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Hydrolysis of sugars catalyzed by water-tolerant sulfonated mesoporous silicas

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Mesoporous silicas are modified with sulfonic acid groups either by one-pot or by grafting method. In the hydrolysis of sucrose and starch, the sulfonated mesoporous silicas work as water-tolerant recyclable solid acid catalysts, showing higher conversion and turnover frequency than conventional Amberlyst-15, Nafion-silica and HZSM-5 catalysts.

KEY WORDS: sulfonated mesoporous silica, solid acid catalyst, sucrose, starch, hydrolysis.

1. Introduction

Homogeneous acid catalysts such as H_2SO_4 and $AlCl_3$ are widely used in the industrial chemical processes to synthesize bulk and fine chemicals, but they have serious drawbacks of hazards in handling, corrosiveness, difficult separation, and production of toxic waste. Solid acids can replace the homogeneous acids for simpler and environmentally more benign processes [1]. Typical solid acids includes zeolites, heteropolyacids, and ion-exchange resins, but most solid acids are subject to poisoning by water in reactions where water is involved as a reactant or solvent. Thus, hydrophobic nature at the acid sites is important to block the poisoning by water. Sulfonated mesoporous silicas are a new class of solid acid catalysts, because they have uniform large pores (2–50 nm) with sulfonic acid groups. So far sulfonated MCM-41 [2–6], SBA-15 [7, 8] and HMM [9] have been known, and their catalytic performances as solid acid were tested in several reactions such as alkylation, esterification, etherification in organic solvents. However, to the best of our knowledge, no recyclable catalytic reaction in water media has been reported using the mesoporous catalysts.

Recently, biomass attracts much attention as a renewable feedstock due to its "CO_2 neutral" impact on the environment. Sugars are key intermediates from biomass to chemicals, and conversion of sugars also requires a green process. However, the present enzyme-catalyzed process for hydrolysis of starch to glucose needs two steps with several drawbacks such as generation of waste, low thermal stability of enzymes, and difficulty in separation of products and enzymes [10]. Heterogeneous catalysts may find an opportunity for replacing the enzyme catalyst if glucose is obtained in one-step reaction with high catalytic activity and selectivity. Glucose would be an important raw material for a variety of chemicals such as sorbitol, glucaric acid and so on. In this communication, we describe that the sulfonated mesoporous silicas work effectively as recyclable water-tolerant solid acid catalysts in the hydrolysis of bulky sugar molecules to yield monosaccharides.

2. Experimental

2.1. Catalyst preparation

Mesoporous silicas HMM-1 [11, 12] with bridging organic groups and FSM-16 [13] were used as precursors. Sulfonation of HMM-1 was performed by one-pot co-condensation [14] or by post-synthesis grafting method.

2.1.1. Synthesis of Et-HMM-One pot

Octadecyltrimethylammonium chloride (ODTMA, 7.93 g) was dissolved in a mixture of ion-exchange water (224.0 mL) and 3 M sodium hydroxide aqueous solution (35.48 g). The mixture of 1,2-bis(triethoxysilyl)ethane (BTEE, 11.0 g) and 3-mercaptopropyltrimethoxysilane (MPTMS, 2.07 g) was added to the above solution. The suspension was stirred at room temperature for 20 h and aged at 368 K for 24 h. The resulting white precipitate was recovered by filtration to yield an as-synthesized sample. Surfactant was removed by stirring the as-synthesized sample (1.0 g) in ethanol (200.0 mL) with 36% HCl (3.0 g) at 343 K for 12 h. The oxidation of –SH group in the mesoporous ethane silica (0.50 g) was carried

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out by treatment with 65 wt.% HNO_3 (10.0 g) at room temperature for 24 h. The resulting powder obtained upon filtration was washed with large amount of hot water and dried under vacuum to yield sulfonated ethylene-bridged HMM (Et-HMM-One pot).

2.1.2. Synthesis of Ph-HMM-One pot

ODTMA (7.93 g) was dissolved in a mixture of ion-exchange water (275.1 mL) and 3 M sodium hydroxide aqueous solution (29.44 g). The mixture of 1,4-bis(triethoxysilyl)benzene (BTEB, 7.92 g) and MPTMS (1.27 g) was added to the above solution. The suspension was stirred at room temperature for 12 h and aged at 363 K for 24 h. The resulting white precipitate was recovered by filtration to yield an as-synthesized sample. The surfactant was removed by stirring the as-synthesized sample (1.0 g) in ethanol (200.0 mL) with 36% HCl (3.0 g) at 328 K for 6 h. The oxidation of –SH group in the mesoporous benzene silica was carried out as mentioned earlier to yield sulfonated phenylene-bridged HMM (Ph-HMM-One pot).

2.1.3. Synthesis of Et-HMM-Graft

MPTMS (2.0 mL) was added dropwise to ethylene-bridged mesoporous silica (Et-HMM, 1.25 g) in chloroform (100.0 mL). The suspension was stirred at room temperature for 5 days. The powder material obtained upon filtration was washed with chloroform and dried at room temperature to yield thiol-functionalized ethylene-bridged mesoporous silica (Et-HMM-SH). The oxidation of Et-HMM-SH was carried out as mentioned earlier to yield sulfonated ethylene-bridged HMM (Et-HMM-Graft).

2.1.4. Synthesis of Ph-HMM-Graft and FSM-Graft

MPTMS (2.0 mL) was added dropwise to phenylene-bridged mesoporous silica (Ph-HMM, 1.28 g) in chloroform (100.0 mL). The suspension was stirred at room temperature for 5 days. The powder material obtained upon filtration was washed with chloroform and dried at room temperature to yield thiol-functionalized phenylene-bridged mesoporous silica (Ph-HMM-SH). The oxidation of Ph-HMM-SH was carried out as mentioned earlier to yield sulfonated phenylene-bridged HMM (Ph-HMM-Graft). Sulfonated FSM-16 was prepared by the similar grafting method (FSM-Graft).

2.1.5. Synthesis of SiO_2-Graft

MPTMS (2.0 mL) was added dropwise to amorphous silica (CARiACT Q10, 1.0 g) in toluene (80 mL). The suspension was refluxed for 4 h. The powder material obtained upon filtration was washed with toluene and dried under vacuum at room temperature to yield thiol-functionalized amorphous silica (SiO_2-SH). The oxidation of SiO_2-SH was carried out as mentioned earlier to yield the sulfonated silica (SiO_2-Graft).

Liquid H_2SO_4 (>96%), zeolite HZSM-5 (Si/Al = 40, Zeolist), Amberlyst-15 (Across Organics) and Nafion-silica (SAC-13, Aldrich) were used to compare the catalytic performances. Structural parameters of the catalysts are summarized in Table 1. Gas adsorption was measured on an Autosorb-6 and a Chembet-3000 (Quantachrome). XRD profiles were acquired on a Rigaku Miniflex using Cu Kα radiation. ^{13}C CP-MAS and ^{29}Si MAS NMR spectra were recorded on a Bruker MSL-400 spectrometer at 100.6 MHz for ^{13}C and 79.5 MHz for ^{29}Si.

Prior to catalytic reactions, all the solid acids were treated in refluxed water for 1 h to remove loosely bonded –SO_3H groups, and the filtered solids were dried under vacuum at 383–423 K for 1 h.

2.2. Hydrolysis of sucrose and starch

Sucrose, starch (potato) and acetonitrile (HPLC grade) were purchased from Wako and used without further purification. The hydrolysis of sucrose (Scheme 1 (1)) was performed in the batch mode in a glass reactor. Typically, sucrose (0.4 g) was dissolved in H_2O (20 mL) and to the solution was added catalyst (0.2 g). The resulting mixture was stirred at 353 K for 6 h. The hydrolysis of starch was performed in an autoclave at 403 K for 6 h. The catalytic reactions at substrate/acid site ratio of 200 were also tested. Products were analysed by liquid chromatography (Shimadzu LC10AT*VP*, column: phenomenex Luna 5μ–NH_2 100 Å, 150×4.6 mm) with a refractive index detector. A mixture of acetonitrile and water (83:17) was used as an eluent.

3. Results and discussion

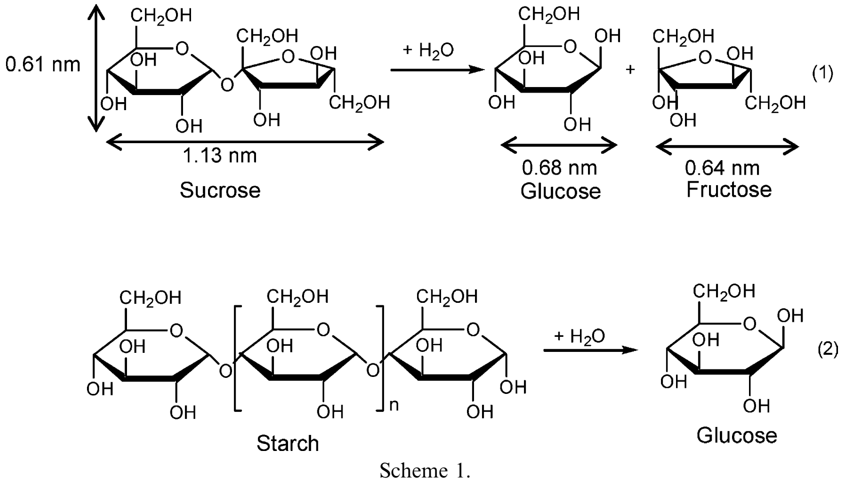
3.1. Hydrolysis of sucrose and starch

Figure 1 depicts time-conversion curves for the hydrolysis of sucrose using acid catalysts. The

Table 1
Textural properties of solid acids[a]

Catalyst	Surface area ($m^2 \cdot g^{-1}$)	Pore diameter (nm)	Acid amount ($mmol \cdot g^{-1}$)[b]
Et-HMM-One pot	814 (717)	2.7 (2.7)	0.36
Et-HMM-Graft	673	2.4	0.69
Ph-HMM-One pot	749 (785)	2.7 (2.7)	0.31
Ph-HMM-Graft	665	2.1	0.90
FSM-Graft	868	2.0	1.11
SiO_2-Graft	280	18	0.45
Amberlyst-15	42 (44)	2–30 (2–30)[c]	4.65
Nafion-silica	215 (184)	3–30 (3–30)[c]	0.17
HZSM-5	364	0.56	0.39
H_2SO_4	–	–	0.50

[a] After water reflux. Values in parenthesis were measured after the catalytic reaction.
[b] Acid amount was determined by titration with 0.01 M NaOH.
[c] Pore diameter is not uniform.



Scheme 1.

sulfonated mesoporous silicas show high conversions, which are comparable to that of Amberlyst-15. On the other hand, Nafion-silica and SiO_2-Graft had a low activity, and no reaction was observed for HZSM-5. Liquid H_2SO_4 gave a slightly higher rate than the solid acids. All the conversion curves obey the first-order dependence on the concentration of sucrose. Table 2 summarizes the results of hydrolysis of sucrose over the acid catalysts. The conversion is over 80% at 353 K after 4 h for the mesosporous silicas, Amberlyst-15 and H_2SO_4, and the corresponding yields of glucose and fructose are obtained. This indicates that no other side reactions take place under the reaction conditions. In Table 2, the catalytic activity is also compared by TOF (initial rate per acid site), because the acid concentration per weight is varied for the solid catalysts. It should be noted that the TOF over the sulfonated mesoporous silicas is higher than that of Amberlyst-15. Therefore, the mesoporous silicas show high conversion and TOF that are not simultaneously obtained over SiO_2-Graft, Amberlyst-15 and Nafion-silica. In the catalytic runs at a substrate/acid site ratio of 200 by varying the catalyst loading, higher conversions are obtained for Et-HMM-One pot and Ph-HMM-Graft than those of Amberlyst-15 and Nafion-silica (Figure 2).

Hydrolysis of starch (Scheme 1, (2)) was carried out at 403 K in an autoclave. The TOF is calculated based on mol% of glucose formed per acid site after 6 h. As shown in Table 2, the mesoporous HMM and FSM catalysts have higher TOF than SiO_2-Graft, Amberlyst-15 and Nafion-silica. Besides glucose, small amount of maltose was also formed. Higher yields of glucose were

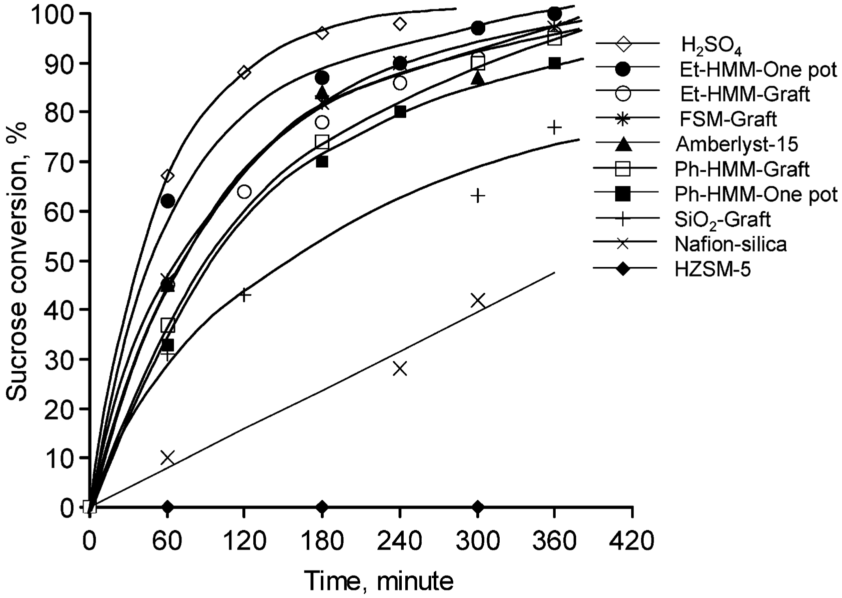


Figure 1. Time-conversion curves for hydrolysis of sucrose over acid catalysts. Sucrose 0.4 g, water 20 g, catalyst 0.2 g, temperature 353 K.

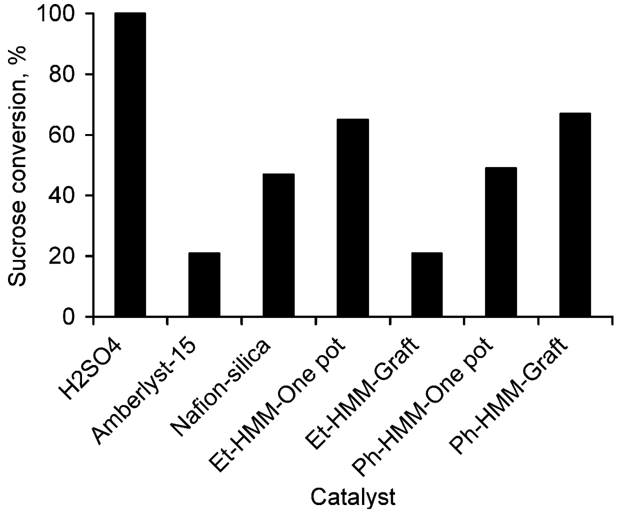


Figure 2. Hydrolysis of sucrose over acid catalyst at substrate/acid site ratio of 200. Sucrose 1.76 mmol, water 1666 mmol, catalyst 0.009 mmol, temperature 353 K, reaction time 24 h.

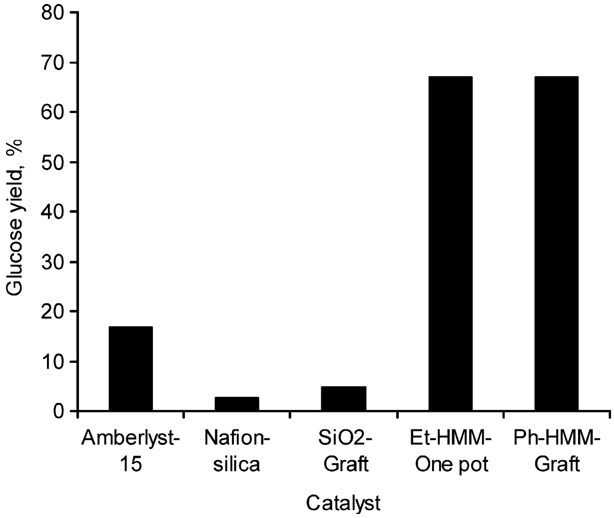


Figure 3. Hydrolysis of starch over acid catalysts at the substrate/acid site ratio of 200. Starch 2.22 mmol, water 1111 mmol, catalyst 0.0108 mmol, temperature 403 K, reaction time 24 h.

Table 2

Results of hydrolysis of sucrose and starch by acid catalysts[a]

Catalyst	Sucrose hydrolysis				Starch hydrolysis		
	TOF (h^{-1})[b]	Conv. (%)	Yield (%)		TOF (h^{-1})[c]	Yield (%)	
			Glucose	Fructose		Glucose	Maltose
Et-HMM-One pot	11.6	90	90	90	1.2	23	12
Et-HMM-Graft	3.0	86	86	82	0.6	21	12
Ph-HMM-One pot	6.8	81	81	80	0.7	23	11
Ph-HMM-Graft	2.3	83	83	82	0.5	27	13
FSM-Graft	3.8	90	90	89	0.6	39	18
SiO_2-Graft	2.1	64	64	64	0.4	11	11
Amberlyst-15	0.5	88	88	87	0.1	25	12
Nafion-silica	3.7	28	28	26	0.3	03	5
HZSM-5	0	0	0	0	–	–	–
H_2SO_4	12.6	98	94	94	–	–	–

[a] Sucrose hydrolysis: catalyst 0.2 g, sucrose 0.4 g, water 20 g, temperature 353 K, reaction time 4 h. Starch hydrolysis: catalyst 0.1 g, starch 0.2 g, water 10 g, temperature 403 K, reaction time 6 h. Products were analyzed by HPLC (column: Phenomenex Luna 5μ –NH_2 100 Å, eluent: acetonitrile : H_2O = 83 : 17).

[b] TOF is an initial rate per acid site [mol of sucrose converted (mol of acid)$^{-1}$ h^{-1}].

[c] TOF = [mol of glucose formed (mol of acid)$^{-1}$ h^{-1}].

also observed in the reaction at the substrate/acid site ratio of 200 for Et-HMM-One pot and Ph-HMM-Graft, where the acid concentration was kept constant (Figure 3). This clearly indicates that the sulfonated mesoporous silicas work efficiently as water-tolerant solid acid catalysts in the hydrolysis of starch.

3.2. *Catalyst recycle experiments*

The sulfonated mesoporous silicas were recyclable in repeated runs. After completion of each reaction, the catalyst was filtered and washed with water, and then used for the next reaction. The reactions were tested upto three recycles, and no decrease in the activity was observed for Ph-HMM-One pot (Figure 4). Further, no reaction occurred after adding sucrose to the filtrate solution. This confirms that no leaching of acid groups happens during the reaction. The reproducible high conversions in repeated runs are indicative of no blocking of the mesoporous channels by the reactant and product molecules.

The recyclable Ph-HMM-One pot catalyst was characterized by XRD and NMR. The XRD patterns in the low and high 2θ regions in Figure 5 indicate that both the 2-D hexagonal structure (*p6mm*) and the crystal-like pore walls [12] are preserved after the catalytic reactions. In the ^{29}Si MAS NMR analysis (Figure 6), three signals are assigned to $T^{2\prime}/T^{3\prime}$ (−60.5, −70.2 ppm) of $\equiv Si(CH_2)_3SO_3H$ and T^2/T^3 (−70.2, −80.0 ppm) of $\equiv SiC_6H_4$, in which the $T^{3\prime}$and T^2 resonances are

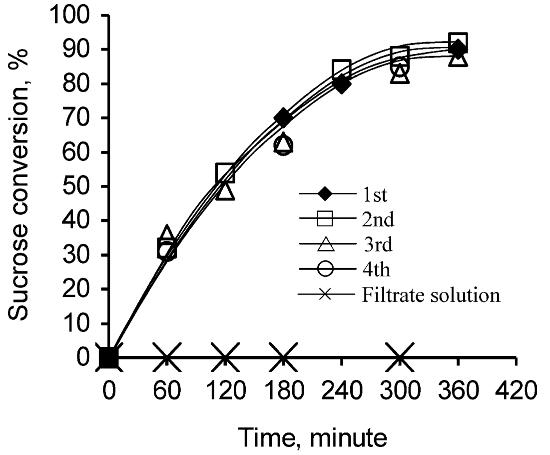


Figure 4. Time-conversion curves for catalyst recycle experiment. Sucrose 0.4 g, water 20 g, Ph-HMM-One pot 0.2 g, temperature 353 K.

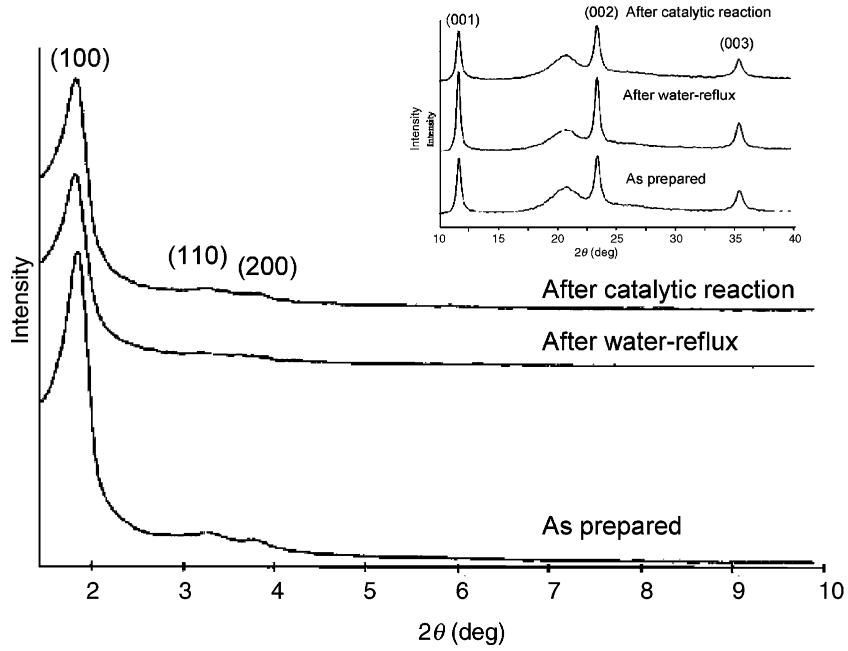


Figure 5. XRD patterns of Ph-HMM-One pot.

overlapped [14]. The absence of Q sites indicates that the Si–C bonds are stable during the catalytic reaction. In the ^{13}C CP-MAS NMR spectra, the signal at 135.4 ppm is assigned to $\equiv SiC_6H_4$. The band at 54.9 ppm is due to the C1′ carbon of the $\equiv Si(CH_2)_3SO_3H$ group, which is overlapped with a spinning sideband. The C2′ and C3′ signals appear at 19.6 and 14.5 ppm, respectively. The two peaks at 59.4 and 18.6 ppm are assignable to $SiOCH_2CH_3$ of the T^2 species [12]. The ^{13}C NMR data and the catalytic recycle experiments indicate that the $\equiv Si(CH_2)_3SO_3H$ group remain unchanged after the catalytic reaction.

An important feature of the mesoporous silicas is its uniform channel structure that bulky reactants can access. Sucrose molecules (0.6 × 1.1 × 0.5 nm) can easily enter the channels and are able to interact with the acid sites. In the hydrolysis of bulky starch by the mesoporous catalysts, TOFs are varied by different initial concentrations of starch. This indicates that diffusional limitations may be present for the starch hydrolysis on the mesoporous catalysts. We suggest that the starch molecule is hydrolyzed by the acid site around the pore window, and the resulting smaller fragments enter into the pore to be hydrolyzed. In contrast, Amberlyst-15, Nafion-silica and SiO_2-Graft have neither a uniform pore diameter nor an ordered channel structure. This reduces the number of acid sites to interact with sucrose/starch molecules (Figure 7). By considering that both the mesoporous HMM/FSM silicas and SiO_2-Graft have similar hydrophilic (silica backbone) and hydrophobic ($Si\text{–}C_3H_6\text{–}SO_3H$) moieties, the unique structural properties of the mesoporous silicas boost the efficiency of the acid sites.

4. Conclusions

We have shown that the new water-tolerant sulfonated mesoporous silicas can be efficiently used as solid acid catalysts in the hydrolysis of sugars. The mesoporous channels are beneficial in converting bulky sucrose and starch molecules into monosaccharides by a green process. The catalysts are recyclable and the reproducible activity is achieved.

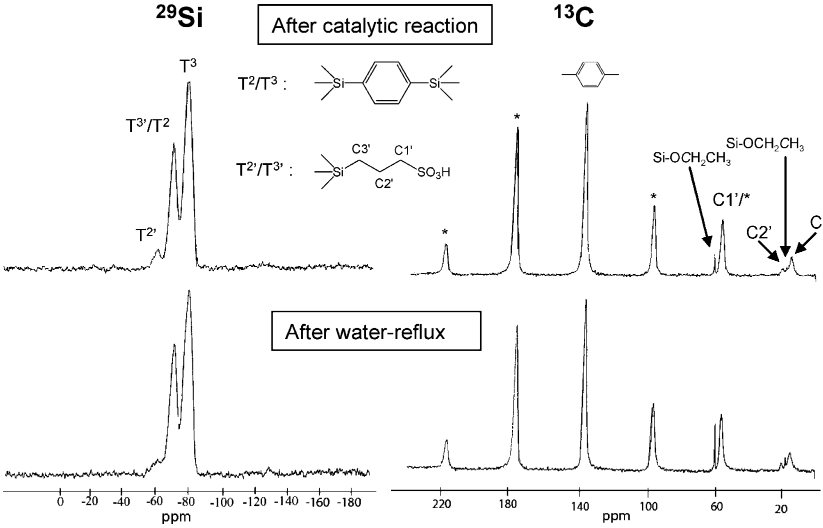


Figure 6. ^{29}Si and ^{13}C NMR spectra of Ph-HMM-One pot. * refers to spinning sidebands.

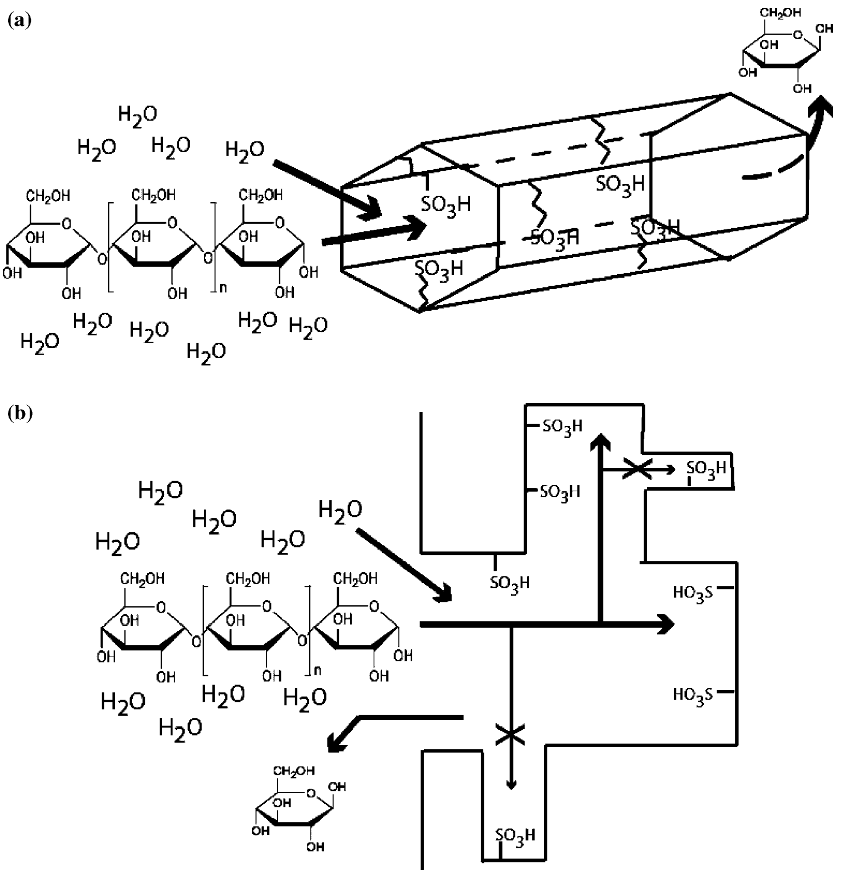


Figure 7. Schematic representation of hydrolysis of starch by (a) sulfonated mesoporous silicas and (b) Amberlyst-15, Nafion-silica and SiO_2-Graft.

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