Direct synthesis of porous organosilicas containing chiral organic groups within their framework and a new analytical method for enantiomeric purity of organosilicas†

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Organosilica porous solids containing chiral organic moieties in the framework with an enantiomeric purity of 95% ee, estimated by eluting organic constituent units from chiral organosilicas, were synthesized from a newly designed chiral (*R*)-(+)-1,2-bis(trimethoxysilyl)phenylethane precursor *via* a surfactant-mediated self-assembly approach.

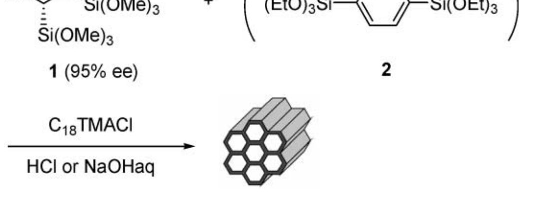
The concept of periodic mesoporous organosilicas (PMOs) possessing a homogeneous distribution of organic and silica moieties in its framework emerged in the late 1990's with the expansion of conventional mesoporous materials.[1] PMOs, synthesized from 100% or less organic-bridged organosilane precursors [$(R'O)_3Si–R–Si(OR')_3$], are widely studied because they offer multiple advantages in designing materials for diverse applications.[2] The introduction of chirality into PMOs is one of the most exciting topics. Several groups reported the synthesis of PMOs from bridged organosilanes containing various chiral organic groups such as bulky vanadyl Schiff base complexes,[3] a binaphthyl group,[4] and diaminocyclohexane groups.[5,6] The PMOs showed optical activity and enhanced activity for asymmetric reactions. They showed the higher potential of the chiral mesoporous organosilicas for applications such as chromatography of optical isomers or enantioselective catalysis. Previous studies have typically employed a large amount of pure silica precursor such as tetraethoxysilane (60–95 mol%) for co-condensation to stabilize the porous framework because the bridging organic groups are too bulky to accommodate in the framework. However, the introduction of a higher amount of chiral organic groups in the framework of mesoporous materials is highly promising from the standpoint of improving the performance of chiral organosilicas. Recently, Polarz *et al.*[7] and Ide *et al.*[8] reported the synthesis of functionalized mesoporous ethylene-silicas from 100% chiral borated ethylene-bridged disilane precursors prepared by enantioselective hydroboration. However, borated ethylene-bridged precursors are limited in that they only yield mesoporous organosilicas functionalized with amino and hydroxy groups. A variety of sol–gel precursors having highly controlled asymmetric centers would open a wide range of opportunities for the development of chiral organosilicas. The development of a simple analytical method for determining the enantiomeric purity of chiral organosilicas is of utmost importance as well.

In this communication, we present a novel synthesis of chiral porous organosilicas *via* surfactant-mediated self-assembly from a newly designed chiral (*R*)-(+)-1,2-bis(trimethoxysilyl)phenylethane, **1**, of 95% ee (Scheme 1), and describe a simple, widely applicable method for determining the enantiomeric purity of organosilica solids.

The hydrosilylation of (*E*)-1-phenyl-2-trichlorosilylethene (14.3 g) with trichlorosilane in the presence of 0.3 mol% palladium–(*R*)-**3** as catalyst, followed by the addition of methanol and triethylamine, gave 18.9 g of **1** in 91% yield and 95% ee (Scheme 2, Supporting Information†).[9]

Further, in a typical synthesis of organosilica, 0.63 g of octadecyltrimethylammonium chloride (C_{18}TMACl) was dissolved in 9 g of deionized water and 4.5 g of HCl (∼36%) was added to obtain a homogeneous aqueous acid solution. Then, 0.87 g of **1** was slowly introduced, and the mixture was stirred vigorously under ambient conditions for 42 h. After heating at 80 °C for 8 h under static conditions, the gel was cooled and kept under ambient conditions for around 16 h, followed by further heating at 80 °C for another 7 h under static conditions. The resultant precipitate was recovered by filtration and suspended in a C_{18}TMACl solution of NH_4F at 70 °C for 6 h to stabilize the framework structure. The surfactant was removed by extraction using an ethanol–HCl solution as described elsewhere.[1]

In the basic synthesis procedure, 0.91 g of precursor **1** was added to a homogeneous solution of C_{18}TMACl surfactant



Scheme 1

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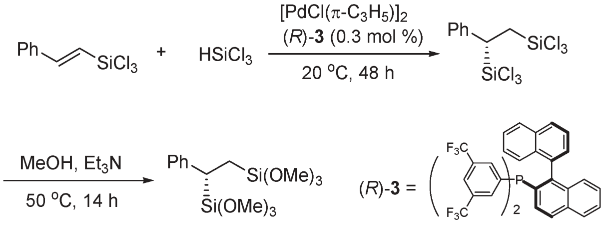

Scheme 2

(0.83 g), 6 N NaOH (1.2 g) and H_2O (15 g) and stirred vigorously for 9 h under ambient conditions. The gel was kept under ambient temperature for 18 h statically and heated at 45 °C for 33 h in a closed vessel. Finally, the solvent was evaporated from the open vessel over a period of 63 h. The material was filtered, recovered and dried prior to characterization.

Further, the synthesis of mesoporous hybrid solids with crystal-like pore walls[10] was attempted using a combination of chiral precursor **1** and 1,4-bis(triethoxysilyl)benzene, **2**, in basic medium. A mixture of precursors **1** and **2** was added into a homogeneous solution of the surfactant C_{18}TMACl and sodium hydroxide (3 N NaOH). The molar ratio of the initial gel was (**1** + **2**) : C_{18}TMACl : NaOH : H_2O = 1 : 0.48 : 1.2–1.4 : 280–400. The suspension was stirred vigorously at ambient temperature for 18 h followed by heating at 95 °C for 20 h. The white precipitate obtained was filtered, washed and dried before the surfactant was removed by extraction using an ethanol–HCl solution. Materials were synthesized with 20 and 40 mol% **1**. Details of the organosilica solids studied are listed in Table 1.

X-Ray diffraction patterns revealed the formation of ordered mesostructures in the organosilicas produced (Fig. 1). The organosilica derived from 100% precursor **1** under acidic conditions showed a broad peak centered with a *d*-spacing of 31.4 Å in the lower angle region. Meanwhile, only the lamellar phase was observed when the synthesis was performed under basic conditions (Table 1 entry 2, XRD not given). The organosilicas derived from the mixture of **1** and **2** (entry 4) showed sharp peaks at a lower angle (d = 45.0 Å) and also several peaks in the medium angle region at *d*-spacings of 7.6, 3.8 and 2.5 Å (Fig. 1A inset) confirming the molecular scale periodicity in the pore walls, in addition to the ordered mesostructure.[10] Transmission electron microscopy confirmed the 2D-hexagonal mesoporous structure in the organosilicas (Fig. 1B). Although the mesostructure ordering was not so significant for both organosilicas, as evidenced by the single peak in the low angle realm of the XRD patterns, the TEM result evidently confirmed the structural ordering, however, its proportion was modest in the materials.

Table 1 Microstructural properties of organosilicas prepared from **1** & **2**

Entry no.[a]	Precursor	BJH pore diameter/Å	Surface area/m^2 g^{-1}	ee (%)	Product structure
1	**1**	9.1	1180	95	microporous
2	**1**	—	—	—	lamellar
3	**1** + **2** (2 : 8)	28	780	—	mesoporous
4	**1** + **2** (4 : 6)	26	770	0	mesoporous

[a] Entry 1 in acidic medium, entries 2, 3 and 4 in basic media.

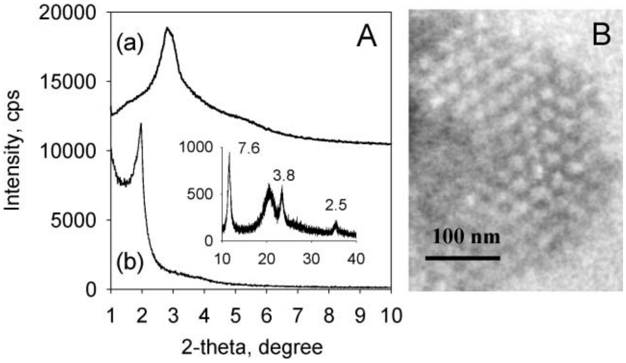

Fig. 1 (A) X-Ray diffraction patterns of organosilicas from (a) **1** (Table 1 entry 1) and (b) **1** and **2** (entry 4). (B) Transmission electron micrograph of mesoporous organosilica (entry 4).

Nitrogen adsorption–desorption isotherms confirmed the presence of uniform micropores (entry 1) or mesopores (entries 3 and 4) in the organosilicas (Fig. 2). The BJH (Barrett–Joyner–Halenda) pore diameters were 9.1 and 26 Å for the organosilicas derived from 100% **1** (entry 1) and a mixture of **1** and **2** (entry 4), respectively. One should notice that the pore size estimated by the BJH method is well under-estimated.[11]

Fig. 3 shows ^{29}Si and ^{13}C MAS NMR spectra. A broad resonance centered at −64.1 ppm was observed for the

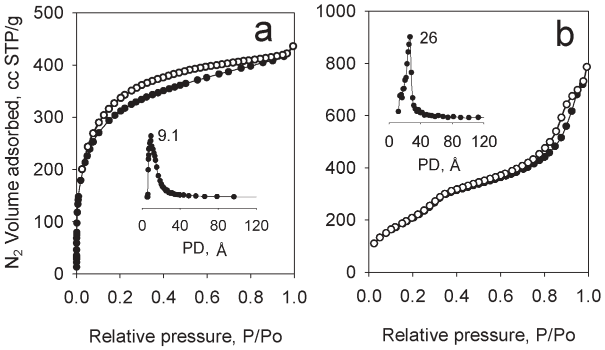

Fig. 2 N_2 adsorption–desorption isotherms and BJH pore size distribution curves (inset) of organosilicas from **1** (entry 1) and **1** and **2** (entry 4).

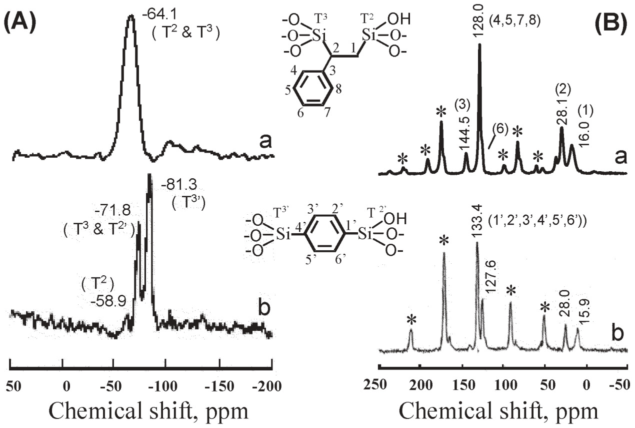

Fig. 3 (A) ^{29}Si MAS NMR and (B) ^{13}C CP-MAS NMR spectra of organosilicas from (a) **1** (entry 1) and (b) **1** and **2** (entry 4). [Spinning side bands are indicated with an asterisk (*).]

organosilica solid derived from 100% precursor **1**. This can be assigned to the combined resonance due to the T^2 and T^3 silicons bridged by a phenylethane moiety. Three resonances were observed at a chemical shift of −58.9, −71.8 and −81.3 ppm for the material derived from the mixture of **1** and **2**. The resonance at −58.9 ppm is attributable to the T^2 silicon bridged by the phenylethane moiety, while the resonance at −71.8 ppm is due to the combination of T^3 and $T^{2'}$ silicon bridged by phenylethane and benzene moieties. The strong resonance at −81.3 ppm is due to the $T^{3'}$ silicon bridged by the benzene moiety. Due to the crystal-like pore walls in the latter materials, the silicon moieties are well arranged in the system, resulting in the sharp resonances in the ^{29}Si MAS NMR spectrum.

All the resonances observed in the ^{13}C CP-MAS NMR spectrum of the organosilica material derived from 100% **1** are assignable and shown in Fig. 3. Meanwhile, the ^{13}C NMR spectrum of the material derived from the mixture of precursors **1** and **2** displayed signals for both phenylethane and benzene moieties. The signal at 133.4 ppm is due to the aromatic carbons of the bridged benzene, while the nearby accompanying resonances at 127.6, 28.0 and 15.9 ppm can be attributed to the phenyl group in phenylethane. Apart from these, the signals at 15.9–16.0 and 28.0–28.1 ppm are due to the carbons of the CH_2– and CH(Ph)– groups, respectively, and confirm the formation of the $(O_{1.5}Si–C_6H_4–SiO_{1.5})_n–(O_{1.5}Si–CH(Ph)CH_2–SiO_{1.5})_m$ network.

Decomposition of the silica network due to cleavage of siloxane bonds (Si–O–Si) in chiral organosilanes by HF treatment, followed by Tamao oxidation,[12] was successfully applied to elute organic constituent units of 1-phenyl-1,2-ethanediol for the determination of enantiomeric purity. The analysis resulted in 95% ee for the organosilica prepared from 100% **1** and showed no racemization during self-assembly. However, the enantiomeric excess of the mesoporous materials derived from the mixture of **1** and **2** was totally lost, indicating that racemization of the chiral center occurred during hydrolysis and condensation processes under basic conditions. Comparison of the ^{13}C NMR spectra of the two materials clearly showed that chemical moieties from **1** were also present in the resultant material. These results clearly indicate that acidic conditions are more suitable for the synthesis of chiral porous hybrid solids.

In summary, chiral porous organosilica was synthesized from 100% organosilane containing bridging organic chiral groups with high enantiomeric purity (95% ee). For the first time, the enatiomeric purity of organic groups in chiral organosilica solids was determined by eluting the organic groups from the solids. These chiral porous organosilicas can be used in chromatographic separation and enantioselective catalysis by attaching active functional species to the framework of the phenyl groups.

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