INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–10

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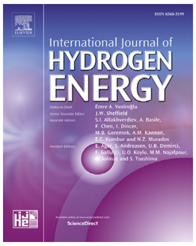

Highly selective CuO/$\gamma-Al_2O_3$ catalyst promoted with hematite for efficient methanol dehydration to dimethyl ether

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ARTICLE INFO

Article history:
Received 16 December 2017
Received in revised form
6 February 2018
Accepted 9 February 2018
Available online xxx

Keywords:
CuO-$Fe_2O_3/\gamma-Al_2O_3$ catalyst
Dimethyl ether production
Methanol dehydration
Hematite
Tenorite

ABSTRACT

A recent alternative for replacing traditional hydrocarbons like gasoline, diesel, and natural gas, is the use of dimethyl ether (DME), which is more environmentally friendly. One of the ongoing challenges is to catalyze methanol dehydration for selectively producing the DME ($2CH_3OH \rightarrow CH_3OCH_3 + H_2O$). It is established that the CuO catalyst over alumina performs the methanol dehydration, but the formation of by-products is the main drawback. For these reasons, we synthesized a CuO/$\gamma-Al_2O_3$ catalyst promoted with hematite aiming to enhance the activity toward DME at atmospheric conditions. The resulting bimetallic catalyst (CuO-Fe_2O_3/Al_2O_3) performed a 70% conversion at 290 °C, which is similar to other catalysts recently reported in the literature but done in harsh conditions. In addition, this bimetallic catalyst exhibited a 100% in selectivity toward the DME production. XPS spectra of the fresh and used catalyst suggested that the chemical oxidation states of Cu and Fe remain without change. After regenerating the catalyst at 600 °C for 2 h in air, it performed at a similar catalytic conversion, confirming the reusability of the as-synthesized material and reducing the environmental impact.

Introduction

Great efforts in technological research are focused on developing new catalysts with bifunctional properties, for example, catalysts capable of generating the desired reaction products while maintaining their activity for long-term [1]. Bimetallic catalysts are subject to study because they have improved physical and chemical properties compared to their one-component counterparts [2–7]. For example, in heterogeneous catalysis some chemical reactions require bifunctional catalysts which focus on having active sites on the metal and

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https://doi.org/10.1016/j.ijhydene.2018.02.051
0360-3199/

Please cite this article in press as: Armenta MA, et al., Highly selective CuO/$\gamma-Al_2O_3$ catalyst promoted with hematite for efficient methanol dehydration to dimethyl ether, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.02.051

acid sites on the support [8–10]. In recent years, Cu-Fe bimetallic material has been studied in different disciplines such as semiconductors, catalysis, and even thin films. The main advantage of using Cu and Fe is their high abundance in the earth's crust [11]. In addition, since in a chemical reaction the contact site of the reagents is on the metal oxide, thus increasing the surface area and reducing the particle size effectively would increase the contact area between the Fe-Cu sites and the reagents [12]. However, there are still some challenges to overcome, such as preventing sintering and carbonization of Cu-Fe catalytic sites [13].

Regarding the DME production, the use of this kind of catalysts could potentially reduce the atmospheric pollutants compared to Diesel combustion [14–16]. The combustion of DME generates lower NO_X smoke amounts, almost near zero [17]. Equally, their range of application relies on replacing chlorofluorocarbons (CFCs), which are responsible to damage the ozone layer [18–22]. The low pollution generated by the combustion of dimethyl ether has led those large cities in countries such as USA, China, Saudi Arabia, and Sweden to encourage the use of DME fuel because of its reduced effect on the environment [23].

Two main processes are utilized to obtain DME [24]. Both indirect and direct methods use solid catalysts, commonly $\gamma-Al_2O_3$ or HZSM-5 zeolite, and CuO-ZnO$-\gamma-Al_2O_3$/HZSM-5 respectively [25,26]. There is a controversial discussion between the use of $\gamma-Al_2O_3$ and HZSM-5 for DME synthesis, since HZSM-5 presents stronger acidic sites, which lead to the formation of light hydrocarbons as by-products, resulting in the catalyst deactivation [27].

Currently, the indirect method uses Al_2O_3 as primary support, due to the fact that is a material with textural properties suitable for the reaction, it also reaches conversion values above 35% at 250 °C and 82% at 375 °C. However, the use of such high temperatures leads to the formation of undesired by-products [28–31]. In particular, high temperatures are required to obtain light olefins [32]. Therefore, great research efforts are being taken to improve the textural properties and catalytic properties of the Al_2O_3 support with the presence of transition metals such as Cu, Fe, Ni, and including bimetallic oxides. For example, ZnO-CuO/Al_2O_3, even though its conversion value at 300 °C is only 80%, its selectivity barely reaches 75% [33].

In this work, we prepared CuO/$\gamma-Al_2O_3$, $Fe_2O_3/\gamma-Al_2O_3$, and CuO-$Fe_2O_3/\gamma-Al_2O_3$ catalysts by the impregnation method. To the best of our knowledge, this is the first time that Fe_2O_3 is used as a promoter in the dehydration of methanol. Fresh and used CuO-$Fe_2O_3/\gamma-Al_2O_3$ systems were characterized to get insight into the relationship between crystalline structure, particle size, chemical composition and morphology of the material for DME production *via* methanol dehydration.

Experimental

Synthesis of the CuO/$\gamma-Al_2O_3$, $Fe_2O_3/\gamma-Al_2O_3$, and CuO-$Fe_2O_3/\gamma-Al_2O_3$ by impregnation method

The impregnation method is simplified into three steps: 1) the impregnation of the active agent on the support, 2) drying, and 3) calcination. Commercial alumina ($\gamma-Al_2O_3$) supplied by Aldrich with a grain size of 58 Å was used as support. For the catalyst synthesis, we used nitrate nonahydrate, $Fe(NO_3)_3\cdot 9H_2O$, and hydrated copper nitrate, $Cu(NO_3)_2\cdot 2.5H_2O$. Before the impregnation, solutions of iron nitrate containing 0.72 g in 50 mL of deionized water (0.25 M) and 0.54 g of copper nitrate in 50 mL of deionized water (0.17 M) were prepared separately and stirred for 4 h at 25 °C until complete dissolution. The precursor amounts were calculated to reach 2 wt. % of Fe and 3 wt. % of Cu. These values represent an equimolar ratio for Cu:Fe (1:1). A third solution was prepared using the same amounts as earlier of Fe and Cu to prepare the bimetallic catalyst. After the impregnations, the catalysts were dried at 80 °C for 10 h with a pH between 6 and 7. Then, the Cu- and Fe-based and bimetallic catalysts were activated at 650 °C for 6 h in a conventional oven in air, and further stored in N_2 atmosphere.

Characterization of materials

The specific surface areas of the samples were determined by adsorption–desorption of N_2 in a Micromeritics model Tristar II equipment at −196 °C by using the Brunauer-Emmet-Teller (BET) method. The acidity of the catalysts was determined by a ChemBET Pulsar TPR/TPD equipment, using NH_3 as a test molecule. The crystalline structures of the materials were analyzed by X-ray diffraction (XRD) employing a Philips X'Pert diffractometer with CuKα radiation ($\lambda = 1.5406$ Å) operated at 45 kV and 30 mA, in the range of 2θ angles from 10° to 80°. The morphology analysis of the samples was performed in a JEOL JSM-5300 scanning electron microscopy (SEM), and the average size of the nanoparticles was determined by a JEOL 2010 high-resolution transmission electron microscopy (HRTEM) at an accelerating voltage of 200 kV. Finally, the material surface was analyzed by X-ray Photoelectron Spectroscopy (XPS) in a SPECS PHI-548 system.

Catalytic activity

Dehydration of methanol was performed in a micro-plant at atmospheric pressure, as follows: i) reagent saturation was dipped into a bath of ethylene glycol to keep constant the saturation temperature at 10 °C, ii) the reaction was carried out within a U-type tubular reactor, and iii) the products were identified using a gas chromatograph FID Varian Model 3400 (Chromosorb Carbowax 1540 column) as reported [34]. Fig. S1 displays the schematic reactor set up. A mixture of methanol (0.825 mL/h) and nitrogen (30 mL/min) was used as a feed, resulting in a Weight Hourly Space Velocity (WHSV) of 1.3 h^{-1}. About 0.15 g of catalyst was deposited on the reactor fiberglass bed to carry out the catalytic reaction. Before the measurements, we removed the physisorbed water from the sample at 150 °C in a nitrogen atmosphere. Subsequently, the temperature was raised at 250 °C at a heating rate of 10 °C min^{-1}. After that, the temperature was raised again up to 290 °C. The reaction was monitored for 5 h, analyzing the reaction products every 10 min. Finally, for the catalyst that reached the highest conversion values, it was subjected to a regeneration treatment by heating at 600 °C for 2 h, in an air atmosphere with a flow of 100 mL/min.

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