RSC Advances

Volume 1 | Number 1 | Jan 2013 | Pages 1–100

RSC Advances

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Conversion of glucose into 5-hydroxymethylfurfural catalyzed by chromium(III) schiff base complexes and acidic ionic liquid immobilized on mesoporous silica

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Abstract:

A series of novel catalysts were prepared by immobilized chromium(III) schiff base complex and acidic ionic liquid onto the surface of MCM-41, and characterized by FT-IR, TG, XRD, SEM, TEM, NH_3-TPD, ICP-OES, and N_2 sorption studies. The catalytic activity of the prepared solid catalysts was investigated for the conversion of biomass (mainly including glucose, fructose, inulin) with the presence of DMSO. The dependencies of catalytic activity on reaction parameters such as temperature, reaction time and solvent were investigated and the reaction conditions were optimized. A HMF yield of 43.5% was achieved from glucose using Cr(Salen)-IM-HSO_4-MCM-41 as the catalyst in DMSO at 140 ^{o}C for 4 h. Furthermore, the catalyst also demonstrated good activity and as high as 83.5% HMF was directly obtained from fructose, and the HMF yield reached 80.2% when inulin was selected as substrate. The immobilized catalysts developed in this study present improved performance over other solid catalyst, and they have been efficiently and easily recycled at least five times without significant loss of activity in glucose conversion and HMF yield.

Keywords: Glucose; Chromium(III) schiff base complex; Acidic ionic liquid; MCM-41; 5-Hydroxymethylfurfural

1 Introduction

Diminishing fossil resources combined with the growing concern about global warming and environment pollution have led to developing novel sustainable routes for the production of fine chemicals and fuels from renewable resources. Biomass has been regarded as the most appropriate substitute for the synthesis of chemicals and transportation biofuels.[1] Currently, 5-hydroxymethylfurfural (HMF), obtained from the dehydration of carbohydrates (e.g. glucose, fructose, inulin, cellobiose and cellulose), has been identified to be a key platform compound[2] for the production of biochemicals, pharmaceuticals, and furan-based polymers.[3-6]

Although HMF could be easily formed by dehydration of fructose using various acid catalysts, fructose is not an ideal feedstock for HMF production due to its high cost. The transformation of glucose in one-pot synthesis has attracted much attention because glucose is the most abundant monosaccharide and less expensive than fructose.[7,8] One of the challenges of using glucose as a raw material is that the stability of the glucose ring makes the processing difficult.[9] Recently, a tandem catalytic system combining isomerization of glucose with subsequent acid-catalyzed dehydration of fructose to HMF has been extensively investigated.[10,11] High yields of HMF from glucose have been shown in ionic liquids and organic solvents using various lewis acid as catalysts.[12,13] In 2007, nearly 70% of HMF yield was firstly reported from glucose in a system consisting of $CrCl_2$ and 1-ethyl-3-methylimidazolium chloride [EMIM]Cl.[14] Subsequently catalysts with chromium as the catalytic center were designed to catalyze the conversion of glucose into HMF. Wu et al[15] reported that the yield of HMF from glucose can reach 83.4% using chromium(III) chloride ($CrCl_3 \cdot 6H_2O$) in DBU-based ILs. It believed that ionic liquids with chromium salts exhibited excellent catalytic performance, and it exists severe drawbacks in terms of separation and recycling. In order to overcome these problems of catalyst while achieving the appropriate catalytic activity, heterogeneous catalysts have been developed. A HMF yield of 90% with a full fructose conversion was obtained using MIL-101(Cr)-SO_3H.[16] Bromberg et al[17] synthesized the novel functional composite materials that are hybrids of MOFs and polymer network, showed high activity in fructose dehydration to HMF. However, the dehydration of glucose is very unselective and the yield is low in these catalytic systems.

Supported ionic liquid nanoparticles[18-20] have excellent catalytic performance for the dehydration of fructose to HMF, but HMF was not detected when glucose was used as the substrate. This is probably because the supported ionic liquid nanoparticles have Brønsted acid sites, which favor the dehydration of fructose, but lack Lewis acid sites. Recently, Liu et al[21] prepared a series of cation-exchange resins modified by metal ion and investigated their activity in glucose conversion in [Bmim]Cl ionic liquid. Yi et al[22] reported that the yield of HMF achieved 48% from glucose using heteropoly acid ionic crystal ($Cs_2Cr_3SiW_{12}$) as the catalyst in both aqueous and DMSO media. As seen in the above mentioned studies, a heterogeneous catalyst combining Lewis with Brønsted acidic sites should be a better choice to degrade glucose into HMF.

Schiff base transition metal complexes have been extensively studied because of their potential uses as catalysts in wide range of reaction, such as epoxidation of olefins,[23] oxidation of alcohol,[24] Suzuki-Miyaura coupling reaction,[25] asymmetric reaction,[26] and so on. Many strategies have adopted to anchor metal complexes on mesoporous silica to overcome the disadvantages of schiff base complexes. Mesoporous silica, especially MCM-41, has been widely used as a heterogeneous support for the immobilization of homogeneous catalyst due to thermal stability, large surface area, high dispersion, ease of surface modification and tunable pore size.[27,28] From our previous work, homogeneous chromium-salen complexes can catalyze the isomerization of glucose to fructose with high activity and selectivity. Moreover, SO_3H-functionlized ionic liquids with a hydrogen sulfate counteranion are suitable candidates for bifunctional catalysts, because the dual acidic functionalized ILs can obviously enhance their acidities.[19,20]

Herein, we synthetized bifunctional catalysts with the anchoring of chromium(III) schiff base moiety and SO_3H-functionalized ionic liquids on the surface of mesoporous silica, MCM-41. Particularly, utilizing an insoluble solid catalyst diminishes the hazardous effect of chromium. This is the first application of the catalysts in the conversion of carbohydrates. Furthermore, the catalysts exhibit efficient activity for the dehydration of glucose into HMF, and could be also used in the production of HMF from other carbohydrates, such as fructose, inulin, cellobiose, sucrose, cellulose, and starch.

2 Experimental

2.1 Materials

5-Chlorosalicylaldehyde, 5-Bromosalicyclaldehyde, Chromium acetate($Cr(OAc)_3$,99%), γ-Chloropropyl Triethoxysilane(CPTES), 3-Aminopropyltriethoxysilane, and 1,3-Propanesultone were purchased from shanghai Aladdin Industrial Inc.; HMF used in the study was obtained from Sigma-Aldrich Co. LLC.; inulin was obtained from Alfa Aesar; fructose, sucrose, glucose, cellobiose, Cetyltrimethylammonium bromide(CTAB), Tetraethyl orthosilicate(TEOS), Ethylenediamine were purchased from Sinopharm Chemical Reagent Co. Ltd.; Solvents and reagents were obtained from commercial sources and were used without further purification. Deionized water was produced by using a laboratory water-purification system (RO DI Digital plus).

2.2 Catalyst preparation

We report a simple and efficient procedure for the immobilized chromium(III) schiff base complex and acidic ionic liquid on the mesoporous silica as an effective and reusable catalyst (Scheme 1).

2.2.1 Preparation of MCM-41 nanoparticles

Mesoporous MCM-41 was prepared according to the literature method,[28] with a slight modification. In a typical procedure, CTAB (1.36 g, 3.7 mmol) was added to deionized water (50 mL) at room temperature to give a clear solution and 5.2 mL TEOS was added dropwise under stirring. Then the aqueous ammonia (25 wt%) was added until the pH of the solution was adjusted to 10.5 and the mixture was stirred for 3 h, then transferred into a Teflon-lined autoclave and heated at 105 ^{o}C for 24 h. The gel was separated by filtration, washed with distilled water and ethanol, dried in air at room temperature, and then calcined at 550 ^{o}C for 6 h .

2.2.2 Synthesis of salen-type ligands

The ligands were prepared and purified according to the literature.[29] The appropriate substituted salicylaldehyde (10 mmol) in ethanol (50 mL) was added to a ethanol (20 mL) solution of ethylenediamine (5 mmol). The mixture was refluxed for 3 h and cooled to the room temperature. The formed solid was collected by filtration. The solid were subsequently recrystallized from ethanol and dried at 60 ^{o}C in a vacuum oven. The ligands were characterized by ^{1}H NMR, FT-IR, and UV-vis (see ESI†).

2.2.3 Synthesis of the chromium(III) complexes

The chromium(III) complexes were prepared essentially as described.[30] In the synthetic procedure: $Cr(OAc)_3$ (2.29 g, 10 mmol) dissolved in 20 mL of ethanol was added dropwise into ethanol solution (15 mL) contanining the 5 mmol of ligand. The suspension was refluxed for 10 h under nitrogen protection, and then cooled to room temperature. On removal of the ethanol and addition of deionized water, the complex precipitated from solution. After filtering, the filter cake was washed with deionized water. The crude product was recrystallized with petroleum ether. After drying under vacuum at 40 ^{o}C, The obtained chromium(III) schiff base complexes were denoted as Cr(Salen), Cr(Salen-Cl), Cr(Salen-Br). The chromium(III) complexes were characterized by FT-IR, and UV-vis (see ESI Fig. S4†).

2.2.4 Synthesis of the APTS-NH_2-Cr(salen)

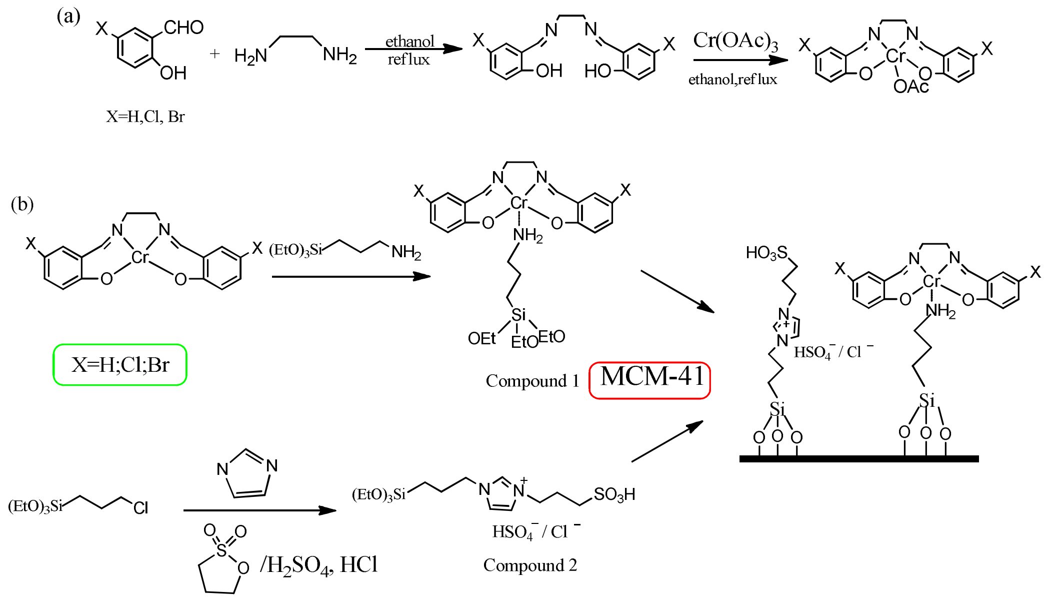
A mixture of Cr(Salen) (10 mmol) and (3-Aminopropyl) triethoxysilane (5 mmol) was heated under N_2 atmosphere refluxing for 24 h. After the reaction, the solvent evaporated under reduced pressure to give the compound 1.

2.2.5 Synthesis of the acidic ionic liquid [CPTES-IM-SO_3H][HSO_4]/[Cl]

The acidic ionic liquid [CPTES-IM-SO_3H][HSO_4]/[Cl] was synthesized as the following process.[31,32] Equivalent mole of imidazole (3.4 g, 50 mmol) and sodium ethoxide (3.4 g, 50 mmol) were dissolved in ethanol with stirring at 70 °C for 8 h. Subsequently, CPTES (12 g, 50 mmol) was added dropwise and the mixture was refluxed for 12 h under N_2 atmosphere. The mixture was filtered to remove the byproduct sodium chloride, the ethanol was evaporated under reduced pressure. A yellowish oil compound was obtained. 1,3-Propanesultone (6.1 g, 0.05mol) was slowly added into the solution in ethanol and the mixture was stirring at 50 °C for 8 h. Then sulfuric acid or hydrochloric acid was added dropwise for another 12 h. The target compound 2 was obtained by washing with diethyl ether for 3 times and drying under vacuum.

2.2.6 Synthesis of the heterogeneous chromium(III) complexes and acidic ionic liquid catalysts

Typically, fresh dried mesoporous silica MCM-41(0.5g) , compound 1 (0.5 g) and the compound 2 (1.0 g) were added in 50 mL of dry toluene, and the mixture was refluxed for 24 h under N_2 atmosphere. Then the resulting suspension was cooled and filtered. The collected powder was washed overnight in a Saxhlet extractor using equivalent ethanol and acetonitrile as solvent and then the solid was dried at 60 ^{o}C overnight. The obtained catalysts were denoted as Cr(Salen)-IM-HSO$_4$-MCM-41, Cr(Salen)-IM-Cl-MCM-41, Cr(Salen-Cl)-IM-HSO$_4$-MCM-41, Cr(Salen-Br)-IM-HSO$_4$-MCM-41, and the synthetic route was followed (Scheme 1).



Scheme 1 (a) Synthetic route of chromium(III) complexes, (b) Synthetic route of Cr-supported catalyst of the mesoporous silica

2.3 characterization techniques

FT-IR spectra were recorded on a Nicolet 360 FT-IR instrument (KBr discs) in the 4000-500 cm^{-1} region. UV-vis spectra were recorded on TU-1901 dual-beam UV-Vis spectrophotometer in the 200-800 nm. ^{1}H-NMR spectra were measured on a Bruker DPX 300 spectrometer at ambient temperature in D_2O or $CDCl_3$ using TMS as the internal reference. TG analysis was carried out using a STA409 instrument in dry air at a heating rate of 20 °C/min from 25 to 800 °C. SEM was performed on a

HITACHI S-4800 field-emission scanning electron microscope. TEM was obtained by using a JEOL JEM model 2100 microscope operated at 200 kV. XRD patterns were collected on a Bruker D8 Advance powder diffractometer using a Ni-filtered Cu/Kα radiation source at 40 kV and 20 mA with a scanning speed of 1°/min. BET surface areas were determined by N_2 adsorption/desorption measurements (Micromeritics ASAP 2020) done at 77 K. Surface areas were calculated using the Brunauer-Emmett-Teller (BET) method over the range $P/P_0 = 0.05$-0.30, where a linear relationship was maintained. Pore size distributions were calculated using theBarrett-Joyner-Halenda (BJH) model. NH_3-TPD temperature-programmed desorption (NH_3-TPD) experiments were carried out on a chemisorption apparatus equipped with a TCD detector. The catalyst in the solids and recovered catalyst were determined by the ICP-OES method with the Optima 7300DV (PerkinElmer) spectrometer.

2.4 Catalytic reactions

All the dehydration reaction experiments were conducted a 5 mL reaction vial equipped with magnetic stirrer. A typical procedure for dehydration of glucose was as follow: fructose (100 mg), catalyst (50 mg) and DMSO (2 mL) were added into the reaction vial. The mixture was stirred vigorously and heated with a thermostatically controlled oil bath for a specific time. The reaction mixture was heated to desirable temperatures with an oil bath under strong stirring for a specific time. After the reaction, the catalyst was separated by centrifugation, the sample was diluted with deionized water, and analyzed by high-performance liquid chromatography (HPLC). HMF was characterized by ^{1}H NMR and ^{13}C NMR (see ESI†).

2.5 Analysis

The liquid samples were analyzed with HPLC using a Agilent Alliance System instrument (1100 Series) equipped with a refractive index detector and a UV detector, and a Shodex SURGER SP0810 (300×8.0) columns for analysis. Deionized water was used as the eluent phase, with a flow rate of 0.7 mL/min and 70 °C column temperature. The amount of HMF and fructose were determined using an external standard. The conversion of glucose and the yield of HMF were evaluated as follows:

$$\text{Glucose conversion (mol\%)} = \left(1 - \frac{\text{moles of remaining glucose}}{\text{starting moles of glucose}}\right) \times 100\%$$

$$\text{HMF yield (mol\%)} = \left(\frac{\text{moles of HMF}}{\text{starting moles of glucose}}\right) \times 100\%$$

3 Results and discussion

3.1 Catalyst characterization

3.1.1 SEM and TEM analysis

The SEM micrographs of the pure MCM-41 and the catalyst Cr(Salen)-IM-HSO_4-MCM-41 are shown in Fig. 1 (a) and (b), this mesoporous silica materials were likely spherical in nature, but some mesoporous molecular sieves generated aggregation because of the incorporation of organic functional groups. As seen from the Fig. 1 (c), the TEM micrograph confirms that the material contain long-range order, one dimensional pore structure, similar to the pure silicon MCM-41.[29,34]

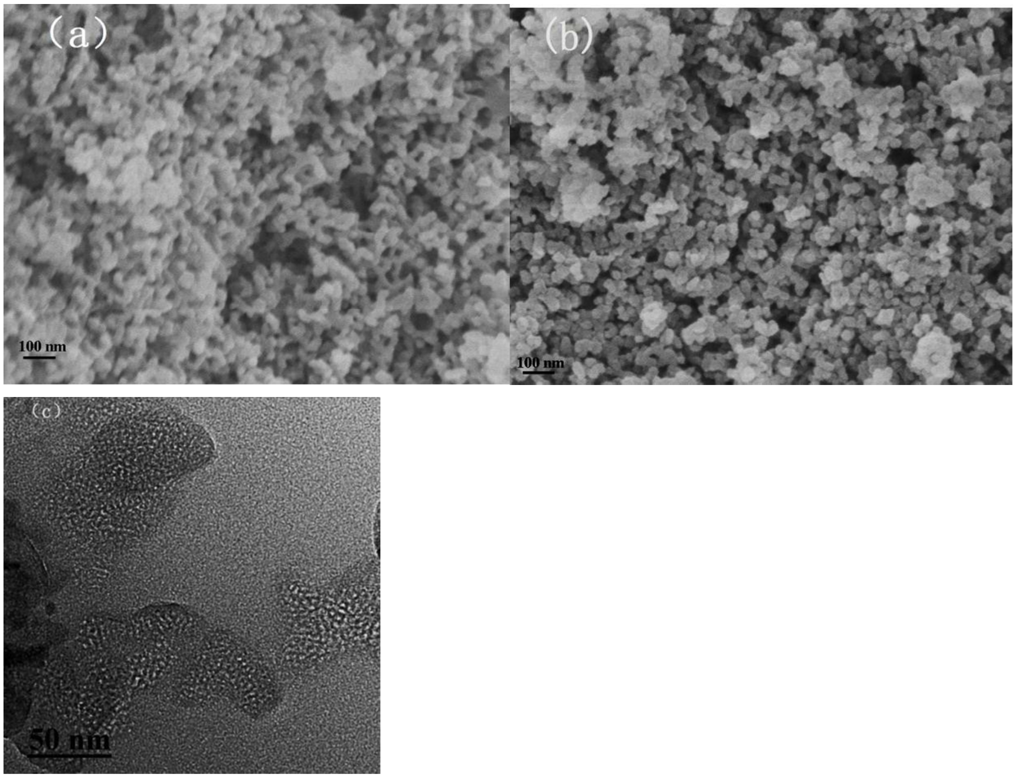


Fig. 1 (a) SEM image of the pure MCM-41, (b) SEM image of the catalyst Cr(Salen)-IM-HSO_4-MCM-41, (c) TEM image of the catalyst Cr(Salen)-IM-HSO_4-MCM-41.

3.1.2 FT-IR spectroscopy

The ligand showed a characteristic band at 1633 cm^{-1} (see ESI Fig.S4†) for the azomethine group (C=N) which were shifted to a lower frequency (1625 cm^{-1}) on complexation, indicating coordination of the schiff-base with chromium.[35] The Si-O-Si vibration at 1091 cm^{-1} was indeed grafted onto the functionalized silica. In the hydroxyl region, the broad band was seen at 3441 cm^{-1} belonging to the stretching vibration of Si-OH groups and H-O-H stretching of absorbed water. Two characteristic peaks were also found at 1459 and 1565 cm^{-1}, which were due to C=N and C=C vibrations of the imidazole ring. In addition, the bands at 1191 and 1048 cm^{-1} were assigned to the S=O stretching vibration of -SO_3H group (Fig. 2).[36] The Cr(Salen)-IM-Cl-MCM-41, Cr(Salen-Cl)-IM-HSO_4-MCM-41, and

Cr(Salen-Br)-IM-HSO_4-MCM-41 were also investigated by FT-IR spectroscopy (ESI, Fig. S6).

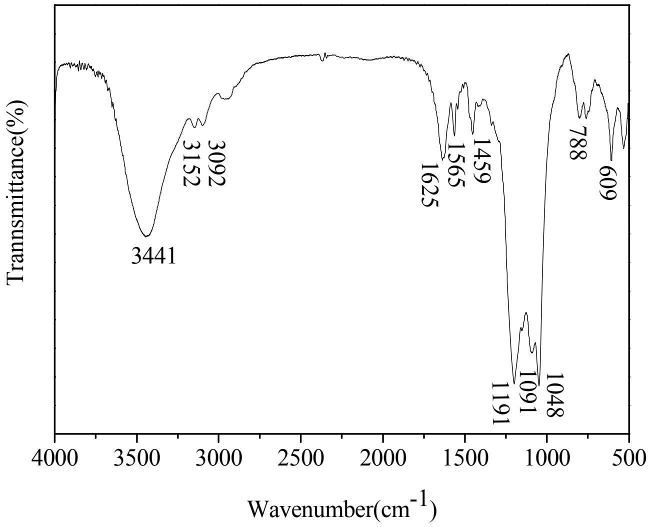


Fig. 2 FT-IR spectra of Cr(Salen)-IM-HSO_4-MCM-41

3.1.3 Thermal analysis

The stability of catalyst was determined by thermogravimetric analysis (Fig. 3). The TG curve indicates an minor weight loss of 1.4% in the range of 25-120 ^{o}C， which is attributed to physically absorbed water in silica. On the other hand, the coordinated water molecules are usually eliminated nearly 1.1% at higher temperature in the range of 120-250 ^{o}C. Complete loss of the acid ionic liquid and chromium complex covalently grafted on to the silica is seen in the temperature at 250-480 ^{o}C, and the amount of organic moiety was about 33.0% against the total solid catalyst. Meanwhile, the peak in the DTG curve showed the fasted loss of the catalyst occurred at 400 ^{o}C. It was demonstrated that the catalyst exhibited good thermal stability below 250 ^{o}C (Fig. 3). The Cr(Salen)-IM-Cl-MCM-41, Cr(Salen-Cl)-IM-HSO_4-MCM-41, and Cr(Salen-Br)-IM-HSO_4-MCM-41 were also investigated by thermal analysis (ESI, Fig. S7).

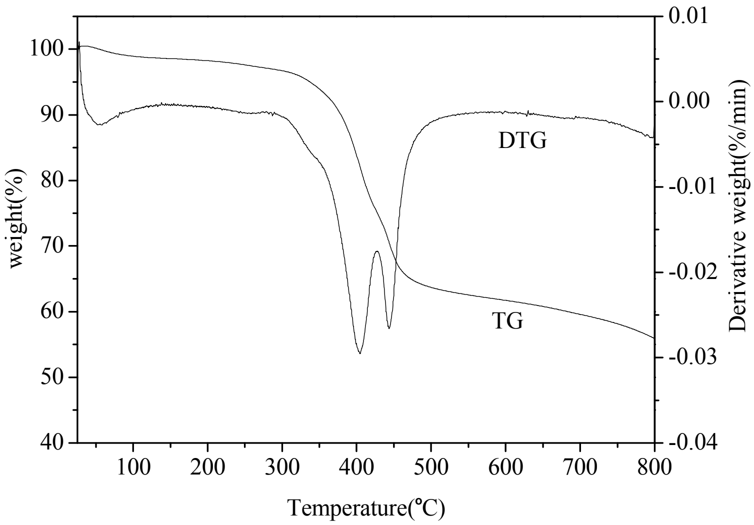


Fig. 3 TG-DTG analysis for the Cr(Salen)-IM-HSO$_4$-MCM-41 catalyst.

3.1.4 Small angle X-ray diffraction studies

XRD patterns of MCM-41 and Cr(Salen)-IM-HSO$_4$-MCM-41 are shown in Fig. 4. The power X-ray diffraction pattern of parent MCM-41 shows a typical three-peak pattern with a very strong d_{100} = 46.29 Å reflection at $2\theta = 1.91°$ and two other weaker reflections at $2\theta = 3.79°$ and $2\theta = 4.51°$ for d_{110} and d_{200}, respectively, indicating a well ordered hexagonal structure.[23,29] Cr(Salen)-IM-HSO$_4$-MCM-41 exhibits a decrease d_{100} reflection with a spacing of 40.04 Å at $2\theta = 2.19°$, and the higher order (110 and 200) diffractions became disappeared. However, the diffraction lines shifted to higher angel and broader after the anchoring of the acidic ionic liquid and chromium complex in MCM-41. This suggests that the mesoporous structure of the MCM-41 remains almost unchanged. [37,38]

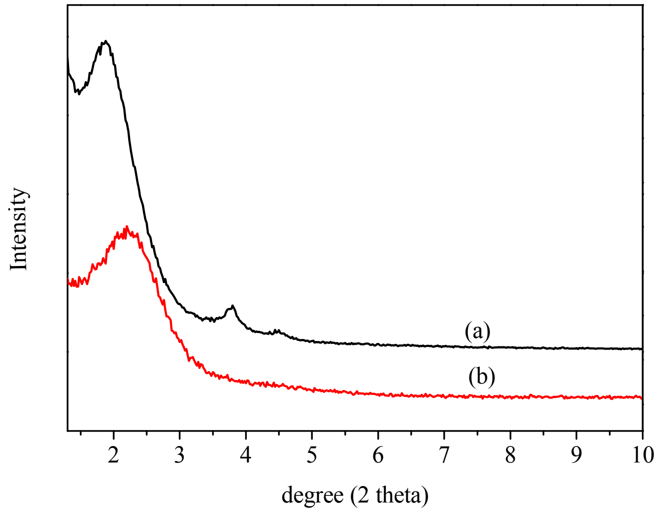


Fig. 4 Low angle powder XRD patterns of MCM-41(a) and Cr(Salen)-IM-HSO_4-MCM-41(b).

3.1.5 N_2 sorption studies

The mesoporous structure of samples was determined by nitrogen adsorption-desorption isotherm, as shown in Fig. 5. The samples display type IV isotherms that are typical for mesoporous materials. This indicates that the mesoporous structure of the parent support was retained in the immobilized catalyst.[39] The surface area and pore size distribution were calculated using BET and BJH methods, shown in Table 1. A decrease in surface area was observed for MCM-41 and Cr(Salen)-IM-HSO_4-MCM-41 from 890.6 to 540.5 m^2g^{-1} and the average pore volume decreased from 1.278 to 1.168 cm^3g^{-1}. The decrease in BET surface area and the loss of uniformity of pore size for Cr(Salen)-IM-HSO_4-MCM-41 in comparison with MCM-41 demonstrated that anchoring of chromium complex and acidic ionic liquid into the mesoporous silica has significant effects on the pore structure of the catalyst. Furthermore, the average pore diameters decreased from 4.83 to 4.33 nm, suggests that acidic ionic liquid and the chromium complex might be confirmed the in-depth functionalization with organic groups in channels of mesoporous silica.[40]

Table 1 Physico-chemical properties of MCM-41 and catalysts

Entry	Sample type	Surface area (m^2g^{-1})	Pore volume (cm^3g^{-1})	Average pore size(nm)	Surface acidity[a] (mmol/g)	Cr[b](wt%)
1	MCM-41	890.6	1.278	4.83	-	-
2	Cr(Salen)-IM-Cl-MCM-41	540.5	1.162	4.32	0.112	2.79
3	Cr(Salen)-IM-HSO_4-MCM-41	576.3	1.168	4.33	0.148	2.83
4	Cr(Salen-Cl)-IM-HSO_4-MCM-41	523.4	1.159	4.34	0.135	2.75
5	Cr(Salen-Br)-IM-HSO_4-MCM-41	515.2	1.143	4.28	0.142	2.79
6	Cr(Salen)-IM-HSO_4-MCM-41[c]	527.8	1.158	4.29	0.139	2.78

[a] Acid concentration values were determined through NH_3-TPD. [b] The chromium content of the catalysts were obtained by using ICP-OES. [c] The recovered catalyst after five times.

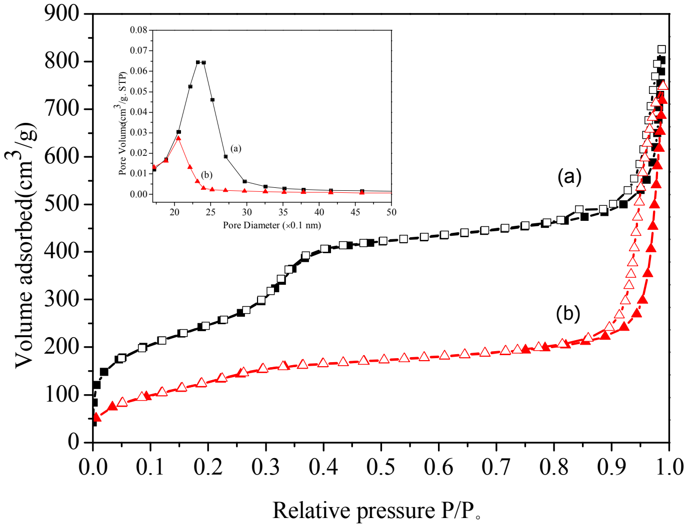


Fig. 5 Nitrogen physisorption isotherms and pore size distribution (inset) for the MCM-41(a) and Cr(Salen)-IM-HSO_4-MCM-41 (b).

3.2 Conversion of glucose to HMF by the homogeneous schiff base complexes

The effect of different metal schiff base complexes on the dehydration of glucose to HMF was investigated in DMSO and the results are listed in Table 2. The homogeneous catalyst Cu(Salen) and Mn(Salen) had little catalytic activity for the dehydration of glucose at 120 °C for 3 h, the yields of Fructose were about 3.2 % and

6.8%, respectively (Table 2, entries 4,5). But Cr(Salen) can catalyze efficiently the isomerization of glucose to fructose under the same conditions (Table 2, entry 1), the fructose yield was 27.8%. The possible reason is that chromium complexes have relatively weaker bound schiff base ligands than manganese and copper complexes. The catalytic activity of chlorine and bromine substituent groups on the chromium(III) schiff base complexes were also discussed about the dehydration of glucose (Table 2, entries 2, 3), indicating that the different substituent groups do not improve the catalytic activity. The possible reason is that electron-accepting character of the substituents leads to a decrease in the delocalization.[41]

Table 2 The catalytic activity of different schiff base complexes on the conversion of glucose to HMF[a]

Entry	catalyst	Temperature(^oC)	Conversion(%)	Fructose Yield(%)	HMF Yield(%)
1	Cr(Salen)	120	75.1	27.8	ND[b]
2	Cr(Salen-Cl)	120	73.4	23.5	ND
3	Cr(Salen-Br)	120	74.8	25.4	ND
4	Cu(Salen)	120	90.5	3.2	ND
5	Mn(Salen)	120	91.5	6.8	ND

[a] Reaction conditions: 100 mg of glucose, 2mL of DMSO, t=3 h, 8 mol% of catalyst.

[b] Not Detected.

3.3 Conversion of glucose to HMF by the heterogeneous schiff base complexes

Based on these considerations above, chromium(III) schiff base complexes can be more active homogenous catalysts for the isomerization of glucose to fructose. Furthermore, high yields of HMF could be easily obtained from dehydration of fructose using various acidic catalysts. Therefore the acidic ionic liquid can effectively promote the dehydration of fructose (ESI Table S1), and shifting the equilibrium from glucose to fructose.[42]

The catalyst Cr(Salen)-IM-Cl-MCM-41 showed good catalytic activity (HMF yield of 31.2%) at 140 °C for 4h, but the catalytic ability (HMF yield of 43.5%) was improved significantly under the same conditions when Cr(Salen)-IM-HSO_4-MCM-41 was used as catalyst (Fig. 6). The Brønsted acidity of the Cr(Salen)-IM-HSO_4-MCM-41 was higher than Cr(Salen)-IM-Cl-MCM-41 (Table 1), indicating that optimization of the Brønsted acidic functionality is an important factor for HMF selectivity. The different catalytic activity of substituent groups heterogeneous catalysts were also discussed about the conversion glucose to HMF. For Cr(Salen-Br)-IM-HSO_4-MCM-41, it can be seen that the yield of HMF increased to 38.6% after 4 h at 140 °C，while the HMF yield was obtained 37.8% using Cr(Salen-Cl)-IM-HSO_4-MCM-41 as catalyst in the same conditions. Based on the results discussed above, Cr(Salen)-IM-HSO_4-MCM-41 showed better catalytic activity toward the dehydration of glucose into HMF.

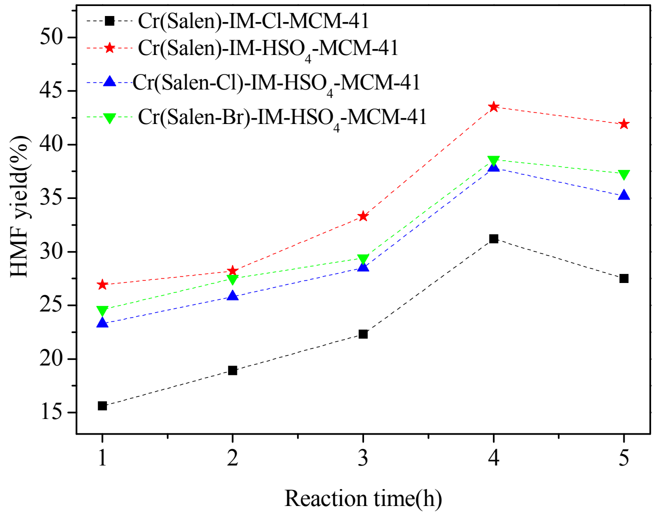


Fig. 6 Influence of different catalysts on the conversion of glucose to HMF.

Reaction conditions: 100 mg of glucose, 2 mL of DMSO, 50 mg of catalyst, T=140 °C.

As shown in Fig. 7, the different temperatures and reaction time in DMSO were optimized to achieve maximum quantity of HMF from glucose. Time ranged from 1 to 5 h were carried out at different temperature of at 120, 130, 140, 150 °C. With the further increasing reaction time, the HMF yield doesnot improve significantly at low temperature (120 and 130 °C). The probably reason might be that the substrates or products are strongly adsorbed on the surface of mesoporous silica materials causing deactivation at low temperature.[22] The desorption become stronger with higher temperature, the initial HMF yield showed obvious improvement. However, increasing reaction temperature and time, the HMF can be decomposed to levulinic acid, formic acid, and the insoluble humins,[43] leading to a decrease in HMF yield. Therefore, 140 °C and 4 h were selected as the optimum condition for the dehydration of glucose to HMF.

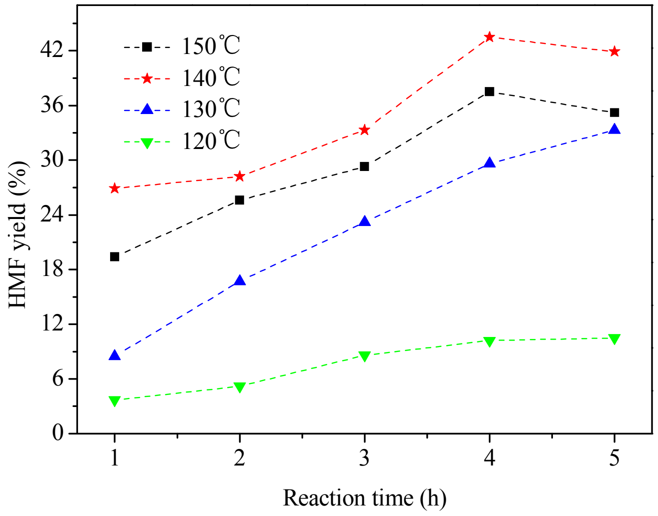


Fig. 7 Glucose transformation into HMF in the presence of

Cr(Salen)-IM-HSO_4-MCM-41.

Reaction conditions: 100 mg of glucose, 2 mL of DMSO, 50 mg catalyst.

Cr(Salen)-IM-HSO_4-MCM-41 is a solid bifunctional catalyst with dual Brønsted-Lewis acidity. The effect of different dosages of catalyst on the conversion of glucose was investigated at 140 °C for 4 h, and the results were given in Fig. 8. It can be seen that increasing the catalyst loading led to an increase in yields of HMF. This may be due to the availability of more active sites of the catalyst. It reached a maximum when the amount of the catalyst was 50 mg. The further increase of the amount of catalyst led to a decrease in the yield of HMF, meaning that the excessive catalyst has not facilitated the transformation of glucose into HMF but into undesired products such as soluble polymers and humins.

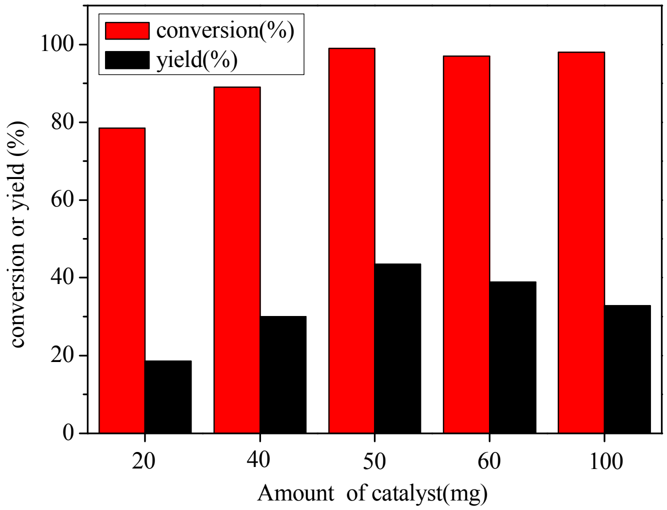


Fig. 8 The HMF yield and conversion of glucose with different amounts of catalyst.

[a]Reaction conditions: 100 mg of glucose, 2 mL of DMSO, T=140 °C, t=4 h.

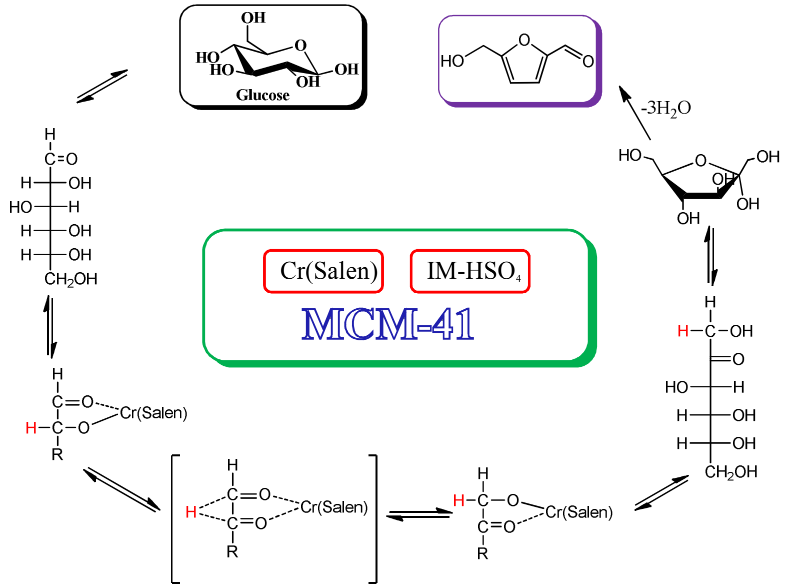
We screened the catalytic activity of Cr(Salen)-IM-HSO_4-MCM-41 using various solvents at 140 °C for 4 h (Table 3). Nearly full conversion with 43.5 % HMF yield was obtained in DMSO, the result is not surprised as DMSO could stabilize HMF and suppress the side reactions.[44] However, DMA, DMF, NMP, and [BMIM]Cl were less effective reaction media in the study. When NMP was used as solvent, HMF yield of 28.9% was obtained from glucose. HMF yield of 14.2% was achieved in [BMIM]Cl. In the polar aprotic solvent, such as DMA and DMF, 15.7% and 12.5% HMF yield were obtained, respectively. In addition, the catalytic activity of the catalyst on the conversion glucose into HMF was also investigated in co-solvent system. It was demonstrated that with the co-solvent gave the lower yields of 16.5-22.1% (entries 6-8). Based on the experiments and referred to the relevant literature, we put forward the possible reaction mechanism for glucose conversion to HMF (Scheme 2).

Table 3 Effect of different solvents for the conversion of glucose to HMF[a]

Entry	Solvent	Temperature(°C)	Conversion (%)	Yield (%)
1	DMSO	140	99	43.5
2	DMF	140	97	12.5
3	DMA	140	89.3	15.7
4	NMP	140	98	28.9
5	[BMIM]Cl	140	95	14.2
6	H_2O-DMSO[b]	140	80.5	21.4
7	H_2O-DMA[b]	140	81.1	16.5
8	[BMIM]Cl-DMSO[b]	140	96	22.1

[a]Reaction conditions: 100 mg of glucose, 50 mg of Cr(Salen)-IM-HSO_4-MCM-41, 2 mL of solvent, t=4 h.

[b]Volume ratio of H_2O/DMSO, H_2O/DMA, [BMIM]Cl/DMSO =1:3.



Scheme 2 Plausible reaction mechanism for the conversion of glucose into HMF on Cr(Salen)-IM-HSO$_4$-MCM-41 catalyst.

3.4 Reusability of the catalyst

The recyclability is of significant importance for applying catalysts in industrial processes. Cr(Salen)-IM-HSO$_4$-MCM-41 was separated from the product mixture by centrifugation, washed with ethanol, and dried in an oven at 70 ^{o}C The reaction temperature and time were 140 ^{o}C and 4h, respectively. The catalyst was successfully recycled five experiments for the conversion of glucose into HMF with only a minor decrease in catalytic activity (Fig. 9). And the loading of chromium complex and acidic ionic liquid of the recovered catalyst were determined (Table 1, entry 6). This results suggested that MCM-Cr(Salen)-IM-HSO$_4$ catalyst can be reused, but the recycling time is limited. It can be mainly attributed to two factors. Firstly, active components leached from silica support surface during vigorous operating conditions. Secondly, the polymer produced in the reaction may be absorbed on the silica, thus poisoning the catalytic activity of the catalyst.

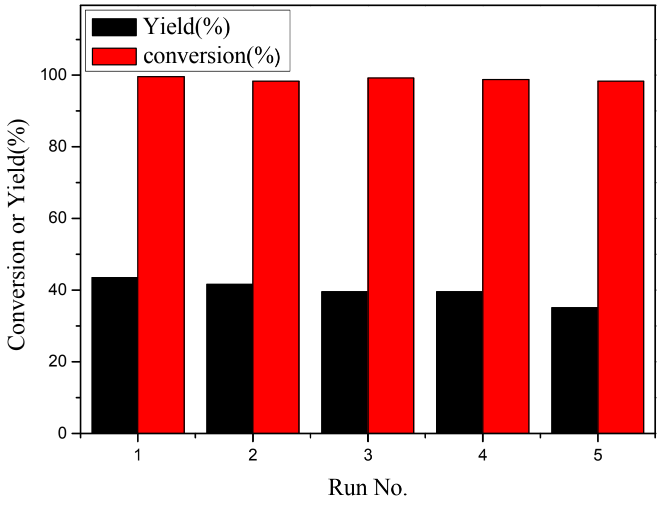


Fig. 9 Reusability of the Cr(Salen)-IM-HSO_4-MCM-41 catalyst in the dehydration glucose. Reaction conditions: 50 mg of catalyst, T=140 °C， t =4 h.

3.5 Conversion of other saccharides to HMF

The Cr(Salen)-IM-HSO_4-MCM-41 catalyst in HMF formation from glucose opens up the possibility of using other carbohydrates, such as fructose, galactose, sucrose, cellobiose and inulin. An HMF yield of 83.5% for the dehydration of fructose was obtained using Cr(Salen)-IM-HSO_4-MCM-41 at 120 °C for 3 h (Table 4, entry 2). The HMF yield reached 80.2% when inulin was selected as substrate, but which is higher than the HMF yield from sucrose. However, the HMF yield from starch and cellulose was low under the same condition because the hydrolysis of starch or cellulose to glucose is difficult in the organic media.

Table 4 Dehydration of different substrates catalyzed by Cr(Salen)-IM-HSO_4-MCM-41[a]

Entry	Substrate	Time(h)	Temperature(°C)	Conversion(%)	HMFYield(%)
1	Fructose	2	120	98.7	65.6
2	Fructose	3	120	99.5	83.5
3	Galactose	5	140	78.9	12.1
4	Sucrose	2	140	94.3	39.6
5	Sucrose	4	140	97.5	43.7
6	Cellobiose	5	140	68.2	25.2
7	Inulin	3	140	96.8	74.4
8	Inulin	4	140	98.5	80.2
9	cellulose	5	140	57.8	7.8
10	starch	5	140	50.3	4.3

[a] Reaction conditions: 100 mg of substrate, 50 mg of catalyst, 2 mL of DMSO.

4 Conclusion

A series of functionalized mesoporous silica materials were tested as catalysts for the selective conversion of glucose into HMF. Owing to the presence of chromium complex and acidic ionic liquid in the framework, the heterogeneous catalysts can serve as a bifunctional catalyst with Brønsted and Lewis acidity. The catalyst Cr(Salen)-IM-HSO_4-MCM-41 has been demonstrated to be the most active, exhibiting high glucose conversion and HMF yield (43.5%) at 140 °C for 4 h in DMSO. The Cr(Salen)-IM-HSO_4-MCM-41 also shows good catalytic activity for the dehydration of biomass-derived, fructose, sucrose, and inulin to HMF, which enabled maximum yields of 83.5%, 43.7%, and 80.2%, respectively. So it is indicated that the novel catalysts have great potential in industry applications used as the heterogeneous catalyst due to their green preparation, high activity, and high reusability.

Acknowledgments

This work was financial supported by National Natural Science Foundation of

China (21206057), and the Natural Science Foundation of Jiangsu Province, China (BK2012118), (BK2012547), and MOE & SAFEA for the 111 Project (B13025).

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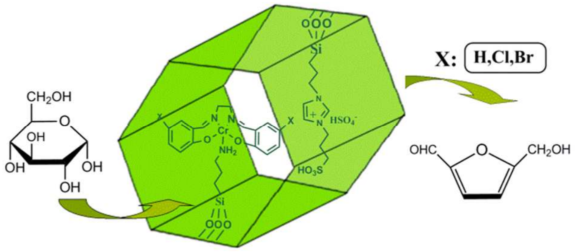
Graphical Abstract



A series of novel catalysts were synthesized by immobilized chromium(III) complex and ionic liquid onto the surface of MCM-41.