Sn-MCM-41 as Efficient Catalyst for the Conversion of Glucose into 5-Hydroxymethylfurfural in Ionic Liquids

Qing Xu, Zhu Zhu, Yukui Tian, Jin Deng, Jing Shi, and Yao Fu *

Recently, much attention has been paid to the development of technologies that facilitate the conversion of biomass into platform chemicals such as 5-hydroxymethylfurfural (5-HMF). In this paper, a tin-containing silica molecular sieve (Sn-MCM-41) was found to act as a bifunctional heterogeneous catalyst for the efficient conversion of glucose into 5-HMF in ionic liquid. In the presence of [EMIM]Br, the yield of 5-HMF converted from glucose reached 70% at 110 °C after 4 h. During the reaction, the active center of the catalyst first catalyzed the isomerization of glucose into fructose and then the dehydration of fructose into 5-HMF. After the reaction, the heterogeneous catalyst Sn-MCM-41 could be easily recovered and reused without a significant loss in activity. The catalyst Sn-MCM-41 was also able to catalyze the conversion of fructose into 5-HMF at an 80% yield. Moreover, the low toxicity of the Sn-based catalyst makes the method a greener approach for the conversion of saccharides into 5-HMF.

Keywords: Glucose; Heterogeneous catalysis; Sn-MCM-41; 5-Hydroxymethylfurfural; Ionic liquids

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INTRODUCTION

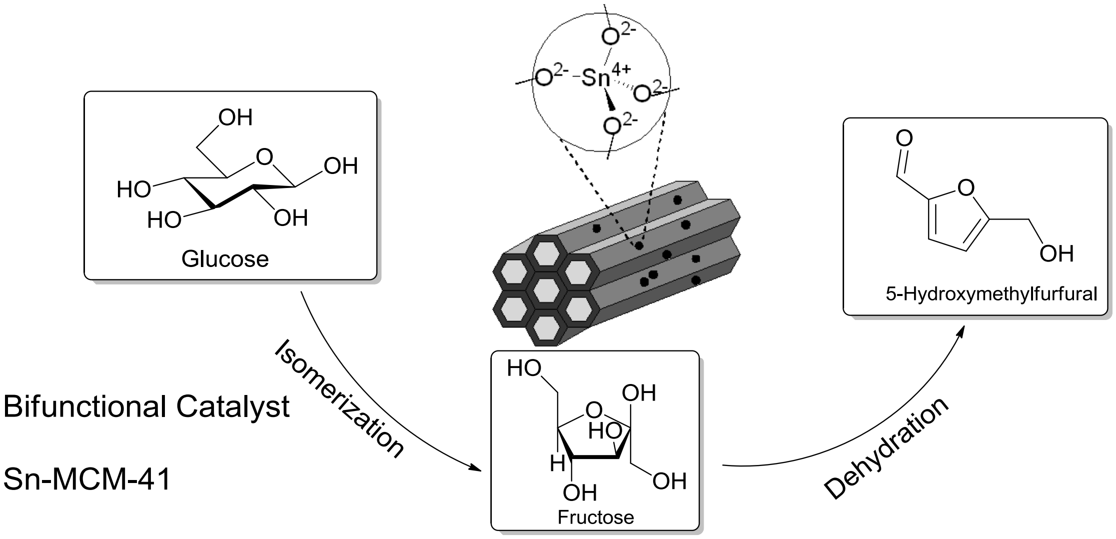
Biomass-derived carbohydrates are a promising carbon-based alternative energy source and renewable chemical feedstock. Recently, there has been increasing interest in the conversion of carbohydrates into 5-hydroxymethylfurfural (5-HMF), which is an important compound that connects biomass to the petrochemical industry (Asghari and Yoshida 2006; Román-Leshkov *et al*. 2006; Chheda *et al*. 2007; Hu *et al*. 2008, 2009b; Ren *et al.* 2013). 5-HMF can be prepared by way of the dehydration of carbohydrates such as fructose and glucose.

Glucose, the most abundant and accessible monosaccharide unit in lignocellulosic biomass, is the most promising feedstock for the production of 5-HMF. Unlike fructose, glucose cannot be directly dehydrated into 5-HMF due to its pyranose structure. Thus, an isomerization step to convert glucose into fructose is required before the dehydration step, which makes the conversion of glucose more challenging (Qi *et al.* 2010; van Putten *et al.* 2013). $CrCl_2$ was found to efficiently catalyze the reaction using 1-ethyl-3-methyl-imidazolium chloride ([EMIM]Cl) as a solvent (Zhao *et al.* 2007) or using N,N-dimethylacetamide (DMA) containing lithium chloride (LiCl) as a solvent (Binder and Raines 2009). Following this discovery, other homogeneous catalysts such as $SnCl_4$ and $GeCl_4$ were developed to catalyze the reaction in ionic liquids (Hu *et al.* 2009a; Ståhlberg *et al.* 2010; Zhang *et al.* 2011b).

Heteropoly acids were also found to be a highly effective catalyst to convert glucose into 5-HMF, and a two-step conversion of glucose into 2,5-dimethylfuran (DMF) was achieved (Chidambaram and Bell 2010). Although satisfactory yields of 5-HMF can be obtained from glucose using these homogeneous catalysts, the development of heterogeneous catalysis systems is desirable due to the ease of product separation and catalyst recovery that their use entails (Zhang *et al.* 2011a). It has been reported that $SO_4^{2-}/ZrO_2-Al_2O_3$ catalysts can be used to synthesize 5-HMF from glucose (Yan *et al.* 2009). The combination of a solid acid (Amberlyst-15) and a solid base (Mg-Al hydrotalcite) can also catalyze glucose into 5-HMF (Takagaki *et al.* 2009). However, the selectivity of 5-HMF is relatively low in these reaction systems.

In recent years, molecular sieve catalysts have attracted considerable interest among researchers due to their excellent characteristics, such as stable frameworks and high specific surface areas (Román-Leshkov *et al.* 2010; Moliner *et al.* 2010; Nikolla *et al.* 2011). For instance, when combined with HCl, Sn-beta zeolite, a heterogeneous catalyst, can catalyze glucose in biphasic systems into 5-HMF with 70% selectivity at 180 °C (Nikolla *et al.* 2011). During the reaction, Sn-beta can efficiently catalyze the isomerization of glucose to fructose, and HCl can catalyze the dehydration of fructose into 5-HMF. However, there are still some disadvantages to using this system, such as the high reaction temperature and the homogeneous catalyst HCl that must be imported. These disadvantages may limit the wide application of the reaction.

Therefore, the development of a bifunctional solid catalyst that can efficiently catalyze the conversion of glucose into 5-HMF is of great importance. In this work, an efficient synthesis approach to producing 5-HMF from glucose by means of a tin-based bifunctional catalyst (Sn-MCM-41) in ionic liquids is reported (Scheme 1). In this catalytic system, Sn-MCM-41 catalyzed both the isomerization of glucose into fructose as well as the dehydration of fructose into 5-HMF under relatively mild conditions. Furthermore, the Sn-MCM-41 could be easily recovered and reused without a significant loss in activity.



Scheme 1. Sn-MCM-41 as catalyst for the dehydration of glucose into 5-HMF

EXPERIMENTAL

Materials

Glucose (99%) and fructose (99%) were purchased from Alfa Aesar (Beijing, China). SiO_2 (99.8%) was purchased from Aladdin reagent Co., Ltd. (Shanghai, China). C_{16}TAOH (10% in water), TMAOH (25% in water), and C_{16}TABr (99%) were purchased from TCI Development Co., Ltd. (Shanghai, China). The other reagents (AR grade) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All reagents were used without further purification.

General Procedure for Carbohydrate Conversion

The catalysts were prepared according to the literature (Corma *et al.* 2001). The glucose, fructose, and catalysts were dried at 60 °C under a vacuum before use. For a typical run, 100 mg of catalyst and 100 mg of carbohydrate were added into 1.0 g of ionic liquid. Then, the mixture was heated at a specified temperature for the desired time with a magnetic stir bar. After the reaction, the samples were cooled to room temperature, diluted with water, and analyzed by HPLC.

General Procedure for Quantification of Reaction Samples

The concentration of 5-HMF was calculated by HPLC with a Cosmosil/Cosmogel packed 5C18-PAQ (4.6×250 mm) column, a Waters 1525 pump, and a Waters PDA-2996 detector at 280 nm. Methanol/water (5/95 v/v) was used as the mobile phase at 1.0 mL/min. The concentrations of glucose and fructose were determined by a HPLC system consisting of a Waters 1525 pump, a Cosmosil/Cosmogel packed Sugar-D (4.6×250 mm) column, and a Waters 2414 refractive index detector. Acetonitrile/water (75/25 v/v) was used as the mobile phase at the flow rate of 1.0 mL/min. Both the 5-HMF yield and carbohydrate conversion were determined using an external standard curve method.

RESULTS AND DISCUSSION

The study was initiated with glucose as the substrate, and a series of mesoporous silica frameworks, which were incorporated with foreign ions, were screened for activity relating to 5-HMF production in ionic liquids. The incorporation of heteroatoms into the framework of the MCM-41 mesoporous molecular sieve has been widely investigated; such heteroatoms include Ti, Cr, Zr, Sn, and Ni (Corma *et al.* 2001; Corma *et al.* 2003; Zhao *et al.* 2009; Szegedi *et al.* 2010).

A 70% yield of 5-HMF was achieved after 4 h when Sn-MCM-41(50) was employed (Table 1, entry 6), while lower yields (Table 1, entries 1 through 5) were obtained when other mesoporous molecular sieves were used as the catalyst. It has been reported that Lewis acids such as $CrCl_2$, $CrCl_3$, and $SnCl_4$ can catalyze the conversion of glucose into 5-HMF through the isomerization of glucopyranose to fructofuranose, followed by the dehydration of fructofuranose (Zhao *et al.* 2007; Hu *et al.* 2009a; Pidko *et al.* 2010). However, when the metal ions were incorporated into the framework of MCM-41, it was found that only Sn-MCM-41 could catalyze the conversion of glucose to 5-HMF with a satisfactory yield. Meanwhile, Sn-MCM-41 was more effective in the reaction than other zeolite-based catalysts such as Sn-beta zeolite (Table 1, entry 14). In the molecular sieve, the Sn atoms that acted as isolated Lewis acid centers could catalyze the isomerization of glucose to fructose, similar to the action of Sn-beta zeolite (Nikolla *et al.* 2011). However, the Lewis acid centers of Sn-MCM-41 were more active and could also catalyze the dehydration of fructose into 5-HMF at an 80% yield without additional mineral acid catalysts under the same reaction conditions.

Other conditions have also been optimized in this reaction, including the choice of solvent and catalyst loading. When ionic liquids were used as solvents, distinctly higher yields of 5-HMF were observed, whereas lower catalytic activities were observed in water or other solvents (Table 1, entries 6 through 11). To study the effects of catalyst loading, Sn-MCM-41 samples with three different Si/Sn ratios (100, 50, and 25) were tested for glucose conversion. As expected, catalysts with higher loadings of Sn provided relatively higher glucose conversions and 5-HMF yields. For example (Table 1, entries 6 and 12), when Sn-MCM-41(50) was employed as a catalyst, a 5-HMF yield of 70% and a turnover number (TON) of 22 was achieved at a glucose conversion of 99%, which was much higher than that produced by Sn-MCM-41(100). However, from the data in Table 1, entries 6 and 13, it can be seen that a further increase in the Sn loading did not lead to a higher 5-HMF yield. This may be explained by the active sites having been saturated at high loadings. The inactivity of the Sn-free material (Si-MCM-41) also suggested that Sn ions contributed greatly to the catalytic activity (Table 1, entry 1).

Table 1. Dehydration of Glucose into 5-HMF

Entry[a]	Catalyst	Solvent	Conversion (%)	Yield (%)
1	Si-MCM-41	[EMIM]Br	17	4
2	Ti-MCM-41(50[b])	[EMIM]Br	25	5
3	Cr-MCM-41(50)	[EMIM]Br	37	11
4	Zr-MCM-41(50)	[EMIM]Br	22	6
5	Ni-MCM-41(50)	[EMIM]Br	8	1
6	Sn-MCM-41(50)	[EMIM]Br	99	70
7	Sn-MCM-41(50)	[BMIM]Br	90	50
8	Sn-MCM-41(50)	[EMIM]Cl	86	48
9	Sn-MCM-41(50)	[BMIM]Cl	75	40
10	Sn-MCM-41(50)	DMSO	75	25
11[c]	Sn-MCM-41(50)	H_2O	35	12
12	Sn-MCM-41(100)	[EMIM]Br	82	42
13	Sn-MCM-41(25)	[EMIM]Br	99	68
14	Sn-Beta(50)	[EMIM]Br	30	15

[a] Reaction conditions: 100 mg glucose, 100 mg catalyst, 1.0 g solvent, at 110 °C for 4 h.
[b] indicates the Si/M(M=Ti, Cr, Zr, Ni) ratio was 50 in the catalyst.
[c] 100 mg glucose, 100 mg catalyst, 1.0 g solvent, at 140 °C for 4 h.

Many studies have shown that various kinds of Lewis acids, including $CrCl_3$, $SnCl_4$, and $GeCl_4$, can catalyze glucose into 5-HMF (Zhao *et al.* 2007; Hu *et al.* 2009a; Zhang *et al.* 2011b). However, the toxicity of the catalysts or the difficulty of catalyst recovery has limited the application prospects of these acids. In contrast, the catalyst Sn-MCM-41 is relatively cheap and can be easily recovered by filtration or centrifugation. Accordingly, the stability and the reusability of the Sn-MCM-41(50) catalyst was examined. The glucose conversion reaction was conducted under the same conditions as those of the reaction seen in Table 1, entry 6. After the reaction, the catalyst was separated by centrifugation, washed with water and ethanol, dried at 333 K for 2 h, and then calcined at 673 K for 5 h to remove adsorbed by-products prior to reuse in the next run. As shown in Fig. 1(a), a slight decrease in 5-HMF yield from 70% to 65% was observed in the second run, but no further loss of activity was observed in the subsequent runs. A similar phenomenon was observed for the conversion of fructose, as shown in Figure 1(b). Meanwhile, the ICP-AES analysis of the catalyst showed a slight increase in the Si/Sn ratio after 3 runs, from 63 to 69, indicating that the Sn loading in the catalysts almost remained the same after being used in the ionic liquids. In other words, a stable 5-HMF yield of about 65% could be obtained. The decrease in catalytic activity in the second run may be attributed to the partial loss of unstable surface active sites.

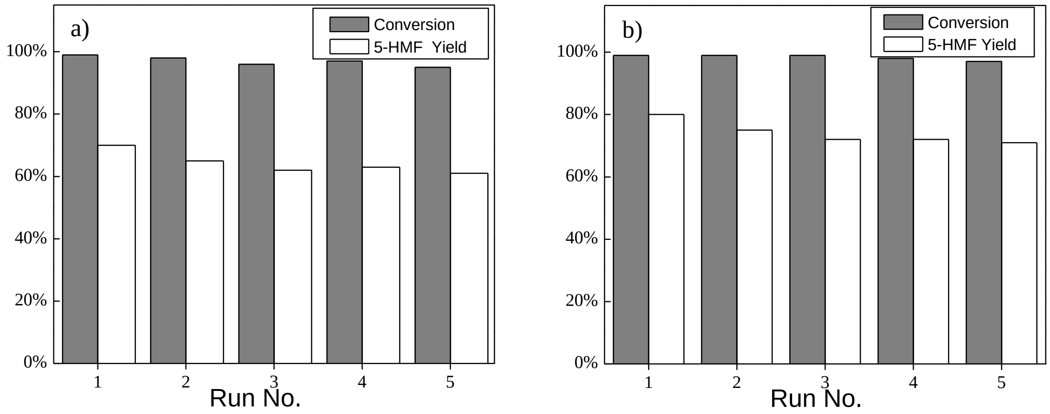


Fig. 1. Reuse of the Sn-MCM-41/[EMIM]Br system for carbohydrate conversion: a) glucose and b) fructose

However, it should be pointed out that the phenomenon of catalyst deactivation was observed in successive runs when the catalyst was reused without calcination, runs in which the 5-HMF yield was poor. Fortunately, the activity of the catalyst could be recovered by calcination, which suggested that the deactivation of the catalyst was mainly caused by the adsorbed by-products; as such, the removal of these species was able to reactivate the catalyst (Qi *et al.* 2009; Lewkowski 2001).

The reaction temperature is an important factor for both the reaction rate and the product yield. To determine the influence of the temperature on the 5-HMF yield, experiments were carried out at 100, 110, 120, and 130 °C. Satisfactory results for the conversion were obtained under these conditions, as seen in Fig. 2.

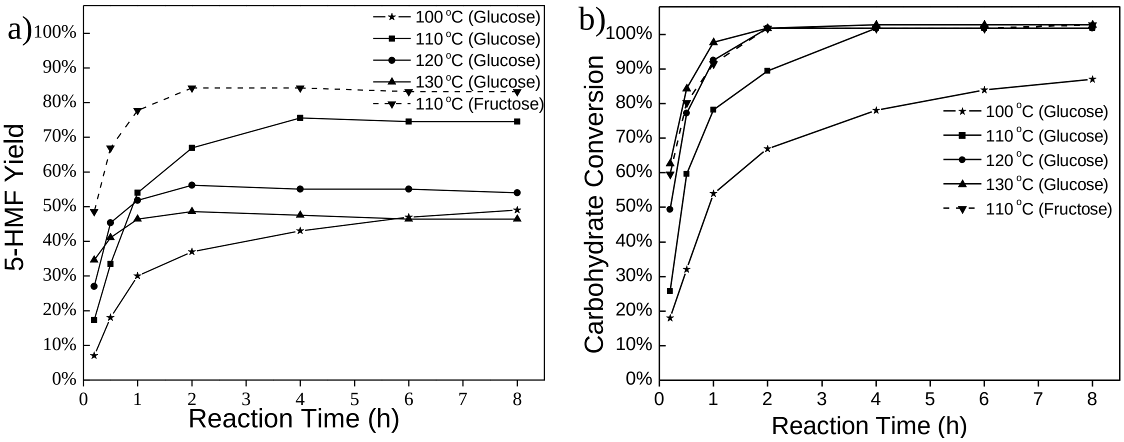


Fig. 2. a) 5-HMF yield with time and temperature for carbohydrate dehydration using Sn-MCM-41(50) in [EMIM]Br; b) carbohydrate conversion with time and temperature using Sn-MCM-41(50) in [EMIM]Br

However, when the reaction was performed at 80 °C, the rates of glucose conversion and 5-HMF formation were rather low. This suggests that higher temperatures promoted the isomerization of glucopyranose to fructofuranose and the dehydration of fructofuranose, as in other catalytic systems (Hu *et al.* 2009a; Román-Leshkov *et al.* 2010). The highest 5-HMF yield of 70% was achieved with 99% glucose conversion at 110 °C after 4 h. As previously reported (van Putten *et al.* 2013), fructose can be easily converted into 5-HMF in the presence of Lewis acid catalysts. As shown in Fig. 2, a 5-HMF yield of 80% with 99% fructose conversion at 110 °C was observed.

Powder X-ray diffraction (XRD), scanning electron microscopy (SEM), and other techniques were used to characterize the catalyst. Figure 3 shows the XRD patterns of the calcined Sn-MCM-41 samples with different Si/Sn ratios [Sn-MCM-41(100), Sn-MCM-41(50), and Sn-MCM-41(25)] and with pure silica [Si-MCM-41]. Similar to pure Si-MCM-41, the Sn-MCM-41(100), Sn-MCM-41(50), and Sn-MCM-41(25) also exhibited peaks around 2θ = 2.0 ~ 3.0 degrees, corresponding to a diffraction pattern of 100, and the results indicated that the ordered mesoporous structures were still retained in the Sn-MCM-41 catalysts. The peaks corresponding to diffraction patterns of 100 and 200 decreased in a manner similar to that of Sn-MCM-41 catalysts as a result of the addition of foreign ions. The slight increase in d100 spacing suggests the presence of Sn in the framework. The X-ray diffraction data for the Sn-MCM-41 before and after reaction in the [EMIM]Br solvent also showed no significant changes in the mesoporous structure.

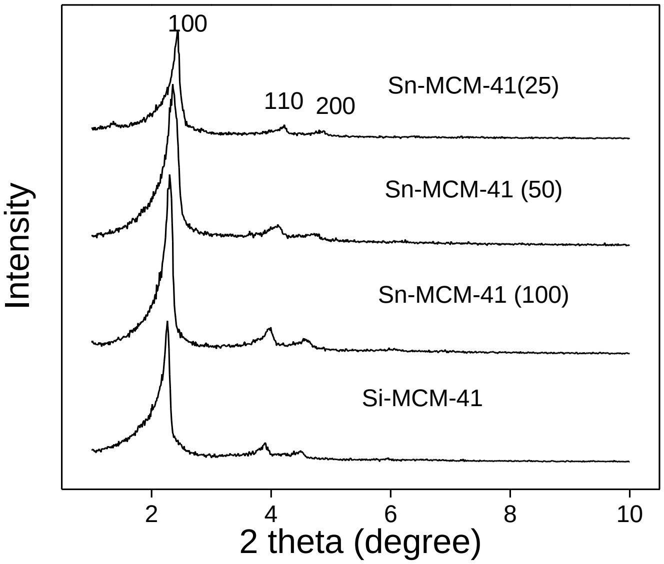


Fig. 3. XRD patterns of Sn-MCM-41 and Si-MCM-41

TEM micrographs of Sn-MCM-41 and Si-MCM-41 are shown in Fig. 4. Consistent with the XRD results, the TEM micrographs indicated that an ordered mesoporous structure was present in the catalysts (Fig. 4 a, b, c, d). The XPS and framework IR spectra (See Fig. S2 and Fig. S3 in Supplementary Information) of Sn-MCM-41 showed the presence of Sn^{4+} on the surface of the catalysts, which is the Lewis acid center in the catalytic process. In the NH_3-TPD analysis of Sn-MCM-41 catalysts, a desorption peak centered at 150 °C indicated weak acid sites, and a broad peak in the range of 280-500 °C suggested the presence of medium and strong acid sites. The total acid strength, surface area, average pore size, and average pore volume data of the catalysts are listed in Table S2 in the Appendix.

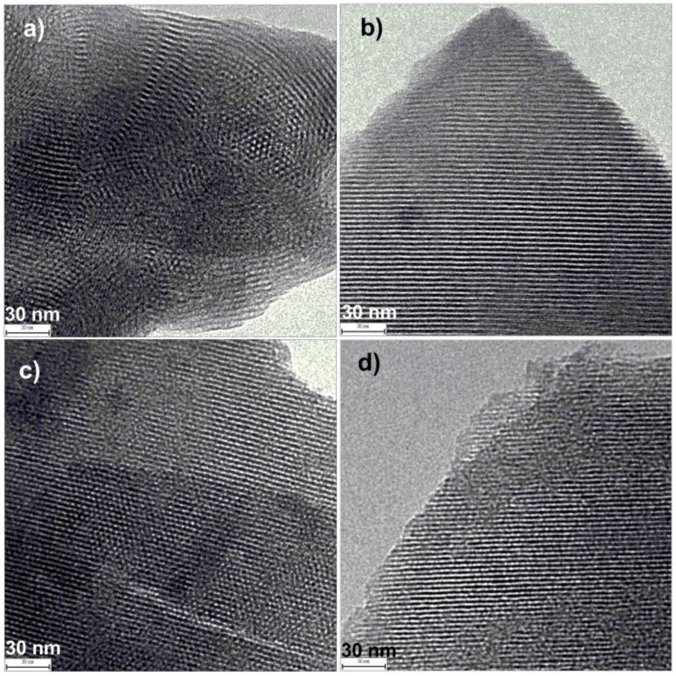


Fig. 4. TEM micrographs: a) Si-MCM-41; b) Sn-MCM-41(100); c) Sn-MCM-41(50); and d) Sn-MCM-41(25)

CONCLUSIONS

1. An efficient method for the conversion of glucose and fructose into 5-HMF catalyzed by a bifunctional solid catalyst Sn-MCM-41 using ionic liquid [EMIM]Cl as solvent has been developed. 5-HMF yields of 70% from glucose and 80% from fructose were obtained at 110 °C using [EMIM]Br as a solvent.
2. During the conversion of glucose into 5-HMF, Sn-MCM-41 catalyzed the isomerization of glucopyranose to fructofuranose and the dehydration of fructose. The Lewis acid sites on the surface of catalysts are the active centers during the reaction. Also, the ionic liquid solvent contributed greatly in respect of promoting the isomerization of glucose and stabilizing the product 5-HMF.
3. Unlike $CrCl_3$, $SnCl_4$, $GeCl_4$, and other homogeneous catalysts, Sn-MCM-41 features low toxicity and can be easily recovered and reused without a significant loss in activity. Therefore, the Sn-MCM-41 catalytic system has the potential for the industrial scale production of 5-HMF.

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APPENDIX: SUPPLEMENTARY INFORMATION

Sn-MCM-41 as Efficient Catalyst for the Conversion of Glucose into 5-Hydroxymethylfurfural in Ionic Liquids

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Materials

Glucose(99%) and fructose(99%) were purchased from Alfa Aesar. (Beijing, China). SiO_2 (99.8%) was purchased from Aladdin reagent Co., Ltd. (Shanghai, China). C_{16}TAOH(10% in water), TMAOH(25% in water) and C_{16}TABr(99%) were purchased from TCI Development Co., Ltd.(Shanghai, China). The other reagents(AR) were purchased Sinopharm Chemical Reagent Co., Ltd.(Shanghai, China). All reagents were used without further purification.

General Procedure for the Reaction

Glucose, fructose and catalysts were dried at 60 °C under vacuum before use. For a typical run, 100 mg catalyst and 100 mg carbohydrate were added into 1.0 g ionic liquid. Then the mixture was heated at a specified temperature for the desired time under atmospheric pressure with a magnetic stirrer. Samples were withdrawn, diluted with water and analyzed by HPLC. The concentration of 5-HMF was calculated by HPLC with a Cosmosil/Cosmogel packed 5C18-PAQ (4.6×250mm) column, a Waters 1525 pump, a Waters PDA-2996 detector at 280 nm. Methanol/Water (5/95 v/v) as flowing phase at 1.0 ml/min. The concentration of glucose and fructose were determined using a HPLC system consisting of a Waters 1525 pump, a Cosmosil/Cosmogel packed Sugar-D (4.6×250mm) column and a Waters 2414 refractive index detector. Acetonitrile/Water (75/25 v/v) was used as mobile phase at flow rate of 1.0 mL/min.

Synthesis of Sn-MCM-41

Sn-MCM-41were prepared as follows.[1] An aqueous solution of hexadecyl-trimethylammonium hydroxide/bromide (C_{16}TAOH/Br) was mixed with an aqueous solution of $SnCl_4 \cdot 5H_2O$ and a tetramethylammonium hydroxide solution (25%). After homogenisation, the silica was added slowly to the above solution under stirring and the stirring was continued for 1 h after completion of addition. The molar composition of the mixture was the following: 1 SiO_2:(0.16-4x) C_{16}TABr:4x C_{16}TAOH:0.26 TMAOH:x $SnCl_4$:24.3 H_2O, where x was between 0.01 and 0.04. The homogeneous gel was transferred to PTFE-lined stainless steel autoclaves and heated at 135 °C under static conditions for 24 h. The resulting solid product was then filtered, washed with deionized water, and dried at 60 °C for 24 h. The product was calcined at 540 °C for 1 h in a flow of N_2 and followed by 6 h in air to remove the organic material.

Catalysts Characterization

Table S1. Si/Sn Ratios of the Catalysts Used in the Ionic Liquids

Catalyst	Reuse of the Catalysts	Si/Sn ratio
Sn-MCM-41(50)	Run 1	63
Sn-MCM-41(50)	Run 2	67
Sn-MCM-41(50)	Run 3	69

The Si/Sn ratios were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Thermo-Jarrell ASH-Atom Scan Advantage).

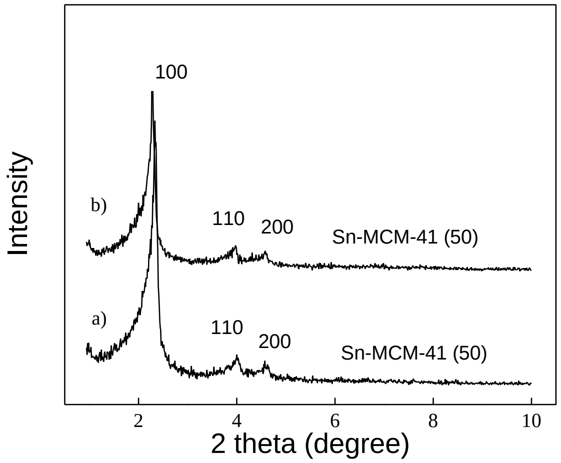

Fig. S1. XRD patterns of Sn-MCM-41(50): a) before reaction and b) after reaction

X-ray photoelectron spectroscopy (XPS) analysis was carried out on a Thermo Scientific Escalab 250 instrument using Al Kα source to excite the photoelectrons from the samples. For energy calibration, the C1s was assigned to be 284.5 eV. The XPS spectrum (Fig. S2) of Sn-MCM-41 shows typical doublets for Sn 3*d*3/2 and 3*d*5/2 electrons with binding energies of 495.7 and 487.2 eV, respectively, indicating the presence of Sn^{4+} on the surface.[2]

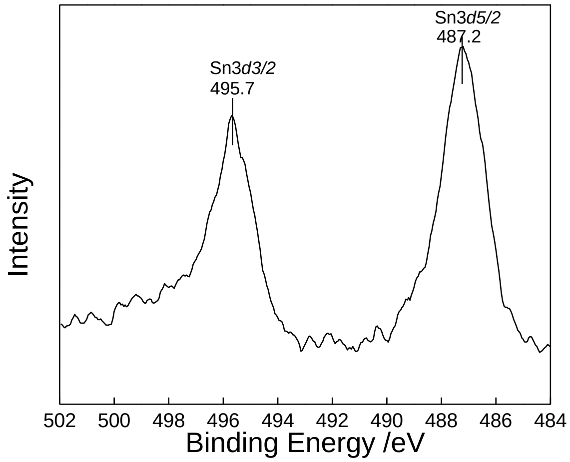

Fig. S2. XPS spectrum of Sn element in Sn-MCM-41

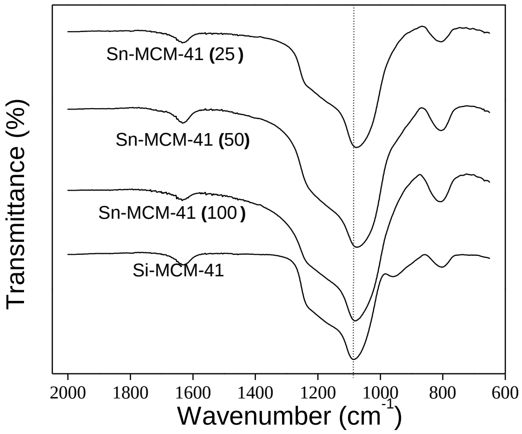

Fig. S3. The framework IR spectra of the Si-MCM-41 and Sn-MCM-41 samples

The framework IR spectra of the Si-MCM-41 and Sn-MCM-41 samples was carried out on a Fourier Transform Infrared Spectroscometer (FT-IR, Nicolet 8700). The T–O–T lattice vibration is found to shift to lower wavenumbers for Sn-MCM-41 with increasing tin content.

Nitrogen adsorption/desorption isotherms were measured with a Micromeritics ASAP 2020 analyzer. The surface area was determined using Barrett-Emmet-Taller (BET) method, and the average pore size and pore volume was determined by Barret-Joyner-Halenda (BJH) method. The relative total acid amount was determined by NH_3-TPD method, with the value of Si-MCM-41 assigned as 1.00.

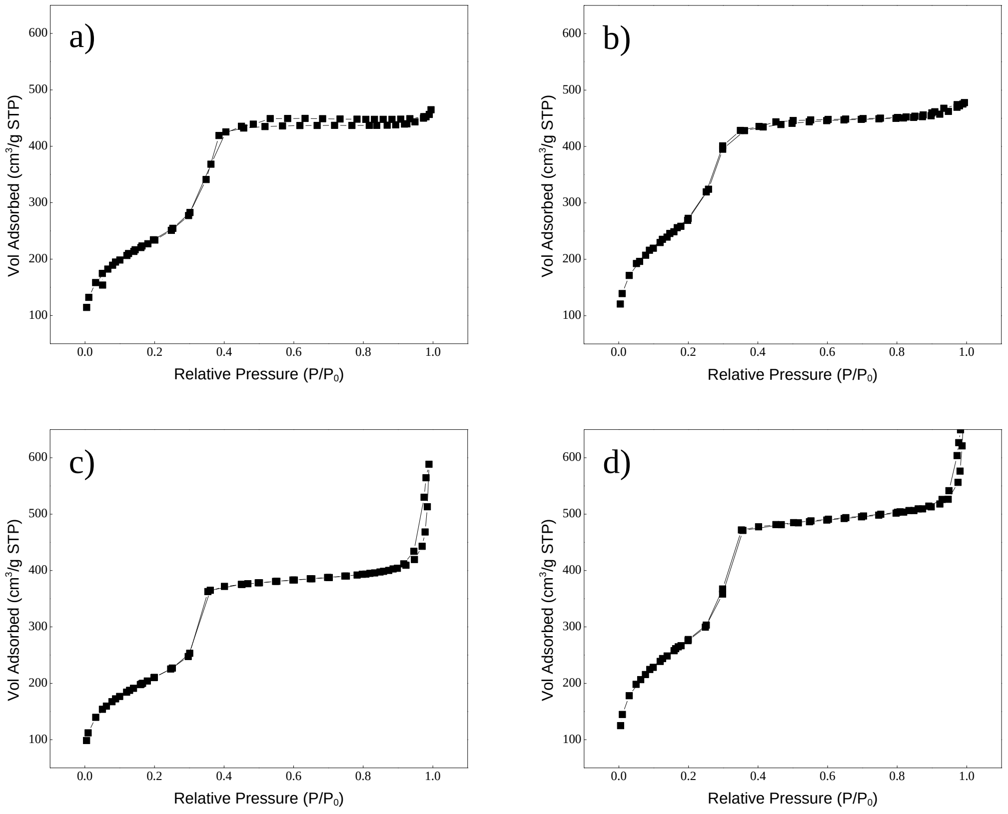

Fig. S4. N_2 adsorption/desorption isotherms of a) Si-MCM-41, b) Sn-MCM-41(100), c) Sn-MCM-41(50) and d) Sn-MCM-41(25)

Table S2. Textural Properties of the Catalysts

Catalysts	D_p/Å	V_p/cm^3 g^{-1}	S_{BET}/m^2 g	Relative total acid amount	Si/Sn ratios
Si-MCM-41	32.9	0.70	813	1.00	—
Sn-MCM-41(100)	29.2	0.72	938	1.31	95
Sn-MCM-41(50)	35.6	0.69	733	1.54	63
Sn-MCM-41(25)	33.9	0.86	961	1.66	33

Transmission electron microscopy (TEM) microphotographs were obtained with a X′ PERT PRO electron microscope operating at 200 kV.

Additional References Cited

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