

# Alkyl sulphonic acid surface-functionalised silica as heterogeneous acid catalyst in the solvent-free liquid-phase addition of acetic acid to camphene

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## Abstract

In search for heterogeneous Brønsted acid catalysts as alternatives for corrosive liquid acid catalysts, silica's were surface-functionalised with linear alkyl chains containing thiol and thioacetic ester end-groups, which were subsequently converted into sulphonic acids by oxidation with  $\text{H}_2\text{O}_2/\text{HOAc}$ . FT-IR, CP/MAS  $^{13}\text{C}$  NMR, XPS, TGA and acid–base titrations established the formation of a surface-bound monolayer of alkyl sulphonic acid groups.

The catalytic properties of the surface-functionalised silica's were evaluated in the solvent-free liquid-phase hydro-acyloxy-addition of acetic acid (**1**) to camphene (**2**), yielding the pine-fragrance isobornyl acetate (**3**). Reaction rates (normalised on the concentration of sulphonic acid groups) were identical to those found using the homogeneous  $\text{CH}_3\text{SO}_3\text{H}$  reference catalyst. The equal rates suggest that a similar reaction mechanism is operative. The reaction rate with the solid surface-functionalised silica catalysts increased by two orders of magnitude upon addition of a small amount of water. In the presence of water the alcohol analogue of **3**, i.e. isborneol (**15**), is an important intermediate. Generation of homogeneous alkyl sulphonic acids via hydrolysis followed by leaching from the silica surface does not occur; the formation of **3** stopped after removal of the solid catalyst from the reaction mixture by filtration. Thus, the alkyl sulphonic acid functionalised silica's act as proper heterogeneous Brønsted acid catalysts.

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*Keywords:* Silica; Surface modification; Sulphonic acid; Isobornyl acetate; Kinetics

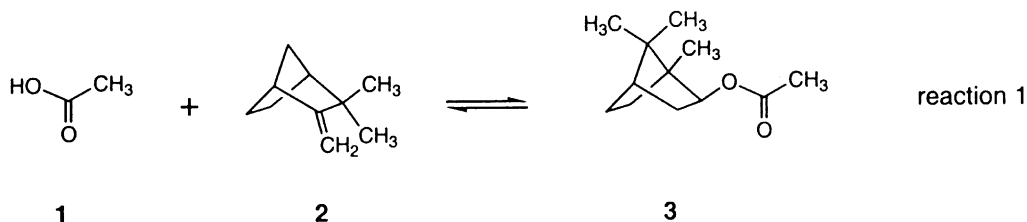
## 1. Introduction

Mineral acids, such as  $\text{H}_2\text{SO}_4$ , find application as acid catalyst in alkylation, hydration, hydrolysis and esterification reactions [1–4]. To avoid corrosion, troublesome work-up procedures and excessive waste streams, there is a search for heterogeneous

solid–acid catalysts. In analogy to  $\text{BF}_3/\text{H}_3\text{PO}_4/\text{SiO}_2$  and  $\text{AlCl}_3/\text{Al}_2\text{O}_3$  catalysts,  $\text{H}_2\text{SO}_4$  can be impregnated into a metal oxide support (e.g.  $\text{ZrO}_2$ ) and subsequently applied as a solid–acid catalyst. With many of such solid–acid systems, however, the occurrence of corrosion due to leaching and volatilisation is not completely prevented, especially when either liquid water or water vapour is present [4,5]. In this paper, an alternative route is explored, involving covalent surface modification of a silica support with organic functionalities containing strong acid groups.

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Although alkyl sulphuric acids ( $\text{ROSO}_3\text{H}$ ) are potential candidates, they readily eliminate  $\text{H}_2\text{SO}_4$  by (auto-catalysed) hydrolysis [6–13]. In contrast, alkyl sulphonic acids ( $\text{RSO}_3\text{H}$ ) combine strong acidity with good hydrolytic stability [14–17]. To obtain silica functionalised with alkyl sulphonic acids, silica surfaces are derivatised with alkyl thiol and alkyl thioacetic ester functionalities, followed by oxidation of the thiol and thioacetic ester groups with  $\text{H}_2\text{O}_2$ . The catalytic performance of these materials is evaluated in the solvent-free liquid-phase hydro-acyloxy-addition of acetic acid (**1**) to camphene (**2**), giving the industrially important pine-fragrance isobornyl acetate (**3**, reaction 1) [2]. For comparison, methane sulphonic acid ( $\text{CH}_3\text{SO}_3\text{H}$ ) will be employed as a homogeneous reference catalyst.



## 2. Experimental

### 2.1. General

Commercial reagents were used without purification. All solvents were purified and dried by standard procedures [18]. Reactions and storage of samples were carried out under a  $\text{N}_2$  atmosphere.

Solution NMR was performed with a Bruker AC 300 spectrometer ( $^1\text{H}$  NMR 300.13 MHz,  $^{13}\text{C}$  NMR 75.47 MHz). Solid state CP/MAS NMR spectra were recorded on a Varian <sup>UNITY</sup>INOVA spectrometer ( $^{13}\text{C}$  NMR 75.47 MHz) equipped with a 7 mm VT-CP/MAS probe. Samples were spun at 5000 Hz in  $\text{Si}_3\text{N}_4$  rotors and the spectra were referenced to external adamantane. Contact times were 4–5 ms.

Transmission FT-IR analyses were done on a Mattson Galaxy Series 5000 FT-IR spectrophotometer using KBr pellets. Liquid samples were measured as a thin film cast on a blank KBr pellet. Spectra were recorded by averaging 512 scans at  $4\text{ cm}^{-1}$  resolution.

X-ray photoelectron spectroscopy (XPS) was carried out using a Vacuum Generators MT-500 (Fisons Instruments) equipped with a non-monochromatic Al X-ray source ( $\text{K}\alpha$  1486.6 keV) and a CLAM-2 hemispherical analyser for electron detection. Samples were applied on carbon adhesive tape. After correction for charging and background scattering the spectra were referenced and scaled on the Si 2p signal.

Thermogravimetric analyses (TGA) were executed by measuring the relative loss of weight in an air flow ( $50\text{ ml min}^{-1}$ , 2 vol.%  $\text{H}_2\text{O}$ ) as a function of temperature and time with a PC-controlled Perkin-Elmer TGS-2 TGA apparatus, autobalance AR-2 (temperature program: isotherm for 1 h at 323 K, followed by heating from 323 to 1123 K (heating rate  $10\text{ K min}^{-1}$ ))

and isotherm for 15 min at 1123 K). Samples of ca. 3.5 mg were used.

Acid–base titrations were used to determine the absolute number of sulphonic acid groups per gram of alkyl sulphonic acid surface-functionalised silica. Prior to the addition of the titration solution (2.89 mM KOH, standardised with potassium hydrogen phthalate) and the thymolblue/EtOH indicator (three drops), the surface-modified silica (0.110 g) was carefully suspended in an aqueous NaCl solution (0.86 mM, 40.0 ml) for 20 min. The reported titration results are average values of six independent titrations.

### 2.2. Synthesis of reference compounds

#### 2.2.1. 1-Hexanesulphonic acid monohydrate (**4**)

To a Schlenk-vessel (100 ml) containing a mixture of glacial acetic acid (50 ml, 0.87 mol) and 35 wt.%  $\text{H}_2\text{O}_2$  in water (7.88 ml, 90 mmol  $\text{H}_2\text{O}_2$ ), 1-hexanethiol (2.20 ml, 15.6 mmol) was added under stirring. The temperature of the reaction mixture was raised to 343 K in 30 min and the mixture was stirred

for an additional 2 h. After evaporation of all volatiles in vacuo at 293 K, 1-hexanesulphonic acid monohydrate (**4**) was obtained in quantitative yield (2.88 g, 15.6 mmol).  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  0.87 (t, 3H), 1.33 (m, 6H), 1.64 (m, 2H), 2.70 (m, 2H), 9.22 (s, 3H) ppm;  $^{13}\text{C}$  NMR (DMSO- $d_6$ )  $\delta$  13.8, 22.0, 24.3, 27.7, 30.9, 51.5 ppm.

### 2.2.2. Decane-1,10-dithioacetate (**5**)

To a solution of 1,10-dibromodecane (5.03 g, 16.7 mmol) in DMF (100 ml), potassium thioacetate (3.84 g, 33.6 mmol) was slowly added under stirring at 303 K. After stirring for 3 days, diethyl ether (100 ml) was added to the reaction mixture. The reaction mixture was washed with water (4  $\times$  100 ml) and the separated organic layer was concentrated at 293 K under reduced pressure. The solid residue was re-crystallised from acetone; crystals were isolated by filtration and dried in vacuo at 293 K. Yield of **5** (57%, 19.2 mmol).  $^1\text{H}$  NMR (CDCl<sub>3</sub>)  $\delta$  1.30 (m, 6H), 1.55 (m, 2H), 2.32 (s, 3H), 2.86 (t, 2H) ppm;  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>)  $\delta$  28.8, 29.0, 29.1, 29.3, 29.5, 30.6, 196.0 ppm.

### 2.2.3. Decane-1,10-disulphonic acid dihydrate (**6**)

Decane-1,10-dithioacetate (**5**, 2.78 g, 9.6 mmol) was added to a mixture of 35 wt.% H<sub>2</sub>O<sub>2</sub> in water (8.5 ml, 97 mmol H<sub>2</sub>O<sub>2</sub>) and glacial acetic acid (50 ml, 0.87 mol) in a Schlenk-vessel (100 ml) under stirring. Next, the temperature was raised to 343 K in 30 min and the reaction mixture was stirred for an additional 2 h. After evaporation of all volatiles in vacuo at 293 K, decane-1,10-disulphonic acid dihydrate (**6**) was obtained in quantitative yield (3.26 g, 9.6 mmol).  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  1.25 (m, 12H), 1.57 (m, 4H), 2.59 (m, 4H), 9.08 (s, 6H) ppm;  $^{13}\text{C}$  NMR (DMSO- $d_6$ )  $\delta$  24.6, 28.1, 28.76, 28.83, 51.4 ppm.

### 2.2.4. Poly[(3-mercaptopropyl)methylsiloxane] (**8**)

To a mixture of EtOH (17.5 ml) and an aqueous solution of HCl (0.10 M, 50 ml), dimethoxy(3-mercaptopropyl)methylsilane (**7**, 10.9 ml, 60.4 mmol) was added under stirring. The reaction mixture was heated at 323 K and stirred for 3 h. After evaporation of all volatiles in vacuo at 293 K, poly[(3-mercaptopropyl)methylsiloxane] (**8**) was obtained as a rubbery material (yield 83%, 6.49 g).  $^1\text{H}$

NMR (CDCl<sub>3</sub>)  $\delta$  0.10 (b, 3H), 0.67 (b, 2H), 1.35 (b, 1H), 1.66 (b, 2H), 2.56 (b, 2H) ppm;  $^{13}\text{C}$  NMR (DMSO- $d_6$ )  $\delta$  -0.4, 15.9, 27.1, 27.5 ppm; CP/MAS  $^{13}\text{C}$  NMR  $\delta$  1.1, 17.7, 29.1 (two  $^{13}\text{C}$  signals) ppm; FT-IR  $\tilde{\nu}$  434(m), 677(w), 791(s), 922(w), 1024(s), 1084(s), 1177(m), 1262(s), 1308(w), 1343(w), 1414(m), 1443(w), 2560(w), 2799(w), 2859(w), 2882(m), 2928(s), 2957(s), 3200–3700(w) cm<sup>-1</sup>.

### 2.2.5. Attempted oxidation of poly[(3-mercaptopropyl)methylsiloxane] (**8**)

Poly[(3-mercaptopropyl)methylsiloxane] (**8**, 1.63 g) was stirred in 100 ml acetic acid for 0.5 h after which 35 wt.% H<sub>2</sub>O<sub>2</sub> in water (6.42 ml, 73 mmol H<sub>2</sub>O<sub>2</sub>) was added. The heterogeneous mixture was heated to 343 K in 30 min, stirred for another 1 h and subsequently filtered over a glass frit.

The scarcely soluble fraction (residue) was dried under reduced pressure: CP/MAS  $^{13}\text{C}$  NMR  $\delta$  1.1, 17.7, 29.1 (two  $^{13}\text{C}$  signals) ppm; FT-IR  $\tilde{\nu}$  434(m), 677(w), 791(s), 922(w), 1024(s), 1084(s), 1177(m), 1262(s), 1308(w), 1343(w), 1414(m), 1443(w), 2560(w), 2799(w), 2859(w), 2882(m), 2928(s), 2957(s), 3200–3700(w) cm<sup>-1</sup>. These spectral data are identical to those of **8**.

The filtrate was concentrated under reduced pressure:  $^{13}\text{C}$  NMR (DMSO- $d_6$ )  $\delta$  20.6, 20.9, 24.5, 28.2, 47.8, 48.7, 59.9, 60.2, 63.0, 72.2 ppm;  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  0.11(s), 1.88(m), 2.60(m), 3.45(t), 4.07(t) ppm. FT-IR  $\tilde{\nu}$  444(w), 527(w), 604(m), 779(m), 1040(s), 1163(s), 1244(s), 1370(w), 1638(m), 1736(m), 2968(w), 3200–3700(m) cm<sup>-1</sup>. NMR analysis showed that degradation of the polymer had occurred. The following low-molecular weight compounds were unequivocally identified: 3-hydroxypropane sulphonic acid, 3-methoxypropane sulphonic acid and [1,2] oxathiolane-2,2,-dioxide [19–22]. No  $^{13}\text{C}$  NMR chemical shifts representative for Si-CH<sub>3</sub> and Si-CH<sub>2</sub> containing species ( $\delta$  < 20 ppm) were found in the spectra of the filtrate.

## 2.3. Synthesis of surface-modified silica's

### 2.3.1. (3-Mercaptopropyl)methylsiloxane surface-functionalised silica's (**9a** and **9b**)

**9a**: A three-necked round bottomed flask (1.0 l) equipped with a reflux condenser containing 20.0 g

(0.33 mol) silica (Aerosil OX50 (Degussa-Hüls),  $50 \text{ m}^2 \text{ g}^{-1}$ ,  $\langle d \rangle = 40 \text{ nm}$ ) [23] was evacuated and exposed to an  $\text{N}_2$  atmosphere three times before being suspended in toluene (300 ml). Subsequently, dimethoxy(3-mercaptopropyl)methylsilane (**7**, 4.80 ml, 26.6 mmol) was added under vigorous stirring and the heterogeneous reaction mixture was heated at reflux temperature for 24 h. After cooling to room temperature, the suspension was filtered over a Büchner-funnel and the residue was washed with *n*-pentane ( $3 \times 250 \text{ ml}$ ) and subsequently dried at 378 K in vacuo for 5 h.

**9b**: A similar procedure was followed with 20 g (0.33 mol) silica (Aerosil 200 (Degussa-Hüls),  $200 \text{ m}^2 \text{ g}^{-1}$ ,  $\langle d \rangle = 12 \text{ nm}$ ) [23], with toluene (800 ml) and 19.2 ml dimethoxy(3-mercaptopropyl)methylsilane (**7**, 106.5 mmol).

For both surface-modified silica's, similar spectroscopic data were obtained: CP/MAS  $^{13}\text{C}$  NMR  $\delta$  -2.2, 16.6, 28.1 (two  $^{13}\text{C}$  signals) ppm; FT-IR  $\tilde{\nu}$  476(vs), 820(vs), 1136(vs), 1418(m), 1650(m), 1879(m), 2565(w), 2803(w), 2863(m), 2884(m), 2924(m), 2961(m), 3100–3730(w)  $\text{cm}^{-1}$ .

### 2.3.2. Methyl(3-sulphopropyl)siloxane surface-functionalised silica's (**10a** and **10b**)

**10a**: A three-necked round bottomed flask (1.0 l) equipped with a reflux condenser containing 18.0 g (3-mercaptopropyl)methylsiloxane surface-functionalised silica (**9a**) was suspended in glacial acetic acid (600 ml). Under stirring, 35 wt.%  $\text{H}_2\text{O}_2$  in water (0.82 ml, 9.3 mmol  $\text{H}_2\text{O}_2$ ) was added and the temperature of the heterogeneous reaction mixture was raised to 343 K in 30 min and the mixture was stirred for an additional 2 h. After cooling to room temperature, the suspension was filtered over a Büchner-funnel and the residue was dried at 378 K in vacuo for 5 h.

**10b**: A similar procedure was followed using 18.0 g (3-mercaptopropyl)methylsiloxane surface-functionalised silica (**9b**) and 3.28 ml 35 wt.%  $\text{H}_2\text{O}_2$  in water (38 mmol  $\text{H}_2\text{O}_2$ ).

For both surface-modified silica's, similar spectroscopic data were obtained: CP/MAS  $^{13}\text{C}$  NMR  $\delta$  -4.4, 15.2, 22.4 and 53.9 ( $-\text{CH}_2-\text{SO}_3\text{H}$ ) ppm. FT-IR  $\tilde{\nu}$  476(vs), 820(vs), 1136(vs), 1418(m), 1650(m), 1879(m), 2863(m), 2884(m), 2924(m), 2961(m), 3100–3730(w)  $\text{cm}^{-1}$ .

### 2.3.3. (11-Bromoundecyl)dichloromethylsilane (**11a**)

Dichloromethylsilane (40.5 ml, 0.4 mol) was added to a stirred solution of 11-bromo-1-undecene (50.0 ml, 0.2 mol) in dry toluene (50 ml). After addition of a catalytic amount of  $\text{H}_2\text{PtCl}_6$  (ca. 50 mg, 0.1 mmol in 2-propanol, 0.05 ml), the reaction mixture was heated at reflux temperature for 2.5 days. By Kugelrohr distillation, a mixture of (11-bromoundecyl)dichloromethylsilane (**11a**) and (10-bromo-1-methyldecyl)dichloromethylsilane (**11b**) was isolated in near quantitative yield (ratio **11a**:**11b** = 83:17%). Mixture of **11a** and **11b**:  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ )  $\delta$  0.76 (s, 3H), 1.11 (m, 2H), 1.41 (m, 16H), 1.84 (m, 2H), 3.40 (t, 2H), 3.52 (t, 0.4H); **11b**) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.2, 6.7 (**11b**) 21.6, 22.4, 22.8 (**11b**), 26.9 (**11b**), 28.2, 28.8, 29.1, 29.3, 29.4, 29.5, 32.3, 32.8, 33.9 ppm.

### 2.3.4. (11-Bromoundecyl)methylsiloxane surface-functionalised silica (**12**)

A three-necked round bottomed flask (1.0 l) equipped with a reflux condenser containing 20.1 g (0.33 mol) silica (Aerosil OX50 (Degussa-Hüls),  $50 \text{ m}^2 \text{ g}^{-1}$ ) was evacuated and exposed to an  $\text{N}_2$  atmosphere three times before being suspended in dry toluene (300 ml). Next, 9.20 ml of the (11-bromo-undecyl)dichloromethylsilane (**11a**) and (10-bromo-1-methyldecyl)dichloromethylsilane (**11b**) mixture (ratio **11a**:**11b** = 83:17%, vide supra) was added under stirring and the reaction mixture was heated at reflux temperature for 2 days. After cooling to room temperature, the suspension was filtered over a Büchner-funnel, washed with *n*-pentane ( $3 \times 250 \text{ ml}$ ) and dried at 293 K in vacuo for 8 h. CP/MAS  $^{13}\text{C}$  NMR  $\delta$  -1.0, 17.3, 22.4, 29.4 (multiple  $^{13}\text{C}$  signals), 32.7 (multiple  $^{13}\text{C}$  signals) ppm. FT-IR  $\tilde{\nu}$  476(vs), 820(vs), 1136(vs), 1414(w), 1466(m), 1661(m), 1881(m), 2855(s), 2928(s), 3120–3710(w)  $\text{cm}^{-1}$ .

### 2.3.5. Methyl(11-thioaceto-undecyl)siloxane surface-functionalised silica (**13**)

A three-necked round-bottomed flask (1.0 l) containing 19.8 g of (11-bromoundecyl)methylsiloxane surface-functionalised silica (**12**) was suspended in DMF (300 ml). After addition of potassium thioacetate (3.13 g, 27.4 mmol) the mixture was stirred at 293 K for 2 days. The suspension was filtered over a Büchner-funnel and the residue was washed with

CH<sub>3</sub>OH (3 × 100 ml) and dried in vacuo for 5 h at 323 K. CP/MAS <sup>13</sup>C NMR δ -1.1, 16.8, 22.7, 29.4 (multiple <sup>13</sup>C signals), 33.2 (multiple <sup>13</sup>C signals) and 190.0 (-CO-S-) ppm. FT-IR  $\tilde{\nu}$  476(vs), 820(vs), 1136(vs), 1414(w), 1466(w), 1655(w), 1672(m), 1703(m), 1881(m), 2855(s), 2928(s), 3120–3710(w) cm<sup>-1</sup>.

### 2.3.6. Methyl(11-sulphoundecyl)siloxane surface-functionalised silica (**14**)

A Schlenk-vessel containing glacial acetic acid (300 ml) and 9.98 g methyl(11-thioaceto-undecyl)siloxane surface-functionalised silica (**13**) was suspended. 35 wt.% H<sub>2</sub>O<sub>2</sub> in water (0.46 ml, 4.4 mmol H<sub>2</sub>O<sub>2</sub>) was added and the suspension was heated at reflux temperature for 90 min. The suspension was filtered over a Büchner-funnel, washed twice with water (100 ml) and dried in vacuo for 12 h at 383 K. CP/MAS <sup>13</sup>C NMR δ -1.3, 16.5, 23.4, 29.4 (multiple <sup>13</sup>C signals), 33.1 (multiple <sup>13</sup>C signals) and 52.1 (-CH<sub>2</sub>-SO<sub>3</sub>H) ppm. FT-IR  $\tilde{\nu}$  476(vs), 820(vs), 1136(vs), 1418(m), 1650(m), 1879(m), 2863(m), 2884(m), 2924(m), 2961(m), 3100–3730(w) cm<sup>-1</sup>.

## 2.4. Catalysis

### 2.4.1. Liquid-phase hydro-acyloxy-addition of acetic acid (**1**) to camphene (**2**)

A mixture of glacial acetic acid (**1**, 0.70 mol), camphene (**2**, 95%, 0.70 mol) and acetic anhydride (to remove traces of water, 1.00 ml) was mechanically stirred (1500 rpm) at 338 K under a N<sub>2</sub> atmosphere for 16 h. Subsequently, either the homogeneous reference catalyst CH<sub>3</sub>SO<sub>3</sub>H (aliquots of 0, 4.25, 8.50, and 17.0 mmol (see Section 3)) or alkyl sulphonic acid surface-functionalised silica (typically 5.0 g) was added as catalyst. The composition of the soluble fraction of the reaction mixture was analysed by capillary GC as a function of reaction time. Samples were prepared as follows: 1.00 ml of the reaction mixture was added to water (25.00 ml) followed by extraction with *n*-heptane (25.00 ml). Next 1.00 ml of the *n*-heptane fraction was diluted with *n*-heptane to 25 ml in a volumetric flask. 1.0 μl of the diluted solution was injected into the GC (Varian 3400, column: DB-5 capillary liquid-phase siloxane polymer (5% phenyl, 95% methyl), 30 m × 0.323 mm, temper-

ature program: 5 min at 333 K, 10 K min<sup>-1</sup> to 553 K, 10 min, carrier gas: N<sub>2</sub>, FID).

Reactions in the presence of added water (1.26 ml, 0.07 mol) were performed without the extra addition of acetic anhydride. To test the possible occurrence of acid (auto-catalysed) hydrolysis of the Si-O and Si-C bonds of the surface-anchored alkyl sulphonic acids, the insoluble catalyst particles were removed from the reaction mixture by filtration with a double-ended glass filter (under a N<sub>2</sub> atmosphere) and the composition of the soluble fraction of the reaction mixture was further analysed by capillary GC as a function of reaction time.

### 2.4.2. Calculation of reaction rate constants

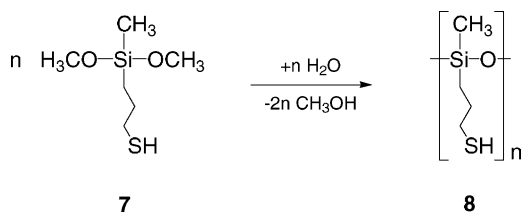
Reaction rate constants for the hydro-acyloxy-addition reaction of acetic acid (**1**) to camphene (**2**), which gives isobornyl acetate (**3**), were obtained after modelling reaction 1 with Eqs. (A.1)–(A.3) (see Appendix A). It was experimentally verified that the volume of the reaction mixture did not significantly change as a result of the conversion of **1** and **2** into **3**. Eqs. (A.1)–(A.3) were employed for the initial stage of the reaction. It was established that similar reaction rate constants were obtained using either a reversible or an irreversible reaction model in the initial stage of the hydro-acyloxy-addition reaction (Eqs. (A.4)–(A.7), see Appendix A). Therefore, the irreversible reaction model was used in the calculation of the reaction rate constants (Table 2).

## 3. Results and discussion

### 3.1. Synthesis and characterisation of reference compounds

For the preparation of heterogeneous sulphonic acid catalysts, the use of oxidising reagents, such as HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and HIO<sub>3</sub>, is undesired because residual quantities can function as homogeneous catalysts. Therefore, H<sub>2</sub>O<sub>2</sub> is the oxidant of choice. It was established that with H<sub>2</sub>O<sub>2</sub> pure alkyl sulphonic acids are obtained in quantitative yield, e.g. 1-hexanesulphonic acid (**4**) is obtained from hexanethiol and decane-1,10-disulphonic acid (**6**) from decane-1,10-dithioacetate (see Section 2, [19,24–33]). Accordingly, silylating agents containing

an ( $\omega$ -)thiol-functionalised oligo-methylene chain were applied for the preparation of alkyl sulphonic acid surface-functionalised materials [34–41]. In contrast to the model compounds 1-hexanesulphonic acid (**4**) and decane-1,10-disulphonic acid (**6**), the silylating agents also contain the reactive Si–O and Si–C moieties. The alkyl sulphonic acid surface-functionalised materials may therefore be susceptible towards hydrolysis and oxidation [34,42–45] and subsequent dissolution of catalytically active sulphonic acid species in the reaction medium. Furthermore, besides surface-functionalisation, self-condensation of the silylating agents may occur, leading to contamination of the alkyl sulphonic acid surface-functionalised materials by (physisorbed) oligo- and polysiloxanes. To gain insight in the importance of these undesired processes, poly[(3-mercaptopropyl)methylsiloxane] (**8**) was synthesised by acid-catalysed polymerisation of dimethoxy(3-mercaptopropyl)methylsilane (**7**, Scheme 1, see Section 2 and [19,24–26,34,40–42,46]). Oxidation of **8** by H<sub>2</sub>O<sub>2</sub>/HOAc resulted in a scarcely soluble and a soluble fraction. CP/MAS <sup>13</sup>C NMR and FT-IR showed that the scarcely soluble fraction consisted of unconverted poly[(3-mercaptopropyl)methylsiloxane] (**8**), whereas <sup>1</sup>H NMR, <sup>13</sup>C NMR and FT-IR revealed that the soluble fraction consisted of degradation products only (see Section 2). This result agrees with the results of a previous investigation of related polysiloxanes [34], and indicates that self-condensation and degradation of the silylating agents has to be taken into consideration. The stability of the (attached) silylating agents strongly depends on the accessibility (and density) of their Si–O and Si–C bonds [43–45]. It is therefore preferred to have the silylating agents attached as a thin monolayer on the rigid silica support. Hence, for the synthesis of surface-functionalised materials by silylation



Scheme 1. Acid-catalysed polymerisation of dimethoxy(3-mercaptopropyl)methylsilane (**7**).

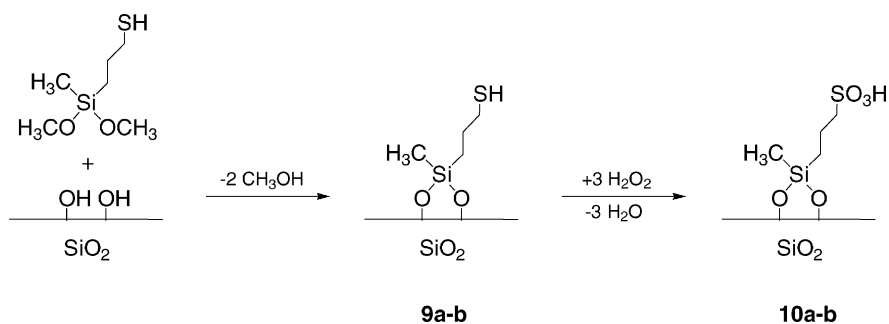
reactions, application of an appropriate solvent (e.g. toluene) is required to induce the silylation agents to mainly react with the silanol groups of the silica surface (vide infra) [47,48].

### 3.2. Methyl(3-sulphopropyl)siloxane surface-functionalised silica's (**10a** and **10b**) and methyl(11-sulphoundecyl)siloxane surface-functionalised silica (**14**)

Two non-porous silica's (Aerosil OX50, 50 m<sup>2</sup> g<sup>-1</sup> (**a**) and Aerosil 200, 200 m<sup>2</sup> g<sup>-1</sup> (**b**)) were used for the covalent surface modification with alkyl sulphonic acids. This allows us to investigate the influence of the number of sulphonic acid groups per gram catalyst on the catalytic performance. Furthermore, a silylation reagent with a short hydrophobic propyl chain as well as one with a more extended hydrophobic undecyl chain were applied to gain insight in possible effects of the alkyl chain length on the catalytic activity.

Silica samples silylated with (short) dimethoxy(3-mercaptopropyl)methylsilane (**7**, Scheme 2) possess characteristic IR  $\nu_{\text{S-H}}$  (2560 cm<sup>-1</sup>) and  $\nu_{\text{C-H}}$  (2800–3000 cm<sup>-1</sup>) vibrations [49,50]. Concomitantly, the characteristic absorptions of free surface silanol groups (3746 cm<sup>-1</sup>) completely disappeared upon silylation. Hence, dimethoxy(3-mercaptopropyl)methylsilane (**7**) is covalently attached to the silica surface. Additional evidence came from <sup>13</sup>C NMR analyses. Upon polymerisation of **7** (vide supra), it was observed that in solution, the <sup>13</sup>C signals of the methyl and methylene group  $\alpha$  to the Si atom shifted from –5.7 ppm (Si–CH<sub>3</sub>) and 12.1 ppm (Si–CH<sub>2</sub>) for **7** to –0.4 ppm (Si–CH<sub>3</sub>) and 15.9 ppm (Si–CH<sub>2</sub>) for poly[(3-mercaptopropyl)methylsiloxane] (**8**). The corresponding CP/MAS <sup>13</sup>C NMR chemical shifts for **8** are 1.1 ppm (Si–CH<sub>3</sub>) and 17.7 ppm (Si–CH<sub>2</sub>), whereas the (3-mercaptopropyl)methylsiloxane surface-functionalised silica's (**9a** and **9b**) gave corresponding resonances at –2.2 ppm (Si–CH<sub>3</sub>) and 16.6 ppm (Si–CH<sub>2</sub>). Hence, the differences in chemical shift between **8** and **9a** and **9b** also support a covalent attachment of the silylating agent without the excessive formation of surface-bound oligo- and polysiloxane species.

The lack of polysiloxane formation protruding from the silica surface is attributed to the application of dry toluene during the condensation reactions [47,48]. The



Scheme 2. Silica surface-functionalisation with dimethoxy(3-mercaptopropyl)methylsilane (**7**) and the subsequent oxidation of the mercapto group to a sulphonic acid group by  $\text{H}_2\text{O}_2$ .

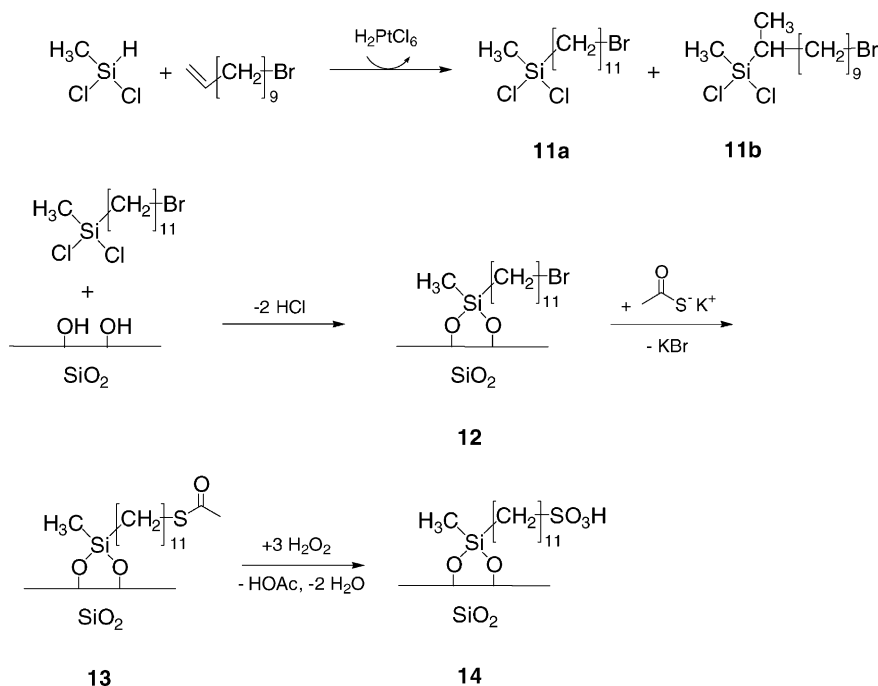
use of this solvent induces the hydrolysable groups from the silylating reagents to react only with the silanol groups of the silica surface. In addition, the accessibility of the hydrolysable groups of the silylating agent will be reduced upon reaction with the silica surface, thus preventing the formation of surface-bound oligo- and polysiloxanes.

Treatment of (3-mercaptopropyl)methylsiloxane surface-functionalised silica's (**9a** and **9b**) with  $\text{H}_2\text{O}_2/\text{HOAc}$  led to the disappearance of the  $\nu_{\text{S-H}}$  vibration ( $2560 \text{ cm}^{-1}$ ) in the IR spectrum, which indicates the successful oxidation of the thiol groups. Assignment of vibrations to the  $\text{SO}_3\text{H}$  group, however, is thwarted due to the presence of intense Si–O and O–H absorptions of the silica support in the spectral region of interest. Nonetheless, CP/MAS  $^{13}\text{C}$  NMR showed the characteristic chemical shifts of a carbon atom  $\alpha$  to a  $\text{SO}_3\text{H}$  group (53.9 ppm) and the chemical shifts of a methyl and methylene group  $\alpha$  to a silicon atom at  $-5$  and  $15$  ppm, respectively.

Methyl(11-sulphoundecyl)siloxane surface-functionalised silica (Aerosil OX50) (**14**) was synthesised according to Scheme 3. The silylating agent (11-bromoundecyl)dichloromethylsilane (**11a**) was obtained as a mixture with (10-bromo-1-methyldecyl)dichloromethylsilane (**11b**, ratio **11a**:**11b** = 83:17%) by hydrosilylation of 11-bromoundecene with dichloromethylsilane. Note that both **11a** and **11b** can be applied as silylating agents (see legend to Scheme 3). In analogy to the preparation of (3-sulphopropyl)methylsiloxane surface-functionalised silica's (**10a** and **10b**), FT-IR and CP/MAS  $^{13}\text{C}$  NMR demonstrated successful silylation of the silica support

with **11a** and **11b**. Subsequent derivatisation of the silica-bound (11-bromoundecyl)methylsiloxane (**12**) to silica-bound methyl(11-thioaceto-undecyl)siloxane (**13**) was indicated by the observation of new carbonyl signals characteristic for thioesters by FT-IR ( $\nu_{\text{C=O}}$  at  $1650\text{--}1715 \text{ cm}^{-1}$  [49,50]) and by CP/MAS  $^{13}\text{C}$  NMR (190.0 ppm). In line with the oxidation of (3-mercaptopropyl)methylsiloxane surface-functionalised silica's (**9a** and **9b**), no characteristic IR vibrations of thioacetic acid *S*-alkyl ester functionalities and mercapto groups were observed after treatment of (**13**) with  $\text{H}_2\text{O}_2/\text{HOAc}$ , which implies the successful oxidation of the ester group. To validate the complete conversion into sulphonic acid groups, CP/MAS  $^{13}\text{C}$  NMR was applied. All characteristic chemical shifts for an undecyl sulphonic acid moiety and a methyl group  $\alpha$  to a Si atom were found in the spectra (see Section 2).

Further evidence for the successful formation of sulphonic acid groups was obtained using XPS. For the (3-sulphopropyl)methylsiloxane surface-functionalised silica's (**10a** and **10b**) as well as for the methyl(11-sulphoundecyl)siloxane surface-functionalised silica (**14**), a weak S 2p signal was found at  $169.4 \text{ eV}$ , which is a characteristic for a sulphonic acid [51]. The S 2p signal of the silica-bound (3-mercaptopropyl)methylsiloxane (**9a**), for comparison, was found with a similar intensity at  $163.7 \text{ eV}$  (characteristic for an organic sulfide [52–54]). Thus, in spite of the low sensitivity of sulphur in XPS [55] and the low surface coverage, the XPS results are in agreement with the NMR analyses and support the presence of sulphonic acid groups.



Scheme 3. Reaction scheme for the synthesis of methyl(11-thioaceto-undecyl)siloxane surface-functionalised silica (**13**). Subsequent treatment of **13** with  $\text{H}_2\text{O}_2/\text{HOAc}$  gives methyl(11-sulphoundecyl)siloxane surface-functionalised silica (**14**). The surface modification with (10-bromo-1-methyldecyl)dichloromethylsilane (**11b**) proceeds analogously to that of (11-bromo-undecyl)dichloromethylsilane (**11a**).

### 3.3. Coverage of the silica surface

The number of sulphonic acid groups per gram alkyl sulphonic acid surface-functionalised silica (Aerosil OX50 and Aerosil 200) was determined by acid–base titration (Table 1). Multiplication of these numbers by the molar mass of the alkyl chains gives the relative loading (wt.%) of these materials. The calculated values are in good agreement with the loss of weight observed by TGA (air) (Table 1). By using the BET specific surface areas, the number of alkyl sulphonic

acid groups per  $\text{nm}^2$  was calculated to be  $\sim 0.70$  for all three samples (Table 1). In addition, by taking a surface density of three silanol groups per  $\text{nm}^2$  [56,57] and under the assumption that two silanol groups are converted into one functionalised site (Schemes 2 and 3), the degree of surface-functionalisation was found to be nearly 50% for all samples (Table 1). Hence, all analytical results converge towards the conclusion that the silica particles are covalently functionalised with alkyl sulphonic acid groups without the excessive formation of oligo- and polysiloxanes.

Table 1

Loading of sulphonic acid groups on the alkyl sulphonic acid surface-functionalised silica's per gram and per surface area

| Catalyst                                                                     | $\text{SO}_3\text{H}$<br>( $\text{mmol g}^{-1}$ )<br>(titrated) | Loading<br>(wt.%)<br>(calculated) | Loading<br>(wt.%)<br>(TGA(air)) | Specific surface<br>area ( $\text{m}^2 \text{g}^{-1}$ )<br>(BET) | $\text{SO}_3\text{H}$ ( $\text{nm}^{-2}$ )<br>(calculated) | Surface functionalised<br>(%) (calculated) |
|------------------------------------------------------------------------------|-----------------------------------------------------------------|-----------------------------------|---------------------------------|------------------------------------------------------------------|------------------------------------------------------------|--------------------------------------------|
| $\text{SiO}_2$ (Aerosil OX50)                                                |                                                                 |                                   |                                 |                                                                  |                                                            |                                            |
| $=\text{Si}(\text{CH}_3)(\text{CH}_2)_3\text{SO}_3\text{H}$ ( <b>10a</b> )   | 0.059                                                           | 0.8                               | 0.8                             | 50                                                               | 0.71                                                       | 48                                         |
| $\text{SiO}_2$ (Aerosil 200)                                                 |                                                                 |                                   |                                 |                                                                  |                                                            |                                            |
| $=\text{Si}(\text{CH}_3)(\text{CH}_2)_3\text{SO}_3\text{H}$ ( <b>10b</b> )   | 0.240                                                           | 3.3                               | 3.5                             | 200                                                              | 0.72                                                       | 48                                         |
| $\text{SiO}_2$ (Aerosil OX50)                                                |                                                                 |                                   |                                 |                                                                  |                                                            |                                            |
| $=\text{Si}(\text{CH}_3)(\text{CH}_2)_{11}\text{SO}_3\text{H}$ ( <b>14</b> ) | 0.056                                                           | 1.4                               | 1.6                             | 50                                                               | 0.67                                                       | 45                                         |



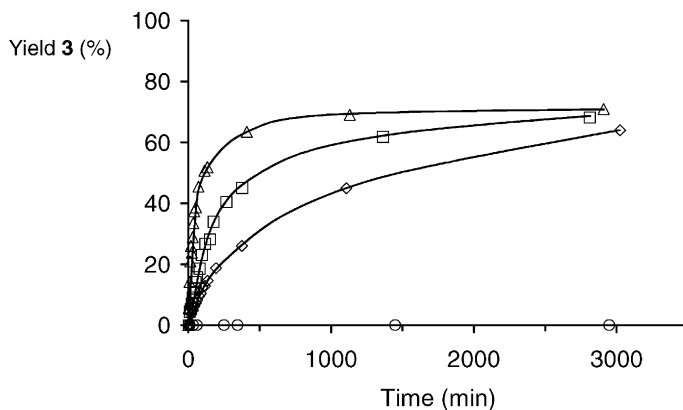


Fig. 1. Formation of isobornyl acetate (**3**) by the solvent-free hydro-acyloxy-addition of acetic acid (**1**, 0.70 mol) to camphene (**2**, 0.70 mol) at 338 K as a function of time with  $\text{CH}_3\text{SO}_3\text{H}$  as catalyst (0.00 M (○), 0.03 M (◇), 0.06 M (□) and 0.12 M (△)).

#### 3.4. Liquid $\text{CH}_3\text{SO}_3\text{H}$ ; a homogeneous reference catalyst

To benchmark the catalytic performance of the alkyl sulphonic acid surface-functionalised silica's, methane sulphonic acid ( $\text{CH}_3\text{SO}_3\text{H}$ ) was used as a homogeneous reference catalyst in the solvent-free liquid-phase hydro-acyloxy-addition reaction of acetic acid (**1**) to camphene (**2**), which yields the industrially important pine-fragrance isobornyl acetate (**3**). This reaction is an equilibrium reaction in which about 70% of **3** is formed when identical initial concentrations of **1** and **2** are used (Fig. 1) [5]. To evaluate the catalytic performance of the solid, alkyl sulphonic acid surface-functionalised silica's

versus that of homogeneous  $\text{CH}_3\text{SO}_3\text{H}$ , reaction 1 was modelled with Eq. (A.7) to obtain reaction rate constants (see Section 2 and Appendix A). The calculated apparent reaction rate constants for the forward reaction ( $k_1$ ) were plotted against the concentration of  $\text{CH}_3\text{SO}_3\text{H}$  (Fig. 2). Notice that the concentration of sulphonic acid groups is not equal to the concentration of dissolved protons, since the dissociation constant of  $\text{CH}_3\text{SO}_3\text{H}$  in glacial acetic acid is very low:  $5.1 \times 10^{-7} \text{ mol l}^{-1}$  [58]. Hence, in acetic acid the reaction rate will depend on the square root of the concentration  $\text{CH}_3\text{SO}_3\text{H}$  if the reaction rate is linearly related to the proton concentration [59]. The results in Fig. 2, however, indicate that at low concentrations of sulphonic acid groups,  $k_1 = k'_1 [\text{RSO}_3\text{H}]$ , whereas

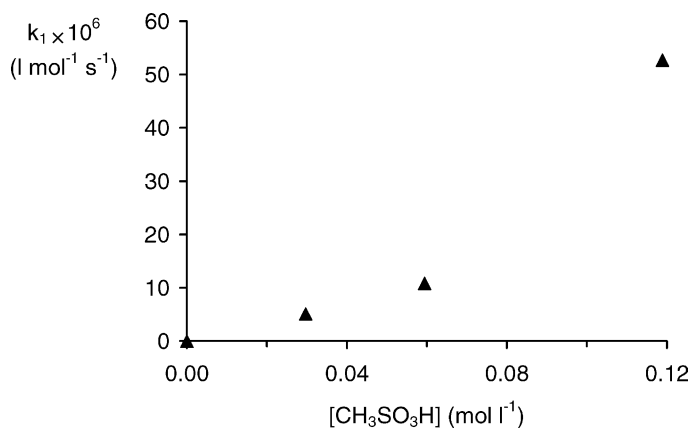
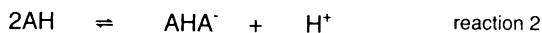


Fig. 2. The reaction rate constant ( $k_1$ , reversible reaction model) as a function of the catalyst concentration ( $[\text{CH}_3\text{SO}_3\text{H}]$ ) at 338 K.

at higher concentrations a higher order dependency is apparent. Similar results were found previously for other electrophilic additions to alkenes, particularly in reaction mixtures of a low dielectric constant. These observations have been rationalised by invoking that the conjugated base of the acid group of the catalyst becomes stabilised by another acid catalyst molecule (reaction 2; AH is representative for the acid group of the catalyst) [58,60–66]. Co-operation of sulphonic acid groups may also contribute in the case of the surface-modified silica samples. For the silica-bound methyl(3-sulphopropyl)siloxane (**10a** and **10b**) and the silica-bound methyl(11-sulphoundecyl)siloxane (**14**), the distance between the Si atom and the proton of the sulphonic acid groups is 0.8 and 1.8 nm, respectively, (assuming an *anti*-periplanar geometry for the alkyl chains). Hence, co-operation between sulphonic acid groups in (**10a**, **10b** and **14**) will not be limited by the length of the alkyl chains at a surface coverage's of one sulphonic acid group per 1.43 nm<sup>2</sup> (Table 1).



### 3.5. Catalytic performance of alkyl sulphonic acid surface-functionalised silica's

The number of sulphonic acid groups per gram of sulphonic acid surface-functionalised silica catalysts (Table 1) is considerably lower than for liquid CH<sub>3</sub>SO<sub>3</sub>H ( $d_4^{20} = 1.48 \text{ g ml}^{-1} = 10.4 \text{ mmol g}^{-1}$ ). Hence, to obtain an equivalent number of sulphonic acid groups as with the homogeneous CH<sub>3</sub>SO<sub>3</sub>H catalyst (0.06 M), an excessively large quantity of alkyl sulphonic acid surface-functionalised silica is required. For this reason, the solid sulphonic acid functionalised silica catalysts were applied in such quantities that the concentration of sulphonic acid groups in the reaction mixture was at least 20 times lower than with CH<sub>3</sub>SO<sub>3</sub>H. As a consequence, the overall rates of the isobornyl acetate (**3**) formation are lower (Figs. 1 and 3). However, when the apparent reaction rate constants are corrected for the total number of sulphonic acid groups present in the reaction mixture, a normalised reaction rate constant ( $k'_1$ ) of  $3.3 \times 10^{-4} \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$  for the silica (Aerosil OX50)-bound propyl sulphonic acid catalyst (**10a**) and  $2.9 \times 10^{-4} \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$  for the silica (Aerosil OX50)-bound undecyl sulphonic acid cata-

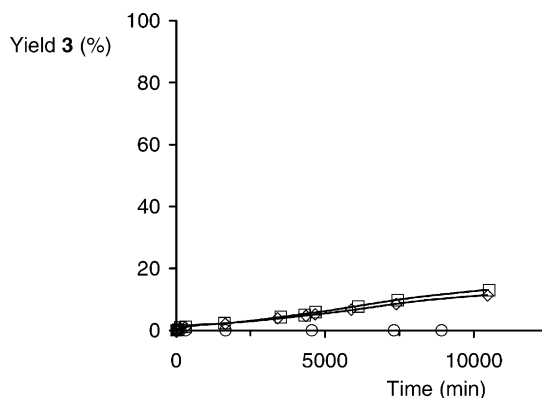


Fig. 3. Formation of isobornyl acetate (**3**) by the solvent-free hydro-acyloxy-addition of acetic acid (**1**, 0.70 mol) to camphene (**2**, 0.70 mol) at 338 K as a function of time with bare silica (Aerosil OX50) (○), silica (Aerosil OX50)-bound propyl sulphonic acid catalyst (**10a**, 0.47 mmol sulphonic acid groups) (□) and silica (Aerosil OX50)-bound undecyl sulphonic acid catalyst (**14**, 0.44 mmol sulphonic acid groups) (◇).

lyst (**14**) were found, which are nearly identical to that obtained for the homogeneous CH<sub>3</sub>SO<sub>3</sub>H catalyst ( $2.1 \times 10^{-4} \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$ , Table 2). Thus, limitation of the reaction rate by diffusion (mass-transfer) near the surface of the solid catalyst can be discarded (see also Appendix A). Since the rate of isobornyl acetate (**3**) formation is neither affected by the length of the

Table 2

Rate constants for CH<sub>3</sub>SO<sub>3</sub>H and alkyl sulphonic acid surface-functionalised silica's, normalised on the concentration of sulphonic acid groups<sup>a</sup>

| Catalyst                                                                                                                                          | $k'_1$ ( $\text{l}^2 \text{ mol}^{-2} \text{ s}^{-1}$ ) |
|---------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------|
| CH <sub>3</sub> SO <sub>3</sub> H                                                                                                                 | $2.1 \times 10^{-4}$                                    |
| SiO <sub>2</sub> (Aerosil OX50)<br>=Si(CH <sub>3</sub> )(CH <sub>2</sub> ) <sub>3</sub> SO <sub>3</sub> H ( <b>10a</b> )                          | $3.3 \times 10^{-4}$                                    |
| SiO <sub>2</sub> (Aerosil OX50)<br>=Si(CH <sub>3</sub> )(CH <sub>2</sub> ) <sub>11</sub> SO <sub>3</sub> H ( <b>14</b> )                          | $2.9 \times 10^{-4}$                                    |
| SiO <sub>2</sub> (Aerosil OX50)<br>=Si(CH <sub>3</sub> )(CH <sub>2</sub> ) <sub>3</sub> SO <sub>3</sub> H ( <b>10a</b> ), 0.47 M H <sub>2</sub> O | $2.8 \times 10^{-4}$                                    |
| SiO <sub>2</sub> (Aerosil 200)<br>=Si(CH <sub>3</sub> )(CH <sub>2</sub> ) <sub>3</sub> SO <sub>3</sub> H ( <b>10b</b> ), 0.47 M H <sub>2</sub> O  | $2.4 \times 10^{-4}$                                    |
| SiO <sub>2</sub> (Aerosil OX50)<br>=Si(CH <sub>3</sub> )(CH <sub>2</sub> ) <sub>3</sub> SO <sub>3</sub> H ( <b>10a</b> ), 0.47 M H <sub>2</sub> O | $3.0 \times 10^{-2b}$                                   |
| SiO <sub>2</sub> (Aerosil 200)<br>=Si(CH <sub>3</sub> )(CH <sub>2</sub> ) <sub>3</sub> SO <sub>3</sub> H ( <b>10b</b> ), 0.47 M H <sub>2</sub> O  | $3.8 \times 10^{-2b}$                                   |

<sup>a</sup> [RSO<sub>3</sub>H] < 0.06 M.

<sup>b</sup> After induction period (Fig. 4).

hydrophobic alkyl chain (Fig. 3 and Table 2), these results indicate that the mechanism for isobornyl acetate (**3**) formation is the same for homogeneous  $\text{CH}_3\text{SO}_3\text{H}$  as for the heterogeneous alkyl sulphonic acid surface-functionalised silica's. Furthermore, co-operation effects do not contribute (vide supra).

### 3.6. Influence of water on the catalytic performance

To improve the catalytic performance, it is expected that a catalyst with a larger content of sulphonic acid groups gives rise to a higher reaction rate. Such a material was obtained by using a silica support material of a larger specific surface area (**10b**), for which the surface coverage was not altered (Table 1). In addition, it is expected that the presence of small quantities of water may enhance and facilitate proton transfer and mobility from the sulphonic acid to the alkene [65–68], giving rise to an increase in the reaction rate.

To establish if a higher content of sulphonic acid groups as well as the presence of water increases the reaction rate, the hydro-acyloxy-addition was performed with a silica-bound propyl sulphonic acid catalyst of a specific surface area of  $50\text{ m}^2\text{ g}^{-1}$  (**10a**) and also with a silica-bound propyl sulphonic acid catalyst with a specific surface area of  $200\text{ m}^2\text{ g}^{-1}$  (**10b**), both in the presence of water (10 mol% with respect to each of the reactants). Fig. 4 shows that a higher content of sulphonic acid groups indeed

accelerates the overall rate of formation of isobornyl acetate (**3**), while the enhancing effect of water on the reaction rate is corroborated by the different reaction rates for **10a** in Figs. 3 and 4. Notice that in the presence of water, but without a catalyst, the reaction rate is almost equal to zero; after 15,000 min only a trace amount of **3** (ca. 1%) is found (Fig. 4). This is rationalised by the fact that acetic acid itself is not sufficiently dissociated and thus does not provide enough protons; the autoprotolysis constant of glacial acetic acid is  $10^{-13}\text{ mol l}^{-1}$  [69], whereas the dissociation constant of methane sulphonic acid in glacial acetic acid is  $5.1 \times 10^{-7}\text{ mol l}^{-1}$  [58].

In the initial stage of the reactions catalysed by the silica-bound propyl sulphonic acids with water present, an induction in the formation of isobornyl acetate (**3**) takes place (Fig. 4). During the induction period (about 1500 and 500 min for **10a** and **10b**, respectively, cf. Fig. 6), the normalised reaction rate constants ( $k'_1$ ) are of the same order of magnitude as obtained without water or with the  $\text{CH}_3\text{SO}_3\text{H}$  catalyst (Table 2). After the induction period, the normalised reaction rate constants are  $3.0 \times 10^{-2}\text{ l}^2\text{ mol}^{-2}\text{ s}^{-1}$  for **10a** and  $3.8 \times 10^{-2}\text{ l}^2\text{ mol}^{-2}\text{ s}^{-1}$  for **10b**. These values are of similar order of magnitude, but two orders of magnitude higher than in the absence of water (Table 2).

To check whether the enhancing effect of water on the reaction rate is caused by the formation of homogeneous alkyl sulphonic acids, i.e. by hydrolysis

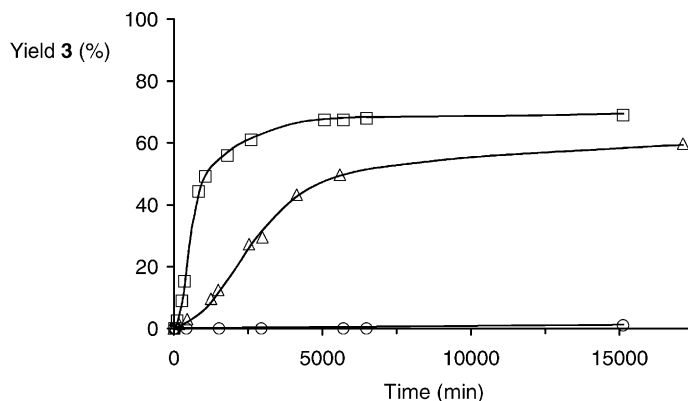


Fig. 4. Formation of isobornyl acetate (**3**) by the solvent-free hydro-acyloxy-addition of acetic acid (**1**, 0.70 mol) to camphene (**2**, 0.70 mol) at 338 K as a function of time in the presence of water (0.07 mol). In the absence of a catalyst (○); in the presence of the silica (Aerosil OX50)-bound propyl sulphonic acid catalyst (**10a**, 0.24 mmol sulphonic acid groups) (△) or the silica (Aerosil 200)-bound propyl sulphonic acid catalyst (**10b**, 0.96 mmol sulphonic acid groups) (□).

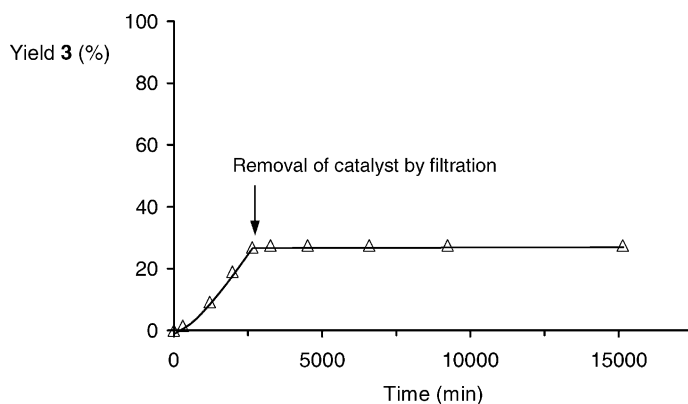


Fig. 5. Formation of isobornyl acetate (**3**) by the solvent-free hydro-acyloxy-addition of acetic acid (**1**, 0.70 mol) to camphene (**2**, 0.70 mol) at 338 K as a function of time in the presence of water (0.07 mol) with silica (Aerosil OX50)-bound propyl sulphonic acid catalyst (**10a**, 0.24 mmol sulphonic acid groups). After removal of the catalyst by filtration, the reaction does not proceed.

of the silyl ether (Si–O–Si) linkages and/or Si–C bonds of the silica-bound alkyl sulphonic acids, the catalyst was removed from the reaction mixture by filtration during the reaction. Since this resulted in a complete stop of the hydro-acyloxy-addition reaction (Fig. 5), the alkyl sulphonic acid surface-functionalised silica's were found to be proper heterogeneous catalysts. Consequently, water must be involved in the mechanism of isobornyl acetate (**3**) formation.

Besides the possibility of facilitating proton transfer (vide supra), water also competes as a nucleophile with acetic acid for capturing the protonated alkene. This is confirmed by the formation of isoborneol (**15**,

Fig. 6). The presence of isoborneol (**15**) (and the absence of leaching) strongly supports that water has to be absorbed near the catalyst surface. Isoborneol (**15**) is present as an intermediate, which is confirmed by the result that its concentration passes through a maximum (Fig. 6) and by the fact that isoborneol (**15**) is in equilibrium with camphene (**2**) and water in the presence of an acid catalyst [70,71]. Since the intermediate formation of isoborneol (**15**) is accompanied by an increased formation rate of isobornyl acetate (**3**), the presence of water facilitates a more favourable, parallel reaction path involving isoborneol (**15**, reactions 3a and 3b).

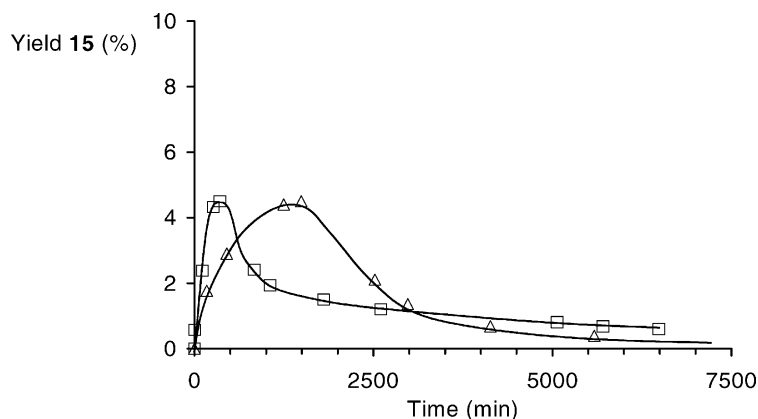
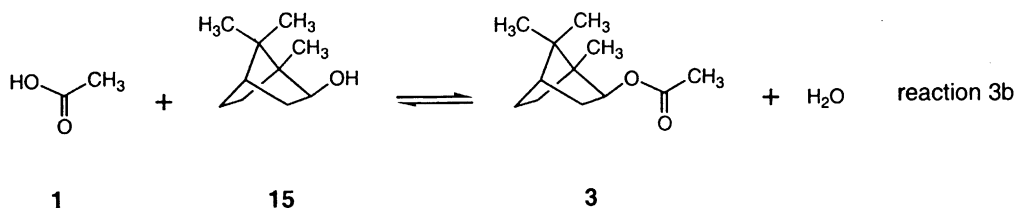
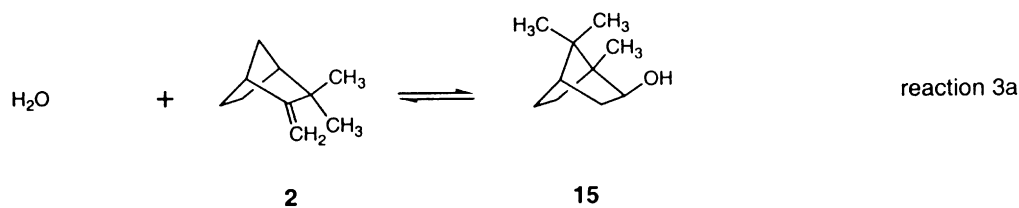


Fig. 6. Formation of isoborneol (**15**) by the solvent-free hydro-acyloxy-addition of acetic acid (**1**, 0.70 mol) to camphene (**2**, 0.70 mol) at 338 K as a function of time in the presence of water (0.07 mol). With the silica (Aerosil OX50)-bound propyl sulphonic acid catalyst (**10a**, 0.24 mmol sulphonic acid groups) ( $\Delta$ ) or the silica (Aerosil 200)-bound propyl sulphonic acid catalyst (**10b**, 0.96 mmol sulphonic acid groups) ( $\square$ ).



#### 4. Conclusions

Methyl(3-sulphopropyl)siloxane surface-functionalised silica's (**10a** and **10b**) and methyl(11-sulphoundecyl)siloxane surface-functionalised silica (**14**) were prepared by surface modification reactions without the formation of protruding polysiloxanes. These non-porous surface-functionalised materials act as proper heterogeneous Brønsted acid catalysts in the solvent-free liquid-phase hydro-acyloxy-addition reaction of acetic acid (**1**) to camphene (**2**), which yields the pine-fragrance isobornyl acetate (**3**). The observation that the reaction rate constants are similar to those of the homogeneous catalyst  $\text{CH}_3\text{SO}_3\text{H}$  (normalised on the concentration of sulphonic acid groups) indicates that the mechanism of isobornyl acetate (**3**) formation is the same for homogeneous and heterogeneous catalysts. Addition of water to the reaction mixture facilitates the formation of **3** via its corresponding alcohol isoborneol (**15**) and gives rise to an increase in the reaction rate of two orders of magnitude, while the sulphonic acid surface-functionalised materials still act as heterogeneous acid catalysts.

#### Acknowledgements

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University) are gratefully acknowledged for performing the XPS measurements.

#### Appendix A. Calculation of reaction rate constants

The hydro-acyloxy-addition of acetic acid (**1**) to camphene (**2**) can be modelled by a reversible reaction:



where  $k_1$  and  $k_2$  are the apparent reaction rate constants of the forward and the reverse reaction, respectively. Then, the reaction rate  $r$  is expressed by the following differential equation, where  $[\text{A}]$ ,  $[\text{B}]$  and  $[\text{C}]$  are the concentrations of acetic acid (**1**), camphene (**2**) and isobornyl acetate (**3**), respectively, (concentrations at  $t = 0$  are indicated by the subscript "0", while concentrations at equilibrium are indicated by the subscript "eq"):

$$\left. \begin{aligned}
 r &= \frac{d[\text{C}]}{dt} = k_1[\text{A}][\text{B}] - k_2[\text{C}] \\
 \text{furthermore : } K_{\text{eq}} &= \frac{k_1}{k_2} = \frac{[\text{C}]_{\text{eq}}}{[\text{A}]_{\text{eq}}[\text{B}]_{\text{eq}}} \\
 \text{experimental conditions : } &[\text{A}] = [\text{B}] \\
 \text{in addition : } &[\text{A}] = [\text{A}]_0 - [\text{C}]
 \end{aligned} \right\} \frac{d[\text{C}]}{dt}$$

$$= k_1([\text{C}]_{\text{eq}} - [\text{C}]) \left( \frac{[\text{A}]_0^2}{[\text{C}]_{\text{eq}}} - [\text{C}] \right) \quad (\text{A.2})$$

Integration of Eq. (A.2) and using  $[C]_0 = 0$ :

$$\begin{aligned} & \int_{[C]_0}^{[C]} \frac{d[C]}{([C]_{\text{eq}} - [C]) \left\{ \frac{[A]_0^2}{[C]_{\text{eq}}} - [C] \right\}} \\ &= \int_0^t k_1 dt \Rightarrow -\frac{1}{[C]_{\text{eq}} + \frac{[A]_0^2}{[C]_{\text{eq}}}} \ln \\ & \times \left| \frac{\frac{[A]_0^2}{[C]_{\text{eq}}} - [C]}{[C]_{\text{eq}} - [C]} \right| = -\frac{1}{[C]_{\text{eq}} - \frac{[A]_0^2}{[C]_{\text{eq}}}} \\ & \times \ln \left| \frac{[A]_0^2}{[C]_{\text{eq}}^2} \right| + k_1 t \end{aligned} \quad (\text{A.3})$$

Units of the apparent reaction rate constants,  $k_1$ :  $1 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $k_2$ :  $\text{s}^{-1}$ .

In the case of  $[C]_{\text{eq}} \rightarrow [A]_0$ , Eq. (A.1) changes to



Consequently, Eq. (A.3) changes to Eq. (A.7) by taking the limit of  $[C]_{\text{eq}} \rightarrow [A]_0$  (which can be found by substituting  $[C]_{\text{eq}} = [A]_0 + a$  and taking the limit  $a \rightarrow 0$ ):

$$\lim_{[C]_{\text{eq}} \rightarrow [A]_0} -\frac{1}{[C]_{\text{eq}} - \frac{[A]_0^2}{[C]_{\text{eq}}}} \ln \left| \frac{[A]_0^2}{[C]_{\text{eq}}^2} \right| = \frac{1}{[A]_0} \quad (\text{A.5})$$

Using  $[C] = [A]_0 - [A]$ :

$$\begin{aligned} & \lim_{[C]_{\text{eq}} \rightarrow [A]_0} -\frac{1}{[C]_{\text{eq}} + \frac{[A]_0^2}{[C]_{\text{eq}}}} \ln \\ & \times \left| \frac{\frac{[A]_0^2}{[C]_{\text{eq}}} - [C]}{[C]_{\text{eq}} - [C]} \right| = \frac{1}{[A]} \end{aligned} \quad (\text{A.6})$$

$$\begin{aligned} \frac{1}{[A]} &= \frac{1}{[A]_0} + k_1 t, \quad : \quad [A] = [A]_0 - [C] \\ & \times \frac{1}{[A]_0 - [C]} = \frac{1}{[A]_0} + k_1 t \end{aligned} \quad (\text{A.7})$$

For both models (Eqs. (A.1) and (A.4)) at low catalyst concentrations:

$$\begin{aligned} k_1 &= k'_1 [\text{RSO}_3\text{H}] \quad (\text{with } k_1 : 1 \text{ mol}^{-1} \text{ s}^{-1}, \\ k'_1 &: \text{l}^2 \text{ mol}^{-2} \text{ s}^{-1}) \end{aligned} \quad (\text{A.8})$$

### A.1. Calculation of diffusion-controlled reaction rate for a non-porous catalyst

To get an indication whether the reaction rate is limited by diffusion-controlled transport of reactants, the diffusion rate of the reactants were calculated and compared with their reaction rate (for isothermal, steady-state conditions without catalyst aggregation and agitation) [72,73].

Consider an imaginary sphere of radius  $p$  surrounding a catalyst particle with radius  $L$ . The molar flux  $J_A$  of a reactant A through the surface is the amount of A molecules that pass through per unit area per unit time. Therefore, the total flow  $F_{\text{diff A}}$ , the amount of A molecules per unit time passing through the entire surface area  $4\pi p^2$ , is:

$$F_{\text{diff}} (\text{mol s}^{-1}) = 4\pi p^2 J_A \quad (\text{A.9})$$

Using Fick's first law  $J_A = \mathbb{D}_A d[A]/dp$ , with  $\mathbb{D}_A$  the diffusion coefficient of A, yields:

$$F_{\text{diff A}} (\text{mol s}^{-1}) = 4\pi p^2 \mathbb{D} \frac{d[A]}{dp} \quad (\text{A.10})$$

Separation of variables and integration using the boundary conditions  $[A]_{p=L} = [A]_{\text{eq}}$  (assuming an equilibrium concentration of reactant A at the particle surface) and  $[A]_{p=\infty} = [A]$  gives

$$F_{\text{diff A}} (\text{mol s}^{-1}) = 4\pi L \mathbb{D}_A ([A] - [A]_{\text{eq}}) \quad (\text{A.11})$$

Hence, for  $N_p$  catalyst particles:

$$F_{\text{diff A, tot}} (\text{mol s}^{-1}) = 4\pi L N_p \mathbb{D}_A ([A] - [A]_{\text{eq}}) \quad (\text{A.12})$$

where

$$N_p = \frac{m/\rho}{(4/3)\pi L^3} \quad (\text{A.13})$$

with  $m$  is the amount of catalyst (kg) and  $\rho$  the catalyst density ( $\text{kg m}^{-3}$ ).

The current experimental conditions  $L = 20 \times 10^{-9} \text{ m}$  (Aerosil OX50) [23],  $m = 5.0 \times 10^{-3} \text{ kg}$  (see Section 2),  $\rho_{\text{catalyst}} \approx \rho_{\text{SiO}_2} = 2.3 \times 10^3 \text{ kg m}^{-3}$ ,  $\mathbb{D}_A = 1.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  (glacial acetic acid, (1)) [74], volume of the reaction mixture  $= 149 \times 10^{-6} \text{ m}^3$  (experimentally determined),  $[A]_0 = 4.7 \times 10^3 \text{ mol m}^{-3}$  and  $[A]_{\text{eq}} = 0.3 \times [A]_0 = 1.4 \times 10^3 \text{ mol m}^{-3}$  give an

initial diffusion-controlled reaction rate of

$$r_{\text{diff A}} (\text{mol m}^{-3} \text{s}^{-1}) = \frac{5.4 \times 10^4}{149 \times 10^{-6}} = 3.6 \times 10^8 \quad (\text{A.14})$$

Since under the current experimental conditions  $[A]_0 = [B]_0$  and by assuming  $\mathbb{D}_A = \mathbb{D}_B$ , a similar diffusion-controlled transport rate is derived for reactant B [camphene (2)].

Using Eq. (A.2), the reaction rate  $r$  ( $\text{mol l}^{-1} \text{s}^{-1}$ ) as a function of reactant A is expressed by

$$r = k_1 \left( [A]^2 + \frac{[A]}{K_{\text{eq}}} - \frac{[A]_0}{K_{\text{eq}}} \right) \quad (\text{A.15})$$

Hence, by using Eqs. (A.8) and (A.15) and  $[A] = [A]_0$  at  $t = 0$ , the initial reaction rate can be expressed as

$$r_i (\text{mol l}^{-1} \text{s}^{-1}) = k' [\text{RSO}_3\text{H}] [A]_0^2 \quad (\text{A.16})$$

By using the results in Tables 1 and 2, values for  $r_i$  obtained are lower by several orders of magnitude than  $r_{\text{diff A, tot}}$  [Eq. (A.14)], which shows that there is no diffusion (mass-transfer) limitation of the reaction rate. For example, for the silica-bound methyl(3-sulphopropyl)siloxane catalyst (10a):

$$\begin{aligned} r_i (\text{mol l}^{-1} \text{s}^{-1}) &= k' [\text{RSO}_3\text{H}] [A]_0^2 = 3.3 \times 10^{-4} \\ &\times [2.0 \times 10^{-3}] [4.7]^2 = 1.5 \times 10^{-5}; \\ r_i (\text{mol m}^{-3} \text{s}^{-1}) &= 1.5 \times 10^{-2} \end{aligned} \quad (\text{A.17})$$

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