Preparation of mesoporous silica/polymer sulfonate composite materials

Masahiro Fujiwara [a],[*], Kumi Shiokawa [a], Yingchun Zhu [b]

[a] *Kansai Center, National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan*
[b] *Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, People's Republic of China*

Abstract

Mesoporous silica/polymer sulfonate composite materials were prepared by simply mixing hexadecyltrimethylammonium bromide, polymer sulfonates and TEOS (tetraethoxysilane) in alkaline aqueous solution. Nafion and poly(sodium 4-styrenesulfonate) were employed as polymer sulfonates. XRD patterns and nitrogen adsorption–desorption isotherms showed that the precipitates obtained had mesostructure similar to MCM-41. Especially, the crystallinity of hexagonal structure of composite materials synthesized with Nafion was high. From all the results obtained here, it is concluded that the polymer sulfonate resins might be incorporated in the wall framework of mesoporous silica matrix. However, when the excess amount of Nafion was mixed, the acid sites of Nafion were significantly lost in the obtained materials. These composite materials present new classes of organically modified mesoporous silicas, where organic polymers are incorporated in the framework of mesoporous silica. They were used as catalysts for α-methylstyrene dimerization and Friedel–Crafts alkylation reaction of aromatics.
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1. Introduction

Researches on mesoporous silicas and related materials are important fields of recent material science [1,2]. Especially MCM-41 and its analogues [2] are actively studied because of their high potentials for various applications. The functionalization of mesoporous silica with organic compounds began with the surface modification using silane compounds such as R-Si(OR′)$_3$ [1,3]. After this kind of approach, the framework modification using disilane compounds followed. These materials are often called periodic mesoporous organosilicas (PMOs) [4–6]. For example, Inagaki and co-workers notified that benzene ring and analogues are completely incorporated into the framework of mesoporous silica materials, and that these materials are effective acid catalysts after sulphonation [7]. Another trend is the polymerizations in the pore voids of mesoporous materials: many researchers produced composite materials with the corresponding polymers by this method [8]. Mesoporous composite materials, where an organic polymer is introduced into their "framework", are also investigated. In 2000, we briefly

reported that Nafion resin, whose structure is illustrated in Fig. 1, was incorporated in the framework of M41S type of mesoporous silica [9]. This material was a unique catalyst for α-methylstyrene dimerization. Recently, another group developed the composite materials with polyacrylate [10]. In Fig. 2, a classification of these composite materials of mesoporous silica with organic components is proposed. Type (A) is surface modification using R-Si(OR′)$_3$ compounds [1,3], and Type (B) is framework modification such as periodic mesoporous organosilicas (PMOs) [4–7]. Type (C) shows composite materials with polymeric compounds in the pore voids [8]. Composite mesoporous materials with polymers in the framework are named Type (D) here [9,10].

In this paper, we wish to report further examination of the composite materials of mesoporous silica with Nafion resin. The matrices of mesoporous materials are expected to offer ordered nanostructures useful as solid support [11]. Nafion resin is also a functional perfluorinated sulfonic acid polymer to be used as acid catalyst [12] and as polymer electrolyte for fuel cell application [13]. Composite materials of Nafion resin with amorphous silica have been utilized in these technologies [14,15]. The ordered nanostructures of Nafion and analogous resins with mesoporous silica matrix are expected to be useful for various applications.

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[*] Corresponding author. Tel.: +81 72 751 9253.
E-mail address: m-fujiwara@aist.go.jp (M. Fujiwara).

$$[(CF_2CF_2)_nCFCF_2]_x$$
$$|$$
$$(OCF_2CF)_mOCF_2CF_2SO_2OH$$
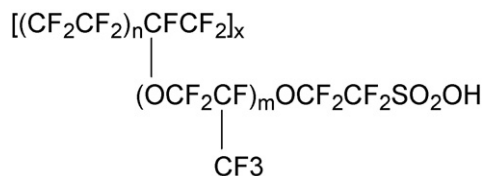$$|$$
$$CF_3$$

Fig. 1. Structure of Nafion resin.

2. Experimental

2.1. Preparation of mesoporous silica/Nafion composite material

The preparation procedure is considerably simplified from our previously reported method [9]. Nafion solution commercial available was directly used and no hydrothermal treatment was performed. A typical synthesis of mesoporous silica/Nafion composite is following: 5.0 g of 5% Nafion alcohol solution (from Aldrich) was added to 200 mL of the aqueous solution of NaOH (1.73 g; 43.25 mmol) and hexadecyltrimethylammonium bromide (3.48 g; 9.55 mmol), and this mixed solution was stirred for a few minutes. To this solution, 16.69 g (80 mmol) of tetraethoxysilane (TEOS) was added dropwise for 5 min, and the resulting solution was further stirred for 12 h at room temperature. An as-synthesized sample thus obtained was filtered, washed with sufficient amount of H_2O and dried at 80 °C for 12 h. Template was removed by refluxing with 1 M H_2SO_4 solution of EtOH (solid sample/EtOH solution = 1 g/150 mL) for 12 h. The filtered solid was refluxed again with pure EtOH (sample/EtOH = 1 g/150 mL) for 12 h, filtered, washed with H_2O at room temperature and dried at 80 °C for 12 h.

2.2. Preparation of mesoporous silica/Nafion composite material from amorphous silica/Nafion composite

The general preparation method of MCM-41 type of mesoporous silica from porous amorphous silica is described in elsewhere [16]. This procedure was applied to amorphous silica/Nafion composite. The amorphous silica/Nafion composite used here was SAC-13 purchased from Aldrich. To the aqueous solution of NaOH (0.15 g; 3.80 mmol) with hexadecyltrimethylammonium bromide (0.37 g; 1.00 mmol) in 4 mL of H_2O, 0.61 g of SAC-13 was added. After stirred for 1 h, the resulting mixture was placed in a stainless autoclave, sealed tightly and heated at 110 °C for 24 h under autogenous pressure. The following procedures were similar to the above-mentioned process.

2.3. Preparation of mesoporous silica/poly(4-styrenesulfonate) composite material

To the solution of NaOH (0.799 g; 19.98 mmol) and hexadecyltrimethylammonium bromide (1.582 g; 4.341 mmol) in 90 mL of H_2O, 0.412 g of poly(sodium 4-styrenesulfonate) dissolved in 10 mL of H_2O was added, and to this homogeneous solution 8.403 g (40.34 mmol) of TEOS was mixed. The resulting solution was stirred for 2 days at ambient temperature. The precipitate thus formed was filtered, washed with sufficient amount of H_2O and air-dried. The following procedures were similar to the above-mentioned process.

2.4. Preparation of mixture of Nafion with hexadecyltrimethylammonium bromide

A 5% alcohol solution of Nafion (7.656 g; Nafion content: 0.353 g; sulfonic acid equivalent: 0.341 mmol) was mixed with NaOH (0.038 g: 0.95 mmol) in 5 mL of H_2O. After removing solvent under reduced pressure, the residue was dissolved in a mixed solution of H_2O (10 mL) and EtOH (10 mL). Finally hexadecyltrimethylammonium bromide (0.125 g; 0.343 mmol) was added. After about 1 day, white precipitate obtained was filtered and air-dried.

2.5. Preparation of mixture of poly(4-styrenesulfonate) with hexadecyltrimethylammonium bromide

The solution of 0.412 g of poly(sodium 4-styrenesulfonate) in 6 mL of H_2O was mixed with the aqueous solution (50 mL) of hexadecyltrimethylammonium bromide (0.728 g; 2.00 mmol). The white precipitate was formed in a few minutes. After stirring for 1 h, the white precipitate was filtered and dried at 60 °C.

2.6. Product characterizations

XRD patterns were recorded with a MAC Science MXP3V diffraction apparatus with Ni filtered Cu Kα radiation ($\lambda = 0.15406$ nm). N_2 adsorption-desorption isotherms were obtained at −196 °C (in liquid N_2) using a Bellsorp Mini instrument (BEL JAPAN Inc.). BJH calculation was performed to esti-
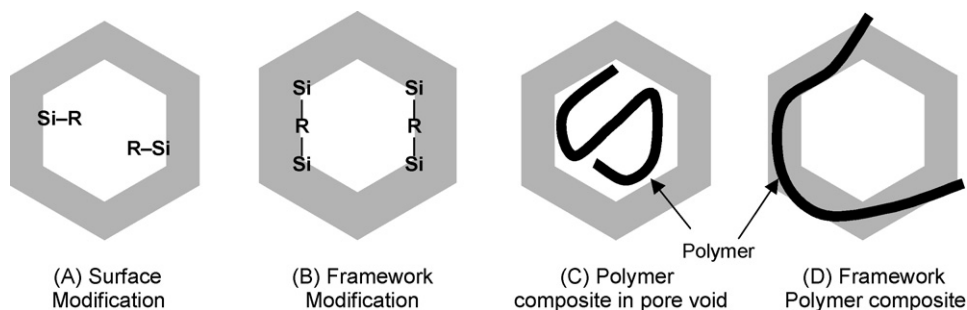

Fig. 2. Conceptual schemes of composite materials of mesoporous silica with organic components.

mate the mesopore size using adsorption branches of isotherms. Elemental analyses of silicon were performed by the alkali fusion-gravimetric method according to JIS G 1212 (Japanese industrial standard). Elemental analyses of fluorine were carried out with the lanthanum-alizarin complexone method using a Shimadzu UV-1600 photometry apparatus after the extraction of alkali fusion method. Elemental analyses of carbon were performed by the common combustion gas quantification method. Thermogravimetric analyses (TGA) were performed on a Shimadzu TGA-50 apparatus. All samples were held in a platinum sample holder and were heated under air from room temperature to 800 °C at the rate of 5 °C/min. FT-IR spectra were measured on a Perkin-Elmer Spectrum One spectrometer. Transmittance electron microscope (TEM) images were obtained using a JEM-2100F (JEOL) high-resolution transmission field emission electron microscope (HRTEM) operated at 300 kV. The acid capacities of composite materials were estimated by the titration method. The composite materials were immersed in 0.1 M of aqueous solution of NaCl, and the acid amounts of the ion-exchanged solutions thus obtained were analyzed by titrating with 0.01 M NaOH using phenolphthalein as indicator.

2.7. Catalytic reactions

The experimental procedure of α-methylstyrene (AMS) dimerization was described in our previous paper [9]. A competitive Friedel–Crafts reaction of toluene and *p*-xylene with benzyl alcohol was performed by the mixed solution of toluene (0.92 g, 10 mmol), *p*-xylene (1.05 g, 10 mmol) and benzyl alcohol (0.22 g, 2 mmol) in the presence of a catalyst (0.05 g) at 90 °C for 7 h with vigorous stirring. After filtering the catalyst, the filtrate was analyzed by a capillary GC.

3. Results and discussion

3.1. Synthesis of mesoporous silica/Nafion composite material

Composite materials made of mesoporous silica and Nafion resin were prepared by a procedure modified for mesoporous
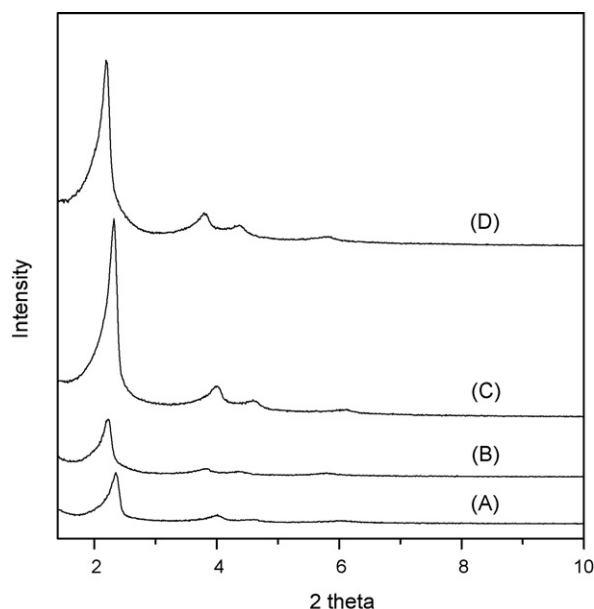

Fig. 3. XRD patterns of as-synthesized and template-free (solvent extracted) mesoporous silica/Nafion composite materials. (A) As-synthesized MCM/Nafion-1. (B) As-synthesized MCM/Nafion-2. (C) Template-free MCM/Nafion-1. (D) Template-free MCM/Nafion-2.

silica synthesis. TEOS was added to a homogeneous alkaline solution of hexadecyltrimethylammonium bromide with Nafion resin. After stirring at room temperature, as-synthesized composite materials of mesoporous silica and Nafion resin were obtained as a white precipitate. Although hydrothermal treatment in an autoclave was given in our previous paper [9], we found that this hydrothermal treatment is not essential for the synthesis after the publication of the paper. The surfactant as template was removed by refluxing in H_2SO_4–EtOH solution (1 M of H_2SO_4). H_2SO_4 is expected to contribute to both the regeneration of sulfonic acid sites in Nafion polymer resin and the surfactant removal. The sample names and the profiles of composite materials are summarized in Table 1. The data of a composite material prepared under hydrothermal conditions [9] are also included in Table 1 as MCM/Nafion-H. Fig. 3 shows XRD patterns of two composite materials (MCM/Nafion-1 and

Table 1
Properties of various mesoporous silica/polymer composites materials

Sample	Starting ratio		d_{100}[a]		SSA[b] (m²/g)	PV[c] (cm³/g)	PPD[d] (nm)
	g/mol[e]	wt%[f]	2θ	nm			
MCM/Nafion-1	3.13	5.21	2.32 (2.34)	3.81 (3.77)	1239	1.12	2.52
MCM/Nafion-2	6.72	11.18	2.20 (2.22)	4.01 (3.98)	1211	1.26	2.75
MCM/Nafion-3	14.87	24.76	2.20 (2.28)	4.01 (3.87)	333	0.26	2.52
MCM/Nafion-H[g]	6.58	10.96	2.25 (2.35)	3.92 (3.76)	918	1.00	2.75
MCM/PSS	8.88	15.19	2.14 (2.24)	4.13 (3.94)	838	0.66	2.75

[a] d_{100}: X-ray diffraction (1 0 0) interplanar spacing. In parentheses, as-synthesized sample.
[b] BET specific surface area.
[c] Primary mesopore volume calculated from adsorption branch of BJH pore size distribution curve.
[d] Peak pore diameter from adsorption branch of BJH pore size distribution curve.
[e] Starting ratio of polymer (as acid type) and TEOS; gram of polymer/molar of TEOS.
[f] Estimated weight percentage when polymer is completely incorporated in solid material and all TEOS converts into silica (SiO_2).
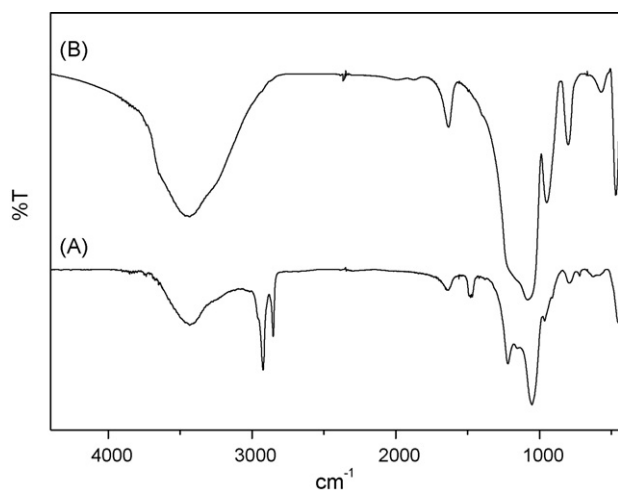[g] MCM/Nafion composite material we reported [9].

Fig. 4. Infrared spectra of as-synthesized (A) and template-free (B) MCM/Nafion-1 composite material.

MCM/Nafion-2) in as-synthesized and template-free forms. XRD patterns indicated the formation of the hexagonal structure characteristically observed in the MCM-41 type of mesoporous silica [2]. The peaks assigned to d_{110}, d_{200} and d_{210} interplanar spacings were found besides those from d_{100} interplanar ones in all four samples. The surfactants were removed successfully by the extraction using H_2SO_4 in EtOH with the hexagonal structure maintained. Template removal by calcination was not performed to avoid thermal decomposition of Nafion resin. The peaks derived from the hexagonally ordered structure became stronger after the template removal in both cases (MCM/Nafion-1 and MCM/Nafion-2).

Infrared spectra of as-synthesized and template-free (extracted) samples are shown in Fig. 4. In the as-synthesized sample, strong absorptions of the surfactant were observed approximately at 2929 and 2850 cm^{-1} (Fig. 4A). These absorptions disappeared after the treatment with H_2SO_4 (Fig. 4B), indicating the complete removal of the surfactant. On the other hand, the absorptions of C–F stretching modes of Nafion resin at 1210 and 1160 cm^{-1} were not found in either spectra, while

they are detected in amorphous silica/Nafion composite [14a]. It seems that in the case of amorphous silica/Nafion composite, the contact time of Nafion resin with alkaline solution is comparatively short (the preparation solution gels immediately), preventing the serious decomposition of C–F bonds [14a]. In our case, Nafion resin was dissolved in the high alkaline solution for a long time, resulting in critical degradation.

The TEM images of MCM/Nafion-1 are shown in Fig. 5. The ordered structure (hexagonally arranged) was confirmed from the layered lines in the solid. The distance between layers is estimated to be 3.0–3.8 nm, approximately according with that from XRD patterns.

The nitrogen adsorption–desorption isotherms of the template-free samples are shown in Fig. 6. Both samples, MCM/Nafion-1 and MCM/Nafion-2, indicated the typical type IV isotherms (IUPAC) of ordered mesoporous silica materials. The pore size of MCM/Nafion-2 was larger than that of MCM/Nafion-1. These results were consistent with the d_{100} interplanar spacings from XRD patterns (Fig. 3). Specific surface areas (BET surface area) and pore volumes of both samples were over 1000 m^2/g and 1 cm^3/g, respectively. These data were at the level similar to the MCM-41 type of mesoporous silicas [1,2], and considerably higher than those of amorphous silica/Nafion composite materials [15]. These properties are similar to those of the sample prepared under hydrothermal conditions (MCM/Nafion-H) in our previous paper [9]. Therefore, a simpler preparation method using the direct use of commercial reagent under ambient conditions proved to be applicable. However, when more than 20 wt% of Nafion resin was added to the starting solution, the ordered structure of the corresponding composite material was considerably collapsed (MCM/Nafion-3). The peak at 2.28 in 2θ observed in the as-synthesized sample (Fig. 7A) indicated its moderately ordered structure. However, this peak almost disappeared after the removal of template (Fig. 7A), showing the destruction of the ordered structure. In Fig. 7B, the nitrogen adsorption–desorption isotherm and the pore size distribution estimated from the BJH method of template-free MCM/Nafion-3 are presented. The porosity of this sample was poor and the peak of the pore diameter was
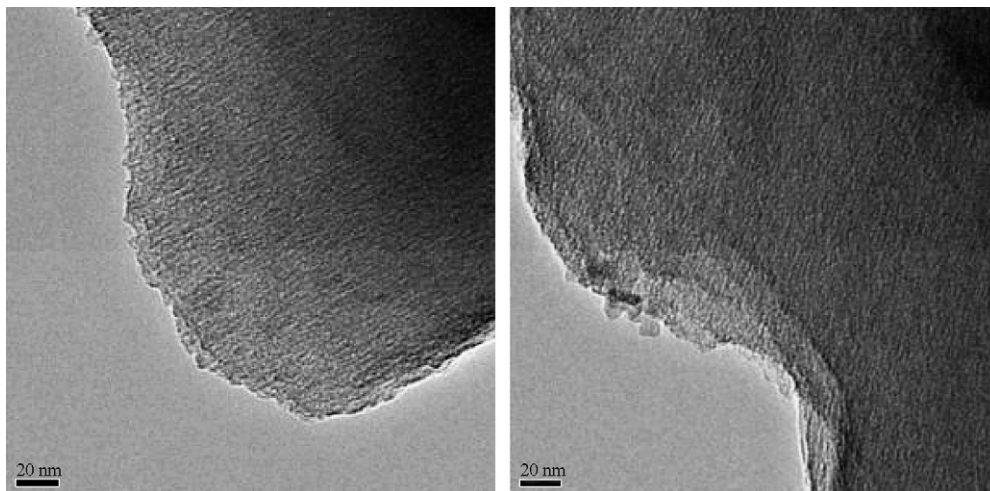

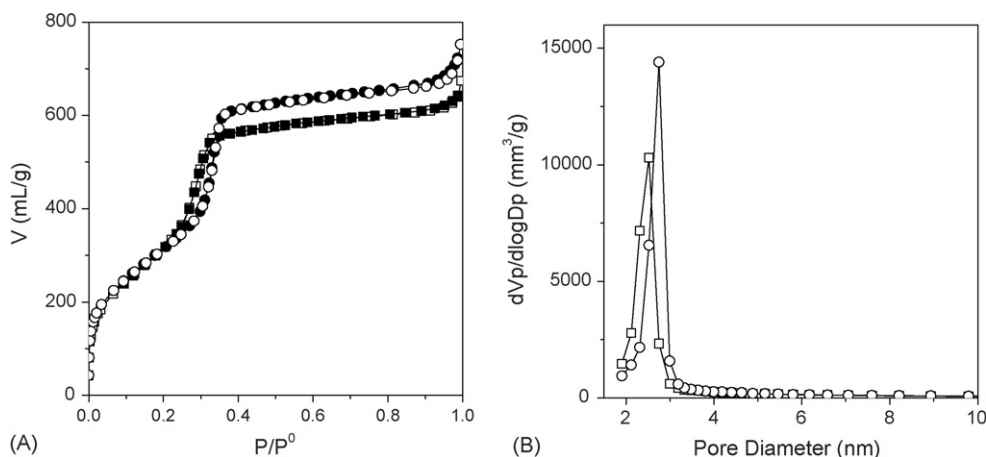
Fig. 5. TEM images of MCM/Nafion-1 (template-free).

Fig. 6. (A) Nitrogen adsorption–desorption isotherms of mesoporous silica/Nafion composite materials. (□) Adsorption branch of MCM/Nafion-1; (■) desorption branch of MCM/Nafion-1; (○) adsorption branch of MCM/Nafion-2; (●) desorption branch of MCM/Nafion-2. (B) Pore size distributions estimated from the adsorption branches of the isotherms by BJH method. (□) MCM/Nafion-1; (○) MCM/Nafion-2.

broad. The specific surface area and the pore volume decreased to 333 m^2/g and 0.259 cm^3/g, respectively. Thus, the addition of excess amount of Nafion resin inhibited the formation of ordered structure.

Another approach to the preparation of the composite material was attempted by using an amorphous silica/Nafion composite. It is well known that porous amorphous silica can be transformed into mesoporous MCM-41 type material in the presence of surfactant in alkaline solution [2,16]. An amorphous silica/Nafion composite material commercially available (SAC-13; Nafion content: approximately 13 wt%) was immersed in an alkaline solution dissolving hexadecyltrimethylammonium bromide. This solution system was placed in an autoclave to be hydrothermally treated by reacted at 115 °C for 24 h [16]. The XRD patterns of as-synthesized and template-free samples thus obtained are shown in Fig. 8. The crystallinity of the as-synthesized sample was poor, and after the removal of template the hexagonal structure nearly collapsed. Even in this case, a comparatively high content of Nafion resin (13 wt%) is thought

to prevent the formation of ordered structure in the case of MCM/Nafion-3.

3.2. Analyses of composition of mesoporous silica/Nafion composite material

The contents of Nafion resin in these composite materials were analyzed by various methods. The results of TGA measurement of these composite materials are listed in Table 2. Nafion resin is thermally decomposed from 150 to 600 °C [17], and the weight decrease of pure mesoporous silica (without Nafion resin) we prepared was measured 4.78% due to the thermal dehydration of silanols in this temperature range. The corrected values of the weight decreases by this blank measurement are shown in the parentheses. Although there are no direct proportional relationships between the starting contents of Nafion and the weight decreases, combustible Nafion contents increased from MCM/Nafion-1 to MCM/Nafion-3. A similar tendency was observed in the elemental analysis shown in Table 2. The
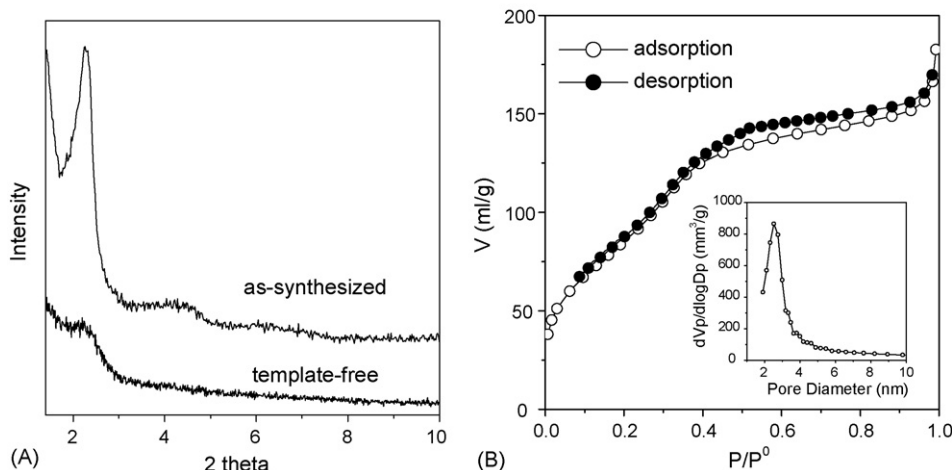

Fig. 7. (A) XRD patterns of as-synthesized and template-free (solvent extracted) MCM/Nafion-3. (B) Nitrogen adsorption–desorption isotherm and the pore size distribution by BJH method from adsorption branch (in inset) of MCM/Nafion-3.
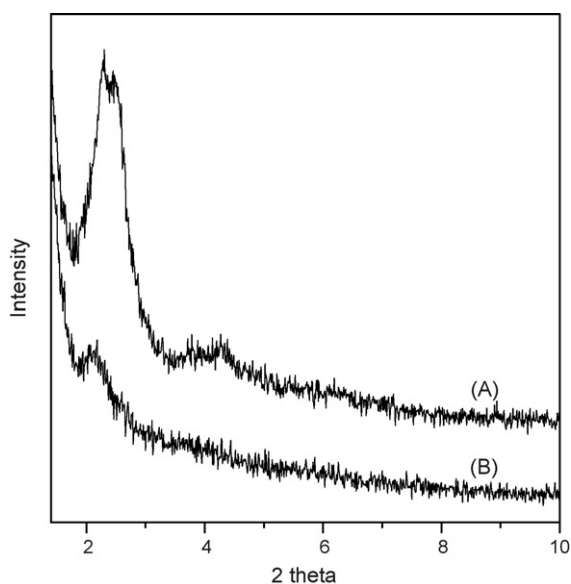
Fig. 8. XRD patterns of as-synthesized (A) and template-free (B) mesoporous silica/Nafion composite material obtained from an amorphous silica/Nafion composite (SAC-13).

carbon and fluorine contents increased with the starting Nafion resin contents. It should be noted that the fluorine contents were low in these composite materials, although the weight ratios of fluorine to carbon must be approximately 3.2 according to the chemical formula of Nafion (Fig. 2) [14a]. These lower contents of fluorine indicated that carbon–fluorine bonds in Nafion resin were significantly cleaved during the preparation process, because aliphatic perfluoro group is known to be unstable under basic conditions (although aromatic C–F bond is reported to be tolerant in alkaline solution) [11a]. No observation of C–F bonds in infrared spectra (Fig. 4), which can be observed in amorphous silica/Nafion composite [14a], was likely to result from the decrease in the fluorine content in the resin.

The acid capacities of these composite materials were estimated by the cation exchange method with NaCl [14]. The acid equivalents are also summarized in Table 2. The acid content of pure Si-MCM-41 (with Nafion resin) was under 0.001 mequiv. H^+/g. Pure Nafion resin (NR-50) and its composite material with amorphous silica (SAC-13; Nafion content: 13 wt%) is reported to have 0.89 or 0.14 mequiv. H^+/g of acid

capacities, respectively [14]. In the parentheses of Table 2, the weight percentages of Nafion in the composite materials calculated from the measured acid capacities are listed on the assumption that all sulfonic acid sites of Nafion resin are active. The calculated Nafion content of MCM/Nafion-1 (5.92 wt%) from acid capacity was reasonably consistent with the estimated values from both starting ratio and TGA measurement. On the other hand, in the case of MCM/Nafion-2, the Nafion content estimated from the acid capacity (17.02 wt%) was in discord with other results. Furthermore, the acid capacity of MCM/Nafion-3 was approximately 0.003 mequiv. H^+/g. From these results, it was concluded that high contents of Nafion in the composite materials led to the some decomposition of Nafion resin, while no significant changes were observed in the case of low Nafion contents.

3.3. Synthesis of mesoporous silica/poly-sulfonate composite material

The formation of composite materials of mesoporous silica with polyacrylate was recently claimed in a report [10], where a procedure analogous to ours was used. We also studied the preparation of a composite material made of mesoporous silica and another poly-sulfonate. Poly(4-styrenesulfonic acid) sodium salt was employed for the synthesis. In a similar manner to Nafion, TEOS was added to the mixed alkaline solution of poly(sodium 4-styrenesulfonate) (PSS) and hexadecyltrimethylammonium bromide, forming a composite material (MCM/PSS) after stirring. The XRD patterns of the as-synthesized and template-free samples are shown in Fig. 9A. Although the peak intensities of these two patterns were lower than those of composite materials with Nafion, an ordered structure in the nano-level was observed. In the as-synthesized MCM/PSS, peaks assigned to d_{110}, d_{200} and d_{210} interplanar spacings were found as well as d_{100} interplanar one. Those peaks are not so clear in the template-free MCM/PSS, and its pore structure might be a wormhole like one [18]. The nitrogen adsorption–desorption isotherms of this MCM/PSS composite material presented in Fig. 9B are basically type IV. The peak pore diameter was found at 2.75 nm (in inset). Thus, a poly(styrenesulfonate) polymer can be successfully introduced into mesoporous silica material as well as Nafion resin.

Table 2
Results of elemental analysis, TGA and acid capacity of mesoporous silica/polymer composite materials

Sample	Stating ratio (wt%)[a]	Elemental analysis (wt%)[b]			TGA (%)[c]	Acid capacity (mequiv. H^+/g)[d]
		C	Si	F		
MCM/Nafion-1	5.21	2.75	39.1	1.65	9.06 (4.27)	0.0527 (5.92)
MCM/Nafion-2	11.18	2.89	39.3	1.71	10.75 (5.97)	0.1515 (17.02)
MCM/Nafion-3	24.76	3.92	36.8	5.87	13.99 (9.21)	0.003 (0.3)

[a] Starting weight composition of Nafion calculated from carbon in Nafion and silicon in TEOS, regarding as Nafion formula are $n = 7$ and $m = 1$ in Fig. 1.

[b] Elemental analyses of C, Si and F were performed by common combustion gas quantification method, alkali fusion-gravimetric method or lanthanum-alizarin complexone method, respectively.

[c] Percentage of weight loss from 150 to 600 °C. In parentheses, the corrected value by deducting the weight decrease (4.78%) by the dehydration of mesoporous silica prepared without Nafion is noted.

[d] Acid capacity estimated from the titration of ion-exchanged solution from NaCl using NaOH solution. In parentheses, the weight percent of Nafion calculated from this acid capacity using the pure Nafion resin acid capacity [14a], 0.89 mequiv. H^+/g (on the supposition that all sulfonic acid sites are active).
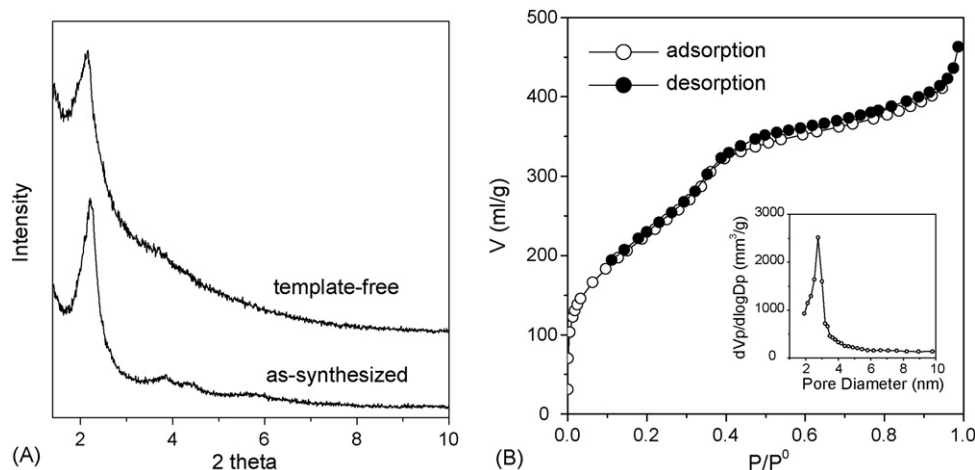
Fig. 9. (A) XRD patterns of as-synthesized and template-free (solvent extracted) mesoporous silica/poly(sodium 4-styrenesulfonate) composite material (MCM/PSS). (B) Nitrogen adsorption–desorption isotherm and the pore size distribution by BJH method from adsorption branch (in inset) of MCM/PSS.

3.4. Mechanistic discussion on the formation of mesoporous silica/poly-sulfonate composite materials

It is well known that the polymer electrolyte such as ion-exchange resin and surfactant readily form their complex by their ionic interaction [19]. When sodium polyacrylate or poly(4-styrenesulfonate) was mixed with hexadecyltrimethylammonium bromide in aqueous solution, their complexes were instantly produced as precipitates. On the other hand, sodium salt of Nafion resin obtained by neutralization with sodium hydroxide scarcely afforded the precipitate with the surfactant in aqueous solution. Only after the considerable evaporation of solvent, a white viscous solid was obtained. Fig. 10 shows XRD patterns of the complexes obtained from sodium salt of Nafion or sodium poly(4-styrenesulfonate) with hexadecyltrimethylam-
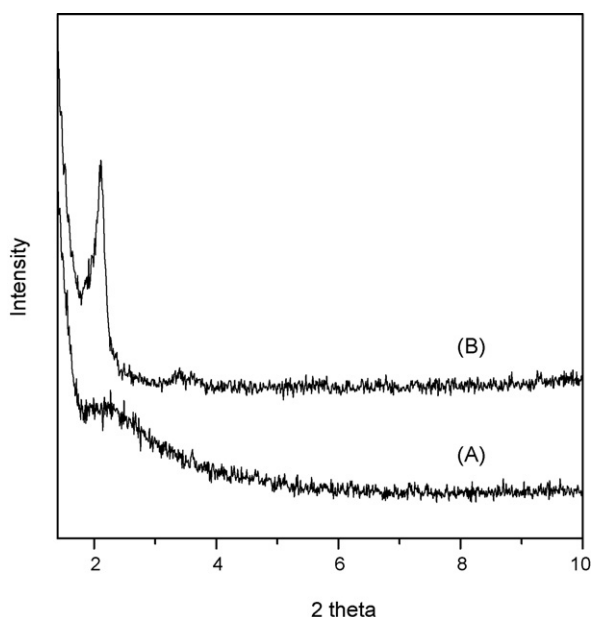
monium bromide. In the XRD pattern of the complex from sodium poly(4-styrenesulfonate) and the surfactant, a sharp peak at 2.11 in 2θ (interplanar space: 4.18 nm) was found (B in Fig. 10). These kinds of XRD pattern often observed in the complexes of polyelectrolytes and surfactants indicate the formation of lamellar structure complexes of polymer electrolytes with surfactants [19d]. On the other hand, in the case of the complex from Nafion resin and surfactant, no clear peak was observed in the XRD pattern (A in Fig. 10), indicating that Nafion forms no ordered complex with cationic surfactant. A broad peak found at 2.22 in 2θ (interplanar space: 3.98 nm) is likely to be derived from the cluster structure of sulfonic acid parts of Nafion resin [20]. This cluster structure might restrict the formation of the complex with surfactant.

In Fig. 11, a possible formation mechanism of composite material consisting of mesoporous silica and polymer sulfonate is displayed. Two routes of composite materials formation are assumed. In the case of MCM/PSS synthesis, some layered phases of poly(styrenesulfonate) and surfactant are formed at first. The hydrolysis of TEOS to silica occurs in this solution. With the progress of the condensation of silanols (Si–OH) to siloxane bonds (Si–O–Si), the hexagonal structure by the influences of surfactant is formed gradually. However, the layered structure of poly(styrenesulfonate) and surfactant is comparatively strong so as to restrict the transformation of the layered structure to the hexagonal one (route A). The lower crystallinity of MCM/PSS is thought to be caused from this effect. On the other hand, complex compounds are scarcely formed from Nafion resin and surfactant, not suppressing the above-mentioned transformation and the fabrication of hexagonal structure (route B). It is thought that the electrostatic interaction between the sulfonate group of Nafion and cationic surfactant compels the mixing of Nafion resin in aqueous phase as shown in route B of Fig. 11, when the amount of Nafion is not overabound. It is not sure that Nafion resin bearing highly hydrophobic perfluoro main chain is incorporated into the aqueous phase of the mixed solution. However, the low fluorine contents in MCM/Nafion composite materials confirmed by the

Fig. 10. XRD patterns of precipitated solids from Nafion resin (A) or sodium poly(4-styrenesulfonate) (B) with hexadecyltrimethylammonium bromide.
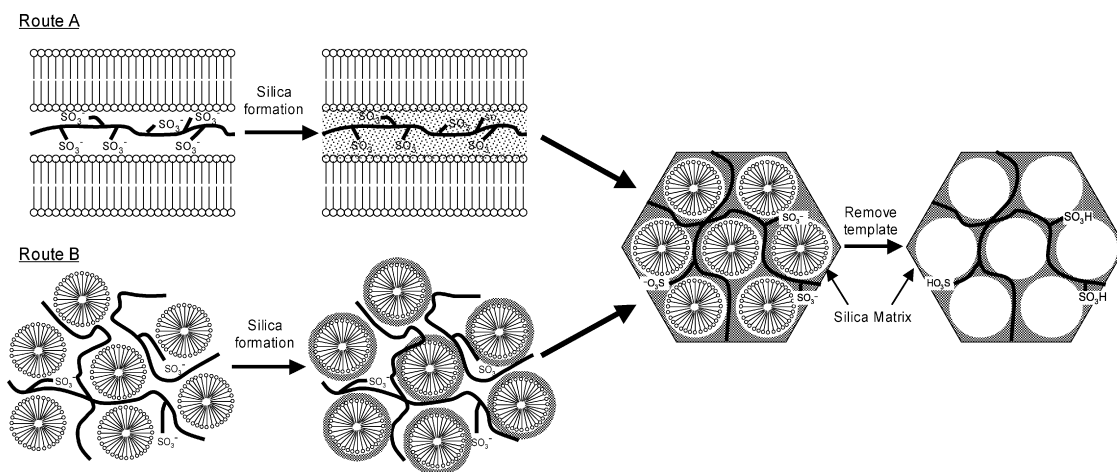
Fig. 11. Expected mechanisms of mesoporous silica/polymer sulfonate composite materials.

elemental analysis suggested that the reaction of carbon–fluorine bond proceeds to eliminate fluorine in high alkaline solution. The main chains of Nafion resin become more hydrophilic by this reaction, increasing the affinity for silica matrix. Finally, the well-defined hexagonal structure of MCM/Nafion composite materials is obtained in the case of low loading of Nafion resin.

3.5. Catalytic Friedel–Crafts reaction by mesoporous silica/Nafion composite materials

We have previously shown the unique behavior of mesoporous silica/Nafion composite materials for α-methylstyrene (AMS) dimerization. Representative results are listed in Fig. 12A. Using this catalyst, intermediate products (products **1** and **2**) are predominantly obtained and the further reaction (intramolecular Friedel–Crafts reaction) to form an indan derivative (product **3**) is inhibited, while the product **3** was yielded effectively by amorphous silica/Nafion composite (SAC-13) [9]. A competitive Friedel–Crafts type reaction of toluene and *p*-xylene with benzyl alcohol was examined using MCM/Nafion-1 and SAC-13 (Fig. 12B). While no selectivity for the benzylation of toluene or *p*-xylene was observed in the reaction by SAC-13, the reaction of *p*-xylene occurred preferably in the case of MCM/Nafion-1 catalyst. These results indicated that Friedel–Crafts reaction catalyzed by MCM/Nafion-1 is more influenced by the substituents on the benzene ring than that by SAC-13. *p*-Xylene with two electron-donating groups is
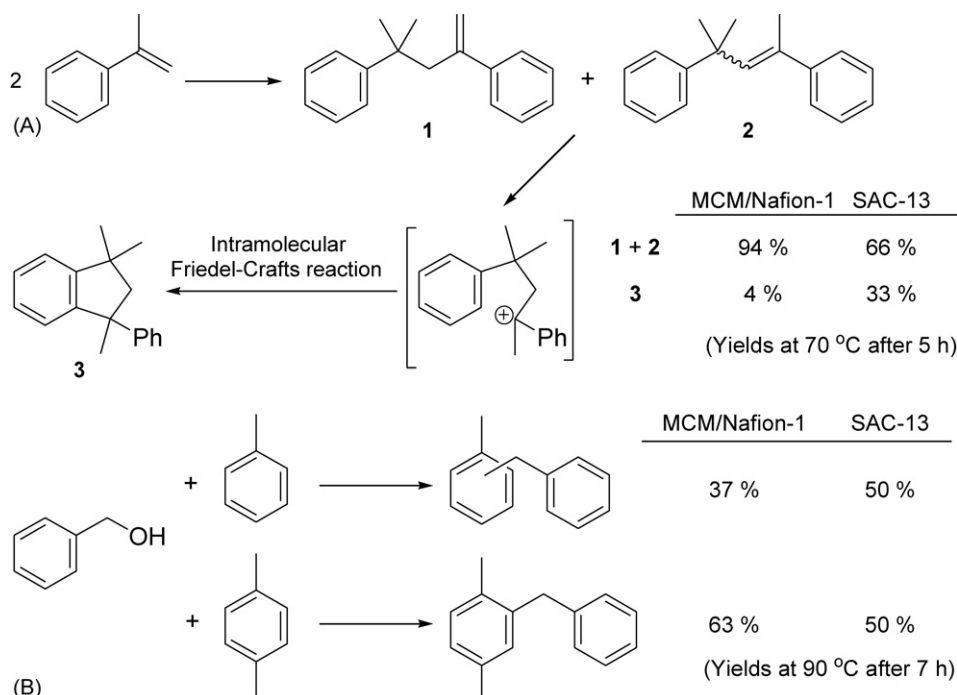

Fig. 12. Results of α-methylstyrene (AMS) dimerization (A) and competitive Friedel–Crafts type reaction of toluene and *p*-xylene with benzyl alcohol (B).

more reactive than toluene with one electron-donating group in the case of MCM/Nafion-1 catalyst. The intramolecular Friedel–Crafts reaction of products **1** and/or **2** bearing one electron-donating group on the benzene ring is required for affording product **3**. However, this reaction is less accelerated by MCM/Nafion-1 than by SAC-13. Therefore, when mesoporous silica/Nafion composite material is used for the catalyst for the AMS dimerization, the formation of product **3** is suppressed to result in the predominant production of intermediate dimers (products **1** and **2**).

4. Conclusions

In this paper, we showed the preparation and the properties of composite materials comprised of mesoporous silica and polymer sulfonates such as Nafion. The polymer sulfonates are incorporated into the wall framework of mesoporous silica matrix, and probably provide an example of the "framework polymer composite" of mesoporous silica. The formation mechanisms of these composite materials are also discussed. These composite materials will present new classes of organically modified mesoporous silicas, which are one of the most exciting fields of current material chemistry.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2006.09.016.

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