

Furfuryl alcohol production by liquid phase catalytic transfer hydrogenation of furfural on alumina as Lewis acid catalyst

C.P. Jiménez-Gómez, J.A. Cecilia, R. Moreno-Tost, J. Santamaría-González, P. Maireles-Torres

Universidad de Málaga, Departamento de Química Inorgánica, Cristalografía y Mineralogía (Unidad Asociada al ICP-CSIC), Facultad de Ciencias, Campus de Teatinos, 29071 Málaga, Spain

Keywords: *biomass; lignocellulose; catalytic transfer hydrogenation; furfural; furfuryl alcohol; alumina*

Currently, much attention is being paid to the development of efficient and environmentally friendly technologies for the sustainable production of energy, fuels and chemicals [1]. In this context, lignocellulosic biomass appears as a renewable alternative feedstock to fossil resources. Thus, dehydration of C5 carbohydrates leads to furfural (FUR), a versatile platform molecule for the synthesis of a large spectrum of chemicals. Among them, the most important is furfuryl alcohol (FOL), accounting for 65% of FUR production, which finds application in the preparation of resins used as high-quality cores and molds for metal casting, reactive solvent for phenolic resins in the refractory industry, chemical building block for the synthesis of tetrahydrofurfuryl alcohol and pharmaceuticals and manufacture of fragrances [2,3]. FOL is prepared industrially by the catalytic hydrogenation of furfural, which can be carried out in vapor or liquid-phases, being the former in the presence of copper chromite the preferred industrial route. However, other products such as 2-methylfuran, tetrahydrofurfuryl alcohol and 2-methyl tetrahydrofuran can result from furfural hydrogenation, besides furan and THF, different pentanediols, 2-pentanone and 2-pentanol, cyclopentanone and cyclopentanol. The selectivity pattern depends strongly on reaction conditions and on the nature of the catalyst used. Nevertheless, a synthetic approach based on the catalytic transfer hydrogenation (CTH), based on the Meerwein-Ponndorf-Verley (MPV) reduction of an aldehyde (or ketone) coupled to the oxidation of a secondary alcohol, has been also proposed, which does not require supply of external hydrogen and the alcohol can be chosen in order to produce an aldehyde or ketone with industrial applications [4,5].

The present contribution deals with the production of FOL from furfural by CTH, using different commercial aluminas as catalysts and a secondary alcohol as hydrogen donor, in liquid phase. The results have demonstrated that the formation of other by-products is minimized and FOL is produced in high yield, at temperatures ranging between 90 and 150°C, by using 2-propanol. Thus, full conversion of furfural and a FOL selectivity higher than 90 mol% are attained after only 2 h, at 150°C, a FUR concentration of 0.25 M in 2-propanol and a catalyst/FUR weight ratio of 1:1 (Fig. 1). A reaction mechanism, involving Lewis acid sites present on the alumina surface in the activation of FUR and 2-propanol, has been put forward. Different experimental parameters (FUR concentration, reaction temperature, catalyst loading, type of alumina and nature of

alcohol) have been optimized in order to achieve suitable FOL yields. Moreover, reutilization has been evaluated to support the advantage of the heterogeneous catalytic process which allows the reuse of the solid catalyst. Finally, and considering that dehydration of xylose to furfural is accomplished in the presence of solid acid catalysts, the one-pot synthesis of FOL from xylose has been undertaken by tuning selected experimental variables.

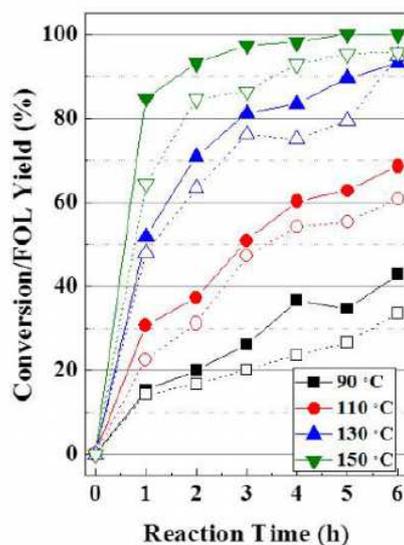


Figure 1. Kinetic of catalytic transfer hydrogenation of furfural in the presence of alumina as a function of the reaction temperature (Experimental conditions: 0.25 M FUR in 2-propanol; cat:FUR weight ratio= 1:1, 100 mg catalyst) Closed symbols: FUR conversion, Open symbols: FOL yield

The authors are grateful for financial support from the Spanish Ministry of Economy and Competitiveness (CTQ2015-64226-C3-3- R project), Junta de Andalucía (P12-RNM-1565), and FEDER (European Union) funds.

[1] A. Corma, S. Iborra, A. Velty, Chemical routes for the transformation of biomass into chemicals, *Chem. Rev.* 2007, 107, 2411-2502.

[2] R. Mariscal, P. Maireles-Torres, M. Ojeda, I. Sádaba, M. López-Granados, Furfural: a renewable and versatile platform molecule for the synthesis of chemicals and fuels, *Energy Environ. Sci.* 2016, 9, 1144-1189.

[3] J.P. Lange, E. van der Heide, J. van Buijtenen, R. Price, Furfural-A promising platform for lignocellulosic biofuels, *ChemSusChem* 2012, 4, 150-166.

[4] M.J. Gilkey, B. Xu, Heterogeneous catalytic transfer hydrogenation as an effective pathway in biomass upgrading, *ACS Catalysis* 2016, 6, 1420-1436.

[5] M.M. Villaverde, T.F. Garetto, A.J. Marchi, Liquid-phase transfer hydrogenation of furfural to furfuryl alcohol on Cu-Mg-Al catalysts, *Catal. Commun.* 2015, 58, 6-10.