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Selective transformations of cellulose derived compounds catalyzed by heterogeneous materials

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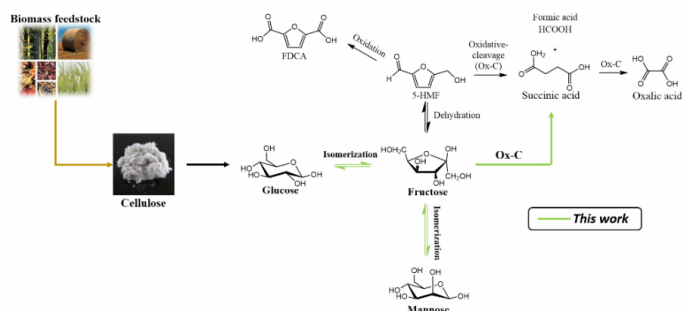
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PURPOSE OF THE ABSTRACT

The transformation of renewable biomass into chemicals is becoming more and more attractive as a way to avoid the aggravation of CO₂ emission and diversify sources of energy and materials.[1] In this context, biomass represents an available carbon-neutral renewable resource for the production of bioenergy, biochemicals, and biomaterials. The use of non-edible biomass as agricultural, wood or paper residues, it is more desirable because it eliminates the competition against food. Cellulose, that is one of the major components of these residues, is a homo-polysaccharide comprising on units of D-Glucose linked together via beta-1,4-glycosidic linkages. The development of cost-effective catalytic processes adapted to the molecular structure of functionalized biomass-sourced molecules is a challenging task. The key reaction to achieve good productivity on the transformations of these cellulose-derived materials is the isomerization of glucose to fructose since the latest one would be the platform for other important derivatives as it is shown in Scheme 1. The use of heterogeneous catalysts and non-toxic solvents is more desirable in order to build a more sustainable process. Following these premises, catalysts based on hydrotalcite-type derived materials comprised by Mg-Ca-Al or by Ca-Al have been used to perform the selective isomerization glucose towards fructose, using water as solvent under mild reaction conditions (Table 1).[2] They showed good performance getting very high activity, conversion=51%, and excellent selectivity (88%) compared with the current industrial process based on the transformation via biocatalysis.[3] The stability and recyclability of the catalysts were tested only detecting a small activity loss after 5 consecutive runs. Results of Table 1 indicates that it was also possible to modulate the selectivity towards fructose or mannose by tuning the number of the basic sites of the catalysts. Therefore, the combination of acid and basic sites plays a key role in the reaction, a fact that will be discussed during the presentation, as well as other important operational parameters, such as reaction pressure and temperature. The synthesis of the catalysts and their characterization will be also discussed since they are one of few cases found in the literature of this kind of hydrotalcite-type materials with a high level of Ca incorporation.

Finally, and in order to increase the added-value of bio-products obtained, an additional transformation of fructose such as its oxidation-cleavage to achieve succinic (SA) or oxalic (OA) acids by using Fe-supported on carbon (Fe@CNT) catalysts was also essayed. These catalysts showed very high activity (fructose conversion = 99%) and selectivity (around 50%) mainly towards OA.[4] More interestingly, none of the reactions shown in this work needs any pre-treatment or additives, such as bases, for obtaining high yield and selectivity of bio-products, using water as solvent and mild reaction conditions.

FIGURES



Entry	Catalyst	M ²⁺ /M ³⁺ Molar ratio	Conversion (%)	Fructose Selectivity (%)	Mannose Selectivity (%)
1	HTC-CaAl	0.8	18.7	99.9	0.0
2		2.3	48.8	87.7	9.2
3		3.0	50.4	87.4	10.6
4		3.4	89.2	27.4	72.5
6	HTC-MgCaAl	1.9	18.7	99.9	0.0
7		2.1	28.1	89.9	0.0
8		2.3	40.4	79.9	1.5

FIGURE 1

Scheme 1

Transformations of cellulose derivatives

FIGURE 2

Table 1

Reaction conditions: Glucose (0.5 g) in water (5 g) with catalyst (0.05g) at 363 K and PN2 = 10 bar during 90 min

KEYWORDS

Heterogeneous catalysts | Biomass | Cellulose | Isomerization

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