

## Immobilization of a $C_2$ -Symmetric *ansa*-Zirconocene Complex on Silica Surfaces Using a Si-Cl Anchor: Catalysts for Isospecific Propene Polymerization

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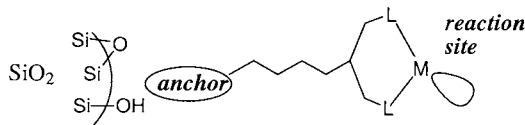
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(Received December 15, 1998; CL-980927)

A  $C_2$ -symmetric *ansa*-zirconocene complex which has a Si-Cl moiety on its bridge was immobilized on  $\text{SiO}_2$  by the reaction of the Si-Cl anchor with Si-OH on the solid surface. The prepared solid catalyst was found to be effective for isospecific propene polymerization. It exhibited higher productivity compared to a catalyst prepared using the zirconocene without a Si-Cl anchor. The effect of pretreatment of silica surfaces with  $\text{Me}_3\text{SiCl}$  on catalyst performance is also described.

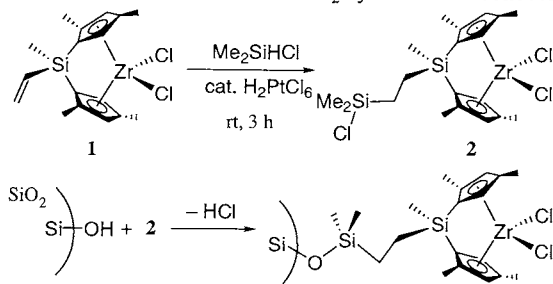
The group 4 metallocene catalysts for olefin polymerization have been extensively investigated in a last few decades.<sup>1</sup> For the purpose of industrial application, heterogenization of the homogeneous catalysts on solid supports is practical and preferred. In fact, in recent years, many reports on supported metallocene catalysts have appeared.<sup>2-8</sup> Adsorption of metallocene compounds on methylaluminoxane(MAO)-treated  $\text{SiO}_2$  supports are successful examples,<sup>2c-f</sup> although desorption of complexes to solution during the polymerization was noted.<sup>3</sup> An alternative approach is to immobilize the complexes on support surfaces with an anchor moiety via chemical reactions. An effective way to keep the front-side (reaction site) of the metallocenes open for incoming olefins would be to tether the complex with its back-side (Figure 1).



**Figure 1.** Immobilization of catalysts with a "back-side anchor".

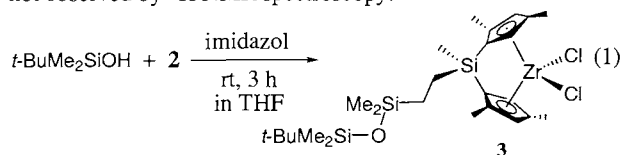
There have been some reports in which ligands were bound to supports first, and then reacted with  $\text{ZrCl}_4$  to prepare such complexes,<sup>4-6</sup> and a few of them could even catalyze syndiospecific olefin polymerization.<sup>4b,6b</sup> However, this method often results in low yields of desired complexes and further purification is difficult. In particular, this methodology is not suitable for isospecific polymerization catalysis, which requires chiral coordination environment, since diastereomeric isomers (*rac*-/*meso*-) of supported complexes can not be

**Scheme 1.** Immobilization of the  $C_2$ -symmetric zirconocene.



separated. For preparation of isospecific immobilized catalysts, to tether well-defined racemic metallocene complexes to the support with anchors appears to be the only route to surface-bound catalysts.<sup>7,8</sup> To the best of our knowledge, however, isospecific catalysts chemically anchored on solid supports have not appeared in the literatures.<sup>9</sup> A major barrier to achieve this aim can be attributed to the difficulty of preparation of racemic complexes with an anchor moiety. Herein we wish to report the synthesis of  $C_2$ -symmetric *ansa*-metallocene with a Si-Cl anchor and its immobilization on silica surfaces (Scheme 1).

We recently reported the preparation of  $C_2$ -symmetric *ansa*-zirconocene complex that has a vinyl group on its silylene bridge moiety **1**.<sup>10</sup> When **1** (*rac*-/*meso*- > 99/1) was treated with  $\text{Me}_2\text{SiHCl}$  in the presence of  $\text{H}_2\text{PtCl}_6$ , as a catalyst, hydrosilylation of the vinyl group cleanly occurred with excellent regioselectivity to give **2**. The other possible regioisomer was not observed by  $^1\text{H}$  NMR spectroscopy.



As a model reaction for immobilization on a silica surface, the homogenous reaction of **2** with a silyl alcohol was examined. Treatment of **2** with 1 equiv of *t*-BuMe<sub>2</sub>SiOH in the presence of imidazol in THF at rt for 3 h gave **3** in a good yield (eq 1).<sup>11</sup> Disappearance of the Si-Cl bond (32.65 ppm) and formation of new Si-O-Si bonds (7.94, 11.18 ppm) was observed in the  $^{29}\text{Si}$  NMR spectra, indicating that the reaction of Si-OH with Zr-Cl was negligible.

This result encouraged us to study the immobilization of **2** on silica by its reaction with surface Si-OH groups (Scheme 1). Typical procedure for the immobilization was as follows. Silica gels were treated under vacuum ( $10^{-3}$  Torr, 1 Torr = 133 Pa) at 500 °C for 16 h. The silica gel (0.5 g) was suspended in dry toluene (10 mL) under Ar, and to the suspension was added a THF solution of **2** (0.05 mmol) at rt. Then imidazol was added, and the mixture was stirred at rt overnight. Toluene/triethylamine was also used as a solvent/base, and appeared to be rather suitable judging from the amount of Zr loaded in the catalysts (Table 1). After washing twice with toluene, the volatiles were removed in vacuo. The Zr content in the prepared catalysts was determined by ICP analysis. CP/MAS solid state  $^{29}\text{Si}$  NMR showed a broad signal at 11-16 ppm and sharp one at -11.7 ppm, which are assignable to O-SiMe<sub>2</sub>CH<sub>2</sub>- of the backside anchor and the *ansa*-bridging silicon, respectively, and indicated the absence of Si-Cl bonds.<sup>12,13</sup> For comparison, **1** was adsorbed on the silica surface similarly without base.

The results of polymerization of propene using Zr/SiO<sub>2</sub>-

**Table 1.** Catalysts with immobilized zirconocene complexes and polymerization of propene<sup>a</sup>

run	complex/base	silica gel	solvent	Zr-atom /wt%	PP yield/g	rate <sup>b</sup>	$M_w$	$M_w/M_n$	[mmmm] /%	mp /°C
1	2/imidazol	A <sup>c</sup>	THF	0.47	0.525	113.2	106000	2.59	91.1	151.0
2	2/Et <sub>3</sub> N	A	toluene	0.75	0.796	107.6	94000	2.45	87.7	150.8
3	2/Et <sub>3</sub> N	B <sup>d</sup>	toluene	0.78	0.641	83.3	74500	2.87	86.9	146.1
4	1/none	A	toluene	0.79	0.073	9.4	65100	1.85	92.4	156.0
5	1/none	B	toluene	0.76	0.137	18.3	106000	2.06	93.2	159.0

<sup>a</sup> reaction conditions: in a 100 mL autoclave, toluene 30 mL, catalyst 30 mg, MMAO: Al = 6 mmol (Al/Zr = ca. 2500 for runs 2-5), propene 3 atm, 30 °C, 1 h. <sup>b</sup> kg-PP/mol-Zr-h-atm. <sup>c</sup> A: Degussa Corporation "Aerosil 300": 300 m<sup>2</sup>/g. <sup>d</sup> B: Fuji Silysia Chemical Ltd. "CARIACT P-10": 281 m<sup>2</sup>/g.

catalysts/MMAO are shown in Table 1. The catalyst from **2** produced polypropylene in moderate catalytic activity (runs 1-3). Isotacticity of the polymers was satisfactory although slightly lower than those observed in homogeneous reaction with **1**.<sup>14</sup> Similar results were obtained with two kinds of silica supports, indicating reproducibility of this method. It should be noted that the catalyst prepared from **1** showed much less catalytic activity than those from **2** in spite of its similar Zr content (runs 4-5). This is probably because the Zr-Cl bonds of **1** reacted with the surface Si-OH of silica. When the amounts of MAO was reduced from 2500 to only 122 equiv of Al/Zr, the catalytic activity was 81.8 kg-PP/mol-Zr-h-atm, which is still comparable to that of run 2.<sup>15</sup> Desorption of **2** under the polymerization conditions was not observed in our investigation according to the reported method.<sup>3</sup>

These results revealed that immobilization of C<sub>2</sub>-symmetric *ansa*-metallocene with a Si-Cl anchor is effective. Their catalytic activities, however, were still not satisfactory when compared to homogenous reactions. A possible reason could be the presence of excess hydroxy groups on the silica surface compared to amount of zirconium used.<sup>16</sup> Thus we reasoned that deactivating part of the surface-OH groups would improve the activity of the catalyst. Indeed, when the silica support was pretreated with Me<sub>3</sub>SiCl before **2** was immobilized on it,<sup>17</sup> the catalytic activity improved remarkably (Table 2).<sup>18</sup> Surprisingly, yield of the polymer increased even though the amount of Zr-atom was smaller (run 7). But, as expected, treatment of SiO<sub>2</sub> with excess Me<sub>3</sub>SiCl resulted in decrease of the polymer yield (run 9). Although the reason for the decrease of isotacticity in the present system is not clear yet, it may be because the active species stays too close to the solid surface. Further study on tethering the complex with a longer spacer to improve this method is now in progress.

**Table 2.** Effect of pretreatment of SiO<sub>2</sub> with Me<sub>3</sub>SiCl: Polymerization of propene<sup>a</sup>

run	Me <sub>3</sub> SiCl /mmol <sup>b</sup>	Zr-atom /wt%	cat. /mg	PP yield/g	rate <sup>c</sup>	$M_w$	$M_w/M_n$	[mmmm]
6	0.3	0.74	30	0.88	121	71000	2.34	84.1
7	0.9	0.47	15	2.03	876	98600	2.60	86.8
8	0.9	0.47	15	4.76	4110 <sup>d</sup>	19500	3.72	75.8
9	1.8	0.13	30	0.46	359	91900	2.42	83.4

<sup>a</sup> Reaction conditions: silica gel = B, MMAO: Al = 2 mmol per 10 mg of cat., toluene = 30 mL, propene = 3 atm, 30 °C, 1 h. <sup>b</sup> mmol of Me<sub>3</sub>SiCl per 1 g of SiO<sub>2</sub>. <sup>c</sup> kg-PP/mol-Zr-h-atm. <sup>d</sup> at 60 °C for 0.5 h.

The authors are grateful to Professor H.-H. Brintzinger for personal communication. Ms. Chieko Kariya is appreciated for ICP analysis. Fuji Silysia Chemical Ltd. is acknowledged for providing CARIACT P-10 silica gel. The authors thank Mr. Katsuo Yasumi (UBE Industry) for useful advice.

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