

# Single-step preparation and catalytic activity of mesoporous MCM-41 and SBA-15 silicas functionalized with perfluoroalkylsulfonic acid groups analogous to Nafion®

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Received (in Cambridge, UK) 17th December 2003, Accepted 18th February 2004

First published as an Advance Article on the web 11th March 2004

Preparation of hybrid organic–inorganic MCM-41 and SBA-15 silicas functionalized with perfluoroalkylsulfonic acid groups has been achieved in a single step by reacting the mesoporous silicas with 1,2,2-trifluoro-2-hydroxy-1-trifluoromethylethane sulfonic acid  $\beta$ -sultone; the catalysts showed higher activity than commercial Nafion®–silica composite for the esterification of long chain fatty acids with ethanol.

Synthesis of different types of hybrid organic–inorganic mesoporous silicas functionalized with alkylsulfonic acid groups has been reported in recent years.<sup>1–5</sup> These hybrid materials exhibited very high activity for many liquid-phase acid-catalyzed reactions including acid esterification,<sup>1,2</sup> aromatic alkylation,<sup>5</sup> and bisphenol-A synthesis,<sup>4</sup> for which acidic zeolites are not very active in solution. Covalent anchoring of the sulfonic acid functional groups onto the silica matrix by alkyl chain tethers has been achieved either by direct synthesis<sup>1–3</sup> or *via* post-synthetic grafting techniques.<sup>1,4</sup> In some cases, a final oxidation of thiol to sulfonic acid is required.<sup>1,4</sup> None of the precedents reported so far has reported perfluorinated sulfonic acid anchored to mesoporous silicas.

Solid acid catalysts containing perfluorinated sulfonic acid groups have been known for many years. Nafion® is one of the most versatile acid catalysts that contain terminal sulfonic acid groups attached to a perfluoro polymeric backbone.<sup>6,7</sup> The presence of electron-withdrawing F atoms in the structure increases significantly the acid strength of the terminal sulfonic acid groups which becomes comparable to that of pure sulfuric acid. However, the catalytic activity of the usual Nafion® preparations is far from optimum due to the low surface area of the polymeric catalyst. In order to overcome this, attempts have been made to support low polymer weight Nafion® on high surface area silica or other inorganic oxides.<sup>7–10</sup> Also co-gels of silica with partially depolymerized Nafion® were found to be able to catalyse different reactions occurring through carbocation intermediates.<sup>7</sup>

In this communication, we report for the first time the synthesis of hybrid organic–inorganic mesoporous materials with terminal perfluorinated sulfonic acid functional groups which are structurally analogous to Nafion®. Purely siliceous MCM-41 or SBA-15 silicas were functionalized with a suitable precursor, 1,2,2-trifluoro-2-hydroxy-1-trifluoromethylethane sulfonic acid sultone (**1**), to get sulfonic acid groups anchored to the silanol groups with perfluoroalkyl tethers (Scheme 1).<sup>†</sup> The cyclic precursor **1** reacts with the surface silanol groups of the mesoporous silicas by opening up the sultone ring and forming a covalent bond between the silica framework and the perfluoroalkyl chain with terminal sulfonic acid functional groups. The simplicity of this method consists in that in a single step the anchoring and the formation of

the sulfonic group is achieved, in contrast with precedents in which a rather inefficient thiol oxidation is needed after the anchoring.<sup>1,2,4</sup> The ratio of **1** to mesoporous silica during the synthesis can be varied over a wide range to get different loadings of perfluoroalkylsulfonic groups. Typically a 0.5–2 wt% loading of sulfur was obtained by altering the amounts of **1** in the treatment solution.

The amount of organic material present in the solids was determined by elemental analysis. For all samples the C/S atomic ratio was found to be very close to the theoretical value of 3. Thermogravimetric analysis (Mettler 851, heating rate 10 °C min<sup>-1</sup> in air stream) of the hybrid materials showed initial loss of weight up to 150 °C attributable to adsorbed water (~8 wt%) followed by a second step that extends up to 350 °C (~3 wt%). Notably the weight loss observed between 150 and 350 °C is relatively minor. This thermogravimetric profile contrasts with that observed for MCM-41 silica functionalized with *n*-propyl tethered sulfonic acid groups for which the loss of organics was almost complete in this temperature region.<sup>4</sup> To confirm the thermal stability of the perfluoroalkylsulfonic groups, TG-MS analyses (Perkin-Elmer TGA thermobalance coupled to a Fisons mass spectrometer) were carried out. Mass spectrometric data of the substance desorbed upon heating showed mostly desorption of adsorbed water in two different profiles up to 350 °C and the evolution of a minor amounts of SO<sub>2</sub> at about 350 °C. Fig. 1 shows a typical thermogravimetric-mass profile for one of the samples prepared.

The small angle X-ray diffraction patterns (Philips X'pert diffractometer, 40 kV, 35 mA) of the solids were very similar to those of the parent MCM-41 or SBA-15 silicas and indicate that under our reaction conditions the long range ordering was unaffected by the anchoring of perfluoroalkylsulfonic acid groups. The main reason to explain the stability of mesoporous silica to the preparation procedure is that according to Scheme 1 the sulfonic groups are only formed when covalent immobilization of the perfluorinated chain has occurred. However, care should be taken to avoid the presence of increasing amounts of free 1,2,2-trifluoro-2-hydroxy-1-trifluoromethylethane sulfonic acid since a partial damage of the mesoporous structure may then occur.

Nitrogen adsorption–desorption isotherms (Micromeritics ASAP 2000, 77K) of the hybrid solids were of Type IV according

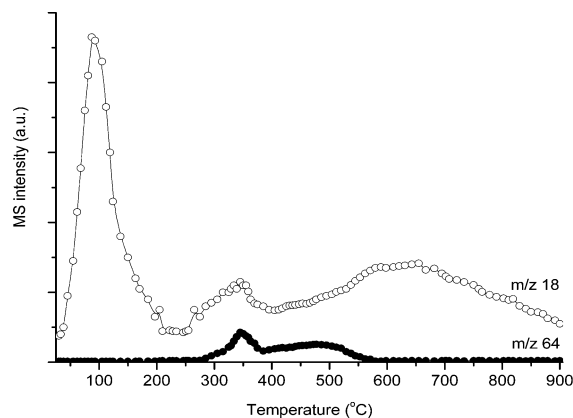
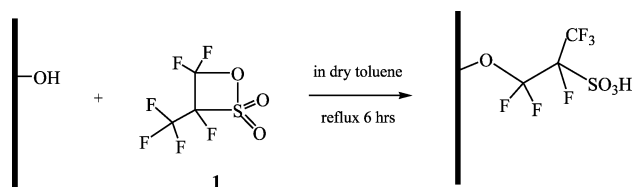


Fig. 1 MS signal intensity curves for selected *m/z* values of perfluorosulfonic MCM-41 sample.



Scheme 1

to the IUPAC nomenclature, which are typical for mesoporous materials. The BET surface area was found to decrease continuously with the loading of the organics. Pore size distribution measurements showed a slight decrease and broadening of the average pore diameter with the anchoring of the organics. Table 1 provides a summary of surface area and pore volume for some of the perfluoroalkylsulfonic acid containing MCM-41 and SBA-15.

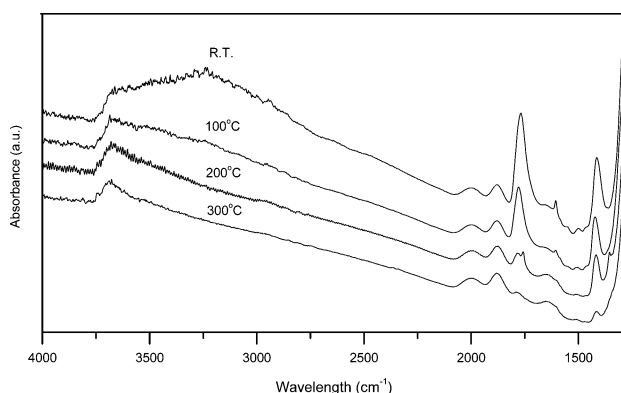
FT-IR spectra (Nicolet 710 FT-IR spectrophotometer) of self-supporting wafers of the solids were recorded at room temperature in sealed cells after degassing under vacuum at 200 or 300 °C for 1 h. Fig. 2 shows a typical example in which the presence of a band at 1420 cm<sup>-1</sup> characteristic of ν(S=O) stretching vibrations of undissociated -SO<sub>3</sub>H groups previously reported in Nafion® films and triflic acid can be observed.<sup>11</sup> The intensity of the band was significantly maintained with increasing degassing temperatures even up to 300 °C indicating strong binding of the perfluoroalkyl-sulfonic acid groups onto the surface of the mesoporous silicas and its thermal stability. Other bands observed at 1650 and 1760 cm<sup>-1</sup> were assigned according to the IR studies on Nafion® to the vibrations of absorbed and protonated water molecules, respectively.<sup>11</sup>

In a preliminary screening, the catalytic performance of the hybrid MCM-41 materials was determined for the esterification of alcohols with long chain aliphatic acid.† Blank reactions performed under identical conditions without any catalyst and also with pure siliceous MCM-41 showed negligible conversion of the acid. All the catalysts showed very high activity for the esterification of octanoic acid with ethanol (Table 1). Conversion of octanoic acid reached almost 95% in 6 h. Comparison under identical reaction conditions showed that the hybrid organic-inorganic mesoporous silica catalysts possess more than double activity than the commercial Nafion® silica composite (Nafion® SAC-13, Aldrich) and Nafion silica co-gels in spite of the much higher density of sulfonic groups of the latter catalysts. Per acid site the turnover

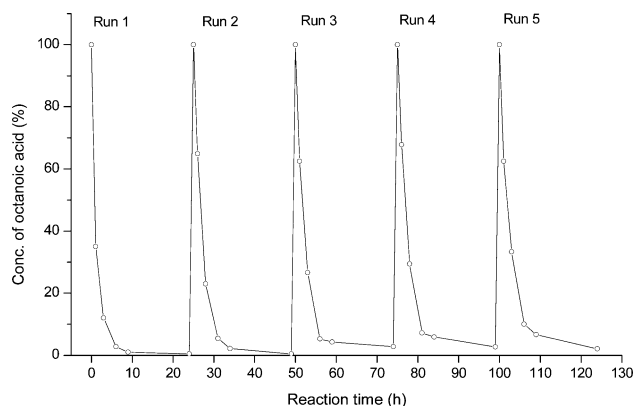
**Table 1** Physical properties and catalytic activity of the catalysts in the esterification of octanoic acid with ethanol

Sample	Amount of <b>1</b> per g of solid	S content/ mmol g <sup>-1</sup>	S <sub>BET</sub> / m <sup>2</sup> g <sup>-1</sup>	C <sub>8</sub> acid conversion <sup>a</sup> (%)
MCM-41	—	—	1030	< 1.0
MFS-10 (MCM)	0.5	0.16	912	34.7
MFS-1 (MCM)	1.5	0.45	680	88.0
SFS-2 (SBA)	1.0	0.25	820	63.8
SFS-1 (SBA)	1.5	0.51	780	87.1
Nafion-SiO <sub>2</sub> gel	—	29% <sup>b</sup>	77	57.7
SAC-13	—	10–20% <sup>b</sup>	200 <sup>c</sup>	37.3

<sup>a</sup> At 3 h. <sup>b</sup> Amount of Nafion® loadings. <sup>c</sup> From manufacturer's data. Reaction temp 60 °C. Ethanol/acid (mol. ratio) 105. Catalyst wt 100 mg.



**Fig. 2** FT-IR spectra of perfluorosulfonic MCM-41 sample at different treatment temperatures.



**Fig. 3** Esterification of octanoic acid with ethanol at 60 °C in the presence of MCM-41 containing perfluorosulfonic acid groups for 5 consecutive runs.

frequency of sulfonic acid groups anchored on MCM-41 ( $9.7 \times 10^{-3} \text{ s}^{-1}$ ) is one order of magnitude higher than that of commercial Nafion® silica ( $1.1 \times 10^{-3} \text{ s}^{-1}$ ) composites.

To check the reusability of the catalysts fresh reactants (0.15 g acid and 1.0 g ethanol) were added after 24 h reaction and the progress of the reaction was monitored by taking small aliquots of samples at different time intervals. Fig. 3 shows the results for 5 successive runs. It can be seen that the catalyst converts almost 90% of the acid in less than 6 h for 5 consecutive runs. Alternatively, if the solid catalyst was filtered after each run, washed with CH<sub>2</sub>Cl<sub>2</sub>, dried and reused, an approximately 25–35% decrease in activity was observed between the 1<sup>st</sup> and 2<sup>nd</sup> use but then it remains fairly constant for consecutive runs.

Thus, we have developed a single-step method of preparing hybrid organic-inorganic mesoporous silica catalysts functionalized with terminal perfluorosulfonic acid groups for which no oxidation step is required. The catalysts analogous to Nafion® with completely fluorinated tethers showed very high activity and can be reused repeatedly without any observed loss of activity.

## Notes and references

† Calcined MCM-41 or SBA-15 (2.0 g) was evacuated at 120 °C for 8 hours, cooled to room temperature and to this added a solution of **1** (1.0 g) in 50 ml dry toluene. The mixture was refluxed for 4 hours, the solid was filtered and washed thoroughly with toluene and finally dried at 100 °C overnight.

‡ 5 g of ethanol and 150 mg of octanoic acid were heated in a three-necked flask at 60 °C and then 100 mg of the catalyst was added. Samples were collected at different time intervals and analysed by gas chromatography (HP5890, HP-5 column).

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