



Reaction temperature controlled selective hydrogenation of dimethyl oxalate to methyl glycolate and ethylene glycol over copper-hydroxyapatite catalysts



Chao Wen^a, Yuanyuan Cui^a, Xi Chen^a, Baoning Zong^b, Wei-Lin Dai^{a,*}

^a Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, PR China

^b State Key Laboratory of Catalytic Materials and Reaction Engineering, Research Institute of Petroleum Processing, China Petroleum & Chemical Corporation, Beijing 100083, PR China

ARTICLE INFO

Article history:

Received 26 May 2014

Received in revised form 8 July 2014

Accepted 10 July 2014

Available online 18 July 2014

Keywords:

Hydroxyapatite

Copper based catalysts

Dimethyl oxalate

Methyl glycolate

Ethylene glycol

ABSTRACT

Copper based hydroxyapatite (HAP) supported (Cu/HAP) catalysts are synthesized by a facile ammonia-assisted one-pot synthesis (AAOPS) method and carefully studied on the selective hydrogenation of dimethyl oxalate (DMO). The Cu/HAP catalysts exhibit different catalytic performance compared with the conventional Cu/SiO₂ ones. When the reaction temperatures are set at 483 K, the optimal Cu/HAP catalyst displays relatively high and stable catalytic performance with methyl glycolate (MG) as the main product. The yield to MG can reach 70% which is the highest value on the copper based catalysts till now. When the reaction temperature is risen to 513 K, the selectivity of the catalysts swifts to the ethylene glycol (EG), and the catalytic behavior is similar to the traditional Cu/SiO₂ catalysts. It was found that the copper phosphate species play important roles in stabilizing the copper particles and the Cu⁺ species. Also, the abundant surface hydroxy groups on the catalysts are responsible for the distinct catalytic performance of the Cu/HAP catalysts.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

As the increasing emerge of the energy crisis and environmental issue, searching for the catalytic methods for the rational and clean utilization of the coal resources and further synthesis of highly value-added chemicals are greatly needed to meet the challenging environmental needs and industrialization requirements, which consequently sparked a rapid global development of the C1 chemistry. Hydrogenation of dimethyl oxalate (DMO) to ethylene glycol (EG) is one of the great productive applications for the C1 chemistry which have been scaled up to industrial levels with a capacity of 10,000 tons per year in 2010 [1]. Furthermore, partial hydrogenation of DMO could obtain methyl glycolate (MG), the latter of which is an essential intermediate for the synthesis of pharmaceutical products, fine chemicals, and perfumes [2]. More encouragingly, ethanol (EtOH), as one of the versatile feed stock for the synthesis of various products and an additive or a potential substitute for gasoline, could also be produced by deep hydrogenation of DMO with a satisfying yield of 91% [3]. The tandem hydrogenation of

DMO could obtain three main products and the development of a proper and efficient catalyst to control the synthesis of the target products continues to be a huge challenge for both academia and industry. As the primary hydrogenation product, the synthesis of MG via DMO needs a moderate reaction condition and a catalyst with relatively weak hydrogenolysis property, and generally, silver based catalysts are usually adopted. For the product of EG and deep hydrogenation product of EtOH, copper based catalysts show excellent catalytic performance and now has been intensively investigated [4–7]. To the best of our knowledge, there is no copper based catalyst with bi-functional active sites that can obtain the high yields of MG and EG respectively with the only modulation of the reaction parameters. Once the reaction products of EG and MG could be selectively controlled by the modulation of the operational conditions such as H₂ pressure, temperature or mole ratio of H₂/DMO, it would be greatly economical and energy-efficient for the DMO hydrogenation process along with the market demands.

The well-established Cu/SiO₂ catalysts are extensively studied due to its high catalytic performance on the gas-phase hydrogenolysis of the DMO to EG and EtOH. Optimized Cu/SiO₂ catalysts now have obtained an inspiring achievements with the EG yield at 100% and EtOH yield at 91% [3,5]. However, the selectivity to MG on

* Corresponding author. Tel.: +86 5566 4678; fax: +86 5566 5572.
E-mail address: wldai@fudan.edu.cn (W.-L. Dai).

the copper based catalysts is extremely low because of the superb hydrogenolysis ability of the copper species and MG would be the main hydrogenation products only when the conversion of DMO is below 70% which also indicates that the catalysts are deactivated [4]. The synthesis of MG is generally based on the carboxylation of formaldehyde over concentrated sulphuric acid or boron trifluoride catalysts [8–10]. This process involves strong acid and high reaction pressure which requires expensive equipment, and also causes severe corrosion of the reactor. Hydrogenation of DMO to MG on the Ru based homogeneous catalysts was extensively studied in 1980s [11,12], and the yield of MG could achieve up to 97%. However, homogeneous noble metal catalysts are scarce, costly and difficult to be recycled thus makes the MG production gloomy. Recently, the flourishing developed coal to ethylene glycol (CTEG) program in China rekindles the research of the hydrogenation of DMO on the heterogeneous catalysts and the synthesis of MG via DMO has gained breakthroughs. Yin et al. have found that the silver based silica catalysts show high selectivity to MG at the temperature of 463 K and could prevent further reaction to EG or EtOH [2,13]. Zheng et al. developed a kind of Ag/SBA-15 catalyst with Ag crystallite size of ca. 3.9 nm. The Ag/SBA-15 catalyst showed superb selectivity to MG with a high TOF value [14]. The Au–Ag bimetallic catalyst supported on SBA-15 is also found to exhibit excellent activity for the selective hydrogenation of DMO to MG under low temperature [15]. Although the hydrogenation of DMO to MG could be obtained with a yield over 90%, the usage of gold or silver enormously increases the production cost and the high sensibility on the reaction environment for the noble metals also blocks the industrialization of the hydrogenation of DMO process. Furthermore, Ag based catalysts are greatly susceptible to the liquid hourly space velocity (LHSV), and these catalysts are active only if the reaction LHSV is below 0.6 h^{-1} . Silica supported Cu–Ag catalysts display better selectivity to MG with a yield at 60% under higher LHSV [16]. Furthermore, the silica support could be a fatal flaw in the DMO hydrogenation process because of the leaching of the silica under the gas phase reaction condition containing methanol [1]. Thus, the development of the non-noble metal and non-silica catalysts for the hydrogenation of DMO operating at high LHSV has increased tremendous interests in both academia and industry. Moreover, it is greatly significant and valuable for the achievement of the co-production of the MG and EG on only one catalyst in the same plant depending on the production requirement or the reaction condition.

In the present work, a novel kind of copper based HAP supported catalyst is systematically studied to investigate the relationship between the structure–function and the selective behavior of the catalysts. HAP is one of the calcium phosphate salts which are the mineral constituent of human hard tissues (bones, teeth, etc.) and are of importance in the biomedical field as a raw material for the preparation of artificial bone graft. It is also a promising material used industrially in sensors, fluorescence materials, chromatography, and environmental phosphorus recovery. As a catalyst, HAP has the unusual property of containing both acidic and basic sites in a single crystal lattice and exhibits superb catalytic performance in formaldehyde combustion [17], catalytic conversion of ethanol [18], and catalytic reduction of NO_x [19]. Furthermore, HAP can be served as a catalyst support thanks to its high specific areas and ion-exchange property [19,20]. The HAP carrier would also afford abundant hydroxyl groups and moderate acid property on the surface of the catalysts which would contribute to the hydrogenation of DMO to MG and EG [2]. The as-prepared Cu/HAP catalysts in the present work show higher selectivity to MG compared with other Cu based catalysts, moreover, the selectivity to EG could be modulated simply only by controlling the reaction temperatures.

2. Experimental

2.1. Catalyst preparation

All the reagents are purchased from Sinopharm Chemical Reagent Co., Ltd. without further purification, unless otherwise specified.

Copper based HAP catalysts are synthesized via a facile ammonia-assisted one-pot synthesis (AAOPS) method. Firstly, 7.56 g of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ is dissolved in 300 ml of deionized water and a certain amount of aqueous ammonia (25 wt.%) are added into the above solution to adjust the pH value to 11.0. Then, 0.1 M of $(\text{NH}_4)_2\text{HPO}_4$ aqueous solution is dripped slowly into the above suspension with the molar ratio of Ca/P to 1.67. The as-prepared suspension is then kept at 313 K for 24 h under stirring. Secondly, certain amount of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ is added into the above suspension, and aqueous ammonia (25 wt.%) solution is added again to maintain the pH value at 11.0. Afterwards, the as-obtained suspension is kept on stirring for 4 h, and then, the bath temperature is risen to 363 K and the mixture is kept on stirring until the pH value of the suspension reaches 6–7. Finally, the filter cake is filtrated and washed with deionized water for three times. The solid is dried at 373 K overnight, and then, calcinated from 573 to 973 K at a ramping rate of 2 K min^{-1} .

Pure HAP can be obtained following the same procedure as mentioned above without the addition of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and the calcination temperature is 773 K.

The added amount of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ are determined by the copper loading. In our study, Cu/HAP catalysts with copper loading from 5 to 30 wt.% are synthesized and calcinated at 773 K, the catalysts are labeled as xCu/HAP, where x stands for copper loading. Furthermore, the 20Cu/HAP catalysts at different calcination temperatures are further studied to confirm the structural evolution and the distinct catalytic sites on the catalysts. These catalysts are labeled as 20Cu/HAP-y, where y denotes the calcination temperatures (K).

All the catalysts are reduced at 573 K for 4 h under the 5% H_2/Ar (V/V) atmosphere prior to the catalytic test.

2.2. Catalyst characterization

Specific surface areas of the samples are measured by nitrogen adsorption–desorption method at 77 K (Micromeritics Tristar ASAP 3000) using Brunauer–Emmett–Teller (BET) method. The pore size distributions are obtained from the desorption isotherm branch of the nitrogen isotherms using Barrett–Joyner–Halenda (BJH) method.

The wide-angle XRD patterns are collected on a Bruker D8 Advance X-ray diffractometer using nickel-filtered Cu $\text{K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) with a scanning angle (2θ) range of $20\text{--}90^\circ$, a scanning speed of 2° min^{-1} , and a voltage and current of 40 kV and 40 mA, respectively. The full width at half maximum (FWHM) of CuO (0 1 1) and Cu (1 1 1) reflection is measured for calculating crystallite sizes using the Scherrer equation.

The copper loadings are determined by the inductively coupled plasma (ICP) method using a Thermo Electron IRIS Intrepid II XSP spectrometer.

TEM micrographs are obtained on a JOEL JEM 2010 transmission electron microscope. Samples for electron microscopy observation are prepared by grinding and subsequent dispersing the powder in ethanol and applying a drop of very dilute suspension on carbon-coated grids.

TPR profiles are obtained on a Tianjin XQ TP5080 auto-adsorption apparatus. 25 mg of the catalyst is outgassed at 473 K

Download English Version:

<https://daneshyari.com/en/article/45671>

Download Persian Version:

<https://daneshyari.com/article/45671>

[Daneshyari.com](https://daneshyari.com)