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Use of delaminated hectorites as supports of copper catalysts for the hydrogenolysis of glycerol to 1,2-propanediol

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ABSTRACT

Delaminated hectorites were used as supports of copper catalysts for the hydrogenolysis of glycerol. Catalytic results were compared with those obtained for copper catalysts prepared with other supports: hectorites, synthesized by conventional heating and with microwaves, and silicate-bearing hectorite. Copper was introduced by impregnation, solids blend with ultrasounds, and ion-exchange methods. Catalytic tests were carried out in liquid phase at 40 bar, 473 K and stirring of 400 rpm. The selectivity to 1,2-propanediol was very high for all catalysts (>90%). The highest conversion (61% after 8 h of reaction) was obtained for a delaminated hectorite impregnated with 40 wt.% of copper. This was related to the highest surface area of this delaminated hectorite together with its lower hydrophilic character (lower C.E.C.), which made possible to best control copper agglomeration. In fact, copper dispersion increased during reaction for this catalyst.

1. Introduction

The recent increase of biodiesel production as renewable combustible has caused some concern oversupply of glycerol in the market. With the use of biodiesel worldwide, glycerol becomes more readily available while descending price [1]. This has promoted the development of novel technologies to convert glycerol into high added-value products, such as 1,2-propanediol (1,2-PDO), which can be used as humectant, in antifreeze mixtures, as brake fluid or as component of polyesters and alkyl resins [2]. However, 1,2-propanediol is currently obtained from petroleum derivatives. Therefore, its production from renewable resources is highly desired [2].

Catalytic hydrogenolysis of glycerol is one of the most attractive green routes to obtain selectively glycols. Supported noble metals, such as Ru, Rh, and Pt are well known active catalysts for this reaction [3–14]. Unfortunately, these catalysts often promote excessive C–C cleavage, resulting in low selectivity to propanediols. The best result at mild reaction conditions (30 bar, 423 K) was recently achieved with a Ru/bentonite catalyst, which led to 67% of selectivity to 1,2-PDO for a 72.5% of conversion [13].

A less expensive and more effective alternative for cracking control is the use of copper catalysts. Cu/ZnO have been the most used catalysts for this reaction [15–19]. In the first studies, high selectivity to 1,2-PDO (80–100%) was reported but working at hard reaction conditions (80–150 bar, 453–545 K) [15,16]. More recently, Balaraju et al., working at softer conditions (20 bar, 473 K), achieved 37% of conversion with 92% of selectivity to 1,2-PDO after 16 h [17] whereas Claus et al. obtained 55% of conversion and 86% of selectivity to 1,2-PDO, at 50 bar and 473 K, after 7 h of reaction. The use of an organic solvent during reaction instead of water reduced the agglomeration of metal particles, the main responsible for catalyst deactivation [18]. These authors proposed that the presence of Ga_2O_3 in Cu/ZnO catalysts can control deactivation yielding high conversion (99%) and high selectivity to 1,2-PDO (80%) working at 50 bar and 493 K [19]. Vasiliadou and Lemonidou attributed deactivation to a collapse of mesoporous network with agglomeration of metal particles when using monometallic Cu (20 wt.%) and bimetallic (5 wt.% Ru–Cu) catalysts supported in mesoporous silica for this reaction [20].

Other supported-copper catalysts were used for this reaction. Huang et al. reported selectivity to 1,2-PDO of 99% for a 29% of conversion with Cu/SiO_2 after 12 h of reaction, working at 90 bar and 453 K [21]. These authors suggested that the mechanism to obtain 1,2-PDO proceeded through the acetol route, as previously proposed by Suppes et al. [22]. This acetol route is favored by the presence of acid sites, but it can also proceed via metal sites that catalyze dehydration of glycerol [14,23]. Lastly, other recent interesting paper by Claus et al., using different oxides (ZnO, SiO_2, CaO, Al_2O_3) as supports of copper catalysts, pointed out that the catalyst with the highest activity (52% of conversion and 98% of selectivity to 1,2-PDO after 7 h at 473 K and 50 bar) was that with the highest metallic area, Cu/ZnO [24].

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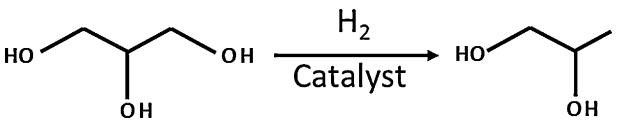

Scheme 1. Hydrogenolysis of glycerol 1,2-propanediol.

Hectorites $(M^{n+}{}_{x/n}\cdot yH_2O[Mg_{6-x}Li_x](Si_8)O_{20}(OH\cdot F)_4)$, and related hectorite compounds, are layered materials with high cation exchange capacity (C.E.C.), and with interesting surface and acidic properties [25], which make them suitable to be used as catalytic supports for this reaction. The main disadvantage of hectorite is the collapse of its structure at relatively low temperatures. This encouraged the design of new methodologies to synthesize stable hectorites, such as pillared clays or delaminated hectorites. Pillared clays are mostly prepared using bulky cations (e.g. $Al_{13}{}^{7+}$) as pillaring species [26–31]. Besides, Torii and Iwasaki reported the synthesis of silicate-bearing hectorites [32], which presented, at short time of hydrothermal treatment, silicate pillars in the interlamellar space. Delaminated hectorites can be synthesized using quaternary ammonium salts during the hydrothermal treatment, as proposed by Iwasaki [33], or by preparing polymer-hectorite clays [34]. The mesoporous of delaminated hectorites are obtained after removing the quaternary salt and the polymer, respectively, during calcination. They correspond to antiparticle space of disk-shaped crystallites aggregated by edge-to-face bonding. Hectorites can be used as supports of copper catalysts. Typical methods used for preparing catalysts include impregnation, solid blend and modification of hectorite by exchange or with copper complexes [35].The aim of this study was to compare the catalytic activity of several Cu/delaminated hectorites with the catalytic behavior of Cu/hectorites and Cu/silicate-bearing hectorite for the glycerol hydrogenolysis to obtain 1,2-propanediol (Scheme 1). For this proposal, different wt.% and dispersion of copper were used.

2. Experimental

2.1. Preparation of catalysts

2.1.1. Synthesis of supports

Two delaminated hectorites were prepared according to the method reported by Iwasaki [33]. The molar ratio of reagents was Si:Mg:Li = 8:5.2:0.8. An acidified silicate solution was mixed with the appropriate amounts of $MgCl_2$ and LiF. Then, a LiOH solution was added until pH 12. The resulting suspension was maintained for 15 min in an ultrasound bath, filtered, washed with deionized water, and finally, dried overnight at 353 K. This solid was suspended in a trimethyldodecylammonium chloride solution (AQ) in a molar ratio Li:AQ = 1:1. The suspension was submitted to hydrothermal treatment in a conventional autoclave at 453 K for 1 h, or 2 h. After that, they were calcined at 893 K for 75 min obtaining HD1 and HD2, respectively.

One silicate-bearing hectorite was prepared by hydrothermal treatment following the procedure proposed by Torii and Iwasaki [32] but using a different quaternary salt. The molar ratio of reagents was Si:Mg:Li = 8:5.4:0.6. A sodium silicate solution, previously acidified with nitric acid 1 M, was mixed with the appropriate amount of $MgCl_2$. Then, a sodium hydroxide solution was added until pH 12. The slurry obtained was dispersed in water and mixed with the appropriate amount of LiF, stirring was maintained for 1 h and heated hydrothermally at 453 K for 2 h, filtered and dried at 353 K. Finally, this solid was mixed with trimethyldodecylammonium chloride, by refluxing at 353 K for 1 h, in molar ratio Li:AQ = 1:1, and then filtered and calcined at 893 K for 75 min (HB).

Two traditional hectorites were prepared following the Granquist and Pollack method [36], and the Vicente et al. method [37], respectively. The preparation was carried out as follows: 135 mL of a slurry composed by SiO_2, fresh precipitate $Mg(OH)_2$ and LiF in a molar ratio of Si:Mg:Li = 6.9:5:2:1.6 was vigorously stirred for 1 h. The SiO_2 amount used was lower than the stoichiometric value to avoid the presence of residual SiO_2 in the resulting hectorite whereas the amount of LiF was chosen considering this reagent as source of Li for the lamellars (0.8) and for the interlamellar space (0.8). In one method the sample was aged in a conventional autoclave at 393 K for 8 days (HC), and in the other the sample was autoclaved in a laboratory microwave oven at 393 K for 8 h (HMw). Samples were filtered and dried at 353 K.

2.1.2. Preparation of supported-copper catalysts

Supported-copper catalysts were prepared by 3 methods: impregnation, solids blend with ultrasounds, and ion-exchange.

Impregnated catalysts were prepared mixing 1.5 g of support with different volumes of a 15 wt.% copper nitrate ethanol solution under ultrasounds for 15 min. Different charges of copper (12.5, 20 and 40 wt.% Cu) were obtained after solvent rotaevaporation, calcination at 723 K for 2 h, and reduction under pure hydrogen (2 mL/s) at 573 K for 2 h. Impregnated catalysts were designated as Cu/support $name_{imp1}$, Cu/support $name_{imp2,}$ Cu/support $name_{imp3}$, where 1, 2 and 3 represent 12.5, 20 and 40 wt.% Cu, respectively.

Solids blend with ultrasounds method consisted of an effective mixture of support and copper nitrate (15 wt.% Cu) until the obtention of a homogeneous solid with a copper charge of 40 wt.%. Then, decane was added, and the mixture was submitted to ultrasounds for 15 min. The solid was separated by decantation, dried, calcined at 723 K for 2 h, and reduced under pure hydrogen (2 mL/s) at 573 K for 2 h. These catalysts were named as Cu/support $name_{sb}$.

Lastly, exchanged copper catalysts were obtained by stirring 1.5 g of support in an aqueous 0.01 M copper nitrate solution for 30 min. Samples were filtered, and washed with deionized water. The reduction step was performed “in situ” under catalytic reaction conditions. Exchanged catalysts were called as Cu/support $name_{ex}$.

2.2. X-ray diffraction (XRD)

XRD measurements were made using a Siemens D5000 diffractometer (Bragg–Brentano parafocusing geometry and vertical θ–θ goniometer) fitted with a curved graphite diffracted-beam monochromator and diffracted-beam Soller slits, a 0.06° receiving slit, and scintillation counter as a detector. The angular 2θ diffraction range was between 5° and 70°. Sample was dusted on to a low background Si(5 1 0) sample holder. The data were collected with an angular step of 0.05° at 3 s per step and sample rotation. Cu Kα radiation was obtained from a copper X-ray tube operated at 40 kV and 30 mA.

The X-ray pattern was analyzed implementing the program TOPAS 3.0 [38]. This approach calculates the contribution to the reflection width produced by a specific instrument configuration. The crystallite size was calculated from the net integral breadth of the reflections, βi [39], according to the following formula that comes from the Scherrer expression: $\beta i = \lambda/\varepsilon \cos \Theta$, where λ is the X-ray wavelength, ε is the crystallite size and θ is the Bragg angle. 0 6 0 reflection was used to calculate the crystallite size of the hectorites.

2.3. N_2 physisorption

N_2-adsorption–desorption isotherms were recorded at 77 K using a Micromeritics ASAP 2000 surface analyzer. Prior to analysis samples were outgassed at 393 K. Specific surface areas were calculated from the BET method.