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Continuous heterogeneous hydrogenation of CO₂-derived dimethyl carbonate to methanol over Cu-based catalyst

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Catalytic mild hydrogenation of carbonates synthesized from the CO₂ captured by alcohols is of significant interest both conceptually and practically, which provides alternative approaches to the indirect hydrogenation of CO₂ to methanol. However, the catalytic efficiency of the process of dimethyl carbonate (DMC) hydrogenation still remains unsatisfactory. Unprecedented gas-solid phase fix-bed catalyzed hydrogenation of DMC to methanol has been made. Herein, we address this issue with the facile Cu/SiO₂ catalysts, reaching complete conversion and highly selective formation of methanol (up to 80% yield) under mild condition (503 K, 2.5 MPa), which is the highest yield that has been reported. Characterization results indicate that the copper dispersion and the synergetic effect between balanced Cu⁰ and Cu⁺ sites are considered to play a critical role in attaining high yields of methanol. The optimized Cu/SiO₂ catalyst displayed excellent catalytic performance in the hydrogenation of diethyl carbonate (DEC) and di-n-propyl carbonate (DPC) as well, presenting a broad substrate scope. Moreover, the comparative catalytic activity (~76% methanol yield) in the hydrogenation of DMC under solvent-free condition shows promise its scalable application in the industry.

1. Introduction

 CO_2 , as a so-called greenhouse gas, has the effect of trapping the sun's heat and is believed to be one of the main contributors to the presently observed global warming phenomena. The input of large amounts of anthropogenic CO₂ emitted has exceeded the needed amount of the natural carbon cycle.¹ Capturing and converting CO₂ gas which as an economical, safe and renewable carbon resource to a liquid fuel has captured much attention during the past four decades, mainly due to its synthetic significance as an important pathway outlined in "The Methanol Economy"² to fundamentally synthetic feed stock such as methanol. Nevertheless, the transformation of chemically stable CO₂ to methanol represents a grand challenge in exploring new concepts and solutions for the academic and industrial development of catalytic processes due to the high activation energy barrier needed for the cleavage of the C=O bond.³ As we know, traditional industrial Cu/ZnO/Al₂O₃ exhibits promising performance for MeOH production from CO and $\rm H_2$ (syngas) with a space-time yield up to 0.842 g_{MeOH} ·g⁻¹_{Catal}·h⁻¹ under certain conditions, and this process is the dominant one for MeOH production.⁴ However, syngas is a synonym of "fossil carbon", as it is generated from fossil fuels, like coals, crude oils and CH₄. Along with the resource exhaustion, the need to reduce the emission of

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carbon dioxide into the atmosphere is pushing toward the use of "renewable carbon", so to avoid as much as possible burning "fossil carbon".⁵ Thus, it would be more valuable to develop new industrial processes for converting CO₂ that can be captured from atmosphere into "working carbon". The solar-driven reduction of CO2 into chemicals and fuels such as formic acid, methane or methanol has been considered as a promising approach to address the problems of global warming and energy crisis.⁶ However, most of reported solar-active catalysts for CO₂ photo-reduction suffer from low energy conversion efficiency, uncontrollable selectivity, instability and incapability to completely suppress the competing hydrogen evolution reaction in the presence of water. The conversions of CO₂ into more valuable products such as CH₄, CH₃OH or C₂H₄, which involve multiple proton-coupled electron transfer, have only been demonstrated with low conversion efficiency and selectivity.⁷ Furthermore, many possible products of CO₂ photoreduction could be presented both in the gaseous and liquid phases, which makes the product separation and detection guite a complex process. Hence, the design and fabrication of highly active photocatalytic systems with high conversion efficiency and selectivity for CO₂ reduction remain a grand challenge. Electrolysis of water, driven by electricity that is derived from renewable energy sources, could provide hydrogen as an ideal energy carrier for clean and sustainable energy technologies, which has been industrialized. Besides, the research of photocatalytic decomposition of water to hydrogen energy with solar energy has made some progress, which can also provide an inexpensive approach for the H₂ production.

Conventional processes for CO_2 hydrogenation involving gas phase catalytic conversion over Cu-Zn based catalysts was

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proceeded at high pressure and temperatures (503-543 K), where methanol production was unfavourable in consideration of the reaction is exothermic (ΔH_{298K} = -49.5 kJ/mol).⁸⁻¹¹ CuO/ZnO/Al₂O₃ catalysts presents methanol productivity of 0.311 g·g⁻¹_{Catal}·h⁻¹ at 553 K and 5 Mpa.¹² Traditional Cu/ZnO/Al₂O₃ catalysts would lead to huge amount of CO as a by-product of methanol via the reverse water-gas shift (rWGS) reaction. As we know, the production of CO not only reduces the yield of methanol but also has a negative effect when methanol is used in fuel cells because CO poisons the metal-based catalyst used.¹³ In view of the great challenge exists in highly efficient production of methanol from CO₂ by direct hydrogenation under mild conditions,^{14,15} indirect hydrogenation of CO₂ has been successfully achieved resulting in establishing a bridge from CO₂ to methanol.

The hydrogenation of a series of CO₂ derivatives including carbonates, carbamates, urea derivatives, formates, polycarbonates and so on, were investigated in the laboratory and in industry.¹⁶⁻¹⁹ Milstein and coworkers pioneered this reaction process and reported the highly catalytic hydrogenation of dimethyl carbonate to methanol using a homogeneous dearomatized PNN/Ru^{II} pincer complex under serious conditions (383 K and 5 MPa H₂).²⁰ Ding and coworkers have developed a novel CO₂ indirect conversion process by selective hydrogenation of cyclic carbonates from readily available CO₂ and epoxides to give methanol and the corresponding ethylene glycol with excellent catalytic efficiency.¹⁷ Considering the difficulties in industrial production of homogenous catalysts in terms of stability, separation, handling, and reuse, heterogeneous catalyst system for the hydrogenation of carbonates under mild conditions with ease of catalyst separation and recycling from industrial viewpoint is in urgent demand. Recently, Li and coworkers firstly achieved the heterogeneous hydrogenation of cyclic ethylene carbonate (EC) over a copper-chromite nanocatalyst with moderate selectivity (60%) for the formation of methanol and good selectivity for production of EG (93%) at 453 K and 5 MPa H_2 ,²¹ however, its practical application might be hindered to some extent due to environmentally unfriendly condition. ${\rm Liu}^{22}$ and ${\rm Chen}^{23}$ reported the application of copper-silica nanocomposite in the hydrogenation of EC, affording methanol and EG in higher yields in batch and fixed-bed continuous flow reactors under relatively mild conditions respectively. Nevertheless, the solid state of EC at room temperature and the separation of hydrogenation products may limit its industrial production. Notably, the liquid phase product of DMC hydrogenation need no separation owing to the unitary MeOH as product compared with other carbonates, while the hydrogenation of linear dimethyl carbonate is particularly difficult due to the two adjacent active methoxyl groups.²⁴⁻²⁵ Very recently, M. Tamura reported the Cu/CeO₂ as an effective catalyst for methanol synthesis from DMC hydrogenation with 94% yield in a batch reactor under 433 K and 6-8 MPa.²⁶ The hydrogenation of DMC technology can be combined with the synthesis of DMC to accomplish the fixation and indirect transformation of CO or CO₂. DMC obtained from the first step can be directly pumped into the hydrogenation device without separation and purification process, which can greatly reduce the production costs. Thus, the methanol from this technology shows advantages in the separation and purification compared with the traditional methanol process. DMC can also be obtained easily by transesterification of ethylene carbonate (EC) with methanol. The transesterification of ethylene carbonate (EC) synthesized from ethylene oxide and carbon dioxide with methanol, ethylene glycol as main product and DMC as coproduction of the whole process. This technology can not only solve

the problem of excess CO_2 , but also provide a low cost pathway for the DMC production. Up to now, no gas-solid phase heterogeneous continuous hydrogenation of DMC has been reported until now.

Herein, we report our preliminary results in the vapor phase hydrogenation of DMC with copper-silica catalysts prepared by evaporating ammonia (AE) method which can not only conveniently and effectively disperse copper species on silica but also the high catalytic activity for hydrogenation of DMC to MeOH results from the copper particle size and the cooperative effect between Cu^0 and Cu^+ . Accordingly, a series of silica supported copper catalysts with different copper contents were fabricated and the relationship between the catalysts structure and activities were investigated.

2. Experimental

2.1 Catalyst preparation

A series of copper catalysts with different Cu loading were prepared by the AE method. Briefly, 4.3 g, 6.4 g, 8.6 g and 10.7 g of Cu(NO₃)₂·3H₂O (A.R., Sinopharm Chemical Reagent Ltd.) yielding 20, 30, 40, and 50 wt.% of Cu in the final catalysts were dissolved in 200 mL deionized water in a beaker, into which 25 wt.% ammonia solution (A.R., Sinopharm Chemical Reagent Ltd.) was added by a dropper in 5 min to form a clear $[Cu(NH_3)_4]_2$ solution. This step was followed by drop-wise addition of 30 wt.% silica sol (Qingdao Grand Chemical Co.) solution over a period of 5 min to form a light-blue precipitate and stirred for 4 h. The initial pH of the suspension was 11-12. The suspension was heated in a water bath preheated to 363 K to allow the evaporation of ammonia. Then, the samples were dried at 373 K for 12 h, followed by calcination at 723 K for 4 h in air. The catalysts were pelletized, crushed, sieved to 40-60 meshes, and denoted as xCu/SiO₂, where x represents the copper mass fraction. The samples with 40 wt.% CuO dispersed by different oxides $(TiO_2, ZrO_2 \text{ and } CeO_2)$ were prepared by the same method. The CuZnAl catalysts with 1:9 mole ratio of Cu/Zn-Al (the mole ratio of Zn/Al was fixed at 4:5) were synthesized by the depositionprecipitation method using Na₂CO₃ as the precipitant according to previous report,²⁷ which was denoted as CuZnAl (1/4/5).

2.2 Catalyst characterization

The BET surface area (S_{BET}) was measured using N₂ physisorption at 77 K on a Micromeritics TriStar 3000 apparatus. The samples were outgassed for 2 h at 523 K before each measurement. The X-ray diffraction (XRD) patterns were collected on a Bruker AXS D8 Advance X-ray diffractometer using Cu *K*\alpha radiation ($\lambda = 0.15418$ nm) with angle (2 θ) range of 20-80°, a scanning speed of 4° min⁻¹, a voltage of 40 kV, and a current of 20 mA. The full width at half maximum (FWHM) of Cu (111) diffraction at a 2 θ of 43.3° was used for calculating the Cu crystallite sizes by using the Scherrer equation.

For the XRD examination of reduced catalysts, to avoid and diminish phase transformation from surface oxidation, a variety of measures were taken to suppress the occurrence of oxidization. Firstly, these catalysts which were reduced one at a time in tube furnace by 5 vol.% H_2/Ar would not be taken out until the temperature of the tube furnace was below 303 K. What more

important is that, to prevent them from being oxidized, the reduced catalysts were loaded immediately into a centrifuge tube full of absolute ethanol which could provide a great effect of isolation from air for these catalysts after reduction. And then the sample was sent to the laboratories for the XRD measurements as soon as possible.

The particle size and distribution were observed by transmission electron microscopy (TEM; JEOL JEM2011) with acceleration voltage of 200 kV. The reduced samples for electron microscopy were prepared by grinding and subsequent dispersing the powder in ethanol and applying a drop of very dilute suspension on carboncoated grids and then quickly moved into the vacuum chamber. The surface species were detected by X-ray photoelectron spectroscopy (XPS; Perkin Elmer PHI 5000C). The spectra were recorded with Mg $K\alpha$ line as the excitation source (hv = 1253.6 eV) at 14 kV and 20 mA. The binding energy (BE) values were referenced to the C 1s peak of contaminant carbon at 284.6 eV with an uncertainty of ± 0.2 eV. XPSPeak 4.1 was employed to deconvolute the Cu 2p peaks using the Shirley-type baseline and an iterative least-squared optimization algorithm. The FWHMs of peaks devided (for $\operatorname{Cu}^{^{\scriptscriptstyle +}}$ and Cu°) are almost consistent. The ratio of Cu^{+}/Cu° was calculated from the ratio of the peak area. Fourier transform infrared spectroscopy (FT-IR) experiments of the catalysts were performed using a Bruker Vector 22 spectrometer equipped with a DTGS detector and a KBr beam splitter.

The TPR profiles were conducted with a homemade apparatus. During the experiments, each sample (20 mg) was outgassed under flowing Ar at 473 K for 1 h and then cooled to ambient temperature. The TPR profiles were obtained with 5 vol.% H₂/Ar flow (40 mL/min). The temperature was increased from 303 to 773 K at a rate of 10 K/min. The H₂ consumption was monitored using a TCD detector. The Cu dispersion was determined by dissociative N₂O adsorption- H₂-TPR reverse titration. The N₂O chemisorption process consists of three sequential steps:

 $CuO + H_2 \rightarrow Cu + H_2O (1)$ (hydrogen consumption = A₁) 2Cu + N₂O → Cu₂O + N₂ (2)

 $Cu_2O + H_2 \rightarrow 2Cu + H_2O(3)$ (hydrogen consumption = A₂)

Step 1 represents the reduction of CuO in the catalysts. In this step, a flow of 5 vol.% H₂/Ar (40 mL/min) was used as the reducing agent, and the temperature was risen from 298 to 773 K with a heating rate of 10 K/min. Step 2 represents the oxidation of surface Cu to Cu_2O by N_2O , which is a well-known method to evaluate the dispersion of Cu based catalysts.^{28,29} This step was conducted after the reduced catalyst was cooled to 333 K in Ar (30 mL/min) and purged with pure Ar flow for 30 min. After then, pure N₂O (30 mL/min) is introduced to the catalyst at 333 K for 0.5 h. Subsequently, the catalyst is purged with Ar (30 mL/min) for 0.5 h to remove the residual N₂O. Step 3 represents the reduction of surface Cu_2O species. In this step, a flow of 5 vol.% H_2/Ar (40 mL/min) is also used as the reducing agent, and the temperature was risen from room temperature to 773 K with a heating rate of 10 K/min. The dispersion (D) of Cu was calculated as the following equation, which has extensively been used in literatures elsewhere. $D = 100\% \times 2A_2/A_1$

The specific area of metallic copper was calculated from the amount of H₂ consumption with 1.46×10^{19} copper atoms per m².³⁰

The activity test was conducted on a continuous flow unit equipped with a stainless-steel fixed-bed tubular reactor. The catalyst bed had an inner diameter of 10 mm with a height of approximately 40 mm. Both sides of the catalyst bed were packed with guartz powders (20-40 meshes). Typically, the sample was loaded into a stainless steel tubular reactor with the thermocouple inserted into the catalyst bed for better control of the temperature. The catalyst was activated in a 5 vol.% H₂/Ar atmosphere at 573 K for 4 h at a temperature ramping rate of 2 K/min from 303 to 573 K. 0.8g of catalyst and 10 wt.% DMC (purity 99.0%) in THF were used in this probe reaction make it convenient for investigation the activities of different samples. After cooling to the reaction temperature, 10 wt.% DMC and H₂ were fed into the reactor at a H₂/DMC molar ratio of 260 and a system pressure of 2.5 MPa. The reaction temperature was first set at 503 K and the roomtemperature liquid hour space velocity (LHSV) of reactant was set at corresponding value for MeOH production. The methanol content in liquid products was analyzed using 1-butanol as internal standard. The gas products collected in the condenser were analyzed offline by SHIMADZU GC-2010 Plus gas chromatography using a flame ionization detector and the tail gas was analyzed online using a flame ionization detector (FID) with a six-way valve as gas sampler.

3. Results and Discussion

3.1 Characterization of catalysts

Fig. S1⁺ showed the wide-angle XRD patterns of the supported Cu catalysts. Evident diffraction peaks of CuO at 35.5° and 38.7° (PDF#45-0937) were observed and the peaks intensify with the increase in copper content. After reduction (Fig. 1), peaks from copper oxides disappeared along with the appearance of the peaks from metallic copper. A strong diffraction peak at 43.3° characteristic of *fcc* Cu (111) (JCPDS04-0836) could be observed. In addition, a diffraction peak at 37.0° (JCPDS34-1354) attributed to Cu₂O was also observed in the reduced catalyst. These findings demonstrated that the metallic copper and Cu₂O coexist in the working catalysts. Cu crystallite sizes calculated by the Scherrer formula were listed in Table 1. The average Cu particle size increased from approximately 10.7 to 15.5 nm with an increase in



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Fig. 1 XRD patterns of xCu/SiO_2 reduced at 573 K: A) $20Cu/SiO_2$, B) $30Cu/SiO_2$, C) $40Cu/SiO_2$, D) $50Cu/SiO_2$.

Catalyst	S _{BET} (m ² g ⁻¹)	V _p (cm ³ g ⁻¹)	d _p (nm)	^a d _{Cu} (nm)	^b D _{Cu} (%)	^b S _{Cu} ⁰ (m ² g ⁻¹)	^c Cu⁺/Cu ⁰	^b Cu⁺/Cu ⁰	^d TOF(h ⁻¹)
20Cu/SiO ₂	367.6	1.03	11.8	10.7	31.5	4.1	0.56	0.51	7.9
30Cu/SiO ₂	279.8	0.81	11.1	14.6	28.7	5.6	0.69	1.01	9.1
40Cu/SiO ₂	257.6	0.54	8.8	15.1	22.6	5.9	1.08	1.73	13.7
50Cu/SiO ₂	232.6	0.49	10.8	15.5	13.0	4.2	0.87	1.43	8.6

Table 1 Structural parameters and catalytic properties of the Cu/SiO₂ catalysts.

^a Cu average diameter of particle size calculated from the XRD. ^b Cu dispersion, surface area of Cu⁰ and Cu⁺/Cu⁰ determined by N₂O titration. ^cCalculated from XPS data of reduced samples. ^d TOF (grams DMC reacted per gram surface Cu per hour) at temperature of 433 K, at conversion below 30%.

Cu content from 10 to 50 wt.%. The coexistence of metallic copper and Cu₂O in the working catalyst inferred that the inadequate reduction of Cu²⁺ species in the calcined catalysts upon H₂reduction. For the well-established Cu/SiO₂ catalysts or other silica supported catalysts, the generation of the copper phyllosilicate species, which could stabilize the Cu⁺ species, was known to form during the preparation of Cu/SiO₂ catalyst by AE method. The incomplete reduced copper species were also found to secure the high catalytic efficiency in the hydrogenation of dimethyl oxalate (DMO), due to the fact that Cu⁺ could adsorb carbonyl group and inhibit the aggregation of copper species.^{31,32}

Table 1 summarizes the chemical compositions and textural properties of xCu/SiO₂ catalysts. The increase of copper content resulted in the gradual loss in both surface area and the Cu dispersion, indicating that the excess amount of copper species in the catalyst adversely impact on the structure of the supports. BET surface area and Cu dispersion with varying Cu amount significantly ranged from 367.6 to 232.6 $\rm m^2g^{-1}$ and 31.5 to 13.0%, respectively. Copper dispersion and Cu⁰ surface area were crucial factors determining the catalytic performance of copper-based catalysts.³³ The highest Cu⁰ surface area (5.9 m²g⁻¹) was obtained on 40Cu/SiO₂. N₂ adsorption-desorption results (Fig. S2 in ESI⁺) showed that all the catalysts displayed the hysteresis loop with type IV, confirming the presence of the mesoporous structures in the catalysts. The elevated Cu content resulted in a decrease of pore volume, as well as BET surface area. The corresponding pore size distributions are shown in Fig. S2⁺. The average pore size of 20Cu/SiO₂ catalyst derived from the desorption branch was at 11.8 nm. With the increase of copper content, the average pore size decreased to 8.8 nm for the 40Cu/SiO₂ catalyst, while it can be seen from the pore size distribution that the presence of more smaller pores in this catalyst probably due to the porosity provided by the laminar structure of copper phyllosilicate. With the copper loading increased to 50 wt.%, agglomeration copper particles filled up some smaller pores and covered the surface of the support, which therefore had relatively larger average pore size.³⁴

H₂-temperature-progammed reduction (H₂-TPR) was performed to further investigate the reducibility and structural evolutions of calcined samples (Fig. 2). The calculations of hydrogen consumption added in Table S1⁺. It can be observed that the uptake of H₂ increased along with the increasing in copper content. The reduction peak covered a range from approximately 460 to 560 K, which could be attributed to the reduction of CuO species. Only one single reduction peak at about 530 K could be observed in the20Cu/SiO₂ catalyst, indicating that the copper species are in well-dispersed state. A shoulder peak at higher temperature appeared when the copper content was higher than 30 wt.%. The high temperature reduction peak was ascribed to the reduction of the bulk CuO, and the low temperature one could be assigned to the reduction of small isolated highly dispersed CuO species on the surface.35-37 With an increase in copper mass ratio, the amount of highly dispersed CuO species decreased gradually, resulting in the relatively large Cu particle. The results were in good accordance with the observations made by XRD and N₂O measurement.



Fig. 2 H_2 -TPR of calcined samples: A) 20Cu/SiO₂, B) 30Cu/SiO₂, C) 40Cu/SiO₂, D) 50Cu/SiO₂.

Table	2 Cata	lytic acti	vities of	various	catalyst
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Entry	Catalyst	DMC conv. (%)	MeOH sel. (%)	STY _{MeOH} (h ⁻¹)	Gas products CO _x (%)	Gas products CH ₄ (%)		
1	20Cu/SiO ₂	100	60.4	0.43	33.0	1.4		
2	30Cu/SiO ₂	100	73.1	0.52	23.1	1.1		
3	40Cu/SiO ₂	100	80.0	0.57	16.7	0.9		

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4	50Cu/SiO ₂	100	71.5	0.54	21.8	1.7
5	40Cu/ZrO ₂	100	13.5	0.10	73.5	1.9
6	40Cu/TiO ₂	100	25.8	0.18	60.3	0.1
7	40Cu/CeO ₂	100	72.1	0.51	25.4	0.4
8	CuZnAl(1/4/5)	100	64.7	0.46	27.6	1.2

Reaction Conditions: liquid hour space velocity (LHSV of DMC) ~0.2 h⁻¹, H₂/DMC ~ 260 (mol/mol), 503 K, 2.5 MPa. CO_x means that CO and CO₂. STY represents the space time yield of MeOH for the catalysts, grams of product per gram of catalyst per hour ($g \cdot g^{-1}_{Catal} \cdot h^{-1}$).



Fig. 3 Cu LMM XAES with different catalysts reduced at 573 K: A)20Cu/SiO₂, B) $30Cu/SiO_2$, C) $40Cu/SiO_2$, D) $50Cu/SiO_2$.

Fourier-transform IR (FTIR) spectroscopy is usually adopted to discriminate the species from copper hydroxide, copper nitrate hydroxide, and copper hydrosilicate according to the structural OH groups.^{38,39} As shown in Fig. S3⁺, the band near 1640 cm⁻¹ appeared corresponding to the bending mode of OH groups of adsorbed water.⁴⁰ The appearance of the δ_{OH} vibration at 668 cm⁻¹ and the v_{SiO} shoulder peak at 1039 cm⁻¹ illustrated that the structure of copper phyllosilicate exists in the samples.

The XPS spectra of the samples as well as the X-ray induced Auger spectra (XAES) of the reduced Cu/SiO_2 catalysts were displayed in Fig. S4⁺ and Fig. 3. The intense and broad photoelectron peak at above 933.4 eV (Cu $2p_{3/2}$) along with the presence of the characteristic shake-up satellite peaks suggested that the copper oxidation state was +2 in all the calcined samples (Fig. S4⁺). In the case of the reduced samples (Fig. S4⁺), the BE

values of Cu $2p_{3/2}$ core levels were located in the range of 932.4-932.7 eV and the absence of Cu 2p satellite peak strongly demonstrated that all Cu²⁺ species had been reduced to a low valence state of +1 or 0 after the reduction. The Cu⁺ species was mainly formed upon the reduction of the copper phyllosilicate under the experimental conditions (reduced at 573 K), since the further reduction of Cu^{\dagger} to Cu^{0} required a temperature higher than 873 K³⁸. The result was consistent with those from FT-IR and XRD. Because the BE values of Cu^{\dagger} and Cu^{0} were almost identical, the distinction between these two species present on the catalyst surface was feasible only through the examination of XAES spectra. Two overlapping Cu LMM Auger kinetic energy peaks centered at about 916.5 and 913.6 eV were observed in the reduced catalyst (Fig. 3). Deconvolution of the original Cu LMM peaks was thus carried out and the Cu⁺/Cu⁰ ratios extracted from the deconvolution were listed in Table 1. As shown in Table 1, the Cu⁺/Cu⁰ ratio derived by fitting the Cu LMM peak first rose and then decreased with the increment of copper loading, and the highest Cu^{+}/Cu^{0} (1.08) was obtained on 40Cu/SiO₂. This finding agreed well with N₂O titration.

The TEM images and copper particles sizes distributions of different Cu/SiO₂ catalysts were shown in Fig. 4. Light gray spherical silica particles are identified along with dark ones assignable to CuO particles. The increased Cu particle sizes and decreased dispersion of copper species with the increase of the copper content can be directly observed in Fig. 4, which is consistent with the XRD and N₂O titration results.

3.2 Catalytic Activity

It is well known that Cu is active for methanol synthesis, serving in the dissociative chemisorption of hydrogen and the dissociative adsorption of C=O. Therefore, a detailed catalytic performance study of the Cu-based catalysts system was performed by changing

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Fig. 4 TEM images of the reduced catalyst: (A)20Cu/SiO₂, (C)30Cu/SiO₂, (E)40Cu/SiO₂, (G)50Cu/SiO₂ with Cu particle size distribution of (B)20Cu/SiO₂, (D)30Cu/SiO₂, (F)40Cu/SiO₂, (H)50Cu/SiO₂.

the amount of Cu. As shown in Table 2, at liquid hourly space velocity (LHSV) of 0.2 h⁻¹, all catalysts achieved 100% DMC conversion, which manifested the high activity of Cu in the hydrogenation of DMC. Different Cu/SiO₂ catalysts showed volcano-type catalytic behavior in terms of MeOH yield. Along with the Cu loading, the yield of MeOH and STY_{MeOH} increased slightly and was maximized on the 40Cu/SiO₂ catalyst (80.0%). Further increase in the Cu loading led to a decrease in MeOH yield. For all the Cu/SiO₂ catalysts, methanol was the main reaction product with CH₄, CO, and CO₂ as main by-products produced through methanation, decarbonylation and decomposition side-reactions. The stability of

40Cu/SiO₂ catalyst was tested, as shown in Fig. S5⁺, the Cu species was not sintered in a 100 h test, besides, the yield of methanol could achieve ~76% when neat DMC as reactant indicating super stability of catalyst and the potential for further industrial applications. The conversion of DMC and yield of MeOH could maintain at ~100% and >75% respectively when the LHSV based on DMC is lower than 1.4 h⁻¹ for the 40Cu/SiO₂ catalyst. Considering the calculation method on the yield of MeOH is complex if the DMC was not converted totally (<100%), the influence of LHSV was not discussed in detail. The Cu component dispersed on oxide supports including TiO₂, ZrO₂, CeO₂ shows large amount of gas products,

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which illustrated that the role of active copper dispersion and the acidic-basic property on the surface.²² Interestingly, when the CuZnAI catalyst was introduced into this reaction, the gas products mainly consist of CO demonstrating that the conventional CuZnAI catalyst showed higher catalytic activity in the hydrogenation of CO_2 derived from DMC hydrolysis, while the CO produced cannot be efficiently converted to methanol, which was in accordance with



Fig. 5 The yield of methanol as a function of reaction temperature on 40Cu/SiO₂ catalyst. Reaction Conditions: liquid hour space velocity (LHSV of DMC) ~0.2 h⁻¹, H₂/DMC ~260 (mol/mol), 2.5 MPa.

yield. Nevertheless, the side reactions were favourable at high temperature. Hence, we speculate that the hydrogenation of DMC over $40Cu/SiO_2$ catalyst is reversible and equilibrium conversion is reached at temperature of 503 K.

3.3 Gas-Phase hydrogenation of other carbonates

In order to investigate the catalytic capacity of Cu/SiO₂ catalysts by the AE method, other two linear CO₂ derivatives including diethyl carbonate and di-n-propyl carbonate were selected to undergo the gas-phase hydrogenation to generate methanol. The 40Cu/SiO₂ catalyst was also very effective in the hydrogenation of these carbonates (Fig. 6), exhibiting 76.5% and 82.0% methanol yield for the hydrogenation of DEC and DPC respectively. The selectivities of ethanol and propanol reach above 99% (Table S2⁺). The above finding indicates excellent catalytic performance of 40Cu/SiO₂ catalyst in the hydrogenation of a series of linear carbonates. It was known that higher melting point (such as diphenyl carbonate) would easily result in the reaction pipe blocking at incomplete conversion due to the low temperature of liquid products collector (270 K). Furthermore, for dibutyl carbonate, it is mainly synthesized from the ester exchange of DMC with butanol in industry not from the reaction of CO₂ and butanol. Considering the economical efficiency, reaction value and implementation possibility, we choose DMC, DEC and DPC as substrates for this reaction.

3.4 Discussion

High dispersion of copper species and strong metal-support interactions are vital for the high activity and super stability in hydrogenation of esters. In particular, copper phyllosilicate with a lamellar structure can enhance the dispersion and metal-support the report that $\rm Cu/ZnO/Al_2O_3$ catalyst did not work well in the hydrogenation of CO. 13

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Fig. 5 demonstrated the dependence of the yield of methanol on reaction temperature from 473 to 553 K. The methanol yield increased with reaction temperature and a maximum was reached at 503 K, when the temperature was lower than 473 K, the conversion could not reach 100%, which lowered the methanol



Fig. 6 Catalytic performance of 40 wt.%Cu/SiO₂ catalyst in the gas-phase hydrogenation of other carbonates. ^a liquid hour space velocity (LHSV of DEC) ~0.2 h⁻¹, H₂/DEC = 260 (mol/mol), 503 K, 2.5 MPa; ^b liquid hour space velocity (LHSV of DPC) ~0.1 h⁻¹, H₂/DPC ~ 260 (mol/mol), 503 K, 2.5 MPa.

interaction significantly. The central copper ions isolated and surrounded by silica can be hardly reduced completely and aggregated to sinter upon high-temperature calcination, which endows copper phyllosilicate with superior catalytic activity and thermal stability. Copper phyllosilicate is known to form during the preparation of Cu/SiO₂ catalyst by the AE method with selective adsorption of Cu(NH₃)₄²⁺ on SiO₂.³⁹ In the Cu/SiO₂ catalyst fabricated via the AE method, initially Cu²⁺ reacted with NH₃·H₂O to form a copper ammonia complex, while the colloid silica was dissolved to yield silicic acid (Si(OH)₄). The neutral Cu complex $Cu(OH)_2 \cdot (H_2O)_4$ generated gradually increased with decreasing pH resulted from the evaporation of ammonia. When the pH of the suspension progressively declined to 7, the evaporation process was terminated. Meanwhile, the heterocondensation reaction of silicic acid with the Cu complex $Cu(OH)_2 \cdot (H_2O)_4$ occurred and subsequently generated copper phyllosilicate monomer.41 The formation of copper phyllosilicate was also corroborated by FT-IR and XRD. Partial copper phyllosilicate transformed to high dispersed CuO during the calcination process, hence the copper ions were homogeneously distributed over the silica support to some extent, even at elevated metal loading. It was generally accepted that the high Cu surface area was beneficial for the catalytic performance of copper-based catalyst. A proper loading amount of copper could be dispersed on the support more uniformly, and larger copper surface area was achieved, which could induce the higher hydrogenation activity. The further increase of copper content would decrease the metal dispersion because the particle sintering dominated over the catalyst. The remaining copper phyllosilicate after calcination in samples was reduced to Cu₂O upon reduction at ~623 K. For the ion-exchanged Cu-O-Si species and copper phyllosilicate, the

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Fig. 7 $S_{Cu}/m^2 g^{-1}_{cat}$ and the mole ratio of Cu^+/Cu^0 as a function of Cu loading.

reduction is ceased at Cu^{+} under the present reduction condition since the progressive reduction of Cu₂O to Cu⁰ required a higher temperature than 873 K.⁴¹ Notably, the catalyst precursor appears also to be the key factor in determining the Cu species distribution and surface chemical state of the Cu/SiO₂ catalyst. The chemical states of surface properties were also changed with the variation of structural parameters. Except for the reducibility of CuO, the proportions of surface Cu⁺ sites of reduced catalyst were modulated. It has been reported that the efficiency of ester hydrogenation greatly relies on the synergistic cooperation of Cu and Cu^{+} present on the catalyst surface. Poels and Brands³¹ suggested that the Cu^0 species activated H₂ while the Cu^+ species adsorbed intermediate species in ester hydrogenation. Moreover, Cu⁺ might function as electrophilic or Lewis acid sites to polarize the C=O bond via the electron lone pair on oxygen, thus improving the reactivity of the ester group. Fridman et al. mentioned that the dissociative adsorption of cyclohexanol on Cu⁰ sites were accompanied by formation of cyclohexanol alcoholate and phenolate species, leading to the poor chemi-selectivity on this site, which did not occur on the Cu⁺ species.⁴² Hence, it can be deduced that the Cu⁺ species is more suitable for the stabilization of intermediate product. Presumably, excessive Cu⁰ species might induce the side reactions, such as decomposition of the reaction intermediates, most probably ethyl formate, which likely result in the increasing amount of gas products. Liu and coworkers²² discovered that the synergistic effect between Cu^0 and Cu^+ plays a critical role for attaining high yields of methanol and diols during the process of EC hydrogenation. The adsorption of ethyl acetate on Cu under reduction conditions has been hypothesized in previous report to proceed via the cleavage of the C-O bond adjacent to the carbonyl group,43 here we tentatively propose that the adsorption of DMC also proceeds in this manner. The yield of methanol rapidly increased with an increase in the Cu^{+}/Cu^{0} value,

Main reaction:



Fig. 8 Proposed hydrogenation mechanism over Cu/SiO₂ nanocatalys

which was probably due to that the Cu⁺ contributed to the adsorption of methoxy and acyl species of DMC during the hydrogenation reactions, while Cu⁰ facilitated the decomposition of H₂. S_{Cu}/m²g⁻¹_{cat} and the mole ratio of Cu⁺/Cu⁰ as a function of Cu loading were shown in Fig. 7. It was notable that the 40Cu/SiO₂ catalyst showed the highest Cu⁺/Cu⁰ ratio and the largest Cu⁰ surface area. Correspondingly, the methanol yield increased significantly owing to the dissociation of H₂ molecules on highly dispersed catalytically active Cu species and the stronger methoxy and acyl species adsorption on the Cu⁺ sites. Remarkably, the TOF increased steadily at low Cu⁺/Cu⁰, reached a maximum at Cu⁺/Cu⁰ of 1.08, and decreased with further increases in the ratio (Table 1). Therefore, the optimal TOF on the 40Cu/SiO₂ catalyst lies in the high surface Cu⁰ site density and the cooperative effect of Cu⁰ and Cu⁺.

On the basis of "The omega process", a possible process for the DMC hydrogenation over Cu/SiO₂ catalyst was proposed (Fig. 8). No gas product could be found when the reactant was methanol instead of DMC with 40Cu/SiO₂ as catalyst, indicating that the methanol could not decompose to CO₂ on the active Cu sites under the H₂ atmosphere. No gas product and methanol was observed for the hydrogenation of DMC without any catalysts, showing that the active Cu species are essential in the hydrolysis process of DMC at relatively high temperature. This transformation begins with the initial reduction of DMC to methyl formate (Step 1), followed by the further reduction of methyl formate to methanol (Step 2). Methanol from the methoxy group was produced in this process. It seems that these competing reaction paths exist in the hydrogenation of DMC. CO₂ could be produced in the analogous "Omega process", in which MeOH is reacted with CO₂ to first afford DMC, followed by catalytic hydrolysis of the DMC with H₂O in the system which comes from solvent and environment to selectively produce MeOH.¹⁷ CO is a problematic by-product in heterogeneously catalyzed hydrogenation of methyl formate.^{16,44}

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 46 Inevitably, the co-existence of Cu⁰ and Cu⁺ can promote the hydrogenation of CO₂ to CO, methanol and small amount of CH₄. Wang's work $^{\rm 47}$ demonstrated the conversion of CO $_{\rm 2}$ rapidly increased with an increase in the Cu⁺/(Cu⁰+Cu⁺) value and reached the maximum when $Cu^{+}/(Cu^{0} + Cu^{+})$ is 1.00, which showed that the Cu⁺ species was the active component in the Cu/SiO₂-AE nanocatalyst for activation and conversion of CO₂. Moderate higher reaction temperature is conducive to the methanol production from direct hydrogenation of DMC and indirect hydrogenation of CO2. The side reactions would be promoted which resulted in more gas products if the reaction temperature was too high. However, methanol produced from CO2 and DMC was inhibited at lower temperature. Both of these factors will result in the decline of methanol yield. Hence, a proper reaction temperature is essential in the gas-solid phase hydrogenation of DMC.

4. Conclusions

In summary, for the first time, a facile and highly efficient route for the indirect synthesis of methanol from CO₂ via gas-solid heterogeneous continuous hydrogenation of DMC, diethyl carbonate, and di-n-propyl carbonate was demonstrated using low-cost Cu/SiO₂ catalysts prepared by the facile AE method. The catalysts possessed remarkable stability and efficiency even though the neat DMC as reactant, which could be ascribed to the high copper species dispersion and the synergistic effect of Cu⁰ and Cu^{\dagger} . The Cu^{0} and Cu^{\dagger} site densities suggested that Cu^{\dagger} was the main active site and primarily responsible for the catalytic performance in the hydrogenation of DMC to methanol. Moreover, the yield of methanol was also affected by the reaction temperature. This indirect synthetic methodology using inexpensive Cu-based catalysts under mild conditions shows promising application potential to convert CO₂ to methanol in industry.

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Continuous heterogeneous hydrogenation of CO₂derived dimethyl carbonate to methanol over Cubased catalyst

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Copper content played significant roles in the catalytic performance of Cu/SiO_2 catalysts in dimethyl carbonate hydrogenation to methanol. Optimized hydrogenation activity was achieved over the 40Cu/SiO₂ sample.

