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Direct conversion of glucose to 5-hydroxymethylfurfural using a mixture of niobic acid and niobium phosphate as a solid acid catalyst



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ABSTRACT

The aim of this work was to optimize the acid-catalyzed conversion of glucose into 5-hydroxymethylfurfural (HMF) in an aqueous medium using niobic acid (NbO), niobium phosphate (NbP) and a mixture of both solid acid catalysts. A simplex-centroid mixture design was applied to optimize the mixture ratio between NbO and NbP. A central composite design was applied to process optimization. The studied variables were temperature (T), time (t) and substrate to catalyst weight ratio ($R_{S/C}$). The mixture design revealed excellent glucose conversion (55%) and HMF selectivity (56%) when the weight ratio between NbO and NbP was equal to 1:1. The experimental results demonstrate that a mixture of both solid acids provides a better combination of Brønsted and Lewis acidity for effective glucose dehydration into HMF than each individual catalyst.

1. Introduction

5-Hydroxymethylfurfural (HMF) is considered one of the “top 10” valued-added bio-based building blocks that can be obtained from biomass rich in carbohydrates [1]. From HMF, it is possible to obtain polymeric materials, biofuels, solvents and fine chemicals [2,3]. This versatile molecule has the potential to replace or at least minimize the dependence of petroleum-based materials.

The platform molecule, HMF, can be produced from the acid-catalyzed dehydration of hexoses (C_6 sugars) with both glucose and fructose explored as feedstocks. This reaction has been catalyzed by both homogeneous [4–6] and heterogeneous [7–11] catalysts in aqueous [7,12], organic [13–15], water/organic [6,9,16], ionic liquid media [17,18] and so on. Among these, heterogeneous catalysts and water media are the most desirable conditions, due to heterogeneous catalysis avoiding serious drawbacks in terms of separation and recycling, as well as equipment corrosion [15]. Water is a convenient solvent for biomass due to its excellent substrate solubilization properties, low cost and environmental friendliness [3].

Fructose can be dehydrated directly to HMF, however, the mechanism to obtain HMF from glucose involves a first step of isomerization to fructose, followed by its dehydration to HMF [8,19,20].

This isomerization process is equilibrium limited, requiring additional and expensive separation and purification steps [20]. Consequently, in order to find an economical and environmentally feasible industrial process for the production of HMF, an efficient direct conversion from glucose would be most beneficial.

The literature has proved that Lewis acid sites (LAS) play an important role in the ratio of glucose isomerization into fructose, whereas Brønsted acid sites (BAS) have a negative effect on isomerization. In contrast, BAS are active to the dehydration of fructose to HMF, while an excess of LAS leads to the formation of many by-products that decrease the yield of the main product [19,21,22].

In reactions where water is used as a reactant, solvent or product, such as carbohydrate dehydration to HMF and other reactions of biomass conversion, very few solid acids can maintain the desirable characteristics of activity and stability without deactivation of their acid sites [12]. Among these materials, niobium-containing catalysts, such as niobic acid ($Nb_2O_5 \cdot nH_2O$, hereafter labeled NbO) and niobium phosphate ($NbOPO_4$, hereafter labeled NbP), have attracted significant interest as catalysts due to their strong acidic properties ($H_0 \leq -5.6$ for NbO and $H_0 \leq -8.2$ for NbP, where H_0 is the acidity function defined by Hammett and Deyrup [23,24]). These catalysts have the capability of maintaining active catalysis in polar and protic solvents

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[12,25,26]. Both NbO and NbP exhibit BAS and LAS, with NbP showing a higher ratio of BAS to LAS than NbO. Nakajima et al. [27], has proved that LAS on the surface of NbO and NbP work even in an aqueous medium. The presence of water-tolerant acidic sites originates from the presence of the NbO₄-H₂O adducts that still having a residual positive charge and thus acting as LAS. Moreover, It is well known that the textural, acidic and catalytic properties of NbP are superior to those of NbO, with the advantage that these properties are preserved at higher temperatures [12,28].

Several studies have been reported in the literature on the performance of NbO and NbP as catalysts of fructose dehydration [7,12,15,29,30], but several studies report glucose as feedstock to produce HMF [21,27]. In the studies where fructose was the feedstock, NbP showed superior catalytic performance than NbO. This results could be attributed to the higher number of BAS present on the surface of NbP than NbO, which improves fructose dehydration to HMF [12]. In contrast, due to a high number of LAS on NbO, a high glucose conversion was observed, but the HMF selectivity was not satisfactory [27]. Perhaps, a mixture between NbP and NbO will provide a better combination balance of BAS and LAS to improve glucose conversion into HMF.

Finding an optimal ratio of BAS/LAS and reaction conditions, like temperature, time, catalyst and solvent, is extremely important to gain selectivity for HMF and improve conversion of the feedstock. For this purpose, the experimental design and response surface methodology (RSM) are effective statistical procedures frequently used for the optimization of processes when there are many factors and interactions among these factors.

To the best of our knowledge, this is the first time a mixture of NbO and NbP has been applied as a catalyst to convert glucose into HMF. Thus, the aim of this work was to determine the optimum process conditions for maximizing the acid-catalyzed glucose conversion into HMF using NbO, NbP and a mixture of both in water. A simplex-centroid design was applied to find an optimal ratio between NbO and NbP, which improves the selectivity of HMF from glucose. A central composite design (CCD) and desirability function approach were used for multi-response optimization.

2. Experimental

2.1. Materials

The Nb₂O₅·nH₂O (NbO) and NbOPO₄·nH₂O (NbP) materials were kindly supplied by Companhia Brasileira de Metalurgia e Mineração (CBMM, Brazil) in powder form. The NbO consisted of 80 wt% Nb₂O₅ and 20 wt% H₂O. The NbP contained 66.7 wt% Nb₂O₅, 15.9 wt% P₂O₅, 2.1 wt% K₂O and 15.3 wt% H₂O. Acetonitrile (99.9%), *n*-butylamine (99.5%), glucose (99.5%), HMF (98%) and levulinic acid (98%) were purchased from Sigma-Aldrich. All materials were used without further purification. Milli-Q water was used for preparation of all aqueous solutions.

2.2. Catalyst characterization

X-ray diffraction (XRD) was measured using a Bruker model D8 Discover diffractometer using Cu K α radiation ($\lambda = 0.1541$ nm) with an angular variation of 5–80° (2 θ) and a 0.05° s⁻¹ scan rate.

Analysis of the specific surface area was determined using the multipoint Brunauer–Emmett–Teller (BET) method. The average pore diameter and volume were calculated from the adsorption branch of the isotherm using the Barrett–Joyner–Halenda (BJH) method. Nitrogen adsorption experiments were performed on a Quantachrome Nova Model 1200E coupled to an automatic nitrogen gas adsorption instrument (Boynton Beach, FL, USA). Prior to measurement, the samples were thermally activated at 120 °C for 6 h.

The acid strength of niobium catalysts was measured by the

potentiometric titration method. The experiment was performed by suspending 0.5 g of catalyst in 30 mL of acetonitrile and stirring for 3 h. The suspension was then titrated with a solution of 0.025 mol L⁻¹ *n*-butylamine in acetonitrile [31]. The variation in the electrode potential was measured with a digital pH meter. The addition of *n*-butylamine continued until no further change of mV was recorded. The acid strength of spent catalysts was evaluated by carried out two consecutive catalytic runs at optimal conditions defined for each studied catalyst. After the first run, the catalyst was regenerated by washing it with hot water and dried at 120 °C overnight. The spent catalysts were then titrated as describe above.

Lewis and Brønsted acidic sites were investigated by Fourier Transform Infrared Spectroscopy (FT-IR) (NICOLET Magna-IR 760) using pyridine as probe molecule. The powder samples (*c.a.* 12 mg) were pressed into KBr disks (*c.a.* 1.2 cm diameter). Drops of pyridine were added in the samples and it were dried under high vacuum at 150 °C. After dried, the FT-IR spectra were recorded. BAS and LAS concentrations, were determined according to the procedure reported by Emeis [32].

2.3. Catalytic experiments and analysis

The catalytic experiments were performed in batch conditions. An appropriate amount of catalyst was added to the 5 mL aqueous solution of glucose and magnetically stirred in a sealed glass flask, with the temperature controlled by a thermostatic oil bath. The reaction proceeded with a set time and temperature. After the reaction was completed, the reactor was rapidly cooled down by immersion in an ice-water bath. Solids were separated from aqueous solution by filtration. The filtrate was analyzed by high performed liquid chromatographic (HPLC) for glucose, HMF and LA.

HPLC analysis was performed on a Shimadzu Prominence system equipped with a SPD-M20A photo diode array detector (PDA), a LT-II evaporative light scattering detector (ELSD LT-II) and Shimadzu LCMS solution software. Glucose, LA and HMF were separated on a Rezex RFQ column (100 mm × 7.8 mm, 8 μ m particle size, Phenomenex, Torrance, CA, USA). Ultra-pure water with 0.08% acetic acid was used as the mobile phase with a flow rate of 0.6 mL min⁻¹ and the column was heated to 80 °C. A guard column of the same material was also used. The temperature of the ELSD drift tube was kept at 50 °C, the carrier gas pressure was 350 kPa and the gain was set at 5. The glucose concentration was determined by the ELSD. LA and HMF were quantified on the PDA detector at 270 and 310 nm, respectively. The total run time was 10 min.

2.4. Design of experiments and statistical analysis

Design of experiments was applied to study the variables that affect the production of HMF from glucose in different conditions, as well as to optimize the levels to perform the reaction. For this purpose, two types of experimental design were applied to evaluate the niobium catalyst performance. The responses measured were HMF selectivity and glucose conversion. All statistical analyses were performed using Statistica software (version 7.0, StatSoft, Inc.) and electronic spreadsheets from Microsoft® Excel 2003 [33].

2.5. Mixture design

In previous studies [27], higher glucose conversion was observed when NbO was used as the catalyst, whereas higher HMF selectivity was found when NbP was used as the catalyst. For this reason, a simplex-centroid mixture design was applied to study the suitable weight ratio between NbO and NbP to increase the glucose conversion into HMF.

Experiments were carried out in water. The typical reaction conditions used were 0.1 g of glucose, a reaction time of 60 min and a

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