

Unique silane modified perfluorosulfonic acids as versatile reagents for new solid acid catalysts

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A new versatile reagent, a perfluorosulfonate/trisilanol [(OH)₃Si(CH₂)₃(CF₂)₂O(CF₂)₂SO₃⁻M⁺], is synthesized and a series of surface bound strong solid acid catalysts developed which are active for catalyzing a range of reactions, for example alkene isomerization, alkylations and acylations.

Over recent years there has been considerable interest in the development of solid acid catalysts¹⁻⁶ as environmentally benign replacements for their homogeneous counterparts such as HF. The importance of this area of research has been highlighted by a number of reviews where the use of strong solid acids such as sulfated zirconia,¹ heteropolyacids,² zeolites,³ aluminosilicates,⁴ perfluorinated resinsulfonic acids⁵ and the weaker polystyrene-based sulfonic acid resins with low thermal stability⁶ has been described. In the case of perfluorinated sulfonic acid resins, access to the acid sites can be restricted giving rise to low activity for reactions in non-polar solvents or in the gas phase. The high acid strength and chemical and thermal stability of perfluorosulfonic acids is well known⁵ and the ability to heterogenize these functional groups, at the same time maintaining ready accessibility, would be a major step forward.

In this paper we describe the synthesis of [(OEt)₃Si(CH₂)₃(CF₂)₂O(CF₂)₂SO₂F] **1** via the direct hydrosilylation of CH₂=CHCH₂(CF₂)₂O(CF₂)₂SO₂F with HSi(OEt)₃ using a platinum catalyst which produces exclusively **1** in 85% yield.† This can be hydrolyzed to [(OH)₃Si(CH₂)₃(CF₂)₂O(CF₂)₂SO₃⁻M⁺] **2**. This new reagent can be surface attached to yield a new type of strong solid acid catalyst.

The triethoxysilyl perfluorosulfonyl fluoride, **1**, can be hydrolyzed by the reaction of **1** in a mixture of distilled water, dimethyl sulfoxide and potassium hydroxide (58% water–30% Me₂SO–12% KOH). Typically compound **1** is left to react at 90 °C for 18 h in water and basic Me₂SO solution, after which time the sulfonyl fluoride is completely hydrolyzed giving a stable, clear solution. The loss of the sulfonyl fluoride peak at 47 ppm can be monitored using ¹⁹F NMR spectroscopy. After hydrolysis only signals at –77.2 (–OCF₂CF₂SO₂F), –83 (–CH₂CF₂CF₂O–), –112 (–CH₂CF₂CF₂–) and –112.3 (–CF₂CF₂SO₂F) ppm are observed in the ¹⁹F NMR spectrum. The ²⁹Si NMR spectrum with a peak at –46.3 ppm, shows the silicon alkoxides are hydrolyzed to –Si(OH)₃ (or ion-dissociated forms), having less than 10% forming –SiOSi– bonds. The new compound, which can be described as [(OH)₃Si(CH₂)₃(CF₂)₂O(CF₂)₂SO₃⁻M⁺] **2**, has been used to synthesize a series of surface-bound strong solid acid catalysts.

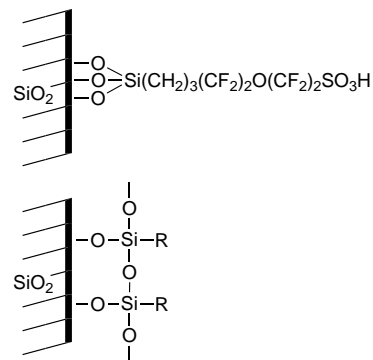
Solid acid catalysts formed from **2** can be made by surface modification and attachment to an existing support or, alternatively, materials can be synthesized using an *in situ* sol-gel technique. Using both of these approaches a covalently bonded perfluorosulfonic acid is attached to the surface (see Scheme 1, the two structures denote low to high loadings). We have found the acid functionality to be readily accessible, stable on the surface and very active for a range of catalytic reactions.

Using an *in situ* sol-gel approach, tetraalkoxysilanes are hydrolyzed and co-condensed in the presence of **2** to yield very high surface area materials with pendent sulfonic acid groups.

The formation of silica networks and organically modified silica networks^{8,9} has been described in detail previously. A typical procedure for these new materials is outlined below. Compound **2** (from heating **1**, 2.6 g in 40 ml of the water–Me₂SO–KOH mixture, overnight at 90 °C), was cooled and the pH was adjusted to 6 (4 M HCl). A solution of hydrolyzed tetramethoxysilane was then added (68 g TMOS, 10.9 g water and 1 g of 0.04 M HCl, stirred for 30 min). Gellation occurs in *ca.* 30 s. The dried modified silica network is then re-acidified by washing with 4 M nitric acid. The final materials (*ca.* 0.5–2 mm in size) are hard, glass-like, with high surface areas. The surface area (determined by BET), pore volume, and pore diameter are found to be 550 m² g⁻¹, 0.75 cm³ g⁻¹ and 55 Å respectively. Successful incorporation of **2** is shown using solid-state ¹⁹F NMR spectroscopy, chemical analysis, thermogravimetry (TG) coupled with measurements of the acid equivalents. The number of acid equivalents (for a material which contains 6 mass% organics from TG in the range 300–500 °C) is 0.18 mequiv. g⁻¹ (determined *via* titration), with F and S contents of 2.77 and 0.69 mass% respectively from pendent –(CH₂)₃(CF₂)₂O(CF₂)₂SO₃H functionalities. The solid-state ¹⁹F NMR spectrum has strong peaks at –84.5 and –122.5 ppm (close to the parent **2**). We estimate *ca.* 90% incorporation of **2** within the silica network. Higher loadings (up to 25 mass% of **2**) have also been developed.

Compound **2** has also been attached to a range of pre-formed supports. The chemistry strongly parallels that of silane coupling chemistry to surfaces (using trialkoxysilanes) which is well documented.¹⁰ A solution of **2** was added to a high surface area silica support (CS-1020E, PQ corporation; *ca.* 400 m² g⁻¹) and the support and surface modifier were treated with acid to neutrality. The material was then dried and re-acidified. The materials are very stable to leaching; for example, when left overnight in 4 M nitric acid at 90 °C no significant leaching occurred.

These materials are catalytically active for a number of acid catalyzed reactions. In some cases the activity of these materials (based upon acid equivalents) compared to Amberlyst resins are orders of magnitude higher reflecting the increased acid strength due to the perfluorosulfonic acid group. In Table 1, we



Scheme 1

Table 1 Catalytic conversions (mol%) shown for reactions over the solid acid catalysts

	Catalyst		
	Surface/Si(CH ₂) ₃ -(CF ₂) ₂ O(CF ₂) ₂ -SO ₃ H	NR50	Amberlyst-15
Acid capacity/ (mequiv H ⁺) g _{cat} ⁻¹	0.2	0.9	4.6
Linear alkylbenzene (LAB) ^a	43	3	5
Toluene alkylation with hept-1-ene ^b	99	5	13
But-1-ene isomerization ^c	95	14	47
<i>m</i> -Xylene acylation ^d	89	99	— ^e

^a Reaction conditions: 1 g catalyst, 21.5 g benzene, 10 g of dodec-1-ene, reacted at 80 °C for 1 h. Dodec-1-ene conversion measured using GC. ^b 1 g catalyst, 8.4 g heptene, 15.6 g of toluene, reacted at 100 °C for 2 h, conversion is based on hept-1-ene. ^c Conversion of but-1-ene to *cis-trans* isomers of He = but-1-ene = 38 ml min⁻¹, MHSV of but-1-ene = 1 h⁻¹ at 50 °C. ^d 1 g catalyst, 14 g benzoyl chloride and 21.2 g *m*-xylene reacted at 140 °C for 6 h, conversion is based on benzoyl chloride, the reaction rates are 76 and 300 mm (mequiv H⁺)⁻¹ h⁻¹ for NR50 and the surface modified catalyst, respectively. ^e Reaction temperature too high for Amberlyst-15 catalyst.

show the catalytic activity of this material for three types of reactions, electrophilic aromatic alkylations, alkene isomerizations and Friedel–Crafts acylation. For comparison we also show the activity of a perfluorinated resin sulfonic acid (Nafion resin NR50) which in non-swelling solvents is known to have limited access to all the acid sites,¹¹ and that of Amberlyst-15. Both the surface modified materials and the *in situ* formed materials show the same kind of activity. The results demonstrate the utility of these new materials as solid acid catalysts. Notice that the acid capacities of Amberlyst-15 and NR50 are significantly higher than that of the surface modified catalyst. The differences of reaction rates based on the same amount of acids in the catalysts are much more pronounced than the conversions. Linear alkylbenzenes (LAB) which are made in large quantities (using HF) are widely used in the manufacture of detergents. The new catalyst was found to be very effective as the alkylation catalyst. Conversion of >99% was obtained with 2 g of catalyst and after 6 h. Similar activity patterns (the optimum being the surface attached fluorosulfonic acid) were observed for the isomerization of longer chain α -alkenes (>C₁₂) which are important for use as lubricants. The higher activity of these materials, compared to the polymer Nafion NR50 resin, indicates that most of the acid sites, which are exclusively on the surface, are readily accessible in contrast to the gel type NR50 where most of the acids are buried inside the polymer particles. Data in Table 1 indicated that the surface modified catalyst and NR50 are very effective heterogeneous catalysts for Friedel–Crafts acylation. This is routinely carried

out using Lewis acids such as AlCl₃, which produces large amounts of waste streams, for use in the fine chemical and other industries. NR50 is more efficient for this reaction mainly due to the higher temperature and polar reagent employed that swells the framework of Nafion resin which enhances the acid sites accessibilities.

A quantitative kinetic study of the dimerization of α -methylstyrene (AMS) catalyzed by sulfonic acid resins was also investigated. A detailed kinetic study has been reported previously.^{6,12} The first order rate constants for the surface attached 2, Nafion NR 50 and Amberlyst-15 (AMS, 6 g in 54 g of cumene as solvent, using 1 g of catalyst, at 50 °C) was found to be 1000, 0.1 and 0.6 [(mequiv. H⁺)⁻¹ h⁻¹], respectively. Supported Nafion also shows low activity. The higher activity, >1000-fold, is striking.

Footnotes and References

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† The perfluoroiodide (213 g), ICF₂CF₂O(CF₂)₂CF₂SO₂F,⁷ was stirred under nitrogen with allyl acetate (57 g) and heated to 100 °C. Benzoyl peroxide (4 g) was added over 4 h. The solution was distilled to yield 200 g of pure product CH₃COOCH₂CHICH₂(CF₂)₂O(CF₂)₂SO₂F, bp 87 °C at 0.1 mmHg. ¹⁹F NMR: δ +45.1 (m, 1F), -82.7 (m, 2F), -87.9 (dt, J 142.4 13.0 Hz, 1F), -88.8 (dt, J 142.4, 12.8 Hz, 1F), -112.7 (m, 2F), -117.3 (ddd, J 262.3, 26, 10.2, Hz, 1F), -118.6 (ddd, J 262, 24 Hz, 1F). The product was added to 35 ml isopropyl alcohol, 42 ml acetic acid and 54.4 g zinc powder (90 °C). The mixture was left for a further 4 h. The residue was washed with water and aqueous sodium hydrogencarbonate solution. Distillation gave 108 g of pure CH₂=CHCH₂(CF₂)₂O(CF₂)₂SO₂F (85% yield), bp 134–135°, ¹⁹F NMR: δ +45.0 (m, 1F), -82.6 (m, 2F), -87.3 (m, 2F), -112.6 (m, 2F), -117.4 (t, J 17.6 Hz, 2F). See G. Caiyun and C. Qingyun, *Huaxue Xuebao*, 1984, 592. (OEt)₃Si(CH₂)₃(CF₂)₂O(CF₂)₂SO₂F: ¹H NMR (C₆D₆) δ 0.51 (t, 2H, CH₂Si), 1.13 (t, 9H, CH₃), 1.66–2.01 (m, 4H, CH₂CH₂), 3.71 (q, 6H, CH₂O). ¹³C NMR (C₆D₆) δ 10.86 (SiCH₂), 15.05 (CH₂), 18.18 (CH₃), 33.54 [t, CH₂CF₂, ²J(CF) 21.6 Hz], 58.94 (OCH₂), 108–123. (m, CF₂). MS (EI) *m/z* 503 (M⁺ - H), 489 (M⁺ - CH₃), 459 (M⁺ - OCH₂CH₃); exact mass for M⁺ - H fragment, C₁₃H₂₀SO₆FSi, calc. *m/z* 503.06061803, found *m/z* 503.060178. Anal. Calc. for C₁₃H₂₁SO₆SiO₆: C, 30.95; H, 4.19; S, 6.36. Found: C, 30.44; H, 3.89; S, 6.46%.

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