



Catalysis of ordered nanoporous materials for fructose dehydration through difructose anhydride intermediate



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ABSTRACT

A fructose reaction network, including difructose anhydride (DFA) – fructose cycle in parallel with fructose dehydration following with 5-hydroxymethylfurfural (HMF) side reactions, was devised. By applying H₂O - MIBK biphasic solvent, MIBK could act as an extractant of HMF and also a promoter for fructose dehydration. By raising reaction severity, molecular sieve catalysed improved HMF selectivity by suppression of DFA formation. While narrow pore zeolites and sulfated mesoporous silica catalysed 90% HMF selectivity at 85–94% fructose conversion, the large pore 12-MR zeolites exhibited low HMF selectivity returning with excessive humin formation due to their shape selective catalysis for HMF oligomerization.

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1. Introduction

5-hydroxymethylfurfural (HMF) is one of the key platform molecules in future bio-refinery for the synthesis of dimethylfuran, levulinic acid (LA), 2,5-furandicarboxylic acid, etc. [1]. Mostly HMF is synthesized from fructose dehydration catalysed with Brønsted acidity. The HMF synthesis involves a complicated reaction network including fructose dehydration through difructose anhydride (DFA) intermediate, HMF re-hydration with formation of formic acid (FA) and LA by-products, and oligomerization for humin formation [2].

Many strong acidic catalyst systems have been reported such as mineral acid liquids [3], acidic ionic liquids [4], or solid acids including resins [5], phosphoric acid treated niobic acid [6], metal oxides [7], zeolites [8,9], mesoporous zeolite [10], sulfated mesoporous metal oxides [2], Nafion-resin supported on mesocellular silica foam [11], etc. Since strong acid could simultaneously catalyse fructose dehydration and also side reactions [12], the general approach in using strong acidic catalyst might be detrimental to HMF product selectivity. Alternatively, weak acidic sulfated mesoporous silica (MS) for the catalysis of fructose dehydration with

minimum side reactions was reported recently [2]. The new catalyst system catalysed high HMF yield at appropriately high reaction temperature.

During fructose reaction, HMF product is reactive for further side reactions with by-product formation, leading to deteriorated HMF product selectivity. Some biphasic reaction systems, such as water - methyl isobutyl ketone (MIBK) [12], BMIMCl - THF [13], water - butanol [6], and NaCl solution - THF [14], etc., have been proposed for enhancing HMF product selectivity. In the biphasic solvent system, the organic solvent acts as an extraction phase to protect HMF from the occurrence of further secondary reactions in aqueous phase.

According to Zhang et al. [10], mesoporous zeolite imposes severe diffusion resistance toward the transportation of carbohydrates during fructose reaction. All different elemental reactions in the complex reaction network are under various diffusion resistances and catalysed by different acid strengths. Porous catalyst design could be optimized by fine tuning solid acidity and pore structure for the selective catalysis of fructose dehydration with respect to side reactions. The present report studies the catalytic characteristics of zeolites and sulfated MS in terms of operating condition and reaction product selectivity. The interplay of fructose reaction, DFA intermediates and HMF formation are studied from perspective of reaction network and optimum catalyst design.

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2. Experimental

Commercial zeolite samples, mordenite (MOR, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 10.5$), ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 25$), Beta ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 15$) and Y ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 10$) were used. ZSM-12, MCM-22 and ITQ-2 were synthesized with hydrothermal method following the procedures of references [15–17]. All the zeolite samples in H-form were dried and calcined at 550 °C in air. Sulfated MS denoted as 5M41S550 was prepared following reference [2], starting with the synthesis of MCM-41 material, following with calcination, H_2SO_4 impregnation and calcination at 550 °C.

Fructose dehydration was conducted in a Carousel 6 Place Reaction Station (Radleys Discovery Technologies). In a typical procedure, a reaction mixture comprising fructose of 1 g and H_2O – MIBK (4:6) solvent mixture of 10 ml, and a catalyst of 33 mg was heated at the desirable reaction temperature under continuously mechanical stirring. For DFA reaction, a reaction mixture of 1 mg DFA, 0.15 mL 0.006M H_2SO_4 (used as catalyst) and 10 g solvent was used. In the end of reaction, the product mixture appearing in two phase was collected. A solution of 4 g H_2O and 11 g MeOH acting as a co-solvent was added to the product mixture to form a one-phase homogeneous solution. The resultant solution was then filtrated to separate solid products and liquid products.

The liquid products were analysed using Hitachi L-2130 HPLC equipped with a refractive index (RI) detector. Chromatographic separation was conducted using an Aminex HPX-87H column (Bio-Rad Laboratories, Inc.) with a mobile phase using 0.005 M H_2SO_4 aqueous solution at flow rate of 0.6 ml/min and 45 °C. The concentrations of product components were determined from calibration curves (See Supplemental Information STable 1 and SFig. 1) using direct calibration method. Material balance calculation was conducted through a serial calculations including (a) determination of product weight from the concentration and product volume; (b) calculation of mass recovery from the product weight; and (c) normalization of mass fragments. Fructose conversion and product selectivity were determined accordingly.

3. Results

3.1. Effect of reaction severity on catalytic performances

The catalytic performances of various zeolite samples during fructose reaction were measured by using 10% fructose solution of 3:7 v/v water – MIBK solvent. As shown in Fig. 1A, during fructose dehydration at reaction temperature of 170 °C, fructose conversion increased with reaction time, reaching a plateau for maximum conversions. Among the zeolite samples tested, mordenite was the least active one.

Fructose dehydration generated HMF product in accompany with some major by-products, including DFA, FA, LA and AGP (anhydroglucose). A general trend in product selectivity was observed. With increasing conversion level, while HMF product selectivity increased to reach a maximum (Fig. 1B), DFA by-product selectivity decreased monotonically (Fig. 1C). All the catalyst samples catalysed remarkable high DFA product selectivity at low conversion level. The reduction of high DFA by-product selectivity along with increasing conversion level was remunerated with the increasing selectivity to HMF product for the most part and to non-DFA product for the remaining part (Fig. 1D). In reference to the sulfated mesoporous silica catalyst 5M41S550, zeolite catalysed lower HMF but higher DFA selectivity at low conversion level. At high conversion level, the HMF product selectivity over most molecular sieve catalysts except zeolite Y and Beta approached to that over 5M41S550. Noticeably, the large pore 12-oxygen-membered ring (12-MR) zeolite Y and Beta catalysed remarkably lower HMF

product selectivity (Fig. 1B) and higher non-DFA by-product selectivity (Fig. 1D) than all other zeolite samples.

Therefore, HMF product selectivity was significantly affected by conversion level. The highest achievable fructose conversions of various catalysts were evaluated at their maximum HMF product selectivity (Table 1). Among the tested molecular sieve catalysts, the sulfated mesoporous silica catalyst 5M41S550 exhibited the highest HMF selectivity of 91% at fructose conversion of 65%. In comparison, the tested zeolites except zeolite beta and Y having pore opening in the range of 6.4–7.4 Å catalysed comparable HMF product selectivity around 79–85% at conversion around 52–82%. Among the zeolite tested, ZSM-5 exhibited the best performance producing a maximum HMF selectivity of 85% at achievable fructose conversion of 82%. The major by-products over most zeolites were FA and LA; and additionally humin for large pore 12-MR zeolites.

The catalytic performances of zeolite samples in fructose dehydration were further measured at reaction temperature of 190 °C. The product selectivity changed with conversion level (Fig. 2). According to HMF product selectivity trend (Fig. 2B), the tested zeolites could be classified into two categories. For **Group A**, the 10-MR and narrow pore 12-MR zeolites, including ZSM-5, mordenite and ZSM-12, HMF product selectivity decreased monotonically with increasing conversion level. For **Group B**, including MCM-22, ITQ-2 (the wide pore 12-MR zeolites) and 5M41S550, a maximum HMF selectivity appeared at fructose conversion at around 75%. While **Group A** catalysed nil DFA selectivity, **Group B** catalysed high DFA by-product selectivity at low conversion level, following a descending trace with increasing conversion (Fig. 2C). Generally speaking, the non-DFA by-product selectivity decreased with increasing conversion level (Fig. 2D). Noticeably, the sulfated MS 5M41S550 exhibited the lowest non-DFA by-product selectivity.

Comparing to the catalytic performances at reaction temperature of 170 °C (Table 1), the tested zeolites all catalysed about the same maximum HMF product selectivity with higher achievable fructose conversion at reaction temperature of 190 °C within a shorter reaction time (Table 2). Over the **Group A** zeolite, the main by-products were LA, FA and sometime AGP. On the other hand, over **Group B** catalyst, humin by-product was remarkably generated. Among the tested molecular sieve catalysts, the sulfated MS catalyst 5M41S550 exhibited the highest HMF selectivity of 90% at fructose conversion of 94%. Among the zeolite tested, the best catalysts ZSM-5 and ZSM-12 produced a maximum HMF selectivity of 88% at achievable fructose conversion of 85%. Higher HMF selectivity could be obtained at lower fructose conversion.

3.2. DFA formation - decomposition during fructose dehydration and their solvent effect

Solvent effect was studied for elucidation of DFA role during fructose dehydration. Comparing to fructose reaction in pure water solvent at reaction temperature of 170 °C, fructose reaction in H_2O – MIBK biphasic solvent system was faster achieving a higher conversion at a same reaction time; and generated a higher DFA by-product selectivity (Table 3). For H_2SO_4 catalyst (Table 3A), since H_2SO_4 concentration was much diluted in case of pure water solvent than that in H_2O – MIBK biphasic solvent, the slow reaction rate in pure water solvent could be attributed to the much diluted H_2SO_4 concentration. Note that at low conversion level, e.g., lower than 30% fructose conversion, while reaction in H_2O – MIBK biphasic solvent generated predominantly DFA and HMF, reaction in pure water solvent produced mainly HMF product. Similar result was observed for 5M41S550 catalyst (Table 3B). Since there was no dilution effect in pure water solvent in case of heterogeneous

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