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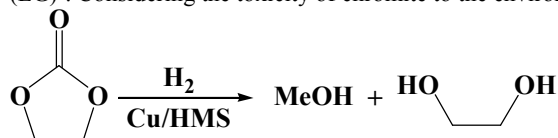
Continuous synthesis of methanol: heterogeneous hydrogenation of ethylene carbonate over Cu/HMS catalyst in fixed bed reactor system

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Xi Chen^a, Yuanyuan Cui^a, Chao Wen^a, Bin Wang^a and Wei-Lin Dai^{a,*}

Continuous fixed-bed catalytic hydrogenation of ethylene carbonate (EC) to methanol and ethylene glycol (EG), an emerging synthetic process of methanol via indirect conversion of CO₂, was successfully performed over Cu/HMS catalysts prepared by ammonia evaporation (AE) method. The catalysts possessed superb performance with conversion of 100% and selectivity to methanol of 74%.

The recycling of carbon dioxide as a primary source for the creation of organic matter and basic feedstock has gained considerable attention recently from the viewpoint of sustainable energy production and greenhouse gas reduction¹. Particularly, catalytic hydrogenation of CO₂ to methanol, a widely used chemical feedstock and one of the significant liquid fuels that can be supplied to fuel cells, is now considered as a key process in devising a methanol economy based on a closed carbon cycle². Although the heterogeneous catalytic system for the direct hydrogenation of CO₂ to methanol has been investigated in depth, the catalysts with high activity and great stability have to be performed under relatively harsh reaction conditions (250°C, 5-36 MPa) by reason of the high activation energy barriers for the cleavage of the C=O bonds of CO₂³, which hampers its large-scale industrial application. Ding and coworkers recently exploited an alternative route for the synthesis of methanol from CO₂ through indirect hydrogenation process by using ethylene carbonate (EC) as the starting material over a homogeneous pincer-type Ru^{II} complex catalyst under relatively mild conditions (140°C, 5 MPa) with excellent activity⁴. However, the applications of homogeneous Ru-based catalysts are limited due to the difficulties in the catalyst-product separation. Indirect heterogeneous hydrogenation of CO₂ to methanol under non-continuous reaction conditions using a copper chromite catalyst has been firstly reported by Li with high selectivities towards methanol and ethylene glycol (EG)⁵. Considering the toxicity of chromite to the environment and



Scheme 1 Hydrogenation of EC to MeOH over Cu/HMS catalyst.

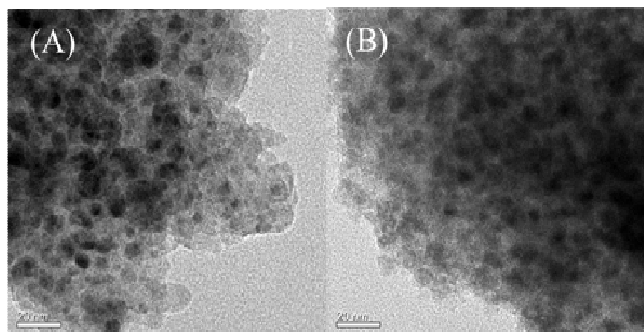
the relatively mediocre productivity of liquid-phase batch hydrogenation process, it is necessary to develop an industrial preferred heterogeneous hydrogenation catalysis system under gas-solid phase reaction conditions. Lately, Cu/SiO₂ prepared by a precipitation-gel method as catalyst in hydrogenation of EC to methanol has been reported by Liu and the catalyst possessed remarkable activity and stability in both batch and fixed-bed continuous flow reactors⁶. However, compared with the elaborate research in batch reaction, there were no detailed discussions in fixed-bed section. Thus, a more systematic investigation is necessary for heterogeneous hydrogenation of EC to methanol in fixed-bed reactor system. Cu/HMS catalyst has been intensively investigated due to the superb performance in the catalytic hydrogenation of esters⁷. Herein, for the first time, we report the gas-phase fixed-bed heterogeneous hydrogenation of EC to methanol and EG systematically. High yields of MeOH (74%) and EG (>99%) have been achieved along with complete conversion of EC (>99%) over 50Cu/HMS catalyst in the fixed-bed reactor.

The textural properties and catalytic performance of Cu nanoparticles supported on different oxide were shown in Table 1. Prior to this, we examined the catalytic properties of Cu/TiO₂, Cu/ZrO₂, Cu/SiO₂, Ni/HMS and Co/HMS catalysts. All these catalysts possess lower selectivity toward methanol compared with Cu/HMS (Table S1, ESI). Thus, Cu/HMS catalysts were chosen for further study in the hydrogenation of EC. To get better understanding of the catalytic reactivity, the catalytic properties were investigated by modulating the copper loading of Cu/HMS samples in the gas-phase hydrogenation of EC. The reactions were conducted at 453 K under 3 MPa of H₂ pressure on a fixed-bed tubular reactor. The main products formed in the hydrogenation process of EC were methanol, ethylene glycol and the gas consisting of CO₂ and CO which demonstrated the existence of side-reactions under the hydrogenation conditions. As shown in Table 1, the 50Cu/HMS catalyst exhibited a superb catalytic selectivity to methanol (74%) compared with the other catalysts. Furthermore, the stability of the optimal 50Cu/HMS catalyst for EC hydrogenation to methanol was measured over a 100-h period shown in Fig. S1 (ESI). It can be found that the catalyst was quite stable at 453 K, with constant conversion of EC (100%) and selectivity to methanol (~74%). The TEM images (Fig. 1) of the reduced and used 50Cu/HMS catalysts clearly revealed that the Cu species was not sintered during the 100-

Table 1 Physicochemical properties and catalytic performance^a

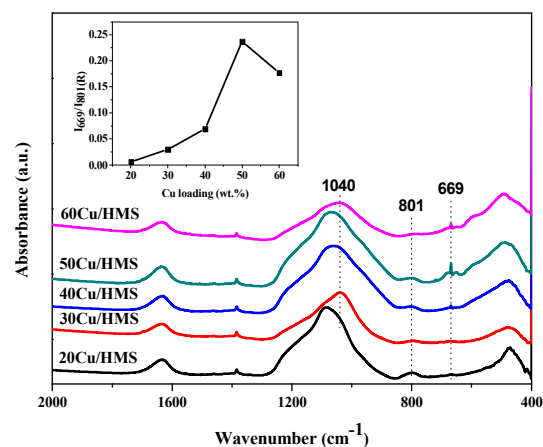
Entry	Catalyst	M loading (%) ^b	Conversion (%)	Yields (%)		Cu dispersion (%) ^c	Scu ⁰ (m ² g ⁻¹) ^d	d _M (nm) ^e	S _{BET} (m ² g ⁻¹)	d _{Pore} (nm)	V _{pore} (cm ³ g ⁻¹)
				MeOH	EG						
1	20Cu/HMS	19.0	97	52.7	>96	32.3	41.6	8.8	417	5.5	0.57
2	30Cu/HMS	27.7	100	56.5	>99	30.1	56.3	10.4	368	4.9	0.45
3	40Cu/HMS	34.3	100	66.3	>99	29.7	69.0	12.8	255	5.6	0.35
4	50Cu/HMS	44.6	100	74.0	>99	25.1	75.8	14.0	227	5.8	0.32
5	60Cu/HMS	53.7	100	68.8	>99	19.1	69.5	15.5	220	6.5	0.36

^a Reaction conditions: liquid hour space velocity (LHSV) = 0.1 h⁻¹, H₂/EC = 257 (mol/mol), 453 K, 3 MPa. ^b Determined by ICP-AES analysis. ^c Cu dispersion and surface area of Cu⁰ were determined by N₂O titration. ^d Cu crystallite size calculated by the Scherrer formula.

**Fig. 1** TEM image of the (A) reduced and (B) used 50Cu/HMS catalysts.

h activity test.

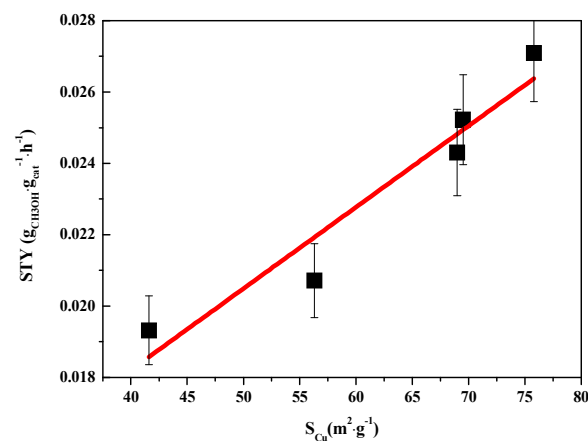
FT-IR spectra were obtained to discriminate the filamentous compounds of phyllosilicates in the catalysts⁸. As shown in Fig. 2, copper phyllosilicate were identified by the appearance of the frequencies of the δ_{OH} bands at 669 cm⁻¹ and the ν_{SiO} shoulder peak at 1040 cm⁻¹ in calcined Cu/HMS samples^{8,9}. Considering the difference in the content of HMS among these catalysts, the integrated intensity of the ν_{SiO} symmetric stretching band of SiO₂ at 801 cm⁻¹ should be revised via dividing the intensity at 801 cm⁻¹ by the corresponding HMS content for calculating the relative amount of copper phyllosilicate accurately. Thus, the relative amount of copper phyllosilicate in these samples was calculated by considering the integrated intensity of the δ_{OH} band at 669 cm⁻¹ normalized to the revised integrated intensity of the ν_{SiO} symmetric stretching band of SiO₂ at 801 cm⁻¹ by terming as $I_{669}/I_{801(R)}$ ^{8,11}. It is necessary to note

**Fig. 2** FT-IR spectra of the calcined Cu/HMS catalysts.

that the $I_{669}/I_{801(R)}$ ratio only provides a qualitative estimation of the amount of copper phyllosilicate, because the extinction coefficients of the corresponding IR bands are unknown. It was clearly found that the values of $I_{669}/I_{801(R)}$ ratios among Cu/HMS samples achieved the highest at 50wt% copper loading, which cues abundant copper phyllosilicate in 50Cu/HMS catalysts after calcination.

After reduction, the Cu⁰ and Cu⁺ coexisted in all the catalysts, as confirmed by diffraction peaks in the XRD patterns (Fig. S3, ESI). A series of diffraction peaks at 43.3, 50.4 and 74.1° are attributed to Cu⁰ (JCPDS 04-0836), while the diffraction peaks at 35.8° are ascribable to Cu₂O (111) plane (JCPDS 05-0667). The average diameters of metallic copper particles calculated by Scherrer equation are listed in Table 1. The particle size grew with the increasing copper loading. This finding could be further proved by TPR profile (Fig. S4, ESI). Besides the main reduction peak at 527 K, a shoulder peak at 545 K, assigned to the reduction of large CuO particles to metallic Cu^{0,11}, appeared when the copper loading was above 30wt.% and achieved the highest at 60wt.%. From the deconvolution results of Cu LMM XAES listed in Table S3 (ESI), the 50Cu/HMS catalyst has the highest X_{Cu⁺} ratio (X_{Cu⁺} = Cu⁺/(Cu⁺+Cu⁰)), corresponding well to the largest amount of copper phyllosilicate in 50Cu/HMS catalyst. It is noteworthy that the Cu⁺ species are formed on the reduction of copper phyllosilicate under the present reduction temperature (573 K) in this work due to the fact that further reduction of Cu⁺ to Cu⁰ needs a temperature above 873 K^{9,11,12}, which meant high Cu⁺/(Cu⁰+Cu⁺) intensity ratio derived from large amount of copper phyllosilicate in the calcined 50Cu/HMS sample prepared by AE method.

Thus, we speculate that the synergetic effect between Cu⁰ and Cu⁺ can greatly influence the catalytic activity of Cu/HMS catalysts in

**Fig. 3** STY of MeOH plotted against copper metal surface area for catalysts with different copper loadings.

the hydrogenation of EC to MeOH. To gain further insight, space-time yield (STY) of MeOH as a function of the effect of S_{Cu^0} was examined and illustrated in Fig. 3. The variation of S_{Cu^0} showed an excellent correlation with the corresponding STY of MeOH, indicating that the Cu^0 surface area contributes importantly to the catalytic performance of Cu/HMS in the hydrogenation of EC to MeOH. On the other hand, the yield of MeOH was also intimately related with the ratio of $Cu^{+}/(Cu^0+Cu^{+})$ from the results shown in Fig. S6 (ESI), implying that Cu^{+} also played an indispensable role in the hydrogenation of EC. A two-site mechanism was proposed that the Cu^0 species activates H_2 and the Cu^{+} species adsorbs the carbonyl group⁹. On the other hand, it has been suggested that in methyl acetate hydrogenation, Cu^{+} acts as the stabilizer of the methoxy and acyl species. In addition, Cu^{+} sites could function as electrophilic or Lewis acidic sites to polarize the C=O bond via the electron lone pair in oxygen, thus improving the reactivity of the ester group. Therefore, it is very likely that the optimal catalytic activity on the 50Cu/HMS catalyst lies in the cooperative effect of Cu^0 and Cu^{+} .

Conclusions

In summary, we have developed a facile and highly efficient catalytic hydrogenation of ethylene carbonate to methanol and ethylene glycol by employing low-cost Cu/HMS catalysts prepared by AE method. The remarkable catalytic activity and hydrogenation stability were observed over 50Cu/HMS catalyst, which could be attributed to the synergetic effect of Cu^0 and Cu^{+} . Moreover, this is the first report for the continuous gas-phase heterogeneous hydrogenation of EC to MeOH and EG with systematic investigations. This indirect synthetic approach, providing a promising strategy for the development of highly efficient conversion of carbon dioxide to generate methanol under mild reaction conditions, in particular, will create new opportunities for industrial applications and green chemistry.

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[†]Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, P. R. China. Fax: (+86-21) 55665572; Tel: (+86-21) 55664678; E-mail: wldai@fudan.edu.cn

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