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An efficient and stable Cu/SiO_2 catalyst for the syntheses of ethylene glycol and methanol via chemoselective hydrogenation of ethylene carbonate

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ABSTRACT

The efficient synthesis of methanol and ethylene glycol via the chemoselective hydrogenation of ethylene carbonate (EC) is important for the sustainable utilization of CO_2 to produce commodity chemicals and fuels. In this work, a series of β-cyclodextrin-modified Cu/SiO_2 catalysts were prepared by ammonia evaporation method for the selective hydrogenation of EC to co-produce methanol and ethylene glycol. The structure and physicochemical properties of the catalysts were characterized in detail by N_2 physisorption, XRD, N_2O titration, H_2-TPR, TEM, and XPS/XAES. Compared with the unmodified $25Cu/SiO_2$ catalyst, the involvement of β-cyclodextrin in $5β\text{-}25Cu/SiO_2$ could remarkably increase the catalytic activity—excellent activity of 1178 mg_{EC} g_{cat}^{-1} h^{-1} with 98.8% ethylene glycol selectivity, and 71.6% methanol selectivity could be achieved at 453 K. The remarkably improved recyclability was primarily attributed to the remaining proportion of $Cu^+/(Cu^0+Cu^+)$. Furthermore, the DFT calculation results demonstrated that metallic Cu^0 dissociated adsorbed H_2, while Cu^+ activated the carbonyl group of EC and stabilized the intermediates. This study is a facile and efficient method to prepare highly dispersed Cu catalysts—this is also an effective and stable heterogeneous catalyst system for the sustainable synthesis of ethylene glycol and methanol via indirect chemical utilization of CO_2.

1. Introduction

Utilization of CO_2 as an important C1 building block for synthesizing high-value chemicals and liquid fuels has recently gained considerable global attention [1–3]. Various routes have been exploited for the conversion of CO_2 into valuable fuels and

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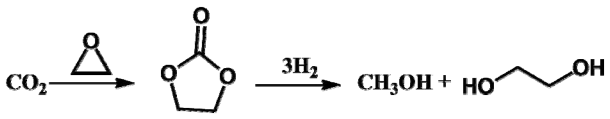
chemicals such as ethanol [4], carbamic ester [5], ethylene carbonate [6], dimethyl ether [7], methanol [8], *etc*. Significant efforts have been devoted to transform CO_2 with renewable hydrogen to methanol [9,10] because methanol is not only a key chemical feedstock for producing various valuable chemicals but is also an alternative transportable fuel [11]. Nevertheless, direct hydrogenation of CO_2 to methanol suffers from low reaction efficiency due to its low thermodynamic stability and the severe reaction conditions required to overcome the kinetic inertia of CO_2 [12].

Coupling of energetic compounds can overcome the thermodynamic and kinetic constraints and result in efficient utilization of CO_2. Thus, the efficient hydrogenation of CO_2 to chemicals via indirect pathways can be performed under relatively mild reaction conditions with satisfactory yields [13–15]. Alternatively, indirect hydrogenation of CO_2 via ethylene carbonate (EC) intermediate to co-produce methanol (MeOH) and ethylene glycol (EG) is a promising approach for environmentally friendly syntheses of sustainable chemical feedstocks and fuels (Scheme 1). EC is industrially available from CO_2 and ethylene oxide, and this process is well established. Therefore, more attention has been devoted to developing an effective catalyst for EC hydrogenation.

The hydrogenation of EC can be effectively catalyzed via Ru(II)-PNP complexes as a homogeneous catalyst [16]. Afterwards, Ru(II)-NHC complexes were also reported, and they showed efficient catalytic performance [17]. In terms of the easy catalyst recovery, increasing attention is given to effective heterogeneous catalyst. In recent years, various types of catalysts, e.g. $CuCr_2O_4$ [18], Cu–SiO_2-PG [19], Cu/HMS [20], Cu/SBA-15 [21], and Cu/SiO_2-AE [14], were reported to catalyze the hydrogenation of EC. The versatile Cu-based catalysts generally exhibited good catalytic activity due to the selective hydrogenation of C=O and C–O bonds without excessive side-reactions [18,22], e.g. the cleavage of C–C bond. Nevertheless, the catalytic performance of Cu-based catalyst still needs improvement because the active Cu particles are readily aggregated, which can lead to irreversible deactivation. In our previous reports [14,21], Cu/SBA-15 and Cu/SiO_2-AE showed relatively high catalytic activities. However, the catalytic activities of these catalysts tend to decline during recycling experiments; the catalyst stability needs to be further improved.

Many efforts have been devoted to improving the catalytic performance and stability of the copper catalyst. In general, the involvement of a second metal to copper catalyst—especially noble metals—is an alternative way to improve the catalytic properties of copper catalysts by forming bimetallic catalysts [23–25]. Nonetheless, the preparation method is relatively complicated, and the involvement of noble metals inevitably results in high costs. In previous reports [26–28], the coating of a highly branched organic polymer to active catalyst was used to fabricate metal catalysts, e.g. iron oxide, copper-based catalysts. The use of polysaccharides could control the particle sizes and could stabilize the active sites to some degree [27]. The development of a facile method for preparing low-cost catalysts with high catalytic activity and stability for the chemoselective hydrogenation of EC is highly desired.



Scheme 1. The syntheses of EG and methanol via hydrogenation of EC derived from CO_2.

A powerful and unique ligand is needed for coordination to transition metals. Examples include copper and β-cyclodextrin with cyclic oligosaccharides of D(+)-glucopyranosyl units linked by alpha-1,4-glycosidic bonds. The β-cyclodextrin is environmentally friendly, low-cost and has unique coordination ability. This makes it a good precursor for preparing modified copper catalysts. Here, a series of β-cyclodextrin-modified Cu/SiO_2 catalysts were prepared via the ammonia evaporation (AE) method. The as-prepared copper catalysts were employed in the hydrogenation of EC to co-produce methanol and EG. The textural and structural properties of the as-prepared catalysts were systematically characterized by N_2 physisorption, X-ray diffraction (XRD), temperature programmed reduction of H_2 (H_2-TPR), N_2O titration, high resolution transmission electron microscopy ((HR)TEM), and X-ray photoelectron spectroscopy/Auger electron spectroscopy (XPS/XAES). Moreover, the catalytic performance of the as-prepared catalysts and reusability were studied. In addition, density functional theory (DFT) calculation was performed to identify the unique roles of Cu species with different valence states on the catalytic performance. A plausible mechanism was proposed based on these results.

2. Experimental

2.1. Materials

$Cu(NO_3)_2{\cdot}3H_2O$ (>99%), β-cyclodextrin (>99%), and p-xylene (98.85%) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Ethylene carbonate (99%) was commercially available from Alfa Aesar. Ammonia aqueous solution (25 wt%) and tetrahydrofuran (THF, 99.8%) were purchased from Xilong Chemical Co., Ltd., China. Hydrogen (99.999%) was purchased from Beijing Haikeyuanchang Practical Gas Co., Ltd., China. Aqueous colloidal silica sol ($mSiO_2{\cdot}nH_2O$, 30 wt%) was obtained from Qingdao Haiyang Chemical Co., Ltd., China. Other reagents were of analytical grade and used as received.

2.2. Catalyst preparation

The *x*β-25Cu/SiO_2 catalysts (Cu loading and β-cyclodextrin loading (*x*) were based on the total weight of the catalyst) were prepared by a one-step AE method described as follows. Briefly, the required amounts of $Cu(NO_3)_2{\cdot}3H_2O$ and β-cyclodextrin were dissolved in 150 mL deionized water under stirring and ultrasonication (313 K) for 15 min. Subsequently, ammonia aqueous solution (25–28 wt%, 30 mL) was gradually added for 45 min. Then, the required amounts of aqueous colloidal silica sol were added into the suspension with vigorous stirring. The resulting suspension was continuously stirred for 4 h. Thereaf-