Gas phase selective hydrogenation of furfural to furfuryl alcohol and 2-methylfuran over Cu-CeO$_2$ coprecipitated catalysts

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Introduction.

Furfural is an important chemical derived from lignocellulosic biomass, in particular from C5 sugars like xylose, and it is considered as a platform molecule of great potential for the synthesis of a broad spectrum of chemicals. In this sense, furfuryl alcohol and 2-methylfuran are two important chemicals which can be produced through furfural hydrogenation, either in liquid or vapor phase, although the latter is preferred because it can be carried out at atmospheric pressure. Industrially, a copper chromite catalyst is used, although this catalyst can become very toxic due to the presence of chromium [1]. Therefore, much attention is being paid to the development of chromium-free catalysts, more sustainable and environmentally friendly, as those based on Cu [2] or Ni [3] which are active and selective towards the formation of furfuryl alcohol and 2-methylfuran. Furfuryl alcohol is mainly used for the production of thermostatic resins, intermediate in the manufacture of lysine, vitamin C and dispersing agents. Meanwhile, 2-methyl furan is used in the synthesis of pesticides, or in the pharmaceutical and fragrance industries.

The aim of this work is the synthesis of a series of copper based catalysts, which have been synthesized by coprecipitation of copper and cerium(IV) and subsequent thermal programmed reduction. This method allows increasing the dispersion of Cu particles, while the use of a support like CeO$_2$ can modify the electronic density of the active phase, which can influence the catalytic activity and resistance to deactivation.

Materials and Methods.

A series of Cu-CeO$_2$ catalysts was prepared by coprecipitation method, with different Cu:Ce molar ratios (0.2-6). This procedure was performed by mixing aqueous solution of the corresponding metal nitrates (0.3 M of Cu(NO$_3$)$_2$·3H$_2$O (Sigma-Aldrich) and Ce(NO$_3$)$_4$·6H$_2$O (Sigma-Aldrich) and varying the metal molar ratio. The pH of the resulting solution was fixed at 11, by means of an aqueous solution of sodium hydroxide as precipitating agent. The solution was stirred at 50°C for 4 h, and, after cooling, it was aged at room temperature for 12 h. Finally, solids were filtered and dried at 90 °C for 12 h, and then calcined at 400 °C for 1 h. Prior to reaction, precursors were reduced at 220 °C under a H$_2$ flow of 60 ml min^{-1} for 1 h to obtain the Cu^0 phase.

The synthesized catalysts were characterized by X-ray diffraction (XRD), N$_2$ adsorption-desorption at -196 °C, H$_2$ thermal programmed reduction (H$_2$-TPR) and X-ray photoelectron spectroscopy (XPS).

The gas phase hydrogenation of furfural was carried out in an atmospheric pressure fixed-bed continuous flow quartz catalytic reactor, operated in the down-flow mode. The reaction temperature was controlled with a thermocouple in direct contact with the quartz reactor. The organic feed consisted of a solution of furfural (5 vol. %) in cyclo pentyl methyl ether, and it was supplied by means of a Gilson 307SC piston pump (model 10SC). For each catalytic test, 0.150 g of precursor was reduced in situ at atmospheric pressure with a H$_2$ flow of 60 ml min^{-1}, at 220 °C for 1 h. The catalytic activity was measured at 190 °C with a H$_2$ flow of 10 ml min^{-1} for 5 h. The evolution of the catalytic process was monitored by collecting liquid samples after 60 min, which were kept in sealed vials, and subsequently analyzed by gas chromatography (Shimadzu GC-14B, equipped with a flame ionization detector and a capillary column). The total conversion was calculated from the ratio of converted furfural/fed furfural. The selectivity toward the different reaction products was considering that furfuryl alcohol, 2-methylfuran and furan were the only products obtained in all cases.

Results and Discussion.

X-ray diffraction patterns of precursors show the presence of diffraction peaks attributed to ceria (CeO$_2$), together with peaks associated to CuO. The intensity of the CeO$_2$ peaks decreases with the copper content. In all cases, broad diffraction peaks are observed for both copper and cerium oxides, thus pointing out that the coprecipitation method leads to the formation of small crystallites of Cu and Ce oxides.

After reduction, the diffraction peaks of CuO disappear, arising new peaks assigned to Cu^0 species.

N$_2$ adsorption-desorption at -196 °C reveals that BET surface areas are lower than 90 m^2 g^{-1} in all cases. The porosity is attributed to the void space between particles.

In order to evaluate the reducibility degree of CuO and CeO$_2$, H$_2$-TPR analysis was carried out. It is well recognized that the reduction of bulk CuO takes place in only one step, about 380 °C, while the reduction of bulk ceria is accomplished in two steps. The first step assigned to coordinative unsaturated surface capping oxygen ions and the second one to bulk oxygen, that requires to be transported to the surface before reduction. The presence of CuO-CeO$_2$ interfacial sites decreases the reduction temperature of copper species to

values ranging between 100 and 220 °C. The H_2-TPR profiles reveal that CuO particles are highly dispersed and strongly interacting with CeO_2.

XPS analysis of the Cu-CeO_2 catalysts shows that the Ce 3d spectra can be decomposed in ten contributions: v, u (Ce $3d^9$ $4f^2$ O $2p^4$) and v'', u'' (Ce $3d^9$ $4f^1$ O $2p^5$); v''', u'''(final state of Ce $3d^9$ $4f^0$ O $2p^6$) assigned to Ce(IV); v_0,u_0 (Ce $3d^9$ $4f^2$ O $2p^5$) and v', u' (Ce $3d^9$ $4f^1$ O $2p^6$) assigned to Ce(III), as a consequence of the hybridization between the Ce 4f levels and the O 2p states. Cu 2p region shows a signal located at 932.8 eV, attributed Cu reduced species (Cu^+ and Cu^0). The absence of the shake-up satellite (940-945 eV) indicates that all Cu^{2+} species have been reduced. In order to discern between Cu^+ and Cu^0, Auger line was also studied. The presence of a maximum of kinetic energy about 919.0 eV corroborates the presence of Cu^0 species.

These catalysts were tested in the gas phase hydrogenation of furfural. Figure 1 shows that catalysts with higher copper content give rise to higher furfural conversion, with a lower deactivation, reaching conversion values close to 83% after 5 h on stream, while the catalysts with a lower copper content only reach conversion values close to 55%
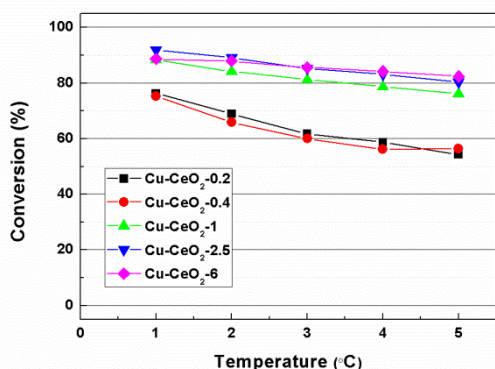

Fig. 1. Furfural conversion of Cu-CeO_2-*x* catalysts at 190 °C, as a function of time on stream. Reaction conditions: m_{cat} = 150 mg, H_2 flow = 10 ml min^{-1}, feed flow = 2.3 mmol h^{-1}.

Concerning the selectivity (Figures 2 and 3), it can be observed that selectivity towards 2-methylfuran decreases with time-on-stream, while the selectivity to furfuryl alcohol increases, reaching yield values of 67% and 15% for furfuryl alcohol and 2-methyl furan, respectively, for the Cu-CeO_2-6 catalyst.
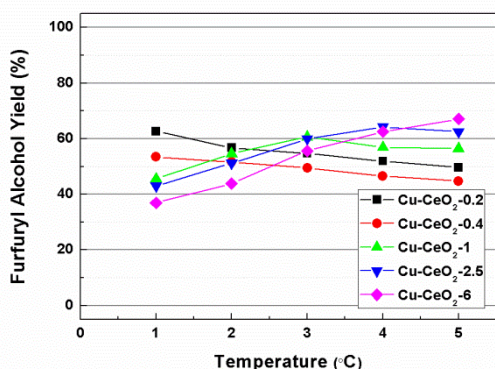

Fig. 2. Furfuryl alcohol yield for Cu-CeO_2-*x* catalysts at 190 °C, as a function of time on stream.
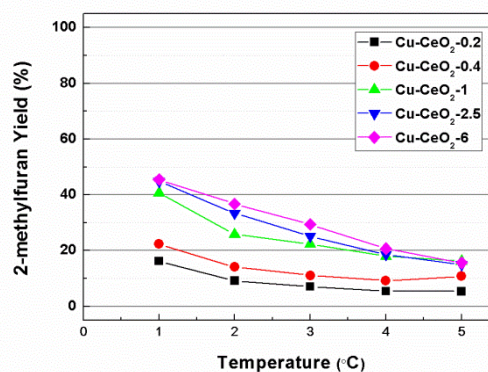

Fig. 3. 2-methylfuran yield for Cu-CeO_2-*x* catalysts at 190 °C, as a function of time on stream.

The spent catalysts have been characterized by using different techniques (CHN analysis, N_2 sorption, XRD and XPS) in order to justify the evolution of the catalytic performance with time-on-stream, and study the modification of textural and structural properties of catalysts after the catalytic process.

Acknowledgements.

References.

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