Synthesis of Hollow Mesoporous Spheres modified with ZrO_2 and non-noble metals for the one-step reaction of furfural to 1,4-pentanediol.

R. Maderuelo-Solera, J.A. Cecilia, C. García-Sancho, R. Moreno-Tost, J. Mérida-Robles, P. Maireles-Torres

Departamento de Química Inorgánica, Cristalografía y Mineralogía, Facultad de Ciencias, Universidad de Málaga, Campus de Teatinos, 29071 Málaga, España.
rocioms@uma.es

To date, the one-pot step from furfural to pentanediols (PDs) only obtains conversions and selectivities referable to noble catalysts. In addition, the most obtained pentanediol has been 1,2-PD followed by 1,5-PD but the direct conversion of furfural to 1,4 pentanediol is the most difficult route. Another problem related to this reaction is the scarcity and the high cost of noble metals, which makes them not the solution for obtaining pentanediols in the nearly future [1-5]. Therefore, this work focuses on the synthesis, catalysis and characterisation of catalysts based on non-noble metals such as Zr, Cu and Co in order to enhance the properties of these catalysts capable of assisting in the hydrogenation of furfural to open its ring and obtain various pentanediols.

The synthesis of these porous SiO_2 nanospheres modified with ZrO_2 was based on a previous work [6] to which different metal loadings were co-precipitated to obtain a family of catalysts ranging from 15% Cu to 15% Co. These were compared with the catalyst without metal loading to check that the addition of non-noble metals contributes an important function to the reaction.

For the synthesis of the nanospheres, SiO_2 of pore size 0.2-0.3 µm was used, previously dried in an oven and avoiding contact with the atmosphere. Toluene was added and once the silica was dispersed, Zr n-propoxide was added taking care that the atmosphere was kept inert with a continuous stream of He. It was stirred at 115°C for 12 hours. The gelatinous solid obtained was centrifuged and filtered with the aid of a Buchner funnel and washed with toluene to avoid the contact with water. Finally, the solid is left to dry in an oven at about 60°C.

For the incorporation of the metal load of the desired metals, the determined amount of nitrate of the metal was dissolved in 100 mL of deionised water and then, the support was added. In the next step, the pH of the solution was increased adding a NaOH solution to reach a pH of 9. After this, the synthesis is aged for at least one hour. Filtration is carried out again with a Büchner funnel, the solid is dried and calcined in an oven at about 500°C for 2 hours.

The EDX images show that the synthesis has generated spheres where Zr, Co and Cu are covering the silica particles. Regarding to the porosity of the catalysts, it can be seen how the introduction of metals decreases both the BET surface area and the pore volume and size, with copper being the metal that most reduces these parameters, which was to be expected since its atomic ratio is lower than that cobalt atomic ratio.

The catalytic tests were carried out at 170°C and (3-48 h) using different H_2 pressures (1-4 MPa). The catalytic results show an almost total conversion of furfural from 3 hours of reaction and an average yield of 10-15% of 1,4-PD, obtaining the highest yield in pentanediols (1,4-PD+1,5-PD) for Zr-HMS-7.5Cu7.5Co catalyst. Other products of interest such as furfuryl alcohol (FOL), tetrahydrofurfuryl alcohol (THFA), 1-pentanediol (1-Pent), 2-methylfuran (2-MF) and 2-methyltetrahydrofuran (2-MTHF) are also obtained.

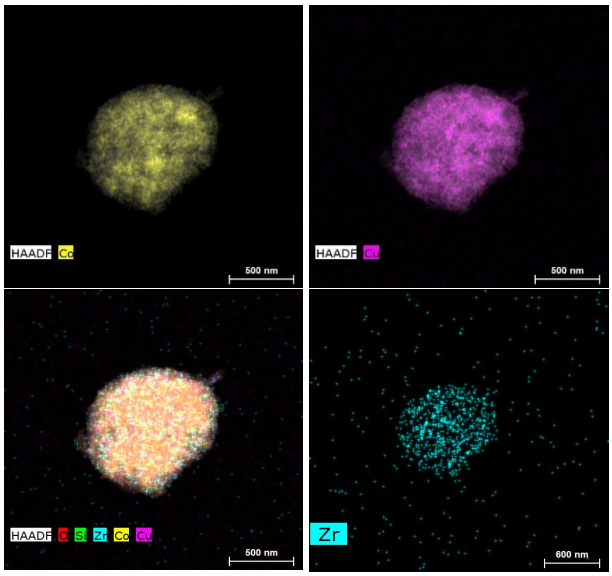

Figure 1: EDX images of Zr-HMS-7.5Cu7.5Co catalyst.

Tabla 1: Textural parameter of the catalysts

Sample	$S_{BET}(m^2g^{-1})$	$t\text{-}_{plot}(m^2g^{-1})$	$V_p(cm^3g^{-1})$	$V_{mic}(cm^3g^{-1})$
Zr-HMS	483	127	0.466	0.0597
Zr-HMS-15Cu	217	26	0.304	0.0072
Zr-HMS-15Co	282	113	0.304	0.0568
Zr-HMS-7.5Cu7.5Co	328	29	0.617	0.0104
Zr-HMS-11.25Cu3.75Co	203	86	0.230	0.0364
Zr-HMS-3.75Cu11.25Co	267	75	0.374	0.0323

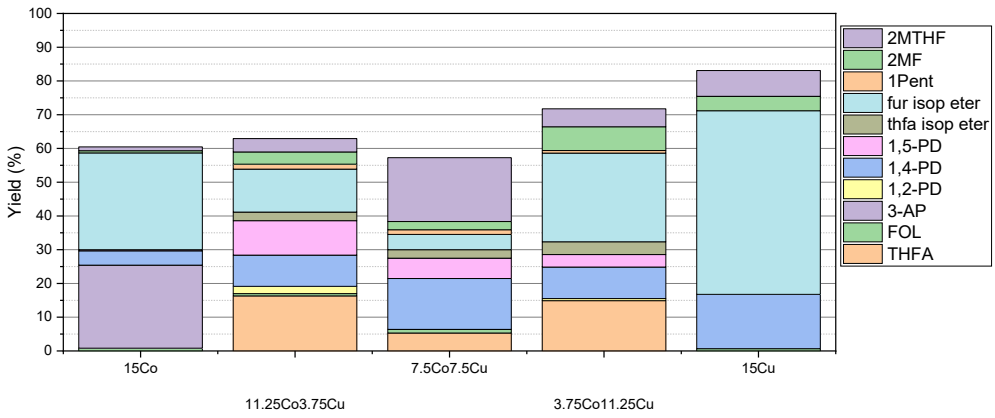

Figure 2: Catalytic results of the catalyst family at 22 hours. Reaction conditions: 170ºC, 4 MPa H_2.

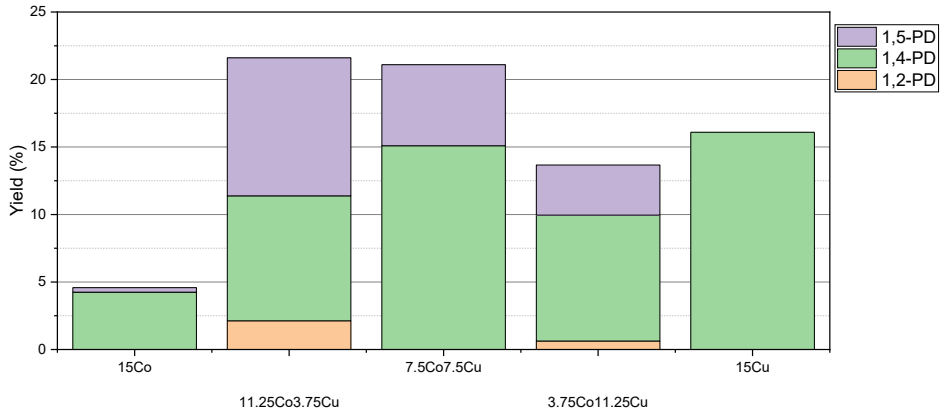

Figure 3: Detail of catalytic results of the pentanediols obtained at 22 hours. Reaction conditions: 170ºC, 4 MPa H2.

References

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