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Conversion and kinetics study of fructose-to-5-hydroxymethylfurfural (HMF) using sulfonic and ionic liquid groups bi-functionalized mesoporous silica nanoparticles as recyclable solid catalysts in DMSO systems†

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Mesoporous silica nanoparticles functionalized with both sulfonic acid (HSO_3) and ionic liquid (ILs) were synthesized and applied as effective and recyclable catalysts for generating 5-hydroxymethylfurfural (HMF) from fructose. For the first time a high HMF yield of 72.5% was achieved in DMSO systems under mild conditions (90 °C and 3 h). We further studied the kinetics of the fructose-to-HMF conversion and compared the rate constants, reaction orders, and activation energies for the systems with and without bi-functional MSN catalysts.

5-Hydroxymethylfurfural (HMF), converted from lignocellulosic biomass, is considered to be one of the “top value-added chemicals”¹ due to its utilization as a building block platform between biomass and promising chemical intermediates, such as 2,5-furandicarboxylic acid (FDCA),² 2,5-dimethylfuran (DMF),³ 5-ethoxymethylfurfural (EMF),⁴ and ethyl levulinate (EL),⁵ which have been studied extensively in recent years, demonstrating the significance of HMF.

HMF has been successfully generated from fructose, glucose, and cellulose using various kinds of reaction systems with homogeneous or heterogeneous catalysts.^{6–8} The mechanism of cellulose-to-HMF conversion is still unclear, but the conversion can be divided into several reactions. First, cellulose is usually pre-treated with alkaline, acid, or certain ionic solutions to destroy its rigid framework. The pre-treated cellulose then goes through the depolymerisation process in an acidic system in order to break the 1,4- β -glycosidic bonds of cellulose and produce glucose. Subsequently, glucose is converted to fructose *via* isomerisation, which is a so-called Lobry de Bruyn–Alberda van Ekenstein transformation.⁹ Finally, the dehydration of fructose generates HMF. The mechanism of fructose-to-HMF

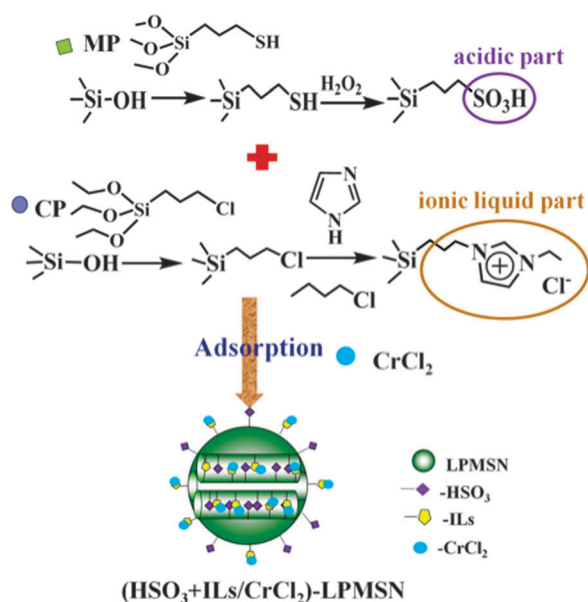
conversion has been discussed in numerous reports.^{10–12} The micro-kinetic model for this three-stage water-removed process¹³ has been constructed to determine an apparent activation energy.¹⁴ In addition, according to their computational results, both the estimated equilibrium constant and activation energy can be greatly influenced by reaction conditions, including temperature, solvent, and catalysts.¹⁵

Different solvents have been used in the fructose-to-HMF conversion because of the contrast between water-soluble reactants (*e.g.*, fructose and glucose) and organic solvent-soluble products (*e.g.*, HMF). Careful selection of solvents can promote a preferential reaction and enhance product yield. The Dumesic group studied the effects of solvents on the dehydration of fructose in biphasic systems, and demonstrated the catalytic ability of dimethylsulfoxide (DMSO), which is able to effectively suppress the undesired side reactions.¹⁵ Recently, ionic liquids have been widely used as both a catalyst and a solvent for producing HMF from lignocelluloses because of their comparatively higher catalytic activity and adjustable composition.^{16,17} However, despite the excellent activity and recyclability of ionic liquids, their potential is restricted to laboratory-scale experiments due to high cost. Therefore, a low-price solvent with desired properties (*e.g.*, high boiling point and low viscosity) such as DMSO can have more potential in industrial applications.

In recent years, several groups have reported the production of HMF from fructose in DMSO-based reaction systems *via* homogeneous and heterogeneous catalysts, including acids, salts, and metal ions.^{18–20} The Dumesic group has investigated the catalytic capabilities of various homogeneous mineral acids.²¹ Recently, Wang *et al.* used carbon-based *p*-toluene-sulfonic acid (TsOH) at 130 °C for 1.5 h resulting in 91.2% of HMF.²² Although these pioneering studies showed high yields of HMF, the relatively harsher reaction conditions are always needed in such homogeneous catalytic systems. From the economic and sustainable viewpoints, scientists have turned to heterogeneous solid catalysts and mild reaction conditions.²³ For example, Sidhuria *et al.* immobilized ionic liquids onto silica particles as an efficient heterogeneous catalyst for fructose-to-HMF conversion with a yield of 63% in a DMSO system.²⁴

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† Electronic supplementary information (ESI) available: Experimental details for synthesis of MSN, functionalization of MSN with sulfonic acid and ionic liquid, and conversion of fructose-to-HMF reaction, HPLC detection, SEM image, nitrogen adsorption–desorption isotherm, solid-state NMR results, and calculation of HMF yield. See DOI: 10.1039/c2cp42751f



Scheme 1 Synthetic process for preparing the bi-functionalized MSN.

Mesoporous silica nanoparticles (MSNs) have been widely used in various applications because of their high surface area, controllable pore size, and controllable surface functionality.^{25–27} Our group has previously functionalized MSNs with carboxylic acids for the immobilization of enzymes (*i.e.*, cellulase) for effective cellulose-to-glucose conversion in an aqueous system.²⁸ Here we propose another strategy: bi-functionalized MSNs with sulfonic acid and ionic liquids were synthesized and used as an efficient and recyclable heterogeneous catalyst for fructose-to-HMF conversion under mild reaction conditions (90 °C and 3 h), producing the highest yield of 72.5%. The proposed MSN-based catalysts are cheaper, selective, and more easily operated at a large scale.

The synthetic process of the bi-functionalized MSN is shown in Scheme 1 and is described as follows: Brij-97 was used as the template and was first dissolved in 180 g of deionized water. Then, APTMS and DOP were added to the Brij-97 solution with stirring at room temperature. After stirring for 30 min, organosilanes (*i.e.*, MPTMS and CPTES) were added to the reaction system along with TEOS, and the whole system, with a composition (in molar ratios) of water : Brij-97 : TEOS : MPTMS : CPTES = 433 : 0.293 : 1 : 0.009 : 0.009, was prepared and kept stirred for 24 h at room temperature. The mixture was subsequently heated at 100 °C overnight. Finally, the precipitated solid was collected by filtration and washed sequentially with water and methanol. It is worth noting that the template can be extracted by this washing step. To further convert the thiol group of (MP + CP)-MSN to a sulfonic group, the (MP + CP)-MSN was oxidized in an H₂O₂ solution with a

composition of (MP + CP)-MSN : H₂O : MeOH : H₂O₂ = 0.5 g : 10 ml : 10 ml : 10 ml. After reaction at room temperature overnight, the obtained sample (*i.e.*, (HSO₃ + CP)-MSN) was washed and dried in vacuum. To further functionalize the (HSO₃ + CP)-MSN with ionic liquid, the (HSO₃ + CP)-MSN sample and solid imidazole were degassed for 3 h before the addition of anhydrous benzene and chlorobutane with the molar ratio of imidazole : chlorobutane = 1 : 2. After one day of reflux, the product (*i.e.*, (HSO₃ + ILs)-MSN) was collected through filtration and washed with anhydrous benzene. Finally, the (HSO₃ + ILs)-MSN sample was immersed in CrCl₂ solution, and the whole mixture was kept stirred overnight. CrCl₂ can be physically absorbed on the surface of (HSO₃ + IL)-MSN. The final product [(HSO₃ + (ILs/CrCl₂))-MSN] was collected by centrifugation.

The morphology and porous properties of the series of synthesized bi-functionalized MSN were characterized with SEM and nitrogen adsorption–desorption isotherms. The SEM image in Fig. S1 (ESI†) shows a uniform and spherical morphology for bi-functionalized MSN with particle size of sub-microns. In Fig. S2-a (ESI†), the bi-functional MSN exhibits a type IV nitrogen adsorption–desorption isotherm, indicating multilayer adsorption by capillary condensation. Moreover, the results of BET specific surface area and pore size distribution calculated from the BJH method are shown in Fig. S2-b (ESI†) and listed in Table 1 together with other structural properties of bi-functional MSN.

Next, we qualitatively and quantitatively investigated the functional groups on the bi-functional MSN using ²⁹Si and ¹³C solid-state NMR. As shown in Fig S3-a (ESI†), the ¹³C NMR spectrum contains ten identified signals, and these results evidenced the successful grafting of the organosilane MPTMS and ionic liquids on the MSN. Additionally, we further quantified the amounts of each functional group on the MSN by ²⁹Si NMR. There are Qⁿ and Tⁿ peaks shown in Fig. S3-b (ESI†), which represent the relative amount of the silica framework and its covalent bonding with organosilanes. The amounts of functional groups are summarized in Table 1. In addition, results of element analysis indicated the presence of sulfonic acid (S around 2.3%) and ionic liquid (N around 1.7%).

In order to demonstrate the effect of bi-functional MSN on the fructose-to-HMF conversion, the reaction was executed without catalysts (blank sample), with MSN and bi-functional MSN. The result including the efficacy of fructose conversion, HMF yield, and selectivity is depicted in Fig. 1a. The cases of blank (no catalyst) and MSN (with non-functionalized MSN as the catalyst) showed low conversion (around 25%) and almost no HMF yield, indicating that the dehydration of fructose to generate HMF was difficult to occur under such reaction conditions (*i.e.*, DMSO solvent, 90 °C, 3 h). In contrast, under the same reaction conditions, the reaction with

Table 1 Summary of characterization of bi-functionalized mesoporous silica nanoparticles

Physical properties			Functionalization					
Specific surface area/m ² g ^{−1}	Pore size/nm	Particle size/nm	# of Si–OH/ mmol g ^{−1}	Functional group/ mmol g ^{−1}	Elemental analysis/mmol g ^{−1}			
					N%	C%	H%	S%
98.0	4.4	400	6.12	1.06	1.7	16.0	27.6	2.3

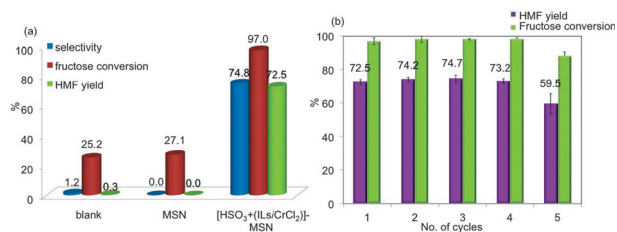


Fig. 1 (a) Results of fructose-to-HMF conversion in different systems. Blank: without any catalyst. MSN: with non-functionalized MSN. [HSO₃ + (ILs/CrCl₂)]-MSN: with bi-functionalized MSN. (b) Recyclability of [HSO₃ + (ILs/CrCl₂)]-MSN in fructose-to-HMF conversion.

the presence of the bi-functionalized MSN surprisingly exhibited enhanced fructose conversion (almost 100%) and HMF yield as high as 72.5%, as shown in Fig. 1a.

The results above clearly demonstrate the effectiveness of the bi-functionalized MSN on the catalytic production of HMF, which was contributed by the functional groups of HSO₃ acid and [EMIM]Cl/CrCl₂ ionic liquid. It has been reported that the dehydration of fructose can be promoted with the assistance of different homogeneous acids and metal chlorides.^{12,16} Here we report that successful functionalization of both sulfonic acid and ionic liquid/metal chloride onto the surface of MSN materials would be a new method to provide efficient heterogeneous catalysts. In addition to the sulfonic acid groups, chloride ions can act as an effective catalyst due to their nucleophilicity and the acidic C-2 proton of the imidazolium part in ionic liquid and also promote the dehydration of fructose.¹² Furthermore, in contrast to other solid nanoparticles, MSN exhibits high surface area and large mesopores, which should be a great benefit to the enhancement of efficiency owing to the increased reaction sites.

Reusability of the [HSO₃ + (ILs/CrCl₂)]-MSN was further studied over five cycles. As shown in Fig. 1b, it is seen that the conversions of fructose almost maintained at 98% till the fifth run. Additionally, no significant loss of HMF yield was observed. It means that the grafted functional groups (*i.e.* sulfonic acid (HSO₃) and ionic liquids (ILs)) did not leach during the complicated reiterating process and further hold their original activity without obvious decay. Therefore, the recyclability of the synthesized bi-functional material has been exactly confirmed.

We further studied the kinetics of the fructose-to-HMF conversion and compared the rate constants, reaction orders, and activation energies for the systems with and without bi-functional MSN catalyst. First, we conducted two reaction systems (*i.e.*, with and without catalyst) at the same reaction temperature (*i.e.*, 90 °C) but for different reaction time periods. We observed the variation of HMF yields with reaction time, as shown in Fig. 2a. The reaction rates of both cases are initially high but tend to be almost constant after a time-span, indicating that the reactants have already run out resulting in no more HMF produced. However, addition of our synthesized catalysts, [HSO₃ + (ILs/CrCl₂)]-MSN, obviously accelerates the generation of HMF to some extent. Three hours later, there is about 73.4% of HMF, which is nearly three times larger than the one (25.3%) in blank. That is to say, our material takes effect in the catalytic fructose conversion.

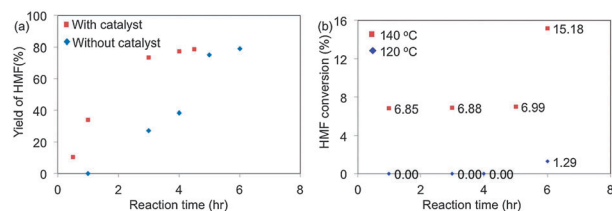


Fig. 2 (a) Effect of reaction time and catalyst on the yield of HMF. (b) The kinetics profiles of HMF decomposition in DMSO at different temperatures (blue: 120 °C and red: 140 °C).

For the purpose of identifying the relationships between kinetic parameters (such as rate constants, reaction orders, and activation energies) and the addition of bi-functional catalyst, we further comprehensively constructed the kinetics profiles at different temperatures for systems w/ and w/o [HSO₃ + (ILs/CrCl₂)]-MSN (Fig. 3). We supposed that the ultimate product of fructose dehydration is HMF only, implying that we did not take other by-products into account. Besides, we assumed that the degradation of HMF would not occur under our designed conditions (90 °C, 0–6 h). This hypothesis can be supported by the testing results of HMF decomposition, as shown in Fig. 2b. In this experiment, HMF is considered as the reactant, placed in an identical environment as before. From the data shown, it is seen that the apparent decay of HMF (15.18%) could be noticed only under sufficient reaction temperature and time (140 °C, 6 h), which is far from our practical operating conditions. That is to say, under milder conditions (90 °C, 3 h), the decomposition of HMF is unconsidered and this outcome bolsters the previous model we have set up.

From Fig. 3, we analyzed the kinetics profiles in order to systematically understand the shifts of each kinetics parameter caused by the catalysts. Referring to the previous published research,¹⁴ we assumed that the transformation of fructose is a 1st order process. The reaction rate could be expressed as follows:

$$\frac{d[\text{HMF}]}{dt} = k[\text{fructose}] = \frac{d[\text{fructose}]}{dt}$$

[] means molar concentration of each chemical and k is the rate constant for fructose conversion at a certain temperature. Next, we transformed this equation into a numerical form and made the [fructose] in terms of conversion X , *i.e.* [fructose]_{*t*} = [fructose]₀ (1 – X). After the subsequently integral calculation, the original equation will become:

$$-\ln(1 - X) = kt + C$$

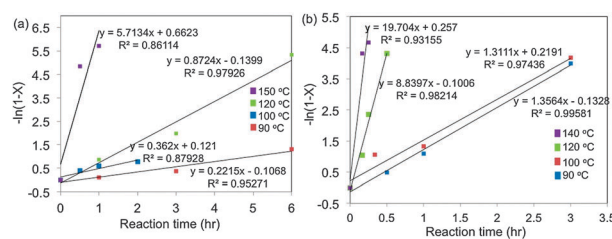


Fig. 3 The kinetics profiles of fructose-to-HMF conversion (fitted by 1st order assumption) (a) without catalysts and (b) with [HSO₃ + (ILs/CrCl₂)]-MSN.

t is the reaction time and C is an arbitrary constant. Therefore, we plotted a figure with $-\ln(1 - X)$ as the y -axis and t as the x -axis, fitting the data linearly and evaluated reaction constants from the slopes. As shown in Fig. 3, there is an obvious increase of k in the presence of bi-functional mesoporous silica nanoparticles, confirming their ability to promote this reaction.

Next, we calculated the activation energy (E_a) of each system from rate constants we obtained by the Arrhenius equation. As the result, the E_a of systems w/ and w/o catalysts are 67.5 and 80.05 kJ mol⁻¹, respectively. This fact indicated that our addition of [HSO₃ + (ILs/CrCl₂)]-MSN has altered the reaction route in a certain degree, consequently lowering the activation energy and leading to a higher reaction rate.

In conclusion, we have demonstrated the synthesis of mesoporous silica nanoparticles with both acid and ionic liquid groups. Such bi-functionalized MSN solid catalysts have enhanced the production of HMF from fructose dehydration under mild conditions using DMSO as the solvent. The kinetics study has indicated that our bi-functionalized MSN could accelerate fructose dehydration by reducing the activation energy. We expect that the bi-functionalized and recyclable MSN catalysts can be also useful for other catalytic applications.

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