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Synthesis and characterization of Supported copper phyllosilicate catalysts for Acetic Ester Hydrogenation to Ethanol

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Graphical abstract



Highlights:

- Supported copper phyllosilicate catalysts were successfully synthetized by a simple coprecipitation method.
- The formation mechanism of copper phyllosilicates during co-precipitation was proposed.
- The co-precipitation method favored the form of the 2:1 copper phyllosilicate rather than the 1:1 copper phyllosilicate
- Addition of ammonium ion and zinc ion drastically promoted copper silicate phase evolution from the 2:1 copper phyllosilicate to the 1:1 copper phyllosilicate during precipitation.

• Supported 1:1 copper phyllosilicate catalysts showed superior activity for acetic ester hydrogenation to ethanol.

Abstract

Supported copper phyllosilicate (Cu/SiO₂) catalysts were prepared by a simple coprecipitation method (CP), and compared with the urea hydrolysis deposition-precipitation method (DP) in terms of phase evolution during synthesis, physicochemical properties, chemical states of copper species after reduction, and catalytic performance in ester hydrogenation to ethanol. Catalysts were characterized by N₂-physisorption, X-ray powder diffraction (XRD), IR spectroscopy, H₂ temperature programmed reduction (TPR), transmission electron microscopy (TEM), in situ X-ray photoelectron spectroscopy (XPS), and FTIR/CO spectroscopy. It was confirmed that copper phyllosilicates species existed in all catalysts but the exact form differed in the Cu-CP catalysts and the Cu-DP catalysts. While the Cu-DP catalyst favored the form of 1:1 copperphyllosilicate, the Cu-CP catalysts tended to have more species of 2:1 copperphyllosilicate which led to only small amount of active copper species on surface after reduction and thus low ester conversion. Addition of ammonium ion and zinc ion during the CP method synthesis promoted the copper silicate phase evolution from 2:1 copperphyllosilicate to 1:1 copper phyllosilicate, and the reactivity of ester hydrogenation was greatly enhanced. Conversion of 99.67%, selectivity of 99.07%, and space-time yield of 1.23 g_EtOH/(g_cat · h) were achieved at 250 °C using a Cu-Zn-NCP catalyst.

Keywords: Cu/SiO_2 Catalyst, Copper phyllosilicate, Co-precipitation, Phase evolution, Cu^0/Cu^+ , Acetic Ester Hydrogenation, EthanolSynthesis.

1. Introduction

Ethanol was an important industrial commodity and a potential alternative synthetic fuel to be used in automobiles. Currently, ethanol was produced by two major processes: (1) fermentation of sugars derived from corn or sugar cane, and (2) hydration of petroleum-based ethylene. Due to the diminishing crude oil resource and potential food crisis, gasification of coal or biomass to syngas ($CO + H_2$), followed by catalytic conversion of syngas to ethanol, became more promising for large ethanol production. However, due to the slow kinetics of the initial C–C bond formation and fast chain growth of C₂ intermediates, the direct conversion process suffered from low yield and poor selectivity ^[11]. Alternatively, several indirect, multi-step processes, such as via hydrogenation of C₂ intermediates such (acetic esters and oxalic esters) to ethanol, had attracted extensive attentions ^[2-3]. Among these key steps, ester hydrogenation to ethanol was the only step that was still under research and development, and thus was the technical bottleneck we needed to overcome for a viable coal-to-ethanol process. This work presented the recent development of hydrogenation catalysts for acetic ester to ethanol conversion.

Catalysts for ester hydrogenation had generally been prepared by mixing hydrogenating metals (e.g., Fe, Co, Ni, Cu, and Zn) with various oxides (e.g., SiO₂, ZrO₂, V₂O₅, Cr₂O₃, and WO₃) ^[4]. Typically, Copper-based catalysts were considered to be suitable for selective ester hydrogenation, because they allowed for selective hydrogenation of C=O bonds but were relatively inactive in C-C bond hydrogenolysis^[5]. However, due to the low melting point (ca. 1083 °C) and thus low $T_{h\bar{u}ttig}$ (ca. 178 °C) and $T_{Tammann}$ (ca. 405 °C) of copper, single copper nano particles were not sintering-resistant or mechanically stable for industrial applications ^[6]. Adkins et al. firstly described the application of a copper-chromium catalyst for ethyl ester

hydrogenation ^[7]. Later on, Cr-free catalysts had been developed due to strong environmental restrictions, among which Cu/SiO₂ catalysts stood out in hydrogenation of dimethyl oxalate to ethylene glycol and ethanol ^[2-3, 8-9]. Research on silica supported copper catalysts indicated that both high dispersion of copper species and strong metal-support interaction were vital to high activity and stability in vapor-phase hydrogenation of ester to alcohols or glycol, which was similar to the Cu-Cr catalyst system ^[3,10-11]. In addition, because of the weak acidic and basic properties of SiO₂, Cu/SiO₂ catalysts had demonstrated highest yield of desired products in hydrogenation of esters at mild conditions ^[12].

In order to obtain desired performance of Cu/SiO₂ catalysts, it was necessary to disperse fine particles onto the support. Conventional methods such as wet impregnation often led to broad size distribution of metal particles and large particle size when the loading was high. Ion-exchange approach could well disperse and stabilize copper species on silica support, but the metal loading was low due to limited amount of terminal –OH groups on the surface of silica ^[13]. As early as 1990, Van der Grift confirmed that Cu/SiO₂ catalysts prepared by urea hydrolysis deposition-precipitation method (DP) could offer good metal dispersion, even at high metal loading, partially due to the formation of "chrysocolla (copper phyllosilicates) - like" precursors ^[10]. Almost at the same time, copper phyllosilicates were reported in Cu/SiO₂ catalysts by ammonia evaporation (AE) methods ^[3, 12, 14] and hydrothermal precipitation techniques ^[5, 10, 15-18].

The chemical states of copper in both calcined and reduced copper phyllosilicates were also of great importance to the catalytic hydrogenolysis of esters. N. Takezaw et al. claimed that isolated cupric precursors were reduced to monovalent copper while small clusters of cupric oxide (CuO) were reduced to metallic copper in copper/silica catalysts prepared by ion-exchange approaches ^[19]. C. J. G. Van Der Grift suggested that calcination at 550 °C, as

well as direct reduction at 277 °C, the "chrysocolla-like" catalyst precursors prepared by DP method led to the decomposition of copper hydrosilicate and reorganization of silica support, furthermore, calcination of the same sample at 427 °C caused the subsequent reduction to occur at a lower temperature, which indicated the presence of small copper oxide particles over silica support ^[17]. J. Gong obtained Cu/SiO₂ catalysts by ammonia evaporation hydrothermal (AEH) method, and found the coexistence of copper phyllosilicates and cupric oxide even after calcination at 400 °C. After reduction, Cu⁰ and Cu⁺ species co-existed and were primarily originated from well–dispersed copper oxide nano-particles and copper phyllosilicates, respectively ^[3]. The synergetic effect between Cu⁰ and Cu⁺ was believed to play an excellent role for Cu/SiO₂ catalysts during the hydrogenolysis of dimethyl oxalate (DMO) to ethylene glycol or ethanol ^[3, 12, 15]. Since copper phyllosilicates contributed to the good dispersion of metal particles and provide active sites upon reduction, they were often considered a key component in Cu/SiO₂ catalysts.

Copper phyllosilicates were copper silicates with a lamellar structure that consists of layers of SiO₄tetrahedra and layers of CuO₆ octahedra. The 1:1 copper phyllosilicate, which was often known as chrysocolla [Cu₂Si₂O₅(OH)₂], was a poorly ordered mineral containing Si/Cu \approx 1 and one of the typical copper phyllosilicates available in nature ^[10, 20]. Another type of copper phyllosilicate was the 2:1 copper phyllosilicate, also called Cu-talc or Cu-smectie, which was less common and only forms when there is large excess amount of Si ^[20]. Several researchers revealed that silica may react with certain metal (Ni ^[21-23], Cu ^[5, 10, 15-18], Co ^[24]) precursors to form phyllosilicates during preparation, depending on the reactivity of silicic species with the metal complexes ^[21]. Formation of silica-supported copper phyllosilicates and nickel phyllosilicates was a well-known case during catalyst preparation by DP method ^[21-23] and selective adsorption of metal tetraammine complex ^[25, 26], EXAFS^[20], and ESR ^[25, 26].

Siffert et al. found that the prerequisites for the formation of phyllosilicates include: (1) silicic species in solution must be monomeric; (2) metal hydroxo complexes must be present in solution; and (3) The pH must be lower than that of the hydroxide precipitation. The mechanism proposed was based on the formation of two types of monomeric species in solution, i.e., monomer 1 [(HO)₃Si]-O-[M(H₂O)₄(OH)] and monomer 2 [(HO)₃Si]-O-[M(H₂O)₄]-O-[Si(OH)₃], whose polymerization would lead to the formation of 1:1 and 2:1 phyllosilicates, respectively ^[27]. In addition, in the case of Ni/SiO₂ and Cu/SiO₂ systems, it was shown that addition of NH₄⁺ could inhibit the formation of phyllosilicates, which could be attributed to the formation of "competitor ion" or the decrease of the concentration of [Cu(OH)₂(H₂O)₄]⁰ complex ^[26].

In the present work, silica supported copper catalysts were prepared by adding acidic copper nitrate solution to a basic sodium silicate solution to co-precipitate copper hydroxo complexes and monomeric silica. As a comparison, another kind of Cu/SiO₂ catalyst with the same composition was prepared by urea hydrolysis deposition-precipitation method (DP). These two types of catalysts were calcined at the same temperature, and the catalytic performance was evaluated by using gas phase hydrogenation of ethyl acetate as the probe reaction. Characterization of physicochemical properties of catalysts by N₂-physisorption, X-ray powder diffraction (XRD), IR spectra, H₂ temperature programmed reduction (TPR), transmission electron microscopy (TEM), in situ X-ray photoelectron spectroscopy (XPS), and FTIR/CO spectroscopy were performed to correlate with activity performance. Special attention was paid to the nature of copper precursors and the valence states of active sites on the surface of reduced catalysts.

2. Experimental Section

2.1. Catalyst preparation

The Cu/SiO₂ Catalysts studied were prepared by two different precipitation methods coprecipitation (CP) and urea hydrolysis deposition precipitation (DP). Copper nitrate Cu(NO₃)₂•3H₂O (A.R., Sinopharm Chemical Reagent, China) was used as copper source. Silica sol (JN-30, 30.62 wt% SiO₂, Qingdao Haiyang Chemical) and sodium silicate Na₂SiO₃•9H₂O (A.R., Sinopharm Chemical Reagent, China) were used as silicon source. After drying, the catalyst precursors were calcined in static air at 450 °C for 4 h. All catalysts were denoted as Cu-x, where x represents the preparation technique (CP, NCP, DP) respectively.

a) Co-precipitation of copper hydroxo complexes and monomeric silica. The Cu-CP sample was prepared as following description: 31.2 g of Na₂SiO₃•9H₂O was dissolved in 200 mL deionized water to form Solution A. According to stoichiometric ratio, 13.0 g of Cu $(NO_3)_2$ •3H₂O and nitric acid $[n_{HNO3}=2(n_{Si}-n_M), M$ represents bivalent metal cation] were dissolved in 150 mL deionized water to form Solution B. Solution A was transferred to an oil bath preheated at 90 °C, then Solution B was added drop-wise into Solution A and stirred to form a suspension, with the pH of the solution changing from 14 to 7. After the precipitation, the suspension was aged at 90 °C with stirring for 5 h. The mixture was filtrated and washed with 500 mL of deionized water five times, and then was dried at 110 °C overnight. When ammonium nitrate was added to the solution B with a Cu²⁺:NH₄⁺ molar ratio of 1:5, the precipitated sample was denoted as Cu-NCP; The Cu-Zn-NCP sample was prepared by adding zinc nitrate and ammonium nitrate to Solution B with a Cu²⁺:Zn²⁺:NH₄⁺ molar ratio of 1:0.1:5.

b) Urea hydrolysis deposition precipitation (DP) method. 13 g of Cu $(NO_3)_2$ •3H₂O and urea (per equivalent of copper three equivalents of urea) were dissolved in 150 mL deionized water. According to the desired formula, 22.5g of acidulated silica sol was added into the

mixed solution and the pH was adjusted to 2 - 3 by adding nitric acid at room temperature. Then the suspension was stirred and kept at 90 °C in an oil bath for 24 h, allowing for urea hydrolysis. The pH of the suspension solution increased gradually, and when it reached 6 -7, the heating process was terminated. The mixture was filtrated and washed with 500 mL of deionized water five times, and then dried at 110 °C overnight. The sample was denoted as Cu-DP.

For comparison, a Cu/SiO₂ sample prepared by the co–precipitation method described by Van der Grift ^[16] was coded as Cu-JTS. In this preparation, sodium silicate solution was added into a copper nitrate solution and the pH of the solution started from 1 and ended at 4.3. Amorphous silica (SiO₂-450) was prepared by adding ammonium nitrate to a sodium silicate solution, which was followed by drying and then calcination 450 °C.

2.2. Catalyst characterization

The chemical composition of the catalysts were determined by X-ray fluorescence spectroscopy (XRF), using a Rigaku ZSX Primus II X-Ray spectrometer which is equipped with an Rh target X-ray tube at the power of 3 kW. The Cu weight loading is expressed in wt% of Cu per gram of the sample:

 $wt\%_{Cu}=m_{Cu}/(m_{Cu}+m_{SiO2})\times 100\%$

Specific surface area and pore volume of the samples were measured from Nitrogen adsorption isotherms at 196 °C, using MicromeriticsTristar 3000 equipment. Sample degassing was carried out at 300 °C for 3h prior to adsorption. BET surface area was calculated using the BET equation, the pore size distribution was calculated following BJH method according to the desorption isotherm branch, and the total pore volume (Vp) was derived from the adsorbed N_2 volume at a relative pressure of approximately 0.99.

IR spectra of powder samples with KBr wafer were recorded at room temperature using a Bruker Vertex 70 FTIR Spectrometer that is equipped with DTGS detector. Spectra were recorded in the 4000 - 400 cm⁻¹ range at a resolution of 4 cm⁻¹.

X-ray powder diffraction (XRD) patterns of samples were scanned using a Bruker D8 Advance X-ray diffractometer with Ni-filtered Cu K_a radiation source ($\lambda = 0.15406$ nm) at 40 kV and 40 mA, The scanning 2 θ range was 10 - 80°, and the scanning speed 2 °/min. For measurements of reduced catalyst samples, Ar was used to protect the cooling sample from oxidation during transfer and sample preparation before XRD analysis.

Transmission electron microscopy (TEM) images were taken with JEOL 2011 Electron Microscope operating at 200 kV. This microscope also has an attached X-ray energydispersive spectrometer (EDS). Before being transferred into the TEM chamber, reduced catalysts samples were quickly dispersed with ethanol and then dropped onto the nickel grid for TEM/EDS analysis.

The reducibility of the calcined catalysts was determined by H_2 temperature programmed reduction (TPR) on a MicromeriticsAutochem II 2920 auto adsorption apparatus. 40 mg of sample was degassed at 120 °C under Ar for 1 h, and after cooling to room temperature the gas was switched to 10 vol% H_2 /Ar with a flow rate of 50 mL/min. The temperature was ramped linearly to 800 °C with a heating rate of 10 °C/min. The thermal conductivity detector (TCD) was used to determine the H_2 consumption during the run.

The dispersion and distribution of the active surface metallic copper sites were determined by dissociative N₂O adsorption at 60 °C and 90 °C, using the procedures described by Van Der Grift et.al. ^[18]. Firstly, The calcined sample was reduced at 300 °C under 10 vol% H₂/Ar (50mL/min) for 1h.and cooled down to the designated oxidation

temperature, the gas was switched to pure Ar, and purged for 20 min. Then, the sample was exposed in the 10% N₂O/Ar (30 mL/min) atmosphere and oxidized for 1h, ensuring that surface Cu atoms were completely oxidized according to the reaction: $2Cu + N_2O \rightarrow Cu_2O +$ N₂, Finally, sample was purged with Ar and cooled to room temperature. Following the same procedures as the first one, a second TPR run was performed, the consumed amount of H₂ consumption was calibrated using known amount of surface Cu₂O, for the sample subjected to oxidation at 60 °C, it was denoted as Y₁, while it was denoted as Y₂ for oxidation at 90 °C. The quantity of loading copper in all reduced catalysts was measured by XRF and denoted as X, and copper dispersion (D) was calculated by dividing the amount of surface copper atoms into total supported copper atoms as follows:

D=(2×Y/X)×100%

To obtain the copper chemical states on surface for catalysts upon calcination, after reduction and after re-oxidation by N₂O, in situ X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (XAES) were carried out on Thermo Scientific K-alpha spectrometer system, which is equipped with monochromatic Al K α (1486.6 kV) X-ray source, a hemispherical energy analyzer and multi-stage samples cabin. All binding energies were calibrated by using the C1s peak at 284.6 eV as the reference. Each calcined catalyst was pressed into pellet and equally placed into the sample chamber. The samples were transferred to the vacuum chamber (2×10⁻⁷ Pa) and the first XPS measurement was performed. Then, the samples were drawn back into the sample chamber and reduced at 300 °C in 10 vol% H₂/Ar (50mL/min) atmosphere for 1 h and cooled down. Second XPS/XAES measurement was performed following the same procedures. Finally, the reduced samples were equally exposed to the 10% N₂O/Ar (30 mL/min) atmosphere at 90 °C for oxidation for 1h, and the third XPS/XAES measurement was performed.

The infrared studies of adsorptive CO on the surface of catalysts were conducted with Bruker Vertex 70 FTIR Spectrometer system which is equipped with an in situ transmission cell (Specac GS05850). The cell is connected to a vacuum-desorption apparatus with a residual pressure below 10^{-4} Pa, can be heated up at different atmospheres. To study reduced samples, each catalyst was pressed into disk and pretreated in situ in the cell at 300 °C under 10 vol% H₂/Ar (50 mL/min) for 1 h. After cooling down to 25 °C, the spectrum was taken as the reference for subsequent spectra of the sample. The catalyst was then exposed to a flowing mixture of 1% CO/Ar for 30 min at 25 °C to reach the adsorption equilibrium. While staying at the constant desorption temperature of 25 °C, spectra were collected at different evacuation pressures. To investigate the CO adsorption behavior of catalyst upon surface reoxidation by N₂O, the sample after reduction was first cooled in H₂/Ar and subsequently evacuated, and surface oxidation was accomplished by flowing 10% N₂O/Ar (30mL/min) in 90 °C for 1 h. After cooling down to 25 °C, spectra could be collected following the above mentioned procedures.

2.3. Catalytic reaction

The vapor-phase hydrogenation of ethyl acetate (EA) was tested in a continuous-flow fixed-bed Micro-reactor. Typically, 1g catalyst (40 - 60 meshes) was placed between plugs of quartz sand in a steel tubular reactor. Before the experiment, all catalysts were activated in situ at 300 °C with a ramping rate of 1 °C/min under pure H₂ (50 mL/min) for 4 hours, and then cooled under H₂ to the reaction temperature. Pure ethyl acetate (A.R, purity > 99%) and H₂ were mixed and preheated, and fed into reduced catalyst bed with a H₂/EA molar ratio of 29 at a total pressure of 3.0 MPa and in a temperature range of 210 °C to 280 °C. Steady-

state was usually obtained after 4 h on stream reaction. Products were condensed to allow for liquid and gas separation. Liquid and gas products were analyzed separately by an off-line gas chromatograph (Shimadzu GC17-A) equipped with a HP-FFAP capillary column (30 m \times 0.25 mm \times 0.3 µm) and a flame-ionization detector (FID). The products were quantified via internal calibration method.

3. Results and Interpretation

3.1. Physicochemical and Morphological properties of catalysts

The chemical compositions and the textural properties of the two types of catalysts were listed in the Table 1. The actual copper loading determined by XRF was close to the nominal value. For calcined co-precipitation (CP) catalysts, the BET surface area of the Cu-CP sample was 515.7 m²/g, which was noticeably higher than that of the Cu-DP sample prepared by urea hydrolysis deposition precipitation (DP) method. By adding NH₄⁺ and Zn²⁺ to the co-precipitation process, the structure of the Cu/SiO₂ catalysts changed rapidly, and their BET surface area decreased to 423.4 m²/g. However, they were all much higher than that of amorphous silica (SiO₂-450).

After calcinations, similar to the DP sample, the color of all co-precipitation catalysts (Cu-CP, Cu-NCP, and Cu-Zn-NCP) changed from bright blue to olive green. The high specific surface area and olive green or bright blue color were often attributed to the presence of copper phyllosilicates and/or copper oxide with a high specific surface area and a two-dimensional dispersion of copper species over the corrugated silica sheets [28]. According to Van der Grift, the bright blue color of the precipitates indicated the presence of hydrated, octahedrally surrounded copper(II) ions in the catalyst precursors, and the olive green was characteristic of decomposed chrysocolla (copper phyllosilicates) with a two dimensional tenorite on silica^[10, 16]. In the Cu-JST sample, the color changed from bright blue to dark gray, suggesting the presence of CuO with some degree of aggregation in silica matrix ^[28]. Hence it was reasonable to assume that the formation of copper phyllosilicates in the copprecipitated catalyst precursors which was dehydrated and partly decomposed after calcination.

It was noticeable that the BET surface area of Cu-DP sample was the higher than Cu-DP sample even with the same copper loading, and could be adjusted by adding NH₄⁺ and zinc to the co-pricipitation process. Because copper phyllosilicates possess high specific surface area ^[10], this larger surface area may be attributed to more copper phyllosilicates, or special type of copper phyllosilicate species preserved in the co-precipitation catalysts.

The N₂ adsorption-desorption isotherms and pore-size distributions curves of all calcined Cu/SiO₂ catalysts samples exhibited a type IV Langmuir isotherm and mesopores dominatedas implied in Fig. 1. The Cu-DP sample was found to possess H₁-type hysteresis loop and show a bimodal pore-size distribution with maxima at radii 3.0 and 7.0 nm, whereas for the co-precipitation catalysts, all samples exhibited H₂-type hysteresis loop and single

pore-size distribution centered at 3.0 nm, implying that "parallel plate narrow slit channels" dominated in these catalysts.

During the co-precipitation of sodium silicate and copper nitrate solution, copper nitrate hydroxide, the mixture of copper nitrate hydroxide with silica gel, or copper phyllosilicates were probably formed. As mentioned in the introduction, the FTIR spectroscopy was well adopted to distinguish between these three copper species in the sample ^[6.26]. As shown in Figure 2a, the copper nitrate hydroxide was characterized by δ_{OH} bands of structural hydroxyl groups at 677, 776 and 887 cm⁻¹, and two sharp bands at 1423 cm⁻¹ and 1347 cm⁻¹ corresponded to the molecular vibration of nitrate. The discrimination between copper hydroxide and copper phyllosilicates can be made from the δ_{OH} bands and the presence or absence of δ_{SiO} band ^[26]. The band at around 690 cm⁻¹ was often attributed to the structural hydroxyl group of Cu(OH)₂ ^[6,29], while the presence of chrysocolla (1:1 copper phyllosilicate) was often characterized by a δ_{SiO} band of SiO₄tetrahedra at ~1040 cm⁻¹ and by δ_{OH} bands of structural hydroxyl groups at 670 cm⁻¹ and 3620 cm^{-1[3,20,26]}. Typically, a sharp band at 3620 cm⁻¹ was attributed to O-H stretching of the structural OH, and a medium intensity band at 670-675 cm⁻¹ was assigned to the deformation mode of OH linked to 3 Cu atoms ^[20].

So for silica supported copper catalyst precursors, in addition to the bands of amorphous silica at about 1100, 800 and 470 cm⁻¹ (Figure 2a), the Cu-JTS sample only exhibited bands at 700, 1088, 1347 and 1423 cm⁻¹, indicating only mixture of copper nitrate hydroxide was formed in the silica gel. While for the dried precursors of Cu-CP and Cu-DP sample, the typical bands at 670, 1024, and 3623 (3645) cm⁻¹ were observed, suggesting the formation of copper phyllosilicates in the catalyst precursors.

However, it was hard to further identify which type of copper phyllosilicates preserved in the Cu-CP and Cu-DP precursors, since the ill-crystallized 1:1 and 2:1 phyllosilicates

cannot be distinguished from their δ_{OH} vibration bands which were very close (~ 670 cm⁻¹), and their SiO stretching vibration bands which were very broad ^[21]. Although the syntheses started with Si/Cu ratios of 2 - 4 which would otherwise lead to the formation of 2:1 copper phyllosilicate, most of products obtained from previous reports ^[10,12,20] were chrysocolla (1:1 copper phyllosilicate) ,or sometimes copper oxides, unless very high temperature were used, in which case the reaction mixtures contained a large excess of active Si , and the 2:1 copper phyllosilicate (Cu-talc) was obtained, when the reaction mixtures did not contain a large excess of active Si, the products were mixture of copper oxides and amorphous silicates, with perhaps some phyllosilicates^[20].

After calcination, copper phyllosilicates were also preserved in all precipitated catalysts, which were characterized by the IR spectra shown in Figure 3. Comparing to the dried samples, the intensity of absorption bands at 670 ,1024, 3623 cm⁻¹ decreased, and the shoulder peak at 1110 cm⁻¹ became obvious. This indicated that part of the copper phyllosilicates decomposed and rearranged after calcination at 450 °C. The relative amount of supported phyllosilicates before and after calcination can be roughly estimated by considering the integrated intensity of δ_{OH} band at 670 cm⁻¹ normalized to the integrated intensity of the symmetric δ_{SiO} band of amorphous silica at 800 cm⁻¹, which was defined as I_{670}/I_{800} ^[26]. The results were summarized in the Table 2. For co-precipitated catalysts, the Cu-CP sample seemed to contain larger amount of copper phyllosilicates and to be more thermally stable than others in terms of phyllosilicates decomposition. Introduction of NH₄⁺ and Zn²⁺ had inhibited the formation of stable type of copper phyllosilicates during the co-pricipitation process.

To further investigate the cupreous species in co-precipitated Cu/SiO₂ catalysts, XRD patterns of bulk CuO and two types of calcined Cu/SiO₂ catalysts were collected and shown

in Fig. 4. The Cu/SiO₂ catalysts by two types of precipitation method exhibited similar XRD patterns, but all were different from the characteristic diffraction peaks of CuO. The broad peak at 22° was generally considered to be amorphous silica as the support in Cu/SiO₂ catalysts, while the strong and broad peaks at ca. 30.5°, 35.8°, 56.9°, 63.3°, and 72° suggested the predominant presence of copper phyllosilicates with poor crystallinity^[3,26,30]. No diffraction peaks for copper oxide were observed, indicating that copper oxide species was highly dispersed in co-precipitated catalysts.

The TEM images of calcined Cu-DP and Cu-CP catalysts were shown in Figure 5. Upon calcination, the dark spherical particles irregularly dispersed on the silica support. The average particle size was about 8.4 nm for the Cu-DP catalyst and 4.2 nm for the Cu-CP catalyst. According to the EDS results, the main component of this particles was copper oxide, which should be attributed to the decomposition products of copper silicates or Cu(OH)₂ on silica. It may be worth noting that some core-shell particles were distributed in the Cu-CP catalyst with a Si/Cu ratio about 11, which suggested that some copper species were buried into silica species in the Cu-CP catalyst after calcination.

The temperature programmed reduction (TPR) profiles for CuO and the synthesized Cu/SiO_2 catalysts were presented in Fig. 6. The reduction peak for bulk CuO was around 225 °C while the peak for the Cu-CP sample 243 °C, implying there was a strong interaction between copper species and silica support. Literatures had suggested that the main peak could be assigned to the reduction of well-dispersed CuO particles to copper metal (Cu⁰) and phyllosilicates to cuprous oxide (Cu₂O) ^[3, 12, 15]. Reduction of cuprous oxide to copper metal may need much higher temperature and the peak may not be visible on the profile. The reduction temperature for the Cu-CP catalyst was higher than other Cu/SiO₂ catalysts, probably because it had more stable copper phyllosilicates. This was consistent with the

semi-quantitative results of IR characterization. Similarly, adding NH_4^+ and Zn^{2+} to samples (Cu-NCP and Cu-Zn-NCP catalysts) inhibited the formation of stable phyllosilicates and thus led to lower reduction peak.

3.2. Characterization of reduced catalysts

3.2.1 Crystalline size

The two types of Cu/SiO₂ catalysts were reduced at 300 °C, and their XRD patterns were shown in Fig. 7. While copper oxide and phyllosilicates disappeared, there were broad peaks for Cu metal and cuprous oxide (Cu₂O). Peaks at 43.3°, 50.3°, and 73.9° could be assigned to Cu metal (111), (200), and (220) plane diffraction, respectively (JCPDS 04-0836). Peaks at 36.4° and 61.4° were characteristic of Cu₂O crystalline. The broad peak at 21° was from amorphous silica. Crystalline size of Cu metal and Cu₂O was calculated using Scherrer Formula and listed in Table 3. It can be seen that both Cu size and Cu₂O size in the DP catalyst were similar to the CP catalysts, with Cu metal in the range of 7.8 – 8.4 nm and Cu₂O 7.5 – 7.9 nm.

The TEM images of reduced catalysts were shown in Fig. 8. The light gray silica supports were identified along with highly dispersed dark spherical particles assignable to Cu species. It was apparent that metal particles were uniformly dispersed onto the silica support in all samples, for the co-precipitation catalysts. The statistical results based on TEM images showed that the copper particles sizes were about 4.3 nm to 5 nm, which were smaller and more uniform than the DP catalyst. It was also noticeable that adding NH₄⁺ and Zn²⁺ during precipitation (Cu-NCP and Cu-Zn-NCP catalysts) did not change the metal particle size.

3.2.2 Dispersion and distribution of metallic copper on surface

To investigate the metal species and their distribution on surface for the reduced Cu/SiO_2 catalysts, oxidation by N₂O was performed for the reduced catalysts at 60 °C and 90

°C, respectively, which was followed by 2nd reduction using the same procures as the 1st TPR. Copper oxide (CuO) was used as reference. Literature had suggested that copper metal species could be oxidized to Cu₂O by N₂O under 90 °C ^[18]. If the quantity of loading copper in all reduced catalysts was denoted as X, and the total hydrogen consumption of the 2nd TPR as Y (in which Y_{60} referred to the 2nd reduction at 60 °C and Y_{90} at 90 °C), dispersion of copper metal can thus be calculated as 2Y/X. The dispersion results of all catalysts were summarized in Table 3.

The 2nd TPR profiles of the samples were shown in Fig. 9. For pure CuO, copper metal species from the 1st TPR could not be oxidized by N₂O even at 90 °C, resulting in no further hydrogen consumption during the 2nd TPR and therefore virtually zero dispersion. For the Cu-DP sample prepared by urea hydrolysis deposition precipitation, the 2nd TPR profiles, including the reduction peak position and area, looked similar when the oxidation treatment was performed at 60 °C and 90 °C. While for the Cu-CP sample prepared by co-precipitation, the 2nd TPR profiles differed in both peak position and area. For instance, in the case of oxidation treatment at 60 °C, the reduction peak was broad spanning from 100°C to 175 °C and the dispersion was 7.47%; while in the case at 90 °C, the peak shifted to 145 °C and the dispersion increased to 19.72%. This suggested that there was less copper metal species on the surface of the Cu-CP catalyst comparing to the Cu-DP one. It should be understandable that the co-precipitation method gave out a more copper enrichment on the surface of silica support than the deposition precipitation method .When the oxidation temperature rose from 60 °C to 90 °C, N₂O penetrated deeper and more copper beneath the surface was oxidized in the Cu-CP catalyst, which soundly explained why more hydrogen was consumed during the 2nd TPR run. Besides, the reduction peak shift to higher temperature was an indication of enhanced interaction between cuprous species and the support.

Adding NH_4^+ and Zn^{2+} to the co-precipitated catalysts seemed to help shift more copper species to the surface. For the Cu-NCP catalyst, the dispersion was 16.14% for the case of oxidation at 60 °C and increased to 19.75% when at 90 °C. For the Cu-Zn-NCP catalyst, the dispersion was high in both cases but the difference already diminished. In summary, with same copper loading, using additives during the co-precipitation synthesis could change the microstructure evolution and enrich copper species onto the surface, and thus greatly improved the copper metal dispersion upon reduction.

3.2.3 In situ XPS analysis of surface chemical states

XPS and XAES were employed to study the chemical status of copper species on surface of four catalysts, i.e., Cu-DP, Cu-CP, Cu-NCP and Cu-Zn-NCP, which were subject to in situ reduction at 300 °C and in situ oxidation by N₂O at 90 °C when needed. The Cu2p XPS spectra of the four as-calcined catalysts were illustrated in Fig. 10. The binding energy for Cu2p3/2 and Cu2p1/2 were centered at 935.1 eV and 954.9 eV, respectively, and the satellite peaks of 2p-3d orbitals were in the binding energy range of 941 – 944 EV. These features were all due to the characteristics of Cu²⁺ species. Moreover, the Cu2p3/2 binding energy of CuO is typically around 933.5 EV, so the main peak at 935.1 eV observed in this study was likely due to the strong interaction of Cu²⁺ and the silica support, i.e., the formation of copper phyllosilicates^[10]. This is consistent with the XRD and IR results.

When the catalysts were reduced in hydrogen at 300 °C, the Cu2p XPS spectra were shown in Fig. 11A. The Cu2p3/2 binding energy shifted to 932.4 – 932.8 eV and the Cu2p1/2 binding energy to 952.1 – 952.5 eV. Meanwhile, the satellite peaks disappeared, suggesting Cu^{2+} species were reduced to Cu^{0} and/or Cu^{+} . When the reduced catalysts were kept in the chamber and further oxidized by N₂O at 90 °C, the Cu2p XPS spectra were shown in Fig.

12A. It could be found the spectra were similar to Fig. 11A and lack of the satellite peaks characteristic to Cu^{2+} . This confirms that oxidation of copper metal by N₂O at 90 °C could only go to Cu_2O ^[3, 12].

The amount of Cu^0 and Cu^+ on surface of the catalysts after reduction and after further oxidation by N₂O could be determined by Cu LMM XAES, as in Fig. 11B and Fig. 12B, respectively. In both figures, the Auger kinetic energy peaks were broad and asymmetric, but could be de-convoluted into two symmetrical peaks centered at 916 and 918 eV corresponding to Cu^+ and Cu^0 species, respectively. Quantitative results were summarized in Table 4. The reduced Cu-DP catalyst had dominant Cu^+ species on surface (96.0%) which further increased to nearly 100% coverage after oxidation by N₂O; For co-precipitation catalysts, the reduced Cu-CP catalysts only had Cu^+ surface coverage of 60.4%. As the promoters were added during the precipitation , however, the Cu^+ surface coverage was increased, the reduced Cu-NCP and Cu -Zn-NCP catalysts exhibited 71.4% and 94.9% of Cu^+ surface coverage respectively, which, upon oxidation, also dramatically increased to 92.9% and 100%, respectively. It is thus found that using NH₄⁺ and Zn²⁺ during the coprecipitation synthesis could not only enrich copper onto the support surface, but also tune the percentage of different copper species on surface.

3.2.4 IR study of CO adsorption on catalysts

IR of CO adsorption on catalysts was also used to probe the chemical status and distribution of copper species on surface. The IR spectra of CO adsorption on the reduced Cu-Zn-NCP catalyst at different equilibrated pressure were shown in Fig. 13A. When the CO pressure was at 1 atm, physisorption and chemisorption co-existed on the catalyst surface, where the bands at 2120 cm⁻¹ and 2170 cm⁻¹were due to stretching of gaseous CO, and band at 2054 cm⁻¹ was due to the CO adsorbed on the silica support via hydroxyl group bonding.

With vacuuming, the gaseous CO and physical adsorbed CO were removed, and chemisorbed CO peak started to appear at 2113 cm⁻¹. When the pressure was further reduced, this weak peak quickly disappeared and a strong and stable chemisorbed CO peak emerged at 2124 cm⁻¹. When the pressure dropped to 4.5×10^{-3} Pa, 2124 cm⁻¹ blue shifted to 2130 cm⁻¹. CO chemisorption is usually considered to occur on the copper species to form Cu⁰-CO , Cu⁺-CO , Cu²⁺-CO species via σ - and π -back bonds, as a result of the synergistic effect between two bonds, the Cu⁺-CO species are characterized by the higher thermal stability than Cu⁰-CO and Cu²⁺-CO species ^[31-35]; besides, it is often thought that the stretching frequency of CO species absorbed onto cupreous surfaces follows the sequence Cu²⁺-CO > Cu⁺-CO > Cu⁰-CO ^[36]. According to these assignments , band at 2130 cm⁻¹ and 2113 cm⁻¹ can be assigned to linear stretching of Cu⁺-CO and Cu⁰-CO species respectively, and the only Cu⁺-CO carbonyls could be preserved at the end of high vacuum.

When the Cu-Zn-NCP catalyst was reduced and further oxidized by N_2O at 90 °C, the IR spectra of CO adsorption were shown in Fig. 13B. The evolution of sorption bands as a function of CO pressure was the same as for the reduced catalyst. The only difference was that, under high vacuum, the Cu⁺-CO band shifted to 2132 cm⁻¹ and the sorption peak area was bigger than the reduced one, which was a good indication of more Cu⁺ species that was due to some Cu⁰ species oxidation by N₂O.

IR of CO adsorption on the Cu-DP, Cu-CP and Cu-NCP catalysts were also performed following the same procedures. The spectra for these reduced catalysts and further oxidized ones were presented in Fig. 14A and B, respectively. A qualitative analysis on the amount of Cu^+ on surface was given in Table 5, which was found to be in good agreement with the quantitative analysis by H₂-TPR and XPS. For the Cu-DP catalyst, there was a big Cu⁺-CO sorption peak at 2132 cm⁻¹ after it was reduced, and the peak area increased after it was

further oxidized by N₂O, suggesting large amount of Cu⁺ species, along with some Cu⁰ species, existed on surface. For the Cu-CP catalyst, only a trace of Cu⁰-CO sorption peak at 2107 cm⁻¹ could be seen when it was reduced, and a weak shoulder peak at 2126 cm⁻¹ appeared after oxidation which could be presumably assigned to Cu⁺-CO sorption. This indicated that the amount of both Cu⁰ and Cu⁺ on the Cu-CP catalyst surface was actually small though the relative percentage of Cu⁰ was high. For the Cu-NCP catalyst, it can be qualitatively seen that the amount of Cu⁺ on surface was more than the Cu-CP catalyst, implying the copper species was more concentrated on surface via the assistance of NH₄⁺ during the synthesis.

3.3. Catalytic performances

The reactivity of the catalysts was probed using vapor-phase hydrogenation of ethyl acetate (EA), and was correlated with the surface structure and active metal species of the catalysts. Under the reaction conditions, the main product was ethanol and ethane was the byproduct that could be detected. The conversion, selectivity, and space time yield over different catalysts were summarized in Table 6.

For the Cu-DP catalyst, the reactivity at 250 °C was as high as 94.0% which was close the thermodynamic equilibrium conversion. As a comparison, for the Cu-CP catalyst, the conversion of EA at 250 °C was only 11.4% but could reach 95.3% when the temperature was raised to 280 °C. Using additives such as NH_4^+ and Zn^{2+} remarkably improved the reactivity. For example, the Cu-Zn-NCP catalyst behaved much better than the Cu-DP one, and when at 250 °C, the conversion of EA reached 99.7% and STY 1.23 g_EtOH/(g_cat · h)

4. Discussions

4.1. Formation of copper phyllosillicates in Cu/SiO₂ catalysts prepared by coprecipitation

The formation of copper phyllosilicates was well known during the preparation of Cu/SiO₂ catalysts by urea hydrolysis deposition-precipitation (DP) method, ammonia evaporation (AE), sol-gel, and selective adsorption of copper tetraammine complex $[Cu(NH_3)_4(H_2O)_2]^{2+}$ on silica. In the present work, copper phyllosilicates were also obtained by co-precipitation method, despite the pH range for precipitation and the precursor for silica was different. Our study showed these preparation methods followed the same type of elementary reaction mechanism. Firstly, monomeric silicic acid reacts with hydrolyzed copper complexes containing H₂O and OH ligands through a hetero-condensation reaction to form Si-O-Cu monomers or Si-O-Cu-O-Si monomers, and secondly, monomers polymerize to form copper phyllosilicates^[26]. It has been reported that the prerequisites for the formation of copper phyllosilicates include: (1) formation of monomeric silicic species in solution; and (2) formation of neutral copper complex with hydroxyl ligands. In addition, the formation of copper phyllosilicates must be faster than the precipitation of copper hydroxide species and gelation of silicic species ^[26-27]. Thus, the pH of the solution is critically important, especially for DP method in which the pH must be lower than that of the hydroxide precipitation^[27]. During the preparation by CP method, the copper hydroxo complexes ($[Cu(OH)_2]^0$) and monomeric silicic acid were formed and co-precipitated by adding acidified copper nitrate solution drop-wise into the alkaline sodium silicate solution. With the pH of the solution gradually decreasing from 14 to 8, the two precipitates reacted to form copper phyllosilicates. Their characteristic IR peaks were strong in all three samples including Cu-CP, Cu-NCP and Cu-Zn-NCP after filtering and drying. Meanwhile, IR peaks for Cu(OH)₂ were not obvious, suggesting most copper species exist as in the compound of copper phyllosilicates.

When the alkaline sodium silicate solution was added drop-wise into the acidified copper nitrate solution, the pH of the solution gradually increased from 3 to 7, which was accompanied by the gradual change of copper species from $[Cu_x(OH)_y^{(2x-y)+}]$ cations to neutral $[Cu(OH)_2]^0$ monomers. Meanwhile, silicate hydrolyzed quickly to silicic acid monomers which further polymerized and condensed along with pH change. The rate difference in forming the two types of monomers led to the precipitation of $Cu(OH)_2$ and amorphous silica separately, as in the case of the reference sample Cu-JTS where these two components were confirmed by IR.

After calcination at 450 °C, copper phyllosilicates tended to decompose but the catalysts prepared by co-precipitation retained more than other catalysts, suggesting the Cu-CP catalysts had higher thermal stability. As shown in the IR, BET, XRD, XPS and TPR characterization, Cu-CP catalysts had higher I₆₇₀/I₈₀₀ ratio, larger BET surface areas, more complete layer structure and higher reduction temperature.

4.2. Structure of the Cu/SiO₂ catalysts prepared by co-precipitation

It was known that during the urea hydrolysis deposition precipitation, with the increase of copper loading, the phase of chrysocollas (1:1 copper phyllosilicates) became more predominant in catalysts as evidenced by the increase of the characteristic I_{670}/I_{800} ratio in IR and the BET surface area ^[10,15]. On the other hand, Van der Grift et al. identified that the TPR profiles of the Cu/SiO₂ catalysts prepared via homogeneous deposition precipitation were independent of metal loading within the range of 1 - 40 wt%, and the strong reduction peak could be ascribed to the reduction of copper phyllosilicates to Cu⁺ and well-dispersed CuO to Cu^{0[3, 12, 15]}. Themonovalent copper species were formed during the reduction of ion-exchanged Cu-O-Si species and copper phyllosilicates in Cu/SiO₂ catalysts, due to the strong interaction between copper species and SiO₂^[12,19]. For Cu/SiO₂ catalysts prepared by the

same procedure, more copper phyllosilicates often led to more monovalent copper under identical reduction conditions ^[12, 15, 30].

As described above, the physicochemical properties and surface structure of the Cu-CP and Cu-DP catalysts were totally different, even with the same copper loading. There were more copper phyllosilicates in the Cu-CP catalyst than in the Cu-DP one, based on which one may think there would be more Cu^+ species in the Cu-CP catalyst after reduction. However, our results of N₂O surface oxidation, In-situ XPS, and FT-IR CO-adsorption showed that the amount of both Cu^0 and Cu^+ on surface of the Cu-CP catalyst was lower than that of the Cu-DP one. Obviously, the difference in the content of copper phyllosilicates could not account for the different properties between the two types of catalysts.

One possible explanation was that these two types of catalysts contained different types of copper phyllosilicates. Paolo Burattin et al. showed that two types of monomeric species of nickel phyllosilicates could be formed under aqueous condition depending on the Metal: Si ratio in the solution, and polymerization of each would lead to the formation of 1:1 and 2:1 phyllosilicates, respectively ^[21]. It was also suggested that the formation of phyllosilicates was a kinetically limited process, and was especially governed by the kinetics of silica dissolution. The 1:1 phyllosilicate was formed dominantly during deposition-precipitation of silica and copper species under normal temperature and atmospheric pressure ^[21-22]. Jun Xiao and Gilles Villemure found that 2:1 trioctahedral copper phyllosilicate (Cu-talc or Cu-smectie) was obtained with the chemical composition of Si/Cu ratios of approximately 1.33, under the hydrothermal treatment of aqueous mixtures of sodium hydroxide, copper chloride and excess sodium silicate at 150 °C. While the 1:1 copper phyllosilicate (chrysocolla) was predominate when increasing the hydrothermal treatment to 250 °C, and it had a lower Si/Cu ratio of approximately 1^[20]. In the present work, all the samples had similar copper loading at

about 35 wt% (Si/Cu ratio = 1.8), but the initial concentration of monomeric silicic acid in the two types of precipitation methods was very different, which thus likely resulted in the formation of two types of copper phyllosilicates. In the co-precipitation (CP) method, the acidified copper nitrate solution was added drop-wise into the alkaline sodium silicate solution. It was easier to form silicic acid with high concentration in this case, as compared with the deposition-precipitation (DP) method. Therefore, the 2:1 copper phyllosilicate rather than 1:1 copper phyllosilicate might be expected to form dominantly in co-precipitation (CP) samples.

Due to poor crystallinity, our IR and XRD results did not distinguish between 1:1 copper phyllosilicate and 2:1 copper phyllosilicate in the Cu-CP samples ^[21]. The Cu-CP catalyst had a reduction peak at 243 °C and was more difficult to reduce than the Cu-DP catalyst. It has been suggested in the literature that the 2:1 phyllosilicate was more difficult to reduce than the 1:1 phyllosilicate, which implied that more stable 2:1 phyllosilicate exist in the Cu-CP catalyst^[21]. In addition, it was well-known that the 1:1 phyllosilicate consisted of a brucitetype sheet containing metal (M) in octahedral coordination and a sheet containing linked tetrahedral SiO₄ units, while in the 2:1 phyllosilicate, two sheets of linked SiO₄ units sandwiched one brucite-type sheet ^[21-23]. After high temperature calcination or reduction, copper phyllosilicates often decomposed by dehydration and partly reorganization of the silica support ^[16, 17, 23]. Characterization of calcined catalysts by TEM and EDS had shown a morphology of core-shell structure in Cu-CP catalysts, which would be easily interpreted as the copper species buried into silica support. In the 2:1 copper phyllosilicate, all the CuO₄ octahedrons were trapped into the two layers of SiO4 rather than linked in one layer, this also explained why smaller amount of active copper was detected on the surface of the Cu-CP catalysts and why enhanced interaction between cuprous species and the support was observed.

4.3. Effect of NH₄⁺ and Zn²⁺ on the evolution of the structure of Cu/SiO₂ catalysts prepared by co-precipitation

Addition of NH₄⁺ and Zn²⁺ during co-precipitation changed the structure of Cu/SiO₂ catalysts dramatically, such as lower reduction peak and more amounts of active copper species after reduction on surface. It should be noted that the Cu-Zn-NCP catalyst actually exhibited almost the same physicochemical properties as the Cu-DP catalyst in which the 1:1 phyllosilicate was predominant. Comparing to the Cu-CP catalyst, the Cu-NCP and Cu-Zn-NCP catalysts seemed to contain more 1:1 phyllosilicate and less 2:1 phyllosilicate.

Thierry Toupance et al. found that addition of ammonium nitrate to the precursor solution prevented the formation of copper phyllosilicates during the preparation of Cu/SiO₂ by selective adsorption of copper tetraammine complex on silica, and in the case of Ni/SiO₂ catalysts, addition of NH_4^+ could inhibit the formation of nickel phyllosilicates ^[26]. Previous reports had suggested that the ammonium ion acted as "a competitor ion", but there were two explanations:

One possible rationalization was that the NH_4^+ ions prevented the formation of phyllosilicates by inhibiting silica dissolution. According to Stumm et al., nucleophiles and anionic ligand adsorption increased the rate of silicate dissolution, whereas cation adsorption had an opposite effect ^[37]. Dove showed that alkaline ions increased the rate of silica dissolution, while multivalent ions such as Zn^{2+} , Cu^{2+} , Al^{3+} , and Fe^{3+} inhibited dissolution. Alkaline ions (such as Na^+ and Li^+) were small cations with a localized positive charge which could easily approach negatively charged silica surface to adsorb and weaken the Si-O-Si bonding and thus to favor silica dissolution ^[38]. In contrast, NH_4^+ was a much larger cation with less localized positive charge. In consequence, when it approached the silica surface, it was less strongly adsorbed, and therefore, silica dissolution is less favored.

Another explanation was that the formation of copper phyllosilicates required the presence of OH bridging ligands in the copper complex $^{[26]}$. It is known that the tetraammine copper complex, which only had non-bridging NH₃ ligands, cannot be involved in the formation of phyllosilicates, only the [Cu(OH)₂(H₂O)₄] complex is zero charged, and it contains two OH bridging ligands. Therefore, it can be considered as a good candidate for participation in the nucleation stage with monomeric silicic species ^[25]. Adding NH₄⁺ to the solution caused the concentration of [Cu(OH)₂(H₂O)₄] to decrease dramatically and the pH to shift to a lower value, which slowed down the rate of silica dissolution and in turn speeded up the polymerization and condensation of monomeric silicic acid. The formation of copper phyllosilicates was thus inhibited ^[26].

Unlike the soluble silica sol in alkaline solution, the monomeric silicic acid came from the hydrolysis of silicate during the co-precipitation. Cations such as NH_4^+ , Zn^{2+} , and even Cu^{2+} could also act as a "promoter" to accelerate the polymerization reaction to form poly silicic acid which further coagulated to inertial silica gel. So introduction of ammonium and zinc ions might have reduced the number of free monomeric silicic acid and changed the ratio of Si and M in the solution. The concentration of free monomeric silicic acid was lower; the probability of forming 1:1 phyllosilicates was higher.

It was reported that zinc species can also react with silica to form the zinc phyllosilicates during impregnation or cation exchange processes ^[21]. But in this study there was no evidence to identify this compound, probably due to the low composition. However, due to the difference in ionic radius between copper and zinc, it still could be inferred that introduction of zinc cation would interfere with the ordered lamellar structures of copper phyllosilicates, and the 1:1 phyllosilicate structure would be more likely to form.

Based on these observations and inferences, the formation of 1:1 and 2:1 copper phyllosilicates during the co-precipitation process was proposed in the scheme1. Hydrolysis of silicate to form the silicic acid firstly occurredby adding the acidic copper solution; some monomeric silicic acid then reacted withfreehydrolyzed copper species through heterocondensation, which led to formation of some monomer species contained Si-O-Cu bridges, such as Si-O-Cu monomers or Si-O-Cu-O-Si monomers. These species further polymerized and constructed the layer structure of 1:1 or 2:1copper phyllosilicates. When the reaction mixtures contained a large excess of free Si species, some well-structured 2:1 copper phyllosilicates were favored to form, in which two linked SiO₄sheets sandwiched the brucitetype sheets. But this 2:1 layer structure was not stable for Cu ^[20]. If the calcination temperature was increased, the 2:1 copper phyllosilicates would be decomposed by dehydration and partly reorganization of the silica support, which led to the formation of the core-shell structure; if some mixed cationsuch as Zn was introduced, there would be Si-O-Zn monomersin the solution, and it would be easy to form the individual 1:1 layer structure rather the symmetricalsandwiched structures, so the 1:1 copper phyllosilicates were resulted.

4.4. Active site on the reduced Cu /SiO₂ catalysts for hydrogenolysis of acetic ester

It has been suggested that several kinds of copper species exist in calcined Cu/SiO₂ catalysts prepared by deposition-precipitation method, 1) undecomposed 1:1 copper phyllosilicate; 2) well dispersed CuO; and 3) ion exchanged Cu-O-Si species. The well dispersed CuO species were often attributed to the decomposition of the 1:1 copper phyllosilicate or well dispersed Cu(OH)₂ species, upon hydrogenation reduction at 273 - 350 °C, and the well disperse CuO species were usually reduced to dispersed Cu⁰.Meanwhile, for copper phyllosilicates and ion exchanged Cu-O-Si species, the reduction was stopped at Cu⁺ due to the strong interaction of copper and SiO₂^[3, 12, 26]. Van der Grift et al. indicated that the

1:1 copper phyllosilicate could also be further reduced to the well dispersed Cu^0 species at higher temperatures ^[16, 17]. For the Cu-CP catalysts, the calcination caused the 2:1 copper phyllosilicate to partly decompose and reorganize, only leaving small amount of well dispersed CuO species on surface and other copper species buried into the bulk phase and covered by the silica. This is because the two sheets of linked SiO₄ units sandwiched the brucite-type sheet in the 2:1 phyllosilicate, and these layers were usually neutral and did not exhibit ion-exchange properties ^[21].

The catalytic steps of ester hydrogenolysis to alcohols were thought to proceed on copper metal ^[39], Jinlong Gong et al. further pointed out that Cu^0 was the sole active sites and primarily responsible for the activity of Cu/SiO_2 catalysts, while Cu^+ facilitated the conversion of intermediates during the hydrogenation of hydrogenation of oxalic ester. Adding NH_4^+ and Zn^{2+} during the co-precipitation process seemed to help the copper silicates evolve from the 2:1 copper phyllosilicates to the 1:1 copper phyllosilicates, and more active copper species emerged onto the silica support. For the Cu-Zn-NCP catalyst in particular, large amount of active Cu^0 and Cu^+ species were dispersed on the surface with an optimum ratio, which led to the outstanding activity during the hydrogenolysis of ethyl acetate to ethanol.

5. Conclusions

A simple co-precipitation method (CP) was employed to synthesize Cu/SiO₂ catalysts for acetic ester hydrogenation to ethanol and compared to the urea hydrolysis depositionprecipitation method (DP). As confirmed by IR spectroscopy, phases of copper phyllosilicates existed in both types of catalysts. However, the exact form of phyllosilicates in the oxide samples, as well as the amount of active copper species on surface of the reduced samples, was different. The Cu-CP catalyst had higher surface area and smaller metal

particles than the Cu-DP catalyst, but on the other hand, had higher reduction temperature and much less active copper species on surface. All the features could be explained by the dominant copper silicate phase, the 2:1 copper phyllosilicate, in the Cu-CP catalyst upon synthesis, as compared to the dominant 1:1 copper phyllosilicate phase in the Cu-DP catalyst. During calcination, the 2:1 copper phyllosilicate partly decomposed and reorganized, and only small amount of copper –containing compounds were left on surface, with other copper species buried into the bulk phase and covered by the silica. After reduction, only small amount of active copper species dispersed on the surface of the Cu-CP catalyst. As a consequence, the catalytic conversion of acetic ester to ethanol was lower for the Cu-CP catalyst.

Adding NH₄⁺ and Zn²⁺ during the co-precipitation process tended to change the copper silicate phase evolution from 2:1 phyllosilicate to 1:1 phyllosilicate, resulting in more active copper species emerging onto the surface of reduced catalysts. Noticeably, the copper particle size remained small and the amount of active copper species on surface increased greatly. For the Cu-Zn-NCP catalyst, high conversion of acetic ester (> 97%), high selectivity of ethanol (> 99%), and good space-time yield of ethanol (1.23 g_EtOH/(g_cat \cdot h)) could be obtained in the temperature range of 230 °C to 250 °C.

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Scheme1.The schematic growth process of 1:1 and 2:1 copper phyllosilicates during the coprecipitation process



Figure 1.Nitrogen adsorption-desorption isotherms (A) and the pore size distributions (B) of the Cu/SiO_2 catalysts prepared by the DP and CP method.



Figure 2.FTIR spectra of (a) copper nitrate hydroxide by precipitation of copper nitrate with ammonia, (b) Cu-JTS sample, (c) dried precursor of Cu-CP, and (d) dried precursor of Cu-DP sample.



Figure3. IR spectra of the calcined samples: (a) SiO₂-450; (b) Cu-CP catalyst; (c) Cu-NCP catalyst; (d)Cu-Zn-NCP catalyst (e) Cu-DP catalyst.



Figure 4.XRD diffraction patterns of calcined Cu/SiO₂ catalysts: (a) Cu-DP catalyst, (b) Cu-CP catalyst, (c) Cu-NCP catalyst, (d) Cu-Zn-NCP catalyst, and (e) CuO.



Figure 5.TEM images and EDS result of calcined Cu/SiO₂catatlyst. (A) Cu-DP sample; (B,C,D) Cu-CP sample



Figure 6.TPR profile of bulk CuO and Cu/SiO₂ catalysts prepared by DP and co-precipitation methods



Figure 7.XRD patterns of reduced catalysts





Figure 8. TEM images of reduced Cu/SiO₂:(A) Cu-DP, (B) Cu-CP, (C) Cu-NCP, and (D) Cu-Zn-NCP



Figure 9.TPR profiles for Cu/SiO_2 catalysts and CuO after N_2O oxidation treatment in 60 $^\circ C$ and 90 $^\circ C$



Figure 10. Cu2p XPS spectra of Cu/SiO₂ catalysts before reduction



Kinetic Energy /eV **Figure 11.**Cu2p XPS spectra (A)and Cu LMM XAES spectra(B) of reducted Cu/SiO₂ catalysts at 300 °C



 $\label{eq:Kinetic Energy / eV} \mbox{Figure 12.} Cu2p \ XPS \ spectra \ (A) \ and \ Cu \ LMM \ XAES \ spectra \ (B) \ of \ oxidized \ Cu/SiO_2 \ catalysts \ by \ N_2O \ at \ 90 \ ^{\circ}C$



Figure 13.IR spectra of CO adsorption on the reduced Cu-Zn-NCP catalyst (A) and on N₂Ooxidized Cu-Zn-NCP catalyst (B) at room temperature. Catalyst was first reduced at 300 °C for 1 hour and then oxidized at 90 °C with 10% N₂O for 1 hour. (a) equilibrium CO pressure of atmospheric pressure, (b-f) gradual decrease of pressure, and (g) equilibrium CO pressure of 4.5×10^{-3} Pa. All spectra were background corrected.



Figure 14.IR spectra of CO adsorption on the Cu/SiO₂ catalysts at equilibrium CO pressure of 4.5×10^{-3} Pa : (A) on reduced Cu/SiO₂ catalysts (B) on N₂O-oxidized Cu/SiO₂ catalysts treated by N₂O.

Sample	Cu Loading	Elemental analysis	S_{BET}	VP	d _P	Color
	wt%	wt%	m²/g	cm ³ /g	nm	
SiO ₂ -450	-	-	169.7	1.00	20.0	
Cu-DP	35.5%	-	455.0	0.75	5.1	Olive green
Cu-CP	35.9%	-	515.7	0.64	4.2	Olive green
Cu-NCP	33.1%	-	503.1	0.75	4.9	Olive green
Cu- Zn-NCP	32.8%	1.96%Zn	423.4	0.76	6.9	Olive green
Cu-JTS	34.3%	-	133.2	0.54	12.8	Dark Gray

Table 1.Structural properties and chemical compositions of Cu/ SiO_2 catalysts

Table 2. Relative amount of copper phyllosilicates before and after calcination in Cu/SiO_2 catalysts

Sample	Relative amount of (<i>I</i> ₆₇₀	$\frac{(I_{670}/I_{800})_{450^{\circ}\text{C}}}{(I_{670}/I_{800})_{110^{\circ}\text{C}}}$	
	110 °C drying	450 °C calcination	
Cu-DP	0.27	0.19	70.4%
Cu-CP	0.55	0.44	80.0%
Cu-NCP	0.49	0.34	69.4%
Cu-Zn-NCP	0.34	0.18	52.9%

Sample	d_{Cu2O}^{a} d /nm /1	d_{Cu}^{a}	$d_{Cu}^{b}/$	Dispersion (2Y/X ratio ^c)		
		/nm	nm	Oxidation at 60 °C	Oxidation at 90 °C	
Cu-DP	7.5	8.2	6.4	16.63%	19.21%	
Cu-CP	7.9	8.4	4.5	7.47%	19.72%	
Cu-NCP	7.6	8	5	16.14%	19.75%	
Cu- Zn-NCP	7.5	7.8	4.3	24.26%	26.05%	
CuO				0	0	

Table 3.Physicochemical properties of reduced Cu/SiO₂ catalysts

^a Cu₂O and Cu crystalline size calculation by the Scherrer formula

^b Cu particle size measured by TEM.

 $^{\rm c}$ Determined by N_2O surface oxidation for Cu^0 .

 $90^{\circ}C/1h/5\%N_2O-Ar$

 Table 4.Surface Cu components of in-situ prepared catalysts based on Cu LMM de

convolution. (Cu+) In-Situ BE of KE(eV) Catalysts preparation $\frac{1}{(Cu^0 + Cu^+)}$ Cu⁰ Cu^+ condition Cu2p_{3/2}(eV) 300°C/1h/10%H₂-Ar Cu-DP 932.3 916.0 918.0 96.0% 90°C/1h/5%N₂O-Ar 932.3 100% 916.2 ---300°C/1h/10%H₂-Ar 932.3 60.4% Cu-CP 916.0 918.1 90°C/1h/5%N₂O-Ar 932.3 85.7% 916.1 918.0 Cu-NCP 300°C/1h/10%H₂-Ar 932.3 916.0 918.1 71.4% 90°C/1h/5%N₂O-Ar 932.3 916.1 918.0 92.9% 300°C/1h/10%H₂-Ar Cu-Zn-NCP 932.3 916.0 918.0 94.9%

932.3

916.0

100%

Table 5.Integration area of Cu⁺-CO IR band at equilibrium CO pressure of 4.5×10^{-3} Pa

before and after the surface oxidation.

Catalysts	In-Situ pretreatment	Cu ⁺ -CO IR band			
	condition	Peak position /cm ⁻¹	integration area /a.u.		
Cu-DP	$300^{\circ}C/1h/10\%H_2$ -Ar	2129	0.27509		
	90°C/1h/5%N2O-Ar	2131	0.51747		
Cu-CP	300°C/1h/10%H2-Ar	2126	0.03647		
	90°C/1h/5%N2O-Ar	2129	0.03839		
Cu-NCP	300°C/1h/10%H ₂ -Ar	2126	0.22141		
	90°C/1h/5%N2O-Ar	2130	0.30003		
Cu-Zn-NCP	300°C/1h/10%H ₂ -Ar	2131	0.30784		
	90°C/1h/5%N2O-Ar	2132	0.56331		

Table 6. Effects of temperature on the activity and selectivity of catalytic hydrogenation of

 ethyl acetate (EA)

Catalysts	Conditions		Conversion	Selectivity	Yield	
	T/°C	P/MPa	LHSV/h ⁻¹	/%	/%	$/(g_{EtOH}/(g_{cat}\cdot h))$
Cu-DP	280	3.0	1.24	97.51%	97.48%	1.22
Cu-DP	250	3.0	1.24	94.04%	97.58%	1.19
Cu-DP	230	3.0	1.24	85.95%	98.94%	1.10
Cu-DP	210	3.0	1.24	39.36%	99.91%	0.51
Cu-CP	280	3.0	1.24	95.31%	99.01%	1.17
Cu-CP	270	3.0	1.24	81.68%	99.83%	1.06
Cu-CP	250	3.0	1.24	11.44%	99.48%	0.15
Cu-CP	230	3.0	1.24	3.23%	99.92%	0.04
Cu-CP	210	3.0	1.24	1.23%	99.93%	0.02
Cu-NCP	280	3.0	1.24	97.59%	97.59%	1.22
Cu-NCP	270	3.0	1.24	98.22%	97.59%	1.23
Cu-NCP	250	3.0	1.24	62.45%	98.91%	0.78
Cu-NCP	230	3.0	1.24	5.23%	99.93%	0.07
Cu-NCP	210	3.0	1.24	2.09%	99.93%	0.03
Cu-Zn-NCP	280	3.0	1.24	98.46%	99.02%	1.21
Cu-Zn-NCP	250	3.0	1.24	99.67%	99.07%	1.23
Cu-Zn-NCP	230	3.0	1.24	97.94%	99.17%	1.23
Cu-Zn-NCP	210	3.0	1.24	51.98%	99.45%	0.67

Reaction conditions: T=210 °C - 280 °C, P=3.0 MPa, $n(H_2)/n(EA)=29$ (molar ratio), and ethyl acetate (EA) LHSV=1.24 h⁻¹.