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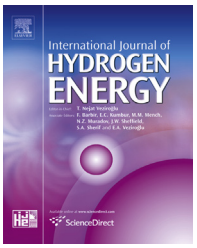

Selective hydrogenation of ethylene carbonate to methanol and ethylene glycol over Cu/SiO_2 catalysts prepared by ammonia evaporation method

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ABSTRACT

A series of Cu/SiO_2-AE catalysts with different copper loadings were prepared by ammonia evaporation method with silica sol as the silica source. The systematic catalyst characterization revealed that different proportions of Cu^0 and Cu^+ species co-existed in the Cu/SiO_2-AE catalysts, which derived from the reduction of CuO and copper phyllosilicate, respectively. The as-prepared catalysts were employed in the hydrogenation of ethylene carbonate (EC) to co-produce methanol (MeOH) and ethylene glycol (EG). Among the catalysts investigated, the $10\%Cu/SiO_2$-AE catalyst with a moderate copper loading exhibited better catalytic activity and product selectivities, which was mainly ascribed to the synergetic effect of Cu^0 and Cu^+ species and the suitable proportion of $Cu^+/(Cu^+ + Cu^0)$. It was proposed that the Cu^0 species promoted the dissociation of H_2, while Cu^+ species adsorbed on the carbonyl group of EC. Under the optimized conditions, EC conversion of 100%, MeOH selectivity of 70.8% and EG selectivity of 98.0% were obtained over the $10\%Cu/SiO_2$-AE catalyst. The catalyst reusability results showed that the agglomeration of Cu and Cu_2O particles was responsible for the gradually decreasing activity of $10\%Cu/SiO_2$-AE catalyst along with recycling runs.

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Introduction

Reduction of CO_2 with renewable hydrogen [1,2] to methanol has gained considerable attention and interests in the viewpoints of CO_2 utilization and "methanol economy" [3–8]. However, direct hydrogenation of CO_2 suffers from the harsh reaction conditions and low reaction efficiency [9–11]. Alternatively, several approaches for indirect hydrogenation of CO_2 to methanol, which could utilize readily available CO_2 derivatives such as ethylene carbonate, methyl formate, dimethyl carbonate, urea derivatives and methyl carbamate, have attracted extensive attention due to the merits of relatively mild reaction conditions and satisfactory yields with a suitable catalyst [12–19]. Among these approaches, indirect hydrogenation of CO_2 via ethylene carbonate intermediate has been regarded as a very attractive and promising approach to co-produce valuable methanol and ethylene glycol indirectly from CO_2, which was first put forward and realized by Ding et al. over a homogeneous pincer-type Ru^{II} complex catalyst [20]. Since ethylene carbonate can be largely and readily available from ethylene oxide and CO_2 [21], more work need to be concentrated on the development of effective catalysts especially recyclable heterogeneous catalysts for the hydrogenation of ethylene carbonate (EC) to co-produce methanol and ethylene glycol. In the previous studies, a few heterogeneous Cu-based catalysts such as $CuCr_2O_4$ [22], Cu-SiO_2-PG [23], Cu/HMS [24] and Cu/SBA-15 [25] were employed in EC hydrogenation to co-produce methanol and ethylene glycol, and showed superior catalytic performances. However, it is still highly desirable to develop more effective, selective and low-cost heterogeneous catalysts and give insight into the active species for EC hydrogenation.

Copper-based catalysts were considered to be feasible for selective ester hydrogenation due to their selective hydrogenation of C=O bonds and were relatively inactive in C–C bond hydrogenolysis [22–28]. For instance, Cu/SiO_2 catalysts stood out in hydrogenation of dimethyl oxalate to ethylene glycol [27] or ethanol [29]. Research on silica supported copper catalysts indicated that both high dispersion of copper species and strong metal-support interaction were very vital to high activity and stability in vapor-phase hydrogenation of ester to alcohols or glycol. In addition, because of the weak acidic and basic properties of SiO_2, Cu/SiO_2 catalysts had exhibited superior yields of desired products in hydrogenation of esters at mild conditions. In order to obtain desired performance of Cu/SiO_2 catalysts, it was necessary to disperse fine particles onto the SiO_2 support. Various approaches have been developed to prepare dispersed Cu nanoparticles, including impregnation [30,31], precipitation-deposition [32,33], sol–gel [34,35], precipitation-gel [23,36], ion exchange [37,38], ammonia evaporation [26–29,39], etc. Among these methods, ammonia evaporation method was widely used for preparing well-dispersed Cu/SiO_2 catalysts as well as facilitating the formation of both Cu^0 and Cu^+ species.

The silica supported copper catalyst prepared by ammonia evaporation (AE) method using silica sol as the silica source has been extensively investigated in the hydrogenation of esters [27,29,39], however, this catalyst has not been reported in the hydrogenation of ethylene carbonate so far. Besides, there were only a few silica supported copper catalysts such as mesoporous HMS supported Cu/HMS [24], mesoporous SBA-15 supported Cu/SBA-15 [25] and precipitation-gel derived Cu-SiO_2-PG [23] have been reported in the hydrogenation of ethylene carbonate. Thus, in this work, various Cu/SiO_2 catalysts with different copper loadings were prepared by ammonia evaporation method, which could conveniently and effectively disperse copper species on SiO_2 support and also enable the formation of different ratio of Cu^0 species and Cu^+ species. The as-prepared Cu/SiO_2-AE catalysts were employed in the hydrogenation of ethylene carbonate to co-produce methanol and ethylene glycol for the first time. The catalysts were systematically characterized by N_2 physisorption, ICP-AES, FT-IR, XRD, H_2-TPR, (HR)TEM, XPS and XAES. The catalytic performances of the as-prepared catalysts, effects of reaction conditions and catalyst reusability were studied. Moreover, the relationship between the catalytic activities of catalysts and the Cu^0 and Cu^+ species was also investigated to disclose the roles of different copper species.

Experimental

Materials

Ethylene carbonate (EC, 99% purity) was obtained from Alfa Aesar. Tetrahydrofuran (THF, 99.8% purity), *p*-xylene (98.85% purity) and $Cu(NO_3)_2\cdot 3H_2O$ (>99% purity) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Aqueous colloidal silica sol ($mSiO_2\cdot nH_2O$, 30 wt%) and silica (SiO_2) were obtained from Qingdao Haiyang Chemical Co., Ltd., China. Ammonia (25 wt%) was purchased from Xilong Chemical Co., Ltd., China. Hydrogen (99.999% purity) was supplied from Beijing Haikeyuanchang Practical Gas Co., Ltd., China. Other reagents were of analytical grade and used as received.

Catalyst preparation

Preparation of 2%–30%Cu/SiO_2-AE catalysts

The 2%–30%Cu/SiO_2-AE catalysts (Cu loading was based on the total weight of the catalyst) were prepared by the ammonia evaporation (AE) method described as follows. Desired amount of 25 wt% ammonia aqueous solution was first added into the desired $Cu(NO_3)_2\cdot 3H_2O$ aqueous solution for 10 min to form a copper ammonia complex solution. Subsequently, 66.7 g aqueous colloidal silica sol ($mSiO_2\cdot nH_2O$, 30 wt%) was dropped into the above copper ammonia complex solution at a rate of 2 mL min^{-1} by a peristaltic pump. After the dropping of aqueous colloidal silica sol was finished, the resulting suspension was continuously stirred for 4 h. The initial pH of the resulting suspension was 11–12. All the above operations were performed under vigorous stirring at room temperature. Then the suspension was transferred into an oil bath to evaporate ammonia and finally to deposit copper species on silica at 353 K. The evaporation process was terminated when the pH of the suspension decreased to 6–7. Then the suspension was filtered, washed with ethanol and deionized water, dried in a vacuum oven at 353 K overnight, calcined at 673 K in static air for 4 h, and finally reduced in 10

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