

Trimethoxy[4-(chloromethyl)-phenyl]silane: Under nitrogen atmosphere, a solution of trichloro[4-(chloromethyl)-phenyl]silane (5 g, 0.019 mol) was added dropwise to a mixture of methanol (5.6 mL), triethylamine (18 mL) and diethyl ether (53 mL) cooled at 0°C. A white precipitate of triethylammonium chloride was rapidly formed. The mixture was then stirred 15 h at room temperature. After removal of the solvent, hexane was added and the resulting ammonium salts were filtered off. Concentration of the filtrate under vacuum afforded the trimethoxy[4-(chloromethyl)-phenyl]silane as a yellow pale liquid (0.015 mol, 80%). ¹H NMR (300 MHz, CDCl₃, 25°C): δ 3.60 (s, 9H, -OCH₃), 4.59 (s, 2H, -CH₂Cl), 7.42 (dd, 2H, ³J_{HH} = 6.45 Hz, -C=CH), 7.65 (dd, 2H, ³J_{HH} = 6.45 Hz, -C=CH).

HMS-Cl: The HMS-Cl silica was prepared according to the Macquarrie procedure. Typically, 5.6 g of dodecylamine was dissolved at room temperature in aqueous ethanol (ethanol/water: 32/36). Then tetraethoxysilane (21.37 g, 0.1 mol) and trimethoxy[4-(chloromethyl)-phenyl]silane (1.65 g, 0.007 mol) was simultaneously but separately added to the template mixture. The resulting solution was stirred for 20 h and the white solid was recovered by filtration. Removal of the dodecylamine was carried out by soxhlet extraction over ethanol for 18h affording the hybrid organic-inorganic HMS-Cl. This latter was finally dried in an oven (50°C, 10⁻¹ mmHg) for 5 h. Yield = 11 g. The chloride content of the HMS-Cl solid was 2.02 mmol/g. IR (KBr) $\bar{\nu}$ = 758, 848 (-CH₂Cl), 1410, 1446, 1625, 2857(-OCH₃), 2930 (-CH₂), 3024 (-C=CH), 3741 (-Si-OH) cm⁻¹. Elemental analysis: %C: 17.04, %H: 2.47). From the N₂ adsorption-desorption isotherms, a very high BET surface of 915 m²/g was obtained.

KG-Cl: Under nitrogen atmosphere, trichloro[4-(chloromethyl)-phenyl]silane (0.01 mol) was added to a suspension of silica (KG-60, 2g) freshly activated (150 °C, 10⁻¹ mmHg, 15 h) in 25 mL of anhydrous toluene. The resulting mixture was stirred for 24h and the KG-Cl solid was collected by filtration and washed with dichloromethane and diethylether. Finally, the modified KG-Cl solid was washed in a soxhlet apparatus with dichloromethane for 15 h. Elemental analysis: %C: 7.87, %H: 1.05. IR spectrum was similar to that of HMS-Cl solid except that a weaker intensity of the $\nu_{\text{Si-OH}}$ band was observed.

KG-TBD and HMS-TBD: Triazabicyclo[4.4.0.]dec-5-ene (TBD, 2.4 g, 0.017 mol) was added to a suspension of 4g of KG-Cl or HMS-Cl in 40mL of anhydrous toluene. The resulting suspension was stirred at reflux for 15h and the white solids were recovered by filtration. Both basic silica were washed with diethylether and three times with 20 mL of a TBD solution (0.1M) in acetonitrile. Then the two resulting hybrid materials were washed in a soxhlet apparatus with acetonitrile for 15h and finally dried under vacuum (10^{-1} mmHg) at 80°C for 8 h in order to remove the physisorbed water. IR (KBr) $\bar{\nu}$ = 796, 848 (residual -CH₂Cl), 951, 1324, 1375, 1445, 1537, 1647 (-C=N), 2860, 2930 (-CH₂), 3024 (-C=CH), 3742 (-Si-OH, lower intensity band for KG-TBD than for HMS-TBD) cm⁻¹. Elemental analysis calculated for KG-TBD %C: 18.94, %H: 2.40, %N: 3.73 and HMS-TBD %C: 33.95, %H: 4.71, %N: 7.24. Thermal analysis: between 250°C and 650°C a weight loss of 20.8% and 38.6% was observed for KG-TBD and HMS-TBD respectively. The N₂ adsorption-desorption isotherms of **HMS-TBD** indicated a BET surface of 660 m²/g with a large pore size distribution (observed using the BJH method). This lower BET surface compared to that of **HMS-Cl** was only due to the presence of the **TBD** species within the pores. Indeed, calcination of both **HMS-TBD** and **HMS-Cl** respectively afforded two mesoporous silica with similar surface areas of 1020 m²/g indicating that the **TBD** grafting over **HMS-Cl** did not lead to any porous framework destruction. The **HMS-TBD** XRD pattern was similar to those reported for HMS silica with a single broad reflection centred on 3.4 nm characteristic of wormhole structure

Si-HMS-TBD: In a typical silylation, HMS-TBD was reacted with HMDS (20 mL) and stirred under reflux for 24 hours. The resulting solid was then filtered off and thoroughly washed with acetone and diethyl ether before drying in an oven (50 °C, 10^{-1} mmHg) for 3 h.