Supporting Information

Conversion and Kinetics Study of Fructose-to-5-Hydroxymethylfurfural (HMF) Using Sulfonic and Ionic Liquid Groups Bi-functionalized Mesoporous Silica Nanoparticles as Recyclable Solid Catalysts in DMSO Systems

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Experimental

Chemicals

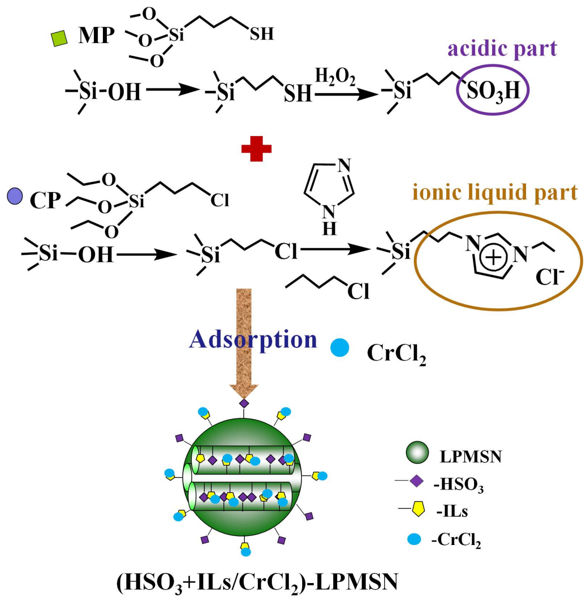
Poly(oxyethylene) oleyl ether (Brij-97, $C_{18}H_{35}EO_{10}$), cetyltrimethylammonium bromide (CTAB, $C_{16}H_{33}N(CH_3)_3Br$), 3-aminopropyltrimethoxysilane (APTMS, 97%), dimethyl phthalate (DOP, >99%), tetraethoxysilane (TEOS), ethanol (99.8%), chromium(II) chloride, benzene, hydrogen peroxide solution (H_2O_2, 30%), chloropropyl trimethoxysilane (97%), and D-(-)-fructose (minimum 99%) were purchased from Sigma-Aldrich. Dried toluene (99.8%) was purchased from Acros. Acetonitrile was purchased from J. T. Baker. 3-mercaptopropyl trimethoxysilane (MPTMS), 3-chloropropyl triethoxysilane (CPTES), chlorobutane, and 5-hydroxymethyl-2-furaldehyde (5-HMF, 98+%) were purchased from Alfa Aesar. Methyl alcohol was purchased from Mallinckrodt Chemical. Imidazole was purchased from Fluka.

Synthesis of mesoporous silica nanoparticles (MSNs)

The synthesis process of the MSN is as follows: Brij-97 was used as the template and was first dissolved in 180 g of deionized water. Then, APTMS and DOP were added to the Brij-97 solution with stirring at room temperature. After stirring for 30 min, 6.7 mL of TEOS was added drop by drop into the mixture, and the whole system, with a composition (in molar ratios) of water: Brij-97: TEOS: AP: DOP = 433: 0.293: 1: 0.058: 0.016, appeared muddy after few minutes. The mixture was kept stirred for 24 hrs at room temperature and subsequently heated at 100 °C overnight. Finally, the precipitated solid was collected by filtration and washed sequentially with water and methanol. It is worth noting that the template can be extracted by this washing step.

Synthesis of bi-functionalized MSN ([HSO_3+ (ILs/$CrCl_2$)]-MSN)

The sulfonic acid and ionic liquid ([HSO_3 + (ILs/$CrCl_2$)] bi-functionalized MSN was prepared using a combination of co-condensation and post-grafting methods, as illustrated in **Scheme 1**. Organosilanes (i.e., MPTMS and CPTES) were added to the reaction system, along with TEOS. The whole system, with a final composition (in molar ratio) of water: Brij-97: TEOS: MPTMS: CPTES = 433: 0.293: 1: 0.009: 0.009, was prepared and kept stirred for 24 hrs at room temperature. The mixture was subsequently heated at 100 °C overnight. Finally, the precipitate (i.e., (MP+CP)-MSN) was collected by filtration and washed sequentially with water and methanol. It is worth noting that the template can be extracted after the washing process.



Scheme 1. An illustration showing the synthesis of [HSO_3+(ILs/$CrCl_2$)]-MSN

To further convert the thiol group of (MP+CP)-MSN to a sulfonic group, the (MP+CP)-MSN was oxidized in an H_2O_2 solution with a composition of (MP+CP)-MSN: H_2O: MeOH: H_2O_2 = 0.5 g:10 ml: 10 ml: 10 ml. After reaction at room temperature overnight, the obtained sample (i.e., (HSO_3+CP)-MSN) was washed and dried in vacuum. To further functionalize the (HSO_3+CP)-MSN with ionic liquid, the (HSO_3+CP)-MSN sample and solid imidazole were degassed for 3 hrs before the addition of anhydrous benzene and chlorobutane with the molar ratio of imidazole: chlorobutane = 1: 2. After one day of reflux, the product (i.e., (HSO_3+ILs)-MSN) was collected through filtration and washed with anhydrous benzene. Finally, the (HSO_3+ILs)-MSN sample was immersed in $CrCl_2$ solution, and the whole mixture was kept stirred overnight. $CrCl_2$ can be physically absorbed on the surface of (HSO_3+IL)-MSN. The final product ([HSO_3+(ILs/$CrCl_2$)]-MSN) was collected by centrifugation.

Characterization

The porous properties of the obtained mesoporous solid catalysts were analyzed with nitrogen adsorption-desorption isotherms measured by the

Micromeritics ASAP 2010 instrument. The specific surface area and pore size were calculated by the BET and BJH methods, respectively. The morphology of the obtained sample was observed with scanning electron microscopy (JEOL JSM-5310 SEM). The organic functional groups modified on the mesoporous silica framework were inspected by solid-state ^{29}Si and ^{13}C NMR spectrometry (BRUKER AVANCE III 400 NMR spectrometer). The elemental composition of the synthesized materials was examined with a Heraeus varioIII-NCSH elemental analyzer.

Fructose-to-HMF conversion

For a typical reaction, 0.015 g of fructose and 4 mg of the synthesized catalyst were added to vials with 0.5 ml of DMSO solvent. Then, the mixture was placed in ultra-sonication for 1 min in order to dissolve the sugar in the organic solvent. Afterwards, the reaction was performed with stirring at various reaction times and temperatures. The reaction was terminated by adding $H_2SO_{4(aq)}$ (5 mM) into the system.

HPLC analysis

After reaction, we removed the catalysts by syringe filter and analyzed the composition of the solution using a high-performance liquid chromatography instrument (ASI500 system) equipped with a HPX-87H column. The eluent was 5 mM H_2SO_4 and the flow rate was 0.6 ml/min. The residue of the reactants and possible products such as 5-HMF were previously identified, and their calibration curves were depicted. The yield of HMF could then be calculated.

Recycle tests of catalysts

For the recycle test, the synthesized mesoporous catalyst was separated from the products and collected by centrifuge, washed with water several times, and dried in lyophilizer. For the second run, the dried catalyst was directly suspended in DMSO, and the whole mixture was then transferred into vials.

Figure S1

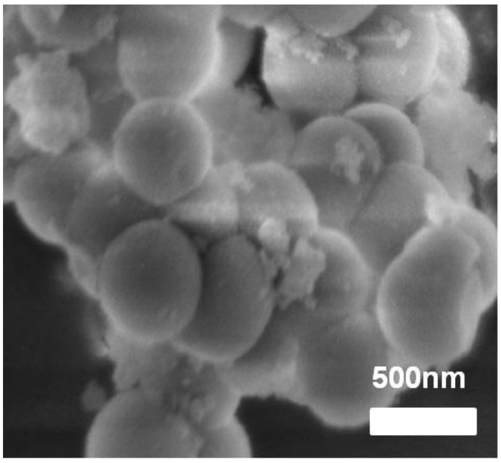


Figure S1. SEM images of [HSO_3+(ILs/$CrCl_2$)] bi-functionalized MSNs.

Figure S2

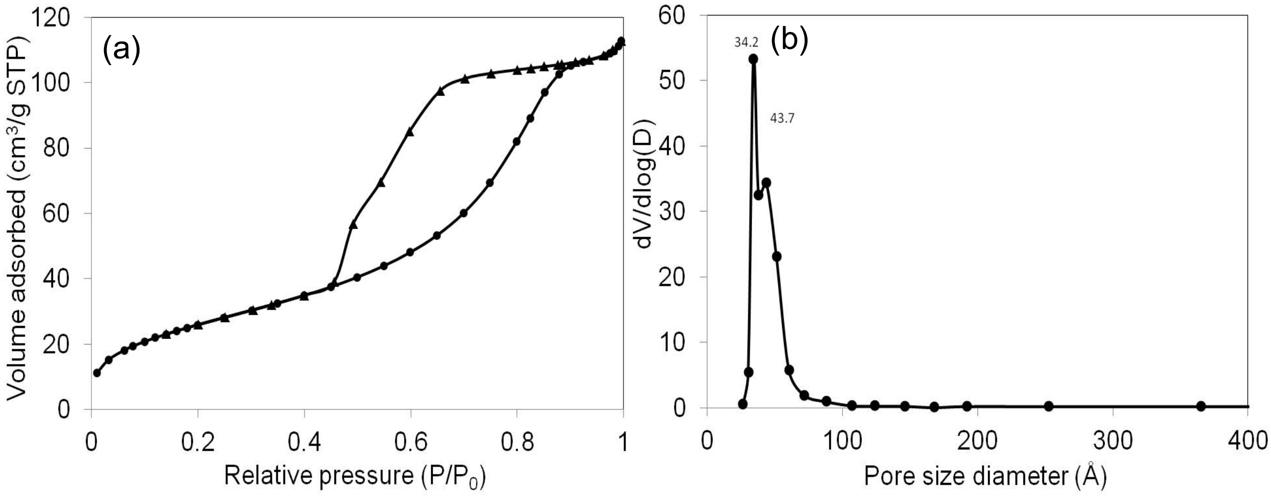


Figure S2. (a) Nitrogen adsorption-desorption isotherm (b) pore size distribution of the synthesized bi-functionalized MSN.

Figure S3

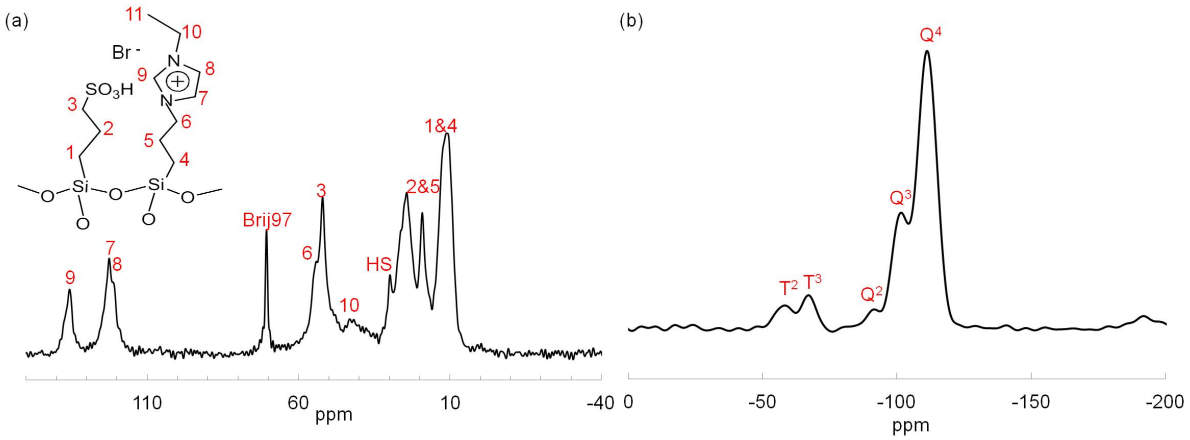


Figure S3. (a) ^{13C} and (b) ^{29}Si solid-state NMR of the synthesized bi-functionalized MSN.

The ^{13}C NMR spectrum contains ten identified signals, and three of them can be assigned to the carbons of the propyl group in the MPTMS. The peak at 10.2 ppm represents to the carbon that is connected directly to the silica framework (C_1). The intensive signals at 70.8 ppm could be assigned to Brij-97 residue. Although theoretically there should be eight signals for the eight carbons of the imidazole-containing organosilane, the signal of C_{11} was overlapped with others peaks. However, the presence of the C_{10} and C_6 peaks indeed proved a successful linkage between CPTES, imidazole and chlorobutane, indicating the successful functionalization of MSN with ionic liquids.

Beside qualitative identification of functional groups, we further quantified the amounts of each functional group on the MSN by ^{29}Si NMR. There were Q^n and T^n peaks appeared in **Fig. S3-b**, which represents the existence of $Si(OSi)_n(OH)_{4-n}$ and $Si(OSi)_n(OH)_{3-n}R$ groups (i.e. $Q^4 = Si(OSi)_4$, $Q^3 = Si(OSi)_3(OH)$, $Q^2 = Si(OSi)_2(OH)_2$, $T^3 = Si(OSi)_3R$, $T^2 = Si(OSi)_2(OH)R$, R = SO_3H or ILs-containing organosilanes in this case).

$$\frac{amount\ of\ functional\ group}{g\ catalyst}$$

$$= \frac{\Sigma(percentage\ of\ the\ signal\ of\ functional\ group)}{\Sigma(molecular\ weight\ of\ each\ signal \times percentage\ of\ each\ signal\ )}$$

$$= \frac{\Sigma(percentage\ of\ T^{n})}{\Sigma(MW(Q^{n}) \times percentage(Q^{n}) + MW(T^{n}) \times percentage(T^{n})}$$