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Development of highly active SO_3H-modified hybrid mesoporous catalyst

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Abstract

Ethenylene groups on the framework of hybrid mesoporous ethenylene-silica (HME) were successfully modified by a two-step chemical modification (Diels–Alder reaction, sulfonation) to obtain hybrid mesoporous solid acid catalyst. The pendant phenylene groups were first introduced at the ethenylene sites on the surface by the Diels–Alder reaction with benzocyclobutene. The introduced phenylene groups were then sulfonated by simple treatment with concentrated H_2SO_4. The successful formation of phenylene–sulfonic acid groups at the ethylene sites was confirmed by ^{13}C and ^{29}Si nuclear magnetic resonance (NMR) analysis. X-ray diffraction (XRD) measurements and N_2 adsorption analysis revealed the preservation of the original mesoscopic ordering and mesoporosity after the modification. The resulting material exhibited high activity for various acid-catalyzed reactions and can be used repeatedly without deactivation.

Keywords: Hybrid mesoporous material; Diels–Alder modification; Sulfonic acid group

1. Introduction

The organic tailoring of the internal surface of mesoporous host has recently received great attention in terms of the application in the fields of catalysis, adsorption, and separation [1]. Periodic mesoporous organosilicas (PMOs) [2–4] are an attractive family of novel mesoporous materials that combine the properties of organic and inorganic components in a composite material. The main focus for developing the PMOs is to introduce bridged-bond organic groups into the highly ordered porous silica framework and thus add either a unique chemical functionality and/or physical property to the materials. To date, several different silicone-bridged organic moieties represented by methylene [4], ethylene [2–4], ethenylene [3,5–8], phenylene [9–11] and its-derivates [12–14] have been incorporated into the silicate framework of highly ordered mesoporous materials. Since the framework of PMOs consists of organic–inorganic hybrid network, homogeneous distribution of the organic groups in the pore wall provides smooth accessibility for the reactant molecules and opens a wide range of new and exciting opportunity for designing materials through the chemical modification. In the previous studies, however, the modification of PMOs has been limited in only simple reactions represented by the bromination of ethenylene [3,5,7,8] and the oxidation of mercaptopropyl group [15–20]. The successful chemical transformation of the organic groups on the surface provides great opportunity of PMOs as a highly functional nanomaterial.

Herein, we proposed the simple methodology to create the hybrid mesoporous solid acid catalyst which has phenylene–sulfonic acid groups as active sites. This proposed approach involves two step chemical reactions shown in Fig. 1; ethenylenes on the surface of hybrid mesoporous ethenylene-silica (HME) are transformed to pendant phenylenes through the Diels–Alder reaction with benzocyclobutene followed by sulfonation of the introduced phenylenes by simple treatment in concentrated H_2SO_4. In this article, we investigate the change in the structural and chemical properties of hybrid mesoporous

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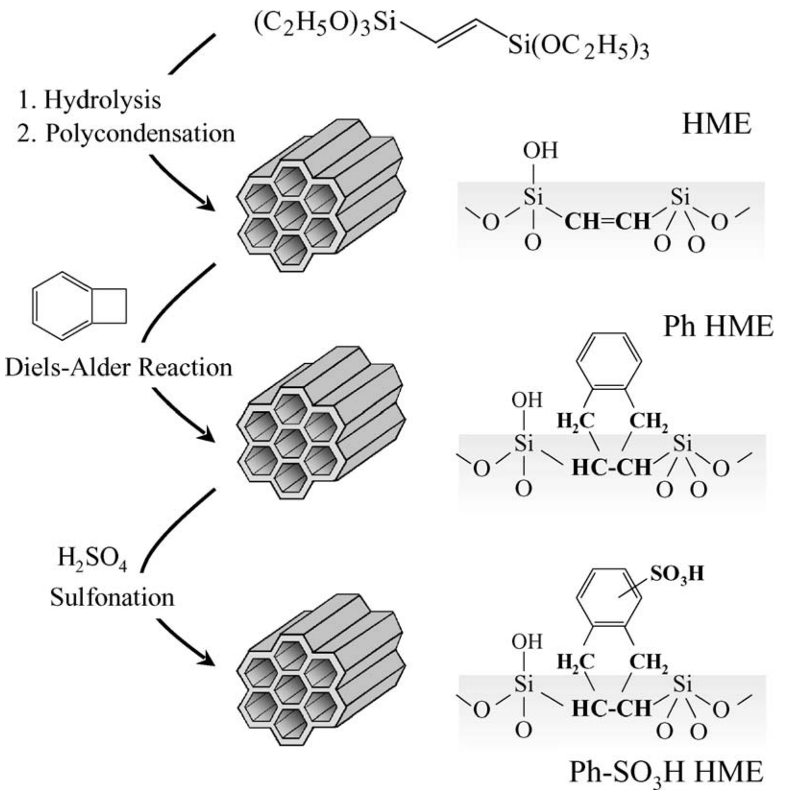

Fig. 1. Schematic representation of the synthetic pathway to hybrid mesoporous solid acid catalyst.

material before and after chemical modification. Esterification of acetic acid, Beckmann rearrangement, and pinacol rearrangement were employed as test reactions to examine the acid properties of the prepared samples. As to mesoporous solid acid catalyst containing sulfonic acid groups, propyl sulfonic acid group, which is obtained by the oxidation of mercaptopropyl groups, was generally adopted as an active site and embedded by grafting technique or one-pot synthesis procedure using silsesquioxane precursor with terminal organic group R-$Si(OR)_3$ [15–20]. However, these modifications suffer from some serious limitations represented by the inhomogeneous distribution of organic groups in the pore, and the loss of mesoscopic ordering and mesoporosity at the oxidation step. Serious problem for use as a solid acid catalyst lies a leaching of sulfur species, which is probably due to the incomplete oxidation of the thiol groups. It is demonstrated that the resulting material exhibits high activity and stability for various acid-catalyzed reactions without deactivation.

2. Experimental

2.1. Synthesis

In the typical synthesis of hybrid mesoporous ethenylene-silica, 2.0 g of P123 ($(HO(CH_2CH_2O)_{20}(CH_2CH(CH_3)O)_{70}(CH_2CH_2O)_{20}OH$, BASF) was completely dissolved in 45 mL of water and 30 mL of 4.0 M HCl solution at 40 °C under constant stirring. To this solution was added 3.53 g of bis(triethoxysilyl)ethylene followed by stirring for 24 h at the same temperature. The resulting mixture was then transferred to an autoclave and heated at 100 °C for an additional 24 h under static conditions. The solid product was collected by filtration and washed with water. The surfactant in 1.0 g of as-synthesized product was removed by stirring in an aqueous solution of 150 mL ethanol and 3.5 g HCl. After repeating this treatment twice, the product was recovered by filtration and washed with 4 M HCl solution and then with water and finally dried in air to obtain HME.

A mixture of 1.5 g mesoporous ethenylene-silica and 1.0 g benzocyclobutene was heated at 200 °C for 24 h. The material obtained was washed in 150 mL of chloroform and then acetone to remove byproducts, yielding the phenylene functionalized hybrid mesoporous ethenylene-silica (Ph HME). This Ph HME was sulfonated by heating at 80 °C for 3 days in concentrated H_2SO_4. The solid was recovered and washed in water at 80 °C for 6 h, repeated twice. The material was finally dried at room temperature to obtain phenylene–sulfonic acid functionalized hybrid mesoporous ethenylene-silica (Ph–SO_3H HME).

2.2. Acid-catalyzed reaction

Esterification of acetic acid was examined in the liquid phase as follows: 0.20 g of the catalyst was evacuated at 423 K for 1 h and then added to a mixture of acetic acid (0.10 mol) and ethanol (1.0 mol). The reaction was carried out at 343 K in an Ar atmosphere, and the liquid phase was analyzed by gas chromatography with capillary columns.

Beckmann rearrangement was examined in the liquid phase as follows: 0.20 g of the catalyst was evacuated at 423 K for 1 h and then added to a mixture of cyclohexene oxime (0.20 g) and DMF (20.0 mL). The reaction was carried out at 403 K in an Ar atmosphere, and the liquid phase was analyzed by gas chromatography with capillary columns.

Pinacole–pinacolone rearrangement was performed in the liquid phase as follows: 0.20 g of the catalyst was evacuated at 423 K for 1 h and then added to a mixture of pinacol (42.3 mol) and solvent. The reaction was carried out at 403 K in an Ar atmosphere, and the liquid phase was analyzed by gas chromatography with capillary columns.

2.3. Analyses

Nitrogen adsorption–desorption isotherms at 77 K were measured using a Micrometrics Coulter SA-3100 system. Prior to measurements, the samples were treated at 423 K for 3 h under vacuum to a final pressure of 1×10^{-5} Torr. The Brunauer–Emmett–Teller (BET) surface area was estimated over a relative pressure (P/P_0) range of 0.05–0.30. The pore size distribution was obtained by analysis of the adsorption branch of the isotherms using the Barrett–Joyner–Halenda (BJH) method. Solid-state ^{13}C and ^{29}Si cross-polarization (CP) magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra were acquired on Bruker ASX200 and ASX400 spectrometers, respectively. The Larmor frequencies of ^{13}C and ^{29}Si were 50.3 and 79.5 MHz, respectively. The following experimental parameters were employed; ^{13}C CP/MAS NMR experiment (4.0 kHz spin rate, 1 s recycle delay, 2 ms contact time); ^{29}Si CP/MAS NMR experiment (4.0 or 3.5 kHz spin rate, 1 s recycle delay, 5 ms contact time). The chemical shifts of the ^{13}C and ^{29}Si NMR spectra were expressed with respect to neat tetramethylsilane.

3. Results and discussion

Fig. 1 shows a schematic representation of the synthetic pathway to hybrid mesoporous solid acid catalyst. The ethenylene-bridged silsesquioxane precursor is hydrolyzed and polycondensed in the presence of block copolymer surfactant, P123, to obtain the HME, which has ethenylene moieties in the silica framework. Ethenylene on the surface are successfully transformed through the Diels–Alder reaction with benzocyclobutene, resulting in the formation of pendant phenylenes. This denoted as phenylene-functionalized HME (Ph HME). The evolved phenylenes are anchored from the silica framework by two alkyl chains with 1, 2 substitution. Finally, the sulfonation of pendant phenylenes is accomplished by simple treatment of Ph HME material in concentrated H_2SO_4. The product was named as Ph–SO_3H functionalized HME (Ph–SO_3H HME).

The change in organic groups on the framework was directly monitored by ^{13}C and ^{29}Si NMR measurement. Fig. 2 displays ^{13}C CP/MAS NMR spectra of HME, Ph HME, and Ph–SO_3H HME. One intense signal at 146 ppm with spinning sidebands in the spectrum of the parent HME is assignable to silicon-bridged ethenylene carbons. The absence of signals derived from residual block copolymer surfactant at 70 ppm indicates successful removal of the surfactant. After the Diels–Alder reaction, three aromatic resonances at 126, 129, and 137 ppm appear. Additional peaks at 28 and 19 ppm are attributed to the two alkyl chains (–CH_2–, –CH–) bonded directly to phenylene and a silicon atom, respectively. The signal at 146 ppm assignable to ethenylene in the framework is simultaneously observed in Fig. 2(b), demonstrating that the ethenylene in the pore walls remained unchanged through the Diels–Alder modification. The formation of Ph–SO_3H groups in the final product can be confirmed by the appearance of a resonance at 139 ppm assignable to the C–SO_3H species of phenylene (Fig. 2(c)). This indicates that the pendant phenylene groups are easily accessible to reactant molecules and converted to Ph–SO_3H groups in the sulfonation reaction.

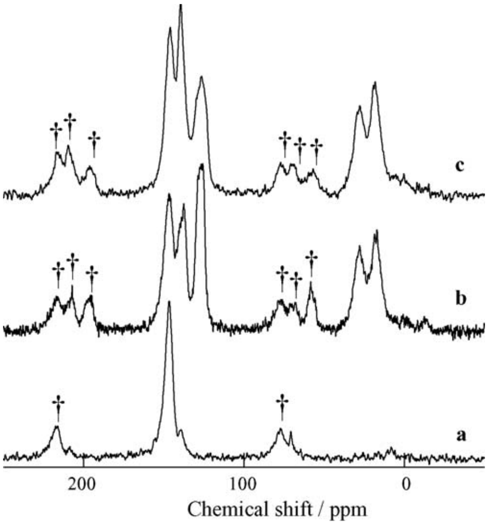

Fig. 2. ^{13}C CP/MAS NMR spectra of HME (a), Ph HME (b), and Ph–SO_3H HME (c). † was denoted as spinning sidebands.

The ^{29}Si CP/MAS NMR spectra are also shown in Fig. 3. Three resonances at −64, −73, and −82 ppm in the spectrum for HME is assignable to Si species covalently bonded to carbon atoms of T_1, T_2, and T_3, respectively. The absence of any resonances assigned to SiO_4 species confirms the absence of carbon–silicon bond cleavage in the Si–CH=CH–Si moiety of the framework. The framework of HME is therefore considered to consist of a covalently bonded network of $O_{1.5}$Si–CH=CH–Si–$O_{1.5}$ units. The spectrum for Ph HME displays two sets of T_n resonances (T_2 and T_3, T'_1 and T'_2) assignable to two different silicon moieties covalently bonded to carbon atoms, representing bridged ethenylene and pendant phenylene groups. As the signals for the Q_n sites are only weak, most of the Si–C bonds have been preserved through the Diels–Alder modification. For the sulfonated sample, two sets of T_n resonances are also observed (Fig. 3(c)), and the intensity for the Q_n sites (−90 to −120 ppm) does not change upon sulfonation. This result indicates that the hybrid network is retained upon sulfonation, supporting the formation of phenylene–sulfonic acid groups on the surface while retaining the original organic–inorganic hybrid network.

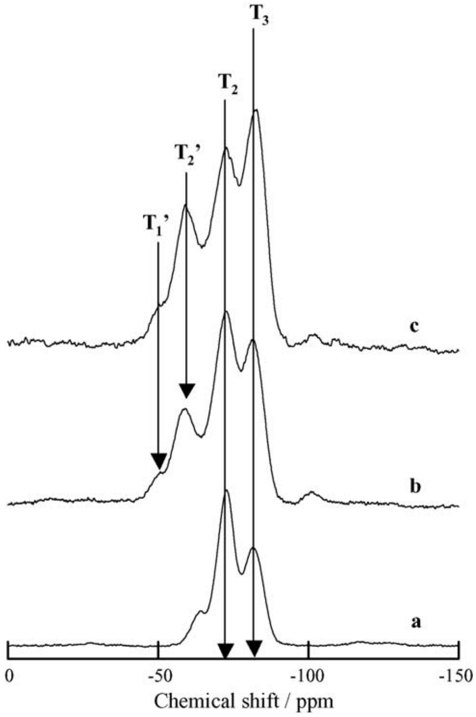

Fig. 3. ^{29}Si CP/MAS NMR spectra of HME (a), Ph HME (b), and Ph–SO_3H HME (c).

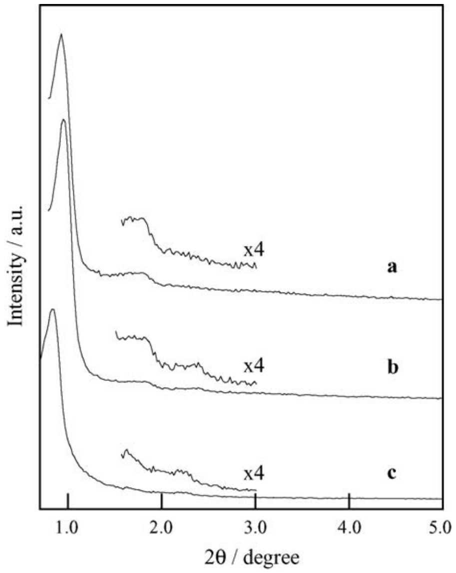

Fig. 4. Small angle XRD patterns of HME (a), Ph HME (b), and Ph–SO_3H HME (c).

The mesoscopic ordering and mesoporosity of samples were evaluated by N_2 adsorption and powder XRD analyses. Fig. 4 compares the XRD patterns of HME samples before and after chemical modification. The profile of the parent HME contains three diffraction peaks indexed as (1 0 0), (2 0 0), and (2 1 0) reflections. These peaks are assigned to two-dimensional (2D) hexagonal *p*6*mm* symmetry, and could also be seen in the spectrum of Ph HME (Fig. 4(b)), indicating that the mesoscopic ordering is completely retained after the Diels–Alder modification. Although the (2 0 0) and (2 1 0) signals become weak, the (1 0 0) reflection appears intensely in the spectrum of Ph–SO_3H HME (Fig. 4(c)). These results thus confirm that the original mesoscopic ordering of HME remains intact after sulfonation in concentrated H_2SO_4.

The N_2 adsorption isotherms and BJH pore-size distributions of samples before and after chemical modification are presented in Fig. 5, and the corresponding textural properties obtained from N_2 adsorption and XRD analyses are summarized in Table 1. All the isotherms in exhibit a typical type-IV pattern with a clear H1-type hysteresis loop in the high relative pressure region. The pore-size distribution of these three samples clearly indicates the presence of uniform mesopores in a narrow range. The BET surface area is slightly decreases upon the Diels–Alder modification due to the partial destruction of micropores by further condensation of the framework. The change in the mesopore diameter from 6.8 to 6.0 nm upon the Diels–Alder reaction strongly suggests the homogeneous modification of ethenylene sites on the surface. The Ph–SO_3H HME has a uniform pore-size distribution, relatively high surface area and mesopore volume, and ordered mesoporous structure identifiable as *p*6*mm* symmetry. Therefore, the chemical modifications were achieved successfully without degradation of the original mesoporosity or mesoscopic ordering.

The concentration of sulfonic acid groups was quantitatively estimated by acid–base titration. The acid amount of Ph–SO_3H HME was determined to be 1.44 mmol g^{-1}. The catalytic performance of the Ph–SO_3H HME material was also tested by several acid-catalyzed reactions.

Fig. 6(A) shows the rate of ethyl acetate formation over Ph–SO_3H HME, perfluorinated sulfonic acid resin (Nafion-H), sulfonated polystyrene resin (Amberlyst-15), and niobic acid. Ph–SO_3H HME exhibits high activity for the formation of ethyl acetate, comparable to that of Ambelyst-15 and Nafion-H. The stability of the sulfonic acid groups during the reaction was conducted by repeating the esterification of acetic acid over Ph–SO_3H HME four times. As shown in Fig. 6(B), both activity for ethyl acetate formation and the acidity remained unchanged throughout these four runs. Thus, the sulfonic acid groups are stable and act repeatedly as acid sites during the reaction.

Table 1
Physicochemical properties of HME, Ph HME, and Ph–SO_3H HME

	S_{BET} (m^2 g^{-1})	V (mL g^{-1})	D (nm)	d (1 0 0) (nm)	α (nm)	Wall thickness (nm)
Original HME	652	0.73	6.8	9.3	10.7	3.9
Ph HME	506	0.70	6.0	9.0	10.4	4.4
Ph–SO_3H HME	565	0.78	6.0	10.2	11.8	5.8

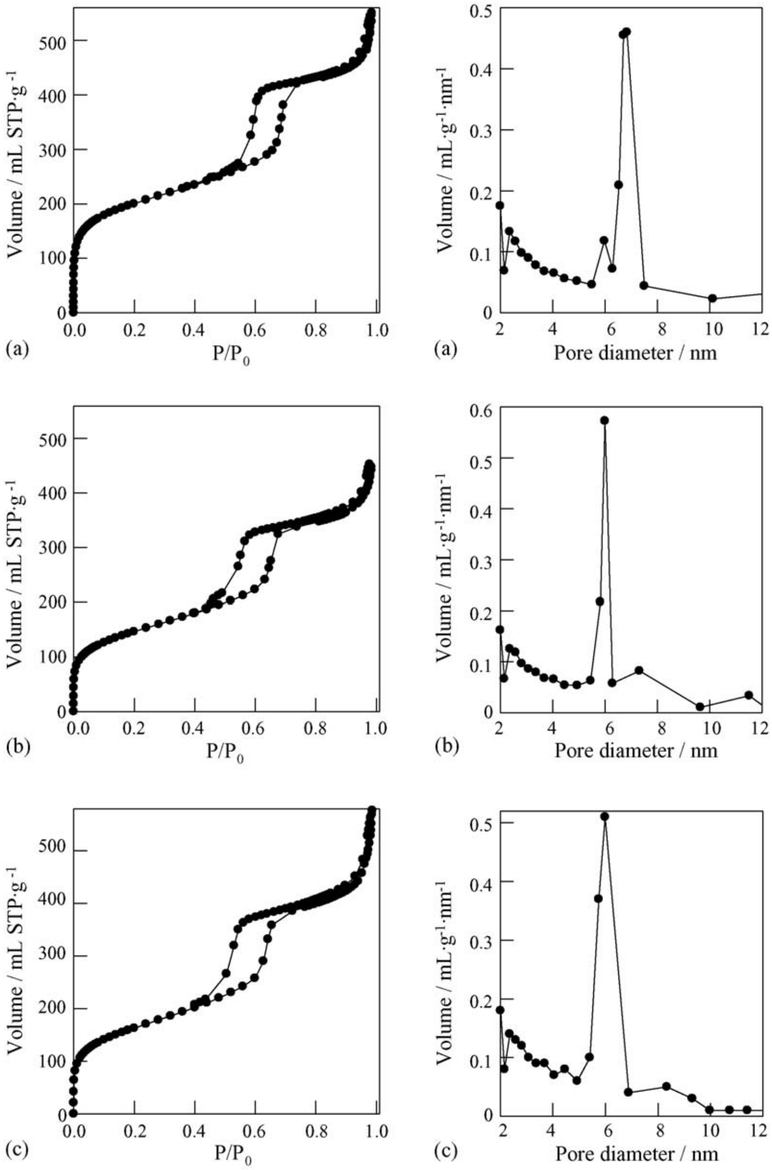

Fig. 5. N_2 adsorption–desorption isotherm and BJH pore size distribution of HME (a), Ph HME (b), and Ph–SO_3H HME (c).

Liquid-phase Beckmann rearrangement is also adopted as a test reaction. Table 2 compares the product distribution over Nafion-H, Ph–SO_3H HME, H-Beta, and H-ZSM5 as solid acid catalyst. The activity in Beckmann rearrangement of Ph–SO_3H HME to the ε-caprolactam shows remarkably higher than that of other three catalysts. Ph–SO_3H HME therefore has the potential for practical application as a stable and highly active acid catalyst.

The acid strength of Ph–SO_3H HME was examined by pinacol rearrangement, which involves the evolution of a cationic intermediate that is stabilized under highly acidic conditions. This conversion is therefore an indicator of the acid strength of the catalyst. Table 3 compares the conversion and selectivity for pinacol rearrangement over several acid catalysts. The conversion by Ph–SO_3H HME is much higher than that for homogeneous catalysts and is comparable to that

Table 2
Conversion and selectivity of liquid-phase Beckmann rearrangement on several acid catalysts

Catalyst	Conversion (%)	Selectivity		
		ε-Caprolactam	Cyclohexanone	5-Hexenenitrile
Ph–SO_3H HME	31.6	78.6	21.4	–
Nafion-H (NR50)	17.7	81.9	18.1	–
H-Beta	8.8	77.2	22.8	–
H-ZSM5	3.0	78.8	21.2	–

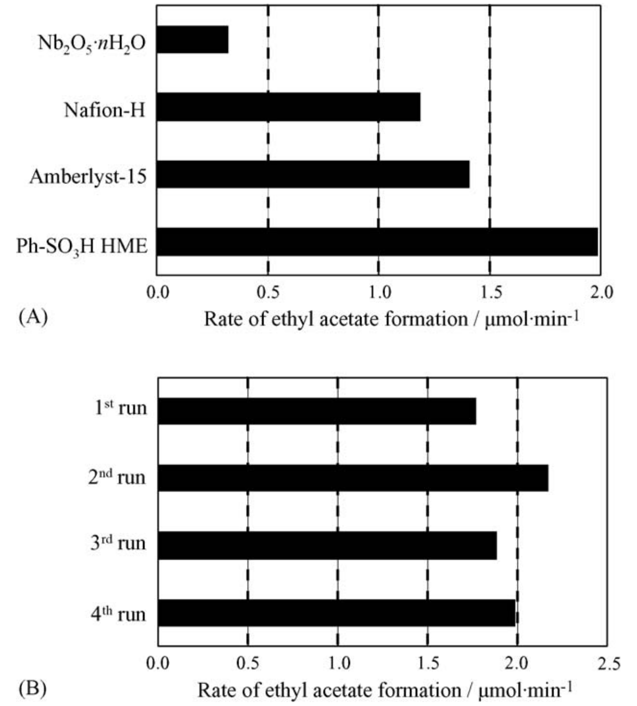

Fig. 6. The rate of ethyl acetate formation on the solid acid catalyst. (A) Comparison the activity over Ph–SO_3H HME, Nafion-H, Amberlyst-15, and niobic acid. (B) Comparison of the activity over repeatedly used Ph–SO_3H HME four times.

Table 3
Conversion and selectivity of pinacol rearrangement on several acid catalysts

Catalyst	Conversion (%)	Selectivity (%)	
		Pinacolone	2,3-Dimethyl-1,3-butadiene
H_2SO_4	98.4	71.7	28.3
Ph–SO_3H HME	92.0	83.5	16.5
$H_3PW_{12}O_{40}$	70.5	90.8	9.2
Amberlyst 15	69.5	83.5	16.5
p-TsOH	42.8	74.4	25.6
Nafion-H (NR50)	42.2	88.2	11.8

for concentrated H_2SO_4 solution. The acid strength of Ph–SO_3H HME is also similar to that of Amberlyst-15, which similarly has benzene sulfonic acid groups as active sites. This high conversion of Ph–SO_3H HME suggests that the incorporation of a large amount of Ph–SO_3H moieties into the restricted mesopores provides high accessibility of the reactant molecules to the active sites, resulting in the promotion of the acid-catalyzed reaction.

4. Conclusion

A new class of hybrid mesoporous solid acid catalyst was prepared by two-step chemical modification technique. The resulting material has high mesoscopic ordering and mesoporosity without degradation of the original material, and also exhibits stability and high activity in acid-catalyzed reactions. The methodology presented here provides a new route to novel PMOs with applications in a wide range of areas in materials science, including the separation of biomaterials, selective ion exchange, and the manufacture of high-performance catalysts.

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References

[1] A. Stein, B.J. Melde, R.C. Schroden, Adv. Mater. 12 (2000) 1403.
[2] S. Inagaki, S. Guan, Y. Fukushima, O. Terasaki, J. Am. Chem. Soc. 121 (1999) 9611.
[3] T. Asefa, M.J. MacLachlan, N. Coombs, G.A. Ozin, Nature 402 (1999) 867.
[4] C. Yoshina-Ishii, T. Afera, N. Coombs, M.J. MacLachlan, G.A. Ozin, Chem. Commun. (1999) 2539.
[5] B.J. Melde, B.T. Holland, C.F. Blandford, A. Stein, Chem. Mater. 11 (1999) 3302.
[6] W. Wang, S. Xie, W. Zhou, A. Sayari, Chem. Mater. 16 (2004) 1756.
[7] K. Nakajima, D. Lu, J.N. Kondo, I. Tomita, S. Inagaki, M. Hara, S. Hayashi, K. Domen, Chem. Lett. 32 (2003) 950.
[8] K. Nakajima, I. Tomita, M. Hara, S. Hayashi, K. Domen, J.N. Kondo, J. Mater. Chem. 15 (2005) 2362.
[9] S. Inagaki, S. Guan, T. Ohsuna, O. Terasaki, Nature 416 (2002) 304.
[10] Y. Goto, S. Inagaki, Chem. Commun. (2002) 2410.
[11] M.P. Kapoor, Q. Yang, S. Inagaki, Chem. Mater. 16 (2004) 1209.
[12] M. Kuroki, T. Asefa, W. Whitnal, M. Kruk, C. Yoshina-Ishii, M. Jaroniec, G.A. Ozin, J. Am. Chem. Soc. 124 (2002) 13886.
[13] M.P. Kapoor, Q. Yang, S. Inagaki, J. Am. Chem. Soc. 124 (2002) 15176.
[14] G. Temtsin, T. Asefa, S. Bittner, G.A. Ozin, J. Mater. Chem. 11 (2001) 3202.
[15] W.M. Van Rhijn, D.E. De Vos, B.F. Sels, W.D. Bossaert, P.A. Jacobs, J. Chem. Soc.: Chem. Commum. (1998) 317.
[16] M.H. Lim, C.F. Blanford, A. Stein, Chem. Mater. 10 (1998) 467.
[17] W.D. Bossaert, D.E. De Vos, W.M. Van Rhijn, J. Bullen, P.J. Grobet, P.A. Jacobs, J. Catal. 182 (1999) 156.
[18] D. Margolese, J.A. Melero, S.C. Christansen, B.F. Chmelka, G.D. Stucky, Chem. Mater. 12 (2000) 2448.
[19] J.G.C. Shen, R.G. Herman, K. Klier, J. Phys. Chem. B 106 (2002) 9975.
[20] Q. Yang, M.P. Kapoor, S. Inagaki, J. Am. Chem. Soc. 124 (2002) 9694.