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PAPER

# Supported ionic liquid silica nanoparticles (SILnPs) as an efficient and recyclable heterogeneous catalyst for the dehydration of fructose to 5-hydroxymethylfurfural†

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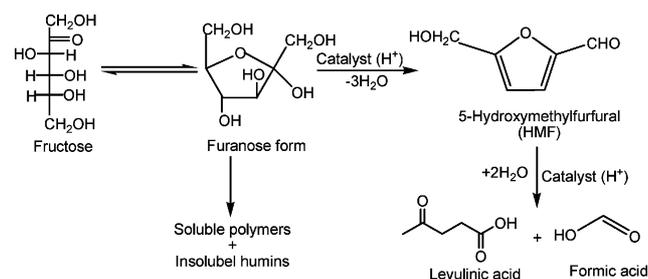
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Supported ionic liquid nanoparticles (SILnPs) having particle size ranging from  $293 \pm 2$  to  $610 \pm 11$  nm have been prepared by immobilization of ionic liquid, 1-(tri-ethoxy silyl-propyl)-3-methyl-imidazolium hydrogen sulfate (IL-HSO<sub>4</sub>) on the surface of silica nanoparticles. The catalytic activity of the prepared SILnPs was investigated for the dehydration of fructose to 5-hydroxymethylfurfural (HMF) in the presence of dimethylsulfoxide (DMSO) as a solvent. The reaction temperature and amount of catalyst have been optimized for dehydration of fructose over SILnPs using experimental design leading to 99.9% fructose conversion and 63.0% HMF yield using silica SILnPs ( $d = 610 \pm 11$ ) nm at 130.0 °C in 30 min reaction time. The SILnPs catalysts developed in this study present improved performances over other zeolites and strong acid ion exchange resin catalysts, and they have been efficiently and very easily recycled over seven times without any significant loss in fructose conversion and HMF yield.

## Introduction

Renewable biomass resources are promising alternatives for the sustainable supply of liquid fuels and chemical intermediates. Diminishing fossil fuel reserves and growing concerns about global warming have attracted the attention of the researchers worldwide to develop alternative sources of energy and chemicals.<sup>1,2</sup> Catalytic conversions of biomass or vegetable materials are important to develop alternatives to crude oil derivatives. Biomass is made up of four major components namely cellulose, hemicellulose, starch and lignin. The hydrolysis of these components results in sugars, which are the raw materials to produce chemicals and fuels.<sup>3</sup> The most important monosaccharides are glucose, fructose and xylose containing 6- and 5-carbon atoms. Among the many biomass-derived chemicals, 5-hydroxymethylfurfural (HMF) is a particularly valuable intermediate for fine chemicals and pharmaceuticals. In fact, HMF has also the potential to become an important biofuel and its oxidative derivative, 2,5-furandicarboxylic acid, may replace terephthalic acid as a monomer in the polymer industry.<sup>4,5</sup> Hence, acid catalyzed dehydration of fructose to

HMF has received substantial attention,<sup>6-14</sup> and its chemistry is described in Scheme 1, in that HMF is again rehydrated to by-products such as levulinic acid and formic acid, and oligomerized or polymerized by-products in the presence of acid catalysts and lowers the HMF yield. Different types of acid catalysts have been employed, such as mineral acids,<sup>6-8</sup> organic acids,<sup>9</sup> supported heteropoly acid (HPA),<sup>10</sup> zeolites,<sup>11,12</sup> cation exchange resins,<sup>11,11</sup> metal ions,<sup>13,14</sup> and metal phosphates.<sup>15</sup> Furthermore, different reaction solvents, including aqueous and organic media, and also a number of biphasic systems have been studied in detail.<sup>1,2,15,16</sup> Homogeneous acid catalyzed processes are effective and can achieve 70.0 to 90.0% fructose conversion with moderate (40.0 to 60.0%) HMF yield,<sup>9</sup> however it has severe drawbacks in terms of equipment corrosion, separation and recycling; while heterogeneous acid catalysts, such as



**Scheme 1** Reaction process and products of the acid catalyzed dehydration of fructose.

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H-form zeolites and metal phosphates can be recycled and have high (60.0 to 90.0%) HMF selectivity, but very low fructose conversion (30.0 to 60.0%) even after a very long (2 h) reaction time.<sup>15,17</sup>

Ionic liquids (ILs) have been used as a sort of novel reaction medium as well as catalysts for the dehydration of hexose to HMF.<sup>2,4,13,18,19</sup> Recently, 1-ethyl-3-methylimidazolium hydrogen sulfate ([EMIM][HSO<sub>4</sub>]) was investigated for fructose dehydration and 88.0% HMF yield was achieved in the presence of isobutylmethyl ketone as a co-solvent at 100.0 °C.<sup>19</sup> However, besides the very large amount (0.3 mL) of IL used (0.3 mL for 36 mg of hexose) which would have an important impact on the economics of the process, homogeneous catalysis has serious drawbacks in terms of the complex separation and recovery of the IL catalyst from the reaction mixture. Heterogeneous catalysis seems more promising for practical applications and Matras and Moreau have reported that neutral ionic liquids such as [BMIm][PF<sub>6</sub>] and [BMIm][BF<sub>4</sub>] were suitable reaction media for the dehydration of fructose to HMF in the presence of Amberlyst-15 acidic catalyst.<sup>20</sup> Moreau *et al.* have efficiently used Brønsted acidic 1-H-3-methyl imidazolium chloride as solvent and catalyst for the dehydration of fructose to HMF (92.0% yield),<sup>18</sup> while Bao *et al.* have demonstrated that Lewis acidic 3-allyl-1-(4-sulfurylchloride butyl)-imidazolium trifluoromethanesulfonate ([ASCBI][Tf]) catalyzed effectively the fructose dehydration under microwave irradiation.<sup>4</sup> In spite of all the studies that have been reported on the use of ionic liquids for the production of HMF, researchers are still far from an adequate understanding of the details and merits of ILs as a reaction medium or as catalysts for the fructose dehydration.

A major limitation on the use of ILs in the above context, relates to their high viscosity that reduces mass transfer ability. As a consequence, just a small fraction of the ionic liquid is active when used in bulk liquid form. Moreover, homogeneous acid catalyzed fructose dehydration processes using ILs are quite effective but present serious drawbacks in terms of separation and recycling of costly ILs, equipment corrosion as well as ILs toxicity. An approach to overcome these limitations is the development of supported ionic liquid catalysts (SILC) that requires smaller amounts of ionic liquid and simultaneously minimizes limitations associated to their viscosity, separation, corrosiveness and toxicity.<sup>21</sup> SILC combine attractive features of homogeneous catalysis such as the uniform nature of the catalytic centres, high specificity and selectivity of the catalyst, with important features of heterogeneous catalysts, such as high interfacial surface area, high system stability, reusability and potential use in fixed-bed reactor.<sup>21</sup> SILC have been successfully used as catalysts in various organic reactions such as hydroformylation,<sup>22,23</sup> alkylations,<sup>24</sup> hydrogenation,<sup>25,26</sup> *etc.*; the use of supported ionic liquids for the dehydration of fructose to HMF has been scarce. Recently, Bao *et al.* have reported the dehydration of fructose to HMF using immobilized Brønsted acidic 3-allyl-1-(4-sulfobutyl)imidazolium trifluoromethanesulfonate and Lewis acidic 3-allyl-1-(4-sulfurylchloride butyl) imidazolium trifluoromethanesulfonate ILs on silica gel.<sup>4</sup> Compared to sulfuric acid and sulfonylchloride modified silica gel, better results have been achieved for the dehydration reaction in terms of activity and reusability.

The main objective of the present study is the development of a new class of SILC. An acid ionic liquid with catalytic activity has been covalently bound to nano-sized amorphous silicas to produce Supported Ionic Liquid nanoParticles (SILnP). In particular, these systems have been developed to acquire the advantages of heterogeneous catalytic systems and the large surface area that is conferred by the nanoparticles. To evaluate the size effects originating from the silica supports, particles with different sizes (~200, 400 and 500 nm) are evaluated on the catalytic performance in the fructose dehydration reaction. The reusability of the SILnPs has been also investigated at the optimized reaction conditions reported in this work.

## Experimental

### Materials

Tetra-ethyl orthosilicate (TEOS) (98.0%), 3-chloropropyltriethoxy silane (95.0%) and diethyl ether (99.0%) were purchased from Sigma-Aldrich. Ammonia solution (25.0% NH<sub>3</sub> in water) and toluene (99.9%) were procured from Riedel-de Haën and BDH, respectively. Ethanol (99.5%) and sodium hydrogen sulfate monohydrate (NaHSO<sub>4</sub>·H<sub>2</sub>O) were obtained from Panreac. Dichloromethane (99.9%) and 1-methyl imidazole were acquired from Fluka. Dimethylsulfoxide (DMSO) (99.5%) was received from SDS. All the chemicals were used as received.

### Synthesis of silica nanoparticles

Silica nanoparticles were synthesized using the Stöber method.<sup>27</sup> This method is based on the hydrolysis of tetra-alkyl silicate in homogeneous alcoholic medium using ammonia as a catalyst. The average particle size of the SiO<sub>2</sub> nanoparticles was controlled by varying the aqueous ammonia [NH<sub>3</sub>(aq)] solution (Table 1).<sup>28</sup> In a typical procedure, TEOS (2.27 mL) was added to an Erlenmeyer flask containing ethanol (42.48 mL), deionised water (4.5 mL) and aqueous ammonia solution under constant stirring. The reaction was allowed to proceed under moderate stirring at room temperature for 24 h. The SiO<sub>2</sub> particles were collected by centrifugation, washed twice with ethanol and then washed thrice using deionised water, and finally the powders were dried at 50.0 °C for 24 h. Three batches of silica nanoparticles having distinct average particle sizes were prepared, as indicated in Table 1.

### Immobilization of IL on silica nanoparticles surface

The immobilization of the ionic liquid on silica nanoparticles surfaces was performed as described below:

**Synthesis of 1-(tri-ethoxy-silyl propyl)-3-methyl imidazolium hydrogen sulfate (IL-HSO<sub>4</sub>).** In a round bottom flask equipped with a reflux condenser and a gas inlet valve, a mixture of 0.05 mol 1-methyl imidazole (4.10 g) and 0.05 mol 3-chloropropyltriethoxy silane (12.04 g) was stirred at 95.0 ± 2.0 °C for 12 h, subsequently the pale yellow product was extracted twice with diethyl ether and dried at room temperature for 24 h.<sup>24</sup> The product was treated with NaHSO<sub>4</sub>·H<sub>2</sub>O for 2 h under ultrasonic treatment to exchange Cl<sup>-</sup> anions by HSO<sub>4</sub><sup>-</sup> anions.<sup>29,30</sup> The resulting mixture was extracted thrice with

**Table 1** Particle size and zeta potential of silica NPs and IL grafted silica NPs (Silica NPs prepared in ethanol using [TEOS] = 0.2 mol L<sup>-1</sup> and [H<sub>2</sub>O] = 5 mol L<sup>-1</sup>, for various amounts of NH<sub>3</sub>(aq))

Sample	NH <sub>3</sub> (aq) (mol L <sup>-1</sup> )/mL	Particle diameter d (nm) ± σ (%)		Zeta potential (mV)	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Sulfur (wt%)	IL loading (wt%)
		d <sub>DLS</sub>	d <sub>SEM</sub>				
Si-1	(0.2)/0.75	214 ± 3	203 ± 22	-31.8	16.7	nil	nil
Si-2	(0.5)/1.87	415 ± 5	391 ± 18	-40.6	11.8	nil	nil
Si-3	(2.0)/7.55	504 ± 9	476 ± 14	-37.9	9.7	nil	nil
Si-1-IL-HSO <sub>4</sub>	—	293 ± 2	257 ± 26	23.7	2.4	1.59	14.6
Si-2-IL-HSO <sub>4</sub>	—	471 ± 5	398 ± 13	26.9	0.1	1.63	15.0
Si-3-IL-HSO <sub>4</sub>	—	610 ± 11	489 ± 14	27.6	0.1	2.17	20.0
Si-4-IL-HSO <sub>4</sub>	—	—	—	24.7	0.2	3.14	28.9

dichloromethane, dried at 50.0 °C to remove any solvent or water content and used for immobilization process.

#### Immobilization of IL- HSO<sub>4</sub> onto nanoparticles surfaces.

Silica nanoparticles were dried in an oven at 50.0 °C for 20 h. In a round bottom flask, 1.4 g of SiO<sub>2</sub> NPs were dispersed in dry toluene. After the addition of 0.7 g of IL- HSO<sub>4</sub> the mixture was stirred under nitrogen atmosphere at 90.0 ± 2.0 °C for 16 h.<sup>24</sup> The solvent (toluene) and ethanol produced during this grafting step were separated by filtration. The excess of physisorbed IL-HSO<sub>4</sub> was removed by boiling dichloromethane extraction during 16 h. Finally the solid was separated by filtration and dried under vacuum followed by drying at 85.0 °C for 3 h. Three batches of supported ionic liquid nanoparticles were prepared corresponding to SiO<sub>2</sub> NPs with three distinct particle size distributions (Table 1). Additionally, to check the effect of additional ionic liquid on catalytic activity, one batch of SILnPs was prepared by using an equal mass of silica NPs (Si-1 = 1.4 g) and IL-HSO<sub>4</sub> (1.4 g) ionic liquid during immobilization process. The remaining procedure for immobilization was kept same and the sample was designated as Si-4-IL-HSO<sub>4</sub> (Table 1).

#### Characterization of the nanoparticles

<sup>29</sup>Si solid-state CP-MAS NMR spectra were recorded using a Bruker Avance 400 spectrometer with a spinning rate of 5.0 kHz. Particle morphology and size distribution was assessed by scanning electron microscopy (SEM) and qualitative elemental composition was assessed by energy-dispersive X-ray spectroscopy (EDX) analysis. SEM and EDX were performed using a Hitachi SU-70 SEM instrument coupled with an EDX Bruker Quantex 400 and operating at an accelerating voltage of 15 and 25 kV. For SEM and EDX analysis an aliquot of a dilute particle suspension was allowed to air dry on glass slides and then were coated with evaporated carbon. The average particle size (D) and the standard deviation (σ) were determined by measuring the size of *ca.* ~25 particles during the SEM analysis of each sample. Transmission electron microscopy (TEM) was carried out on a Hitachi H-9000 microscope operating at 300 kV. The samples were prepared by evaporating ethanol dilute suspensions on a copper grid coated with an amorphous carbon film. Hydrodynamic particle sizes were measured by Dynamic Light Scattering (DLS) and the zeta potential was measured by electrophoretic measurements, both using a Malvern Zetasizer NanoZS instrument. Water was used as the dispersion medium

for powdered samples and the measurements were recorded at 25.0 °C using quartz cells. Sulfur (wt%) was determined by elemental microanalysis technique using an elemental analyzer model-Thermo Finnigan Flash1112. The specific surface area of the SiO<sub>2</sub> NPs was determined by nitrogen adsorption BET measurements using Gemini Micromeritics instrument. In order to eliminate physisorbed moisture, the solid samples were degassed under vacuum at 120.0 °C for 4 h, prior to measurements.

#### Catalytic activity measurements and product analysis

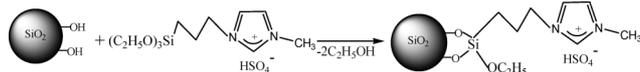
All the dehydration reaction experiments were performed in a 25 mL round bottom flask under magnetic stirring and equipped with a Liebig condenser. In a typical procedure, D-fructose (50.0 mg), DMSO (0.5 mL) and the required amount of powdered catalyst (SILnPs) were charged into the flask. The reaction mixture was stirred magnetically at 1000 rpm and heated with a thermostatically controlled (0.1 °C) oil bath for a specific time. After reaction, the mixture was decanted to a volumetric flask and diluted with miliQ water and then analyzed by HPLC in isocratic mode. D-Fructose was analyzed and quantified using a Gilson HPLC equipped with a Rezex 250 × 4.6 mm (i.d.) column and a refractive index detector (RID). The column temperature was maintained at 60.0 °C and water was used as mobile phase (flow rate: 0.15 mL min<sup>-1</sup>). HMF was quantified using a Gilson 306 HPLC pump and a Spherisorb ODS S10 C18 column, coupled to a Gilson 118 UV-vis detector (280 nm). The mobile phase consisted of 30.0% (v/v) methanol in an aqueous solution of 10.0% methanol (flow rate 0.7 mL min<sup>-1</sup>).<sup>19</sup> Known samples of both reagents and products were used as standards and calibration curves were used for quantification. To ensure the reproducibility of the reaction, repeated experiments were carried out under identical reaction conditions. The obtained results including conversion and yield data were found to be reproducible in the range of ± 5.0% variation. Statistical analysis was made using Statistica 8.0 from Statsoft<sup>©</sup> with 95.0% confidence level.

## Results and discussion

### Synthesis and surface modification of nanosilica catalysts

To obtain morphological well-defined Stöber SiO<sub>2</sub> particles of distinct particle sizes, the reaction conditions were kept

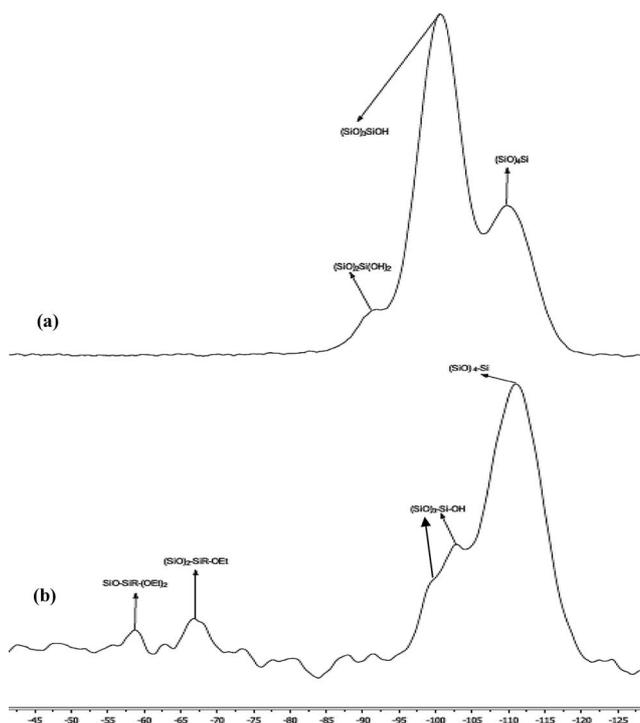
through out all the synthesis experiments but varying the amount of aqueous ammonia  $[\text{NH}_3(\text{aq})]$  solution. As such, the  $\text{NH}_3(\text{aq})$  concentration was varied from 0.2 to 2 mol  $\text{L}^{-1}$  to produce  $\text{SiO}_2$  particles with average size of 214 nm to 504 nm, in diameter (Table 1).<sup>28</sup> These  $\text{SiO}_2$  NPs were then used as substrates to immobilize 1-(tri-ethoxy silyl-propyl)-3-methylimidazolium hydrogen sulfate (IL-HSO<sub>4</sub>) *via* covalent grafting through reaction of the ethoxy groups with  $\text{SiO}_2$  surface silanol, as illustrated in Scheme 2.



**Scheme 2** Schematic representation of 1-(tri-ethoxy silyl-propyl)-3-methylimidazolium hydrogen sulfate (IL-HSO<sub>4</sub>) immobilization on silica nanoparticles.

The ionic liquid can be bounded or supported on a solid support surface *via* two distinct approaches. The first approach involves the simple adsorption of the ionic liquid onto the surface of the solid support (physical bonding) whereas the second approach involves the covalent attachment of ionic liquids to the solid support surface (chemical bonding).<sup>22</sup> The former has a serious drawback of leaching of ionic liquid during vigorous reaction conditions, and the chemical bonding would thus be more advantageous for catalytic applications. In this approach, the ionic liquid could be covalently bonded with the solid support surface *via* the IL cation or anion.<sup>24</sup>

Fig. 1 shows<sup>29</sup> Si-cross polarised MAS-NMR spectra for silica nanoparticles before (Si-3) and after (Si-3-IL-HSO<sub>4</sub>) the immobilization of the ionic liquid. Other silica samples showed similar behaviour. Preliminary evidence for covalent



**Fig. 1** <sup>29</sup>Si CP-MAS NMR of silica nanoparticles (a) before (Si-3 sample) and (b) after (Si-3-IL-HSO<sub>4</sub> sample) immobilization of the ionic liquid.

grafting of the ionic liquid is the disappearance of the peak corresponding to surface Si-OH groups of the silica support after immobilization. NMR signals centred at  $-91$  and  $-101$  ppm, assigned to  $(\text{SiO})_2\text{Si}(\text{OH})_2$  and  $(\text{SiO})_3\text{Si-OH}$  groups, respectively, are strongly diminished, indicating extensive grafting of the IL at the silica surface. A very small peak at  $-101$  ppm and the small shoulder at  $-100$  ppm assigned to  $(\text{SiO})_3\text{Si-OH}$  are observed along with the broadening of the peak at  $-111$  ppm assigned to  $(\text{SiO})_4\text{Si}$  groups, indicating the presence of residual silanol groups. Similar observations have been reported by Hölderich *et al.*<sup>24</sup> Additionally, the two peaks observed at  $-59$  ppm and  $-67$  ppm (Si-3-IL-HSO<sub>4</sub> sample) assigned to Si-O-SiR-(OEt)<sub>2</sub> and (Si-O)<sub>2</sub>-SiR-OEt, respectively,<sup>24</sup> further confirm the ionic liquid attachment at the silica surface from organic cation moiety either *via* one or two Si-O-Si covalent bonds (Scheme 2).

SEM and TEM images for typical  $\text{SiO}_2$  samples before and after IL immobilization are shown in Fig. 2. It should be first noted that the morphological homogeneity that characterized these amorphous  $\text{SiO}_2$  particles was maintained after IL grafting. However, the SEM images also reveal particle coalescence through formation of interparticle necks that are possibly due to the presence of the IL covering the silica surfaces. EDX peaks due to sulfur have been detected on the IL surface modified samples which are consistent with the presence of IL at the surface of the particles; this result was further confirmed by elemental microanalysis performed on the same samples (Table 1). Ionic liquid (wt%) loading was also calculated from the elemental microanalysis (Table 1). Additionally, the zeta potential of aqueous suspensions (pH 7) of the silica nanoparticles and IL immobilized samples were measured at 25.0 °C (Table 1). For example, the zeta potential of the sample Si-3 varied from  $-37.9$  mV to 27.6 mV after IL immobilization. A similar trend has been observed for the other analysed  $\text{SiO}_2$  samples. Furthermore, after immobilization of ionic liquid on the silica surface, the hydrodynamic diameters of Si-1, Si-2 and Si-3 samples increased from 214 to 293, 415 to 471 and 504 to 610 nm, respectively (Table 1).

Both the zeta potential measurements and the increase observed in the hydrodynamic diameter of the above samples are strong evidence for the successful IL surface modification of  $\text{SiO}_2$  nanoparticles. This surface modification is probably better described as a multi-layered process, in which additional IL molecules interact with those covalently attached to the silica surfaces. This type of behaviour would explain the increase in the hydrodynamic diameters of IL modified silica samples, as compared to the starting silica samples. The BET surface area of as such silica nanoparticles and ionic liquid immobilized silica nanoparticles are indicated in Table 1. Surface area has been decreased from 16.7 to 9.7  $\text{m}^2 \text{g}^{-1}$  with increasing size from 214 to 504 nm, respectively. As expected the  $\text{SiO}_2$  NPs surface area after IL immobilization decreased due to IL surface coverage. These values are in good agreement with previous studies.<sup>31</sup> Although particle aggregation in the dry form *via* inter-particle necking can not be ruled out, as clearly observed in Fig. 2, the DLS results also indicates narrow particle size distributions. This is in agreement with aqueous samples of homogeneously dispersed IL modified  $\text{SiO}_2$  NPs with no relevant NPs aggregation.

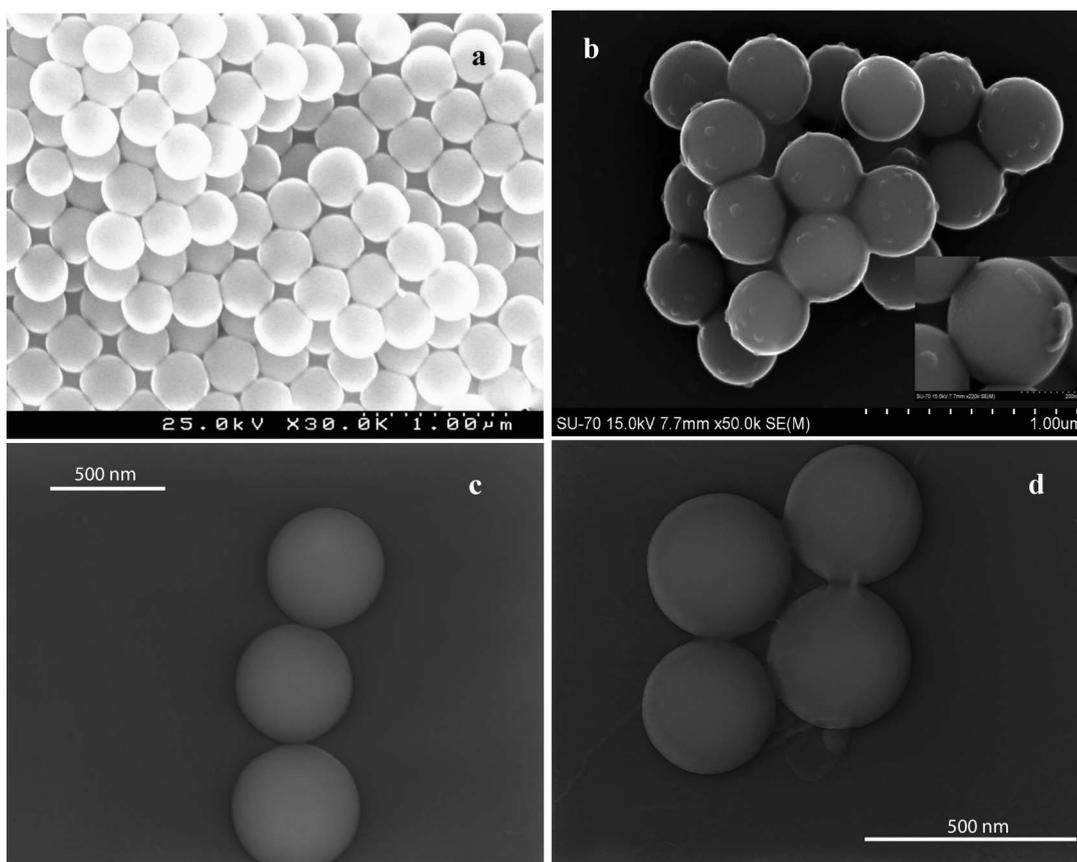


Fig. 2 SEM (a & b) and TEM (c & d) images of Si-2 and Si-2-IL-HSO<sub>4</sub>, respectively.

### Catalytic activity measurements for fructose dehydration

Dehydration of fructose to 5-hydroxymethylfurfural (HMF) involves a number of elementary steps in which the three water molecules per fructose molecule are removed in the presence of acid catalyst (Scheme 1).<sup>1,2,12</sup> During this dehydration process, HMF is rehydrated again in the presence of acid catalyst and gave undesired products such as levulinic acid and formic acid. In the literature, it is reported that solvent plays an important role in fructose dehydration,<sup>2,32</sup> and various solvent systems were used as reaction media such as water,<sup>9,33,34</sup> organic solvents and organic-water mixtures,<sup>6,14,32</sup> ionic liquids,<sup>13,35,36</sup> and biphasic water-organic systems.<sup>37,38</sup> Water based processes are more advantageous in terms of environmental and ecological aspects, however, in the presence of water HMF further rehydrates into levulinic and formic acids. It is reported that the highest selectivity for HMF has been obtained in the presence of DMSO as a solvent because the furanoid form is preferred in DMSO.<sup>2,20</sup> For that reason, DMSO was also used as a solvent in the present study. The yellow colour of the reaction mixture after reaction is a significant test for the absence of polymeric substances commonly known as humins.<sup>18</sup>

### Optimization of the reaction conditions using experimental design

The optimization of a process involves the identification of its most important parameters and the impact of their variation on

the process. One way to accomplish this identification would be testing each variable at a time which would be an exhaustively long and costly task. This simplistic approach would also ignore the interactions between process variables. However these problems can be overcome by using experimental design techniques, in which the factors are analyzed simultaneously and can also focus on more than one answer at the same time.<sup>39</sup> Factorial designs are sufficient to estimate the linear and interaction models, and require a limited number of experimental runs. Some advantages of using a factorial design are based on the fact that averages are more stable than single observations and the more data one averages, the more reliable results are obtained.

A Box-Wilson central composite design (CCD) was defined with the purpose of identifying the most important parameters and their interactions to optimize the reaction conditions for the dehydration of fructose to HMF. Circumscribed central composite (CCC) designs are the balance and original form of experimental design with circular, spherical or hyperspherical symmetry and require 5 levels for each factor. In our case, experimental design is used to find the experimental conditions with the major influence on the HMF% yield. Our aim was to find the combination of the control factors to obtain higher values for HMF% yield.

Two parameters such as reaction temperature ( $T/^\circ\text{C}$ ) and catalyst amount ( $C$ , mg) were tested for the dehydration of fructose to HMF using the Si-3-IL-HSO<sub>4</sub> sample. A central composite design, 2<sup>2</sup>, with four replications of the central point

**Table 2** Experimental data for the central composite design  $2^2$  of fructose dehydration reaction

X1	X2	C (mg)	T/°C	% Conversion
-1	-1	20.0	90.0	23.0
1	-1	40.0	90.0	25.5
-1	1	20.0	130.0	99.2
1	1	40.0	130.0	99.9
0	0	30.0	110.0	99.4
0	0	30.0	110.0	99.4
-1.414	0	15.9	110.0	97.2
1.414	0	44.1	110.0	98.8
0	-1.414	30.0	81.8	14.1
0	1.414	30.0	138.2	99.9
0	0	30.0	110.0	99.4
0	0	30.0	110.0	99.3

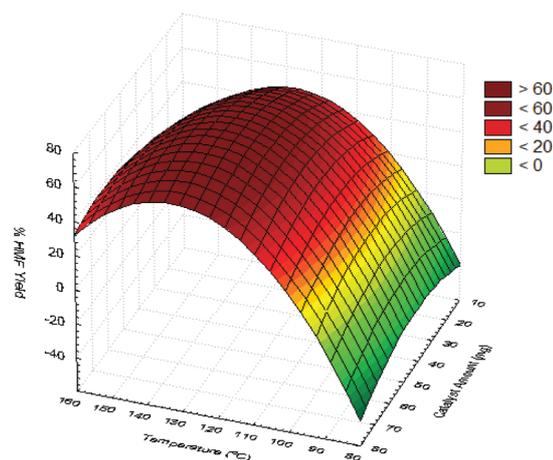
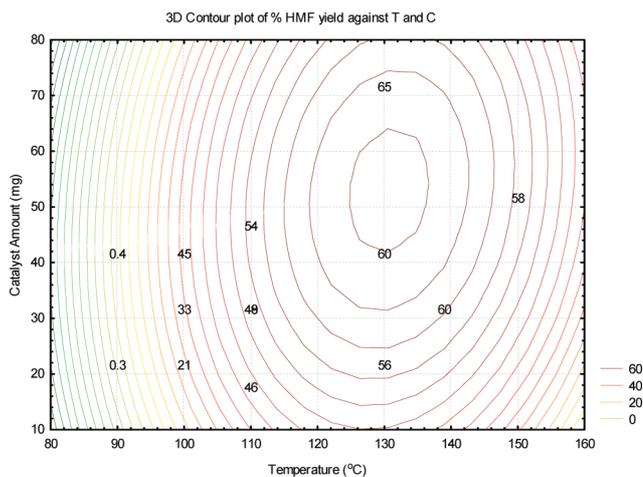
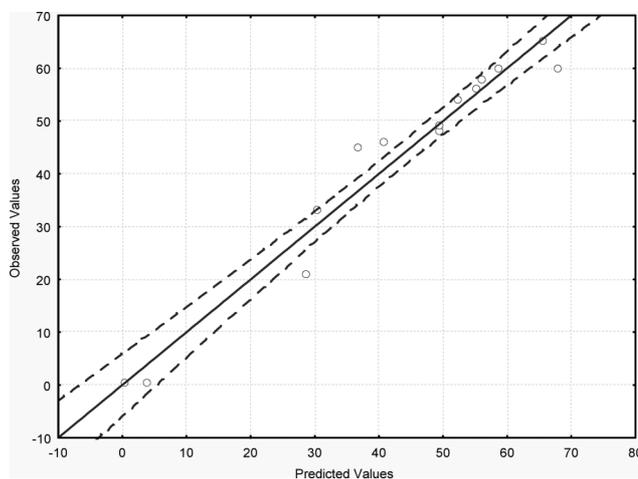
was used (Table 2). The conditions were defined for zero level (central point) and one level (+1 and -1, the factorial points). The design was extended up to the axial points which are at a distance of  $\alpha$  coded units from the central point,  $\alpha = (k)^{1/2}$ , where  $k$  is number of variables.

As mentioned in Table 2, fructose conversion is found in the range of 23.0 to 99.9% in the employed experimental design reaction conditions. The fructose conversion was of 23.0% using 20.0 mg catalyst, which is slightly increased and reached 25.5% by adding double quantity of Si-3-IL-HSO<sub>4</sub> catalyst (40.0 mg) at the temperature of 90.0 °C; while with an increase in temperature from 90 to 110.0 °C, the conversion of fructose increased from 25.5 to 99.0%, over 40.0 mg of Si-3-IL-HSO<sub>4</sub> catalyst. These results suggest immediately that temperature has a more important effect than catalyst amount for the conversion of fructose.

The contour plot and response surface plot of the HMF yield against reaction temperature and catalyst amount are presented in Fig. 3 for the Si-3-IL-HSO<sub>4</sub> catalyst sample. The response surface and contour plot indicate that the reaction is favoured by a reaction temperature (T) at 130.0 °C, and is disfavoured for higher temperature. At 130.0 °C, HMF% yield is between 60.0% over 44.1 mg catalyst, which is decreased to 58.0% with increasing temperature to 150.0 °C at 50.0 mg of catalyst amount. HMF% yield was observed 65.0% with higher amount of catalyst (70.0 mg) at 130.0 °C, however, 60.0% HMF yield is observed at 130.0 °C reaction temperature and 40.0 mg of catalyst amount and hence these conditions were chosen as optimized reaction conditions. We have derived a second order mathematical model, presented in eqn (1), for the experimental results obtained for the fructose dehydration reaction over Si-3-IL-HSO<sub>4</sub> catalyst sample using Statistica 8.0 statistical software.

$$\% \text{ HMF yield} = -580.9 + (9.733 T) + (0.5371 C) - (0.0383 T^2) + (0.0055 T C) - (0.0118 C^2) \quad (1)$$

Fig. 4 shows the correlation between the model predicted values of % HMF yield and experimental data (observed values). As can be seen the predicted values obtained by eqn (1) provide a good description of the experimental results. The significance of the estimated effects was tested by analysis of variance (ANOVA). The ANOVA test indicates that the model adequately describes the % HMF yield. The analysis of variance of experiment is presented in Tables 3 and 4. Normally, the parameters with  $p < 0.05$  are considered as significant

**Fig. 3** 3D Contour plot and response surface plot of % HMF yield against reaction temperature ( $T/^\circ\text{C}$ ) and catalyst amount ( $C, \text{mg}$ ).**Fig. 4** Correlation between observed and predicted values of % HMF yield (symbol O represents experimental results).

parameters and correlation factor ( $R^2$ ) value greater than 0.85 is desired for the mathematical model to be considered as a good approximation of the reaction,<sup>39,40</sup> however in our case, the significance of each coefficient was determined through a  $p$  value test ( $p < 0.00001$ ) considering 95.0% of confidence in which low  $p$  values indicate high significance of the corresponding

**Table 3** Regression coefficients for the response HMF% yield for experimental designs of 2 variables (T and C) for fructose dehydration over Si-3-IL-HSO<sub>4</sub> catalyst

Term	Coefficients	Standard deviation	<i>t</i> -Value	<i>p</i> -Level
Intercept	-587.695	65.595	-8.955	0.000009
T	9.998	1.129	8.853	0.000010
C	-0.040	0.820	-0.048	0.962643
T <sup>2</sup>	-0.040	0.005	-7.757	0.000028
T × C	0.012	0.008	1.504	0.166694
C <sup>2</sup>	-0.014	0.006	-2.225	0.53119

R<sup>2</sup> = 95.8%; Adjusted R<sup>2</sup> = 93.5%; *t*-value for coefficients (absolute value).

**Table 4** ANOVA table for experimental designs for fructose dehydration over Si-3-IL-HSO<sub>4</sub> catalyst

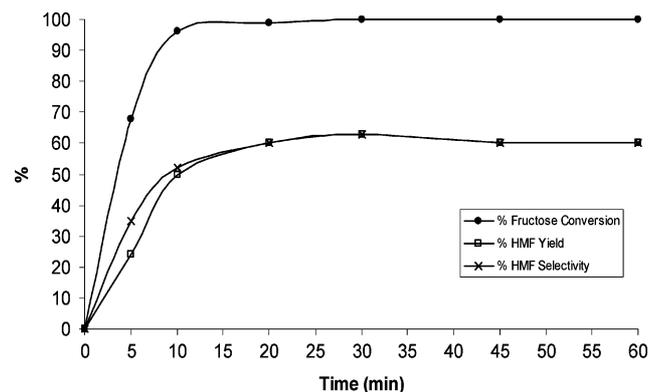
Source	SS	df	MS	F	<i>p</i> -Level
Regression	5663.17	5	1132.63	41.46	0.000006
Residuals	245.871	9	27.31		
Total	5909.04				

SS = sum of squares; df = degree of freedom; MS = mean square.

coefficient. The square regression is more adequate for our purposes than the linear regression given that the *p* value of 0.000006 and R<sup>2</sup> of 0.95, which shows that our theoretical model is very good fit with the experimental data for the fructose dehydration over Si-3-IL-HSO<sub>4</sub> catalyst. The *p* value obtained for T and T<sup>2</sup> variable is lower than the usual statistical value (*p* < 0.05), indicating that the variable with the largest effect on HMF% yield was the temperature (T) and square of temperature (T<sup>2</sup>).

### Effect of reaction time on fructose dehydration

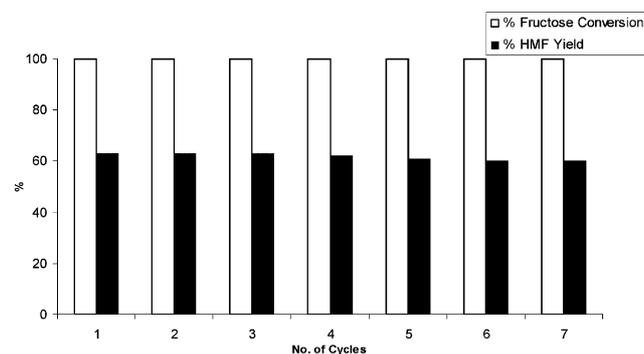
To study the effect of reaction time, kinetic experiments were carried out at the reaction temperature and catalyst amount previously selected. Fig. 5 shows the effect of reaction time on the fructose dehydration reaction at 130.0 °C over Si-3-IL-HSO<sub>4</sub> catalyst (40.0 mg). It was observed that within 5 min of reaction time fructose conversion and HMF% yield reached to 68.0% and 24.0%, respectively. With increasing time from 10 min to 30 min fructose conversion and HMF% yield increased from 96.0 to 99.9% and 50.0 to 63.0% respectively. It is clearly seen that the yield and selectivity of HMF increased gradually during the first 30 min of reaction time. When the time was extended to 45 min and longer (60 min), the yield and selectivity of HMF decreased, which suggested that the HMF is further rehydrated in the presence of acid catalyst and converted into by-products as per reaction Scheme 1. Tong and Li also reported a similar kind of behaviour over a reaction time for fructose dehydration using *N*-methyl-2-pyrrolidonium methyl sulfonate ([NMP][CH<sub>3</sub>SO<sub>3</sub>]) ionic liquid in a homogeneous catalytic system.<sup>2</sup> Consequently, we have considered 30 min as the optimized reaction time for dehydration of fructose over Si-3-IL-HSO<sub>4</sub> and used in further studies.



**Fig. 5** Effect of reaction time on the fructose dehydration over Si-3-IL-HSO<sub>4</sub> catalyst. Reaction conditions: Fructose = 50.0 mg, DMSO = 0.5 mL, Catalyst = 40.0 mg, *T* = 130.0 °C.

### Reusability of Si-3-IL-HSO<sub>4</sub> catalyst in fructose dehydration

To study the reusability of the catalyst, the solid powder sample was separated from the reaction mixture using centrifugation, washed with methanol and dried at 70.0 °C in oven prior to reuse. The regenerated catalyst Si-3-IL-HSO<sub>4</sub> was used for the dehydration of fructose to HMF at optimized reaction conditions derived from previous experiments: 130.0 °C reaction temperature, 40.0 mg Si-3-IL-HSO<sub>4</sub> catalyst and 30 min reaction time. Reusability of catalyst Si-3-IL-HSO<sub>4</sub> was studied over seven cycles and beyond that the catalyst recyclability test was not performed. No significant loss in the conversion of fructose (99.9%) was observed over seven cycles (Fig. 6). Furthermore, the yield of HMF was maintained constant at 63.0% during the first three recycling test and then decreased slightly from 63.0% to 60.0% after seven cycles. These results suggested that there is no significant leaching of the ionic liquid from silica support surface during vigorous operating conditions and the catalyst is efficiently recycled for seven times without considerable loss in its activity and selectivity in the dehydration of fructose.



**Fig. 6** Reusability of the Si-3-IL-HSO<sub>4</sub> catalyst in the dehydration of fructose. Reaction conditions: Fructose = 50.0 mg, Catalyst = 40.0 mg, *T* = 130.0 °C, DMSO = 0.5 mL, Time = 30 min.

### Dehydration of fructose over SILnPs of various sizes and other solid acid catalysts

Dehydration of fructose was examined over various solid acid catalysts at optimized reaction conditions (Table 5). Dehydration of fructose was performed without adding any catalyst

**Table 5** Dehydration of fructose to HMF using different catalysts

Entry No.	Catalyst	Time (min)	% Fructose conversion	% HMF yield
1.	No catalyst	30	0.3	—
2.	Si-1	30	1.0	—
3.	Si-1-IL-HSO <sub>4</sub>	5 <sup>a</sup>	29.6	12.9
		30	99.9	63.5
		60	99.9	62.1
4.	Si-2-IL- HSO <sub>4</sub>	5 <sup>a</sup>	33.2	15.2
		30	99.9	63.0
		60	99.9	60.0
5.	Si-3-IL- HSO <sub>4</sub>	5 <sup>a</sup>	43.5	17.7
		30	99.9	63.0
		60	99.9	60.0
6.	Si-4-IL-HSO <sub>4</sub>	30	99.9	63.3
7.	Si-4-IL-HSO <sub>4</sub> <sup>b</sup>	60	99.9	60.2
8.	Si-3-IL- HSO <sub>4</sub> <sup>c</sup>	60	99.9	63.5
9.	Na-ZSM-5 (Si/Al = 900)	30	1.0	0.8
10.	Na-ZSM-5 (Si/Al = 24)	30	1.0	0.5
11.	H-ZSM-5 (Si/Al = 24)	30	93.9	48.3
12.	Na-β (Si/Al = 25)	30	99.0	49.4
13.	H-β (Si/Al = 25)	30	99.9	65.2

**Reaction Conditions:** Fructose = 50.0 mg, catalyst = 40.0 mg,  $T = 130.0\text{ }^{\circ}\text{C}$ , DMSO = 0.5 mL. <sup>a</sup> Catalyst = 20.0 mg. <sup>b</sup>  $T = 150.0\text{ }^{\circ}\text{C}$ , catalyst = 50.0 mg. <sup>c</sup> 300.0 mg molecular sieve was added to adsorb water.

(entry 1) and almost no conversion was observed at the selected reaction conditions. Pure silica sample (entry 2) having particle size of 214 nm (Si-1) was also used to examine the activity of support in supported ionic liquid nanoparticles catalysts. Only 1.0% fructose conversion was obtained over pure silica sample (Si-1), suggesting that silica is essentially an inactive species in fructose dehydration. Silica supported ionic liquid nanoparticles of various sizes were examined to study the effect of particle size of the SILnPs on fructose dehydration. For these, the reaction was performed using 20.0 mg of catalyst at 130.0 °C over a time of 5 min (entries 3 to 5). There was no significant correlation observed between particle size, % conversion and HMF% yield at a low reaction time (5 min) over a less amount of catalyst (20.0 mg). Si-3-IL-HSO<sub>4</sub> sample gave higher fructose conversion (43.5%) and HMF yield (17.7%), while 29.6% fructose conversion and 12.9% HMF yield was observed over Si-1-IL-HSO<sub>4</sub> sample. The observed differences in catalytic activity results may be due to the variation in the amount of IL loading (Table 1) in the final SILnPs samples. Almost the same fructose conversion (99.9%) and HMF yield (~63.0%) was observed over a 40.0 mg of catalyst after 30 min of reaction time (entries 3 to 5). The fructose dehydration reaction was performed on Si-4-IL-HSO<sub>4</sub> sample having a higher amount of IL loading (28.9 wt%) on the silica surface (entries 6 and 7) and 99.9% fructose conversion with 63.3% HMF yield was observed. Higher amount of IL loading resulted into higher amount of acid site density; nevertheless these results suggest that higher acid site density has no advantage to achieve higher conversions or yields. Furthermore, after 60 min of reaction time HMF% yield was slightly decreased (~60.0%) indicating that HMF is further rehydrated into by-products in the presence of acid catalysts (entries 3 to 5). Hence, we have performed one reaction (entry 8) by adding 300.0 mg molecular sieve with Si-3-IL-HSO<sub>4</sub> catalyst to adsorb the water generated during dehydration reaction that is responsible for the side reaction. No significant increase in HMF% yield was achieved in the presence

of molecular sieve for Si-3-IL-HSO<sub>4</sub> catalyst; however, HMF% yield is maintained after 60 min of reaction time.

Fructose dehydration was carried out in the presence of the commercially available ZSM-5 and beta (β) zeolites (entries 9 to 13) to compare with the results of SILnPs catalyst. Only 1.0% fructose conversion was observed in the presence of Na-ZSM-5 zeolite catalyst having Si/Al ratio of 24 and 900 with 0.5 and 0.8% HMF yield respectively, while Na-β zeolite gave 99.0% fructose conversion with 49.4% HMF yield after 30 min of reaction time. The H-ZSM-5 catalyst sample gave 93.9% fructose conversion with 48.3% HMF yield (entry 11), while 99.9% fructose conversion and 65.2% HMF yield was observed over H-β zeolite (entry 13). HMF% yield observed over H-β zeolite was slightly higher than the SILnPs developed in this study. Nevertheless, it is reported that H-mordenite (Si/Al = 11) gave 54.0% fructose conversion with 50.0% HMF yield after 30 min of reaction time at 165.0 °C in water/methyl isobutyl ketone solvent mixture (1 : 5 v/v).<sup>12</sup> Additionally, dehydration of fructose to HMF was investigated on a 1.0 g (5.6 mmol) scale at 90 °C using DMSO and water as a solvent over an acidic IL (7.5 mol%) *N*-methyl-2-pyrrolidonium hydrogen sulfate [NMP][HSO<sub>4</sub>], which possess the same acidic group as the ionic liquid used in our study.<sup>2</sup> After 2 h of reaction time, 69.4% and 2.4% HMF yield were observed in DMSO and water, respectively. The SILnPs developed in the present study gave 63.0% HMF yield but over 30 min of reaction time at 130.0 °C. Also, unlike the above system<sup>2</sup> the IL modified particles used in this research can be easily separated from the reacting mixture. Moreau *et al.* obtained only 52.0% HMF yield after 3 h in the presence of 120.0 mg of Amberlyst-15 (sulfonic ion-exchanged resin) catalyst and 1-butyl-3-methyl imidazolium tetrafluoroborate ([BMIM][BF<sub>4</sub>]) as a solvent,<sup>20</sup> while Qi *et al.* observed 59.1% fructose conversion with 51.6% HMF yield after 60 min of reaction time in 70 : 30 w/w acetone-water reaction medium at 120.0 °C in microwave heating over strong acid cation exchange resin Dowex 50wx8-100.<sup>1</sup>

Under microwave heating, 84.0% fructose conversion with *ca.* 63.0% HMF yield was observed after 30 min of reaction time over a sulfated zirconia ( $\text{SO}_4^{2-}/\text{ZrO}_2$ , 20 mg) using a mixture of acetone-DMSO (70:30 w/w) as a solvent at 160.0 °C.<sup>32</sup> In this context, the present results are promising for fructose conversion (99.9%) at a lower reaction temperature (130.0 °C). Furthermore, it is reported that sulfonylchloride ( $\text{SiO}_2\text{-SO}_2\text{Cl}$ ) and sulfuric acid ( $\text{SiO}_2\text{-SO}_3\text{H}$ ) modified silica gel catalysts gave high conversions of fructose (92.0 and 95.0%, respectively) and moderate yields of HMF (60.0 and 63.0%, respectively) under microwave irradiation (200 W),<sup>4</sup> which are almost identical with the results obtained over SILnPs. However, the activities of both catalysts decreased to almost zero after the three recyclability tests, while the present results show a catalyst with high efficiency and that can be recycled over seven times without significant loss in its activity and selectivity. Therefore, our experiments in conjunction with results from the literature indicate that the silica supported ionic liquid nanoparticles catalysts synthesized in this study are more promising catalysts than H-form of ZSM-5 and mordenite zeolites as well as Amberlyst-15, commercially available Dowex 50wx8–100 ion exchange resin, sulfonylchloride ( $\text{SiO}_2\text{-SO}_2\text{Cl}$ ) and sulfuric acid ( $\text{SiO}_2\text{-SO}_3\text{H}$ ) modified silica gel. Higher % HMF yields (80.0 to 90.0%) were reported using some homogeneous ionic liquid catalytic systems,<sup>2,19</sup> but they use very large amounts of ionic liquid for the dehydration of fructose to HMF and required vigorous post reaction work-up to recover the costly IL from the reaction mixture, while the SILnPs catalyst developed in the present study is easy to separate from reaction mixture, easily and efficiently recycled and contains a small amount of ionic liquid on the surface of silica nanoparticles, which will also be beneficial from the economic and environmental point of view.

## Conclusions

Silica supported ionic liquid nanoparticle catalysts having varied particle sizes (293 to 610 nm) have been synthesized and successfully employed as solid acid catalysts for the dehydration of fructose to HMF. Supported ionic liquid nanoparticles (SILnPs) were characterized by techniques that confirmed the covalent bonding between the IL cation and the silica surface. The morphology of SILnPs catalyst samples observed by TEM and SEM further confirmed that ionic liquid covered the surface of silica support.

The simultaneous effects of different reaction parameters such as reaction temperature and catalyst amount on % HMF yield were investigated using experimental design and found that reaction temperature is the key parameter in fructose dehydration over Si-3-IL- $\text{H}_2\text{SO}_4$  catalyst. Based on the measured results, a statistical model was developed that provided a good description of the experimental data and the ANOVA analysis indicates that the variable temperature (T) and square of temperature ( $T^2$ ) have a far more significant effect on HMF% yield than the catalyst amount. At optimized reaction conditions, 99.9% fructose conversion and 63.0% HMF yield was achieved over SILnPs indicating that the SILnPs catalysts here synthesized are better than H-form of ZSM-5 and mordenite zeolites as well as Amberlyst-15, commercially available Dowex 50wx8–100 ion exchange resin, sulfonylchloride ( $\text{SiO}_2\text{-SO}_2\text{Cl}$ ) and sulfuric

acid ( $\text{SiO}_2\text{-SO}_3\text{H}$ ) modified silica gel for fructose dehydration. No significant effect of support particle size was observed. The catalyst was efficiently and easily recycled over seven times without significant loss in its activity and selectivity in dehydration of fructose to HMF.

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