



Efficient and stable solid acid catalysts synthesized from sulfonation of swelling mesoporous polydivinylbenzenes

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ABSTRACT

Efficient and stable solid acid catalysts, sulfonic groups functional swelling mesoporous polydivinylbenzenes (PDVB-*x*-SO₃Hs), were synthesized from sulfonation of swelling mesoporous polydivinylbenzenes (PDVB-*x*s) by chlorosulfonic acid in CH₂Cl₂. Nitrogen adsorption–desorption isotherms showed that PDVB-*x*-SO₃Hs have high surface area and abundant mesoporosity. Elemental analysis and acid–base titration techniques showed that PDVB-*x*-SO₃Hs have high concentration of sulfonic groups. Esterifications of acetic acid with cyclohexanol, hexanoic acid with ethanol, lauric acid with ethanol and acylation of anisole with acetyl chloride showed that PDVB-*x*-SO₃Hs are more active than arenesulfonic, propyl-sulfonic groups functional mesoporous silicas (SBA-15-Ar-SO₃H, SBA-15-Pr-SO₃H) and strongly acidic ion-exchange resin (Amberlyst 15). The superior performance of PDVB-*x*-SO₃Hs is attributed to their unique features including large surface area, abundance of mesoporosity as well as high content of sulfonic groups.

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1. Introduction

The replacement of mineral liquid acids by solid acids for the production of fine chemicals has been paid much attention due to the advantages of easy separation of the catalyst from the reaction medium, reductive corrosion, improved regenerability, and enhanced product selectivity [1–19]. Typically, solid acids are zeolites [6–12], heteropolyacids [13,14], sulfated metal oxides [15], and ion-exchange resins [16–21].

Among these solid acid catalysts, zeolites are of great importance because of their high surface area, versatile framework, controllable acid strength, and shape-selectivity [6,7,10,12]. However, bulky molecules cannot get access to the catalytically active sites in relatively small micropores in zeolites, which strongly influences the catalytic conversion of bulky substrates [6]. Synthesis of ordered materials such as MCM-41 and SBA-15 offers a totally new route to solve the limitation of micropores [22–24], but the amorphous nature of mesoporous walls hinders their catalytic applications as strong acidic catalysts for conversion of bulky molecules [6,22]. To achieve strong acidic sites, sulfonic groups have been successfully incorporated into the mesoporous walls by various routes [25–30], giving excellent catalytic properties in a series of acid-catalyzed reactions [31–36]. Notably, there is a strict limitation on the concentration of sulfonic groups on mesoporous

materials because a large amount of sulfonic groups normally lowers the sample mesoporosity [29,37]. Additionally, the presence of hydrophilic terminal silanols on the surface of mesoporous materials also influence their catalytic properties [38,39]. For example, in the etherification of vanillyl alcohol with 1-hexanol, water which is produced as a by-product of the reaction co-adsorbs near the sulfonic acid centers, resulting in their partial deactivation due to competition with the alcohol reactant species [38].

Compared with mesoporous silica walls, organic frameworks have hydrophobic features, which might result in new solid acids by modification of sulfonic groups [16–21,40]. For example, sulfonated resins are good acidic catalysts, but their shortcomings such as low surface area and stability are still challengeable [16–21]. Recently, Xing et al. have successfully synthesized SO₃H-functional FDU-type mesoporous phenol–formaldehyde resins (FDU-*n*-SO₃H, *n* = 14 and 15) [40], which showed superior catalytic activities in the liquid-phase Beckmann rearrangement of cyclohexanone oxime and the condensation of bulky aldehydes with alcohols. These novel solid catalysts have high surface areas (up to 539 m²/g) and controllable hydrophobicity, but their acidic concentration is still blocked by the limitation to sulfonation in the phenolic rings due to the strong steric hindrance. Therefore, SO₃H-functionalized porous organic materials with large surface area and high concentration of sulfonic groups as well as good stability are strongly desirable.

More recently, we have synthesized mesoporous polydivinylbenzenes (PDVB-*x*s) with large surface area and pore volume

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[41]. When compared with mesoporous phenol–formaldehyde resins, they exhibited excellent stability, good swelling property, high capacity for functionalization, and super hydrophobicity due to the unique polymerization of divinylbenzene (DVB) under hydrothermal conditions [41]. We demonstrated here a successful synthesis of sulfonated mesoporous PDVB-*x*s (PDVB-*x*-SO₃Hs) with large surface area and high content of sulfonic groups. Catalytic tests showed that these PDVB-*x*-SO₃Hs are more catalytically active in esterification and Friedel-Crafts acylation than conventional strongly acidic ion-exchange resin (Amberlyst 15: copolymer of sulfonated polystyrene with PDVB), arenesulfonic and propyl-sulfonic groups functional mesoporous silicas (SBA-15-Ar-SO₃H and SBA-15-Pr-SO₃H).

2. Experimental

2.1. Chemicals and reagents

All reagents were of analytical grade and used as purchased without further purification. Amberlyst 15, 3-mercaptopropyltrimethoxysilane (3-MPTS), 2-(4-chlorosulfonylphenyl)-ethyltriethyltrimethoxy silane (CSPTMS), and nonionic block copolymer surfactant poly(ethyleneoxide)-poly(propyleneoxide)-poly(ethyleneoxide) block copolymer (Pluronic 123, molecular weight of about 5800) were purchased from Sigma–Aldrich Company, Ltd. (USA). DVB, azobisisobutyronitrile (AIBN), tetrahydrofuran (THF), chlorosulfonic acid, tetraethyl orthosilicate (TEOS), cyclohexanol, acetic acid, hexanoic acid, ethanol, anisole, acetyl chloride, dichloromethane (CH₂Cl₂), dodecane were obtained from Tianjin Guangfu Chemical Reagent. H-form of Beta zeolite and ultrastable Y zeolite (USY) was supplied by Sinopec Catalyst Co.

2.2. Catalyst preparation

2.2.1. Preparation of mesoporous PDVB-*x*s

Swelling mesoporous PDVB-*x*s (*x* stands for volume ratio of tetrahydrofuran with water) were hydrothermally synthesized by polymerization of DVB with starting system of DVB/AIBN/THF/H₂O at molar ratio of 1/0.02/16.1/0 or 7.23 [41]. As a typical run, 2 g of DVB was added into a solution containing 0.05 g of AIBN and 20 mL of THF, followed by addition of 2 mL of H₂O. After stirring at room temperature for 3 h, the mixture was hydrothermally treated at 100 °C for 2 days. After evaporation of the solvents at room temperature, the PDVB-0.1 sample was obtained. In contrast, mesoporous PDVB with little swelling property designated as PDVB-W was synthesized at 80 °C with the same starting system as PDVB-0.1 except for hydrothermal treatment.

2.2.2. Sulfonation

Sulfonation of swelling mesoporous PDVB-*x*s and PDVB-W was performed by chlorosulfonic acid in CH₂Cl₂. As a typical run, 0.75 g of PDVB-*x*s or PDVB-W was outgassed at 100 °C in a three-necked round flask for 3 h. Then, 50 mL of CH₂Cl₂ containing chlorosulfonic acid (10 mL) was slowly added into the flask at 0 °C, stirring for 12 h under nitrogen atmosphere. Finally, the products were obtained from filtering, washing with a large amount of water, stirring in dioxane, and drying at 80 °C. The samples were denoted as PDVB-*x*-SO₃Hs or PDVB-W-SO₃H.

The samples can also be sulfonated by H₂SO₄, which were denoted as PDVB-S-SO₃Hs under oil bath. As a typical run, 1.5 g of PDVB-0.1 was outgassed at 100 °C in a three-necked round flask for 3 h, and then 100 mL of 98% H₂SO₄ containing 30 mL of CH₂Cl₂ was slowly added; meanwhile, 0.02 g of Ag₂SO₄, which act as catalysts, was also added. The reaction mixture was

heated at 80 °C for 12 h in the oil bath. Finally, the products were obtained after filtration, washing with a large amount of water, and drying at 80 °C.

For comparison, SBA-15-Ar-SO₃H and SBA-15-Pr-SO₃H with molar ratios of S/Si at 0.1 were synthesized according to the literature [29,37].

2.3. Characterization

Nitrogen isotherms were measured using a Micromeritics ASAP 2020M system. The samples were outgassed for 10 h at 150 °C before the measurements. The pore-size distribution for mesopores was calculated using the Barrett–Joyner–Halenda (BJH) model. CHNS elemental analysis was performed on a Perkin–Elmer series II CHNS analyzer 2400. FTIR spectra were recorded using a Bruker 66V FTIR spectrometer. Differential thermal analysis (DTA) and thermogravimetric analysis (TG) were performed on a Perkin–Elmer TGA7 and a DTA-1700 in flowing air, respectively. The heating rate was 20 °C/min. The acid-exchange capacity of the catalysts was determined by acid–base titration with NaOH solution. The MAS ¹³C NMR spectra were recorded on a Bruker AVANCE-400WB, 12 kHz of spinning rate.

2.4. Catalysis

Esterifications of hexanoic acid with ethanol, acetic acid with cyclohexanol, lauric acid with ethanol and acylation of anisole with acetyl chloride were chosen as model reactions. In these reactions, the products were analyzed by gas chromatography (Varian CP-3800 and Shimadzu 14C) with a flame ionization detector (FID) and dodecane was used as an internal standard. The column was OV-1 (30 m); the initial temperature was 80 °C, temperature rate was 25 °C/min, and final temperature was 220 °C (for analysis of esterification of bulky lauric acid with ethanol, the final temperature was 235 °C); the temperature of FID detector was 280 °C. In these reactions, the stirring rate was higher than 800 rpm and catalyst granules were larger than 400 mesh.

2.4.1. Esterification

Esterification of acetic acid with cyclohexanol (EAC) was performed by mixing and stirring 0.2 g of catalyst and 11.5 mL (0.11 mol) of cyclohexanol in a three-necked round flask equipped with a condenser and a magnetic stirrer. After heating the mixture to 100 °C by oil bath, 17.5 mL (0.305 mol) of acetic acid was rapidly added and the reaction was continued for 5 h. In this reaction, the molar ratio of acetic/cyclohexanol acid was 2.6 and the mass ratio of catalyst/cyclohexanol was 0.018. The product was cyclohexyl acetate (CHA) with selectivity for near 100%.

In the esterification of hexanoic acid with ethanol (EHE), 0.3 g of catalyst and 6.26 mL (50 mmol) of hexanoic acid were added into a three-necked round flask equipped with a condenser and a magnetic stirrer. After the temperature rising to 80 °C, 11.67 mL (0.2 mol) of ethanol was rapidly added, the reaction was continued for 5 h, the molar ratio of ethanol/hexanoic acid was 4.0, and the mass ratio of catalyst/hexanoic acid was 0.051. The product was ethyl hexanoate (EH) with selectivity for near 100%.

In the esterification of lauric acid with ethanol (ELE), 4 mmol of lauric acid and 0.15 g of catalyst were added into a three-necked round flask equipped with a condenser and a magnetic stirrer, followed by addition of 80 mmol of ethanol. When the temperature reached 70 °C, the reaction was continued for 5 h. The molar ratio of ethano/lauric acid was 20, and the mass ratio of catalyst/lauric acid was 0.187. The product was ethyl laurate (EL) with selectivity for near 100%.

2.4.2. Acylation

The acylation of anisole with acetyl chloride (AAA) was carried out in a three-necked round flask equipped with a condenser and a magnetic stirrer. In a typical run, 0.3 g of fresh catalyst, 5.5 mL of anisole (50 mmol) and 0.71 mL of acetyl chloride (10 mmol) were added into the reactor while stirring at 60 °C. After 5 h, the products were collected by a syringe after regular intervals. The molar ratio of anisole/acetyl chloride was 5.0, and the mass ratio of catalyst/acetyl chloride was 0.33. The products were *p*-acetylanisole (*p*-AA) with selectivity for about 96–98% and *o*-acetylanisole (*o*-AA) with selectivity for about 2–4%.

3. Results and discussion

3.1. Preparation and sulfonation of samples

Swelling mesoporous PDVB-*x*s were synthesized by polymerization of DVB under hydrothermal treatment [41]. A hydrothermal

route was used in this work to provide a sealed media where most of the solvents remained in the liquid-phase at relatively high temperature (100 °C) and high pressure (5–6 atm). When DVB monomers started to polymerize under these conditions, a loose but highly cross-linked network was gradually formed in solvents (THF) which is considered to act as both solvent and 'template'. After the removal of a large amount of the solvent as the guest, PDVB samples with open disordered mesoporosity were finally obtained. In contrast, a classical porous polymer is formed by polymerization in open system at relatively low temperature and pressure (1 atm). In this case, the solvent, as the guest, cannot be effectively included in the polymer samples. The various synthetic routes result in a big differences in the textural parameters of the samples, giving quite distinguishable swelling properties [41].

Fig. 1A and B shows photographs of the same amount of PDVB-0.1 before and after addition of CH₂Cl₂. Clearly, after making contact with CH₂Cl₂, the volume of PDVB-0.1 is significantly expanded, demonstrating that PDVB-0.1 has excellent swelling property. Fig. 1C shows the photograph of sulfonated PDVB-0.1-SO₃H,

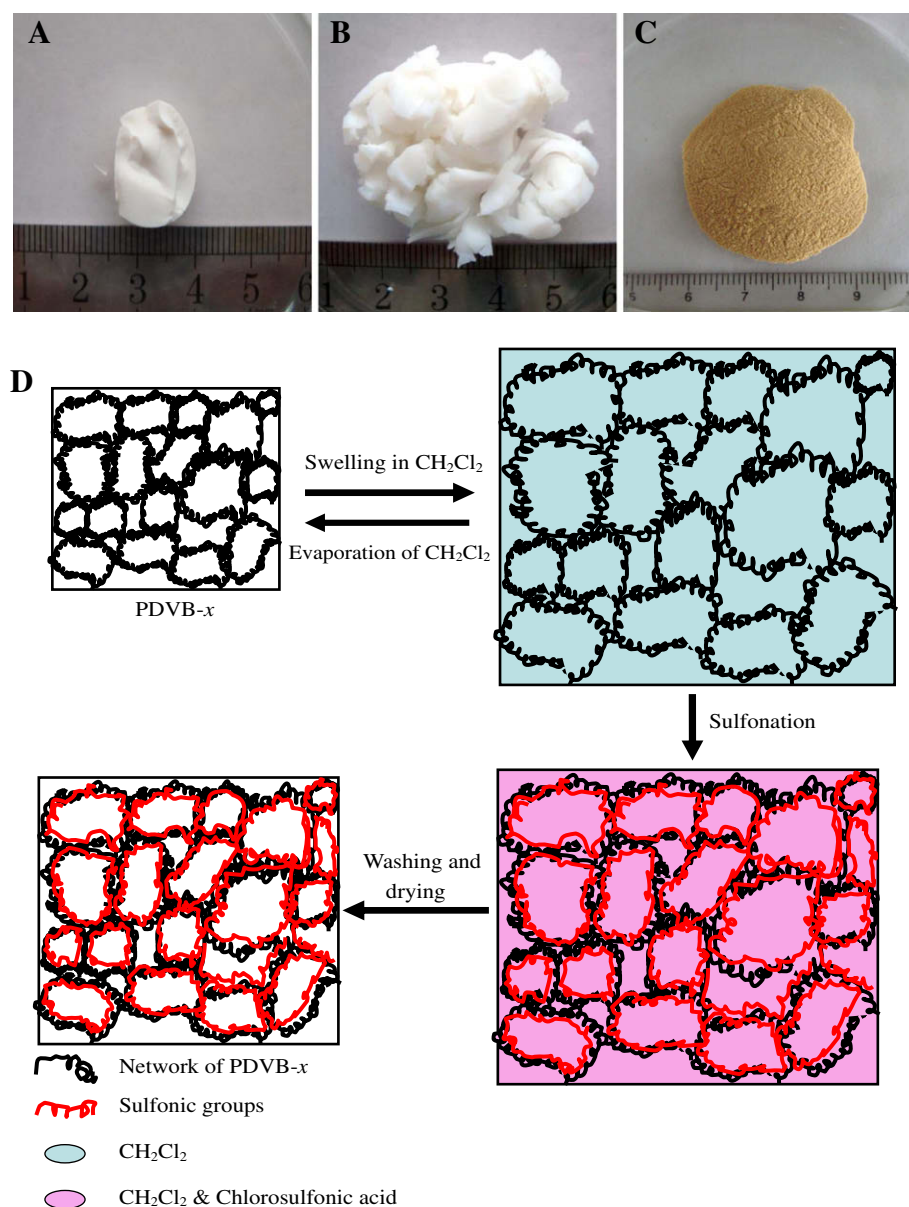


Fig. 1. Photographs of PDVB-0.1 (A) before, (B) after swelling in CH₂Cl₂, and (C) sulfonated PDVB-0.1 as well as (D) proposed sulfonation of PDVB-*x* samples by chlorosulfonic acid in CH₂Cl₂. The weight amount of polydivinylbenzene (PDVB) in the samples of (A), (B), and (C) is the same.

Table 1

The textural and acidic parameters of various solid acid catalysts.

Samples	S content ^a (mmol/g)	Acid sites ^b (mmol/g)	S _{BET} (m ² /g)	V _p (cm ³ /g)	D _p ^c (nm)
PDVB-0.1	0	0	702	1.35	22.0
PDVB-0.1-SO ₃ H	3.72	4.1	380	0.90	23.5
PDVB-0.1-SO ₃ H ^d	3.68	3.9	360	0.80	30.3
PDVB-0.1-SO ₃ H ^e	3.66	3.8	340	0.76	30.4
PDVB-0.1-SO ₃ H ^f	3.63	3.7	336	0.68	30.5
PDVB-0.1-SO ₃ H ^g	3.60	3.6	320	0.62	40.1
PDVB-0	0	0	557	0.51	3.9
PDVB-0-SO ₃ H	3.64	3.9	280	0.32	3.6
PDVB-W	0	0	523	0.39	4.0
PDVB-W-SO ₃ H	1.68	1.89	310	0.25	3.9
PDVB-S-SO ₃ H	2.13	2.45	377	0.61	21
Amberlyst 15	4.3	4.7	45	0.31	40.0
Amberlyst 15 ^d	4.17	4.2			
Amberlyst 15 ^e	4.1	3.85	43	0.30	41.0
Amberlyst 15 ^f	4.0	3.5			
Amberlyst 15 ^g	3.9	3.1	40	0.28	41.2
SBA-15-Pr-SO ₃ H	1.36	1.26	820	1.40	7.3
SBA-15-Ar-SO ₃ H	1.33	1.34	626	0.72	6.3
USY			623	0.26	14.7
H-Beta ^h			550	0.20	0.67
FDU-14-SO ₃ H ⁱ	2.2	2.5	539	0.34	3.2
FDU-15-SO ₃ H ⁱ	1.8	2.1	447	0.33	2.5

^a Measured by elemental analysis.^b Measured by acid–base titration.^c Pore-size distribution estimated from BJH model.^d Recycled catalysts for 1st time.^e Recycled catalysts for 2nd times.^f Recycled catalysts for 3rd times.^g Recycled catalysts for 4th times.^h Si/Al ratio at 12.5.ⁱ Parameters from Ref. [40].

exhibiting khaki color due to the introduction of the sulfonic groups in the sample. Notably, elemental analysis and acid–base titration (Table 1) show that PDVB-0.1-SO₃H has high concentration of sulfonic groups (4.1 mmol/g). In contrast, PDVB-W-SO₃H

sulfonated from PDVB-W with little swelling property shows relatively low concentration of sulfonic groups (1.89 mmol/g). These results indicate that the swelling property plays an important role for the sulfonation. Possibly, the excellent swelling property of PDVB-xS enables the completely exposed framework to react with chlorosulfonic acid in the solvent, as proposed in Fig. 1D. Interestingly, the content of sulfonic groups in PDVB-0.1-SO₃H is even comparable with that (4.7 mmol/g) of industrial acidic resin catalyst of Amberlyst 15. Additionally, PDVB-0.1 sulfonated by H₂SO₄ shows relatively low concentration of sulfonic groups (2.45 mmol/g), which is reasonably related to the low solubility of H₂SO₄ in CH₂Cl₂, when compared with sulfonation by chlorosulfonic acid.

3.2. Characterization

Fig. 2A shows nitrogen isotherms of PDVB-0.1, PDVB-0.1-SO₃H, and recycled PDVB-0.1-SO₃H samples. Before and after sulfonation by chlorosulfonic acid in CH₂Cl₂, the samples show typical type-IV isotherms, giving a steep increasing at a relative pressure $0.7 < P/P_0 < 0.95$, which is characteristic of the presence of mesoporosity. Correspondingly, the two samples show similar pore-size distribution. Notably, PDVB-0.1 has surface area at 702 m²/g, while the surface area of PDVB-0.1-SO₃H is 380 m²/g. The significant reduction in the surface area in PDVB-0.1-SO₃H is attributed to a successful introduction of a large amount of sulfonic groups in the mesoporous PDVB-xS because sulfonic groups almost do not have any contribution for surface area, and similar phenomenon has also been reported previously [25]. Additionally, it is possible that the presence of SO₃H groups might block the pores, reducing the surface area and pore volume of the samples.

After catalytic recycles, the samples still show typical isotherms associated with mesostructured materials (Fig. 2A c–f). Their surface areas (320–360 m²/g) are still comparable with the surface

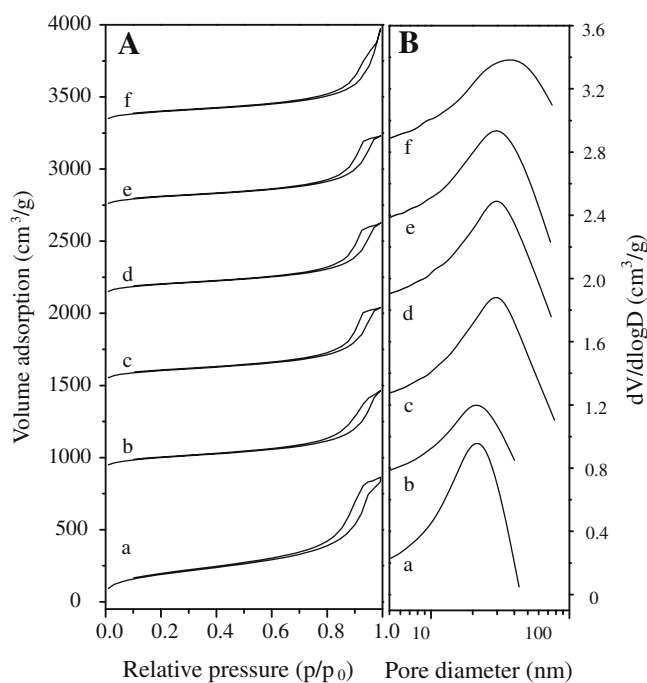


Fig. 2. (A) Nitrogen isotherms and (B) pore-size distribution of (a) PDVB-0.1, (b) sulfonated PDVB-0.1-SO₃H, (c) PDVB-0.1-SO₃H recycled for 1st, (d) PDVB-0.1-SO₃H recycled for 2nd, (e) PDVB-0.1-SO₃H recycled for 3rd, and (f) PDVB-0.1-SO₃H recycled for 4th. The isotherms for (b–f) are offset by 900, 1500, 2100, 2700, and 3300 cm³/g along the vertical axis for clarity, respectively.

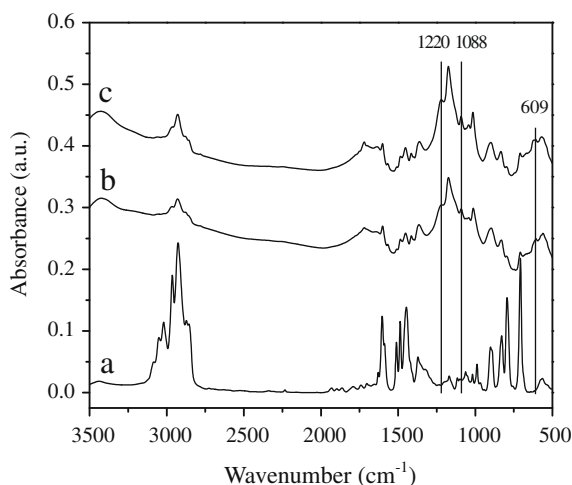


Fig. 3. FTIR spectra of (a) PDVB-0.1, (b) PDVB-0.1-SO₃H, and (c) PDVB-0-SO₃H samples.

area of PDVB-0.1-SO₃H (380 m²/g), indicating that PDVB-0.1-SO₃H has stable mesostructure. The textural parameters of various samples are also summarized in Table 1.

As observed in Table 1, the various samples exhibited quite different surface area, pore volume, and the contents of sulfonic groups. Conventional solid acid resin of Amberlyst 15 had high content of sulfonic groups (4.7 mmol/g), but its surface area was very low (45 m²/g). Conventional SBA-15-Pr-SO₃H and SBA-15-Ar-SO₃H had high surface area (820 and 626 m²/g), but their contents of sulfonic groups were relatively low (1.26 and 1.34 mmol/g). FDU-14-SO₃H with pure organic framework had high surface area (539 m²/g), but its content of sulfonic groups was still low (2.5 mmol/g) [40]. Compared with the solid acid catalysts reported previously, PDVB-0.1-SO₃H had relatively high surface area (380 m²/g) and high content of sulfonic groups (4.1 mmol/g), which would be greatly helpful to search for novel solid acid catalysts with high activities because catalysis is a surface phenomenon.

Fig. 3 shows IR spectra of PDVB-0.1, PDVB-0-SO₃H, and PDVB-0.1-SO₃H samples. Notably, sulfonated samples (PDVB-0.1-SO₃H and PDVB-0-SO₃H) exhibit new bands at 609, 1088, and

1220 cm⁻¹ associated with sulfonic groups, confirming the successful sulfonation of the samples.

Fig. 4 shows ¹³C NMR spectra of PDVB-0.1 before and after sulfonation. The strongest signal at around 38 ppm is attributed to aliphatic carbon chain on the aromatic ring, which is due to the polymerization of vinyl groups on PDVB-0.1 [42]. Compared with the classical resins (the copolymer of styrene and DVB), the signals associated with aliphatic carbon chain on PDVB-0.1 are very strong, indicating its very high cross-linking degree [42,43]. The very small signals at 112 and 137 ppm associated with the residual vinyl groups confirm the high cross-linking degree of the framework for PDVB-0.1. Interestingly, a small peak at around 142 ppm is resulted from the aromatic carbon coordinated with SO₃H groups, indicating the successful sulfonation on aromatic rings in PDVB-0.1 [40].

Fig. 5 shows TG-DTA curves of PDVB-0.1-SO₃H and Amberlyst 15. In TG curves (Fig. 4A), two samples exhibit the weight loss at 35–150, 250–380, and 450–580 °C, which are assigned to desorption of water, decomposition of sulfonic groups, and destruction of polymer framework, respectively [44–46]. Correspondingly, in DTA curves (Fig. 4B), they show three peaks at 35–180, 300–430, and 460–600 °C. Interestingly, the destruction temperature (574 °C) for polymer framework of PDVB-0.1-SO₃H is obviously higher than that of Amberlyst 15 (535 °C), demonstrating that PDVB-0.1-SO₃H has much better framework stability than Amberlyst 15, which is possibly attributed to their differences in monomer structure and cross-linking degree.

3.3. Catalytic results

Table 2 presents catalytic activities in esterifications of hexanoic acid with ethanol, acetic acid with cyclohexanol, and lauric

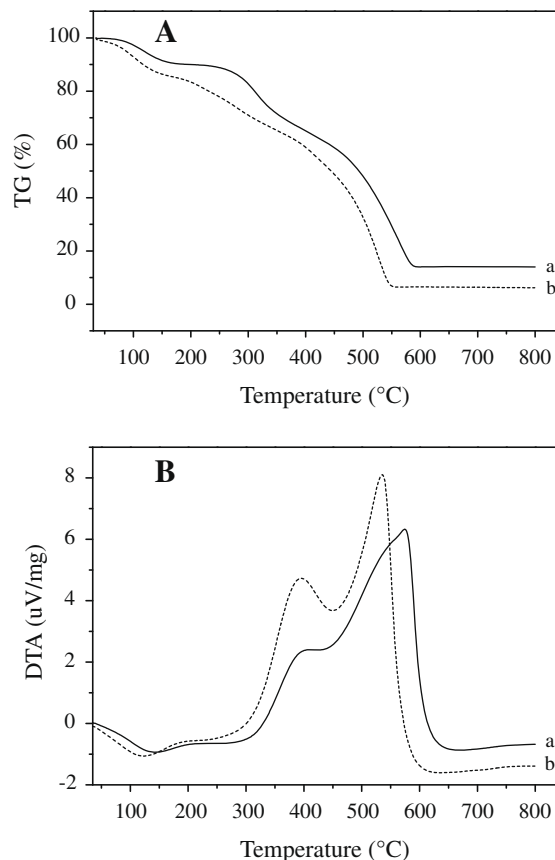


Fig. 5. (A) Thermogravimetric (TG) and (B) Differential thermal analysis (DTA) curves of (a) PDVB-0.1-SO₃H and (b) Amberlyst 15 samples.

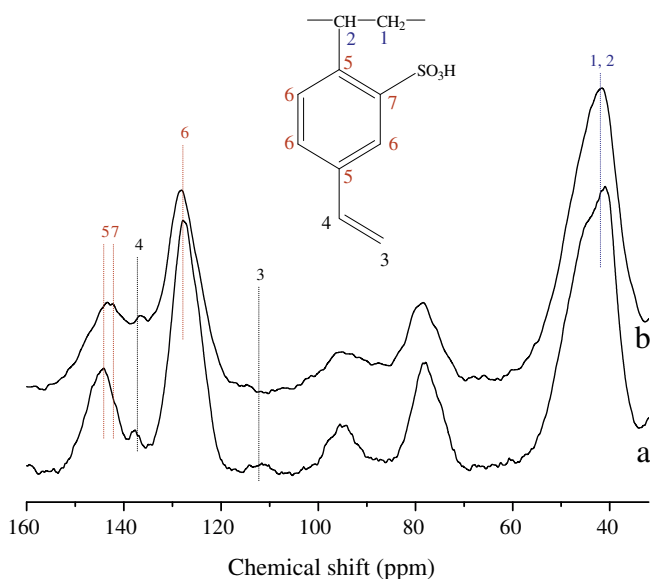


Fig. 4. ¹³C NMR spectra of (a) PDVB-0.1 and (b) PDVB-0.1-SO₃H samples.

Table 2

Conversion and selectivity of catalytic esterifications and acylation over various solid acid catalysts.

Run	Catalyst	EAC		EHE		ELE		AAA		
		Sel. EH (%)	Conv. (%)	Sel. CHA (%)	Conv. (%)	Sel. EL (%)	Conv. (%)	Sel. <i>p</i> -AA (%)	Sel. <i>o</i> -AA (%)	Conv. (%)
1	PDVB-0.1-SO ₃ H	~100	77.5	~100	88.2	~100	99	97.7	2.3	76.5
2	PDVB-0.1-SO ₃ H ^a	~100	71.4	~100	78.9					
3	PDVB-0.1-SO ₃ H ^b			~100	55.2					
4	PDVB-0.1-SO ₃ H ^c			~100	47.8					
5	PDVB-0.1-SO ₃ H ^d	~100	61.6							
6	PDVB-0.1-SO ₃ H ^e	~100	61.0							
7	PDVB-W-SO ₃ H	~100	62.5	~100	72.5	~100	89.4	97.5	2.5	61.8
8	PDVB-W-SO ₃ H ^a	~100	55.7							
9	PDVB-0-SO ₃ H	~100	75.0	~100	84.6	~100	99	97.4	2.6	71.2
10	PDVB-0-SO ₃ H ^a	~100	70.3							
11	PDVB-0-SO ₃ H ^d	~100	60.1							
12	PDVB-0-SO ₃ H ^e	~100	60.0							
13	Amberlyst 15	~100	58.1	~100	56.5	~100	75.2	96.8	3.2	54.3
14	Amberlyst 15 ^a	~100	50.9							
15	Amberlyst 15 ^d	~100	28.4							
16	Amberlyst 15 ^e	~100	20.1							
17	SBA-15-Pr-SO ₃ H	~100	40.5	~100	52.0	~100	61.5	97.1	2.9	44.1
18	SBA-15-Pr-SO ₃ H ^a	~100	36.4							
19	H-Beta					~100	11.0			
20	USY	~100	36.8	~100	29.4	~100	75.8	95.8	4.2	45.6
21	SBA-15-Ar-SO ₃ H	~100	44.6	~100	54.8	~100	76.3	97.3	2.7	43.2

^a 0.1 g of PDVB-0.1-SO₃H catalyst.^b 0.06 g of PDVB-0.1-SO₃H catalyst.^c 0.043 g of PDVB-0.1-SO₃H catalyst.^d 0.2 g of catalysts has been recycled for four times in the esterification of acetic acid with cyclohexanol. The catalyst recycles were performed by centrifugation, washing with dioxane and water at room temperature, and drying at 80 °C, followed by activation of catalysts in 0.1 M H₂SO₄ at room temperature for 4 h and dryness at 80 °C for 10 h.^e 0.1 g of catalysts has been recycled for four times in the esterification of acetic acid with cyclohexanol under the conditions of 0.1 g of catalyst, 11.5 mL (0.11 mol) of cyclohexanol, 17.5 mL (0.305 mol), 100 °C for 5 h.

acid with ethanol and acylation of anisole with acetyl chloride over various solid acid catalysts. Notably, PDVB-0.1-SO₃H (Run 1) and PDVB-0-SO₃H (Run 9) showed much higher activities than those of SBA-15-Pr-SO₃H (Run 17), SBA-15-Ar-SO₃H (Run 21), Amberlyst 15 (Run 13), and PDVB-W-SO₃H (Run 7). For example, in esterification of hexanoic acid with ethanol, PDVB-0.1-SO₃H and PDVB-0-SO₃H showed the conversion at 88.2% and 84.6%, while PDVB-W-SO₃H, SBA-15-Pr-SO₃H, SBA-15-Ar-SO₃H, and Amberlyst 15 gave the conversion at 72.5%, 52.0%, 54.8%, and 56.5%, respectively. Considering the similarity of PDVB-*x*-SO₃Hs to Amberlyst 15 for active sites (the content of sulfonic groups), the higher catalytic activities over PDVB-*x*-SO₃Hs than Amberlyst 15 should be directly assigned to the contribution of high BET surface area and abundant mesoporosity of PDVB-*x*-SO₃Hs. The high surface area is favorable for exposure of catalytically active sites to reactants, and the abundant mesoporosity has an advantage for mass transfer. Comparing PDVB-*x*-SO₃Hs with SBA-15-Pr-SO₃H or SBA-15-Ar-SO₃H, it was clear that SBA-15-Pr-SO₃H or SBA-15-Ar-SO₃H had low concentration of sulfonic groups. Additionally, the presence of hydrophilic surface silanols in SBA-15-Pr-SO₃H or SBA-15-Ar-SO₃H might result in their partial deactivation [38]. When compared with PDVB-W-SO₃H, the higher activities of PDVB-*x*-SO₃Hs are mainly due to their higher concentration of sulfonic groups.

Interestingly, when the amount of catalyst PDVB-0.1-SO₃H was reduced to 1/3 of conventional run, nearly similar number of acid sites in SBA-15-Pr-SO₃H, PDVB-0.1-SO₃H also gave high activity (78.9%, Run 2), compared with that (52.0%, Run 17) of SBA-15-Pr-SO₃H. Further decreasing the catalyst amount to 1/5 of conventional run, PDVB-0.1-SO₃H still showed high activity (55.2%, Run 3). Because SBA-15-Pr-SO₃H has much larger surface area (820 m²/g) than PDVB-0.1-SO₃H (380 m²/g), and total sulfonic sites of PDVB-0.1-SO₃H in Run 3 (0.8 mmol/g) were less than those of SBA-15-Pr-SO₃H (1.26 mmol/g), the higher activity of PDVB-0.1-SO₃H than that of SBA-15-Pr-SO₃H cannot be attributed to the change in both surface area and sulfonic sites over the catalysts.

One possibility was assigned to the difference in their composition. PDVB-0.1-SO₃H had hydrophobic organic walls, while SBA-15-Pr-SO₃H with hydrophilic terminal silanols could adsorb by-product of water near the sulfonic acid centers, resulting in the reduction in catalytic activity, in good agreement with those reported in literature [38].

Fig. 6 shows dependences of catalytic activities on the time in the esterification of acetic acid with cyclohexanol over various catalysts. All curves showed three-step stage. The first stage is the early 5 h, and the reactions are performed at high reaction rate. However, PDVB-0.1-SO₃H and PDVB-0-SO₃H exhibit much higher rates than SBA-15-Pr-SO₃H and Amberlyst 15; the second stage is in the period of 5–9 h, and all the reaction rates gradually decrease; After reaction for over 9 h, all reactions reach equilibrium and the conversion is basically kept constant even after reaction for 24 h. Additionally, the decrease in conversion was not observed, suggesting that the reverse reaction almost does not occur even after a long reaction time up to 24 h.

Catalytic recycles of PDVB-*x*-SO₃Hs and Amberlyst 15 in esterification of acetic acid with cyclohexanol are also presented in Table 2. Notably, PDVB-*x*-SO₃Hs have much better stability than Amberlyst 15. For example, after recycling for four times, both PDVB-0.1-SO₃H and PDVB-0-SO₃H still showed high conversion (61.0% in Run 6 and 60.0% in Run 12). In contrast, Amberlyst 15 has relatively low activity (20.1% in Run 16). These results are reasonably related to their changes in the factors such as acidic concentration and textural parameters. After recycling for four times, PDVB-0.1-SO₃H still exhibits high acidic concentration of 3.6 mmol/g (loss of 12% when compared with fresh PDVB-0.1-SO₃H), while Amberlyst 15 shows a big decrease in acidic concentration from 4.7 (fresh Amberlyst 15) to 3.1 mmol/g (Amberlyst 15 recycled for four times, loss of 34%). Additionally, the recycled PDVB-0.1-SO₃Hs still give high surface area (320–360 m²/g). In contrast, the surface area of recycled Amberlyst 15 further decreases to about 40 m²/g. Apparently, the sulfonic groups in PDVB-0.1-SO₃Hs have much better

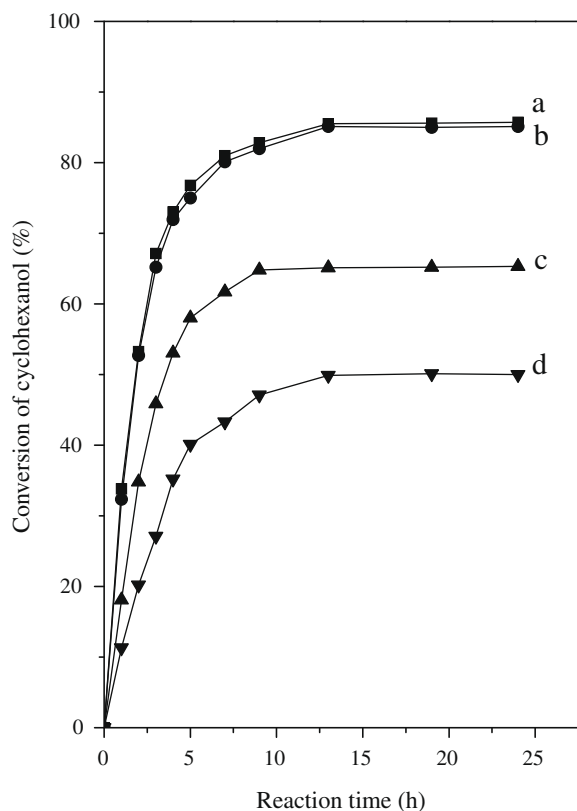


Fig. 6. Dependences of catalytic activities on the time in the esterification of acetic acid with cyclohexanol over (a) PDVB-0.1-SO₃H, (b) PDVB-0-SO₃H, (c) Amberlyst 15, and (d) SBA-15-Pr-SO₃H catalysts.

stability than those in Amberlyst 15 for catalytic esterification of acetic acid with cyclohexanol, which might be assigned to their distinguishable framework stability of the catalysts. Normally, the framework stability of polymers is related to their cross-linking degree. Amberlyst 15 with low cross-linking degree [16] is the copolymer of sulfonated styrene with DVB where the content of DVB as a cross-linker is about 20% [16]. However, PDVB-*x*-SO₃Hs samples are fully composed of DVB polymer, which have very high cross-linking degree. TG-DTA curves (Fig. 4) have confirmed that PDVB-0.1-SO₃H has better framework stability than Amberlyst 15.

In esterification of bulky lauric acid with ethanol, PDVB-*x*-SO₃Hs exhibited very high conversion (~99%, Runs 1 and 9). In contrast, microporous Beta and USY zeolites give the conversion at 11% and 75.8% due to their small pore sizes (Run 19 and Run 20). These results indicate that PDVB-*x*-SO₃Hs are also efficient solid acid catalysts for the conversion of bulky molecules. Moreover, PDVB-*x*-SO₃Hs also showed much higher catalytic activities (76.5% in Run 1 and 71.2% in Run 9) in Friedel-Crafts acylation of anisole with acetyl chloride than Amberlyst 15 (54.3% in Run 13), SBA-15-Pr-SO₃H (44.1% in Run 17) and SBA-15-Ar-SO₃H (43.2% in Run 21), indicating that as novel solid acid catalysts, these sulfonated mesoporous polymers are not only limited to catalytic esterification but can also be used in other reactions such as Friedel-Crafts acylation of anisole with acetyl chloride.

4. Conclusions

Efficient solid acid catalysts (PDVB-*x*-SO₃Hs) are successfully synthesized from sulfonation of swelling mesoporous PDVB-*x*s, and these solid catalysts with pure organic framework have large

surface area (280–380 m²/g), abundant mesoporosity, and high contents of sulfonic groups (3.9–4.1 mmol/g). They exhibited much higher activities in esterifications of hexanoic acid with ethanol, acetic acid with cyclohexanol, and lauric acid with ethanol and acylation of anisole with acetyl chloride than solid catalysts of Amberlyst 15, SBA-15-Pr-SO₃H, and SBA-15-Ar-SO₃H. Recycling in catalytic tests showed that PDVB-*x*-SO₃Hs show superior stability when compared with Amberlyst 15.

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