

Cellulose conversion into hydroxymethylfurfural (HMF): catalysis under sustainable conditions in aqueous media in absence of polluting chemicals

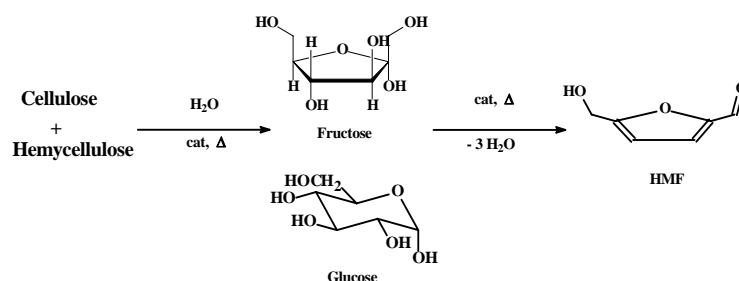
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Introduction

5-Hydroxymethylfurfural (HMF), which can be prepared by dehydration of saccharides, is known to be a starting material in a possible production of biomass-derived fuels as well as a key platform molecule for non-petroleum derived chemicals [1]. One of its derivatives, 2,5-furandicarboxylic acid, may replace terephthalic acid as a monomer in the preparation of plastics [2]. The most convenient synthetic method of HMF is based on the acid-catalyzed triple dehydration of fructose. Several types of acid catalysts have been used in this process, such as mineral acids, strong acid cationic exchange resins, and zeolites in their H-form [3]. The moment being, fructose is the preferred feed for optimal HMF yield, but it is clear that for a large and sustainable scale use of HMF, cellulosic biomass should be used as feed. Such approach involves depolymerization and hydrolysis of cellulose to form glucose, followed by its conversion into HMF. (Scheme 1)



Scheme 1. Cellulose conversion into HMF: key steps in the process.

Although “there is an abundant amount of literature available on HMF (over 1000 references),...”[4] the conversion of saccharides into HMF with heterogeneous catalysts is not fully understood and documented. Heterogeneous acid catalysts offer the advantage of a very easy separation from the reaction products and recycling, thus appearing the most suitable catalysts for a potential industrial application.

In this work we present our approach to a direct conversion, under selective, mild, and catalytic reaction conditions, of cellulose or glucose into HMF.

The direct conversion of cellulose into HMF is working at high temperature (250°C) in water, but the harsh conditions required and the high lability of starting and final organic compounds, produce a low yield because of a high loss of material.

Our aim is to avoid the use of organic solvents, ionic liquids, mineral acids and poisoning-metals (frequently used in the last years) [5], working under heterogeneous catalysis, in the mildest possible conditions avoiding any loss of starting cellulose or glucose in the form of humins or any other by-products. Our strategy consists in the hydrolysis of cellulose into glucose, converting the latter into fructose under basic conditions, and to finally dehydrating the fructose into HMF under acid catalysis using a single bi-functional (basic-acid) catalyst.

Experimental

Our Group has expertise in the synthesis of bifunctional oxides as shown by the scientific and patent literature [6]. In fact we have already used bi-functional catalysts in the direct carboxylation of alcohols to afford dialkylcarbonates. In particular we have used cerium(IV)oxide as host structure, modified with hetero-metals such as aluminium and niobium

Such mixed oxides have been synthesised by calcinations of the mixed hydroxides obtained using a Zinsser Analytic Sophas Automatic Synthesizer. The mentioned mixed hydroxides have been prepared by precipitating with ammonia (10%w) a solution obtained by mixing in the correct ratio different metal solutions of (NH₄)₂Ce(NO₃)₆, Al(NO₃)₃ and [Nb(OEt)₅]₂. Each step has been carried out in the Automatic Synthesizer in order to have reproducible results.

The catalysts have been fully characterized (surface analysis: BET, TPD, XPS, DRIFT; structural analysis: XRD, elemental analysis ecc) before and after use in catalysis in order to determine their modification upon use. The catalytic tests have been carried out using a steel autoclave equipped with four parallel reactors (see Figure 1).

In each reactor 20 mg of catalyst and 2 mL of a 5%w glucose solution have been charged and heated at 423 K for 3 h. At the end of the reaction, the solution has been filtered and analyzed using HPLC equipped with a Biorad HPX87H column (60°C) and a RI detector.

Results and Discussion

Figure 1 reports the conversion of the starting glucose into HMF using different catalysts.

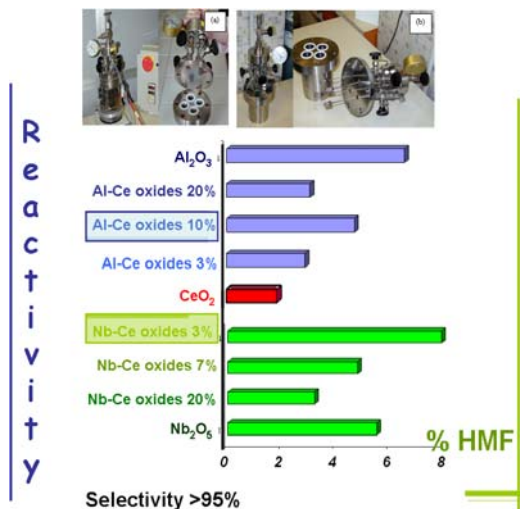


Figure 1. Catalytic conversions of glucose into HMF.

From Figure 1, it is evident that the best catalyst is the Nb/Ceria (3/100) mixed oxide. In each case, a very high selectivity has been observed. We have fully characterized each system used in catalysis and have found that the presence of niobium (already in small amount) modifies drastically the ceria properties by:

- increasing the number of basic-acid sites;
- increasing the number of strong sites (basic and acid);
- increasing the BET surface area.

The Nb(3%)CeO₂ catalysts has also been used in a flow reactor with the same performance as in bulk.

Conclusions

In this work we have presented a direct and very selective conversion of glucose into HMF under unprecedented mild conditions using bifunctional catalysts. The best catalyst has also been used in a continuous flow reactor which improved the overall conversion.

References

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