

$M_x-O_y-Si_z$ Bonding Models for Silica-Supported Ziegler–Natta Catalysts

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Three reactants, polyhedral oligosilsesquioxanes (POSS) ($(c-C_6H_{11})_7(Si_7O_9)(OH)_3$), butylethylmagnesium (2) and titanium tetrachloride $TiCl_4$ (3), react in three different ways according to the order of addition to form three model catalysts, A2, B2 and C2. A2, which is characterized as a bimetallic siloxane cage model catalyst $[(c-C_6H_{11})_7(Si_7O_{12})MgTiCl_3]_n$ ($n = 1,2$), contains a singly bonded $(Ti-O-Si)$ with a doubly bonded $Mg(-O-Si)_2$. B2 contains a doubly bonded $Ti(-O-Si)_2$ with a singly bonded $Mg(-O-Si)$. C2 contains a triply bonded $Ti(-O-Si)_3$. As catalyst precursors the model catalysts demonstrate different activity and catalytic behavior toward ethylene polymerization in the presence of triethylaluminum. Three types of $M_x-O_y-Si_z$ bonding structures are proposed as bonding models for silica-supported Ziegler–Natta catalysts. Copyright © 1999 John Wiley & Sons, Ltd.

Keywords: model; bonding; catalyst; support; silica; polyhedral oligosilsesquioxanes (POSS); butylethylmagnesium; titanium tetrachloride; polymerization

communication.¹ Heterogeneous silica-supported Ziegler–Natta catalysts play an important role as commercial catalysts in the petrochemical and polymer industries.^{2–4} Both commercial importance and scientific significance have stimulated an intense interest in identifying active surface species of such catalysts. Although advances in spectroscopic techniques have revealed some information on the reaction chemistry on silica surfaces, the structures of such catalysts and the metal–silica interactions are still difficult to define at a molecular level. The inherent complexity of the silica-supported catalysts leaves many unanswered questions for direct study of such catalysts. Feher and co-workers have shown that the incompletely condensed silsesquioxane frameworks are effective models for silica surfaces and several monometallic polyhedral oligosilsesquioxane (POSS) complexes.^{5–11}

An attractive approach to this problem is to design, synthesize and characterize model catalysts based by incorporating $M_x-O_y-Si_z$ interactions as models for silica-supported catalyst (Refs 1, 12 and Jia-Chu Liu, J. R. Shapley and F. J. Feher unpublished results). Three $M_x-O_y-Si_z$ interactions are proposed in this paper as bonding models for bimetallic silica-supported Ziegler–Natta catalysts.

INTRODUCTION

The catalyst $[(c-C_6H_{11})_7(Si_7O_{12})MgTiCl_3]_n$ ($n = 1,2$) as a bonding model for silica-supported catalysts was synthesized, characterized and evaluated in ethylene polymerization in a previous

EXPERIMENTAL

Except where noted, all operations and reaction procedures were performed under a nitrogen atmosphere and on a vacuum line with modified techniques. Heptane was used as solvent in the synthesis and fed under nitrogen with a moisture level less than 0.02 ppm. The reactions of POSS with BEMg (10% solution in heptane; Akzo) and $TiCl_4$ in heptane were carried out in a dry, round-bottomed flask with a magnetic stir bar under

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nitrogen at a temperature in the region of 45 °C. After separation, products of each reaction were dried on a vacuum line for 1–2 h and kept in a glove box.

Polymerizations were performed in a 1-liter slurry reactor under the following conditions: 550 psi (3800 kpa) ethylene; 180 mmol hydrogen, [Al]/[Ti] ratio = 25–60:1, polymerization temperature 90 °C. Molecular weights (weight-average M_w , number-average M_n) and molecular weight distribution (MWD) determinations for the polyethylene produced were completed by established methods of GPC analysis.

Infrared spectra were recorded on Nicolet 710sx and 60sx FTIR spectrometers with solution samples prepared in a 0.1 mm KBr Model SL-2 cell under a nitrogen atmosphere. ^1H , ^{13}C and ^{29}Si NMR spectra were recorded on a Varian Unity-300 NMR spectrometer at 299.949, 75.429 and 59.591 MHz, respectively. Chemical shifts (ppm) were reported downfield from tetramethylsilane but were most often measured relative to residual ^1H , or ^{13}C resonance in deuterated CDCl_3 solvents (7.260 ppm for ^1H ; 77.000 ppm for ^{13}C). The elemental analysis data were obtained on an ICP PS-1000 spectrometer.

Mass spectra (MS) were measured on a VG 70-VSE high-resolution mass spectrometer in the Mass Spectrometry Laboratory of the School of Chemical Sciences at the University of Illinois at Urbana-Champaign. The samples were scanned in the 500–2800 molecular weight range and recorded by electron impact (EI) with high resolution under a nitrogen atmosphere. The simulation signals of corresponding proposed structures were conducted on a VG OPUS data system (1990). In addition to standard library searches, the OPUS software includes computer-generated fragmentation of chemical structures and interactive mass peak fragment and loss interpretation.

In a typical experiment, reaction of polyhedral oligosilsesquioxane (POSS) trisilanol 1 with 1 mol equiv of butylethylmagnesium (BEMg) 2 was conducted in heptane at 45 °C. After separation, A1 was treated with TiCl_4 in a further reaction at 45 °C to give A2.

Spectroscopic data

For POSS (1): FTIR (CDCl_3 ; 25 °C) cm^{-1} : 3400br (3 Si—OH), 2920s, 2850s(C—H, in c-hexyl), 1450m, 1270, 1250sh, 1195m, 1110vs (Si—O—Si), 1038sh, 1028sh, 895m (Si—O—H), 845m. ^1H

NMR (300 MHz; CDCl_3 ; 25 °C): δ = 6.96 (s, 3H for Si—OH), 0.70 (br, 7H), 1.21 (br, 35H), 1.71 (br, 35H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.429 MHz; CDCl_3 ; 25 °C): δ = 26.7, 26.9, 27.6 (s, 2:1:2 for CH_2); 23.1, 23.6, 23.9 (s, 1:3:3 for CH). $^{29}\text{Si}\{^1\text{H}\}$ NMR (59.591 MHz; CDCl_3 ; 25 °C): δ = 60.398, -68.180, -69.753 (s, 3:1:3 for three groups of Si). MS (70 eV, 200 °C): m/z 871 ($\text{M}^+ - \text{C}_6\text{H}_1 - \text{H}_2\text{O}$), 789 ($\text{M}^+ - 2\text{C}_6\text{H}_{11} - \text{H} - \text{H}_2\text{O}$).

For BEMg 2. FTIR (heptane; 25 °C) cm^{-1} : 2802vs, 2763vs (C—H), 540w, 470m, 410w (C—Mg—C).

For A1: FTIR (CDCl_3 ; 25 °C) cm^{-1} : 3400br (Si—OH); 2920s, 2850s(O—H in c-hexyl), 1110–1120vs (Si—O—Si); 1105sh, 1085sh, 1075s, 1060s, 935m [(Si—O—) $_2$ Mg]; 895w (Si—O—H). ^1H NMR (300 MHz; CDCl_3 ; 25 °C): δ = 2.80 (s, H for Si—OH in A1a), 2.39 (s, H for Si—OH in A1b, A1c), 0.70 (br, 5H), 0.77 (s, 2H), 0.84 (s, 1H), 1.21 (br, 35H), 1.71 (br, 35H).

For the mixtures of A2: FTIR (CDCl_3 ; 25 °C) cm^{-1} : 1040s (Ti—O—Si); 1105sh, 1085sh, 1075s, 1060s, 935m [(Si—O—) $_2$ Mg]. ^1H NMR (300 MHz; CDCl_3 ; 25 °C): δ = 0.75 (br, 5H), 0.77 (s, 2H), δ 0.84 (br, 1H), 1.21 (br, 35H), 1.71 (br, 35H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.429 MHz; CDCl_3 ; 25 °C): δ = 26.6, 26.8, 27.6 (s, 2:1:2 for CH_2); 22.6, 22.7, 23.0, 23.7 (s, 2:1:3:1 for CH). $^{29}\text{Si}\{^1\text{H}\}$ NMR (59.591 MHz; CDCl_3 ; 25 °C): δ = 65.770, -67.307, -68.126, -69.188 (s, 2:1:1:3 for three groups of 7Si in A2a); -58.345, -66.619, -67.983, -69.372, -69.716 (1:1:1:3:1 for five groups of 14 Si in A2b); the integrated intensity ratio for A2a/A2b was determined to be 3:1. MS (EI, 70 eV, 200 °C): m/z 1039 (M^+ of A2a-3H-3Cl); 1890 (M_2^+ of 4b-6H-6Cl-2C₆H₁₀-Mg); 2160 (M_2^+ of A2b-3H-3Cl-Mg).

For 4: ^1H NMR (500 MHz; CDCl_3 ; 25 °C): δ = 2.79 (s, H for Si—OH), 0.75(br, 5H), 0.65 (br, 2H), 1.24(br, 35H), 1.75 (br, 35H).

For 5: ^1H NMR (500 MHz; CDCl_3 ; 25 °C): δ 2.09 (s, 2H for Si—OH), 0.77 (br, 8H), 1.23 (br, 40H), 1.75 (br, 40H).

Elemental analyses

Compound A2: Calcd: Ti, 4.18; Mg, 2.11; Si, 17.53. Found: Ti, 4.15; Mg, 2.14 Si, 17.64%.

Compound B2: Calcd: Ti, 4.09; Mg, 2.09; Si, 16.8. Found: Ti, 3.63; Mg, 2.04 Si, 15.2%.

RESULTS AND DISCUSSION

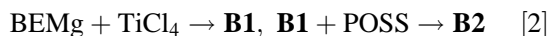
Three types of reactions, A, B and C, and products, A2, B2 and C2

Three reactants, polyhedral oligosilsesquioxane (POSS, $R_7Si_7O_9(OH)_3$, (**1**) R =cyclohexyl), butyl ethylmagnesium (BEMg) (**2**) and titaniumtetrachloride ($TiCl_4$) (**3**), react in three different ways according to different orders of reaction addition to form three products containing three bonding structures. Reactions A, B and C (Eqs. 1, 2 and 3) were carried out in heptane at 45 °C from three reactant materials in a mol ratio of 1:1:1, with different orders of reaction addition as follows:

Reaction A:



Reaction B:



Reaction C:



After separation and removal of solvents, **A2** (a white solid), **B2** (a dark brown solid) and **C2** (a brown solid) were obtained.

Characterization of reactions A, B and C, and the corresponding products A2, B2 and C2

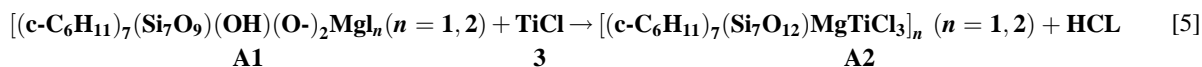
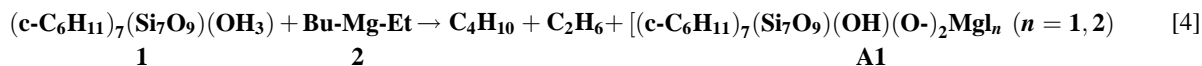
Reactions A and product **A2** were reported briefly in a previous communication.¹ The details are described in this paper. Compound **A2** was characterized as a bimetallic siloxane cage model catalyst, $[(c-C_6H_{11})_7(Si_7O_{12})MgTiCl_3]_n$ ($n = 1, 2$), which exists as a monomer/dimer. The synthesis is summarized in the following reactions 4 and 5. In a typical experiment, reaction of polyhedral oligosilsesquioxane (POSS) trisilanol **1** with 1 mol equiv. of butyl-ethylmagnesium (BEMg) **2** was conducted in heptane at 45 °C. After separation, **A1** was treated with $TiCl_4$ in a further reaction 5 at 45 °C to give **A2**.

A1 is proposed to be a mixture of **A1a**, **A1b** and

reactions were followed by FTIR, NMR (1H , ^{13}C , ^{29}Si) and mass spectroscopy.

FTIR and NMR data shown in the Experimental section indicate that a magnesium–siloxane cage complex **A1** is formed by the condensation of two of the three OH groups of **1** with two alkyl groups of **2**, leaving one unreacted OH group in **A1**. The FTIR signal at 3400 cm^{-1} for three OH in **1** decreased to one-third of its original intensity, and the 1H NMR signal of three OH (total integrated intensity = 3) in **1** at $\delta = 6.96$ ppm changed to new signals for one OH (total integrated intensity As 1) at $\delta = 2.80$ and 2.10 ppm in **A1**. The signals at $\delta = 2.80$ and 2.10 ppm are close to a single isolated OH and separated OH in POSS derivatives in the data¹¹ (Ref. 11, compound 4 and 5), respectively, and are therefore assigned to a single isolated OH in the monomer **A1a** and separated OH in the dimer **A1b/A1c**.

The C–H stretching vibrations of alkyl groups in **2** at 2763 cm^{-1} and 2802 cm^{-1} and the vibration of the C–Mg–C framework in **2** at 540 , 470 and 410 cm^{-1} all disappeared in **A1**. Also, new FTIR signals ($1105sh$, $1085sh$, $1075s$, $1060s$, $1025m$, $935m\text{ cm}^{-1}$) are assigned to the formation of (Si–O–)₂ Mg. FTIR, NMR and MS spectra also indicate the formation of Ti–O–Si and remaining of (Si–O–)₂ Mg in the **A2a/A2b** mixtures. The FTIR signals of OH at 3400 cm^{-1} and $895w\text{ cm}^{-1}$ in **A1** disappeared and new signals at 1040 cm^{-1} (stretching), 785 cm^{-1} and 730 cm^{-1} (pseudo-symmetric stretching) are assigned to Ti–O–Si in **A2**. The peaks at 700 – $600w\text{ cm}^{-1}$ are assigned to the vibration of Cl–(Ti–O–Si). FTIR signals of bonding types obtained are comparable and consistent with those of the same bonding of a catalyst species on silica surfaces.^{13–15} 1H NMR signals at $\delta = 2.80$ and 2.10 ppm assigned to one OH in the mixtures of **A1a**, **A1b** and **A1c** disappeared in the formation of the Si–O–Ti structure unit. The ^{13}C NMR and ^{29}Si NMR data of **A2a** and **A2b** indicate structural changes with respect to the C_{3v} symmetry of structure **1** and are consistent with the proposed structures. The mole ratio of **A2a** to **A2b** is determined as 3:1 based on the integrated intensity



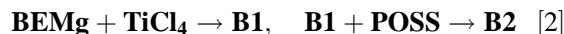
A1c and **A2** is a mixture of **A2a** and **A2b**. The

ratio (3:1) of the monomer to the dimer signals.

The mixture of **A2a** and **A2b** was successfully detected by EI MS in three fragments at $m/z = 1039$ ($M^+ - 3 \text{ Cl} - 3 \text{ H}$), 1890 ($M_2^+ - 6 \text{ H} - 6 \text{ Cl} - 2 \text{ C}_6\text{H}_{10} - \text{Mg}$) and 2160 ($M_2^+ - 6 \text{ H} - 3 \text{ Cl} - \text{Mg}$). The signal at $m/z = 1039$ (nine peaks) can be simulated successfully 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, the monomer **A2a** 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 2160 (12 peaks) are also similar to the simulated spectra of the proposed fragments; therefore dimer **A2b** is formulated as $[(c\text{-C}_6\text{H}_{11})_7(\text{Si}_7\text{O}_{12})\text{MgTiCl}_3]_2$ ($M = 2297.12$). Three strong signals at $m/z = 1039$, 1890 and 2160 in the mass spectra of **A1** and **A2** have the same peak number and signal isotopic shape as those of simulated theoretical spectra by using the identified final formulæ of **A1** and **A2**. In addition to the dimer reported in this paper, a series of trisium cluster-siloxane cage dimers were synthesized and characterized (Jia-Chu Liu, J.R. Shapley and F.J. Fehes, unpublished results).

Product **A2** contains a doubly bonded $\text{Mg}(\text{—O—Si})_2$ and a singly bonded $\text{Ti}(\text{—O—Si})$. According to the FTIR spectra, the reaction pathway for Reactions (B) (Eq. 2) and the corresponding products are proposed as follows:

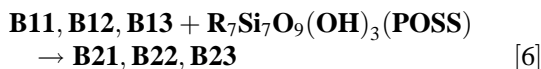
Reaction B:



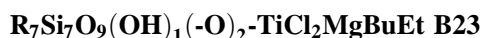
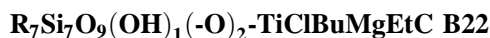
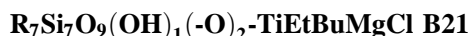
B1 contains:



which react with POSS:



where the products are:

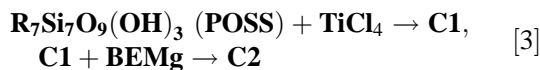


In the first step of the reactions, the products are complicated and probably consist of the components shown in the above pathway. On the basis of FTIR spectra, three intermediates, **B11**, **B12** and **B13**, may be formed by ligand transfer between Mg and Ti. In the second step, **B21**, **B22** and **B23** are

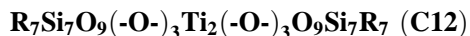
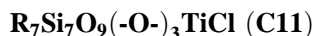
formed by eliminating the molecules of HCl and ethane, respectively.

The solution of these products in heptane is dark brown and cannot be separated up on TLC. The FTIR spectrum^{13–15} of the solution showed strong signals at 930, 1090 and 1070 cm^{-1} . The signal at 930 cm^{-1} is assigned to the formation of a doubly bonded titanium structural unit $(\text{Si—O—})_2 \text{Ti}$, and signals at 1090 and 1070 cm^{-1} are assigned to the formation of a singly bonded magnesium structural unit $(\text{Si—O—})\text{Mg}$ (see 4) below.

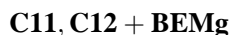
According to the FTIR spectra of the products, the reaction pathway for the process of reactions C and the corresponding products are speculated to be as follows:



Product C1 contains:



which react with BEMg:



The solution of the product **C2** in heptane is brown. The FTIR spectrum shows strong signals at 1030 and 870 cm^{-1} , which are assigned as a triple titanium bonded to POSS in bonding type $(\text{Si—O—})_3 \text{Ti}$. The dimeric product **C12** which has two triply bonded $(\text{Si—O—})_3 \text{Ti}$ units, two bridge bonded Ti—O—Ti and one Ti—Ti metal-metal bond, was identified by Feher. This dimer **C12** is extremely air-sensitive and insoluble in most solvents. If a small amount of **C12** reacts with BEMg in heptane, the product probably exists as a monomeric structure shown in **C2**. The product **C11** (major product), **C12** (minor) and **C2** all contain a triply bonded structural unit $\text{Ti}(\text{—O—Si})_3$ as shown in Table 4 (below). The bonding structures of POSS (**1**), **A1a**, **A1b**, **A1c**, **A2a**, and **A2b** are shown in Figs 1–6, respectively.

A2 contains one doubly bonded $\text{Mg}(\text{—O—Si})_2$ and one singly bonded $\text{Ti}(\text{—O—Si})$, **B2** contains one doubly bonded $(\text{Si—O—})_2 \text{Ti}$ and one singly bonded $\text{Mg}(\text{—O—Si})$, and **C2** contains one triply bonded $\text{Ti}(\text{—O—Si})$. These three bonding structures for (Ti,Mg)-containing silica serve as three models for silica-supported Ziegler–Natta catalysts and are shown in Fig. 7.

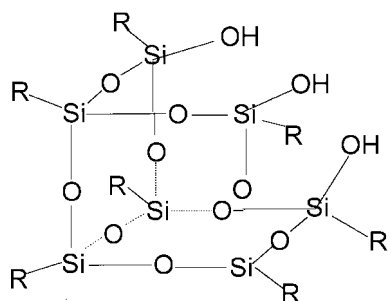


Figure 1 POSS (1).

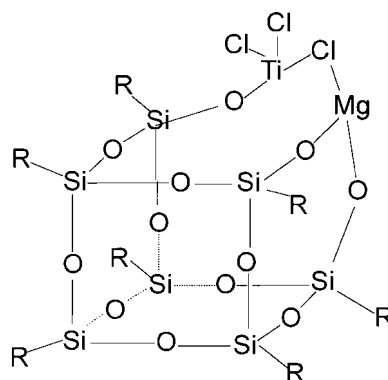


Figure 5 A2a.

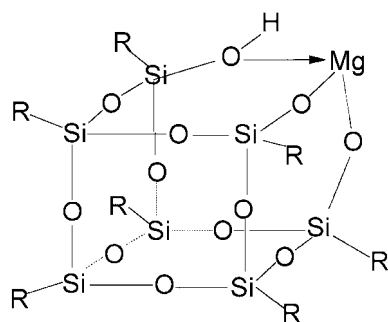


Figure 2 A1a.

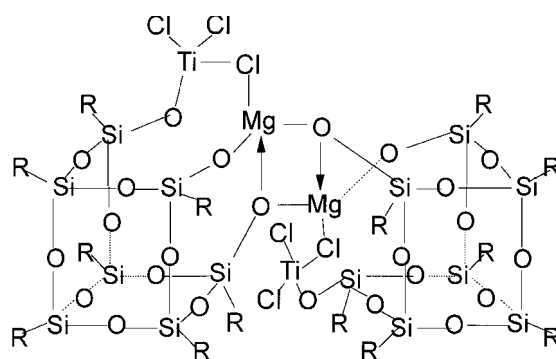


Figure 6 A2b.

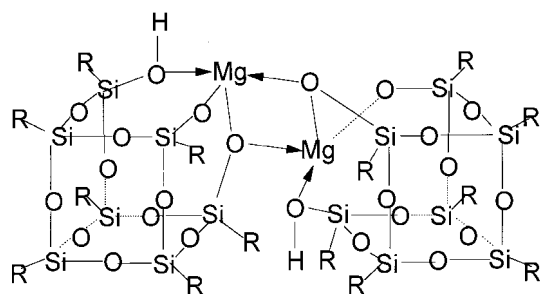


Figure 3 A1b.

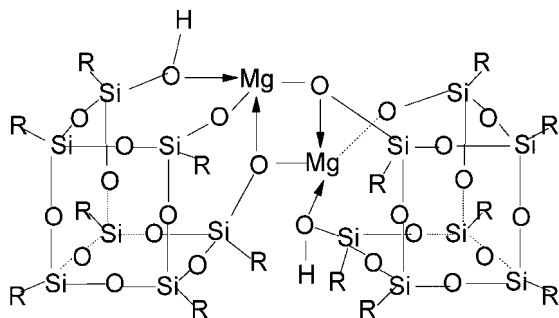


Figure 4 A1c.

Catalytic behavior in ethylene polymerization

Products **A2**, **B2** and **C2** demonstrated very different catalytic behavior in ethylene polymerization in the presence of triethylaluminum co-catalyst. The results of polymerization and the properties of the polyethylene produced are listed in Tables 1 and 2.

Products **A2**, **B2** and **C2** exhibit different activities in ethylene polymerization under the same conditions. The PE resins produced by **A2**, **B2** and **C2** have different M_w , M_n and MWDs as well as different properties such as MI, HLMI and MIR. The following conclusions are drawn from the results of ethylene polymerization under the same conditions:

- (1) The model catalyst **A2** demonstrated a significant catalytic activity for ethylene polymerization in the presence of triethylaluminum. The second product **B2** is the product from reactions B and demonstrates a lower activity at 33% of **A2**. The third one

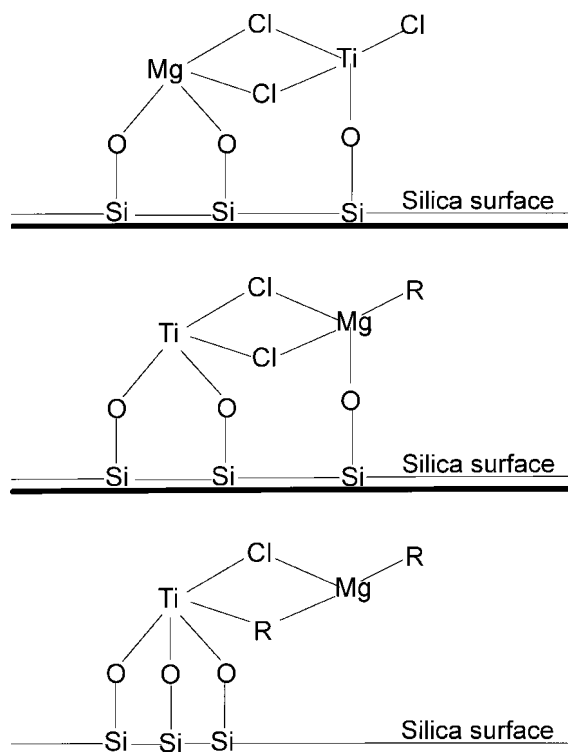


Figure 7 Bonding models (A, B and C) for (Ti,Mg)-containing silica-supported Ziegler-Natta catalysts (Ti,Mg/SiO₂).

C2 came from reactions C and exhibits very low activity at 5–7% of **A2**.

- (2) M_w and M_n and MWD (M_w/M_n) data showed an increase in the order. **A2** < **B2** << **C2**.
- (3) Reasonably, a higher MW compound has a lower MI. The MI and HLMI data showed decrease in order **A2** > **B2** >> **C2**.

Three $M_x-O_y-Si_z$ bonding models for active species on silica surfaces

As the main reactions of organometallic compounds with silica surfaces are related to reactions of hydroxyl groups on silica surfaces, the bonding types and concentrations of hydroxyl groups on silica surfaces are key points in the formation of surface species. A comparison of four types of main structural units containing Si—OH shown in Fig. 8. The numbers of bonding types of Si—OH, and Si—O—Si for (a)–(d) are listed in Table 3.

The comparison in Table 3 indicates that the number of Si—O—Si bonds in the silicon atom unit involving hydroxyl increases from 0 to 3 in (a), (b) and (c) to a real silica surface (d). The compounds with structure model (a) have been used as the simplest model compounds for about 40 years, but each Si structural unit of model (a) contains three of Si—R bonds and one Si—OH bond and is very different from the structures of silica surfaces. POSS has structure model (c), each Si structural unit in which contains one Si—OH or none, only one Si—R bond and three or two Si—O—Si bonds. This structure is close to that of actual silica surfaces. Therefore, the incompletely condensed silsesquioxane framework of POSS is considered to be an effective model for silica surfaces.^{5–11} Several organometallic POSS model compounds have been synthesized and characterized (Refs 1,5–12 and Jiachun Liu, J. R. Shapley and F. J. Feher, unpublished results).

Although all the structures of $M_x-O_y-Si_z$ bonding models are complicated, several main types may be classified and proposed as bonding types of active species on silica surfaces to serve as bonding models for silica-supported catalysts.

Table 1. Comparison of **A2**, **B2** and **C2** activity and meltindex (MI) data.

Catalyst	Activity ($\text{g g}^{-1} \text{h}^{-1}$) $\text{kg g}[\text{Ti}]^{-1} \text{h}^{-1}$	Melt Index (MI) (HLMI)	High Load MI (HLMI)	MIR (=HLMI/MI)
A2	4500 (108.4)	1.02	32.37	28.3
B2	1500 (36.7)	0.01	0.56	46.7
C2	300 (7.3)	Close to 0	Close to 0	NA

Table 2. Comparison of **A2**, **B2** and **C2** activity and molecular weight data

Catalyst	Relative Activity (%)	M_w	M_n	MWD (= M_w/M_n)
A2	100	140000	26000	5.4
B2	33.8	414700	55000	7.5
C2	6.7	750000	78000	9.6

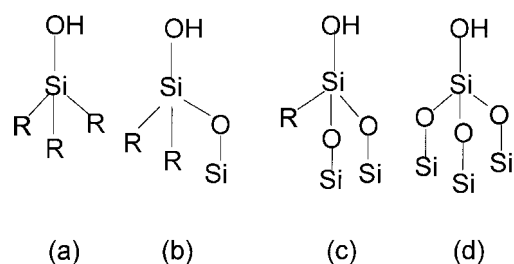


Figure 8 Few types of structures containing Si—OH.

For a bimetallic transition-metal complex bonded in POSS on the basis of the characterization and identification described in this paper, **A2** contains one Mg(O—Si—)₂ doubly bonded and one Ti—O—Si single bonded to POSS; **B2** contains one Ti(O—Si—)₂ doubly bonded and one Mg—O—Si— singly bonded to POSS; **C2** contains one Ti(O—Si—)₃ to POSS. These three M_xO_ySi_z bonding models **A**, **B** and **C** corresponding to structural units in the products **A2**, **B2** and **C2** are shown in Fig. 7. Table 4 also shows a comparison of vibration IR spectra of transition-metal bonding

structures on SiO₂ surfaces and in POSS. For different bonding units such as Si—O—H, Si—O—Ti, (Si—O—)₂ Ti, (Si—O—)₃ Ti, Si—O—Si, Si—O—M and others, the vibration numbers of POSS complexes are very close to those of species on silica surfaces.

A silica-supported catalyst **D**, Ti₂Mg/SiO₂, was prepared by the same procedures as the model catalyst **A2**. Table 5 shows a comparison of this silica-supported catalyst with the model catalyst **A2**. **D** and **A2** have the same components based on elemental analysis of Ti, Mg and Al. Under the same polymerization conditions, **D** and **A2** exhibit similar catalytic behavior in ethylene polymerization.

According to the similarities in the FTIR data (Table 4) and in their components, preparation procedures, polymerization behavior and properties of the PE resins produced (Table 5) between bimetallic POSS and silica-supported catalysts, this silica-supported catalyst **D** contains the same bonding structures as those of the catalyst **A2**, e.g. the M_xO_ySi_z bonding model of **A2** can serve as a

Table 3. Comparison of bonding structures with Silica in models (a) – (b), Fig. 8

Bonding	(a)	(b)	(c)	(d)
Si—OH	1	1	1	1
Si—R	3	2	1	0
Si—O—Si	0	1	2	3
Typical Formula	R—Si—OH	R ₂ Si(OH)—O—Si—R ₃	POSS	SiO ₂

Table 4. FTIR data (cm⁻¹ for bonding types related to SiO₂ surfaces and in POSS

Bonding	Bonding on SiO ₂ Surface ^a		Bonding in POSS	
	Source of vibration	Wavenumber (cm ⁻¹)	Source of vibration	Wavenumber (cm ⁻¹)
Si—O—H	H-bonded OH	3530 (br)	H-bonded OH	3400 (br)
	Non-H-bonded OH	3720		
Si—OH	Stretching	980	Bending	895
	Bending	900–760	Stretching	1040
Si—O—Ti	Stretching	1045/1030	Pseudo-symmetric stretching	785, 730
	Pseudo-symmetric stretching	790, 730	Stretching	930
(Si—O—) ₂ Ti	Stretching	920	Stretching	1030, 870
(Si—O—) ₃ Ti			Stretching	1120–1110
Si—O—Si	Stretching	1150–1050	Stretching	1100–900
Si—O—M	Stretching	1100–900	Stretching	1090, 1070
Si—O—Mg				1105sh, 1085sh, 1075s, 1060s, 935m
(Si—) ₂ Mg				700–400w
Si—Cl		700–400w		700–600w
Ti—Cl		700–600w		

^a Refs 13–15.

Table 5. Comparison of catalyst A2 with silica-supported catalyst D* having the same components

Property	A2 (Mg, Ti/POSS)	Catalyst D (Ti, Mg/SiO ₂)
Activity (kg g[Ti] ⁻¹ h ⁻¹)	108.4	82.5
M _w	140000	120000
M _n	26000	27000
MWD (M _w /M _n)	5.4	4.4
MI (g/10 min)	1.02	1.15
HLMI	32.37	40.48
MIR (HLMI/MI)	28.3	35.2

bonding model for a commercial silica-supported catalyst. On the basis of the analogy in synthesis, structural characteristics and polymerization behavior, these three bonding models **A2**, **B2** and **C2** are proposed as bonding models for (Ti,Mg)-containing bimetallic silica-supported Ziegler–Natta catalysts shown in Fig. 7. An understanding of the bonding structures of active species on silica surfaces is useful in designing new generations of silica-supported Ziegler–Natta catalysts at a molecular level for producing the desired polyolefin resins.

CONCLUSIONS

Three different products (**A2**, **B2** and **C2**) were made by three different reactions, A, B and C, using the same three reactants with different orders of addition. **A2**, **B2** and **C2** contain three types of bonding structures: **A2** contains one doubly bonded Mg(—O—Si)₂ and one singly bonded Ti (—O—Si); **B2** contains one doubly bonded Ti (—O—Si)₂ and one singly bonded Mg(—O—Si); **C2** contains one triply bonded Ti (—O—Si)₃.

The bimetallic siloxane cage model catalyst A2, [(c-C₆H₁₁)₇(Si₇O₁₂) MgTiCl₃]_n (n = 1,2), exists as a monomer/dimer characterized by FTIR, NMR (¹H, ¹³C, ²⁹Si) and mass spectroscopy.

A2, **B2** and **C2** exhibit different catalytic behavior toward ethylene polymerization in the presence of triethylaluminum co-catalyst under the same conditions. A bonding–catalytic property relationship has been established. The activities and the properties of MI and HLMI decrease in the order **A2** > **B2** >> **C2**. The PE resins produced by using catalysts **A2**, **B2** and **C2** have different

molecular weights. M_w, M_n and MWD (=M_w/M_n) and MIR (=HLMI/MI) increase in the order **A2** < **B2** << **C2**.

The model catalyst **A2** and a silica-supported catalyst **D** were prepared in similar procedures and have the same components based on elemental analysis of Ti, Mg, Si and Al. Under the same polymerization conditions, **A2** and the silica-supported catalyst **D** demonstrate similar catalytic behavior toward ethylene polymerization.

On the basis of the analogy between bimetallic POSS model catalysts and silica-supported catalysts, three M_x–O_y–Si_z compounds, corresponding to the main bonding structures of **A2**, **B2** and **C2**, shown in Fig. 7 are proposed as bonding models for silica-supported Ziegler–Natta catalysts.

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