# Novel mesoporous silica–perfluorosulfonic acid hybrids as strong heterogeneous Brønsted catalysts

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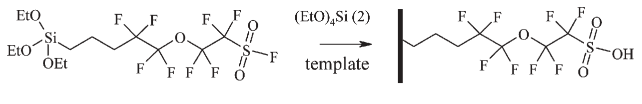
**Perfluorinated sulfonic acids have been immobilised into mesoporous silica frameworks by a one-step process, representing the first example of the successful incorporation of charged silanes using this route, and have been shown to be excellent catalysts for Brønsted acid catalysed transformations.**

The development of strongly Brønsted acidic solids with controlled mesostructures is an area of significant interest in catalysis. Micelle templated sol-gel routes to such materials have been shown to be effective and several mesostructured silicas containing framework alkyl- and aryl-sulfonic acids have been prepared, usually from the thiol with oxidation either during synthesis,[1] or after template extraction.[2,3] Oxidation during extraction, while attractive, often leads to degradation of the template, and a direct, non-oxidative route to the acids would be beneficial. Such routes have been demonstrated for arene sulfonic acids[4,5] but the products are water-sensitive and undergo desulfonylation readily. A further route to strong heterogeneous Brønsted acids consists of the formation of Nafion-H® silica composites,[6–8] which, due to the perfluorinated nature of the organics, are stronger acids than the hydrocarbon based materials. However, they suffer from limited availability of the acid groups due to the imperfect dispersion of the resin within the silica pores. We now present preliminary results relating to the non-oxidative direct synthesis and application of mesoporous silica–perfluorosulfonic acid materials, combining the acidity of Nafion with the excellent dispersion available with sol-gel templated synthesis.

The materials were prepared using the silane **1** and tetraethoxysilane (TEOS, **2**) using the sol-gel co-condensation route first described by one of us (Fig. 1)†.[9,10] Using a molar ratio of **1** : **2** of 0.02 : 0.98 gave a well-ordered material **3** with complete incorporation of both silanes and a sulfonic acid loading of 0.2 mmol $g^{-1}$ (Fig. 1). Monitoring the progress of the reaction by $^{19}$F MAS NMR spectroscopy indicated that the S–F bond cleaves during synthesis such that the as-synthesised product, before template extraction, consists of $RNH_3^+$ $^-O_3SR'$ ion pairs (and presumably also $RNH_3^+F^-$ pairs). Exhaustive acid extraction of the template (0.1 M $H_2SO_4$ in 50 : 50 aqueous ethanol) leads to the sulfonic acid product directly. Interestingly, addition of (trimethoxy)propylsilane **4** in a molar ratio **1** : **2** : **4** of 0.02 : 0.98 : 0.1 led to material **5** with a narrower framework pore size distribution, although in addition to the framework pores *ca.* 10% of the pore volume resides in a small amount of textural pores not present in **3**. In both cases $^{19}$F MAS NMR demonstrated the incorporation of the perfluorinated chain, and indicated that the S–F bond was completely cleaved. As can be seen from the porosimetry data (Table 1 and Fig. 2) both materials are templated, although the silanes utilised, being hydrophobic, partition into the micelle palisade layer, keeping the fluorinated segments away from the solvent, leading to reduced pore diameters compared to most other organic–inorganic hybrids prepared by this route.



1 3

**Fig. 1** Synthesis of mesoporous fluorinated sulfonic acids.

The presence of charged template molecules (with bulky sulfonate counterions) is likely also to increase the head group size, and thus reduce the pore diameter. Importantly, both materials have narrow pore size distributions, the uniformity of the framework pores being significantly enhanced in **5**. To the best of our knowledge, these materials are the first examples of the successful incorporation of charged silanes using the neutral

**Table 1** Summary of porosimetry data for **3** and **5** ($V_{fr}$ and $V_{tex}$ refer to the volume of pores derived from the micelle templating mechanism and from the larger, non-templeted pores ($p/p_o \leqslant 0.5$ and $p/p_o \geqslant 0.8$) respectively).

| | $V_{fr}$/ $cm^3$ $g^{-1}$ | $V_{tex}$/ $cm^3$ $g^{-1}$ | Pore diameter/nm | Specific surface area/$m^2$ $g^{-1}$ |
|---|---|---|---|---|
| **3** | 0.485 | 0.015 | 2.5 | 885 |
| **5** | 0.425 | 0.035 | 2.6 | 860 |

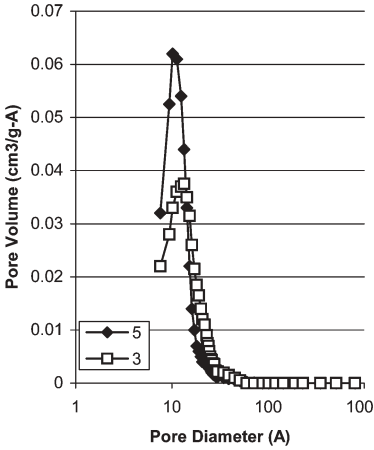


**Fig. 2** Pore size distributions for materials **3** and **5**

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templating method.[11] The increased uniformity induced by the addition of a third silane into the synthesis gel is also unprecedented.

The solid acids synthesised by this route were then tested in important acid catalysed reaction types to probe activity. The Friedel–Crafts acylation of anisole is an important example of such a reaction, where the relatively activated aromatic nucleus means that selectivity is the key goal. Thus, anisole (5 g) was reacted with benzoyl chloride (0.5 g) with 0.1 g of **3** (molar ratio 13 : 1 : 0.0056) in the absence of solvent. The same reaction was repeated with **5** in the same proportions. Conversions are given in Fig. 3a and isomer ratios for **5** at 100 °C are shown in Fig. 3b. After relatively rapid initial conversion to a mixture containing predominantly the *ortho* isomer, a slower conversion takes place, where more acylation occurs, but slowly, and the major process is the conversion of *ortho*- to *para*-benzoyl anisole. Separate experiments with a mixture of *ortho*- and *para*-benzoyl anisole and with a mixture of *ortho*-benzoyl anisole and anisole indicate that this reaction is not a unimolecular isomerisation, but rather a transacylation between *ortho*-benzoyl anisole and anisole. What is also clear is that the propyl-containing material **5** gives a much more rapid reaction than **3**, consistent with the accelerating effects seen in previous catalytic systems containing hydrophobic groups,[12–14] and that **5** leads to the most complete isomerisation (62.5 : 1 *p* : *o*). These groups are considered to improve activity by reducing the polarity of the surface, aiding adsorption/desorption kinetics and thus speeding up reactions. Melero *et al.* have recently reported the related acetylation of anisole (using acetic anhydride and a mesoporous silica–arene sulfonic acid) and they found that the *para* isomer predominated, even at the lower conversions achieved in their system.[15] Thus, the catalysts described here are capable of rapid acylation of anisole, but are also capable of providing high selectivity to *ortho* (at low conversions) or high selectivity to *para* (at high conversions) isomers.

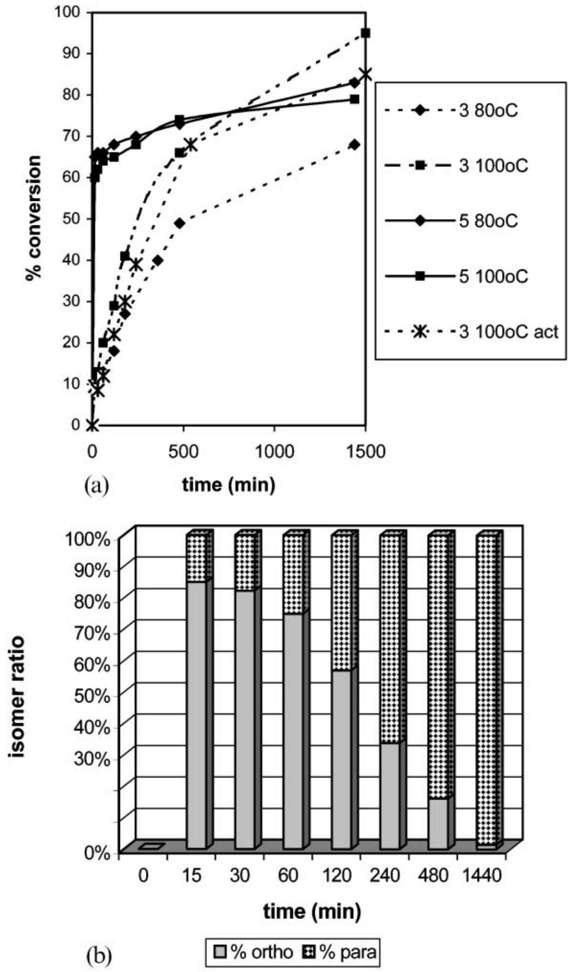
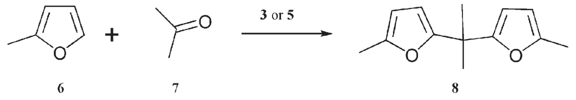


**Fig. 3** (a) Upper conversion *vs.* time for the benzoylation of anisole. 100 °C act refers to a catalyst pre-treated at 100 °C before reaction, other catalysts were used directly from the jar; (b) isomer ratio at different levels of conversion for **5** at 100 °C.

**Table 2** Formation of bis-furyl-propane using catalysts **3** and **5** in comparison with literature precedents (all reactions carried out under identical conditions; TON defined as mol product/mol active site)



| Catalyst | Time/ h | Yield (%) | Selectivity (%) | **6** : Catalyst | TON |
|---|---|---|---|---|---|
| **3** | 24 | 73 | 97 | 340 | 241 |
| **5** | 6 | 86 | 98 | 340 | 292 |
| HMS-propyl$SO_3H$[a] | 24 | 73 | 95 | $\leqslant 55$[b] | $\leqslant 40$[b] |
| MCM-41-propyl$SO_3H$[a,c] | 24 | 57 | 92 | $\leqslant 55$[b] | $\leqslant 31$[b] |
| MCM-41-propyl$SO_3H$[a,d] | 24 | 85 | 96 | $\leqslant 55$[b] | $\leqslant 47$[b] |

[a] Ref. 2. [b] Based on a 1mmol $g^{-1}$ loading of acid groups, the lowest in the range quoted in ref. 2. [c] Catalyst silylated. [d] Catalyst prepared by coating.

By contrast, Friedel–Crafts alkylation of toluene with alkenes (1-hexene or 1-dodecene) failed to give more than traces of alkylation product, although alkene isomerisation and oligomerisation were evident.

The reaction between 2-methylfuran **6** and acetone **7** to give the bis-furan **8** (Table 2) is a useful model for macromolecular chemistry, and has been investigated with success using solid sulfonic acids.[2] We have investigated this reaction using **3** and **5** and found that **5** gives exceptional results both in terms of conversion and selectivity compared to other systems. Reaction of **6**, **7** and catalyst (molar ratios 340 : 850 : 1) in refluxing acetone for 24 h led to a 73% yield (97% selectivity) with **3**, comparable to results in the literature (entry 3), but with less than 15% of the amount of catalyst. With **5** the rate and yield were again substantially increased, with a yield of 86% (selectivity 97%) obtained after only 6 h, and again with a much lower amount of catalyst.

In conclusion, we demonstrate the synthesis of novel well structured fluorinated solid acids using neutral templating with charged silanes. The resultant materials are excellent catalysts for two electrophilic aromatic substitution reactions.

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## Notes and references

† **1** and **2** (0.002 moles and 0.098 moles respectively) were stirred in a solution of 40 ml water, 60 ml ethanol and 5.1 g *n*-dodecylamine at 20 °C for 18 h. After filtration, $^{19}$F MAS NMR indicates the retention of peaks at $\delta$ −117, −88 and −83 ppm, corresponding to the four chain environments (solution phase NMR of the silane: $\delta$ −120, −116, −87, −83 and +44 ($SO_2F$) ppm) but loss of the +44 ppm resonance of the $SO_2F$. Removal of template using 1 M $H_2SO_4$ gave the final products.

1 D. Margolese, J. A. Melero, S. C. Christiansen, B. F. Chmelka and G. D. Stucky, *Chem. Mater.*, 2000, **12**, 2448.

2 W. M. Van Rhijn, D. E. De Vos, B. F. Sels, W. D. Bossaert, P. J. Grobet and P. A. Jacobs, *Chem. Commun.*, 1998, 317.

3 M. H. Lim, C. F. Blanford and A. Stein, *Chem. Mater.*, 1998, **10**, 467.

4 J. A. Melero, G. D. Stucky, R. van Grieken and G. Morales, *J. Mater. Chem.*, 2002, **12**, 1664.

5 F. Mohino, I. Diaz, J. Perez-Pariente and E. Sastre, *Stud. Surf. Sci. Catal.*, 2002, **142**, 1275.

6 M. A. Harmer, W. E. Farneth and Q. Sun, *J. Am. Chem. Soc.*, 1996, **118**, 7708.

7 M. A. Harmer, W. E. Farneth and Q. Sun, *Adv. Mater.*, 1998, **10**, 1255.

8 M. A. Harmer, Q. Sun, A. J. Vega, W. E. Farneth, A. Heidekum and W. F. Hölderich, *Green Chem.*, 2000, **2**, 7.

9 D. J. Macquarrie, *Chem. Commun.*, 1996, 1961.

10 D. J. Macquarrie, J. E. G. Mdoe, D. B. Jackson and J. H. Clark, *New. J. Chem.*, 1999, **23**, 539.

11 R. J. P. Corriu, A. Mehdi and C. Reyé, *C. R. Acad. Sci., Ser. IIc: Chim.*, 1999, 35.

12 I. Díaz, F. M. Márquez-Alvarez, J. Pérez-Pariente and E. Sastre, *J. Catal.*, 2000, **193**, 283.

13 I. Díaz, F. M. Márquez-Alvarez, J. Pérez-Pariente and E. Sastre, *J. Catal.*, 2000, **193**, 295.

14 D. J. Macquarrie, *Green Chem.*, 1999, **1**, 195.

15 J. A. Melero, R. van Grieken, G. Morales and V. Nuno, *Catal. Commun.*, 2004, **5**, 131.