



Structure evolution of mesoporous silica supported copper catalyst for dimethyl oxalate hydrogenation

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ABSTRACT

A modified ammonia evaporation method with an ordered mesoporous silica as the precursor of the support was applied to prepare the well dispersed copper-based catalysts. Appropriate amount of ammonia was used during the aging stage to prevent the destruction of the ordered mesoporous structure, which can ensure the homogeneous pre-distribution of the copper precursor ($[\text{Cu}(\text{NH}_3)_4]^{2+}$) in the mesopores. Then the formation of copper phyllosilicate or surface Cu–O–Si species can be prompted during the ammonia evaporation stage, resulting in large surface areas of both Cu^0 and Cu^+ species in the final catalysts. It was also revealed that the formation of copper phyllosilicate led to the destruction of mesoporous silica structure in the ammonia evaporation stage especially at the higher copper loading. The catalysts with various copper loading were systematically characterized and applied in the hydrogenation of dimethyl oxalate to ethylene glycol (EG). An excellent low-temperature catalytic performance and stability were achieved on 20Cu/OMS with EG selectivity of 98.2% at 453 K, due to the superior surface areas of both Cu^0 and Cu^+ , as well as the highest ratio of $\text{Cu}^+ / (\text{Cu}^0 + \text{Cu}^+)$.

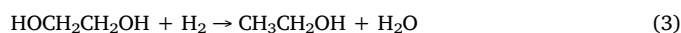
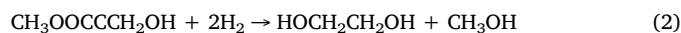
1. Introduction

Ethylene glycol (EG) is an important chemical product, which has been versatily applied in the manufacturing of polyester, lubricant and antifreeze [1,2]. Traditionally, EG is industrially produced by the direct hydration of ethylene oxide. Nevertheless, the shrinking of the fossil-fuel resource and the sustained increasing of demand of EG hinder its wide application. The indirect route for the production of EG from syngas via dimethyl oxalate (DMO) is one of the most attractive approach owing to its advantages in economy and environmental benign feature [3–6]. This route includes two main steps: the oxidative coupling of CO to DMO and then the hydrogenation of DMO to EG. Plentiful works have been involved in the homogeneous hydrogenation of oxalate upon ruthenium-based homogeneous catalysts [7,8]. However, the lower selectivity and the difficulties in the products separation limited its practical applications.

Due to the excellent activity in the hydrogenation of C=O group and lower ability to dissociative adsorption of the C–C bonds, copper-based catalysts have been applied in the hydrogenation of DMO [9,10]. Although CuCr catalysts show reasonable performance [11], the toxicity of the chromium restricts its application. Accordingly, increasing research focused on Cr-free Cu-based catalysts with various

supports, such as SiO_2 , Al_2O_3 , ZnO, and La_2O_3 [12,13]. Strong acid sites of the support would lead to the intramolecular dehydration of EG to ethanol, and strong basic sites would promote the formation of 1,2-butanediol (1,2-BDO) by Guerbet reaction between EG or DMO and ethanol [14,15]. Up to now, the Cu/ SiO_2 catalysts showed the superior performances due to the neutral properties of SiO_2 and the suitable interaction between the copper species and silica. Various method, including impregnation [16], sol-gel [17], deposition precipitation [18], ion-exchange [19] and ammonia evaporation (AE) method [20] have been applied to prepare copper-based catalysts for the hydrogenation of DMO. Among these preparation methods, the AE method was found to be an efficient method and the as-prepared catalyst showed higher activity in the hydrogenation reactions.

It is well known that the hydrogenation of DMO involved three main reactions: first the hydrogenation of DMO to methyl glycolate (MG), then the further hydrogenation of MG to EG, and the deep hydrogenation of EG to ethanol (Eqs. (1)–(3)).



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Table 1
Textural parameters of xCu/OMS catalysts and support.

Catalyst	Cu loading ^a (%)	S_{BET}^b (m ² /g)	V_p^b (cm ³ /g)	D_p^b (nm)	$S_{\text{Cu}^0}^c$ (m ² /g)	Cu dispersion ^c (%)	Crystallite size ^d (nm)
OMS	–	1019	1.10	2.7	–	–	–
10Cu/OMS	10.7	394	0.51	6.0	17.8	27.6	2.08 ± 0.29
15Cu/OMS	15.8	426	0.85	6.2	20.8	22.5	2.12 ± 0.25
20Cu/OMS	20.5	518	1.06	6.9	36.9	21.9	2.33 ± 0.30
25Cu/OMS	25.2	527	1.07	7.0	34.9	18.6	2.74 ± 0.22
30Cu/OMS	29.3	574	1.26	8.4	32.6	16.3	3.16 ± 0.23

^a Determined by ICP-AES analysis.

^b Determined by N₂ isotherm adsorption.

^c Determined by the N₂O titration method.

^d Determined by the TEM images (counting more than 80 particles).

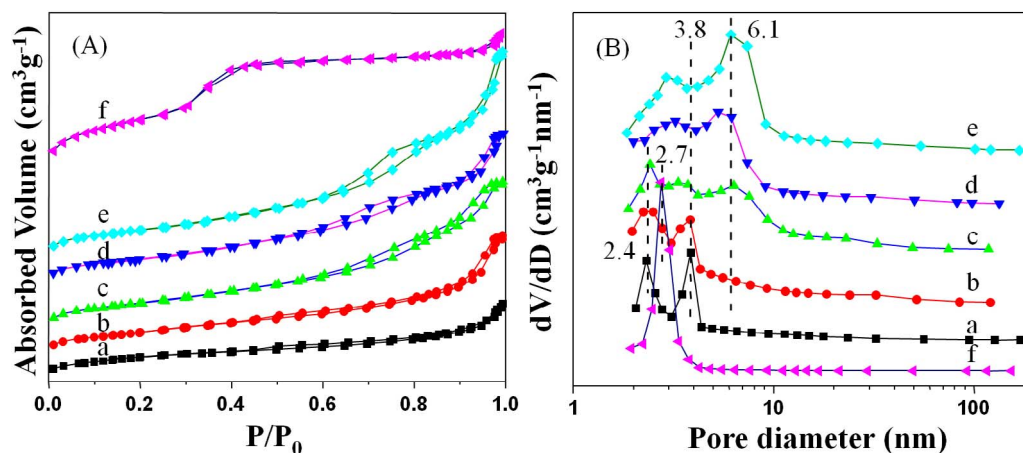


Fig. 1. (A) N₂ adsorption–desorption isotherms, (B) pore-size distribution curves. (a) 10Cu/OMS, (b) 15Cu/OMS, (c) 20Cu/OMS, (d) 25Cu/OMS, (e) 30Cu/OMS, (f) OMS (signal of f in Fig. 1B was attenuated to 1/5).

Raising temperature benefits the further hydrogenation of MG to EG, while the copper species would irreversibly deactivate due to the particle agglomeration under high temperature. Moreover, the Guerbet reaction can occur easily at high temperature with the formation of 1,2-BDO byproduct, which is difficult to be separated from EG. As reported in the earlier literatures, temperature around 473 K is favored for the hydrogenation of DMO to EG [5,16,19]. The preparation of catalyst with perfect hydrogenation performance at lower temperature is still a challenge.

Mesoporous materials have drawn much attention in many fields of chemistry since the successful synthesis of the M41S materials [21]. The ordered mesoporous materials are used as the catalyst support, due to its high specific surface area and pore volume, regular structure, uniform pore size distribution, and excellent thermal stability [22]. Immobilization of copper species into ordered mesoporous materials would improve copper dispersion and promote the catalytic performance in DMO hydrogenation. Yin et al. [16] reported HMS as support could promote the uniform dispersion of copper species. Guo et al. [18] reported Cu/SBA-15 catalyst with ultra-high copper loading had high dispersion and small nanoparticle size. Ma et al. [20] identified that copper could be well incorporated into MCM-41 through the AE method and Cu/MCM-41 showed high dispersion and excellent catalytic performance in DMO hydrogenation. However, although it is crucial important in designing more efficient catalyst, the structure effect of these mesoporous materials on the formation of the final catalyst has not yet revealed up to now.

In this work, series of ordered mesoporous silica (OMS) were synthesized and used for the preparation of Cu/OMS by a modified AE method under weaker alkaline environment. The structure evolution of the ordered mesoporous structure at different stage during the preparation process was systematically study. The structural affect on

the dispersion and formation of copper species were explored. The catalytic performance of the Cu/OMS was examined in the low-temperature hydrogenation of DMO to EG, and the structure–activity relationship was revealed.

2. Experimental

2.1. Catalyst preparation

Ordered mesoporous silica (OMS): tetraethyl orthosilicate (TEOS), cetyltrimethylammonium bromide (CTAB), water and ammonia aqueous were mixed at room temperature in a ratio of 1:0.2:160:1.5 to obtain a homogeneous mixture. Then the mixture was stirred continuously until turning into a white gel. The white gel was loaded into a PTFE-lined stainless steel autoclave and heated at 373 K for 48 h. After cooling to room-temperature, the products were separated by filtering, washed with deionized water, and dried in air at 373 K for 3 h. The resulting solid was calcined in air by heating at a rate of 2 K/min to 823 K and then maintained at this temperature for 6 h.

Cu/OMS: Cu/OMS catalysts were prepared by the AE method described as follows: a certain amount of Cu(NO₃)₂·3H₂O was dissolved in deionized water, and then 25 wt% ammonia aqueous was added and stirred for 0.5 h at 303 K, followed by the addition of ordered mesoporous silica powder and stirring for 4 h with the initial pH value of 10. This process was named aging stage. The suspension was heated from 303 to 353 K to remove ammonia. The temperature was kept at 353 K about 2 h until the pH value of the suspension decreased to 6–7. This process is called evaporation stage. The filtrate was washed with deionized water and then dried at 373 K overnight. Finally, the resulting solid was calcined at 673 K in air for 4 h. The catalysts were denoted as xCu/OMS. The x represents the weight percentage of copper

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