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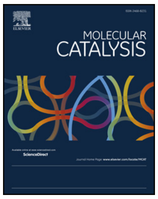

Promotion effect of Ce or Zn oxides for improving furfuryl alcohol yield in the furfural hydrogenation using inexpensive Cu-based catalysts

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ABSTRACT

Kerolite/Mg-smectite mixed layer was used as inexpensive material to support metallic copper, with metal loadings (5–30 wt.%). These catalysts are active in gas-phase furfural hydrogenation, maintaining conversion values higher than 80 mol%, at 210 °C, after 5 h of time-on-stream, with high copper loading (15–30 wt.% Cu) catalysts, being furfuryl alcohol and 2-methylfuran the only detected products. The incorporation of Ce and Zn as promoters causes a decrease in the furfural conversion, although catalysts become much more selective toward furfuryl alcohol, reaching a maximum furfuryl alcohol yield above 80%, at 190 °C, after 5 h of TOS, after CeO_2 addition.

1. Introduction

Nowadays, the world population is looking for and developing alternative energy sources to the traditional fossil fuels, due to progressive depletion. Moreover, their combustion leads to the emission of harmful gases provoking adverse effects on population and environment. Last decades, several sustainable energy sources have been proposed to replace them, but, individually, these are not able to supply the world energy needs for themselves, so it is necessary the complementary use of these different energy sources.

Biomass is becoming a very important alternative energy and carbon-based chemicals source [1], due to its availability on Earth, although this must not interfere with the food chain to be a sustainable option. Lignocellulosic biomass is considered the main non-edible biomass feedstock, which is composed by cellulose (40–50%), lignin (15–25%) and hemicellulose (20–35%) [2]. Among them, hemicellulose has high potential since its hydrolysis and dehydration can give rise to furfural, which is considered as a building block molecule [2,3].

The presence of an aldehyde group and an α,β-unsaturation in the furan ring confers high reactivity to the furfural molecule. Thus, it can be converted into a large variety of high value-added products via hydrogenation, opening-ring, decarboxylation, oxidation or dehydration reactions [4]. In this sense, hydrogenation of furfural can lead to furfuryl alcohol (FOL), tetrahydrofurfuryl alcohol (THFOL), 2-methylfuran (MF), 2-methyltetrahydrofuran (MTHF), furan (F), tetrahydrofuran (THF) or C4-C5 alkanes, depending on experimental conditions [2,4]. The furfural hydrogenation can be carried out in gas or liquid phase. Among them, gas-phase is more sustainable, since it is a continuous process and requires softer temperature and pressure conditions [2].

The industrial catalyst used in gas-phase furfural hydrogenation is copper chromite; however, the presence of chromium species, which can be highly toxic, and catalyst deactivation are issues that must be overcome for the development of a most efficient catalytic process [5–7]. Several active phases, such as Cu [8–16], Ni [9,17–20], Ni_2P [21]. Co [22], Pd [9,23,24], Pt [25–27] or Mo_2C [28–30], have been proposed. The catalytic results have revealed that the hydrogenating character of the active phase is a key factor in determining the activity and selectivity pattern. Thus, the more hydrogenating catalysts, such as those based on Ni or Pd, tend to cleavage the C—C bonds, even the opening ring to obtain alkanes. Moreover, this high catalytic activity can also lead to a faster deactivation. Catalysts with lower hydrogenating behavior, such as Cu, Co, Ni_2P or Mo_2C, do not favor the C—C scission, originating MF and FOL as main products. These chemicals have a great commercial interest, since FOL is used in the manufacture of foundry resins due to their excellent chemical, thermal and mechanical properties, synthesis of fibers or dispersing agents, and intermediate for the synthesis of lysine or vitamin C [4,31]. On the other hand, MF possesses a high potential to be used as gasoline additive,

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since increases the octane value (103), the synthesis of heterocycles and solvent in the synthesis of antimalarial drugs or methylfurfural [4,32].

Among metal active phases, copper is the most inexpensive active, and it has been reported in the literature that basic or amphoteric supports, such as MgO [13], ZnO [11] or CeO_2 [12], or even slight acidic, such as clay minerals or silica, improve the catalytic behavior [8–10,15]. In fact, the presence of small Cu particles supported on SiO_2 allows to attain a high FUR conversion, obtaining MF as main product, since the hydrogenolysis of FOL is favored [16,33]. However, supports with stronger acidity do not favor the FUR hydrogenation in gas phase, but FUR polymerizes.

In order to develop sustainable catalysts on a larger scale, inexpensive supports have emerged as alternative. Thus, raw especial clays, such as bentonite and sepiolite, have been proposed as catalytic support due to their high specific surface area and low acidity [15,34]. The present research aims at the preparation of copper supported on a kerolitic clay, a randomly mixed layer formed by disordered turbostratic talc (kerolite) and Mg-smectite (stevensite) [35,36]. Previous research has established that kerolite can be associated to other Mg-rich clay minerals, such as stevensite or sepiolite [35,36]. Considering that Cu/MgO systems have shown to be active in the FUR hydrogenation [13] and the particular characteristics of kerolitic clay, this could be a suitable support for highly dispersed Cu nanoparticles.

This work has also evaluated the influence of the addition of ZnO or CeO_2, as promoters, on the catalytic performance, because the electronic density of Cu nanoparticles can be modified by the presence of these metal oxides [11,12].

2. Experimental section

2.1. Reagents

The synthesis of the Cu-based catalysts was carried out using copper nitrate trihydrate, $Cu(NO_3)_2{\cdot}3H_2O$ (Sigma-Aldrich, 99%), zinc nitrate tetrahydrate, $Zn(NO_3)_2\ 4H_2O$ (Merck, 99%), cerium nitrate tihydrate, $Ce(NO_3)_4\ 3H_2O$ (Aldrich, 99%), ethanol, CH_3CH_2OH (Prolabo, 95% vol.), ethylene glycol, $C_2H_6O_2$, (Sigma-Aldrich, 99%), sodium carbonate, Na_2CO_3(Sigma-Aldrich, 99%).

Kerolitic clay was collected from the Esquivias deposits (Madrid Basin, Spain). Previous research has established that these deposits are composed mostly of mixed layered kerolite-stevensite [35]. More recently, it has also been reported the presence of sepiolite and saponite in the Esquivias deposits [36–38].

Chemicals employed in furfural hydrogenation were furfural (Sigma-Aldrich, 99%), cyclopentyl methyl ether (Sigma-Aldrich, 99.9%) as solvent, and o-xylene (Sigma-Aldrich, 99.9%) as internal standard. The gases employed were He (Air Liquide 99.99%), H_2 (Air Liquide 99.999%), N_2 (Air Liquide 99.9999%) N_2O/He (5 vol.% in N_2O) and H_2/Ar (10 vol.% in H_2, Air Liquide 99.99%).

2.2. Synthesis of catalysts

Copper-based catalysts were synthesized by a co-precipitation-deposition method, according to previous research reported in the literature [15]. Briefly, 1 g of kerolitic clay was dispersed under stirring in 75 mL of water for 30 min. Later, a solution composed by 10 mL H_2O, 20 mL ethylene glycol, 50 mL ethanol and the corresponding percentage of copper precursor, for achieving a final copper loading ranging between 5 and 30 wt.%, was added to the clay suspension. In order to precipitate the Cu-species, pH was increased until pH = 11 by dropwise addition of a Na_2CO_3 (0.5 M) aqueous solution, at 80 °C. After the addition of the precipitant solution, the resulting solution was cooled and aged at room temperature for 24 h, without stirring. The solid was filtered and dried at 90 °C for 12 h, and calcined at 400 °C for 1 h.

In the case of the catalysts with ZnO or CeO_2, the synthetic procedure was similar to that previously indicated. The Ce or Zn-species was incorporated, using the nitrate precursor, together with the Cu-species considering a Cu/Ce or Cu/Zn molar ratio equal to 1. The catalysts were labeled as K-*x*Cu, K-*x*CuZn or K-*x*CuCe, where *x* is the wt.% of copper loading.

2.3. Characterization of catalysts

The textural properties were evaluated from the N_2 adsorption-desorption isotherms at −196 °C, as determined by an automatic ASAP 2020 system from Micromeritics. Prior the measurements, the samples were outgassed overnight at 200 °C and 10^{-4} mbar. The surface areas were determined with the Brunauer, Emmett and Teller (BET) equation [39], considering a N_2 cross-section of 16.2 $Å^2$. The total pore volume was calculated from the adsorption isotherm at $P/P_0 = 0.996$, and the average pore size was determined by applying the Barrett–Joyner–Halenda (BJH) method to the desorption branch [40]. The Density Functional Theory (DFT) method was employed to determine the pore-size distributions [41].

H_2-temperature programmed reduction (H_2-TPR) experiments were performed with the catalyst precursor (0.080 g), previously treated with a He flow (35 mL min^{-1}) at 100 °C, for 45 min. After the sample cooled to room temperature, the H_2 consumption was monitored between 50 and 500 °C in an Ar/H_2 flow (48 mL min^{-1}, 10 vol% of H_2), at a heating rate of 10 °C min^{-1}. The water formed in the reduction reaction was trapped by passing the exit flow through a cold finger immersed in a liquid N_2/isopropyl alcohol bath (−80 °C). The H_2 quantification was registered on-line with a thermal conductivity detector (TCD).

XRD patterns of catalysts were obtained with a PANanalytical X'Pert Pro automated diffractometer. The patterns were recorded in a Bragg–Brentano reflection configuration, by using a Ge (111) primary monochromator (CuKα_1) and an X'Celerator detector with a step size of 0.017° (2θ), between 2θ = 10 and 70°, with an equivalent counting time of 712 s per step. The crystallite size (D) was calculated by using the Williamson–Hall equation, $B \cos(\theta) = (K\lambda/D) + (2\ \varepsilon \sin(\theta))$, in which θ is the Bragg angle, B is the full width at half-maximum (FWHM) of the XRD peak, K is the Scherrer constant, λ is the X-ray wavelength, and ε is the lattice strain [42]. The analysis (major elements) of untreated kerolite/Mg-smectite was carried out by means of the MagiX X-ray fluorescence spectrometer of PANlytical. A Varian 220-FS QU-106, atomic absorption spectrometer was used for the determination of sodium. Loss ignition was determined at 950 ºC.

The particle morphology was studied by Transmission Electron Microscopy (TEM), using FEI Talos F200X equipment (Thermo Fisher Scientific). This equipment combines outstanding high-resolution S/TEM and TEM imaging with industry-leading energy dispersive X-ray spectroscopy (EDS) signal detection, and 3D chemical characterization with compositional mapping. The samples were suspended in isopropyl alcohol and dropped onto a perforated carbon film grid.

Metal surface area and dispersion were evaluated by N_2O titration [11,12]. This method is based on the formation of a monolayer of Cu_2O by oxidation of superficial Cu^0 with a N_2O flow, according to the reaction: $2Cu^0 + N_2O \rightarrow Cu_2O + N_2$. Before analysis, the CuO phase is reduced under a 10 vol.% H_2/Ar flow (48 mL min^{-1}) and a rate of 5 °C min^{-1}, until 300 °C during 1 h, for all catalysts except in the case of K15CuCe, which was reduced at 230 °C. Then, samples were purged under a He flow and cooled down to 60 °C. The oxidation of Cu^0 to Cu^+ is carried out by chemisorption of N_2O (5 vol.% N_2O/He) at 60 °C during 1 h. Later, the catalyst was again purged with an Ar flow and cooled to room temperature. After this, the reduction of Cu_2O to metallic Cu was accomplished by raising the temperature up to the aforementioned values for all catalysts (300 °C), except for K-15CuCe catalyst (230 °C).

XPS spectra were obtained with a Physical Electronics PHI 5700 spectrometer with non-monochromatic MgKα radiation (300 W, 15 kV, 1253.6 eV) with a multichannel detector. The spectra were recorded in the constant-pass energy mode at 29.35 eV with a 0.72 mm diameter