

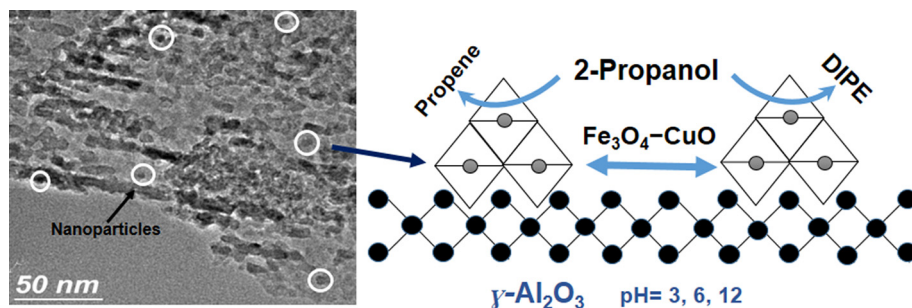


Full Length Article

Diisopropyl ether production via 2-propanol dehydration using supported iron oxides catalysts

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GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Diisopropyl ether
2-Propanol dehydration
Iron catalyst
Alumina
Acidity

ABSTRACT

In this work, we studied the DIPE ($C_6H_{14}O$) production as an oxygenated compound from the catalytic performance of Fe and Cu oxides supported over alumina, on the 2-propanol dehydration reaction. The impregnation acidity effect was investigated. Samples at acid, moderately acidic, and basic pH were prepared. They were tested at 250 °C in a pilot micro-plant at atmospheric pressure. Catalytic results concluded the $Fe_3O_4/\gamma-Al_2O_3$ impregnated to an acid pH showed the highest selectivity toward DIPE with adequate activity. All the catalysts at basic pH showed a complete selectivity to propylene (C_3H_6). The yield of DIPE on the acidity reflects that is a linear function, which is valuable for a more rational design of new catalysts. The catalysts were characterized by adsorption-desorption of N_2 , X-ray diffraction, high-resolution transmission electron microscopy, and energy dispersive X-ray spectroscopy. The correlation between the textural and morphological properties of our catalysts and their catalytic activity was discussed.

1. Introduction

In recent years, there is great concern about the use of methyl tert-butyl ether (MTBE) because of groundwater contamination associated with leaks from storage tanks and gasoline spills [1,2]. Prolonged

exposure to this compound causes headaches, eyes irritation, and health risks caused by its carcinogenic nature. Based on these reasons, it is essential to produce fuels throughout clean and cost-effective approaches [3,4]. A promising strategy is replacing MTBE with another tertiary alkyl ether such as the diisopropyl ether (DIPE). DIPE is a

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Received 2 April 2018; Received in revised form 22 June 2018; Accepted 29 June 2018

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gasoline additive that enhances the octane number, improving the combustion, and reducing CO and hydrocarbons emissions. The DIPE demand increased from 16.4 million tons in 1980, to 69 million tons in 2006, and its consumption is expected to reach 350 million tons by 2020 [5]. Several acid catalysts such as zeolites, sulfonic acid resin (Nafion®), and clays are employed in the selective production of DIPE [6,7]. Zeolites are widely preferred in comparison with others acid catalysts because of their homogeneous pore size distribution, high thermal stability, and selectivity of the desired product [6].

Among the catalysts for efficient 2-propanol dehydration, the Pt/Al₂O₃ performed 100% selectivity to diisopropyl ether at 300 °C [8]. However, the use of precious metals is expensive for practical applications. Besides, it has been proposed low-cost materials such as activated carbon-based catalysts to perform 2-propanol dehydration [5]. These catalysts have obtained a selectivity of 20% toward DIPE at 125 °C, but at this temperature, the catalysts produced undesirable byproducts [5]. This reaction should be cost-effective when converting alcohols into value-added products. DIPE is a solvent highly used in chemical synthesis and the industry (e.g., nitrocellulose synthesis) [9]. Additionally, propylene is used in everyday life in a wide variety of products such as plastics and textiles. It is manufactured using fossil sources such as oil (petrol) and natural gas. The global production of propylene is around 90 million tons per year and projected to increase to 130 million tons by 2023 [10,11].

It is accepted that copper oxides are efficient catalytic materials for the reduction of NO₂ and the regeneration of CO₂ oxidation [12,13]. Fe-based transition metals have suitable physical and chemical properties to catalyze chemical reactions that involve the H₂ adsorption. In this step, the hydrogen-hydrogen bond is broken and then replaced by two iron-hydrogen bonds. On the other hand, the approach of producing bimetallic nanoparticles is interesting because it can lead to an enhancement of their synergic properties in comparison to their individual properties. These improved properties usually depend of the crystal structure, chemical composition, and nanoparticle shapes [14]. Regarding the support, alumina has remarkable textural properties, as well as high thermal and hydrothermal resistance, chemical stability, and significant acid-base characteristics [15–18].

In this work, we modified the impregnation pH of alumina as support to prepare Fe, Cu, and Fe–Cu catalysts through the impregnation method. The resulting materials were tested in the 2-propanol dehydration, at 250 °C in a pilot micro-plant, and characterized by several techniques; adsorption-desorption of N₂, X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), and energy dispersive X-ray spectroscopy (EDX). In addition, we discussed the correlation between the textural and morphological properties of our catalysts and their catalytic activity.

2. Experimental

2.1. Preparation of the catalysts

The Fe, Cu, and Fe–Cu catalysts, with atomic ratio of 1:1 regarding to the transition metal, supported on alumina with different acidity were prepared by the impregnation method. The acidity of the solution was modified with 10 mL of nitric acid (HNO₃) 1.42 M and 15 mL of sodium hydroxide (NaOH) 3 M [7]. The impregnation pH values were 3 (acid), 6 (weakly acid), and 12 (basic) for all the catalysts. The method can be described in three main steps: the impregnation on the support of the active agent, drying out, and calcination. We used commercial alumina (γ -Al₂O₃) as the support with a grain size of 58 Å, supplied by Aldrich. Iron nitrate nonahydrate, Fe(NO₃)₃·9H₂O, and hydrated copper nitrate, Cu(NO₃)₂·2.5H₂O was used for the catalysts synthesis. Separately, solutions of iron nitrate 0.25 M, and copper nitrate 0.17 M were prepared and stirred for 4 h at 25 °C until their complete dissolution for the impregnation. As in a previous work, the amount of the precursors were weighed so that they resulted in % wt., 2% Fe and 3% Cu. A third

solution was prepared using the same atomic ratio as earlier of Fe and Cu to prepare the Fe–Cu bimetallic catalysts [19]. Also, the catalysts were dried at 80 °C for 10 h subsequently to the impregnation step. After that, the catalysts were activated at 350 °C in a conventional oven in air atmosphere for 6 h.

2.2. Catalyst characterization

The surface areas of the materials were calculated from N₂ adsorption-desorption isotherms by the Brunauer-Emmet-Teller (BET) equation at –196 °C in a Micromeritics ASAP 2000 equipment. Before the analysis, the materials were degassed at 200 °C for 4 h. The diffractograms of the catalysts were recorded in a Philips X'Pert diffractometer with CuK α radiation ($\lambda = 1.5406$ Å) at 45 kV and 30 mA. The morphology of the samples was explored using a JEOL 2010 high-resolution transmission electron microscope at an accelerating voltage of 200 kV. For HRTEM measurements, the samples were dispersed in *n*-heptane and afterward deposited on lacey carbon Cu grids. For elemental analysis, we used a JEOL JSM-5300 scanning electron microscopy (SEM) equipped with an energy dispersive X-ray spectrometer from Oxford Instruments.

2.3. Catalytic activity

The 2-propanol dehydration was performed in a pilot micro-plant at atmospheric pressure. A bath of ethylene glycol was used to control the saturation temperature at 5 °C where the saturation reagent was dipped in. The reaction was performed out with a U-type reactor, and the outcomes were analyzed using a gas chromatograph FID Varian Model 3400 (Chromosorb Carbowax 1540 column). A mixture of 2-propanol (0.825 mL/h) and nitrogen (30 mL/min) was used as a feed, resulting in a weight hourly space velocity (WHSV) of 1.5 h^{–1}, a relatively low value. We deposited about 0.3 g of catalyst on the reactor bed to perform the 2-propanol dehydration reaction. We removed the physisorbed water from the sample at 150 °C in a nitrogen atmosphere, before the measurements. Subsequently, the temperature was upraised to 250 °C at a heating rate of 10 °C min^{–1}. This reactor setup allowed N₂ gas to be carried through the saturator that contained 50 mL of 2-propanol. The catalytic reaction was monitored for 30 min, taking samples every 5 min.

3. Results and discussion

3.1. Textural properties

The specific surface areas (S_{BET}) of the samples are listed in Table 1, indicating the pure support with an impregnation pH of 6 has the highest surface area of 172 m²/g. By modifying the pH impregnations of the support either to 3 or 12, the surface area of the support slightly decreased to 140 m²/g and 157 m²/g, respectively. Table 1 shows that the surface areas of the Fe-based catalysts over alumina do not have a linear trend in accordance to pH modifications; S_{BET} at pH of 12 > S_{BET} at pH of 3 > S_{BET} at pH of 6. Fe–Cu bimetallic catalysts presented similar surface areas at different alumina pH values. Otherwise, the surface areas of the Cu catalysts over alumina were lower than the pure support, showing similar values for acid and weakly acid pH conditions, but a higher value at basic pH. In fact, all the samples at basic pH presented higher surface area than the other samples.

In Table 1, we can observe that the pore diameter for the basic catalysts is higher than the other catalysts in each set of samples. In our case, the surface area of the materials increased with the average pore diameter. In some cases, having high surface areas and high pore diameters does not assure high performance of a desired catalytic reaction. It is commonly accepted that greater values of surface area can yield greater values of catalytic activity [20].

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