SUPPORTING INFORMATION

Elaboration of Porous Silicon Carbide by Soft Templating Molecular Precursors with Semi-Fluoroalkanes

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1,3,5-trisilacyclohexane (TSCH)

¹H NMR (400MHz, CDCl₃) δ (ppm): 4.09 (m, 6H, Si*H*₂), 0.00 (m, 6H, SiC*H*₂Si). ¹³C NMR (100.5MHz, CDCl₃) δ (ppm): -10.4 (Si*C*H₂Si).

Synthesis of bis(cyclopentadienyl)-bis(phenoxy)titanium (Cp2Ti(OPh)2)

 $(C_5H_5)_2TiCI_2 + 2PhOH + 2NaH \rightarrow (C_5H_5)_2Ti(OPh)_2 + 2NaCI + H_2$

To a suspension of Cp_2TiCl_2 (2.0g, 8.0mmol, 1.0eq) and NaH (0.46g, 19.3mmol, 2.4eq) in 20ml of Toluene in a two-neck flask under inert atmosphere equipped with an dropping funnel and a reflux condenser with a bubbler, was added dropwise a solution of phenol (1.51g, 16.1mmol, 2.0eq) dissolved into 60ml of toluene during 30 minutes under stirring at room temperature. After refluxing for 45 minutes, the mixture was cooled down and filtered. Toluene was evaporated and the obtained product was purified by recrystallization from cyclohexane. After filtration 2.37g of an orange solid is obtained.

Yield: 81 %

¹H NMR (400MHz, CDCl₃) δ (ppm): 7.23 (td, J = 7.6, 1.2Hz, 4H, H_{meta} Ph), 6.81 (tt, J = 7.6, 1.2Hz 2H, H_{para} Ph), 6.66 (dd, J = 8.4, 1.2Hz, 4H, H_{ortho} Ph), 6.28 (s, 10H, Cp₂Ti).

¹³C NMR (100.5MHz, CDCl₃) δ (ppm): 170.4 (Ph, CO), 129.1 (Ph, C_{meta}), 118.8 (Ph, C_{para}), 117.9 (Ph, C_{ortho}), 115.9 (Cp).

Note: This compound is extremely hygroscopic and needs a drying under vacuum before each use.

Synthesis of the (1H,1H,2H,2H-perfluorotetradecyl)triethylsilane (CF₃(CF₂)₁₁CH₂CH₂SiEt₃) (F12H2SiEt3)

1H,1H,2H-perfluoro-1-tetradecene (3.60g, 5.57mmol, 1eq.), triethylsilane (6.48g, 55.7mmol, 10eq.) and Karsted catalyst (52mg, 2.8*10⁻²mmol, 0.5%mol) were introduced in a sealed Schlenk flask. The solution was heated at 120°C during 20 hours under stirring. The crude product was distilled under reduced pressure (150°C/15mmHg). 3.70g of a white wax was collected.

Yield: 90%

 $Mp = 72-75^{\circ}C$

¹H NMR (400MHz, CDCl₃) δ (ppm): 2.01 (m, 2H, CH₂CH₂Si), 0.95 (t, J = 8.0Hz, 9H, CH₃CH₂Si), 0.76 (m, 2H, CH₂CH₂Si), 0.56 (q, J = 8.0Hz, 6H, CH₃CH₂Si).

¹⁹F NMR (376.5MHz, CDCl₃) δ (ppm): -80.8 (t, J = 9.8Hz, 3F, CF₃), -116.7 (s, 2F, CF₂), -121.7(s, 10F, CF₂), -121.9 (s, 4F, CF₂), -122.7 (s, 2F, CF₂), -123.3 (s, 2F, CF₂), -126.1 (s, 2F, CF₂).



Figure S1 ¹H-¹³C Heteronuclear single quantum coherence spectroscopy (¹H-¹³C Hsqc) of the catalyst $Cp_2Ti(OPh)_2$.



Figure S2 Raman spectra of the catalyst $Cp_2Ti(OPh)_2$ ($\lambda = 532nm$) (a) and of the SDA F12SiEt₃ ($\lambda = 633nm$) (b).



Figure S3 Raman spectra at $\lambda = 633$ nm of TSCH, pTSCH and pSMP10.



Figure S4 SAXS absolute intensity on a binary mixture TSCH/F12SiEt₃ ($x_w = 0.1$) as function of the scattering distance d_L and the temperature. Illustration of the lamellae thickness (dotted line) in function of the temperature and the smectic phase transition between 0 and 5°C.



Figure S5 Thermogravimetric Analysis (TGA) of cross-linked SMP10 and pTSCH.



Figure S6 Wide-angle XRD patterns of SiC obtained from the pyrolysis at 1000°C of (i) pTSCH and (ii) pTSCH obtained by polymerization of TSCH into a x_w = 0.1 F12SiEt₃ organogel.



Figure S7 SEM images of porous SiC resulting from the pyrolysis at 1000°C of pTSCH obtained by 25° C polymerization of TSCH into (a) a $x_w = 0.2$ and (b) a $x_w = 0.35$ F12SiEt₃ organogel.



Figure S8 SEM images showing the grain interconnections in porous SiC (SiC resulting from the pyrolysis at 1000°C of pTSCH obtained by 25°C polymerization of TSCH into a $x_w = 0.2$ organogel).

Calculation of the specific surface area of spherical grains of SiC of diameter 100 nm.

We consider a spherical grain of SiC of 100nm diameter of volume V, of surface S and density d. Therefore its mass m is egal to V*d. The specific surface area A of the grain is given by the following equation: A=S/(V*d). Given that $S=4*\pi*R^2$ and $V=4/3*\pi*R^3$, we have A=3/(R*d) with $R=50*10^{-9}$ m. Note that the density of the SiC obtained at 1000°C is unknown. It should be included between the density of SMP10 (0.998*10^6g/m3) and that of crystalline SiC (3.21*10^6g/m3). As a result, the resulting specific surface area should be included between 18 and 60m2/g.