

New nanocatalyst for hydrolysis of biomass to levulinic acid

Maria Sarno^{1,2*}, Mariagrazia Iuliano³

*1*Department of Physics “E.R. Caianiello”, University of Salerno, via Giovanni Paolo II, 132 - 84084 Fisciano (SA), Italy

*2*NANO_MATES Research Centre, University of Salerno, via Giovanni Paolo II, 132 - 84084 Fisciano (SA), Italy

*3*Department of Industrial Engineering, University of Salerno, via Giovanni Paolo II, 132 - 84084 Fisciano (SA), Italy

*Italy**Corresponding author E-Mail: msarno@unisa.it

1. Introduction

In the last decade, biofuels have attracted significant attention as potentially viable renewable substitutes. In particular, the manufacture of fuels and chemicals [1,2] from biomass will reduce total CO₂ emission and global warming. Recently, considerable research attention is concentrated on the development of attractive techno-economical and environmentally benign approaches for the transformation of waste feedstock into platform chemicals, to obtain various biofuels, foods, and medicines,...

Lignocellulosic biomasses are ideal starting materials for fuel manufacturing, as 150 billion tonnes of LCBs are produced per year [3]. Various catalytic approaches have been attempted on pure cellulose, already derived from biomasses, such as: H₂SO₄, HCl and HBr homogeneous acid hydrolysers, supercritical water hydrolysis, heterogeneous acid hydrolysis and enzymatic hydrolysis. Acid-catalyzed hydrolysis, a process generally conducted at a relatively mild temperature (100–250 °C), has been regarded as an essential step for bioenergy production, and furfural, glucose, 5-hydroxymethylfurfural (HMF) and levulinic acid (LA) are regarded as key intermediate platform chemicals. The hemicellulose can be converted to xylose and furfural, while cellulose can be hydrolyzed to glucose, HMF, and LA. The lignin and humins are solid residues left from hydrolysis of biomass. The furfural, glucose, HMF and LA obtained can be further upgraded to biofuels and biofuel additives, and the solid residues can be used for heat generation and aromatic bio-oil production. Moreover, LA is a chemical bridge connecting biomass and petroleum processing, has also been regarded as a desirable feedstock for liquid fuel production. In particular, LA can be converted to a family of valerate esters (e.g., methyl, ethyl, and propylvalerate) using as gasoline additive. In addition, LA can be converted to resins, solvents, polymers, and chemical intermediates. LA is also an important source for spice, cosmetics, pharmaceutical, pesticide, and fungicide production.

However, some distinct drawbacks are present in the traditional methods such as the corrosion and harsh reaction conditions, which limits the practical utility. The use of heterogeneous catalysts may overcome the above-mentioned drawbacks. Recently, hydrolysis of cellulose over heterogeneous catalysts has been widely investigated [4]. Although heterogeneous catalysts are often recycled more easily than their homogeneous counterparts, the tedious recovery procedure via filtration or centrifugation and the inevitable loss of solid catalysts in the separation process still limited their application, particularly for the small nano-sized particles. Magnetic nanoparticles (MNPs) based catalysts have recently been receiving growing attention, as

they can be readily separated from the reaction mixture by a permanent magnet. In particular, for the hydrolysis of cellulose, the surface of NPs can be functionalized with several functional groups to build different catalysts. Herein, a simple one-step strategy, using a new magnetic acid catalyst, based on Rh and Ru supported magnetite, for hydrolysis of lignocellulosic biomass to obtain levulinic acid, was presented.

2. Methods

NPs after sonication was monitored under TEM (Transmission electron microscopy) (FEI-Tecnai; 200 KV) analysis. For thermogravimetric analyses, an SDTQ 600-TA Instruments was used under an airflow at 10 °C/min. By applying KBr technique, and using a Vertex 70 apparatus (Bruker Corporation), FT-IR spectra were obtained. X-ray diffraction measurements were also performed by a Bruker D8 X-ray diffractometer using CuK α radiation. Soluble product after hydrolysis was analysed with Thermo-Fischer gas chromatography equipment, capillary column (0.25 μ m \times 0.25 mm \times 60 m), and high-performance liquid chromatography (HPLC, Thermo Scientific) with Dionex CarboPac SA10 Analytical, column and refractive index detector, and calibrated with standards, was used for sugars analysis.

3. Results and discussion

The hydrolysis was carried out by using a ratio of 1 mg_{catalyst}/mg_{biomass} at 190 °C. The yields of levulinic acid increased during the time, up 65.3% after 4 h. The nanocatalyst showed relatively high stability, moreover after 5 cycle yield of levulinic acid is still about 40%.

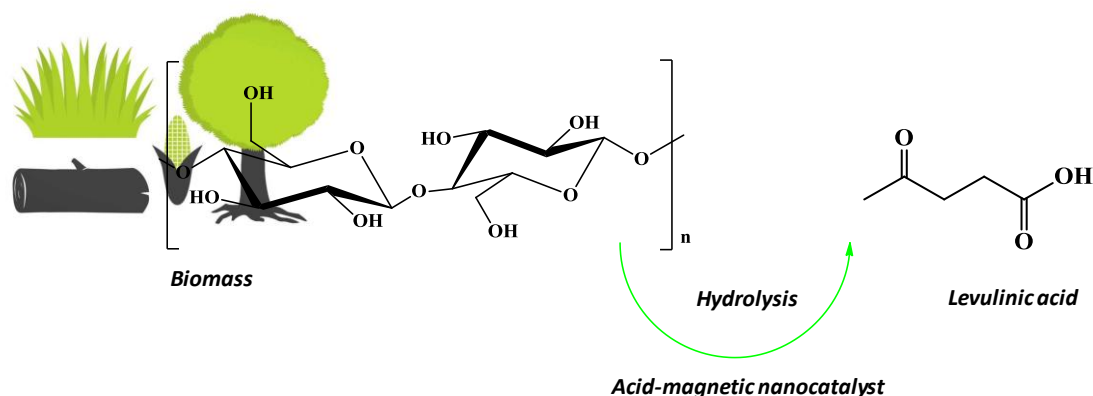


Figure 1. Schematic hydrolysis of biomass

4. Conclusions

A new metal-acid nanocatalyst was successfully synthesized through a “green” process. The direct hydrolysis of biomass was due to a combination of projected factors. The results, further, evidence the role of acid nanocatalyst in improving products yield and selectivity during cellulose hydrolysis in water.

References

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