The direct transformation of ethanol to ethyl acetate over Cu/SiO₂ catalysts that contain copper phyllosilicate

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Abstract. Cu/SiO₂ catalysts that contain copper phyllosilicate, were successfully prepared using the ammonia-evaporation method. The catalysts were characterized via XRD, ICP, BET, FTIR, TPR, XPS, NH₃-TPD and FTIR of Pyridine Adsorption techniques. The results demonstrated that the formation of the copper phyllosilicate species significantly affected the structural properties and caused the CuO nanoparticles to become highly dispersed, and the copper phyllosilicate would provide access to the Lewis acidic Cu⁺ species. It was found that the catalyst with a 23.7 wt% copper loading exhibited the best ethanol conversion and ethyl acetate selectivity. When compared to a catalyst with the same copper loading which was prepared with the impregnation method, the higher activity and selectivity of catalysts might be ascribed to the homogenous distribution of copper nanoparticles, which was the active site for the dehydrogenation, and the amount of Lewis acidic Cu⁺ sites active for esterification. The synergetic effect between the Cu⁰ and Lewis acidic sites was the key factor to achieve direct transformation of ethanol to ethyl acetate.

Keywords. Ethanol; ethyl acetate; copper phyllosilicate; lewis acid sites.

1. Introduction

Ethyl acetate is an important environment-friendly solvent which is used industrially across a wide range of applications. The direct transformation of ethanol to ethyl acetate has been afforded a significant amount of attention because both components are simple, non-corrosive, and relatively non-toxic. Several studies detailing the direct transformation of ethanol to ethyl acetate using Cu-based catalysts have been published. For example, Colley *et al.*¹ reported that the formation of ethyl acetate from ethanol could be achieved over a Cu/Cr₂O₃ catalyst. They proposed that the metallic copper species are the major active components in the catalyst and that the Brønsted acid site on the surface of Cr₂O₃ facilitates the selectivity for ethyl acetate. Inui *et al.*^{2–4} and Zonetti *et al.*⁵ used Cu-Zn-Zr-Al-O multi-component catalysts in a dehydrogenation process and the results indicated that ethanol was first dehydrogenated to form acetaldehyde before reacting

with another equivalent of ethanol or ethoxide to form a hemiacetal, which was then dehydrogenated to furnish ethyl acetate. Moreover, Wang *et al.*⁶ studied the formation of ethyl acetate from ethanol with Cu/ZrO₂ catalysts which were prepared via the co-precipitation method. They proposed that the molar ratio of copper and zirconium had a significant effect on the catalytic performance, and the addition of zirconium improved the selectivity to favour ethyl acetate.

Recently, metal-silica hybrid nanostructures have been investigated widely because silica has a high thermal stability that does not alter the physical nature of the metal components when used as a support. In some cases, silica reacts with metals to form metal phyllosilicates (or metal silicate hydroxides), which make the supported metal nanoparticles more stable, highly dispersed and less crystalline.^{7,8} Silica-supported phyllosilicates have been formed during the preparation of Ni phyllosilicate,^{9,10} Mg phyllosilicate,^{11,12} Co phyllosilicate,^{13,14} Zn phyllosilicate,¹⁵ Cu phyllosilicate.^{16,17} Copper phyllosilicate, which is also called chrysocolla, is a copper silicate with a lamellar structure

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that consists of layers of SiO_4 tetrahedra sandwiched between discontinuous layers of CuO_6 octahedra. Toupance *et al.*¹⁶ were the first to note that the copper phyllosilicate formed in Cu/SiO_2 samples that were prepared by using cationic exchange, and they investigated the formation conditions of copper phyllosilicate when using the selective adsorption method.¹⁷ Huang *et al.*¹⁸ prepared silica-supported, dispersed copper nanomaterials via the precipitation-gel method. They noted that the copper phyllosilicate was rather stable and affected both the structure and thermal stability of the samples profoundly. Many studies have investigated the activity of CuSiO_2 catalysts that contain copper phyllosilicate in some reactions. For example, several authors^{8,19–21} reported that certain Cu/SiO_2 catalysts, which were prepared by ammonia-evaporation method and urea hydrolysis deposition-precipitation method, could hydrogenate dimethyl oxalate to form ethylene glycol. They suggested that copper phyllosilicate species were formed in the Cu/SiO_2 catalysts. Additionally, the Cu^+ from the copper phyllosilicate participated in hydrogenation of dimethyl oxalate to ethylene glycol and cooperated with the Cu^0 to enhance the catalytic performance. Gong *et al.*²² used a Cu/SiO_2 catalyst that was prepared by using the ammonia evaporation method to produce ethanol. They demonstrated that Cu^0 and Cu^+ coexisted within the Cu/SiO_2 catalysts; the Cu^0 and Cu^+ originated from well-dispersed CuO nanoparticles and copper phyllosilicate; and the Cu^0 was primarily responsible for the catalytic activity in the active site. Cu^+ facilitates the conversion of intermediates.

The effect of copper phyllosilicate species on an ethanol dehydrogenation reaction that forms ethyl acetate has not been reported. In this paper, silica-supported copper catalysts, which contain a copper phyllosilicate species, were successfully prepared and applied to the dehydrogenation of ethanol to form ethyl acetate. The catalyst's properties were investigated using XRD, ICP, BET, TPR, FTIR, XPS, NH_3 -TPD and FTIR of Pyridine Adsorption techniques. This research studies the structure and active sites of a Cu/SiO_2 catalyst. The highly dispersed Cu^0 and Lewis acid sites from the copper phyllosilicate are the active sites for the dehydrogenation and esterification processes.

2. Experimental

2.1 Catalyst preparation

The Cu/SiO_2 catalysts were prepared by using the ammonia-evaporation method (AE).¹⁹ The process

entailed the following: ammonia solution added dropwise to a known amount of aqueous $\text{Cu}(\text{NO}_3)_2$ solution (0.2 mol/L) and stirred for 30 min. An appropriate amount of silica sol (30 wt %) was added to the copper-ammonia solution (pH of the solution was 12) before the mixture was stirred for another 4 h. Subsequently, the solution was stirred in oil bath at 363 K to evaporate the ammonia until the pH = 6–7. Next, the product was filtered, washed with distilled water (the pH of precipitation was held at 6–7), and dried in the vacuum oven at 373 K for 4 h before being calcined in air at 673 K for 2 h. The obtained catalysts were named CuSi-1 (7.5 wt %), CuSi-2 (23.7 wt %), and CuSi-3 (36.6 wt %). For comparison, a Cu/SiO_2 catalyst with a 23.9 wt % copper loading was prepared by impregnating the silica with an aqueous solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$. The impregnation method (IM) was followed by drying at 393 K for 4 h with stirring and calcination at 673 K for 4 h in flowing air. This catalyst was named CuSi-IM.

2.2 Catalyst characterization

Powder X-ray diffraction (XRD) patterns were recorded with a Shimadzu Lab XRD-6000 X-ray Diffractometer with nickel-filtered $\text{Cu K}\alpha$ radiation. Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) analysis was conducted with a Perkin Elmer emission spectrometer. The BET specific surface areas of the samples were measured by using N_2 as the adsorbate on a Micromeritics ASAP 2010 system at liquid- N_2 temperature. IR spectra were recorded with a Nicolet 410 FT-IR spectrometer. H_2 -TPR analysis, NH_3 -TPD analysis and N_2O chemisorption were carried out on a self-made instrument. The measurement process was carried out according to previous literature reports.^{6,23} The X-ray photoelectron spectroscopy (XPS) measurement was carried out with a VG ESCA LAB MK II XPS spectrometer that used $\text{AlK}\alpha$ radiation. Pyridine adsorption Fourier transform infrared spectrum was performed according to literature.²⁴

2.3 Catalytic activity

The activity of catalyst was studied with a continuous flow fixed-bed reactor under the following conditions: $P = 1$ atm, $T = 543$ K, $\text{LHSV} = 1$ h^{-1} . In each experiment, 2 mL of the appropriate catalyst was used, and the ethanol was fed into the reactor via a plunge pump. Before the reaction, each catalyst was reduced in situ with a 10% H_2/Ar mixture. The temperature was increased at 5 K/min. until the temperature reached 573 K, which was maintained for 2 h. The reactor was

connected to gas chromatography using a six-port high temperature valve. The effluent streams from the reactions were analyzed with an online gas chromatograph (Shimadzu GC-14C) that was equipped with a flame ionization detector (FID) and a 3 m PEG 20000 column.

3. Results and discussion

3.1 XRD analysis

Figure 1 depicts the XRD patterns for the CuSi-*x* catalysts. From the data for the calcined catalysts shown in figure 1a, it was observed that no diffraction peaks attributed to copper oxide species were detected on the AE catalysts, and a broad and diffuse diffraction peak, which was centered at $2\theta = 22.7^\circ$, was ascribed

to amorphous silica for catalyst CuSi-1.²⁵ With an increased Cu loading, the peak attributed to the amorphous silica disappeared at the same time corresponding to two weak peaks, which were attributed to copper phyllosilicate (approximately $2\theta = 31.2^\circ$ and 35.8°). These data demonstrate that the copper phyllosilicate species was formed.^{8,17} However, severe aggregation of the copper species occurred in the IM sample (CuSi-IM), which was indicated by the strong diffraction peaks for CuO observed at $2\theta = 35.5^\circ$ and 38.9° .²⁵ This result suggests that the Cu/SiO₂ catalysts that were prepared by the AE method, formed copper phyllosilicate [Cu₂SiO₅(OH)₂] and exhibited greater dispersion than what was observed in the product of the IM method.²²

In the XRD patterns of the reduced catalysts (figure 1b), a broad and diffuse diffraction peak, which was centered at $2\theta = 22.7^\circ$, was attributed to amorphous silica in the AE catalysts. This result suggests that the copper phyllosilicate species had disappeared and therefore the amorphous SiO₂ species were formed after the AE catalysts were reduced. The diffraction peaks of Cu⁰, which were at approximately 43.3° and 50.5° , on the CuSi-2 catalyst were broader and less intense than those that were observed for the reduced CuSi-IM catalyst with the same copper loading. This result suggests that the presence of copper phyllosilicate could inhibit the sintering of the Cu particles of the CuSi-2 catalyst during reduction. The Cu⁰ species were markedly aggregated on CuSi-3 catalyst because the copper loading was high. Notably, the CuSi-2 catalyst exhibited a different Cu₂O diffraction peak than what was measured with the CuSi-IM catalyst. A portion of copper exists as Cu⁺, which is reduced from both the ion exchange Cu-O-Si and copper phyllosilicate on the AE catalyst that occurs after the reduction.¹⁹

Figure 1. XRD patterns of the CuSi-*x* catalysts, (a) calcined, (b) reduced.

3.2 Textural properties of the catalysts

The physicochemical properties of the CuSi-*x* catalysts are summarized in table 1. The BET surface area increased from 302 to 460 m² g⁻¹ when the Cu loading was increased for catalysts generated with the AE method, it should be attributed to the copper phyllosilicate species of the AE catalysts. As observed, the BET surface area of the AE catalyst was higher than the IM catalyst, which might be due to the copper species aggregated on the IM catalyst. The copper dispersion of the catalysts obtained from N₂O chemisorption for AE catalysts was decreased with increasing copper loading, and they were higher than the IM catalyst. This is in agreement with XRD.

Table 1. (a) Cu loading conducted by ICP; (b) Cu dispersion determined by N₂O chemisorption; (c) Cu⁰ crystallite size calculated by the Scherrer formula.

Sample	Cu loading (wt %) ^a	S _{BET} (m ² g ⁻¹)	V _p (cm ³ g ⁻¹)	d _p (nm)	Cu Dispersion (%) ^b	Cu ⁰ particle size (nm) ^c
CuSi-1	7.5	302	0.61	6.3	44	—
CuSi-2	23.7	453	0.81	5.7	40.2	9.8
CuSi-3	36.6	460	0.54	4.1	22.3	21.5
CuSi-IM	23.9	206	0.52	7.2	18.2	25.9

3.3 FTIR analysis

FTIR spectra of the CuSi-x catalysts are displayed in figure 2. The formation of copper phyllosilicate was supported by the appearance of an δ_{OH} band at 670 cm⁻¹ and a ν_{SiO} shoulder at 1042 cm⁻¹ on the low-frequency side of the asymmetric stretching ν_{SiO} band of SiO₂ at 1100 cm⁻¹.¹⁶ The magnitudes of these resonances grew as the copper loading increased. These resonances were not observed with the CuSi-IM catalyst, which was prepared by the impregnation method. The relative amount of supported phyllosilicate in these samples could be evaluated by dividing the integrated intensity of the δ_{OH} band at 670 cm⁻¹ by the integrated intensity of the symmetric ν_{SiO} band of amorphous silica at 800 cm⁻¹, which can be written as I_{670}/I_{800} .¹⁶ Copper phyllosilicate could be formed during the AE method of preparation. This species was more abundant when the copper loading was increased.

3.4 TPR analysis

The TPR profiles of CuSi-x catalysts are depicted in figure 3. For the IM catalyst, three reduction peaks were observed. The lower temperature reduced peak, which was centered at 513 K, was attributed to the reduction

of the highly dispersed CuO. The higher temperature reduced peaks at 653 K and 614 K were ascribed to the reduction of larger particles of CuO on the SiO₂ surface.^{26,27} These results suggest that the Cu species were poorly dispersed on the surface of Cu/SiO₂ catalyst which was prepared with the IM method. For the AE catalysts with different copper loadings, only one broad and asymmetric reduction peak was observed (520 K - 526 K). Chen *et al.*¹⁹ reported that the main reduction peak for the Cu/SiO₂ catalysts that are prepared via ammonia evaporation is attributed to the reduction of the well-dispersed CuO to Cu⁰, as well as the reduction of the ion-exchanged Cu-O-Si and copper phyllosilicate to form Cu⁺. Marchi *et al.*²⁸ determined that the reduction of the ion-exchanged Cu-O-Si species to Cu⁺ overlapped with the reduction peak of the well-dispersed CuO to Cu⁰. Therefore, under our conditions, the results suggested that Cu⁰ and Cu⁺ coexist in the AE catalysts.

3.5 XPS analysis

The chemical state of CuSi-x catalysts were investigated by XPS (figure 4). As displayed in figure 4a, the binding energy of the Cu2p_{3/2} peak, which was

Figure 2. FTIR spectra of calcined CuSi-x catalysts. **Figure 3.** TPR spectra of calcined CuSi-x catalysts.

Figure 4. XPS spectra of CuSi-*x* catalysts (a) calcined (b) reduced.

935.0 eV–935.4 eV with a shake-up feature at approximately 943.5 eV, provided conclusive evidence that the copper species on the catalyst surface was Cu^{2+} .²⁹ The higher BE of CuSi-AE catalyst, which contained copper phyllosilicate, might be caused by a strong interaction between the Cu^{2+} and the support.³⁰ This observation was in agreement with the FTIR and XRD data. After reduction (figure 4b), the satellite peak disappeared, and a simultaneous shift in the $\text{Cu}2p_{3/2}$ peak toward lower binding energy (BE) occurred. These phenomena provided conclusive evidence that the copper species on the catalyst's surface were Cu^0 or Cu^+ ,³¹ which was because the binding energies for these Cu^+ species typically overlap with those of the Cu^0 species in Cu 2p XPS analysis.^{32,33} After combining these data with those of the XRD and TPR, we concluded that the main Cu species on the reduced catalysts was Cu^0 , although a small portion of Cu^+ was formed during the reduction.

For the BE values of Cu^+ and Cu^0 are almost identical, the distinction between these two species present on the catalyst surface is feasible only by their different kinetic energies in the XAES Cu LMM line position or the modified Auger parameters α' . It was reported that α' is 1851.0 eV for Cu^0 and 1847.0 eV for Cu^+ .¹⁹ In figure 5, it was obvious that each Cu LMM spectrum possessed the broad and asymmetrical peak shape, implying the coexistence of Cu^0 and Cu^+ on the catalysts surface. Deconvolution of the original Cu LMM peaks was performed, obtained two symmetrical peaks centered at near 914.6 and 918.0 eV, corresponding to Cu^+ and Cu^0 species, respectively. The deconvolution results are listed in table 2. For AE method, the $\text{Cu}^+ / (\text{Cu}^+ + \text{Cu}^0)$ intensity ratio derived by fitting the Cu LMM peak increased with the copper loading, and the intensity ratio reached maximum for CuSi-2 sample of 49.3%. It was attributed to the hindered reduction of Cu^{2+} in ion exchanged Cu-O-Si species and copper phyllosilicate. For IM method, the Cu^+ species also existed on the catalyst surface, but the $\text{Cu}^+ / (\text{Cu}^+ + \text{Cu}^0)$ intensity ratio was lower than the CuSi-2 catalyst; the reason might be the weak interaction between copper species and support.

3.6 NH_3 -TPD analysis

The NH_3 -TPD profiles of the reduced CuSi-*x* catalysts are displayed in figure 6. CuSi-2 and CuSi-3 catalysts exhibited a broad peak, which began at approximately 388 K with a long tail that extended to 673 K, and the CuSi-1 and CuSi-IM catalysts showed two NH_3 desorption peaks between the same temperature range. This result indicated that a large distribution of acid

Figure 5. Cu LMM XAES spectra of the reduced CuSi-*x* catalyst.

Table 2. (a) Kinetic energy (b) Auger parameter (c) Mole ratio of Cu to Si of the catalysts after reduction determined by XPS (d) $X_{Cu}^+ \% = Cu^+ / (Cu^+ + Cu^0) \times 100\%$ by deconvolution of Cu LMM XAES spectra.

Catalyst	K.E.(eV) ^a		α' (eV) ^b		B.E. of Cu 2p _{3/2} (eV)	R _{Cu/Si} ^c	X _{Cu+} ^d %
	Cu ⁺	Cu ⁰	Cu ⁺	Cu ⁰			
CuSi-1	915	918	1847	1851	932.7	0.1	38
CuSi-2	915	918	1847	1851	932.7	0.3	49.3
CuSi-3	915	918	1847	1851	932.7	0.4	39.9
CuSi-IM	915	918	1847	1851	932.6	0.1	36.5

sites that varied from weak to medium were present on the catalysts surface.^{34–36} It can be observed from the data in figure 6 that the areas of reduced CuSi-x desorption peaks increased in size as follows: CuSi-1 < CuSi-IM < CuSi-3 < CuSi-2. The number of acid sites on the AE catalysts increased when the copper loading increased to peak with the CuSi-2 catalyst. This effect occurred because the amount of copper phyllosilicate species grew with higher copper loading, and a portion of the copper phyllosilicate could be reduced to highly dispersed Cu⁺ species, which were regarded as Lewis acid sites.³⁷ However, when the copper loading was increased further, the copper species aggregated, which influenced the reduction of Cu²⁺ to Cu⁺. For the IM catalyst, the acid sites also came from the Cu⁺ species.

3.7 FTIR of pyridine adsorption

FTIR spectra of pyridine adsorbed reduced CuSi-x catalysts are displayed in figure 7. According to the published work,^{36,38,39} the spectra of pyridine adsorbed on various catalysts displaying bands around 1595 cm⁻¹, 1611 cm⁻¹ and 1445 cm⁻¹ were assigned to pyridine coordinated to Lewis acid sites. The band at 1540 cm⁻¹

was due to a combination band associated with Brønsted acid sites, while the band at about 1480 cm⁻¹ could be attributed to Lewis acid and Brønsted acid sites. As shown in figure 7, the main acid type was Lewis acid site, and the trend of the mount of acid sites was consistent with NH₃-TPD. This result further confirmed that the Cu⁺ could be used as Lewis acid sites.

3.8 Catalytic tests

The direct transformation of ethanol to ethyl acetate was carried out to study the catalytic properties of the CuSi-x catalysts. The catalytic performances are listed in table 3. The catalyst with low copper content demonstrated lower activity to achieve only a 44.5% conversion of ethanol and a 34.4% selectivity for ethyl acetate. The catalytic activities increased with greater copper content and peaked with the CuSi-2 catalyst, which yielded an approximately 65.3% conversion of ethanol and a 48.9% selectivity for ethyl acetate. Further increasing copper content causes decrease in ethanol conversion and ethyl acetate selectivity. For the IM catalyst with the same copper

Figure 6. NH₃-TPD spectra of reduced CuSi-x catalysts.

Figure 7. FTIR of Pyridine Adsorption spectra of reduced CuSi-x catalysts.

Table 3. Catalytic performance during the direct transformation of ethanol to ethyl acetate over CuSi-x catalysts.

Catalysts	Conversion of Ethanol (%)	Selectivity to Ethyl acetate (%)	Selectivity to Acetaldehyde (%)	Yield to Ethyl acetate (%)
CuSi-1	44.5	34.4	54.5	15.3
CuSi-2	65.3	48.9	17	31.9
CuSi-3	52.9	36.7	35.5	19.4
CuSi-IM	49.3	32.5	48.9	16

loading as CuSi-2, the conversion of ethanol reached 49.3% and the selectivity for ethyl acetate was 32.5%, both of which were lower than the values for the CuSi-2 catalyst.

Metallic Cu phases act as active centers for the dehydrogenation of alcohols. However, both copper particle size and metal dispersion affect the dehydrogenation activity. Tonner *et al.*⁴⁰ studied copper catalysts during a methanol dehydrogenation for the formation of methyl formate. They proposed that both the degree of dispersion and the metallic surface area of the copper were important during the selection of the most active catalyst. Crivello *et al.*⁴¹ investigated the reaction of *n*-octyl alcohol dehydrogenation over copper catalysts, and the Cu⁰ sites were discovered to be the active ones. The addition of magnesium into copper catalyst increased its stability and dispersion. The previous reports^{4,6} proposed that the direct transformation of ethanol to ethyl acetate required the active centers for dehydrogenation (Cu⁰) and esterification (acid site). First, the ethanol was dehydrogenated to produce acetaldehyde, which was adsorbed on the acid sites to form a hemiacetal. Finally, the hemiacetal was dehydrogenated rapidly to produce ethyl acetate.

The reduced XRD results of AE catalysts indicated that the number of Cu⁰ sites increased with the copper loading to a point, but the Cu⁰ species were seriously aggregated with too high of a copper loading. It could be observed from table 3 that the conversion of ethanol over CuSi-2 was highest of all of the AE catalysts, the CuSi-3 was in a middle position, and the CuSi-1 was at the lowest position. Simultaneously, the selectivity toward acetaldehyde displayed an inverse trend. The catalytic activity results suggested that the metallic Cu phase acted as an active center for the dehydrogenation of alcohols. Interestingly, the conversion of ethanol over the CuSi-2 catalyst was higher than was observed with the CuSi-IM catalyst with the same copper loading. From the reduced XRD results, we determined that the Cu⁰ species on CuSi-2 catalyst were highly dispersed and had a small particle size, and the results (table 2) showed that the content of surface copper species on the CuSi-2 catalyst was higher than that on the IM

catalyst. These traits might be because the copper phyllosilicate could inhibit the sintering of the Cu particles during reduction, and made the copper species highly dispersed on the catalyst surface. This result suggested that the Cu/SiO₂ catalyst, which was prepared by AE method and contained the copper phyllosilicate, was more effective for the conversion of ethanol.

NH₃-TPD and FTIR of Pyridine Adsorption analyses indicated that the number of acid sites increased in the following order: CuSi-1<CuSi-IM<CuSi-3<CuSi-2, and the main type of acid site is Lewis acid. The selectivity to ethyl acetate demonstrated a similar trend. After reduction, the XRD of the AE catalyst exhibited a small diffraction peak for Cu₂O when the copper loading was increased. This peak became weaker when the copper loading increased further. The XAES spectra showed that both Cu⁰ and Cu⁺ coexisted on the surface of reduced catalysts. The Cu⁺/(Cu⁺+Cu⁰) intensity ratio of AE catalysts increased with the copper loading, and maximized for CuSi-2 sample. The Cu⁺/(Cu⁺+Cu⁰) intensity ratio of the IM catalyst was lower than the AE catalyst. Zhang *et al.*³⁷ and Zhu *et al.*⁴² proposed that the electropositive copper species, which are generated by strong interactions between the copper and the SiO₂ surface, might be strong Lewis acid sites. Gong *et al.*⁴³ and Benaliouche *et al.*⁴⁴ discovered that the number of Lewis acid sites increased on zeolites after Cu⁺ and Ag⁺ were exchanged, which may be because the metal cations are the electron acceptors. Therefore, after reduction, the Cu⁺ sites could function as Lewis acidic sites to absorb the acetaldehyde, thus improving the esterification. The high ethyl acetate selectivity compared with IM catalyst was attributed to the abundant Cu⁺ species.

Therefore, after considering all the above results, we propose that the presence of copper phyllosilicate can improve the dispersion of Cu⁰, as well as generate a Lewis acidic Cu⁺ species. The catalytic performance, (which is higher than observed for the AE catalyst), is superior because of the synergistic effect between the highly dispersed Cu⁰ and Lewis acid sites which are generated from Cu⁺.

4. Conclusions

A series of Cu/SiO₂ catalysts have been synthesized via the ammonia-evaporation method. The formation of copper phyllosilicate had wide effects on the texture and structure of the materials. Compared to the IM catalyst, the AE catalysts exhibited a much higher dispersion, a smaller copper particle size and a larger surface area, in addition to the formation of copper phyllosilicate, which could be reduced to Cu⁺. The AE catalysts exhibited superior ethanol conversion and selectivity for ethyl acetate formation when enacting the direct transformation of ethanol to ethyl acetate. The synergistic effect of Cu⁰ and appropriate amount of Lewis acidic sites generated from Cu⁺ cause this effect.

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