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Preparation of Anchored Metallocene Complexes on Dehydroxylated Silica and Their Use in the Polymerization of Ethylene

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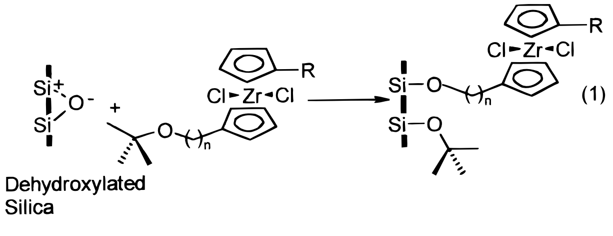
Organometallic compounds including group IV metallocenes have received great attention from both academic and industrial laboratories as single-site catalysts for the polymerization of olefins.[1] Such homogeneous catalysts should be immobilized on solid support in order to use in slurry or gas-phase process, in which the morphology and the bulk density of the polymer particles are of importance. Reactor fouling, a phenomenon where polymer sticks to reactor walls and agitator blades, should be avoided by supporting the catalyst. Among the various ways of the immobilization of homogeneous metallocene catalysts,[2] one of the most promising methods is by the reaction between a functional group of the metallocene compounds and another functional group on solid surface.[3,4] The supported catalysts so prepared are normally used for the polymerization with cocatalyst methylaluminoxane (MAO) in solution.

When silica is employed as a support, the surface hydroxyl group has been used frequently for anchoring but causes some decomposition of the metallocene. Later it was shown that a strained siloxane group generated by dehydroxylation over 900 K could react with alkoxysilane groups.[5] Such reactivity of dehydroxylated silica was utilized for anchoring the metallocene complex having a trimethylsilyloxy group, but the synthetic yields of the complexes having such a labile group were too low for commercial application.[4] We also showed that catalyst decomposition was reduced by decreasing the residual hydroxyl group of the dehydroxylated silica.[6] We envisaged that such electron-deficient strained siloxane sites might be as reactive as trimethylsilyl iodide,[7] which is an efficient reagent for cleaving acetals, ketals, or *tert*-butyl ethers. Then metallocene complexes containing a *tert*-butyl ether functionality could be anchored on silica by a simple reaction (eq 1).

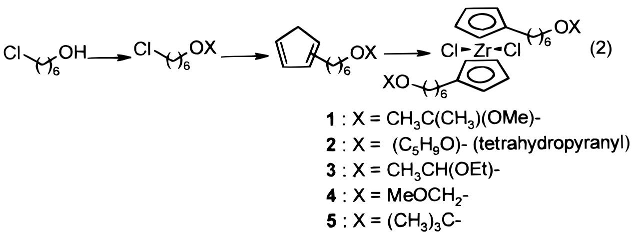


Metallocene complexes having acetal, ketal, or *tert*-butyl ether groups as a substituent on the cyclopentadienyl ring were easily synthesized from 6-chlorohexanol (eq 2).[8] Compound **1**, having a very acid-labile ketal group, is so unstable that it cannot be stored, and the metalation yield was below 30%. For compounds **2**−**5**,the metalation yields were quite good (76−92%).

Table 1. Ethylene Polymerization Data of the Anchored Catalysts

catalyst	activity (kg/(g-cat h))	bulk density (g/mL)	M_w ($\times 10^3$)	M_w/M_n
1	0.70	0.36	248	2.5
2	0.80	0.38	240	2.4
3	0.79	0.37	234	2.5
4	0.53	0.39	241	2.5
5	1.01	0.36	226	2.6
6[a]	0.07	0.08	377	2.6
7[a]	0.51	0.04	290	2.5

[a] Reactor fouling occurred.



The anchored metallocene catalysts were prepared by the reaction of compounds **1**−**5** (0.10 g) with dehydroxylated silica[9] (1.0 g) in hexane (30 mL) at 85 °C for 3 h. HCl was not detected during the anchoring reaction. Nothing was detected in solution, indicating that all metallocene complexes added were immobilized on solid surface. The anchored catalysts rarely leached out upon activation with MAO.[10] Table 1 shows the activities of ethylene polymerization[11] of the anchored catalysts and the properties of polymers obtained. For comparison, immobilized catalysts were prepared according to the same procedure from $[2\text{-EtOCH}_2\text{CH}_2{-}\text{O}{-}(\text{CH}_2)_6{-}\text{C}_5\text{H}_4]_2\text{ZrCl}_2$, **6**,[8] which has relatively acid-stable primary ether group, and bis(*n*-butylcyclopentadienyl)zirconium dichloride, **7**.

The morphologies and bulk densities of the polymer particles obtained form the anchored catalysts **1**−**5** were quite acceptable for the hexane-slurry commercial process.[12] No reactor fouling was observed. In the case of immobilized catalysts **6** and **7**, however, severe fouling occurred, and the morphology and bulk density were not desirable. Figure 1 shows the optical microscope picture of anchored catalyst and polymer particles. Figure 2 shows the polymer particle size distribution derived from the well-anchored catalyst **5**. In general, the morphology of the polymer particles resembles that of the supported catalysts when the activated catalyst does not leach out during the polymerization. Consequently, the bulk density of the polymer is high. The good morphologies and high bulk densities of the polymer particles from anchored catalysts **1**−**5** suggest that the immobilization took place adequately by the reaction proposed in eq 1. However, in the cases of **6** and **7**, the activated catalyst leached out, giving poor morphology and reactor fouling. The molecular weights (M_w) of the polymers obtained from the anchored catalyst **1**−**5** were within the same range (220 000−250 000), but those from **6** and **7** were quite different (377 000 and 290 000,

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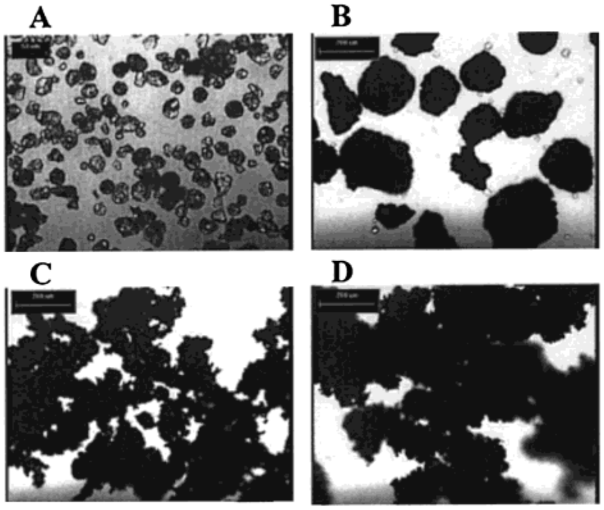


Figure 1. Microscope images of the anchored catalyst **5** (A, ×100) and the polymer particles obtained from anchored catalyst **5** (B, ×40), **6** (C, ×40), and **7** (D, ×40).

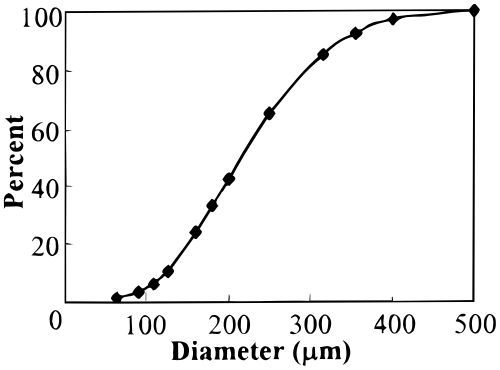
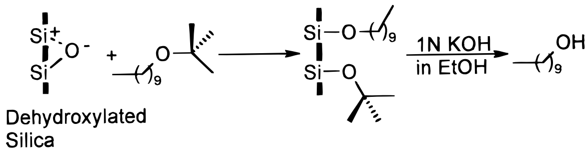


Figure 2. Particle size distribution of the polymer particles obtained from anchored catalyst **5**.

respectively). The ethylene polymerization activities of the well-anchored catalysts (**1**−**5**) were quite good while the supported catalysts of **6** and **7** gave rather low activities. The activity reached up to 1.01 kg/(g-cat h) or 6.8×10^5 g/(mol h bar) in the case of the anchored catalyst **5**.

To determine whether the reaction proposed in eq 1 has actually taken place, a model reaction was devised. Neat *tert*-butyl decyl ether reacted with dehydroxylated silica[9] at 90 °C for 2 h to give modified silica (6.3% carbon content, 0.38 mmol/g). A slight higher carbon content of 7.03% (0.45 mmol/g) was obtained at the same condition using decyl trimethylsilyl ether. While *tert*-butyl decyl ether was intact with a basic ethanol solution (1 N KOH), decyl alcohol leached out from the silica modified with *tert*-butyl decyl ether.[13] This suggests that the carbon−oxygen bond in *tert*-butyl decyl ether was certainly cleaved by the reaction with the dehydroxylated silica (eq 3). As predicted from the bad morphology of the polymer particles in the case of anchored catalyst **6**, primary ethers such as dibutyl ether barely reacted with the dehydroxylated silica (0.6% of carbon content (0.06 mmol/g) observed under similar conditions).

In conclusion, the novel reactivity of dehydroxylated silica toward the acid-labile acetal, ketal, or *tert*-butyl



(3)

ether group has been elucidated. This reactivity of dehydroxylated silica can be applied to the preparation of commercially acceptable immobilized metallocene catalysts. The immobilized catalysts, activated with MAO, gave the polymer in the presence of ethylene with suitable bulk densities and polydispersities.

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Supporting Information Available: Experimental procedures, preparation, and characterization data for **1**−**5** and details of the preparation of anchored catalyst and the polymerization reaction. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) For recent reviews, see: (a) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 428. (b) McKnight, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2587. (c) Kamnisky, W. *J. Chem. Soc., Dalton Trans.* **1998**, 1413.

(2) For leading recent references, see: (a) Kageyama, K.; Tamazawa, J.; Aida, T. *Science* **1999**, *285*, 2113. (b) Abbenhuis, H. C. L. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1058. (c) Sano, T.; Doi, K.; Hagimoto, H.; Wang, Z.; Uozumi, T.; Soga, K. *J. Chem. Soc., Chem. Commun.* **1999**, 733. (d) Roscoe, S. B.; Fréchet, J. M. J.; Walzer, J. F.; Dias, A. J. *Science* **1998**, *280*, 270. (e) Kamfjord, T.; Wester, T. S.; Rytter, E. *Macromol. Rapid Commun.* **1998**, *19*, 505. (f) Alt, H. G.; Schertl, P.; Köppl, A. *J. Organomet. Chem.* **1998**, *568*, 263.

(3) (a) Galan-Fereres, M.; Koch, T.; Hey-Hawkins, E.; Eisen, M. S. *J. Organomet. Chem.* **1999**, *580*, 145. (b) Antberg, M.; Lüker, H.; Böhm, L. Eur. Pat. 293815, 1988.

(4) Sancho Royo, J.; Hidalgo Llinas, G.; Munoz-Escalona Lafuente, A.; Martinez Nunez, F.; Martin Marcos, C.; Lafuente Canas, P.; Pena Garcia, B. Eur. Pat. Appl. 839836, 1998.

(5) Blümel, J. *J. Am. Chem. Soc.* **1995**, *117*, 2112.

(6) Lee, B. Y.; Oh, J. S. PCT/Kr 99/00169, 1999.

(7) Bhatt, M. V.; Kulkarni, S. U. *Synthesis* **1983**, 249.

(8) Lee, B. Y.; Oh, J. S. *J. Organomet. Chem.* **1998**, *552*, 313.

(9) Dehydroxylated silica was prepared by heating silica (XPO 2412 made by Grace Davison, mean particle size, 21 μm) to 800 °C for 15 h under vacuum.

(10) After activation of the anchored catalyst **5** (100 mg) with MAO (Al/Zr, 120) in hexane (100 mL) at 40 °C for 1 h, the solution was decanted, and the Zr content was measured on an ICP. Only 3% of total Zr leached out.

(11) Anchored catalyst (100 mg) was activated in hexane (50 mL) with MAO (heptane solution, Al/Zr, 60) and then prepolymerized. The prepolymerized catalyst was fed into a 1 L reactor containing hexane (660 mL) and triethylaluminum (1.0 mmol) as a scavenger. Polymerization was performed by continuous feed of ethylene at 130 psig for 1 h.

(12) The anchored catalyst **5** was tested in a pilot plant (200 L, continuous hexane-slurry process) for several days without any difficulties.

(13) When the silica (0.5 g) treated with *tert*-butyl decyl ether was reacted with 1 N KOH ethanol solution (5.0 mL) at room temperature for 5 h, 18 mg of organic compounds was obtained. The ^{1}H NMR spectrum showed that they were composed of decyl alcohol (ca. 85 mol %) and *tert*-butyl decyl ether (ca. 15 mol %).

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