

Synthesis of Ethanol via Syngas on Cu/SiO₂ Catalysts with Balanced Cu^0-Cu^+ Sites

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Supporting Information

ABSTRACT: This paper describes an emerging synthetic route for the production of ethanol (with a yield of $\sim 83\%$) via syngas using Cu/SiO2 catalysts. The remarkable stability and efficiency of the catalysts are ascribed to the unique lamellar structure and the cooperative effect between surface Cu⁰ and Cu⁺ obtained by an ammonia evaporation hydrothermal method. Characterization results indicated that the Cu⁰ and Cu⁺ were formed during the reduction process, originating from well-dispersed CuO and copper phyllosilicate, respectively. A correlation between the catalytic activity and the Cu⁰ and Cu⁺ site densities suggested that Cu⁰ could be the sole active site and primarily responsible for the activity of the catalyst. Moreover, we have shown that the selectivity for ethanol or ethylene glycol can be tuned simply by regulating the reaction temperature.

E thanol (EtOH) is a versatile feedstock for the synthesis of various products (e.g., chemicals, fuels, and polymers) and has also been commercially used as an additive or a potential substitute for gasoline.¹ The primary method for EtOH production is based on microbial fermentation processes using agricultural feedstocks, such as sugar cane, potato, manioc, and corn.² Conversion of cellulosic materials, although promising,³ requires considerable R&D effort prior to the achievement of commercial scale.¹ Alternatively, a direct synthesis of EtOH from syngas could complement the existing technologies.⁴ However, major disadvantages of this catalytic process include low yields and poor selectivity of EtOH due to slow kinetics of the initial formation of the C–C bond and fast chain growth of the C₂ intermediates.^{40,5}

This paper describes an alternative approach for the synthesis of EtOH via syngas (Scheme 1). This process is an integrated technology consisting of the coupling of CO with methanol to form dimethyl oxalate (DMO) and subsequent hydrogenation to give EtOH. The byproduct of the second step, CH_3OH , can be separated and used in circulation as the feedstock for the coupling step. In fact, the first step has been scaled up into commercial production with a capacity of 10 000 tons per year as of 2010.⁶ Thus, this paper focuses on understanding the origin of the high efficiency and stability of Cu-based catalysts for hydrogenation of DMO to EtOH. In particular, the formation of the bifunctional catalytic sites of Cu species (i.e., Cu^+ and Cu^0) and their contribution to the reaction were

Scheme 1. Alternative Approach for the Synthesis of EtOH from Syngas



explored by correlating the surface concentrations of catalyst species with initial rates of reaction.

Cu-based catalysts were chosen primarily because of their high activity for vapor-phase hydrogenation reactions.⁷ It has been reported that Cu sites account for the selective hydrogenation of C-O bonds and are relatively inactive for the hydrogenolysis of C-C bonds.^{7a} Our previous work and the literature on Cu catalysts supported on silica (e.g., SiO₂, hexagonal mesoporous silica, SBA) indicated that high dispersion of copper species and strong metal-support interactions are vital for the high activity and stability in hydrogenation of oxalates to ethylene glycol (EG).8 In particular, the formation of copper phyllosilicate $[Cu_2SiO_5(OH)_2]$ with a lamellar structure can enhance the dispersion and metal-support interactions significantly.^{8a,d} Accordingly, we have developed the ammonia evaporation hydrothermal (AEH) method [see the Supporting Information (SI)] to produce catalysts with phyllosilicate phases.

Table 1 illustrates the physicochemical properties and catalytic performance of Cu nanoparticles (NPs) supported on oxides. Al_2O_3 was chosen as a representative acidic oxide support, and ZrO_2 (or TiO_2) and SiO_2 were selected as weakly amphoteric and neutral oxides. Cu/TiO₂, Cu/Al₂O₃, and Cu/ ZrO_2 catalysts possess lower activities than the Cu/SiO₂ catalyst, which could be ascribed to the lower Cu dispersions, numbers of surface Cu atoms, and Brunauer–Emmett–Teller (BET) surface areas, as indicated by N₂O titration (Table 1), H₂ temperature-programmed reduction (TPR) (Figure S1 in the SI), and N₂ adsorption, respectively. Indeed, the number of accessible surface Cu atoms was reported to account for the

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 Table 1. Physicochemical Properties and Catalytic Performance^a

		yields (%)											
entry	catalyst	M loading (%) ^b	EtOH	EG	MG	C ₃ -C ₄ diols	Cu dispersion (%) ^c	$(m^2 g^{-1})^c$	$(m^2 g^{-1})^d$	$d_{\rm M} \over ({\rm nm})^e$	${\displaystyle \mathop{S_{BET}}\limits_{\left(m^{2}~g^{-1} ight)}}$	d _{pore} (nm)	$V_{m^{3}}$ (m ³ g ⁻¹)
1	8Cu/SiO ₂	7.6	28.1	70.7	0	1.2	28.5	15.6	57.8	2.1	285.9	8.1	0.74
2	$15 Cu/SiO_2$	14.7	49.3	35.6	0	15.1	27.3	28.2	76.2	2.7	355.1	8.7	0.93
3	$20 Cu/SiO_2$	19.2	83.0	0	0	17.0	25.8	35.3	72.6	2.8	483.0	9.2	0.89
4	$25 Cu/SiO_2$	23.6	70.7	1.6	0	27.7	20.1	34.7	85.7	4.4	424.5	6.8	0.84
5	$30 Cu/SiO_2$	27.3	58.7	39.8	0	2.3	14.4	26.3	42.2	4.9	389.4	5.9	0.69
6	$40 \text{Cu}/\text{SiO}_2$	36.8	53.5	34.5	0	12.0	12.7	23.8	28.5	7.8	424.0	5.2	0.72
7	20Cu/SiO ₂ – IM	19.1	17.9	54.0	21.9	6.2	11.1	15.3	0.5	12.4	283.6	4.7	0.81
8	$20Cu/TiO_2$	13.4	4.6	39.4	54.7	1.3	2.4	3.3	0.2	26.3	62.1	18.2	0.25
9	$20Cu/Al_2O_3$	17.2	9.8	61.3	20.7	2.5	5.6	7.6	0.7	10.7	300.1	6.1	0.56
10	$20Cu/ZrO_2$	14.6	3.3	40.3	52.1	2.0	3.2	4.9	0.3	15.2	54.2	10.2	0.15
11	20Ni/SiO ₂ ^f	18.3	47.0	0	0	0	_	_	-	8.4	384.4	13.0	1.34
12	20 Co/SiO $_2^{f}$	17.6	64.2	0	0	1.8	_	_	-	4.3	378.6	8.9	0.41

^{*a*}Conditions: liquid hour space velocity (LHSV) = 2.0 h⁻¹, H₂/DMO = 200, 553 K. MG: methyl glycolate. C_3-C_4 diols: 1,2-propanediol and 1,2butanediol. ^{*b*}Determined by ICP-AES analysis. M denotes Cu, Ni, or Co. ^{*c*}Cu dispersion and surface area of Cu⁰ (S_{Cu^0}) were determined by N₂O titration. ^{*d*}Surface area of Cu⁺ (S_{Cu^+}) was determined from irreversible CO adsorption isotherms. ^{*c*}Diameter of metallic particles calculated from the XRD data of the (111) peak broading of Cu by Scherrer equation. ^{*f*}Other gaseous products (e.g., CH₄, CO, and CO₂) were also formed.

catalytic hydrogenation performance.^{8b} Other nanoclusters (e.g., Ni and Co) supported on silica were also tested: Ni/ SiO_2 and Co/ SiO_2 were found to be active for the reaction but suffer from a low EtOH selectivity as a result of alcohol decomposition to form CO and subsequent methanation of CO to form methane.⁹ Notably, neutral SiO₂-supported Cu catalysts prepared by the AEH method exhibited better activity than those prepared by conventional impregnation.

To understand the origin of the catalytic reactivity over Cu/ SiO₂ catalysts, we further investigated the catalytic performance for the gas-phase hydrogenation of DMO by tuning the Cu loading. Table 1 shows that the 20% Cu/SiO₂ (20Cu/SiO₂) catalyst exhibited superior catalytic reactivity in comparison with the others. Figure 1 presents the performance of the 20Cu/SiO₂ catalyst for hydrogenation of DMO as a function of reaction temperature (453–573 K) and the results of a stability test at 553 K for 200 h. Remarkably, the DMO conversion remained at 100% at temperatures above 473 K, and the selectivity for EtOH increased with increasing temperature, exceeding 80% at 553 K. One interesting feature is that formation of EG is favorable at temperatures lower than 553 K, whereas elevated temperatures (e.g., above 553 K) induce the intermolecular dehydrogenation of EtOH and methanol with EG to form C_3-C_4 diols,^{8a} which diminishes the selectivity for EtOH. The catalyst was quite stable at 553 K, with constant conversion of DMO (100%) and selectivity for EtOH (~83%). Transmission electron microscopy (TEM) and powder X-ray diffraction (PXRD) results for the reduced and used samples (Figures S2 and S3) provide basic clues concerning the high activity and stability of the catalysts . The Cu species was not sintered in a 200 h test, indicating that the unique structure of phyllosilicate hampers the sintering of the Cu NPs. In addition, the change in content of surface Cu and the chemical environment was nearly negligible as determined by X-ray photoelectron spectroscopy (XPS) (Figure 2 and Table S1 in the SI). The excellent stability lies in the formation of copper phyllosilicates, as confirmed by the lamellar structure in the TEM image of the calcined 20CuSiO₂ catalyst (Figure 3A). The structure could stem from its unique preparation method; it is formed via reaction of the Cu²⁺ complex with the silanol groups



Figure 1. Performance of the 20Cu/SiO₂ catalyst in catalytic hydrogenation of DMO. (A) DMO conversion and product selectivities as functions of reaction temperature (453–573 K). (B) DMO conversion and EtOH selectivity vs time on stream at 553 K. Reaction conditions: liquid hour space velocity (LHSV) = 2.0 h^{-1} , H₂/DMO = 200 (mol/mol). Trace byproducts include MG and C₃–C₄ diols.

of the silica surface via hydrolytic adsorption to form \equiv SiOCu^{II} monomer and subsequent further polymerization.^{8a,b,10} Because of the strong interaction between the metal and SiO₂, this complex could supply stable Cu species on the surface that would remain intact even after our experimental calcination, reduction, and reaction.

We hypothesize that the high catalytic activity for hydrogenation of DMO to EtOH results from a cooperative effect between Cu^0 and Cu^+ . To understand the structure of the Cu



Figure 2. Cu 2p XPS spectra and (inset) Cu LMM XAES spectra of calcined, reduced, and used $20Cu/SiO_2$ samples.



Figure 3. (A) TEM image of the calcined $20CuSiO_2$ catalyst. (B) FTIR spectra of as-prepared, calcined, and reduced $20Cu/SiO_2$, SiO_2 , and pure $Cu(OH)_2$ samples.

species and the formation process leading to the coexistence of Cu⁰ and Cu⁺ in our Cu/SiO₂ catalysts prepared by the AEH method, we characterized the Cu species in the synthetic process. Fourier-transform IR (FTIR) spectroscopy was used to discriminate the copper hydroxide and copper phyllosilicate species.^{10b,11} Because of their structural OH groups, the frequencies of the δ_{OH} bands for copper hydroxide are at 938 and 690 cm^{-1,11} while those for copper phyllosilicate are at 1040 and 670 cm^{-1,8a,10b} For the as-prepared 20Cu/SiO₂ catalyst (Figure 3B), the peaks appearing at 690 and 937 cm^{-1} suggest the presence of $Cu(OH)_2$. This was also confirmed by the diffraction peaks for Cu(OH)₂ species (JCPDS no. 13-0420) in the PXRD pattern (Figure S3). The appearance of the $\delta_{\rm OH}$ vibration at 670 cm⁻¹ and the $\nu_{\rm SiO}$ shoulder peak at 1040 cm⁻¹ indicated that the structure of copper phyllosilicate existed in the samples; these were not seen for the 20Cu/SiO₂-IM sample prepared by the impregnation method (Figure S4). Upon calcination, the absorption bands associated with $Cu(OH)_2$ disappeared, indicating the complete decomposition of $Cu(OH)_2$ to CuO. However, the presence of the δ_{OH} vibration at 670 cm⁻¹ in the calcined 20Cu/SiO₂ sample suggests the existence of the structure of copper phyllosilicate even after calcination at 673 K. The XPS data for the calcined samples (Figure 2) shows that the Cu oxidation state is +2 with a d⁹ electron configuration in

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the calcined sample, as evidenced by the Cu $2p_{3/2}$ peak at ~933.3 eV, the Cu $2p_{1/2}$ peak at ~952.5 eV, and the $2p \rightarrow 3d$ satellite peak between 942 and 944 eV.^{8a} The asymmetry of the Cu $2p_{3/2}$ envelope allowed the peak of the calcined sample to be deconvoluted into two contributions entered around 933.4 and 936.0 eV, corresponding to dispersed CuO and copper phyllosilicate, respectively.¹²

The formation of Cu⁺ and Cu⁰ occurs during the reduction process, as indicated by the disappearance of the Cu 2p satellite peak at 942-944 eV in the XPS spectrum and the appearance of two overlapping peaks at 334.8 and 338.2 eV in the Cu LMM X-ray excited Auger spectroscopy (XAES) spectrum for the sample after reduction (Figure 2).^{8b} The distinguishability was also confirmed via diffraction peaks in the PXRD patterns (Figure S3). Strong diffraction peaks of the reduced catalysts at 35.8° are ascribable to the Cu₂O(111) plane (JCPDS no. 05-0667), while the diffraction peaks at 43.3, 50.4, and 74.1° are characteristic of Cu⁰ (JCPDS no. 04-0836). The Cu⁺ species is formed upon the reduction of the copper phyllosilicate under the experimental conditions (e.g., 623 K), since the further reduction of Cu⁺ to Cu⁰ requires a temperature higher than 873 K.^{8a} Since the reduction of CuO to Cu⁰ occurs at ~510 K,¹³ the single TPR peak at \sim 516 K (Figure S1) could be attributed to the collective contribution of the stepwise reduction of the welldispersed CuO to Cu⁰ and copper phyllosilicate to Cu⁺.^{13,14}

To further gain insight into the effect of the Cu valence state on the hydrogenation of DMO to EtOH, we examined the effect of Cu loading on the EtOH yield and turnover frequency (TOF) of EtOH as a function of $Cu^0/(Cu^0 + Cu^+)$ (Figure 4).



Figure 4. (A) Yield of EtOH as a function of Cu loading. (B) Correlation of the TOF of EtOH with $Cu^0/(Cu^0 + Cu^+)$.

It is notable that the TOF of EtOH increased steadily at low $Cu^0/(Cu^0 + Cu^+)$, reached a maximum at $Cu^0/(Cu^0 + Cu^+) = 0.33$, and decreased with further increases in the ratio (Figure 4B). Therefore, the optimal TOF of EtOH on the $20Cu/SiO_2$ catalyst lies in the high surface Cu^0 site density (Table 1) and the cooperative effect of Cu^0 and Cu^+ . Moreover, the strong correlation between the surface Cu^0 site density and the formation rates of EtOH and C_3-C_4 diols and the intercept of the trend line (Figure S5A) suggest that the catalytic activity depends on the number of Cu^0 sites. In comparison, there is no clear correlation between the specific activity and the number of Cu^+ sites (Figure S5B).

Two general mechanisms were accordingly proposed and tested on the basis of our experimental results indicating a synergetic effect. In the first, the catalyst has only one active site, Cu^0 , on which H_2 is activated, and the reactant is adsorbed through the hydroxyl group and cleaved. The second is a two-site mechanism in which the Cu^0 species activates H_2 and the

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 Cu^+ species adsorbs the carbonyl group.¹⁵ The correlation in Figure 4 and Figure S5 indicates that Cu^0 is the active site but cannot rule out the role of Cu^+ in a two-site mechanism. However, it has been suggested that in methyl acetate hydrogenation, Cu^+ acts as the stabilizer of the methoxy and acyl species, which are intermediates in DMO hydrogenation.¹⁵ In addition, Cu^+ sites could function as electrophilic or Lewis acidic sites to polarize the C=O bond via the electron lone pair in oxygen, thus improving the reactivity of the ester group in DMO.^{8b} Therefore, it is very likely that Cu^0 acts as the primary active site, which is consistent with the hydrogenation of dimethyl maleate,¹⁶ diethyl oxalate,¹⁷ and furfural and crotonaldehyde,¹⁸ while the Cu⁺ species facilitates conversion of intermediates.

Another interesting feature is the tunability of the products as a function of reaction temperature (Figure 1). For example, a high yield (ca. 95%) of EG can be obtained at a lower temperature (e.g., 473 K). EG is an important chemical used in a variety of industrial applications, such as antifreeze, polyester, H₂ energy, and fuel cells.¹⁹ At present, the technology of ethylene oxidation/hydration accounts for the major share of the EG market.²⁰ As ethylene oxide is commercially produced from ethylene via petroleum cracking, and the global market demand for EG always surpasses its production capacity, increasing efforts have been devoted to exploring alternative processes.²¹ Therefore, this emerging synthetic route for the main production of EtOH or EG from syngas using the same catalytic system through control of the temperature (Scheme S1) could become considerably significant and promising in industry.

In summary, we have demonstrated a facile and highly efficient route for the synthesis of EtOH using low-cost Cu/ SiO₂ catalysts prepared by the AEH method. The catalysts possess remarkable stability and efficiency, which could be ascribed to the coexistence of Cu⁰ and Cu⁺ primarily originating from well-dispersed CuO NPs and copper phyllosilicate, respectively. The correlation between the activity and the Cu⁰ and Cu⁺ site densities suggests that Cu⁰ is the active site and primarily responsible for the activity of the catalyst, while Cu⁺ facilitates the conversion of intermediates. Moreover, the selectivity for EtOH and EG can be tuned simply by regulating the reaction temperature. This indirect synthetic methodology using inexpensive Cu-based catalysts under facile conditions is a promising process that has the potential to enable a sustainable EtOH and EG synthesis using syngas from practical point of view.

ASSOCIATED CONTENT

Supporting Information

Details of experimental procedures, catalyst characterization, TPR profiles, TEM images, PXRD patterns, XPS and FT-IR spectra, and correlation of formation rate with the Cu^0 and Cu^+ surface areas. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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