Cr-free Ni/MgO catalysts for hydrogenation of furfural

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1. Introduction

In the last century, the industrial development and the increase of the world population have caused the depletion of fossil reserves. This fact together with others factors have led to the search of alternative. Biomass is emerging as a widely available source to produce energy and, excluding fossil fuels, is the only source that can provide liquid fuels and chemicals. Lignocellulose is formed by cellulose, hemicellulose, lignin and other extractable components[1]. In the case of hemicellulose, its hydrolysis leads to the formation of xylans and pentosans, which after dehydration can give rise to furfural.

The high interest for furfural is attributed to its chemical structure, which provide high reactivity, making it potentially interesting for the synthesis of a vast variety of high value-added chemicals. Two of these important chemicals are furfuryl alcohol (FOL) and 2-methylfuran (MF), can be synthesized through hydrogenation of furfural, either in liquid or vapor phase. FOL is mainly used for the production of thermostatic resins, intermediates in the manufacture of lysines, vitamin C and dispersing agents. Meanwhile, MF is used in the synthesis of pesticides, in the pharmaceutical or perfume industries. Industrially, copper chromite catalyst is used, although the toxicity associated to the presence of chromium species has prompted the search of Cr-free catalysts[2]. Therefore, much attention is being paid to the development of more sustainable and environmentally friendly catalysts, among them, catalytic systems based on Cu or Ni have demonstrated to be active and selective towards the formation of FOL and MF.[3,4] The dispersion of metal species and their interaction with the support are key parameters that affect the catalytic activity and stability of catalysts. The use of metal oxides as supports can allow to obtain highly active and stable catalytic systems, and the electronic density of metal sites can be modified. The present work is aimed at the synthesis by Ni/MgO catalysts and the evaluation of their catalytic performance in the gas phase hydrogenation of furfural, at atmospheric pressure.

2. Experimental

A series of Ni/MgO catalyst were prepared by coprecipitation method, with different nickel: magnesium molar ratios (0.1-0.3). This procedure was performed by the simultaneous mixing of an aqueous solution of metal nitrates, and the pH was increased until 11 by adding a NaOH aqueous solution to precipitate the corresponding metal hydroxides. The suspension was stirred for 12 hours and later cooled. Finally, Solids were filtered and dried at 90 ℃ for 12 hours, and then calcined at 400 ℃ for 1 hour. Prior to reaction, precursors were reduced at 500 ℃ under a H_2 flow of 60 ml min^{-1}, for 1 h to obtain the Ni^0 phase.

The synthesized catalysts were characterized by N_2 adsorption-desorption at -196 ℃, X-ray diffraction (XRD), H_2-thermoprogrammed reduction (H_2-TPR) and X-ray photoelectron spectroscopy (XPS). The gas phase hydrogenation of furfural was carried out by using a fixed-bed continuous-flow quartz reactor, at atmospheric pressure. The organic feed consisted of a solution of furfural (5 vol. %) in cyclopentyl methyl ether. The catalytic activities were measured in a range of temperature (170 -230 ℃) with a H_2-flow of 10 ml min^{-1} for 5 hours. The evolution of the reaction was followed by collecting liquid samples after 60 min.

3. Results and discussion

X-ray diffraction patterns off the precursors show the presence of diffraction peaks, which can be associated to magnesium oxide (Figure 1 (A)), although crystalline NiO signals appear very close to those of

MgO. The intensity of these peaks decreases with the increase of the nickel content in the catalyst. After the reduction process, new diffraction peaks assigned to Ni^0 species arise.

The determination of textural parameters reveals that an increase of the nickel content provokes a decrease of the specific surface area (S_{BET}) from 84 m^2g^{-1} for the catalyst 0.10-Ni_MgO to 143 m^2g^{-1} for the 0.30-Ni_MgO catalyst (Table 1). The porosity could be mainly attributed to interparticle voids.

Table 1. Metal characteristics of nickel-based catalyst.

Sample	S_{BET} (m^2g^{-1})	t_{plot} (m^2g^{-1})	V_p (cm^3g^{-1})	V_{microp} (cm^3g^{-1})
0.10-Ni_MgO	84	4	0.318	0.0027
0.15-Ni_MgO	199	8	0.408	0.0033
0.20-Ni_MgO	179	2	0.380	0.0018
0.25-Ni_MgO	244	1	0.337	0.0008
0.30-Ni_MgO	143	2	0.353	0.0002

The catalysts were tested in the selective hydrogenation of furfural. The catalyst with an intermediate nickel loading (0.20-Ni_MgO) shows conversion values close 100%, after 5 h TOS, and yield values of 85% and 10% for furan and furfuryl alcohol, respectively. However, catalysts with a lower and higher nickel contents exhibit conversion values lower to 80%.
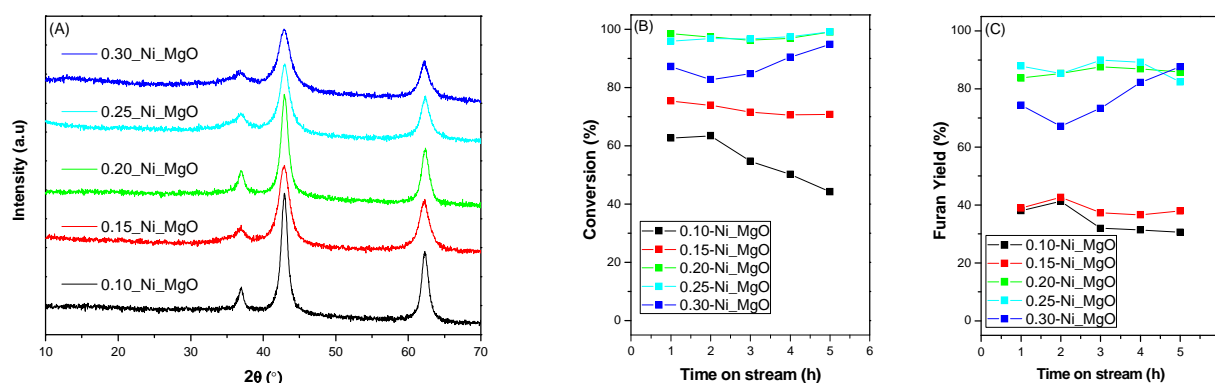

Figure 1. (A) Powder X-ray diffraction patterns of x-Ni_MgO catalysts after calcination at 773 K and (B) furfural conversion and (C) furan yield of x-Ni_Mg catalysts at 190 °C, as a function of time on stream.

4. Conclusions

x-Ni_MgO catalysts have been tested in the furfural hydrogenation, attaining the full furfural conversion with the 0.20-Ni_MgO catalyst, after 5 h of TOS, at 190 °C, by feeding a 5% furfural solution in cyclopentyl methyl ether, at a constant flow of hydrogen of 10 ml min^{-1}. In all cases, catalysts are highly selective to furan. The analysis of the influence of the reaction temperature has revealed the existence of a volcano distribution, attaining the best catalytic performance at 190 °C. However, all catalysts suffer a progressive deactivation with TOS, by deposition of reactants and product.

5. Acknowledgments

References

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