spectra of adsorbed intermediates [7,8], and on transient kinetic studies [9]. It has even been reported that methanol synthesis from mixtures of H_2 and CO does not occur on Cu/SiO_2 [10]. Methanol synthesis rates reach a maximum at intermediate CO_2 concentrations, above which its promoting effect is offset by the oxidation of the active Cu metal sites into inactive species [2]. Thus, the oxidation state of Cu depends not only on catalyst

composition and pre-treatment conditions, but also on the feed and product compositions during steady-state catalysis.

The oxidation state of Cu during methanol synthesis is difficult to establish. Various studies have shown that Cu single-crystal or polycrystalline foil surfaces catalyze methanol synthesis from CO_2/H_2 mixtures [11,12]. X-ray diffraction studies provide an incomplete picture, because Cu-containing phases become detectable only when present as catalytically irrelevant large crystallites and only infrequently on well-prepared active catalysts, whether or not reaction conditions were maintained [13,14]. X-ray photoelectron spectroscopy (XPS) studies have detected significant Cu(I) and Cu(II) concentrations in materials prepared in a treatment cell and then transferred into a vacuum chamber for surface analysis [4]. This approach cannot detect Cu species present during catalysis, because they are likely to be modified by the quenching protocol, by oxidation with air during transfer into the vacuum system, or by autoxidation using protons formed during the initial reduction of the Cu oxide catalyst precursors.

X-ray absorption spectroscopy (XAS) is well suited for in-situ studies of the Cu oxidation state and structure during methanol synthesis, and several groups have applied it. XAS provides element-specific information, so that the Cu and Zn species can be studied independently, even though all mixed phases may exist.

The study that first reported the use of Fourier transforms to obtain radial distribution function around the absorber from the XAS fine structure (i.e. extended X-ray absorption fine-structure spectrum, EXAFS) used a Cu catalyst and stated the significance of the study to methanol synthesis catalysis [15].

Several reports describe X-ray absorption studies of Cu-based catalysts prepared in reactors and then transferred into the X-ray absorption cells using protocols designed to minimize exposure to air. Vlaic et al. [16,17] investigated Cu–ZnO/Al$_2$O$_3$ catalysts reduced at 503 K. After reduction, the catalysts were pressed into wafers and X-ray spectra taken in a He atmosphere. Analysis of the X-ray absorption spectra near the edge showed that some catalysts contained only Cu(0), while others contained residual CuO, although the reason for the difference was not discussed. No Cu(I) was detected in reduced samples. A separate study reported XPS and XAS data on Cu/ZnO catalysts prepared ex-situ and transferred into an absorption cell or a vacuum chamber [4]. Catalysts were activated at 493 K for 4–8 h in a CO$_2$/CO/H$_2$/N$_2$ (4/0.5/2.25/93.25%) mixture saturated with H$_2$O (temperature not specified). Cu K-edge XAS at room temperature detected Cu(0), Cu(I), and Cu(II), but the relevance of these findings to the state of Cu during steady-state catalysis or even after initial pretreatment is questionable because the mild ex-situ treatment is unlikely to reduce Cu atoms that would reduce during more realistic pre-treatments or even during reactions of CO/H$_2$/CO$_2$ mixtures. Sankar et al. [18,19] reduced Cu/ZnO catalysts containing 10, 20, and 33 wt.% Cu at 523 K in H$_2$ for 5 h, then transferred them into a spectroscopic cell. They detected Cu(0) and substantial amounts of Cu(I) and Cu(II). The relative amounts were not reported, but the average number of oxygen neighbors around a Cu atom was highest in the catalyst with the lowest Cu loading, most likely indicating the highest fraction of oxidized Cu in that sample. Another in-situ study by this group also detected Cu in all three oxidation states [20], but sample wafers contained a binder that may not be completely removed during reduction and may have protected some CuO from contact with H$_2$.

Several recent reports demonstrate how XAS studies at reaction conditions are essential to determine the oxidation state and structure of Cu species during methanol synthesis [21–23]. Cu crystallites in Cu–Zn binary catalysts were completely reduced to Cu(0) after treatment with H$_2$ at 493 K, but remained as Cu(II) in Cu–Zn–Al ternary catalysts after H$_2$ treatment at 493 K [21]. Cu(II) in a ternary with 5 wt.% Cu reduced completely to Cu(0) at 533 K and formed Cu clusters too small to produce X-ray diffraction lines. Larger Cu crystallites presenting a radial distribution function characteristic of bulk Cu formed on ternary catalyst with higher Cu content (27 wt.% Cu) after similar treatments [21,22]. Cu(I) or Cu(II) species were not detected in any of the catalysts after reduction at 533 K by these first true in-situ studies of methanol synthesis catalysts.

Several groups have reported the results of combined XRD/XAS in-situ studies of methanol synthesis catalysts. Couves et al. [23] prepared a material resembling a methanol synthesis catalyst by treating the mineral aurichalcite (Cu$_{5-x}$Zn$_x$ (OH)$_6$(CO$_3$)$_2$) in air at 723 K and then reducing in H$_2$ at 543 K and then 773 K. XAS spectra and XRD patterns were measured simultaneously. Cu(0) crystallites of about 10 nm diameter were detected after reduction at 543 K. As the reduction temperature was increased to 773 K, the Cu(0) XRD lines narrowed, and the amplitude of the EXAFS signal declined. This decrease in the EXAFS signal and in the corresponding intensity of the radial distribution function typically reflects a decrease in the average coordination number of Cu atoms (higher dispersion, smaller crystallites) or greater structural disorder. The apparently contradictory results from XRD and EXAFS measurements were attributed to incorporation of Zn atoms into the Cu lattice resulting in greater structural disorder. However, this interpretation may be faulted insofar as structural disorder also broadens X-ray diffraction lines.

An alternative interpretation was suggested in a combined XAS/XRD in-situ study, using a thin quartz capillary as a cell with hydrodynamics resembling those in well-designed tubular plug-flow reactor [24]. A comparison was made between 5% Cu/SiO$_2$ and 5% Cu/ZnO catalysts, reduced in CO/CO$_2$/H$_2$/Ar (0.5/4/4/91.5) mixtures at 493 K and then used in methanol synthesis with either CO$_2$/H$_2$ (10/90), CO/CO$_2$/H$_2$ (5/5/90) or H$_2$O/CO/CO$_2$/H$_2$ (3/4.85/4.85/87.3) mixtures, all at atmospheric pressure [24,25]. In both catalysts and with all synthesis gas compositions, Cu(0) was the most abundant species at 493 K. The structures and coordination

numbers of Cu species on the SiO₂ support were not sensitive to the composition of the gas phase. In contrast, the Cu–Cu coordination number for Cu metal particles on ZnO changed reversibly as feed composition was varied. Cu particles increased in dispersion (i.e. became smaller) when water was removed from the synthesis gas stream. These data led to a model that correlated the relative interfacial area between Cu metal and ZnO in Cu–ZnO with the reduction potential of the gas mixture, which determined the extent of reduction of the ZnO component and the consequent spreading of Cu metal species on ZnO [26]. A rate law was developed that incorporated H_2O partial pressure only in a term that predicted its effect on Cu surface area. This successfully predicted rates measured under conditions differing only in H_2O concentration. The authors conclude that reconstruction of Cu particles in the presence of H_2O provide a more reasonable explanation than competitive adsorption for the observed inhibition of methanol synthesis reaction rates by H_2O [27]. In reference [23], a simultaneous sharpening of XRD lines for Cu metal, and a decrease in Cu EXAFS amplitude, was observed as the reduction temperature was increased from 543 to 773 K. Since XRD is most sensitive to the largest particles, but EXAFS also detects the smallest, it appears that Couves et al. [23] detected the evolution of a bimodal distribution of crystallite sizes, with the largest Cu particles getting larger and the smallest getting smaller. XAS alone cannot detect a bimodal particle size distribution, but disagreement between XAS and XRD on average crystallite size provides circumstantial evidence for bimodal distributions.

All available in-situ XAS data support the role of Cu(0) as the active species and as the most abundant Cu species in working methanol synthesis catalysts using $CO_2/CO/H_2$ feeds. The small Cu particles required for high volumetric productivity form in a narrow range of pre-treatment temperatures. Crystallite growth is rapid in H_2 well below 700 K, but complete reduction requires temperatures above 500 K. Brands, et al. [28] recently reported that Cu in 14% Cu/7% Zn/SiO₂ became reduced in H_2 at 693 K but spontaneously re-oxidized when He or vacuum replaced the H_2 atmosphere. Tohji et al. [29] reported similar behavior for Cu in a Cu/ZnO catalyst reduced in H_2 between 400 and 550 K, with re-oxidation observed below 400 K in non-reducing environments. The authors

attributed these results to spontaneous autoxidation by protons left behind during the initial reduction. Highly dispersed Cu would efficiently scavenge oxygen from O_2 or H_2O in the absence of a reducing atmosphere. However, these workers appear to have used the appropriate measures to remove oxygen from the inlet gas. The argument for autoxidation would have been strengthened if an indicating oxygen trap had also been placed at the outlet of the in-situ cell, to confirm that the cell itself was not leaking.

In this paper, we report a structural study of a catalyst comprising 2.1 wt.% Cu/SiO₂. This same catalyst was used in a previous study to establish the role of metallic Cu in methanol synthesis [6]. Silica supports have not been as extensively studied as ZnO, Al₂O₃, or ZrO₂ in methanol synthesis catalysts. However, SiO₂ provides a good model system because it is widely regarded as unreducible under synthesis conditions. Although Cu/SiO₂ is not used commercially for synthesis of methanol, the observed rate of CO/CO₂ hydrogenation to CH_3OH with this catalyst, expressed per Cu-site, was within a factor of three of the rates reported by others over Cu/ZnO and Cu/ZnO/Al₂O₃ catalysts under comparable conditions [6].

2. Experimental

A Cu/SiO₂ catalyst (2.1 wt.% Cu) was prepared by urea-assisted decomposition of aqueous copper nitrate onto Davison 62 silica, as described in reference [6]. The Cu dispersion measured by N_2O frontal chromatography was 18% [6]. A pre-reduced and passivated sample (0.3 g) was pressed into a 1 in diameter wafer at 35 MPa and the wafer was mounted in an in-situ XAS cell designed and built by Lytle [30]. The catalyst was treated in-situ in a $CO/H_2/N_2$ (31/62/7 mol) mixture or a $CO_2/CO/H_2/N_2$ (10/10/70/10 mol) mixture at a total pressure of 0.42 MPa. X-ray absorption spectra were measured on beamline X-10C at the NSLS facility at Brookhaven National Laboratory. Beamline resolution was approximately 2.5 V at the Cu K edge (8979 eV). Data were taken using a 0.35 eV increment in the near-edge region and a 3.5 eV increment through the EXAFS region. For data analysis, the edge position for Cu metal was defined as 8979 eV, which corresponds to the position of the first inflection point. Data were
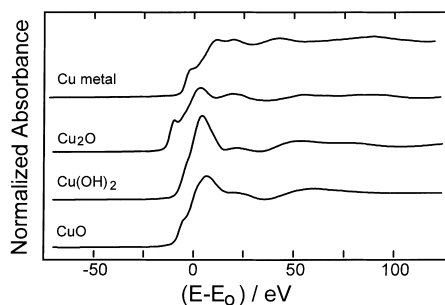
Fig. 2. X-ray absorption near-edge spectra from standard compounds used in this work. The position E_o of the Cu K-edge is 8979 eV.

analyzed using programs EXANES, EXAPLT, and EXAFIT and procedures described previously [31].

3. Results

Near-edge spectra were analyzed by fitting linear combinations of spectra from Cu metal, CuO, $Cu(OH)_2$, and Cu_2O standards from -20 to $+60$ eV energies with respect to the edge [32]. The standard spectra were allowed to shift in energy and were adjusted in amplitude, and added together to find the best fit to the sample spectra. Fractions of Cu occupying sites resembling those in the standard compounds, were given by the fraction of each standard spectrum needed to describe the near-edge spectra of actual catalysts. Near-edge spectra for standard compounds are shown in Fig. 2. In all cases, excellent fits were obtained using only Cu metal and CuO as the standards. A representative fit for an edge spectrum from the catalyst at 530 K in the CO/H_2 mixture is shown in Fig. 3. The $Cu(OH)_2$ and Cu_2O standard spectra were not necessary to describe any of the spectra from catalyst samples.

EXAFS was analyzed after background subtraction and Fourier transformation of the k^1-weighted data in the range from 3 to 16 Å^{-1}. Fourier transform magnitudes from the standard compounds in Fig. 2 are shown in Fig. 4. Our analysis was restricted to the calculation of the number of Cu and O neighbors for an average Cu atom, although EXAFS can also be used to quantify the relative abundance of co-existing phases [33]. Back-transforms were calculated using Fourier-transformed data between 1.4
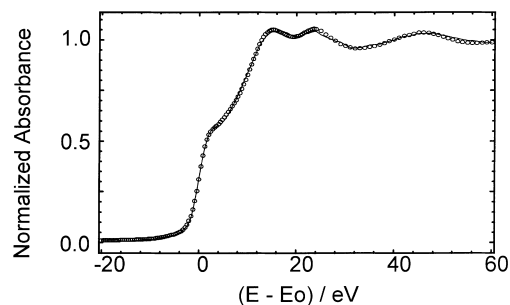

Fig. 3. Representative fit (circles) to Cu K-edge X-ray absorption spectrum from 2.1 wt.% Cu/SiO_2 at 510 K in H_2. Fit was calculated between -20 and $+60$ eV. The fit comprises 14 and 86% contributions from the CuO and Cu metal standard spectra, respectively.
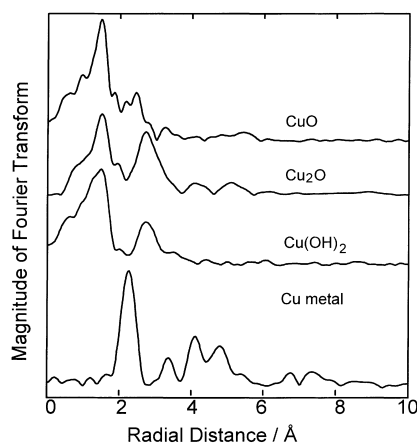

Fig. 4. Fourier transformed k^1-weighted EXAFS from standard compounds, representing possible phases in methanol synthesis catalysts. All traces are on the same scale, except that the Cu metal trace is reduced by a factor of 3.

and 3.4 Å. Back-transformed EXAFS data were fit in the range from 3 to 15 Å^{-1} using oxygen and Cu back-scattering and phase shift functions derived from CuO and Cu metal standard spectra. A representative fit is shown in Fig. 5 for the catalyst after reduction at 530 K. The reported Cu–Cu coordination numbers are likely to be underestimated by 20–30%. This is because the harmonic form of the Debye-Waller factor used to describe disorder is inadequate for Cu atoms at this temperature, in particles which present a significant fraction of atoms at their surface, since the pair-distribution function for such atoms is asymmetrical [34]. Relative values of coordination numbers, however, are correct.
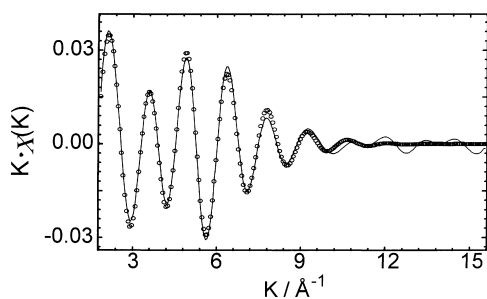
Fig. 5. Representative fit (circles) to EXAFS from the first shell of Cu and O neighbors in 2.1 wt.% Cu/SiO_2 in H_2 at 510 K. Back-scattering and phase shift functions derived from Cu K-edge X-ray absorption spectra from Cu foil and CuO, measured at room temperature, were used to calculate the fit. Fit was calculated between 3 and 15 Å^{-1}. Fit parameters for Cu–Cu pairs were coordination number 6.6, interatomic distance 2.537 Å, and $\Delta\sigma^2 = 0.01$ Å^2. Parameters for Cu–O pairs were coordination number 0.6, interatomic distance 1.836 Å, and $\Delta\sigma^2 = 0.0006$ Å^2.
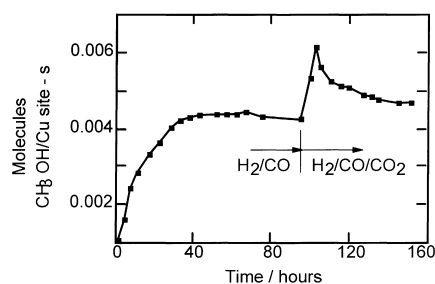

Fig. 6. Rates of production of CH_3OH over 2.1% Cu/SiO_2. Catalyst was pre-reduced in 4.2 MPa H_2 at 523 K for 4 h. Reaction was also at 523 K. Gas compositions were 31% CO/62% H_2/7% N_2 or 10% CO_2/10% CO/70% H_2/10% N_2.

The methanol synthesis rates shown in Fig. 6 were reported previously [6]. In a CO/H_2/N_2 (31/62/7 mol) mixture at 4.2 MPa, CH_3OH synthesis rates at 523 K increased slowly over a period of about 40 h before reaching steady-state values. When a mixture containing CO_2/CO/H_2/N_2 (10/10/70/10 mol) was introduced, the rate increased sharply, and then gradually declined to a new level higher than the rate in the absence of added CO_2 (Fig. 6). The apparent increase in rate upon introduction of CO_2 results from hydrolysis of methoxy groups from the support surface, which is more rapid than the synthesis reactions themselves [8,35].

Figs. 7 and 8 show how the oxidation state and coordination number of Cu atoms responded when catalysts were contacted with synthesis gas compositions
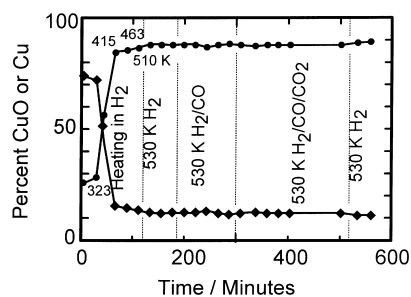

Fig. 7. Fractions of Cu-containing phases identified by analysis of Cu K-near-edge spectra. (●) Cu metal; (◆) CuO-like phase. Conditions were 0.42 MPa, heating rate 2°min^{-1}.
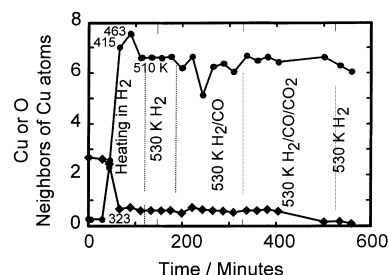

Fig. 8. Average physical environments of Cu atoms from analysis of Cu EXAFS. These results are from the same spectra that provided the edge analyses in Fig. 7. (●) Cu neighbors; (◆) O neighbors.

leading to these transients. XAS data were measured in-situ, except at a total pressure of 0.4 MPa (instead of 4.2 MPa) because of XAS cell pressure limitations. Analysis of the Cu K near-edge region shows that Cu reduction reached a constant value at about 473 K, but 10% of the Cu atoms remain as CuO, even at 530 K (Fig. 7). The Cu environment, characterized by the number and identity of neighboring atoms, also reached a stable state after less than 2 h at 473 K in H_2 (Fig. 8). Cu atoms became increasingly coordinated to other Cu atoms during reduction, consistent with Cu crystallite formation, but retained some oxygen neighbors, as expected from the residual CuO detected by the near-edge analysis shown in Fig. 7. Since support oxygen was not detected in our previous XAS studies of metals supported on SiO_2 [31], we conclude that this oxygen coordination reflects a residual CuO-like phase. The data in Figs. 7 and 8 show that there are no detectable chemical or morphological changes in Cu crystallites as the synthesis gas composition is varied in a range that causes the marked changes in methanol

synthesis rates shown in Fig. 6. We conclude there were no changes in the environment or oxidation state of Cu atoms including surface atoms. Because a large fraction of the Cu atoms were at the surface (18%), such changes would have been detected.

The rates of methanol synthesis presented in Fig. 6 were measured at 4.2 MPa, but the spectra summarized in Figs. 7 and 8 were measured under similar conditions except at only 0.42 MPa due to limitations of the cell. It is reasonable to assume the slow approach to steady-state synthesis activity would be observed also at the lower pressure. Fisher and Bell used IR spectroscopy to study methanol synthesis from H_2/CO_2 (3 : 1) at 0.65 MPa and 523 K on a Cu/SiO_2 catalyst [8]. They observed a 22.6 h transient upon switching from pure H_2 to the H_2/CO_2 mixture, during which both the rate of production of CH_3OH and the concentration of methoxy groups anchored to the SiO_2 increased. Clausen et al. reported reconstruction of Cu particles in Cu/ZnO, but not Cu/SiO_2, upon switching from dry to wet $CO_2/CO/H_2$ at only 0.1 MPa pressure and 493 K [26].

XAS is also applicable to Zn. Several of the reports cited herein report no detectable changes in the Zn component at any point in the catalyst treatments. We are not aware of any report of XAS-observable changes in the Zn component of Cu–ZnO catalysts.

4. Discussion

The results presented here are consistent with earlier work that found Cu(0) to be the dominant Cu species under synthesis conditions, and rejected the presence of Cu(I). They also add indirect evidence for a bifunctional mechanism for methanol synthesis involving support hydroxyl groups, by eliminating an alternative explanation for the initial activation periods observed in H_2–CO feeds. Incomplete reductions of Cu–ZnO/Al_2O_3 at 503 K [16,17] and of Cu/SiO_2 at 500 K [28,36,37] have been reported and the reduction of CuO_x phases may lead to an increase in reaction rates with time on stream. van der Grift et al. [36,37] found by temperature programmed reduction (TPR) that several copper hydrosilicate phases reduced only above 600 K. Brands et al. [28] found that Cu metal surface area increased, when a Cu/SiO_2 catalyst previously reduced at 600 K was re-reduced

at 700 K. Clausen et al. [26] reported that the morphology of Cu particles formed on SiO_2 by reduction in various synthesis gas mixtures at 493 K was insensitive to gas composition. Although Cu particle sizes were not reported, inspection of the EXAFS data presented with the paper indicates that the Cu particles on SiO_2 were similar in size to the particles on ZnO, for which dynamical behavior was clearly observed.

In our study, methanol synthesis rates increased from 1×10^{-3} to 4.5×10^3 CH_3OH/Cu site-sec (Fig. 6), but neither the fraction of Cu that was oxidized (Fig. 7), nor the Cu dispersion indicated by the average Cu–Cu coordination number (Fig. 8), changed. These structural observations are consistent with the conclusions of Clausen et al. [26] also concerning Cu supported on SiO_2. Thus, the origin of the activity changes shown in Fig. 6 must lie in the slow accumulation of a species on the support, which participates in bifunctional methanol synthesis pathways required for CO/H_2 reactant mixtures. One possibility is that support surface hydroxyl groups are required for the formation of formate from CO/H_2 on the support, although not from CO_2/H_2 on the Cu [11,38,39].

Other studies have shown that, on Cu/ZnO catalysts, CO_2/H_2 mixtures produce a formate species that is an intermediate to CH_3OH on both Cu and ZnO surfaces, but that CO/H_2 mixtures produce formate only on the ZnO support surface [8,38–43]. SiO_2 has few hydroxyl groups, but slow methanation side reactions (Eq. (2)) form water molecules, which can hydroxylate the surface of SiO_2 and increase the surface density of required hydroxyl groups:

$$CO + 2H_2 \rightarrow CH_3OH \tag{1}$$

$$CH_3OH + H_2 \rightarrow CH_4 + H_2O \tag{2}$$
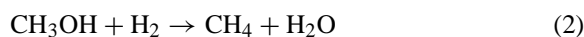
The proposed bifunctional pathways become available only after hydroxyl groups are formed by hydrolysis of Si–O bonds on the support surface. This hypothesis is supported by the observation of a transient increase in production of CH_3OH upon introduction of CO_2 shown in Fig. 6. Fujita et al. [35] showed that introduction of CO_2 following pretreatment of ZnO in a CO/H_2 mixture yielded a similar transient that was due to hydrolysis of methoxy groups from the ZnO surface. The slow approach to steady-state methanol synthesis rates was also observed on Cu–ZnO catalysts. For example,

Lee et al. [42] reported that steady-state rates were reached on Cu/ZnO/Al$_2$O$_3$ after 5 and 20 h on stream for CO$_2$/H$_2$ and CO/H$_2$ feeds, respectively. These transients were attributed to the spillover of reactive intermediates or hydrogen atoms from Cu to ZnO. Such spillover and a bifunctional synthesis mechanism were demonstrated by infrared spectroscopy to occur during methanol synthesis from CO$_2$-containing reactants [8,38]. There is also evidence that reconstruction of Cu particles supported on ZnO [26–29] contributes to these transients, but we detected no structural changes during our transients. It is possible that the unreduced Cu species in our Cu/SiO$_2$ catalysts can adsorb reactive species in the same manner as the ZnO surface. More generally, residual Cu oxide species acting as a promoter in the same capacity as ZnO, may reconcile our successful CH$_3$OH synthesis over Cu/SiO$_2$ from CO/H$_2$, with other studies which show that Cu/SiO$_2$ does not catalyze CH$_3$OH synthesis from CO/H$_2$ mixtures [10].

Although we detect Cu(II) in our Cu/SiO$_2$ catalyst, the fraction of the Cu atoms in this form does not correlate with the rate of methanol synthesis. Other groups have already concluded that Cu metal is the only required form of Cu at least for CO$_2$-containing synthesis gas reactants [11,12], and have explicitly rejected the presence of Cu(I) in working catalysts. Chemical evidence from Han et al. [44,45] eliminates at least one possible role of oxidized Cu as an acceptor site for a formate intermediate in methanol synthesis. They showed that copper formate, or copper formate mixed with Al$_2$O$_3$ yielded formic acid as the exclusive product upon heating in either He or H$_2$. In contrast, zinc formate and mixtures of copper formate with ZnO yielded substantial methanol and methyl formate when heated in H$_2$.

5. Conclusions

As currently practiced, methanol synthesis employs a catalyst prepared from Cu, Zn, and Al or Cr oxides. ZnO and Cu, with or without other oxides, are also effective catalysts. The feed may contain CO$_2$, CO, and H$_2$. The same catalysts are used for water-gas shift reactions, so H$_2$O is likely to be present in the reactor. This system has been the subject of many in-situ and ex-situ studies using X-ray absorption spectroscopy

(XAS). This body of work provides a useful test of the XAS technique, since it is relatively new and the data analysis is still evolving. The consistency among different groups is reassuring.

Most groups that have brought XAS to bear agree that copper is mostly or entirely reduced in the working catalyst. Residual Cu oxide is present following low temperature reduction treatments sometimes employed. Substantial mixed oxides of Cu with Zn were detected in some cases in which the catalyst was prepared in a reactor and then transferred to a spectroscopic cell, under conditions intended to avoid exposure to air. Autoxidation of Cu(0) by protons was reported when Cu/ZnO catalysts were reduced at low temperature and then removed from the reducing environment. Reconstruction of Cu particles in Cu/ZnO catalysts, in response to H$_2$O in the feed, was also observed.

Our own XAS study of a Cu/SiO$_2$ catalyst showed no changes in the Cu metal function during the initial gradual increase in methanol synthesis activity after contact with a CO/H$_2$ mixture. We suggest that methanol synthesis from CO/H$_2$, but not from CO$_2$/H$_2$, requires a bifunctional mechanism involving support hydroxyl groups. The induction of activity for synthesis from CO/H$_2$ reflects hydroxyl formation from hydrolysis of Si–O bonds, which is slow because water is only available from very slow methanation side reactions.

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