

A bimetallic siloxane cage model catalyst. Synthesis, characterization and polymerization behaviour of $[(c\text{-C}_6\text{H}_{11})_7(\text{Si}_7\text{O}_{12})\text{MgTiCl}_3]_n$ ($n = 1,2$)

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Butylethylmagnesium reacts with polyhedral $(c\text{-C}_6\text{H}_{11})_7(\text{Si}_7\text{O}_9)(\text{OH})_3$ to give $[(c\text{-C}_6\text{H}_{11})_7(\text{Si}_7\text{O}_9)(\text{OH})_2\text{Mg}]_n$ ($n = 1,2$), which upon reaction with TiCl_4 gives $[(c\text{-C}_6\text{H}_{11})_7(\text{Si}_7\text{O}_{12})\text{MgTiCl}_3]_n$ ($n = 1,2$) as a monomer/dimer mixture; this new bimetallic siloxane cage model catalyst, in the presence of triethylaluminium, shows a high catalytic activity for ethene polymerization.

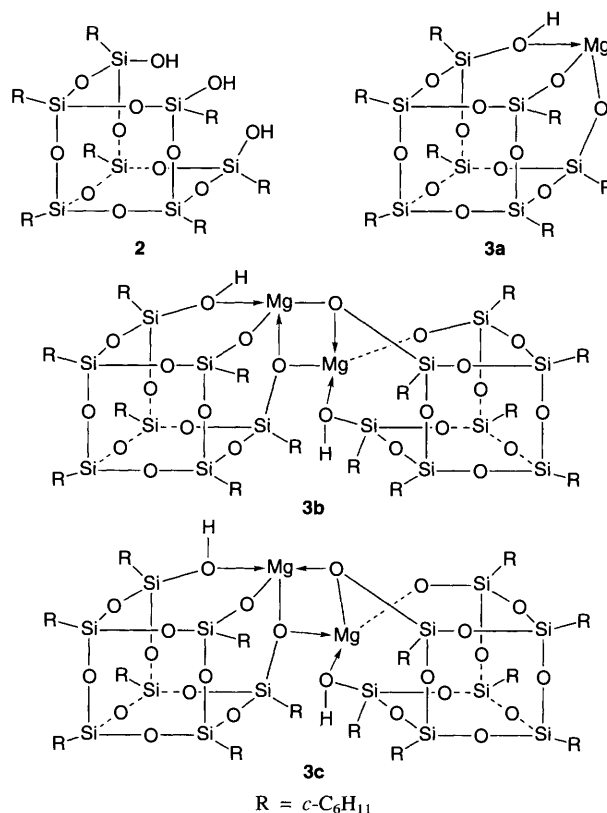
Heterogeneous silica-supported transition-metal catalysts play an important role as commercial catalysts in the petrochemical and polymer industries.¹⁻³ Both commercial importance and scientific significance have stimulated an intense interest in identifying the surface species of such catalysts. Although advances in spectroscopic techniques have revealed some information of the reaction chemistry on silica surfaces, the structures of such catalysts and the metal-silica interactions are still difficult to define at the molecular level. The inherent complexity of the silica-supported catalysts leaves many unanswered questions and direct study of such catalysts is still a surmountable challenge. Feher *et al.* have shown that the incompletely condensed silsesquioxane frameworks are effective models for silica surfaces and several monometallic polyhedral oligosilsesquioxanes (POSS) complexes have been reported.⁴ An attractive approach to the problem is to design, synthesize and characterize model catalysts based by incorporating $\text{M}_x\text{-O}_y\text{-Si}_z$ interactions as models for silica-supported catalysts.⁵

We now report the synthesis, characterization, speculative structures and polymerization reactivity of the new bimetallic siloxane cage model catalysts $[(c\text{-C}_6\text{H}_{11})_7(\text{Si}_7\text{O}_{12})\text{MgTiCl}_3]_n$ ($n = 1,2$), which exists as a monomer/dimer, as well as comparison of this model catalyst to a typical silica supported catalyst having the same magnesium and titanium content.

The synthesis is summarized in Scheme 1. In a typical experiment, reaction of butylethylmagnesium **1** with 1 mol equiv. of polyhedral oligosilsesquioxane (POSS) trisilanol **2** was conducted in heptane at 45–90 °C. After separation, **3** was treated with TiCl_4 at 45 °C to give **4**.

Both reactions were followed by FTIR, NMR and MS. Complex **3** is proposed to be a mixture of **3a**, **b**, **c** and complex **4** as a mixture of **4a**, **b**. FTIR and NMR spectra† indicate that a magnesium-siloxane cage complex **3** is formed by the condensation of two OH in **2** with two alkyl groups of **1**, but that one OH remains unreacted and is present in **3**. The intensity of the broad FTIR signal at 3400 cm^{-1} (three OH) in **2** decreased to

one third of the original intensity, similarly a ^1H NMR signal of three OH (total integrated intensity = 3) in **2** at δ 6.96 decreases to one OH (total integrated intensity = 1) at δ 2.80, 2.10 in **3**. These signals for **3** are at positions close to a single isolated OH and separated OH respectively, in POSS derivatives,^{4c} and are therefore assigned to a single isolated OH in the monomer **3a** and separated OH in the dimer **3b**, **c**. New FTIR signals (1105sh, 1085sh, 1075s, 1060s, 1025m, 935m cm^{-1}) are assigned to the formation of $(\text{Si-O})_2\text{Mg}$ moieties. FTIR, NMR and MS spectra† also indicate the formation of Ti-O-Si bonds and retention of $(\text{Si-O})_2\text{Mg}$ in the mixture **4a**, **b**. The FTIR signal of OH at 3400 cm^{-1} in **3** disappeared and new signals at 1040 cm^{-1} (stretching), 785, 730 cm^{-1} (pseudosymmetric stretching) were assigned to Ti-O-Si in **4**. FTIR signals of bonding units obtained are comparable with those of catalyst species on silica surfaces.⁶⁻⁸ ^1H NMR signals at δ 2.80 and 2.10 assigned to one OH in the mixture **3a**, **b**, **c** disappeared in the formation of **4** as Ti-O-Si bonds form. ^{13}C and ^{29}Si NMR data of **4a**, **b** indicated structural changes with respect to the C_{3v} symmetric structure of **2**, and are consistent with the proposed structures. The mole ratio of monomer **4a** to dimer **4b** was determined as 3 : 1 based on the integrated intensity ratio (3 : 1) of the monomer to the dimer signals. (Elemental analysis of **4a**, **b**: Ti, 4.15 (4.18); Mg, 2.14 (2.11); Si, 17.64 (17.53%). Both **4a** and **4b** were successfully detected by EI-MS [m/z 1039 ($\text{M}^+ - 3\text{Cl} - 3\text{H}$), 1890 ($\text{M}_2^+ - 6\text{H} - 6\text{Cl} - 2\text{C}_6\text{H}_{10} - \text{Mg}$) and



Scheme 1

2160 ($M_2^+ - 6\text{H} - 3\text{Cl} - \text{Mg}$]). The signal at m/z 1039 (9 peaks) can be successfully simulated by the proposed fragment $[(c\text{-C}_6\text{H}_{11})_7(\text{Si}_7\text{O}_{12})\text{MgTiCl}_3 - 3\text{Cl} - 3\text{H}]$ (m/z 1039.25). Thus, monomer **4a** is formulated as $[(c\text{-C}_6\text{H}_{11})_7(\text{Si}_7\text{O}_{12})\text{MgTiCl}_3]$ ($M = 1148.56$). Signals at m/z 1890 (11 peaks) and m/z 2160 (12 peaks) are also similar to the simulated spectra of the proposed fragments; therefore dimer **4b** is formulated as $[(c\text{-C}_6\text{H}_{11})_7(\text{Si}_7\text{O}_{12})\text{MgTiCl}_3]_2$ ($M = 2297.12$). In addition to the dimer reported in this communication, a series of triosmium cluster-siloxane cage dimers have been synthesized and characterized.^{5b}

The model catalyst **4a, b** demonstrated a significant catalytic activity for ethene polymerization. In a typical polymerization, 20 mg of **4a, b** and triethylaluminium as co-catalyst (mole ratio Al:Ti = 25:1) were charged into a reactor (1 l). The ethene polymerization was performed using a slurry under the following conditions: 90 °C, 500 psi of ethene, 180 mmol H₂ and 500 ml of 2-methylpropane as solvent. Polymerization was catalysed with an activity of 110.8 kg PE (g[Ti] h)⁻¹, higher than that, 60.0 kg PE (g[Ti] h)⁻¹, of a typical commercial Ti/Mg/SiO₂ silica-supported catalyst with the same bimetallic content. GPC analysis of the polyethylene indicated $M_w = 140\,000$ and $M_n = 26\,000$, with a molecular mass distribution

(M_w/M_n) of 5.5. The physical properties of the polyethylene (PE) including melt index data: MI = 1.02, HLMI = 32.37, MIR = 28.3, were suitable for potential applications such as blow moulding. MW and MI data of PE obtained with the model catalyst were similar to those obtained with a commercial silica-supported catalyst with the same components. On the basis of the analogy in synthesis, structural characteristic and polymerization behaviour, the systems $[(c\text{-C}_6\text{H}_{11})_7(\text{Si}_7\text{O}_{12})\text{MgTiCl}_3]_n$ ($n = 1, 2$) (Ti/Mg/POSS) have potential use as a bonding model for Ti, Mg-containing bimetallic silica-supported catalysts Ti/Mg/SiO₂ (Scheme 2). An investigation employing this model catalyst should be potentially helpful to design silica-supported catalysts for alkene polymerization.

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Footnotes

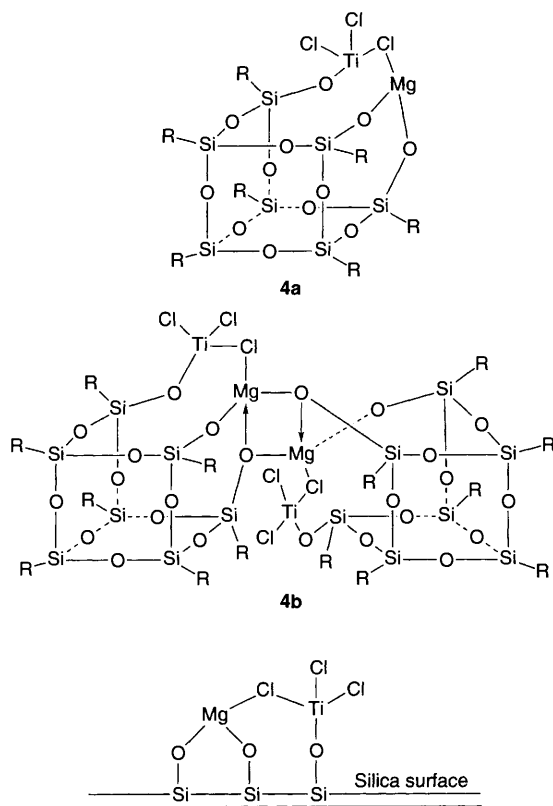
† Spectroscopic data for **3a, b, c**: FTIR (CDCl₃; 25 °C) ν/cm^{-1} : 3400br (Si-OH); 1105sh, 1085sh, 1075s, 1060s, 935m [(Si-O)₂Mg]. ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 2.80 (s, Si-OH **3a**), 2.39 (s, Si-OH in **3b, c**), 0.70 (br, 5 H), 0.77 (s, 2 H), 0.84 (s, 1 H), 1.21 (br, 35 H), 1.71 (br, 35 H).

‡ Spectroscopic data for **4a, b**: FTIR (CDCl₃, 25 °C) ν/cm^{-1} : 1040s (Ti-O-Si); 1105sh, 1085sh, 1075s, 1060s, 935m [(Si-O)₂Mg]. ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 0.75 (br, 5 H), 0.77 (s, 2 H), 0.84 (br, 1 H), 1.21 (br, 35 H), 1.71 (br, 35 H); ¹³C{¹H} NMR (75.429 MHz, CDCl₃, 25 °C): δ 26.6, 26.8, 27.6 (s, 2:1:2, CH₂); 22.6, 22.7, 23.0, 23.7 (s, 2:1:3:1, CH); ²⁹Si{¹H} NMR (59.591 MHz, CDCl₃, 25 °C): δ 65.770, 67.307, 68.126, 69.188 (s, 2:1:1:3 for three groups of 7 Si in **4a**); 58.345, 66.619, 67.983, 69.372, 69.716 (s, d, m, 1:1:1:3:1 for five groups of 14 Si in **4b**); the integrated intensity ratio of **4a**:**4b** was determined as 3:1. MS (EI, 70 eV, 200 °C): m/z 1039 (**4a** - 3 H - 3 Cl), 1890 (**4b** - 6 H - 6 Cl - 2 C₆H₁₀ - Mg), 2160 (**4b** - 3 H - 3 Cl - Mg).

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Scheme 2 Bonding model for Ti/Mg/SiO₂ catalysts (R = *c*-C₆H₁₁)