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Brönsted and Lewis acid ZSM-5 zeolites for the catalytic dehydration of glucose into 5-hydroxymethylfurfural

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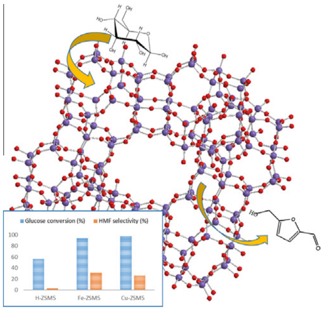
HIGHLIGHTS

- Brönsted and Lewis acid ZSM-5 zeolites have been prepared and characterized.
- They are active in glucose dehydration to HMF in a H_2O/MIBK system, at 195 °C.
- The addition of NaCl allows reaching a HMF yield of 42% after 30 min with H-ZSM-5.
- HMF is not rehydrated to levulinic acid.

GRAPHICAL ABSTRACT



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ABSTRACT

Three different acid ZSM-5 zeolites (H-, Fe- and Cu-ZSM-5) have been prepared and tested in the catalytic dehydration of glucose into 5-hydroxymethylfurfural (HMF). A commercial NH_4-ZSM-5 zeolite (MFI) was modified by thermal or ion-exchange treatments in order to create Brönsted and Lewis acid sites. The zeolitic structure is preserved, and the resulting acid zeolites have demonstrated to be active in the glucose dehydration. The influence of different experimental variables, such as reaction time and temperature, substrate:catalyst molar ratio, volume of the organic solvent and aqueous phase, as well as the density and nature of acid sites, on the catalytic behaviour was investigated. Under the optimal reaction conditions, by using a biphasic NaCl (20 wt%) aqueous solution/methyl isobutyl ketone (MIBK) system, a glucose conversion of 80% and a HMF yield of 42% were achieved at 195 °C, after only 30 min, using H-ZSM-5, which has the lowest Lewis/Brönsted molar ratio among the prepared zeolites. The reutilization of this catalyst was also examined.

1. Introduction

5-Hydroxymethylfurfural (HMF), obtained from biomass, is a potential "carbon-neutral" feedstock for the synthesis of a large spectrum of chemicals and biofuels. Thus, resins derived from HMF can be used as substitute for formaldehyde and HMF oxidation gives rise to highly valuable intermediates such as 2,5-furandicarboxylic acid (FDCA) (proposed as alternative of terephthalic acid for the production of polyesters) or 2,5-dimethylfuran (DMF) (a liquid biofuel). Since the first patented production of HMF in 1960 [1], and having been identified as one of the top ten most valuable platform chemicals by the United States Department of Energy in 2004 [2], HMF has not been industrially produced until 2014, at the AVA Biochem company [3].

The loss of three water molecules by glucose or fructose leads to the formation of HMF, although this is not a simple and easy synthetic route, due to the occurrence of others side reactions, which originate humins (insoluble) and polymers derived from a cross-polymerisation, as well as levulinic (LA) and formic acids derived

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from the HMF rehydration [3,4]. In order to optimize the HMF production, the reaction mechanisms have been extensively studied, but no definitive conclusions have been raised. In this sense, Antal et al. [5] identified a key intermediate supporting a cyclic pathway for the fructose dehydration catalysed by mineral acids. Haworth and Jones [6] and Mednick [7] also pointed to a cyclic pathway involving a fructofuranosyl cationic intermediate. However, Moreau et al. [8] have suggested an acyclic route for the dehydration of fructose using H-mordenite as catalyst, because of the detection of glucose and mannose, which was supported by Wolfrom et al. [9] from the identification of an enediol intermediate.

Nevertheless, glucose as feedstock is preferred over fructose, due to its higher abundance and lower cost. It means that it is necessary to integrate the glucose isomerisation to fructose and the glucose and fructose dehydration, which requires the presence of both Brönsted and Lewis acid sites. Nakajima et al. [10] obtained a HMF yield of 12% in water within 3 h, at 120 °C, using $Nb_2O_5 \cdot nH_2O$ as Lewis acid solid catalyst, and 48% combining this solid catalyst with H_3PO_4. Ordomsky et al. [11] studied the glucose dehydration over different metal phosphates, obtaining selectivities towards HMF varying between 30 and 60%, depending on the Lewis to Brönsted (L/B) acid sites ratio. They concluded that the excess of Lewis acid sites (high L/B ratio) leads to the undesirable transformation of glucose into humins. The reaction was carried out in a biphasic medium formed by water and MIBK, or 2-methyltetrahydrofuran (MTHF), at 135 °C. Weingarten et al. [12], studying the role of the Brönsted and Lewis acid sites for the dehydration of xylose to furfural, reported that the selectivity is also correlated with the L/B ratio, although the catalytic activity depended mainly on the active Lewis acid sites.

Increasing the HMF yield means to minimize side reactions that lead to humins and soluble and insoluble polymers, which take place mainly in aqueous medium. An interesting approach to overcome this drawback consists of the addition of a co-solvent, immiscible with water, to extract the formed HMF, thus suppressing side reactions. However, the use of a biphasic system requires additional steps to recover the HMF, where its purity and easiness of separation are crucial for developing a competitive process from both economic and environmental viewpoints. The partition coefficient (R) of HMF between organic and aqueous phases determines the effectiveness of the solvent extraction in this reaction. However, not only the nature of the co-solvent determines this R coefficient, but also the addition of inorganic salts to the aqueous phase improves the R value, and consequently the HMF production. Thus, Tan and Aravinth [13] tested the effect of the addition of sodium and potassium chlorides on the liquid–liquid equilibrium of a water/acetic acid/1-butanol system, particularly at high salt concentrations, concluding that salts decreased the mutual solubility and increased the concentration in the organic phase. Roman-Leshkov and Dumesic [14] studied the selectivity towards HMF in the presence of NaCl, in biphasic systems, with C3 to C6 solvents (aliphatic alcohols, ketones and ethers), and they found that C4 solvents gave rise to higher HMF yields, due to the increase of the partition coefficient.

In addition to the L/B ratio, the porosity and the hydrophobicity of solid catalysts are essential to carry out the dehydration of glucose into HMF. Mesoporous and microporous acid solids have demonstrated to be suitable for sugar dehydration. Thus, HMF yields ranging between 32 and 77% where obtained from different feedstocks over large-pore mesoporous tin phosphate, under microwave-assisted heating at 150 °C, in a water/MIBK biphasic medium, being the reaction order: fructose > glucose ~ sucrose > cellobiose > cellulose [15]. However, a mesoporous tin phosphate with smaller pore size only attained a HMF yield of 12%, confirming the important role of mesoporosity. On the other hand, 69% of glucose conversion and 23% of HMF yield were obtained by using a mesoporous tantalum oxide (S_{BET} of 79 $m^2 g^{-1}$, average pore diameter of 3.3 nm), at 175 °C, in 1.5 h [16]. It has been also reported the use of a mesoporous MCM-41 aluminosilicate (Si/Al molar ratio of 10), reaching a 87% of glucose conversion and 36% of HMF yield, at 195 °C, after 150 min [17]. In relation to microporous materials, Jae et al. [18] studied the influence of the pore size of zeolites on the conversion of glucose to aromatics, obtaining the best results with medium pore sizes, internal pore space and steric hindrance, such as ZSM-5 and ZSM-11. Besides, H-ZSM-5, H-mordenite and H-beta zeolites were tested for fructose dehydration to HMF at 165 °C in water and also in biphasic water/MIBK medium. In water, 80% of glucose conversion and 25% of HMF selectivity were reached with a H-ZSM-5 zeolite, with an average pore size about 5 Å. When MIBK was added, glucose conversion increased up to 80% and the HMF selectivity exceeded 60% [19]. Hu et al. [20], studying the catalytic behaviour of different zeolites in ionic liquid, observed a synergistic effect between Lewis and Brönsted acid sites, which explained that H-β-zeolite attained a HMF yield close to 50% from glucose, at 150 °C, after 50 min. The influence of the modification of the acidity of several zeolites, by chemical or thermal treatment, has been also evaluated in order to establish the role of the concentration and nature of acid sites on carbohydrate conversion and selectivity to HMF [21,22]. Recently, the state of the art of the dehydration of carbohydrates, mainly C6, for the production of HMF has been reviewed [23,24].

The aim of this work is a thorough study of the glucose dehydration using modified ZSM-5 zeolites, where the influence of experimental variables, such as volume of solvent and salt addition effects, reaction time and temperature, catalyst loading and the evaluation of catalyst reutilization, has been evaluated.

2. Experimental

2.1. Catalyst preparation

In order to obtain a H-ZSM-5 catalyst, a commercial ZSM-5 zeolite (*Zeolyst*), in ammonia form (NH_4-ZSM-5), was calcined in air at 550 °C for 6 h, at a heating rate of 1 °C min^{-1}.

The introduction of Lewis acidity into the ZSM-5 zeolite was carried out by putting in contact 1 g of NH_4-ZSM-5 with 30 mL of an iron(II) sulphate aqueous solution (0.1 M), under nitrogen atmosphere to avoid the oxidation of Fe(II) to Fe(III), and stirring for 24 h. This process was repeated twice. The Fe-ZSM-5 zeolite was filtered, washed with water, dried at 60 °C for 8 h and finally calcined at 550 °C for 6 h. Similarly, a Cu-ZSM-5 zeolite was synthesized by using 1 g of NH_4-ZSM-5 and 100 mL of a copper(II) acetate aqueous solution (0.005 M), under stirring for 24 h. The cationic exchange process was also repeated twice, and the treatment of the resulting Cu-ZSM-5 was analogous.

2.2. Characterization of catalysts

X-ray diffraction (XRD) patterns were recorded on an EMPYREAN PANanalytical using strictly monochromatic Cu K_α radiation ($\lambda = 1.54059$ Å) (Ge (1 1 1) primary monochromator) and working in reflection geometry ($\theta/2\theta$). The X-ray tube worked at 45 kV and 40 mA. The optical configuration was a fixed divergence slit (1/2°), a fixed incident anti-scatter slit (1°), a fixed diffracted anti-scatter slit (1/2°) and PIXCEL detector, working in scanning mode with maximum active length. Energy Dispersive X-ray Fluorescence (EDXRF) technique, used for the elemental analysis of catalysts, was run in a XGT-5000WR (Horiba) spectrometer, and the XGT-5000 software package was used for the acquisition and data analysis.