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The effects of emulsion on sugar dehydration to 5-hydroxymethylfurfural in a biphasic system†

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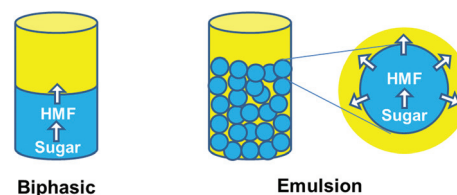
Alkyl/amino functionalized silica nanoparticles to create an emulsion in a biphasic system for sugar dehydration to HMF were successfully developed. As a proof-of-concept, more than 10% increase of HMF yield and 20% increase of selectivity were achieved for both fructose and glucose dehydrations in the emulsion system as compared to the conventional biphasic system. The excellent recyclability of the nanoparticles also further widens the potential of the biphasic system to be scaled up for industrial application.

5-Hydroxymethylfurfural (HMF) has been known as a product of hexose dehydration for over 100 years and is considered to be one of the most promising platform molecules that can be converted into a variety of interesting chemicals.^{1–8} Various approaches have been developed for the production of HMF from biomass, however, using green solvents and environmentally benign conditions for a cost-efficient transformation is still a challenge. Although solvents such as dimethyl sulfoxide (DMSO)^{9,10} and ionic liquids (ILs)^{11,12} are effective in giving high HMF yield by suppressing undesired side reactions, the separation of HMF from these solvents is still energy intensive due to their high boiling points and high HMF solubility. The aqueous–organic biphasic solvent system represents a great improvement pertaining to this issue.^{13,14} Its easy separation and *in situ* HMF extraction prevents HMF decomposition in the aqueous layer and/or humin formation, making the biphasic system a potentially suitable system for scalable industrial applications. In the biphasic system, HMF generated in the aqueous phase should theoretically be extracted into the organic phase instantly. However, this extraction efficiency is limited due to the poor contact surface area between both phases, as well as the low partitioning ratios of HMF to the organic phase. The limited extraction efficiency has resulted in large extracting solvents required for the biphasic system

which can be costly and pose negative impacts to the environment.

Recently, various papers reported using Pickering emulsions for more efficiency, better selectivity or separation to the two-phase systems.¹⁵ Xiao *et al.* have also recently reported the importance of catalyst wettability on catalytic performance¹⁶ and demonstrated this on the conversion of sugars to HMF in the tetrahydrofuran (THF)–DMSO system by adjusting the catalyst wettability to prevent the occurrence of side reactions.¹⁷ However, to the best of our knowledge, the steady emulsion effect on sugar dehydration to HMF in a biphasic system to improve extraction efficiency has not been demonstrated. Herein, we report alkyl/amino functionalized silica nanoparticles to create an emulsion in a biphasic system for sugar dehydration to HMF. The emulsion formed creates a microphasic interaction between phases, resulting in a large contact surface area and hence improving the extraction efficiency of the system (Scheme 1) which also helps to prevent HMF decomposition/polymerization in the aqueous layer. This creation of an emulsion in a biphasic system is the first to demonstrate and serve as a proof-of-concept for increased selectivity and yield for the sugar dehydration to HMF as compared to the conventional biphasic system.

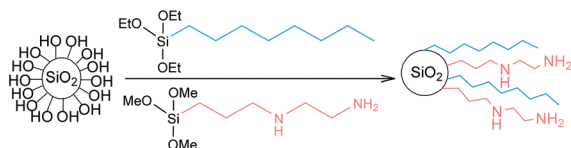
Recently, our group developed a novel and efficient polystyrene-based ammonium chloride resins for the production of HMF from sugars.¹⁸ It was hence of great interest to us to modify the polystyrene resins to create an emulsion for sugar dehydration in the NaCl–H₂O/MIBK (methyl isobutyl



Scheme 1 Sugar dehydration in biphasic and emulsion systems.

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Scheme 2 Functionalization of silica nanoparticles.

ketone) biphasic system. However, preliminary results showed that there is no significant increase in yield and selectivity as compared to the control experiment. This may be due to the inability of these resins to form a stable emulsion due to their large particle size ($>1 \mu\text{m}$). It was shown that functional silica microspheres can form a pH-responsive Pickering emulsion in the biphasic system.^{15c} Inspired by this, silica-based functionalized nanoparticles were adopted to form a Pickering emulsion for the sugar dehydration to HMF. The silica nanoparticles were purchased or synthesized based on the well-established Stöber process.¹⁹ The nanoparticles were then functionalized with different loadings of octyl and diamine chains (Scheme 2) by modifying the synthetic procedure reported.^{15c}

Two different sizes of round, regular silica nanoparticles were synthesized (200 nm and 300 nm) based on the Stöber process. The size of the nanoparticles was measured using TEM and the images are shown in the ESI, Fig. S1.† The synthesized particles were then loaded with various amounts of octyl and diamine groups (Scheme 2 and Table S2†). The loading amounts and ratios were calculated based on the elemental analysis results (Table S2†). These functionalized nanoparticles were then used in fructose dehydration to HMF to test the effect of emulsion on the NaCl–H₂O/MIBK biphasic system (Fig. 1). Firstly, control reactions with no particles, unfunctionalized particles and functionalized silica particles

(synthesized 200 nm particles and commercial particles) were tested in fructose dehydration in the typical biphasic system (Table S1†). Un-functionalized silica particles did not show any increase in HMF yield, while the synthesized 200 nm particles loaded with diamine/octyl chains (2.5/1, Si-12) demonstrated promising increase in HMF yield and selectivity (Table S1,† entry 3). In contrast, commercial silica nanoparticles after functionalization (diamine/octyl 2.5/1, Si-12*) gave no increase in HMF yield (Table S1,† entry 4). This may be due to the small and irregular morphology of the purchased silica nanoparticles. For the synthesized silica particles, smaller nanoparticles (200 nm) performed better in general and the diamine : octyl ratio of 2.5 (2N, Si-12) gave the best results. It was shown that a stable emulsion can also be obtained by loading triamine and octyl groups onto silica nanoparticles.^{15cf} Based on the elemental analysis results (Table S2,† entries 8–12), the triamine : octyl ratio of 1.9 (3N, Si-30) gave the highest yield which was comparable to the yield given by the diamine : octyl ratio of 2.5. This can be explained by the diamine : octyl ratio of 2.5 which is approximately equal to the triamine : octyl ratio of 1.9.

The nanoparticle loading also has an effect on the emulsion, with an established conclusion that the emulsion droplet size decreases as the particle concentration increases.^{15f} This will increase the interfacial contact surface area between both phases for our reaction, leading to an increased HMF yield as shown in Fig. 1d. However, further increasing the nanoparticle loading caused the HMF yield to decrease which may be due to polydispersity of emulsion droplets, resulting in non-uniformity of the emulsion droplet size and lowering the overall surface contact area. The stirring rate also plays an important role in this reaction (Fig. S2†).^{15f,20} Due to the addition of NaCl in the biphasic system, the stability of the emulsion is affected to a certain extent. As shown in Fig. S3,† the emulsion was unstable against sedimentation after being allowed to remain undisturbed for some time when NaCl was added. A mechanical force such as stirring is required to form and maintain the emulsion. Hence, the reaction efficiency increased when the stirring rate was increased to 1000 rpm. At an even higher stirring rate, the yield drops as stirring may also result in the droplet breakage.²⁰

It is well-known that the addition of NaCl in the biphasic system for sugar dehydration to HMF was to improve the extraction efficiency where HMF can be extracted to an organic layer easily due to the saturated aqueous layer. However, as mentioned above, the addition of NaCl affects the emulsion stability to a certain extent. Hence, different amounts of NaCl were being added into the system to test the reaction efficiency against control reactions. The results showed that the NaCl-saturated biphasic system was still required. Various salts and solvents were also screened with NaCl and MIBK found to be the best salt and solvent respectively (Fig. S4–S5†). Increased reaction rates and product selectivity were shown with polar aprotic solvents.²¹ Such solvents like THF and 2-butanone were also tested in this system. Generally, alcohol and ketone solvents with 4–6 carbon alkyl chains gave better results as

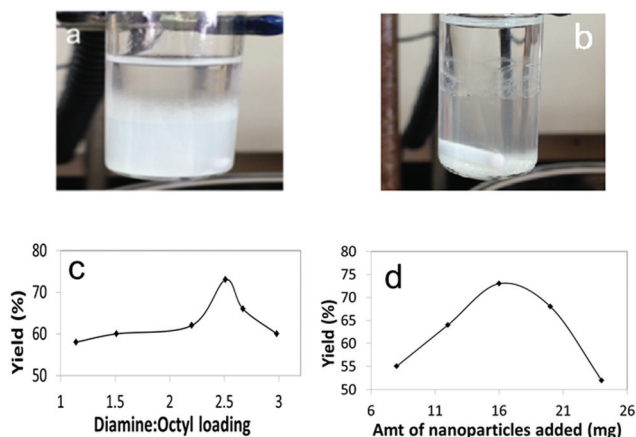


Fig. 1 (a) Emulsion system and (b) non-emulsion system; the effect of (c) diamine : octyl ratio (200 nm particles) and (d) nanoparticles loading on fructose dehydration to HMF. Reaction conditions: fructose (0.5 mmol), aq. HCl (2 mL, 0.25 M), NaCl (0.7 g), MIBK (6 mL), functional nanoparticles (16 mg), 100 °C, 2 h.

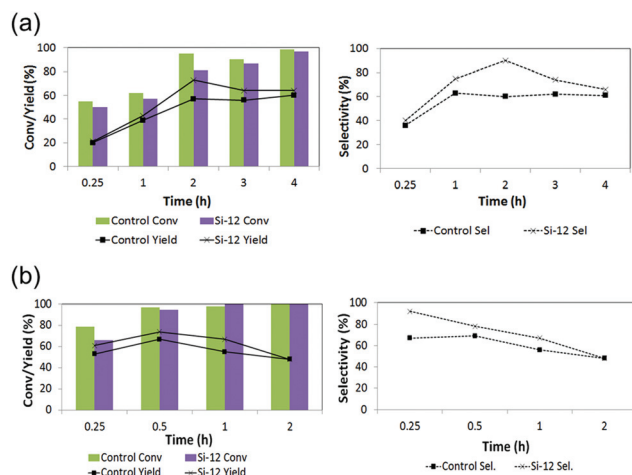


Fig. 2 Kinetic studies of fructose dehydration to HMF at temperatures of (a) 100 °C and (b) 120 °C. Reaction conditions: fructose (0.5 mmol), aq. HCl (2 mL, 0.25 M), NaCl (0.7 g), MIBK (6 mL), Si-12 (16 mg). For control reaction, no nanoparticles were added.

compared to their respective control reactions. Interestingly, 2-propanol showed a slower reaction despite having the most stable emulsion against sedimentation.

With these, kinetic studies for fructose dehydration to HMF were carried out at 100 °C and 120 °C. 5-Chloromethylfurfural (CMF), an analogue of HMF was also observed in the reaction mixture (Scheme S1†). A maximum total yield of 73% and a high selectivity of 90% was obtained at 100 °C for 2 h (Fig. 2a). This is >10% increase in yield and >20% increase in selectivity as compared to the control reaction. It was also indicated that the fructose dehydration rate is much faster in the emulsion system. At a higher temperature of 120 °C, there is also generally an increase in yield and selectivity as compared to the control reaction (Fig. 2b), especially at the initial stage (within 30 min) as the reaction at 120 °C is much faster. The highest yield and selectivity can be reached at a shorter time as compared to that carried out at 100 °C. This shows that the efficiency of the emulsion can be maintained at a higher temperature. A control reaction was also carried out using the non-functionalized silica nanoparticles to confirm that the improvement in the reaction efficiency is solely due to the emulsion in the system (Table S1,† entry 2). Although the partitioning ratio of HMF to the organic phase is the determining factor for the HMF yield and selectivity, the fast HMF diffusion rate in the emulsion system would accelerate the fructose dehydration steps. This would result in the fructose conversion reaching a maximum in a short time while in the control, HMF was still being produced during the reaction time of 2 h and 4 h and thereby HMF selectivity remained almost constant during the above mentioned time period. This has been demonstrated in Fig. 2a (100 °C reaction systems) and supported by the HMF stability test (Table S4†).

To further justify the effectiveness of this system, recyclability of the nanoparticles was also investigated as shown in

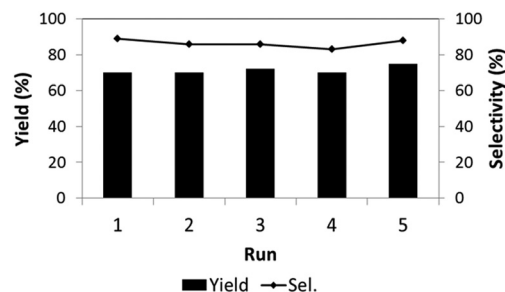


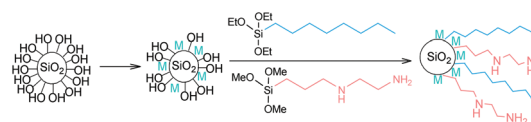
Fig. 3 Recycling of nanoparticles. Reaction conditions: fructose (0.5 mmol), aq. HCl (2 mL, 0.25 M), NaCl (0.7 g), MIBK (6 mL), Si-12 (16 mg), 100 °C, 2 h. The nanoparticles were centrifuged, washed with H₂O and MeOH, dried in a vacuum oven and used directly for subsequent runs.

Fig. 3. To our delight, consistent yield (bar chart) and selectivity (line chart) were observed up to at least 5 runs.

Encouraged by the results from fructose dehydration, the effect of emulsion in the biphasic system for glucose dehydration to HMF was also investigated. It is of great interest to produce HMF from other carbohydrates such as glucose, sucrose or even cellulose due to their abundance in nature and lower cost. The strategy here is to develop bifunctional nanoparticles by loading Lewis acid metal catalysts on the silica nanoparticles for catalyzing glucose isomerization reactions.

Various metals were first loaded onto the bare silica nanoparticles. These M/SiO₂ particles (without further loading of alkyl and amine groups) were then tested in the glucose dehydration reaction. Al/SiO₂ particles gave the highest glucose conversion and fructose yield (~20%) among the metals tested (Table S3†). Increasing the amount of Al/SiO₂ does not further improve the glucose conversion or fructose yield. It was also observed that varying the calcination conditions during the preparation of Al/SiO₂ does not affect the HMF yield (Table S3†).

The bifunctional silica nanoparticles Al/SiO₂ were then obtained after functionalization with octyl and diamine groups (Al/Si-12, Scheme 3) and tested in the glucose dehydration reaction in emulsion. A control reaction was also carried out using the non-functionalized Al/SiO₂ nanoparticles. As shown in Fig. S6a,† there is no significant increase in yield for the emulsion and non-emulsion systems. Using them separately as monofunctional nanoparticles (Al/SiO₂ + Si-12) yielded similar results (Fig. S6b†). We hypothesized that the emulsion might have blocked the accessibility to the heterogeneous Al site, resulting in a slower and less



Scheme 3 Functionalization of M/SiO₂ nanoparticles.

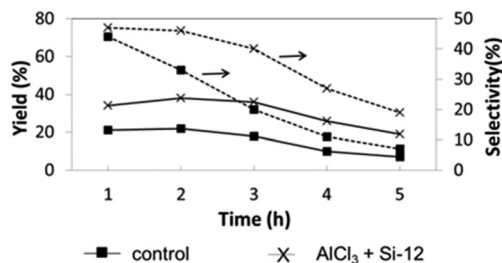


Fig. 4 Effect of monofunctional nanoparticles on glucose dehydration to HMF using AlCl_3 as the isomerization catalyst. Reaction conditions: glucose (1 mmol), NaCl-saturated aq. HCl (1 mL, 0.25 M), MIBK (3 mL), 2.5 wt% Al, Si-12 (90 mg), 150 °C. For control reaction, no nanoparticles were added.

efficient reaction. However, there is also no significant increase in yield as compared to the control reaction when an attempt to double the amount of Al/SiO_2 and halve the amount of Si-12 was carried out (Fig. S7†).

Monofunctional nanoparticles were then used in the glucose dehydration system with homogeneous AlCl_3 as the isomerization catalyst. To our delight, there is >10% increase in yield and 20% increase in selectivity as compared to the non-emulsion AlCl_3/HCl catalytic system (Fig. 4). Here, the emulsion system again demonstrated increased efficiency for AlCl_3/HCl catalyzed glucose dehydration due to the improved HMF extraction efficiency.

In conclusion, we have developed alkyl/amino functionalized silica nanoparticles to create an emulsion in a biphasic system for sugar dehydration to HMF. This creation of emulsion in a biphasic system apparently increases the contact surface area between both phases and therefore greatly improves the HMF extraction efficiency in the sugar dehydration process. As a proof-of-concept, more than 10% increase of HMF yield and 20% increase of selectivity were achieved for both fructose and glucose dehydrations in the emulsion system as compared to the conventional biphasic system. The excellent recyclability of the nanoparticles also further widens the potential of the biphasic system to be scaled up for industrial application.

Acknowledgements

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