Carbohydrate Research 351 (2012) 35–41

Contents lists available at SciVerse ScienceDirect

Carbohydrate Research

journal homepage: www.elsevier.com/locate/carres

Selective dehydration of fructose to 5-hydroxymethylfurfural catalyzed by mesoporous SBA-15-SO_3H in ionic liquid BmimCl

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ARTICLE INFO

Article history:
Received 16 November 2011
Received in revised form 4 January 2012
Accepted 6 January 2012
Available online 17 January 2012

Keywords:
5-Hydroxymethylfurfural (HMF)
Fructose
Dehydration
Acid catalysts
Ionic liquids

ABSTRACT

Mesoporous SBA-15 materials functionalized with propylsulfonic acid groups (SBA-15-SO_3H) were synthesized through a conventional one-pot route. It was used as a catalyst for the selective synthesis of 5-hydroxymethylfurfural (HMF) from dehydration of fructose using BmimCl as solvent. Reaction time, temperature and fructose concentration were investigated during the HMF synthesis procedure. The catalyst SBA-15-SO_3H exhibits high fructose conversion (near 100%) and HMF selectivity (about 81%) with good stability in the HMF synthesis. It was a suitable catalyst to produce HMF from renewable carbohydrates in potential industrial process.

1. Introduction

Biomass is a promising alternative for sustainable supply of precious intermediates and platform chemicals to the chemical industry.[1,2] Amongst many possible biomass derived chemicals, 5-hydroxymethylfurfural (5-HMF) can be used as valuable intermediate for fine chemicals, pharmaceuticals and furan-based polymers. It is considered to have the potential to be a sustainable substitute for petroleum-based building blocks.[3–5]

Acid catalyzed dehydration of D-fructose is the most convenient and efficient method for preparing HMF. Due to the increased interest and demand for industrial application, many efficient catalytic systems were recently developed.[6] It is no doubt that developing a cheap, non-toxic or low-toxic, easily handled catalytic system is highly desirable but challenging. Many types of acid catalysts have been used in this process, such as mineral acids,[7,8] strong acid cation exchange resins,[9–11] H-form zeolites[12,13] and supported heteropolyacids.[14] Among these acid catalysts, heterogeneous acid catalysts offer the advantage of easy separation from the reaction products and can be recycled, thus appearing as the most suitable catalysts for a potential industrial process. However, up to now, the performances of different heterogeneous acid catalysts are still unsatisfactory. A progressive decrease of selectivity to HMF has been observed with time, due to the formation of formic and levulinic acids as well as of polymeric by-products, such as insoluble humins, as shown in Scheme 1.[15] Furthermore, the above mentioned heterogeneous catalysts were not readily regenerated.[16] Thus, more research is being conducted to find more efficient solid catalysts for fructose dehydration. Karam et al. reported[17] that the mesoporous structure of SBA-SO_3H was preserved after five catalytic runs for the reaction of indole with benzaldehyde in water. The drop in the yield can be attributed to a decrease of the acid strength of SBA-SO_3H caused by a solvation of the catalytic sites by water. SBA-15 is a promising candidate for the catalyst supports due to its unique mesoporous structure and high thermal stability, which can be functionalized with different catalytic active groups. It has been reported that the monofunctionalized organo-sulfonic acid modified ordered mesoporous silica materials showed relative high performance for many heterogeneous acid-catalyzed reactions such as the dehydration of monoaccharides.[18] Crisci synthesized a supported bifunctional acid catalyst and silica-supported alkylsulfonic acids for the selective conversion of carbohydrates which are efficient and selective fructose dehydration catalysts under batch conditions, the co-condensed material suffered loss of its mesopore ordering and most of its functional groups during the secondary derivatization step.[19,20]

Both catalyst and solvent are crucial in the conversion of fructose into HMF. In an effort to achieve a high HMF yield, a great deal of work has been reported in the literature, using various media, such as water,[21,22] highly polar organic solvents,[23,24] and ionic liquids.[25–29] Environmental concerns favor water as a solvent for the reaction, but water is not very selective for the production of HMF and many by-products comprising insoluble polymeric compounds (i.e. humins) and soluble polymers are often formed, leading to a

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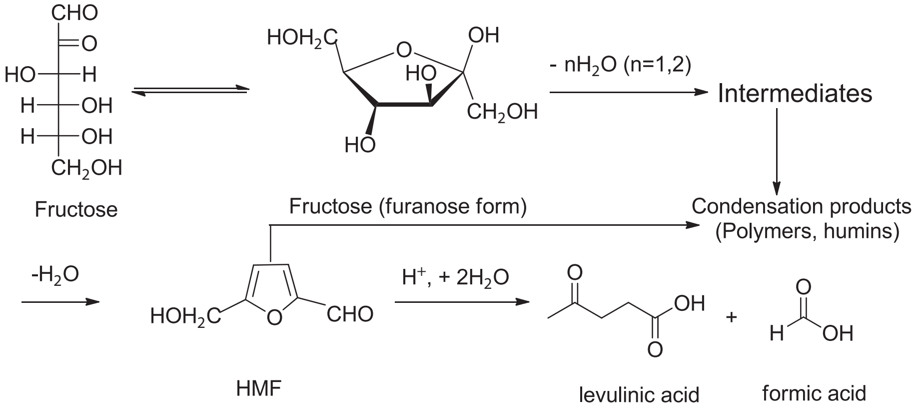
doi:10.1016/j.carres.2012.01.003



Scheme 1. Acid-catalyzed synthesis of HMF from fructose and possible by-products.

comparably low HMF yield.[30] Although high yields of HMF can be achieved in some high-boiling point organic solvents such as dimethyl sulfoxide (DMSO) and dimethylacetamide (DMA), the disadvantage of using those solvents is the high energy consumption during separation.

Ionic liquids are a group of salts that exist as liquids at low temperatures (<100 °C). They have many attractive properties, including chemical and thermal stability, nonflammability, and immeasurably low vapor pressure, which is favorable for a catalytic reaction.[31] Some authors studied the dehydration of fructose in ionic liquids. Zhao et al.[32] reported that chromium(II) chloride was found to be uniquely effective, leading to the conversion of glucose to HMF with a yield near 70%, but the toxicity and recovery of the ionic liquids was not clear. Moreau et al., have demonstrated that neutral ionic liquids such as $[Bmim]PF_6$ and $[Bmim]BF_4$ can act as a suitable reaction medium for the dehydration of fructose to HMF in the presence of the acidic catalyst, Amberlyst-15.[33] Recently, metal chlorides in neutral ionic liquid [Emim]Cl have been found to be effective catalysts for converting fructose and glucose to HMF. The water generated from the dehydration of fructose is diluted in the IL phase thus avoiding the important deactivation of catalytic sites. These results suggest that ionic liquids as solvents or catalysts can play a positive role in the development of effective processes for the dehydration of hexose to HMF.[34,35]

In summary, many attempts have been made to develop new catalytic processes, mainly basing on heterogeneous catalysis, for the transformation of fructose and fructose-precursors into HMF. Although multiple solvents have been reported for the production of HMF, we indicated that HMF can be produced in high yields by the acid-catalyzed dehydration of fructose in BmimCl.

In this work, functional propyl-sulfonic acid groups were grafted onto the pore surface of mesoporous SBA-15. The structure of the materials was investigated with electron microscopic and BET surface area techniques etc. Furthermore, the SBA-15-SO_3H, was first used as a heterogeneous solid acid catalyst for the selective synthesis of 5-hydroxymethylfurfural (HMF) from dehydration of fructose in ionic liquids.

2. Experimental

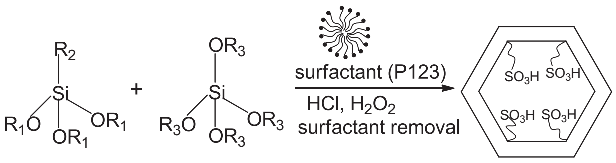
2.1. Materials

Fructose (99%), 5-hydroxymethylfurfural (99%) and HCl (37 wt %) were purchased from Sigma–Aldrich and were used without further purification. Triblock copolymer P123 (EO20PO70EO20, Aldrich), tetraethoxysilane (TEOS) and (3-mercaptopropyl) trimethoxysilane (MPTMS) were purchased from Aladdin Reagent Limited Company (China). Deionized water was used for the preparation of aqueous solutions. 1-Butyl-3-methylimidazolium chloride (BmimCl) (99%) was purchased from Shanghai Chengjie Chemical Co., Ltd.

2.2. Catalyst preparation

The preparation procedures of ordered mesoporous silica SBA-15 functionalized with sulfonic acid groups (SBA-15-SO_3H) were similar to those reported by Zheng et al.[36] Briefly, 4 g of Pluronic 123 (EO20PO70EO20, Mav = 5800) was dissolved in 105.2 g of deionized water at 40 °C by stirring, and then 24.42 g of hydrochloric acid (37 wt %) was added. After that, tetraethyl orthosilicate (TEOS) was added for prehydrolysis, and then a certain amount of 3-mercaptopropyltrimethoxysilane (MPTMS) was slowly added. The resulting mixture was stirred for 24 h at 40 °C followed by aging at 100 °C for another 24 h under static conditions. The molar composition of the mixture was $(1 - x/100)$ TEOS:$(x/100)$ MPTMS:6.1 HCl:0.017 P123:165 H_2O, where $x = (\text{MPTMS}/(\text{TEOS} + \text{MPTMS})) \times 100$ varied from 0 to 20. The solid product was then filtered and subsequently washed with deionized water. The template was removed from the synthesized material by washing with ethanol under reflux for 24 h.

Oxidation of thiol to sulfonic acid groups was carried out according to the following procedures: 0.15 g SBA-15-SH was dissolved in 20 g 2 M HCl aqueous solution, and 0.75 g 30 wt % H_2O_2 was then added. After stirring for 5 min at ambient temperature, the mixture was transferred into an autoclave and then statically treated for 6 h at 100 °C. Finally, the solid product was filtered, washed with deionized water and ethanol, and air-dried at 80 °C overnight to obtain sulfonic acid functionalized SBA-15 (denoted as SBA-15-SO_3H-x).[37,38] The whole procedure is illustrated in Scheme 2.



Scheme 2. Formation of mesoporous materials SBA-15-SO_3H by co-condensation. R_1, R_2 and R_3 represent CH_3-, SH-CH_2-CH_2-CH_2- and CH_3-CH_2-, respectively.

2.3. Catalyst characterization

The catalyst was characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and BET surface area techniques. XRD measurements were done on a Bruker D8 Advance X-ray diffractometer, using Cu Ka radiation (λ = 1.5404 Å) at 40 kV and 20 mA in the 2θ range of 0.5° to 5°. TEM measurements were performed on a Hitachi H-7650 at an accelerating voltage of 120 kV under a low electron dose. The specific surface area was calculated by the BET method and the pore size distribution was calculated by the Barrett–Joyner–Halenda (BJH) method with an ASAP 2000 (Micromeritics) analyzer. The Brönsted acidity on the samples was determined by the ion-exchange capacity, using aqueous solutions of sodium chloride as exchange agents. The method for the Agilent GC/MS system consisted of an Agilent 7890A GC (Agilent Technologies, Shanghai, China) fitted with a Polyethylene Glyco capillary column (30 m × 0.25 mm i.d. and 0.25 μm film thickness), coupled to an Agilent 5975C mass-selective detector (Agilent Technologies, Santa Clara, CA, USA). The detector was operated in electron impact (EI) ionisation mode (electron energy 70 eV). Helium with a purity of 99.999% from Qingdao Ruifeng Gas Co., Ltd (Qingdao, China) was used as the carrier gas. The oven temperature programme was 313 K (held for 5 min) to 503 K at 10 K/min (held for 2 min).

2.4. General procedure for the conversion of fructose to 5-HMF

Dehydration of fructose was performed in a sealed pressure-stable glass tube charged with fructose, catalyst, ionic liquids and a magnetic stirrer. In a typical reaction, a 25 mL reaction tube was charged with 2 g ionic liquids (such as BmimCl), 0.2 g fructose and 0.02 g catalyst in a glovebox and then sealed. The tube with the reaction mixture was placed in a pre-heated oil bath employed with a temperature controller for a specified time under stirring (reaction time were measured after a stable oil bath temperature had been reached). After the reaction, the tube was removed from the oil bath and cooled to room temperature before a sample was taken for analysis.

Sample analyses were performed by HPLC using Waters 2424 and Waters 2489 systems. Fructose conversion was monitored with an NH_2P-50 4E (250 × 4.6 mm) column (Shodex Asahipak), using a mobile phase CH_3CN–H_2O (78:22) at a flow rate of 1.0 mL/min, with an ELSD 2424 detector of drift tube temperature at 80 °C and gas pressure at 0.59 MPa. HMF was quantified with a Zorbax Eclipse XDB-C18 (150 × 4.6 mm, 5 μm) reverse phase column, using a mobile phase CH_3OH–H_2O (1:4) at a flow rate of 0.6 mL/min with a UV/vis 2489 Detector (284 nm) and a column temperature of 35 °C.

3. Results and discussion

3.1. Characterization of the catalyst

The powder XRD patterns of SBA-15-SO_3H samples are shown in Figure 1. All samples show one intense peak of (1 0 0) and two weak diffraction peaks of (1 1 0) and (2 0 0). The XRD patterns of SBA-15-SO_3H indicate that the crystallographic order of mesopores is preserved after the incorporation of MPTMS into SBA-15. The well resolved (1 1 0) and (2 0 0) reflections for the samples reveal highly ordered mesopores in the SBA-15-SO_3H materials. However, when x = 20, the reflections (1 1 0) and (2 0 0) are less resolved and less intense. The results show that the mesoporous order decreases with higher concentrations of MPTMS.

The nitrogen adsorption–desorption isotherms of SBA-15-SO_3H samples are shown in Figure 2a. SBA-15-SO_3H materials exhibited higher BET surface area (631.9–737.3 $m^2\,g^{-1}$), big pore volume (0.95–1.06 $cm^3\,g^{-1}$), as well as large N_2 adsorbed amount. Moreover, the BET surface area and pore volume of the SBA-15-SO_3H materials gradually decreased with increasing MPTMS content in the synthesis gel (Table 1). The isotherms are of type IV with a narrow hysteresis loop indicating the existence of mesoporous structure. The position of hysteresis loops shifts slightly to lower relative pressure and the step becomes less steep with the increase of MPTMS/(MPTMS + TEOS) ratio. Furthermore, the BJH pore size distribution broadened. This further suggested that the mesoporous structure order decreased with the increase of x. However, even at the highest MPTMS content (MPTMS/(MPTMS + TEOS) = 0.2), the SBA-15-SO_3H still exhibited considerably

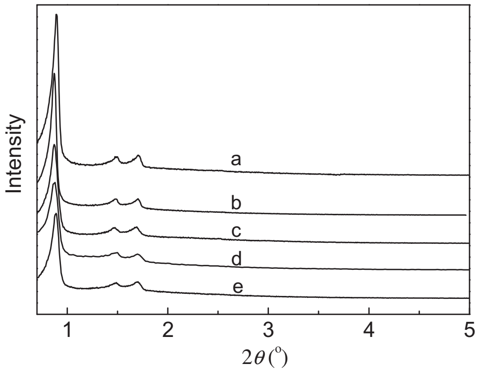


Figure 1. XRD powder patterns of the catalyst samples: (a) SBA-15, (b) SBA-15-SO_3H-5, (c) SBA-15-SO_3H-10, (d) SBA-15-SO_3H-15, (e) SBA-15-SO_3H-20.

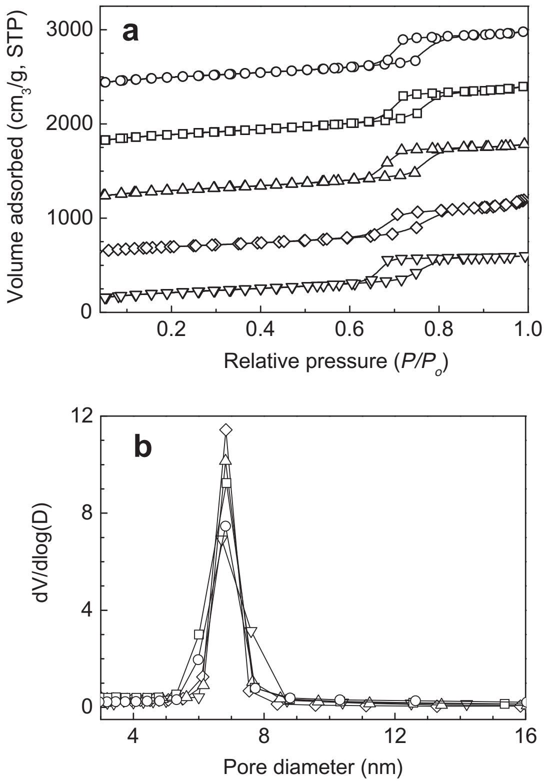


Figure 2. Nitrogen adsorption/desorption isotherms (a) and pore size distribution (b) of SBA-15-SO_3H materials prepared at different n(MPTMS)/n(TEOS + MPTMS) ratios: (▽) SBA-15, (◇) SBA-15-SO_3H-5, (△) SBA-15-SO_3H-10, (□) SBA-15-SO_3H-15, (○) SBA-15-SO_3H-20.

Table 1
Textural parameters of SBA-15-SO_3H samples

Sample	Sulfur content (wt %)	S_{BET} (m^2/g)	d_{100} (nm)	V_p (cm^3/g)	D_p (nm)	H^+ content[a] (mmol/g)
SBA-15	0	806.0	11.20	1.17	8.90	–
SBA-15-SO_3H-5	2.40	737.3	10.20	1.09	7.25	0.47
SBA-15-SO_3H-10	3.84	688.6	10.00	1.06	5.92	0.83
SBA-15-SO_3H-15	4.45	690.3	9.81	0.96	5.77	0.92
SBA-15-SO_3H-20	5.06	631.9	9.86	0.95	5.73	1.16

[a] H^+ content determined by titration.

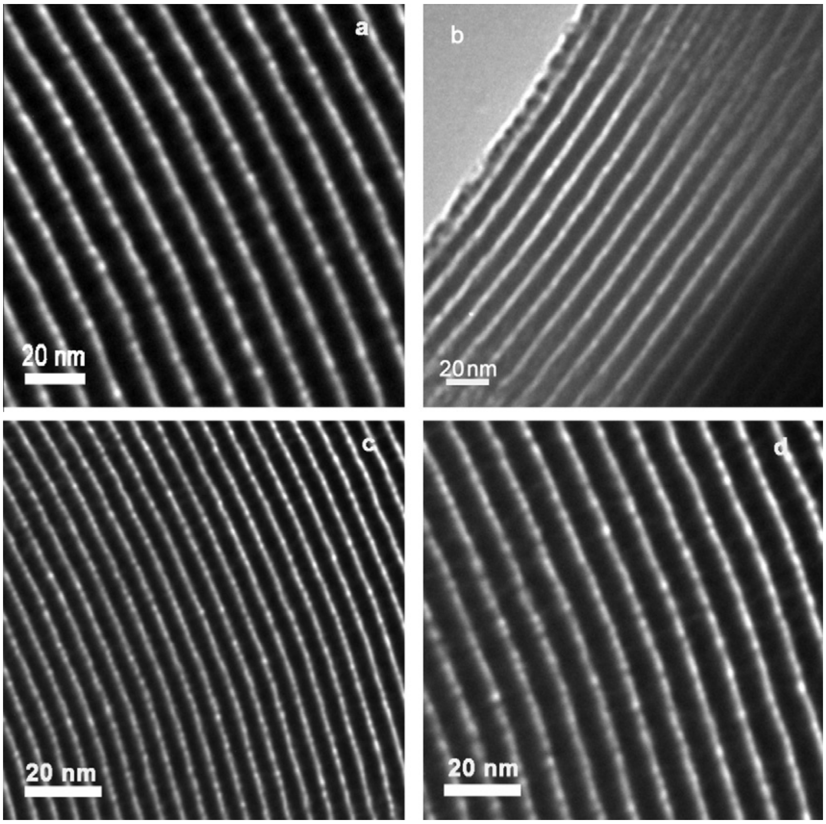


Figure 3. TEM images of SBA-15-SO_3H with different MPTMS concentrations in the initial mixture: (a) 0%, (b) 10%, (c) 15%, and (d) 20%.

high BET surface area and pore volume,[37,38] which satisfies the requirements for the catalytic reaction.

Nevertheless, the TEM micrographs confirm that the SBA-15-SO_3H materials contain well-ordered, one-dimensional pore structure, similar to that of the extracted pure SBA-15 (Fig. 3). The distance between two consecutive centers of hexagonal pores is 11 nm estimated by the TEM images. The average thickness of the wall is 4–5 nm and the pore diameter is around 6 nm, which is in agreement with the results measured by N_2 adsorption.

The thiol groups of MPTMS were in situ oxidized to sulfonic acid groups with H_2O_2 under acidic condition. The accessibility of the sulfonic acids in the materials was determined by ion-exchange capacities with aqueous solutions of sodium chloride (NaCl), and the results are shown in Table 1. The acid capacities of the materials ranging between 0.48 and 1.16 mmolH^+/g SiO_2 increased with the increase in MPTMS contents in the initial mixture.[39–41]

3.2. Catalytic activities of various catalysts under BmimCl

The reaction results of fructose dehydration to HMF using different catalysts are presented in Table 2. The yield of HMF reached a value as high as 41.9% when SBA-15 is used as a catalyst. Pure silica SBA-15 material has no acid sites[42] and indicates that acid is not required as catalyst for the dehydration of fructose in BmimCl. This has been proven by previous work, which found fructose can be dehydrated to form HMF in acidic ionic liquids that act as both solvent and catalyst.[25,43] However, highest HMF yields of 81% can be obtained through catalysis by SBA-15-SO_3H materials (entry 4 in Table 2) and it is very close to that of sulfuric acid, 82.3% (entry 1 in Table 2). As we have known, sulfuric acid was

Table 2
Catalytic activities of various catalysts for dehydration of fructose under BmimCl

Entry	Catalyst	Catalytic performance	
		Conv. (%)	Yield (%)
1	H_2SO_4	100.0	82.3
2	SBA-15	89.2	41.9
3	SBA-15-SO_3H-5	98.2	74.9
4	SBA-15-SO_3H-10	99.2	81.0
5	SBA-15-SO_3H-15	98.5	80.4
6	SBA-15-SO_3H-20	97.4	79.3

Reaction conditions: *m*(ionic liquids)/*m*(fructose)/*m*(catalyst) = 100:10:1, reaction temperature: 120 °C, reaction time: 1.0 h.

an efficient homogenous catalyst in this reaction, but with some serious drawbacks in the process. This result showed that the catalysts of SBA-15-SO_3H possessed a very high activity and selectivity in this catalytic system, indicating that a catalyst with suitable acid base properties is essential for the formation of HMF under these conditions. Compared with sulfuric acid, SBA-15-SO_3H appeared more suitable for industry process and is worth researching further.

SBA-15-SO_3H materials with $x = 5–20$ (entries 3–6 in Table 2) has similar activities for the dehydration of fructose to HMF, and SBA-15-SO_3H-10 showed the highest selectivity and mass yield for HMF of 81%. The GC-MS analysis results show it is found that the HMF is the main product, and neither levulinic acid nor formic acid is found, indicating that the hydrolysis reaction do not take place in current catalytic system.

Table 2 shows that the sulfonic acid functionalized materials are very active and selective in the synthesis of HMF from dehydration of fructose. The yield of HMF reached 74.9, 81.0, 80.4, and 79.3 mol % over SBA-15-SO_3H-5, SBA-15-SO_3H-10, SBA-15-SO_3H-15 and SBA-15-SO_3H-20, respectively. The selectivities for HMF was all found more than 74% at 120 °C for 1 h. The observed results could be rationalized by the fact that the larger surface areas in the mesoporous catalysts can promote the activity and sufficient acidic sites easily accessible for the reactants were responsible for the stabilization of the cationic intermediate formed during the reaction,[44] and also to be more easily accessible for the reactants. However, the catalytic performance of SBA-15-SO_3H depended on both the sulfonic group content and the integrality of mesoporous structure. The mesopore ordering of SBA-15-SO_3H decreased with the increase of propylsulfonic acid amounts in the catalyst. Higher propylsulfonic acid content does not give better catalytic results.

3.3. Effect of reaction temperature and time

The effects of reaction temperature and time on dehydration of fructose to HMF were examined with SBA-15-SO_3H-10 as catalyst and the results are given in Figure 4. High temperature did favor for acid-catalyzed dehydration of fructose to HMF. When the dehydration of fructose was performed at a relatively low temperature of 90–140 °C, by-product formation was negligible. At temperatures lower than 100 °C, no significant effect on HMF yield occurred. HMF yield increased almost linearly with reaction temperature reaching an optimum of 81%, at 120 °C. However, with further increasing the reaction temperature up to 140 °C, the HMF yield was at the same level. Therefore, a temperature of 120 °C was proper for fructose dehydration to HMF over SBA-15-SO_3H. At the same time, higher temperatures may bring on serious side reactions and speed up the loss of active components.

The effect of reaction time on the dehydration of fructose catalyzed by SBA-15-SO_3H is also shown in Figure 4. It was found that the yield of HMF increased gradually during the reaction from 0.5 to 1.0 h. When the time was extended to 1.5 h and longer, the yield of HMF showed almost no increased due to the accompanying decrease in HMF selectivity. These results showed that the optimal reaction time was 1 h in the dehydration of fructose in BmimCl.

3.4. The effect of the initial fructose concentration

A high substrate concentration is usually preferred in terms of process economics. Although a number of HMF production strategies have been available, few of them have satisfactory selectivity and/or yield at high fructose concentrations.[45] Qi et al. achieved 54% HMF yield when 20 wt % fructose was treated at 150 °C for 5 min in the presence of an ion-exchange resin in an acetone/water mixture.[46] Dumesic performed the same reaction in H_2O–salt–organic solvent systems with 30 wt % fructose at 180 °C and attained 55–66% HMF yield.[7]

Our experiments with initial fructose concentrations at 10–60 wt %, according to the results in Figure 5, near 69.5% HMF yield can be achieved with 50 wt % fructose concentration when SBA-15-SO_3H is added. As fructose concentration reaches 60 wt %, as high as z 60.8% HMF yield is obtained. We can always keep higher fructose conversion and satisfied HMF yield with increasing initial fructose concentration. The amount of by-products is not increased even at higher initial fructose concentrations according to HPLC analysis. Obviously, our strategy offers an opportunity to use a high fructose concentration under mild conditions without significantly compromising the HMF yield. Because a higher substrate concentration can greatly reduce solvent use, this method is expected to have great potential in terms of improved process economics and environmental friendliness. The reported conditions with short reaction time at high concentrations may allow for high space-time yields, which may be of interest for the development of efficient continuous processes for the conversion of carbohydrates into HMF.

3.5. Stability and recycling of SBA-15-SO_3H-BmimCl catalytic system

The stability of the SBA-15-SO_3H-BmimCl catalytic system was studied. The SBA-15-SO_3H-BmimCl catalytic system was reused successively for three times under the same reaction conditions. It was found that the whole system could be recycled several times

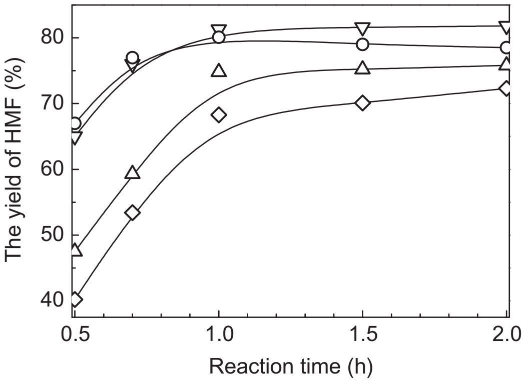


Figure 4. Effect of reaction time and temperature on HMF yield. ◇, 90 °C; △, 100 °C; ▽, 120 °C; ○, 140 °C. (Reaction conditions: 2.4 g BmimCl, 0.6 g fructose, 0.03 g catalyst.)

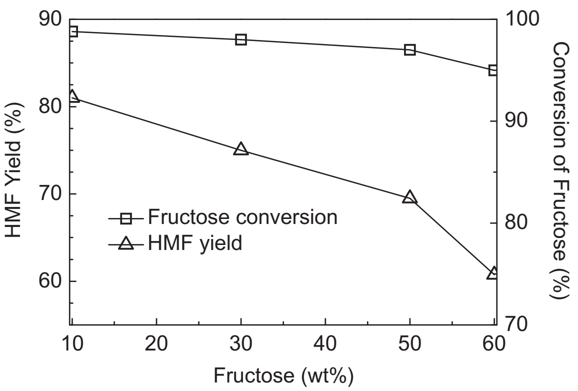


Figure 5. Effect of fructose concentration on HMF yield (△) and conversion of fructose (□). (Reaction conditions: 2.4 g BmimCl, 0.03 g catalyst, 120 °C, 1.0 h.)

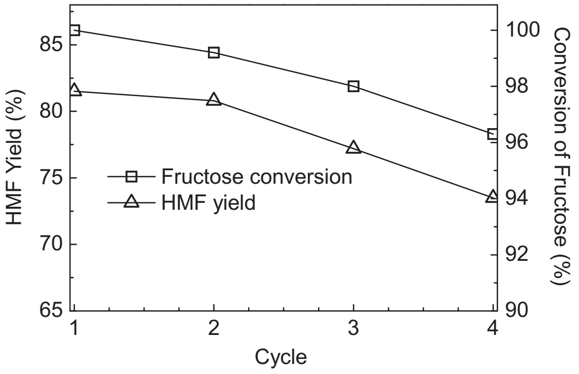


Figure 6. Stability of SBA-15-SO_3H upon catalyst recycling. (Reaction conditions: 2.4 g BmimCl, 0.6 g fructose, 0.03 g catalyst, 120 °C, 1.0 h.)

without using any additional SBA-15-SO_3H catalyst. The HMF product was extracted after each run, and fructose was added directly for the next run. The fructose conversion stabilized at 97–100% (Fig. 6), a slight decrease in the selectivity of HMF was observed. These results clearly showed that the heterogeneous catalysts were active in the dehydration of fructose and can be reused without significant decrease in the catalytic activity and with almost similar selectivity after three recycles.

3.6. Separation of HMF by THF (tetrahydrofuran) extraction

Separation of HMF from the reaction system is another challenge. Extraction is widely applied in the separation and purification of HMF[25,37,47,48] as the solubility of HMF in several organic solvents is high. To be used as an extracting reagent, the organic solvent must not only be immiscible with the reactive catalytic system but also possess a low boiling point, which will facilitate its separation from the extracted HMF via evaporation. THF with its boiling point of only 66 °C, the BmimCl/fructose/SBA-15-SO_3H system was most reactive at 120 °C, a temperature far above the boiling point of THF, was reported to be a good choice in the extraction of HMF. So THF was screened as an HMF extraction solvent in this work.

The extraction method was operated with the similar procedure as described previously.[49] After the reaction, some THF was added into the reaction systems, the semi continuous process for the conversion of fructose to HMF in a THF-BmimCl/SBA-15-SO_3H/fructose biphasic system. The lower phase contains BmimCl, fructose and SBA-15-SO_3H, whereas the upper phase contains THF. HMF is extracted into the THF phase and separated through an evaporation step. Fructose and THF were added to the system at the beginning of each consecutive bath of the operation.

The amounts of the residual HMF and fructose in the reaction phase were analysed using HPLC. In the whole process operation, a total of 99.4% of the fructose was reacted and the selectivity towards HMF was 81.1% and corresponding to 93% of the HMF produced during the whole process was isolated by the THF extraction.

At suitable temperatures, the high HMF yield, low catalyst cost and toxicity make this simple SBA-15-SO_3H-BmimCl system a promising choice for fructose dehydration.

4. Conclusions

SBA-15-SO_3H as a heterogeneous catalyst exhibits excellent performance in the selective synthesis of HMF from dehydration of fructose. It is tolerant to high concentration fructose and can be reused. High fructose conversion (near 100%) and HMF selectivity (about 81%) were obtained, which almost was the same with that of sulfuric acid. The activity of SBA-15-SO_3H may be ascribed to the materials with suitable acidic sites as the active centers and the unique surface textural properties. The separation of HMF was successfully achieved in a THF/BmimCl biphasic system. These made this simple SBA-15-SO_3H-BmimCl system a promising choice for fructose dehydration to HMF.

Acknowledgments

The authors are grateful for the financial support of the National High Technology Research and Development Program of China (No. 2009AA05Z410), the National Natural Science Foundation of China (No. 20803038), the Natural Science Foundation of Shandong Province, China (No. O92003110C) and the Knowledge Innovation Program of the Chinese Academy of Sciences (No. KSCX2-YW-G-075-13).

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