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2,5-DMF production through hydrogenation of real and synthetic 5-HMF over transition metal catalysts supported on carriers with different nature

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ABSTRACT

Catalytic hydrogenolysis reaction of 5-hydroxymethylfurfural platform molecule to produce 2,5-dimethylfuran conversion was studied. For that purpose noble (Pt and Ru) and non-noble (Ni and Cu) metal catalysts supported on acid (HYAL_2O_3 and Al_2O_3) and basic (ZrO_2 and TiO_2) supports were used. All of the tested catalysts were able to convert completely HMF. However, among the mentioned catalysts, the Cu catalyst supported on ZrO_2 showed the best behavior in terms of DMF selectivity, probably due to the neutral nature associated to ZrO_2 support. Moreover, this catalyst was studied in order to know the influence of some reaction parameters on DMF selectivity. As results obtained with CuZr catalyst concluded, a temperature increase had not influence on the aforementioned parameter because the reaction is exothermic. However, the type of feed, the increment of the pressure and the space velocity decrease improved the DMF selectivity.

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1. Introduction

Nowadays fossil resources, such as petroleum, coal and natural gas, are the most important suppliers to world energy system, around 80% of the primary energy consumption [1,2]. This fact involves serious problems related to the concerns about depletion of this kind of energies [2–5], energy security and economics due to their centralized production, and greenhouse emissions, which are related with the increase of global warming [5,6]. However, it is important to remark that petroleum plays dominant role in chemical industry because of its use in a wide range of products including plastics, carpets, curtains, wall paints, varnishes, soaps, perfumes and hairsprays [7], and in transportation sector in which properties of the used fuels are fulfilled by non-renewable petroleum-derived liquids fuels [8]. In order to reduce the problems derived from uses of petroleum, searching and developing of sustainable and environmental friendly energy sources have become essential topics to achieve.

According to the literature [1,9], the biorefinery, and therefore highly abundant and carbon-neutral biomass [4], can be a good alternative to the current needs of energy, chemicals and unconventional fuels. Regarding to the first generation biofuels, biodiesel

and bioethanol, they had a great introduction on transportation sector until a few years ago. However, their production from food crops came in conflicts with food industry [10]. Moreover, these biofuels present several drawbacks that limit their use as transportation fuels, such as low oxidation stability, corrosive nature and poor cold flow properties [11]. This fact leads to the development of a second generation of biofuels or fuels bioadditives, which are derived from non-food residual lignocellulosic biomass [4,10,11].

Although there is a wide variety of chemical building blocks obtained from lignocellulosic biomass, 5-hydroxymethylfurfural (HMF), which is also considered “chemical platform”, seems to be the most promising intermediate as it can be produced from different raw materials (glucose, fructose, sucrose), and it can also be converted into biofuels, such as 2,5-dimethylfuran (DMF), and other fine chemical molecules (levulinic acid (LA), 2,5-furandicarboxylic acid (FDCA), ethyl levulinate (EL)) [1,3,8,9,12]. The production of HMF dates back to 19th century when the HMF was separated from reaction mixture of fructose, sucrose and oxalic acid [12]. Nowadays, the most extended reaction to produce HMF is dehydration of the aforementioned carbohydrates over acid, homogeneous or heterogeneous catalysts [1,8,9,12], because its high volume production from petroleum derived feedstocks suppose a great cost and therefore a low availability [13].

Regarding the DMF, it is produced from selective hydrogenation of HMF [11] under H_2 atmosphere, also called hydrogenolysis process [2,8]. This reaction involves different pathways [1,11,14] in

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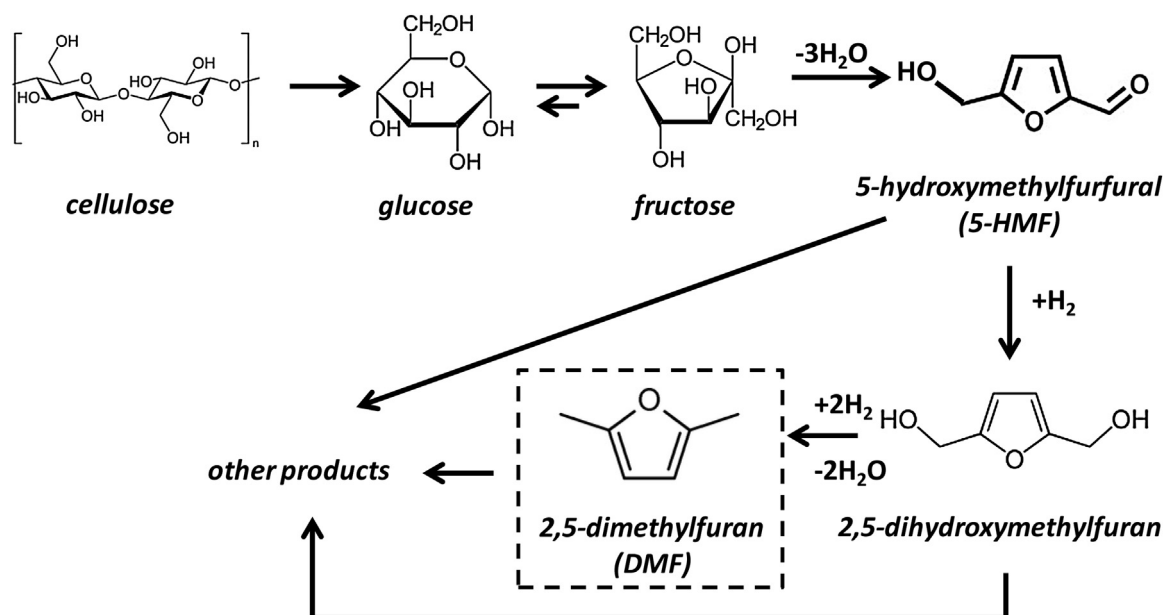


Fig. 1. Desirable main route to transform HMF into DMF through hydrogenolysis reaction.

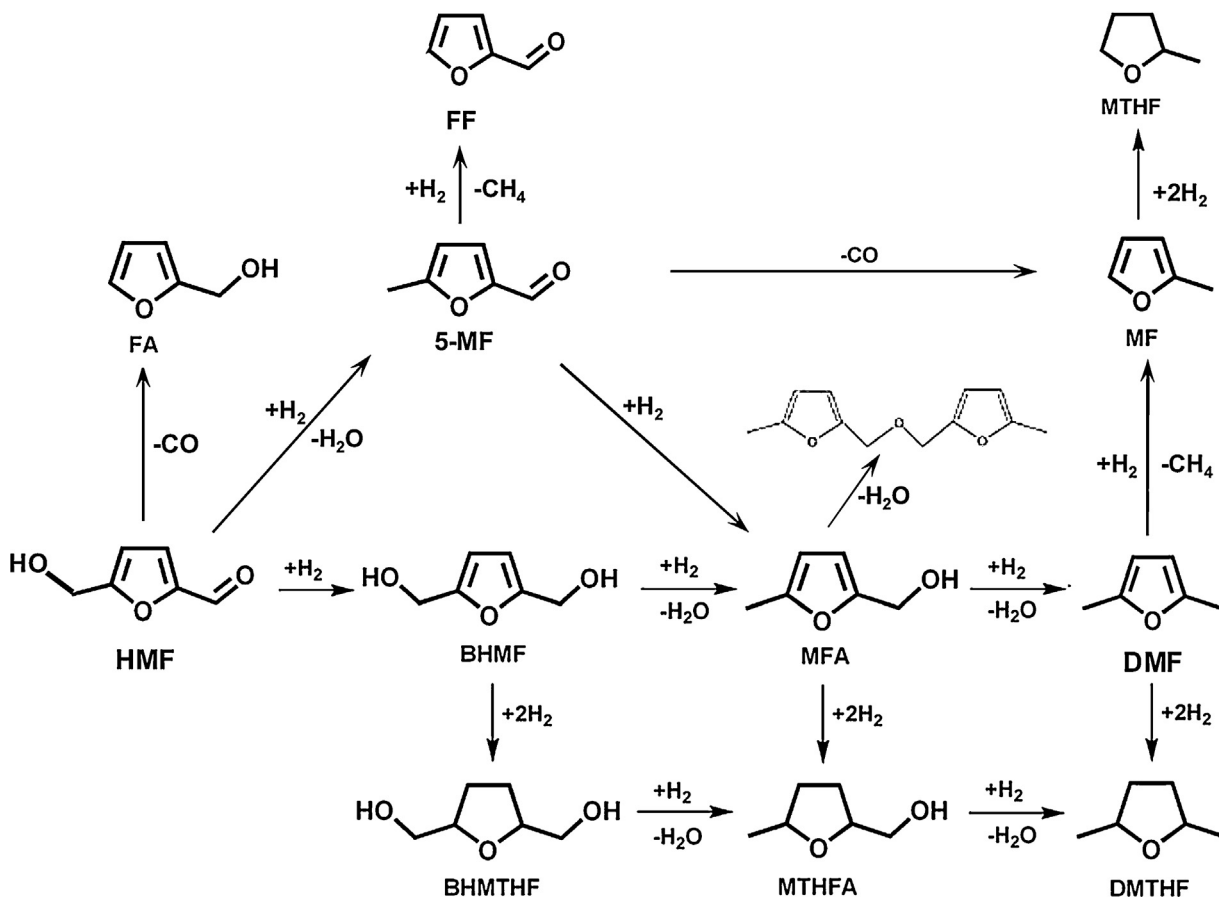


Fig. 2. Reaction mechanism for the conversion of HMF.

which dehydration and hydrogenation reactions are predominant. These pathways are shown in Fig. 1. Nevertheless, according to the literature [2,15,16], apart from dehydration and hydrogenation reactions, secondary reactions could occur during the HMF conversion, such as demethylation and decarbonylation. Fig. 2 shows

a complete reaction scheme of HMF conversion, which have been adapted from the aforementioned literature.

DMF high-quality fuel is considered, as ethanol, an ideal renewable and sustainable substitute or additive of the conventional gasoline [2], because of its high energy density, similar to that of gasoline and higher than ethanol [3,11], and research octane

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