

# Covalently linked ethylmercaptophenyl sulfonic acid and ethylmercaptobenzyl sulfonic acid silica materials—Synthesis and catalytic activity

Amanmamet Bugrayev<sup>a</sup>, Nazli Al-Haq<sup>a</sup>, Rukeme A. Okopie<sup>a</sup>, Asma Qazi<sup>a</sup>,  
Michael Suggate<sup>b</sup>, Alice C. Sullivan<sup>a,\*</sup>, John R.H. Wilson<sup>b</sup>

<sup>a</sup> Department of Chemistry, Queen Mary, University of London, Mile End Road,  
London, E1 4NS, UK

<sup>b</sup> PhosphonicS Ltd., 114 Milton Park, Oxford, OX14 4SA, UK

Received 14 October 2007; accepted 23 October 2007

Available online 30 October 2007

## Abstract

New covalently linked sulfonic acid modified silicas have been formed and characterised and their catalytic Brønsted activity evaluated. Thus phenylmercaptoethyltrimethoxysilane,  $(\text{MeO})_3\text{SiCH}_2\text{CH}_2\text{SC}_6\text{H}_5$  and benzylmercaptoethyltrimethoxysilane,  $(\text{MeO})_3\text{SiCH}_2\text{CH}_2\text{SCH}_2\text{C}_6\text{H}_5$ , were used to prepare the corresponding T-functional silica derivatives silica  $\sim\text{CH}_2\text{CH}_2\text{SC}_6\text{H}_4\text{-4-SO}_3\text{H}$  and silica  $\sim\text{CH}_2\text{CH}_2\text{SCH}_2\text{C}_6\text{H}_4\text{-4-SO}_3\text{H}$  by grafting on commercial silica, followed by sulfonation of the aryl group. Solid-state NMR, DTA and surface area characteristics of the materials are reported. The mercaptophenylsulfonic acid materials are thermally robust highly efficient solid catalysts for a range of transformations including, esterification, etherification and carbonyl group protection. An apparent pore size effect on rate of conversion was observed. The mercaptobenzylsulfonic acid materials were comparatively unstable.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** Sulfonic acid; Silica; Solid acid; Catalyst; Ethylmercaptophenylsulfonic acid; Esterification; Etherification; Carbonyl group protection; Condensation

## 1. Introduction

There is considerable interest in covalently linked sulfonic acid modified silicas owing in part to their application in solid acid catalysis of liquid phase reactions. Silica supports offer benefits of mechanical, thermal and chemical stability in addition to facilitating substrate transport (wide pore silicas) and offering broad solvent compatibility. A driving force for much of the work in this area is focused on the need for thermally robust solid acid catalysts for liquid phase organic transformations on relatively large molecules. Immobilised sulfonic acid functionality may be introduced starting from mercaptoalkyltrialkoxysilane compounds with subsequent oxidation of the immobilised mercapto group. An

alternative option is to start from arylalkyltrialkoxysilanes introducing the sulfonic group by sulfonation of the immobilised aryl group [1,2]. The latter route gives materials with higher acid strength and higher conversions to sulfonic acid in the post-modification step [2]. In pursuit of catalysts with greater acid strength, silica perfluoroalkylsulfonic acids have also been reported [3,4]. Numerous catalytic studies utilising these materials have been reported some of which deal with important esterification chemistry relevant to bio-diesel or emulsifier synthesis [5]. Other studies have variously focussed on carbon–carbon bond forming chemistries such as condensations [6] or protecting group chemistries [7]. We report here on new silica immobilised ethylmercaptophenyl and benzyl sulfonic acids of the type silica  $\sim\text{CH}_2\text{CH}_2\text{SC}_6\text{H}_4\text{-4-SO}_3\text{H}$  and silica  $\sim\text{CH}_2\text{CH}_2\text{SCH}_2\text{C}_6\text{H}_4\text{-4-SO}_3\text{H}$  and initial results on their performance as solid acid catalysts in reactions covering esterification, condensation, and carbonyl group protection. The position of the sulfur atom in the linker chain has a marked

\* Corresponding author.

E-mail address: [a.c.sullivan@qmul.ac.uk](mailto:a.c.sullivan@qmul.ac.uk) (A.C. Sullivan).

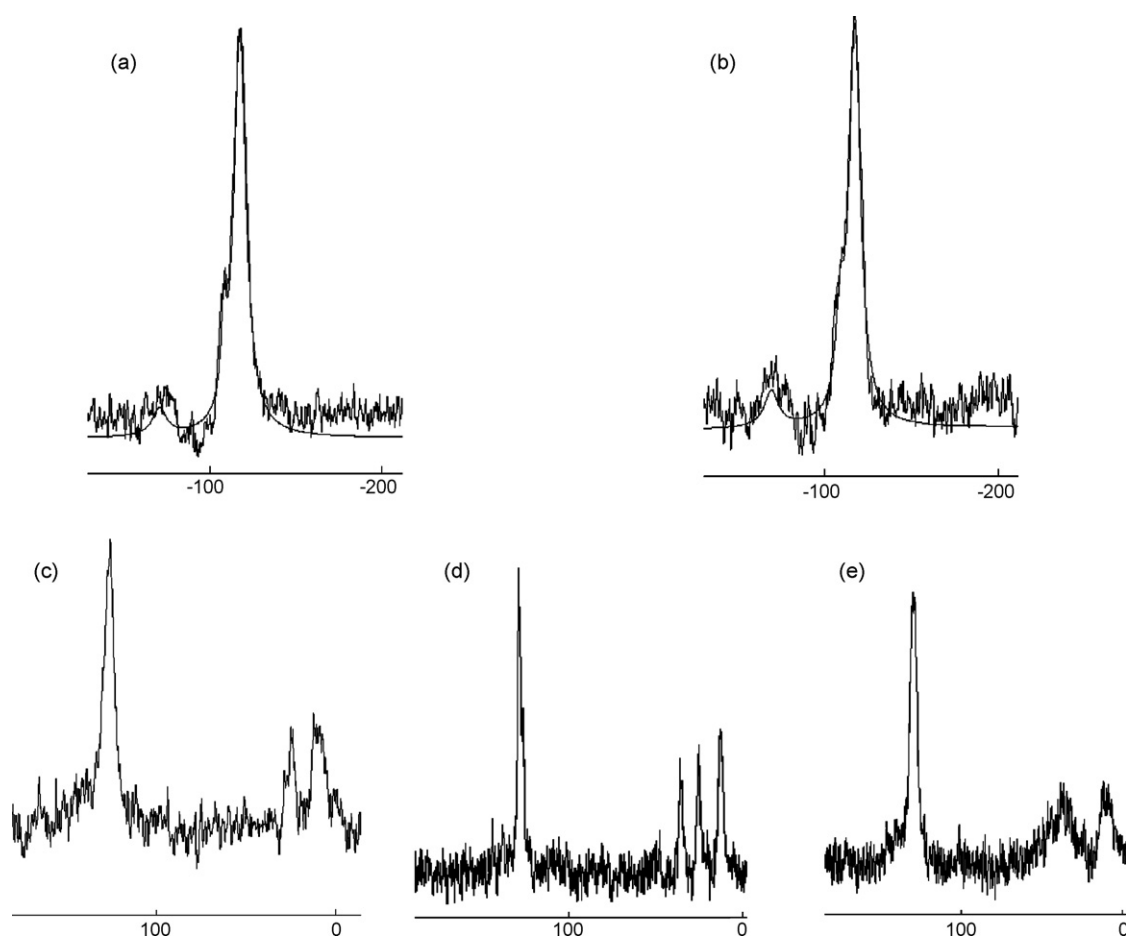
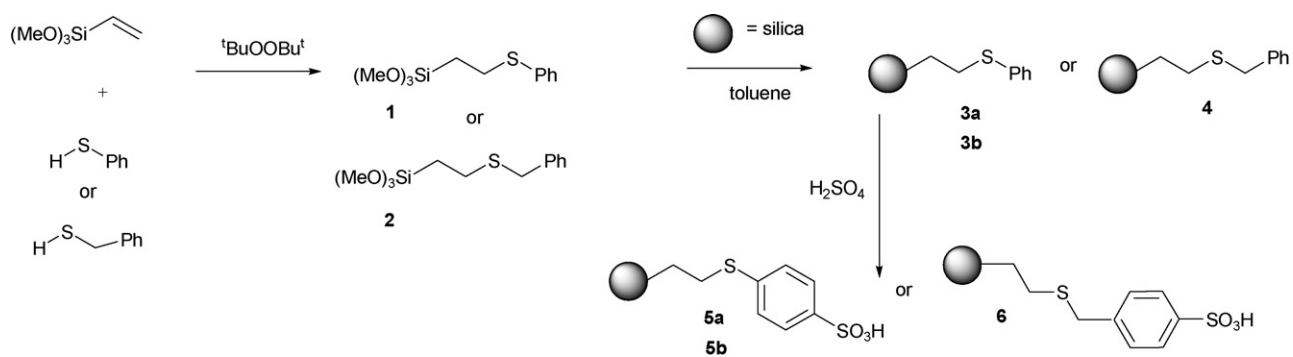


Fig. 1. (a) Fitted  $^{29}\text{Si}$  MAS NMR **5b**, (b) Fitted  $^{29}\text{Si}$  MAS NMR **6**, (c)  $^{13}\text{C}$  CPMAS NMR **5a**, (d)  $^{13}\text{C}$  CPMAS NMR **4**, (e)  $^{13}\text{C}$  CPMAS NMR **6**.

Table 1  
Key parameters of **5a**, **5b** and **6**

Material	Surface area ( $\text{m}^2/\text{g}$ )	$^{\text{a}}\text{SO}_3\text{H}$ loading ( $\text{mmol g}^{-1}$ )	$^{\text{b}}(\%)$ Sulfonation of aryl precursors
<b>5a</b>	165	0.7	69 ( <b>3a</b> )
<b>5b</b>	358	0.7	99 ( <b>3b</b> )
<b>6</b>	206	0.5	56 ( <b>4</b> )

<sup>a</sup> Values from titration with base.

<sup>b</sup> Values obtained by comparison of  $[\text{H}^+]$  mmol/g and  $[\text{S}]$  mmol/g.

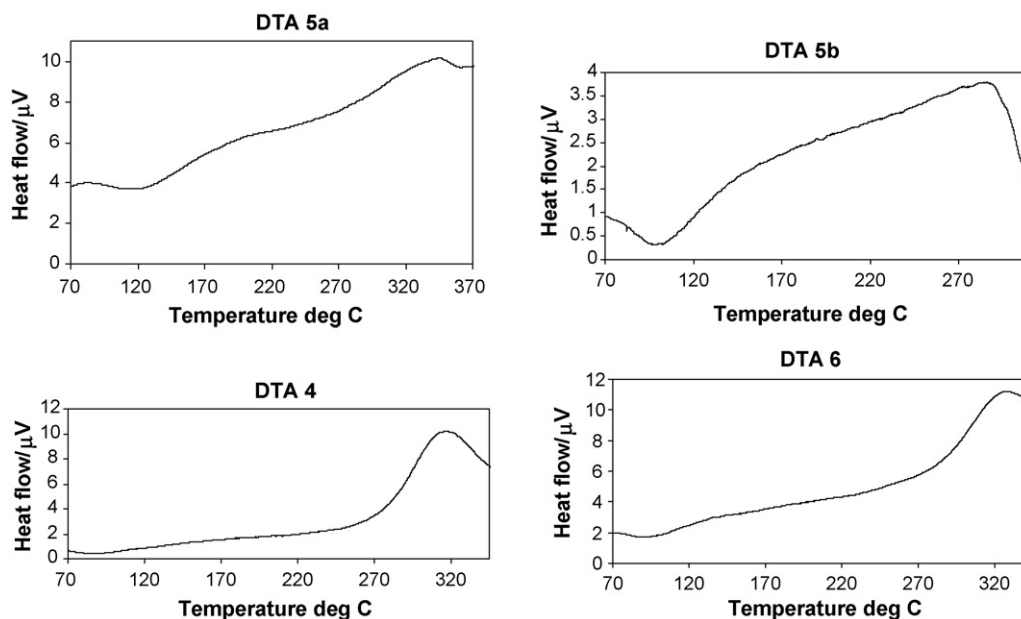


Fig. 2. DTA (in ambient air) profiles (a) **5a**, (b) **5b** and (c) **4** and (d) **6**.

effect on the stability of the function and our results show that the ethylmercaptophenylsulfonic acid system is an excellent Brønsted acid catalyst.

## 2. Results and discussion

### 2.1. Materials synthesis

The new sulfonic acid modified silicas are derived from the compounds  $(\text{MeO})_3\text{SiCH}_2\text{CH}_2\text{SC}_6\text{H}_4$  **1** and  $(\text{MeO})_3\text{SiCH}_2\text{CH}_2\text{SCH}_2\text{C}_6\text{H}_4$  **2** which are readily obtained by addition of the mercaptobenzene or mercaptobenzyl compounds to vinyl trimethoxy silane as previously described [8,9]. The ethylmercaptophenyl- or ethylmercaptobenzyl silica materials, silica  $\sim\text{CH}_2\text{CH}_2\text{SC}_6\text{H}_5/\text{CH}_2\text{C}_6\text{H}_5$  are formed from the trimethoxysilyl compounds using sol-gel or grafting methods. The work herein is focused on materials derived from the latter route. Thus materials **3a** and **3b** were produced from **1** and commercial silicas with mesopore diameters of 60 and 150 Å respectively while material **4** was produced from **2** and the wider 150 Å pore silica. Sulfonation was achieved using sulfuric acid to give materials **5a**, **5b** and **6** (see Scheme 1).

The presence of the functional groups was confirmed by solid state  $^{29}\text{Si}$  NMR (both T and Q Si environments seen) and  $^{13}\text{C}$  NMR (resonances due the alkyl and aryl carbon environments seen). Examples of solid-state spectra are shown in Fig. 1. Data are summarised in Table 1. For the materials used in the study reported here, comparison between the loading of sulfonated functionality, determined by titration and total sulfur indicated that the % of T sites sulfonated in each case was 69% **5a**, 99% **5b** and 56% **6**. Subsequent optimisation of the sulfonation process (see experimental) routinely affords >95% conversion. The measured surface area of the wider pore grafted material **5b** from 150 Å silica was significantly higher than that of material **5a** from 60 Å silica.

For **5a** and **5b** the  $^{13}\text{C}$  CPMAS spectra showed strong broad single peaks due to the phenyl carbons and broad peaks due to the linking ethyl carbons Fig. 1(c). The aryl, benzylic and ethyl linker carbons appear as sharp singlets in **4** but the resonances due to the benzylic and ethyl carbons merge into a broad multiplet in **6** suggesting multiple benzylic environments are present following sulfonation (Fig. 1(d and e)).

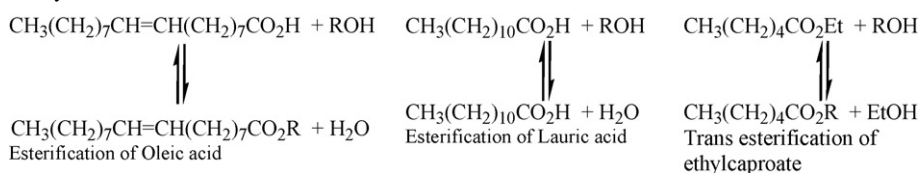
The DTAs of the three materials stored in air prior to analysis, were recorded in an atmosphere of ambient air and show endothermic loss of water at 100  $^{\circ}\text{C}$  (Fig. 2). Further endothermic processes begin at 350  $^{\circ}\text{C}$  for **5a** and 280  $^{\circ}\text{C}$  for **5b**. These events are likely to include endothermic oxidative decomposition of the immobilised sulfonic acids. It is interesting that the decomposition starts at a lower temperature for the wider pore material. For material **6** in contrast, there is exothermic oxidative decomposition which begins at 280  $^{\circ}\text{C}$ . The difference in the enthalpy change between **5b** and **6** reflects the relative thermal/oxidative stabilities of the mercaptobenzyl and mercaptophenyl bonds in these arene sulfonic acid materials and the latter is obviously more stable. The stability difference was also observed in the catalytic studies undertaken.

### 2.2. Catalytic studies

The materials **5a**, **5b** and **6** were evaluated as catalysts in reactions typically catalysed by protic acids. In the first set of experiments esterification of fatty acids was investigated. The studies provided useful comparative data on pore diameter effect, specifically between 60 Å, **5a** and 150 Å, **5b** as well as effect of linker to the sulfonic group, specifically **5b** versus **6**. The results are summarised in Table 2. The reactions typically employed 5 mmol of fatty acid and 0.1 g of catalyst (equivalent to 1.4 mol % acid **5a**, **5b**, and 1 mol % acid **6**). Esterification of oleic acid with methanol, ethanol and butanol proceeded cleanly to completion for all three catalysts in 6–8 h for **5a** and **5b** while **6**

Table 2

Catalytic esterification and transesterification



Entry	Catalyst	Temperature (°C) Time (h)	–1 (%)	–2 (%)	–3 (%)
A-Oleic acid and methanol	<b>5a</b> <sup>a</sup>	64(8)	99	99	99
	<b>5b</b> <sup>b</sup>	64(8)	99	99	99
	<b>6</b> <sup>c</sup>	64(6)	96		
	Blank	64(7)	4%		
B-Oleic acid and ethanol	<b>5a</b>	80(8)	99	99	99 <sup>d</sup>
	<b>5b</b>	80(8)	99	99	
	<b>6</b>	80(8)	80	41	
	Blank	64(8)	4		
B-Oleic acid and butanol	<b>5a</b>	118(9)	98	–	–
	<b>5b</b>	118(8)	99	99	
	Blank				
C-Lauric acid and methano	<b>5a</b>	65(6)	99	–	–
	<b>5b</b>	64(6)	99		
	Blank				
D-Lauric acid and ethanol	<b>5a</b>	80(7)	99	99	99
	<b>5b</b>	80(7)	99	99	
	Blank				
E-Lauric acid and butanol	<b>5a</b>	118(9)	98	–	–
	<b>5b</b>	118(7)	99		
	Blank				
F-Ethyl caproate and butanol	<b>5a</b>	118(10)	97	–	–
	<b>5b</b>	118(10)	98		
	Blank				
G-Ethyl caproate and pentanol	<b>5a</b>	118(10)	98	97	–
	<b>5b</b>	118(9)	99		
	Blank				

<sup>a</sup> Leaching test: 1 h contact with catalyst then hot filtration; conversion at 1 h 14 % and at plus 5 h in filtrate 15%.

<sup>b</sup> Leaching test: 1 h 47%, plus 5 h 47%.

<sup>c</sup> Leaching test: 1 h 50%, plus 5 h 62%.

<sup>d</sup> Recycled 11 times without loss.

took noticeably longer to reach completion in each case. A similar trend was seen with esterification of lauric acid and trans esterification of ethylcaproate. The phenylsulfonic acid catalysts showed similar activity while the benzyl sulfonic catalyst appeared less active than both. The catalyst **5a** was recycled for ethyl oleate formation eleven times without loss in activity. The catalyst **5b** was also recycled several times without loss in a number of cases. **6** on the other hand showed decreasing levels of activity on recycle. Leaching tests were performed using formation of methyl oleate as the test example. The reaction mixtures were filtered hot after 1 h and the reaction was allowed to proceed without catalyst for a further 5 h. No further conversion was seen for the mercaptophenylsulfonic catalysts **5a** and **5b** but filtered solutions from the mercaptobenzylsulfonic acid showed further conversion. This implied some leaching or decomposition of **6**. Indeed **6** was less active in the formation of methyl oleate when the catalyst was pre-treated by stirring in refluxing MeOH for several hours, filtering and drying before use

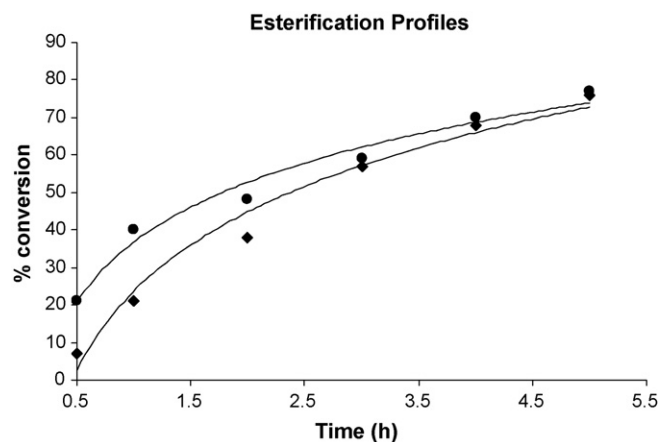
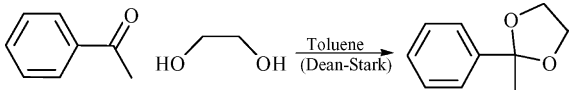
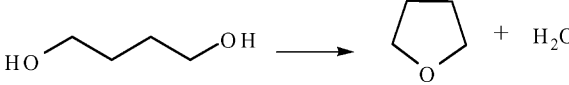
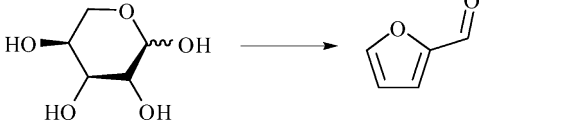
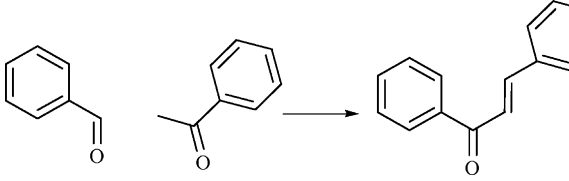


Fig. 3. Reaction profiles for the esterification of oleic acid with ethanol using **5a** (diamond) and **5b** (sphere).

Table 3  
Catalytic carbonyl protection and etherification

Entry		Catalyst	°C (hours)	(%)
H-Ketalisation of acetophenone		<b>5a</b>	110(7)	99 <sup>a</sup>
I-Etherification		<b>5a/5b</b>	120(7)	99 <sup>b</sup>
J-Dehydration of D-Xylose		<b>5b</b>	140(24)	99
L-Aldol condensation		<b>5a</b>	110(24)	51
		<b>5b</b>	110(24)	95

<sup>a</sup> The catalyst was recycled three times without loss.

<sup>b</sup> The diol was replenished five times.

(conversion was 9% after 1 h compared to 50% for the untreated material). The presence of aryl proton signals in the proton NMR of the evaporated MeOH washings confirmed that decomposition of the immobilised functional group had occurred. When pre-treated and assessed in a similar fashion neither **5a** nor **5b** showed evidence of decomposition.

The esterification of oleic acid with ethanol using **5a** and **5b** was examined more closely. A kinetic effect was observed in the early stages of the process was observed (Fig. 3). The wider pore material **5b** converted at roughly three times the rate of **5a** during the first hour. The catalysts had the same acid loading but **5a** had additional non-sulfonated aryl T-functions ~0.3 mmol/g. The rate of conversion in **5b** slowed after the first hour leading to similar conversions for both **5a** and **5b** by the fourth hour.

This suggests that transport to the active site is more efficient for the wider pore material in the early stages of the reaction but this apparent pore size benefit disappears in the latter stages presumably as the pore environment becomes saturated with product. Materials **5a** and **5b** proved to be active catalysts for carbonyl group protection and cyclic ether formation (Table 3). For transformations with more significant steric demand such as aldol condensation, the wider pore material **5b** appeared to be more efficient.

### 3. Conclusions

The new silica immobilised ethylmercaptophenyl sulfonic acid materials described in this paper displayed excellent and recyclable solid acid catalytic activity without leaching. The analogous ethylmercaptobenzyl sulfonic acid system is apparently not stable under the aerobic conditions employed in these

studies. The benzylic carbon may be vulnerable to nucleophilic attack. We are currently exploring the applications of these materials for esterification and transesterification of glycerol and triglycerides in both pure and waste oils.

### 4. Experimental section

All reagents used were purchased from Aldrich, Avocado or Lancaster and were used without further purification, unless otherwise stated. Instruments: solution state <sup>1</sup>H NMR and <sup>13</sup>C NMR were recorded on a JEOL JNM-EX270 spectrometer (solvent CDCl<sub>3</sub> unless otherwise specified, lock and standard obtained automatically from the solvent used at 68 MHz); solid state NMR, Bruker AMX 400 MHz (<sup>29</sup>Si SPE MAS, frequency 119.2 MHz, spinning speed 12 kHz; 1 min recycle delay, with 2 μs ~45° pulse; <sup>13</sup>C CP MAS; frequency 150.9 MHz, spinning speed 10 kHz, 1 ms contact time, 5 s delay, 90° pulse for 3.5 μs). Mass spectra were recorded on a Micro-mass QuattroII mass spectrometer. Surface areas were measured using a Micromeritics Flowsorb II 2300 single point surface area analyzer silica ~CH<sub>2</sub>CH<sub>2</sub>SC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H **5a** and **5b** and silica ~CH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H **6**. A mixture of phenylmercaptoethyltrimethoxysilane, (MeO)<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>SC<sub>6</sub>H<sub>5</sub> or benzylmercaptoethyltrimethoxysilane (28 mmol) and silica (15 g) in toluene (30 mL) was refluxed 6 h. The cooled mixture was filtered and the solid washed with toluene (30 mL) and methanol (3 mL × 30 mL) whence the solid was completely odourless. It was then stirred in sulphuric acid (fuming) (5 g in 20 mL) at 45 °C for 1.5 h. The cooled mixture is filtered and the solid washed with water (2 mL × 20 mL) and methanol (20 mL) and finally oven dried at 80 °C for 24 h.

- $^{13}\text{C}$  CPMASNMR 10.1 (s, SiCH<sub>2</sub>), 26 (s, SCH<sub>2</sub>) 126 (C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H and C<sub>6</sub>H<sub>5</sub>).
- $^{29}\text{Si}$  MASNMR 71 (br s, T-sites), –109, –118 (br m, Q-sites).
- Found % S: 5.64% **5a**, 4.48% **5b**.
- Degree of sulfonation: 69% **5a**, 99% **5b**.

The ethylmercaptobenzylsulfonic acid material was prepared in the same way starting from 1-benzylmercapto-2-(trimethoxysilyl)ethane.

- $^{13}\text{C}$  CPMASNMR 9.5 (s, SiCH<sub>2</sub>), 36 (br m, CH<sub>2</sub>S/SCH<sub>2</sub>Ph) 126 (C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H and C<sub>6</sub>H<sub>5</sub>).
- $^{29}\text{Si}$  MASNMR 70 (br s, T-sites), –109, –118 (br m, Q-sites).
- Found % S: 4.39% **6**. Degree of sulfonation 56%.

Materials used in this work were prepared and had the analyses described above.

Subsequent optimisation of the sulfonation process whereby silicaethylmercaptobenzene (**3a** or **3b**) 20 g is stirred at room temperature for 12 h in a mixture of 98% sulphuric acid (50 mL) and 20% oleum (2.5 mL) and worked-up as described above, routinely gives >95% sulfonation.

#### 4.1. Esterification of oleic and lauric acid

Oleic acid (1.41 g, 5 mmol, 1.58 mL) or lauric acid (1.01 g, 5 mmol) and alcohol (10 mL) and catalyst, (0.1 g) were stirred and heated under reflux at the temperatures and for the times shown in Table 1. The reaction was monitored by TLC (90% petrol, 10% ethyl acetate). The mixture was cooled to room temperature and the catalyst filtered off. The volatiles were evaporated from the filtrate using a rotary evaporator to afford the product. Conversion was determined by integration of the alkene and ester OCH<sub>2</sub> proton environments for oleic acid esterification and either the terminal CH<sub>3</sub> or CH<sub>2</sub> β to carbonyl and ester OCH<sub>2</sub> protons for lauric acid esterification.

#### 4.2. Esterification of ethylcaproate

Ethyl caproate (0.72 g, 5 mmol, 0.82 mL), butanol (10 mL) and catalyst (0.1 g) were stirred and heated under reflux for times and temperatures given in Table 1. The reaction was monitored by TLC (90% petrol, 10% ethyl acetate). The mixture was cooled to room temperature and the solvent removed from the filtered product using a rotary evaporator to give a colourless oil. Conversion was determined by integration of the terminal CH<sub>3</sub> or the CH<sub>2</sub> β to carbonyl and ester OCH<sub>2</sub> protons.

#### 4.3. Ketalisation reaction of acetophenone with ethylene glycol (Isolation of 2-methyl-2-phenyl-[1,3]dioxolane)

A mixture containing acetophenone (2.4 g, 20 mmol, 2.33 mL), ethylene glycol (5 g, 8 mmol, 4.49 mL), catalyst (0.2 g) and toluene (25 mL) was refluxed using a Dean-Stark apparatus for 7 h. The catalyst was filtered off and washed with toluene. The combined filtrate and washings were then washed

with water and dried over MgSO<sub>4</sub>. The solvent was removed by rotary evaporation. The product was pure ketal by NMR.

#### 4.4. Etherification of 1,4-Butanediol

1,4-butanediol (10.2 g, 112 mmol, 10 mL) and catalyst (0.1 g) was heated at 130 °C under reflux and the THF collected via a pressure equalized dropping funnel. The diol was replenished five times. Conversion was determined by the amount of THF produced. Catalyst activity was maintained during these five sequential runs.

#### 4.5. Aldol condensation reaction between benzaldehyde and acetophenone (Isolation of 1,3-Diphenyl-propenone)

A mixture of benzaldehyde (2.12 g, 20 mmol, 2.03 mL), acetophenone (2.40 g, 20 mmol, 2.33 mL), catalyst, (0.2 g) and toluene (25 mL) was refluxed using a Dean-Stark apparatus for 24 h. The catalyst was filtered and washed with toluene and the combined washings and filtrate washed with water and dried over MgSO<sub>4</sub>. The solvent was removed by rotary evaporation. Conversion was determined by integration of proton NMR signals due to acetophenone and alkene protons.

#### 4.6. Dehydration of D-Xylose

D-Xylose (0.2 mmol) and **5b** (23 mg) in DMSO (1 mL) was heated at reflux for 24 h. Conversion to furfural was determined on the basis of appearance of resonance due to the aldehyde and absence of resonances due to the starting D-xylose.

### Acknowledgements

We are very grateful to Mr. Greg Coumbarides for the solid state NMR spectra and to EPSRC and PhosphonicS for CASE award to AQ.

### References

- [1] R.D. Badley, W.T. Ford, *J. Org. Chem.* 54 (1989) 5437–5443.
- [2] J.A. Malero, G.D. Stucky, R. van Grieken, G. Morales, *J. Mat. Chem.* 12 (2002) 1664–1670.
- [3] M. Alvaro, A. Corma, D. Das, V. Fornés, H. García, *Chem. Commun.* (2004) 956.
- [4] D.J. Macquarrie, S.J. Tavener, M.A. Harmer, *Chem. Comm.* (2005) 2363.
- [5] W.M. Van Rhijn, D.E. De Vos, B.F. Sels, W.D. Bossaert, P.A. Jacobs, *Chem. Commun.* (1998) 317; I. Diaz, C. Marquez-Alvarez, F. Mohino, J. Perez-Pariente, E. Sastre, *J. Catal.* 193 (2000) 295–302.
- [6] D. Debasish, J.-F. Lee, S. Cheng, *Chem. Commun.* (2001) 2178–2179; K. Wilson, A.F. Lee, D.J. Macquarrie, J.H. Clark, *Appl. Catal. A Gen.* 228 (2002) 127–133; I.J. Dijkstra, H.L.F. vanOchten, C.A. van Walree, J.W. Geus, L.W. Jenneskens, *J. Mol. Catal. A Chem.* 188 (2002) 209–224.
- [7] S. Shylesh, S. Sharma, S.P. Mirajkar, A.P. Singh, *J. Mol. Catal. A Chem.* 212 (2004) 219–228.
- [8] M.G. Voronkov, *J. Gen. Chem. USSR (Engl. Transl.)* 49 (1979) 529–536; *Zh. Obshch. Khim.* 49 (1979) 605–614.
- [9] C.G. Overberger, J.E. Mulvaney, F. Marshall, *J. Org. Chem.* 21 (1956) 1311.