

Catalytic application of sulfonic acid functionalized mesoporous benzene–silica with crystal-like pore wall structure in esterification

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Received 3 September 2004; received in revised form 10 December 2004; accepted 12 December 2004
Available online 23 January 2005

Abstract

The first catalytic applications of sulfonic acid-functionalized hydrophobic mesoporous benzene–silica with lamellar pore wall structure are reported. The mesoporous benzene–silica attached with propylsulfonic groups to the crystal-like periodic pore walls exhibited the catalytic activity in the esterification of acetic acid with ethanol. The catalytic results show the higher conversion compared to the commercial Nafion-H. © 2004 Elsevier B.V. All rights reserved.

Keywords: Mesoporous benzene–silica; Crystal-like pore wall; Nafion; Esterification; Sulfonic group functionalization; Acidic acid and ethanol

1. Introduction

The replacement of the conventional acid catalysts such as H₂SO₄ and AlCl₃ with solid-acids has been the subject of many researchers because of the safety, low cost and ease of recovery derived from the heterogeneous catalysis [1–3]. Surfactant-templated mesoporous silicas functionalized with alkylsulfonic acid groups onto the pore surface have been reported to be efficient solid acid catalysts for esterification [4]. Indeed, the hydrophobicity of the framework plays an

important role in the esterification due to the water generated during the reaction. To improve the hydrophobicity, organic groups such as methyl and benzyl groups were also incorporated on the surface of the sulfonic acid functionalized mesoporous silicas [5]. Recently, our [6] and other groups [7,8] have reported the synthesis of hybrid mesoporous organosilicas having bridging organic groups as an integral component of framework from 100% of bridged organosilane precursors (R'O)₃Si-R-Si(OR')₃ in the presence of surfactant. Especially, phenylene [9] and biphenylene-bridged [10] mesoporous materials exhibited novel crystal-like periodic structures in the pore walls. These mesoporous materials have unique surface structures with alternatively arranged hydrophobic phenylene (or biphenylene) and hydrophilic silica layers with a periodicity of 0.76 nm (1.16 nm). In subsequent report [11], we described the synthesis of sulfonic acid-functionalized benzene–silica by co-condensation of 1,4-bis(triethoxysilyl)benzene [BTEB: (EtO)₃Si-C₆H₄-

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Si(OEt)₃] and 3-mercaptopropyltrimethoxysilane [MPTMS: (MeO)₃Si-C₃H₆-SH] using a surfactant template followed by post-synthesis oxidation using HNO₃. The bifunctional mesoporous material has sulfonic groups attached to the silica layers of the crystal-like periodic pore walls. It has better catalytic environment than the sulfonic acid functionalized mesoporous silica because the periodic pore surface will be of great advantages for the enhanced selectivity and activity in catalysis.

In the present communication, we disclose the catalytic application of the sulfonic acid functionalized mesoporous benzene-silica with crystal-like wall structure in the esterification of acetic acid with ethanol and catalytic activity is compared to the commercially available Nafion-H (NR50; beads 7–9 mesh; eq. molecular weight, 1250; exchange capacity H⁺ = 0.8 meq g⁻¹). Esterification of carboxylic acids with alcohols is an important industrial reaction because esters are widely used as emulsifiers in the food, pharmaceutical and cosmetic industries [12].

2. Experimental

2.1. Catalyst preparation

Two different types of sulfonic acid functionalized mesoporous benzene-silicas were synthesized: first via co-condensation of 1,4-bis(triethoxysilyl)benzene and 3-mercaptopropyltrimethoxysilane using a surfactant template in basic conditions and second by grafting of MPTMS onto the periodic mesoporous benzene-silica (Ph-HMM) with crystal-like wall structure.

In a typical synthesis, octadecyltrimethylammonium chloride [C₁₈TMAC] was dissolved in a mixture of ion-exchanged water and sodium hydroxide aqueous solution. The mixture of BTEB and MPTMS was added to the above solution, and the suspension was stirred at room temperature for 12 h and aged at 90 °C for 24 h. The resulting white precipitate was recovered by filtration to yield an as-synthesized sample. The reagent ratio was Si: C₁₈TMAC: NaOH: H₂O = 1: 0.96: 2.67: 559 for Ph-MP₄₀ (where, 40 represent the mole percentage of MTPMS in the starting materials). The surfactant was removed by stirring 1.0 g of as synthesized sample in 200 mL ethanol with 3.0 g HCl (36%) at 55 °C for 6 h before filtration and the sample (Ph-MP₄₀) was used for the esterification reaction.

For the grafting procedure, MPTMS (2 mL) was added drop-wise into Ph-HMM (1.28 g) dispersed in chloroform (100 mL) beforehand. The suspension was stirred at room temperature for 5 days. The powder material obtained upon filtration was washed with copious amount of chloroform and dried at room temperature to yield thiol functionalized mesoporous benzene-silica (GPh-SH).

The sulfonic acid-functionalized mesoporous material were derived by the oxidative transformation of the thiol (-SH) into sulfonic (-SO₃H) groups that was accomplished

by the treatment with 65 wt.% HNO₃ as oxidant [11]. The sample was designated as GPh-SO₃H.

2.2. Characterization

The powder X-ray diffraction patterns of the materials were recorded on a Rigaku RINT-2000 X-ray diffractometer using nickel filtered Cu K α radiation. Nitrogen adsorption/desorption isotherms were obtained at 77 K using an Autosorb-1. The volume of adsorbed nitrogen was normalized to standard temperature and pressure (STP). The specific surface area was determined from the linear part of the BET plot ($P/P_0 = 0.05-0.3$). Mesopore size distribution was calculated using the adsorption branch of the nitrogen isotherm and the Barrett-Joyner-Halenda (BJH) formula. The ²⁹Si and ¹³C NMR spectra were recorded on a Bruker MSL-300 spectrometer. Sulphur content was measured by elemental analysis and the ion exchange capacity of the catalysts was determined by acid-base potentiometric titration.

2.3. Reaction

Prior to catalytic runs, the catalysts (0.2 g) were evacuated at 200 °C for 1 h and reaction environment was changed to inert upon charging argon in the three neck round bottom reaction flask. Dehydrated ethanol (1.0 mol) and acetic acid (0.10 mol) were introduced using a syringe. Reaction proceeded in a close air tight environment at 70 °C maintained using a temperature controlled oil bath. The reaction aliquots were taken every hour and analyzed using a gas chromatograph equipped with an FID detector. As an internal standard the 2-butanol was added.

3. Results and discussion

The detailed characterization of the Ph-MP₄₀ materials was reported elsewhere [11]. Powder X-ray diffractions (PXRD) profiles of GPh-SH sample exhibited a sharp peak ($d_{100} = 4.69$ nm) along with two peaks for [1 1 0] and [2 0 0] reflections in the lower-angle diffraction region ($2\theta < 6^\circ$). In addition, three additional peaks [9] at d spacings of 0.76, 0.38 and 0.25 nm were also observed at medium scattering angles ($2\theta = 6-40^\circ$), indicating that a periodicity with a d spacing of 0.76 nm exists in the pore wall (Fig. 1). The PXRD pattern was essentially unchanged after oxidation (GPh-SO₃H), except a decrease in d_{100} peak intensity, confirming that both the mesopore and crystal-like wall structure survived after the oxidation process.

The nitrogen adsorption/desorption isotherms of both GPh-SH and GPh-SO₃H showed type IV isotherms with uniform pore size distribution (Fig. 2). The BET surface area, BJH pore diameter and pore volume of grafted GPh-SH sample were lowered compared to the parent mesoporous benzene-silica sample [9]. It is noteworthy that the oxidized GPh-SO₃H sample exhibit somewhat similar textural

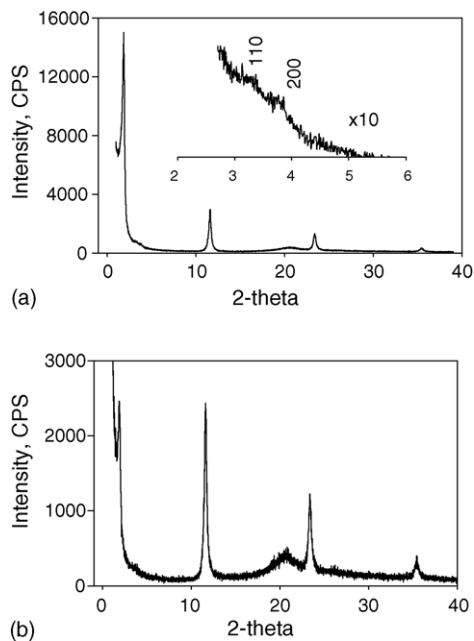


Fig. 1. X-ray diffraction patterns of mesoporous hybrid materials. (a) GPh-SH and (b) GPh-SO₃H.

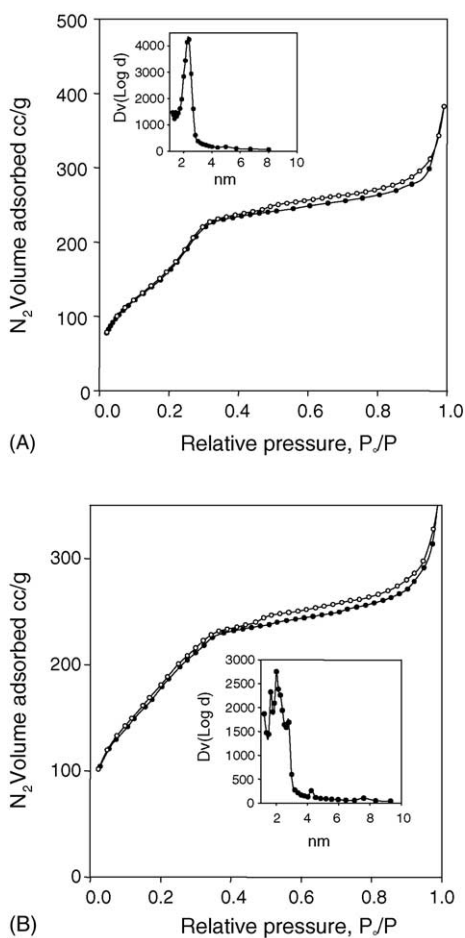


Fig. 2. Nitrogen adsorption (closed circle)-desorption (open circle) isotherms of mesoporous hybrid materials (A) GPh-SH and (B) GPh-SO₃H.

Table 1
Textural properties of the functionalized mesoporous benzene-silicas

Sample	BET (m ² g ⁻¹)	Pore diameter (nm)		H ⁺ (mmol g ⁻¹) ^b
		BJH	DFT	
GPh-SO ₃ H	665	2.1	3.2	0.90
Ph-HMM ^a	818	2.8	3.8	–
Ph-MP ₄₀ ^a	722	2.6	3.7	0.30
Nafion	–	–	–	0.80

^a After oxidation.

^b Measured by potentiometric titration with 0.05N NaOH [11].

properties to that of GPh-SH, confirming the stable mesophase of the material. The textural properties of these functionalized benzene-silicas are summarized in Table 1.

In addition, the transformation of GPh-SH to GPh-SO₃H was monitored by ¹³C NMR spectroscopy and confirmed by the potentiometric titration with NaOH [13]. Elemental analysis of the GPh-SH sample showed a sulfur content of 1.5 mmol g⁻¹ that is higher than the sulfur content of 1.15 mmol g⁻¹ of Ph-MP₄₀ sample. However, the potentiometric titration of GPh-SO₃H results in an acidity of H⁺ = 0.9 mmol g⁻¹, which is relatively low compared to the sulfur content of GPh-SH (1.5 mmol g⁻¹) and about three times as much as that of the Ph-MP₄₀ sample (H⁺ = 0.3 mmol g⁻¹) (see Table 1).

The entity of the mercaptopropyl group after grafting was also confirmed by ¹³C and ²⁹Si NMR spectroscopy. The ¹³C resonance at 11.0 and 26.8 ppm in Fig. 3A are assignable to the mercaptopropyl group and due to the C³ carbon directly bonded to a Si atom and the combination of C¹ carbon bonded to –SH moieties and C² carbon of the propyl chain, respectively [10]. The signal for the bridging phenylene fragment appeared at 133 ppm [9].

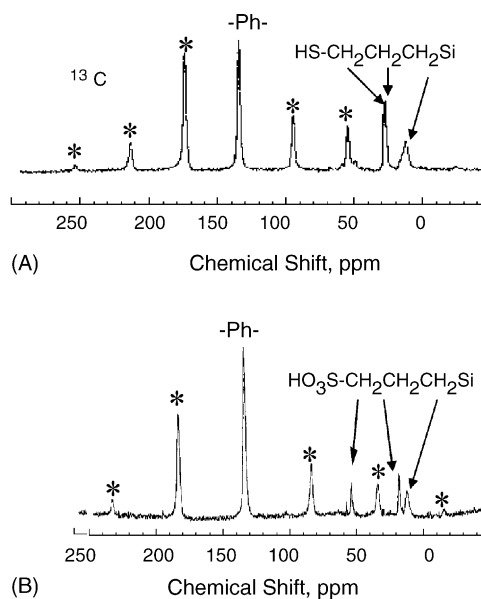


Fig. 3. ¹³C CP MAS NMR spectra of mesoporous hybrid materials. (A) GPh-SH and (B) GPh-SO₃H.

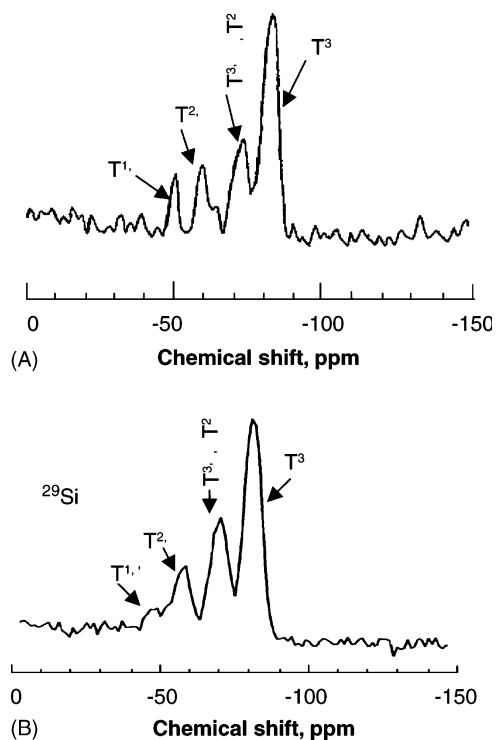


Fig. 4. ^{29}Si MAS NMR spectra of benzene-bridged mesoporous hybrid materials. (A) GPh-SH and (B) GPh-SO₃H.

^{13}C NMR spectroscopy of GPh-SO₃H clearly evidenced the formation of –SO₃H group by the resonances at 53.6 ppm (C¹ bonded with –SO₃H), 18.2 ppm (C²) and 12.1 ppm (C³) (Fig. 3B). No peak at 26.8 ppm was observed, indicating that no –SH moieties remained on the sample after oxidation [13].

The intense signals at –71.4 and –81.6 observed in the ^{29}Si NMR spectrum (Fig. 4A) of GPh-SH are of T² and T³ of phenylene-bridged silicon and at –48.3, –61.2, and –71.4 are of T^{1'}, T^{2'} and T^{3'} of mercaptopropyl fragment bonded silicon [10]. No Q sites silicon species were observed either, confirming the stable Si–C bond upon oxidation (Fig. 4B), but the intensity of T^{1'} silicon of GPh-SO₃H decreased sharply compared to the GPh-SH, while the intensity of T^{2'} silicon remained almost the same. Connected with the potentiometric result, it implies that the loosely bonded SiCH₂CH₂CH₂SH species was removed from the benzene–silica surface during the oxidation process and thus, resulting in the lower acidity compared to the initial S content.

The esterification of acetic acid with ethanol was performed under optimal reaction conditions under argon atmosphere. Fig. 5 demonstrates the reaction profiles observed with three different catalysts GPh-SO₃H, Ph-MP₄₀ and commercially available Nafion-H along with Ph-HMM without sulfonic acid group. Ethyl acetate was the only product detected. Under identical reaction conditions, the conversion of acetic acid on Ph-HMM was below 8%, while it was above 90% on GPh-SO₃H after 6 h of reaction. This result implies that the sulfonic acid group mainly contributes to the formation of ethyl acetate. GPh-SO₃H exhibited higher

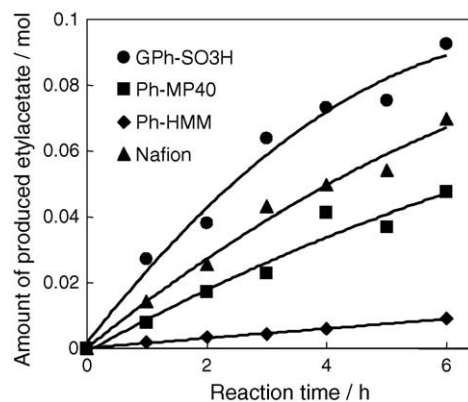


Fig. 5. Esterification of acetic acid with ethanol catalyzed by sulfonic acid functionalized mesoporous benzene–silica solids. Reaction condition: acetic acid, 0.1 mol; ethanol, 1.0 mol; catalyst, 0.2 g; reaction temperature, 343 K.

catalytic activity than Nafion-H. Since the GPh-SO₃H and Nafion-H have almost comparable acidic strength and hydrophobic surface properties, it is evident that apart from acidity and hydrophobicity of the material other constraints are also the governing factor for the catalytic activity. Furthermore, some diffusion limitation occurs to Nafion where the resultant activity might be limited by diffusion control. Due to the swelling of the Nafion beads it is quite possible that participation of at least some of the exchange sites is restricted. Therefore, an active role of crystal-like walls and unique surface structure can be proposed as the reason for the enhanced catalytic activity of GPh-SO₃H. Moreover, the rather different hydrophobic properties of the two materials respond differently to hydrophilic substrates (acetic acid and ethanol) due to varied hydrophobic–hydrophilic interactions.

On the other hand, the significant difference in activity of Ph-MP₄₀ compared to GPh-SO₃H may be due to the different ion-exchange capacity, structural integrity, and mesoscopic nature of Ph-MP₄₀ and GPh-SO₃H, where the latter two parameters could facilitate diffusion of reactants and products during the reaction. The ion-exchange capacity of Ph-MP₄₀ was one-third of that of the GPh-SO₃H catalyst. After reaction, GPh-SO₃H and Ph-MP₄₀ were filtered off and recycled for further use. About 25% loss of its original catalytic activity was monitored after the recycle of GPh-SO₃H, while no obvious loss of catalytic activity was observed for the recycled Ph-MP₄₀. The loss of catalytic activity for GPh-SO₃H may be due to the leaching of weakly bonded SiCH₂CH₂CH₂SO₃H species during the reaction. The participation of leached species in esterification was not evident. However, the differences in the catalytic performance of original and recycled materials depends on the location from where the active species were leached. The easily accessible catalytic active species of GPh-SO₃H are preferentially located on the external surface or near the pore mouth, which result in the higher catalytic activity of original GPh-SO₃H catalyst. This result also indicates that more stable network (O_{1.5}Si–C₆H₄–SiO_{1.5})_n–(SiO_{1.5}CH₂CH₂CH₂SH)_m could be formed by one step co-condensation process compared to the

post-synthesis grafting method, which eventually leads to the stable $(\text{O}_{1.5}\text{Si}-\text{C}_6\text{H}_4-\text{SiO}_{1.5})_n-(\text{SiO}_{1.5}\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{H})_m$ network to oxidation. On the other hand, the post-synthesis grafting leads to the weakly bonded $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$ species. However, the relative effectiveness of the grafting versus the one step co-condensation method for the synthesis of GPh-SO₃H and Ph-MP₄₀ materials in terms of resultant catalytic activity can be concluded either from the enhanced ethyl acetate yield and/or the stability of the network. The results demonstrate that both the hydrophobic character and the acidity contribute to the catalytic activity of the materials. It is noteworthy that the grafting mechanism in conjunction with hybrid networks possibly modified the availability of active surface species that are not available with any regularly structured or amorphous silica. Thus, it is always advantageous to have the hydrophobic surface properties which are associated with the organic moieties in the sulfonated mesoporous silicas.

4. Conclusion

In summary, we have successfully demonstrated the first application of the mesoporous benzene–silica with crystal-like wall structure in the esterification of acetic acid with ethanol. The improved catalytic activity was obtained with grafted materials. The excellent catalytic activity of these sulfonic acid-functionalized mesoporous benzene–silica compared to Nafion clearly suggests that unique surface properties as well as crystal-like wall structure play an important role

in the catalytic reaction. Further investigation for expanding the application fields of these materials is under way.

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