Exceptional performance of sulfonic acid-incorporated-MCM-41 mesoporous materials prepared using a silane containing polysulfide linkages in the acetylation of anisole†

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Sulfonic acid-incorporated-MCM-41 mesoporous materials prepared using a silane containing tetrasulfide linkages showed exceptional yields of the acetylated product in the acetylation of anisole due to their high content of strong acid sites.

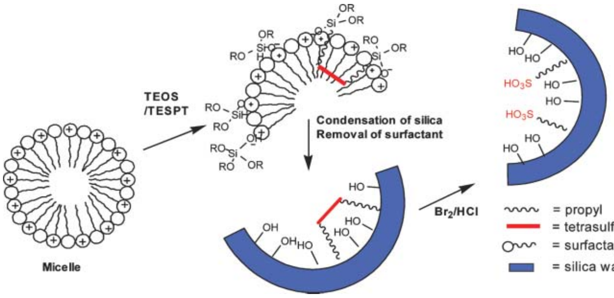
Sulfonic acid has been widely employed as a homogeneous catalyst in various organic syntheses because of its high activity and selectivity, in spite of the severe difficulties involved in separating it from the products and disposing of it after use. The addition of mercaptopropyltriethoxysilane (MPTES) to synthetic mixtures of mesoporous materials is an ordinarily used method of introducing mercapto groups on their pore walls, which can then be converted into sulfonic acid (–SO_3H) groups through oxidation. The incorporation of sulfonic acid groups on porous silica supports produces highly convenient solid acid catalysts exhibiting the advantages of homogeneous catalysts.[1–6] However, too large a content of MPTES in the synthetic mixtures lowers the regularity of the mesopores, and thus there is a strict limitation on the concentration of acid sites on mesoporous materials.[1,3] Otherwise, the addition of fluorocarbon surfactant to the synthetic mixture is essential for the preparation of ordered mesoporous materials containing a high content of sulfonic acid groups.[6]

In this study, we prepared sulfonic acid-incorporated-MCM-41 mesoporous materials using the silane bis(3-triethoxysilylpropyl)-tetrasulfide (TESPT), which contains polysulfide linkages. The low miscibility of the polysulfide linkages with silica sources expels them to the outside of the mesopores, thereby suppressing the negative contribution of the silane in the synthesis of mesoporous materials. The conversion of polysulfide linkages to sulfonic acid groups using Br_2–HCl inhibits the oxidation of organic chains, producing highly convenient solid acid catalysts with a high concentration of acid sites.[7]

Sulfonic acid groups incorporated on MCM-41 mesoporous materials were prepared following Scheme 1. A part of tetraethylorthosilicate (TEOS) was substituted by TESPT. Synthetic mixtures containing cetyltrimethylammonium bromide (C_{16}TABr) were prepared following the procedure described in the literature.[8] Their compositions were: C_{16}TABr : TEOS : TESPT : NH_4OH : H_2O = 120 : 100 − x : x : 800 : 11 400, where x denotes the mole percentage of silicon atoms from TESPT in the mixture. We prepared various synthetic mixtures having values of x in the range of 0–80 to examine the effect of TESPT content on the regularity of the obtained mesoporous materials. MPTES was also employed as a sulfur-containing silane to compare its role as a reagent for introducing sulfonic acid groups to that of TESPT.

The hydrothermal reaction of the synthetic mixtures was carried out at 90 °C for 48 h, followed by washing and filtering. The treatment of the filtered cakes with a mixture of hydrochloric acid (2 N) and methanol removed the surfactant molecules from the mesopores. The oxidation of the sulfide groups exposed on the pore walls with Br_2–HCl, followed by washing with methanol, produced MCM-41 mesoporous materials incorporating sulfonic acid groups. The mesoporous materials that were prepared are named as TESPT-x-MCM and MPTES-x-MCM: TESPT and MPTES denoted the sulfur containing silanes used in the preparation.

Fig. 1 shows the XRD patterns of the MCM-41 mesoporous materials incorporating sulfonic acid groups. The MCM-41 prepared from the synthetic mixture without a sulfur-containing silane showed a sharp diffraction peak which was attributed to the presence of highly ordered mesopores. The addition of TESPT up to x = 10 did not lower the intensity of the diffraction peak, but further increasing the content of TESPT caused a gradual decrease in the intensity of the diffraction peak. The TESPT-50-MCM catalyst obtained from the synthetic mixture with a large amount of TESPT showed a very small diffraction peak, indicating that too high a content of TESPT deteriorated the regularity of the mesopores. However, the diffraction peaks of TESPT-x-MCM catalysts were considerably higher than those of the corresponding MPTES-x-MCM catalysts prepared from the synthetic mixtures containing the same amount of MPTES. The TESPT-10-MCM



Scheme 1 Incorporation of –SO_3H into MCM-41 mesoporous materials using TESPT.

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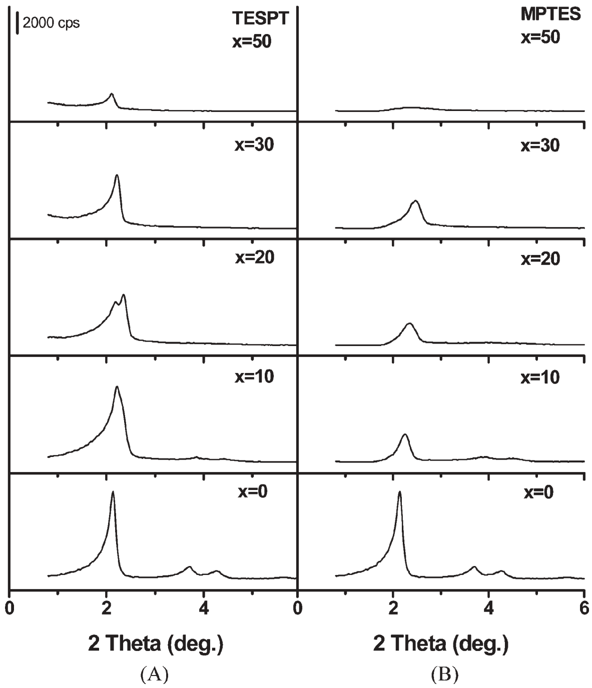
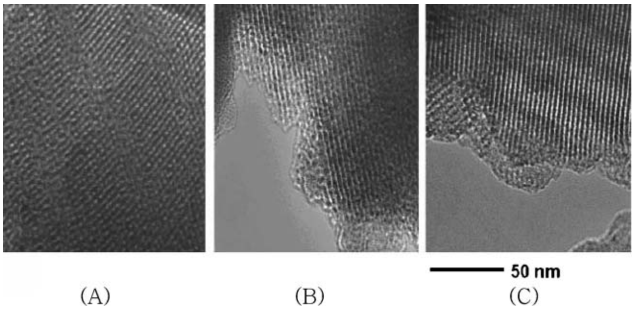


Fig. 1 XRD patterns of (A) TESPT-*x*-MCM and (B) MPTES-*x*-MCM catalysts.

showed a very high diffraction peak, but even the MPTES-10-MCM catalyst showed an extraordinarily small diffraction peak, indicating the poor regularities of mesopores in MPTES-*x*-MCM catalysts.

The regularities of mesopores on the TESPT-30-MCM and MPTES-10-MCM catalysts were compared from their TEM photos in Fig. 2. The TESPT-30-MCM with a large content of TESPT still showed highly ordered mesopores, but ordered mesopores were observed in the case of the MPTES-10-MCM catalyst. The regular arrangement of mesopores was not observed on the MPTES-30-MCM catalyst. Even though the addition of TESPT to the synthetic mixtures lowered the regularity of the mesopores, the mesoporous materials prepared using TESPT showed considerably higher regularity than those prepared using MPTES.

The high regularity of the mesoporous materials resulted in large amounts of nitrogen adsorption on them. As shown in Fig. S1 (see ESI†), the mesoporous materials prepared using either TESPT or MPTES showed clearly the presence of mesopores on their nitrogen adsorption isotherms when *x* did not exceed 30. The size of mesopores on the TESPT-*x*-MCM and MPTES-*x*-MCM were in the range of 2.5–3.2 nm, regardless of the content and species of silane.



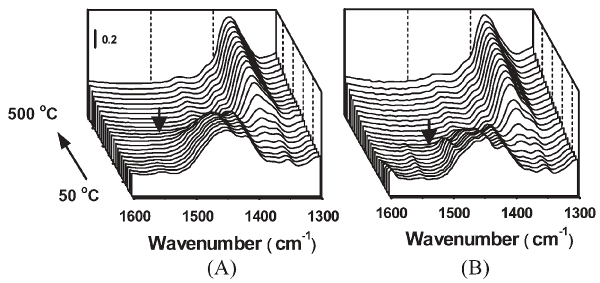
(A) (B) (C)

Fig. 2 TEM images of (A) TESPT-10-MCM, (B) TESPT-30-MCM, and (C) MPTES-10-MCM catalysts.

The chemical state of TESPT was not changed, even though it was incorporated into the mesoporous materials. Fig. S2 (see ESI†) shows ^{13}C NMR spectra of TESPT-20-MCM recorded before and after the oxidation of the polysulfide linkages with Br_2–HCl. These spectra very much resemble those obtained during the incorporation of sulfonic acid groups on mesoporous materials using disulfide linkages.[1] The complete disappearance of the peak at δ = 28.72 ppm showed the generation of sulfonic acid groups from polysulfide linkages.

The sulfonic acid groups incorporated on MCM-41 adsorbed ammonia and produced ammonium ions on them. Fig. 3 shows the IR spectra recorded during the desorption of ammonia from the TESPT-20-MCM and MPTES-20-MCM catalysts. The strong absorption band at 1446 cm^{-1} was attributed to ammonium ions produced on the sulfonic acid groups.[9] The desorption of ammonia at elevated temperatures regenerated the absorption band at 1377 cm^{-1} attributed to sulfonic acid groups. Ammonia molecules adsorbed on sulfonic acid groups incorporated on the TESPT-20-MCM catalyst were retained at 200 °C even under evacuation, indicating the presence of strong acid sites. The MPTES-20-MCM catalyst showed similar behavior regarding the desorption of ammonia, while the band at 1446 cm^{-1} was relatively small. Furthermore, the desorption of ammonia from the MPTES-20-MCM catalyst started at 70 °C, and this temperature was considerably lower compared to the start temperature of 120 °C for the TESPT-20-MCM. The bands at 1446 cm^{-1} in the case of the TESPT-*x*-MCM, which appeared after the adsorption of ammonia, were consistently larger than those on the corresponding MPTES-*x*-MCM catalysts. ^{29}Si MAS NMR spectra of the TESPT-30-MCM and MPTES-30-MCM also supported these results. As shown in Fig. S3 (see ESI†), the T peak of the TESPT-30-MCM was higher than that of the MPTES-30-MCM catalyst. This means that TESPT is more effective than MPTES in introducing sulfonic acid groups to MCM-41.

A high content of mesopores was strongly required to achieve high catalytic activities, because the large surface areas of the sulfonic acid-incorporated-MCM-41 were indispensable to incorporate large numbers of sulfonic acid groups on them. The amounts of sulfonic acid groups on the TESPT-*x*-MCM and MPTES-*x*-MCM catalysts were also limited by the amounts of TESPT and MPTES that were added, respectively. Therefore, large amounts of acid sites could be obtained on these catalysts



(A) (B)

Fig. 3 Desorption of ammonia from (A) TESPT-20-MCM and (B) MPTES-20-MCM catalysts.

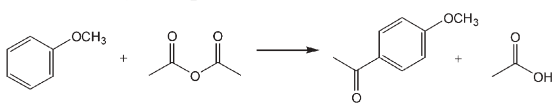
Table 1 Surface areas and amounts of acid sites of the TESPT-*x*-MCM and MPTES-*x*-MCM catalysts

Catalyst TESPT-*x*-MCM			Catalyst MPTES-*x*-MCM		
x	Surface area/m^2 g^{-1}	Amount of acid sites/mmol g^{-1}	*x*	Surface area/m^2 g^{-1}	Amount of acid sites/mmol g^{-1}
10	970	2.64	10	905	0.80
20	960	3.08	20	860	1.45
30	740	3.32	30	749	1.61
50	420	5.63	50	347	2.01
60	213	1.52			
80	24	1.50			

when the mesoporous materials prepared from the mixture of large amounts of TESPT or MPTES showed high regularity in the mesopores.

The amounts of active acid sites on the sulfonic acid-incorporated-MCM were determined from the decrease in pH of their aqueous slurries caused by the addition NaCl solution. The exchange of protons of the sulfonic acid groups with sodium ions was responsible for the decrease in pH. Table 1 lists the surface areas and amounts of acid sites in the sulfonic acid-incorporated-MCM catalysts. Increasing the amount of TESPT in the synthetic mixtures decreased the surface area of TESPT-*x*-MCM catalysts, while increasing the amounts of acid sites up to the TESPT-50-MCM catalyst. The same trends were also observed in MPTES-*x*-MCM catalysts, but their amounts of acid sites were considerably lower than those of TESPT-*x*-MCM catalysts.

The acetylation of anisole with acetic anhydride (eqn (1)) is a typical acid-catalyzed reaction. Various homogeneous and heterogeneous acids were reported to be active for the acetylation, but their activities and selectivities vary remarkably according to the catalysts employed.[5,10,11] Homogeneous acid catalysts such as $AlCl_3$ and $FeCl_3$ showed a high yield of the acetylated product of more than 90%. However, the generation of harmful chlorine gas and a large amount of waste water lower the feasibility of these catalysts for commercial applications.[12] The incorporation of 1,2,2-trifluoro-1-trifluoromethylethane sulfonic acid (Nafion) into mesoporous materials introduced extremely strong acid sites on them. Too strong acid sites, however, accelerated the formation of adducts between the ketone and anisole molecules, and thus, the yield of the acetylated product did not exceed 65%.[5]



(1)

The performance of TESPT-*x*-MCM and MPTES-*x*-MCM as catalysts in the acetylation of anisole was strongly dependent on the type of silane used for the incorporation of sulfonic acid groups, as shown in Table 2. The conversion on the TESPT-30-MCM catalyst, which was defined as the percentage of anisole consumed, was as high as 98%.[13,14] The yield of the acetylated product was also the highest (97.5%) over the TESPT-30-MCM catalyst, due to its exceptional selectivity for the acetylation. MPTES-*x*-MCM catalysts showed similar variations in the conversion and yield with the amount of MPTES added, but the conversions and yields were considerably lower than those obtained using the corresponding TESPT-*x*-MCM catalysts.

Table 2 Acetylation of anisole with acetic anhydride over TESPT-*x*-MCM and MPTES-*x*-MCM catalysts at 90 °C for 1 h

Catalyst TESPT-*x*-MCM			Catalyst MPTES-*x*-MCM		
x	Conversion (%)	Yield (%)	*x*	Conversion (%)	Yield (%)
10	62	62	10	31	31
20	71	71	20	50	49
30	98	98	30	52	51
50	88	81	50	68	65
60	75	73			
80	67	66			

A large amount of sulfonic acid groups with strong strength is essential to obtain high conversion and yield in the acetylation of anisole. The TESPT-*x*-MCM catalysts prepared using TESPT showed large surface areas and large amounts of acid sites compared to the corresponding MPTES-*x*-MCM catalysts. Although MPTES is a well-known material used for the introduction of sulfonic acid groups into mesoporous materials, TESPT, having tetrasulfide linkages, was more effective than MPTES, without inducing a significant loss in the regularity of the mesopores. The acid strength of the sulfonic acid groups in the TESPT-30-MCM catalyst was suitable to achieve an exceptional yield of the acetylation product. The 97.5% yield of the acetylated product obtained from anisole on the TESPT-30-MCM catalyst has not previously been reported even in the case of Nafion-incorporated solid acid,[5] sulfated zirconia,[15] and zeolite H-Beta.[16]

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