Glucose dehydration to 5-hydroxymethylfurfural on zirconium containing mesoporous MCM-41 silica catalysts

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Nowadays, the search for alternatives to platform chemicals derived from fossil sources has been intensified. In this respect, waste lignocellulosic biomass is becoming an attractive renewable feedstock for platform chemicals and biofuels. Agriculture waste and energy crops consist of three main products: cellulose (40-50%), hemicellulose (25-35%) and lignin (5-20%), with glucose being the building block of cellulose. High glucose yields can be achieved via enzymatic hydrolysis of cellulose, although this hydrolysis can be also performed under more drastic conditions, using mineral acids at elevated temperatures. 5-hydroxymethylfurfural (HMF) is a very interesting platform molecule prepared by dehydration of saccharides; thus, one of its derivatives, 2,5-furandicarboxylic acid, may replace terephthalic acid as a monomer in the preparation of plastics. The most usual method for HMF production is the acid-catalysed triple dehydration of fructose, a quite easy reaction, whereas other saccharides like glucose requires special catalysts for the formation of HMF. However, the principal drawback of fructose is its high price and scarcity. As a consequence, the use of glucose as a starting substrate for the HMF production could be more beneficial.

On the other hand, the use of mesoporous solids as catalysts has resulted in significant improvements for many catalytic reactions when compared to conventional ones. MCM-41 silica and its derivatives present attractive properties to be used as supports or catalysts, such as narrow pore size distributions, very high specific surface areas, suitable acidity and high thermal stability. The aim of the present work is to compare the catalytic behaviour in the dehydration of glucose of different zirconium containing silica catalysts, prepared by varying the method of zirconium incorporation into a MCM-41 silica: a) MCM-41 doped with zirconium in the synthesis step and activated at 550 ºC and 750 ºC (Zr-MCM-550 and Zr-MCM-750) [1]. b) Zr-MCM-41 impregnated with sulphuric acid (12 wt.%) and calcined at 750 ºC (12S-Zr-MCM) and c) zirconium sulphate impregnated (30 wt.%) on MCM-41 and calcined at 750 ºC (Zr-30-MCM).

For the dehydration reaction of glucose, a two-phase reactor system, consisting in water-methylisobuthylketone (MIBK), was used. This solvent has been employed successfully by other authors [1]. The catalytic reaction was carried out in a glass reactor of 15 mL provided with a screw top of Teflon, at 175 ºC and 2.5 h of reaction time. Zero time was taken when temperature of the reactor reached 175 ºC; the stirring rate was 600 rpm. The amount of catalyst was 50 mg, 0.15 g of substrate in deionized water (1.5 g) and 3.5 ml of MIBK. After reaction time, the reaction was quenched by introducing the reactor in a bath with cooled water; the liquid phases were separated and filtered and the analysis of products was done in both phases. Glucose conversion and the product selectivity were calculated according to the following equations:

Glucose conversion (wt.%)= (mass of starting glucose – mass of remaining glucose) * 100 / mass of starting glucose

Product selectivity (mol%)= moles of produced product * 100 / moles of glucose reacted

Both the aqueous and the organic layers were analyzed HPLC.

All catalysts were characterized by powder XRD to confirm their mesostructure and exhibit in the low angles region a peak close to $2\theta = 2.05^{\circ}$ corresponding to a d_{100} parameter close to 4.3 nm.

Textural characteristics were evaluated from nitrogen adsorption-desorption isotherms (Table 1). All zirconium containing materials exhibit reversible type IV isotherms. Surface area and pore volume of Zr-MCM-750 sample decrease with respect to Zr-MCM-550, which can be explained by the reorganization and slight shrinkage of the mesoporous structure after the thermal activation. The textural parameters for 12S-Zr-MCM and Zr-30-MCM are slightly lower than those of their pristine supports, possibly as a consequence of the thermal treatment and the presence of nanoparticles of ZrO_2 blocking the access to the mesoporous network.

Ammonia TPD was used to determine the total acidity of catalysts, and the corresponding values are compiled in Table 1.

Table 1

Catalyst	S ($m^2 g^{-1}$)	V_p ($cm^3 g^{-1}$)	dp (nm)	NH_3 desorbed ($\mu mol\, g^{-1}$)
Zr-MCM-550	635	0.68	4.3	563
Zr-MCM-750	553	0.46	3.3	359
12S-Zr-MCM	470	0.48	3.3	282
Zr-30-MCM	359	0.21	2.3	371

Firstly, the influence of the temperature on the catalytic reaction has been evaluated by using the Zr-MCM-550 catalyst. The catalytic results reflect that glucose conversion rises with temperature, achieving a value close to 82 % at 185 ºC. The slight increasing in glucose conversion from 175 to 185ºC can be explained by the rapid formation of humins on the catalyst surface, thus covering some acid sites and limiting the transformation of glucose; in fact, the catalyst became brown after 15 min of reaction at the highest temperature. As reaction products, only fructose and HMF were found, being the former favoured at low temperatures, whereas the selectivity to HMF ameliorates at higher temperatures. That means that glucose is rapidly transformed, in a first step, into fructose, which is subsequently dehydrated to HMF, mainly at high temperatures. This fact reveals the existence of basic centres, which favour the glucose to fructose isomerisation, which is faster than the dehydration to HMF at low temperatures. However, at high temperatures, the dehydration rate of fructose to HMF increases, achieving the maximum HMF yield (25.4 %) at 185 ºC. Nevertheless, at 175 ºC, the HMF selectivity and yield values are quite similar, and this temperature was selected to study the influence of other parameters on the catalytic performance. The activity of this Zr-MCM-550 catalyst was expected since this solid exhibits a suitable acidity (563 μmol NH_3 g^{-1}).

The next step in the catalytic study was to evaluate the influence of the reaction time at 175 ºC. The obtained data indicate that the transformation of glucose to fructose is very fast, since 47 % of fructose selectivity was achieved after 30 min, but for increasing reaction times, the selectivity toward fructose decreases owing to its transformation into HMF. Thus, the selectivity toward HMF monotonously increases with the reaction time, attaining the maximum value of 28 % after 2.5 hours. Nevertheless, higher reaction times barely improve the formation of HMF, possibly due to the preferential formation of soluble polymers and humins, as well as the deposition of residues formed from intermediates condensation on the active sites. From these data, 2.5 h of reaction time was considered as optimal reaction time to study other parameters of the catalytic process.

Once the most suitable experimental conditions have been selected (temperature = 175 ºC, reaction time = 2.5 h and 50 mg of catalyst weight), all the catalysts have been evaluated in this catalytic process (Figure 1). From these data, it is deduced that the catalytic response depends upon the acidity of the catalyst. Thus, Zr-MCM-550 is the most active, according with its higher acidity amongst the zirconium containing MCM-41 silica catalysts, achieving the maximum HMF yield (23 wt.%), whereas Zr-30-MCM is the less active. This last catalyst exhibits good acidity, but the existence of smaller pores (Table 1) could difficult the accessibility of reactants to the acid sites. In any case, all the studied catalysts are moderately active in this catalytic reaction with TOFs varying between 1.3 and 1.8 mmol of HMF g^{-1} h^{-1}.

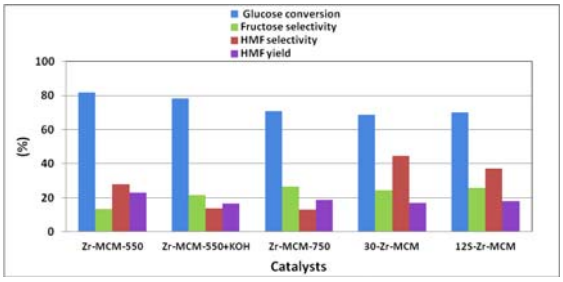

Figure 1

In summary, among the catalysts based on ZrO_2/MCM-41 assayed in the dehydration of glucose to HMF in a biphasic reactor system, Zr-MCM-550 catalyst has demonstrated to be the most active, exhibiting high glucose conversion (82 %) with exclusive formation of fructose (13.2 % selectivity) and HMF (23 wt.% yield) at 175 ºC and after 2.5 h of reaction time. Moreover, this catalyst is stable in the reaction medium and can be reused at least for three cycles of reaction. After calcination at 500 ºC (2 h) its activity is fully recovered

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