

NOTES

Ethylene Polymerization with Silica-Supported $\text{Cr}[\text{CH}(\text{SiMe}_3)_2]_3$ Catalyst. Effect of Silica Calcination Temperature and Cr Content

Takashi MONOI,[†] Haruhiko IKEDA, Yasuaki SASAKI, and Yasumichi MATSUMOTO*

Research & Development Center, Japan Polyolefins Co., Ltd., 10-1 Chidori-cho, Kawasaki-ku, Kawasaki 210-8547, Japan

**Department of Applied Chemistry, Faculty of Engineering, Kumamoto University, 2-39-1 Kurokami-cho, Kumamoto 860-8555, Japan*

(Received March 14, 2003; Accepted April 26, 2003)

KEY WORDS Tris[bis(trimethylsilyl)methyl]chromium(III) / Silica / Ethylene Polymerization / Silanol / Calcination /

We have reported on the results of ethylene polymerization with a silica-supported $\text{Cr}[\text{CH}(\text{SiMe}_3)_2]_3$ catalyst ($\text{Cr}[\text{CH}(\text{SiMe}_3)_2]_3/\text{silica}$).¹ This catalyst showed a high degree of activity in ethylene polymerization—without organoaluminum compounds as cocatalysts or scavengers in slurry-phase polymerization—under conditions comparable to actual industrial conditions for producing polyethylene with a silica-supported chromium oxide catalyst ($\text{CrO}_3/\text{silica}$), the so-called Phillips catalyst.^{2,3} The catalyst showed very similar behavior to the Phillips catalyst, with respect to the effect of the polymerization temperature on the molecular weight of the polyethylene, the broad molecular weight distribution, the presence of long-chain branching and copolymerization abilities with 1-hexene.

In a previous paper,¹ we fixed the silica calcination temperature at 600 °C and the Cr content to silica at 0.1 wt% in the $\text{Cr}[\text{CH}(\text{SiMe}_3)_2]_3/\text{silica}$ catalyst to simplify the comparison of the performance of the catalyst with the Phillips catalyst. In this article, we report on the effect of the silica calcination temperature and Cr content of the catalyst on its activity and the obtained polyethylene. The interesting characteristics of the catalyst are presented and a mechanism for active site formation is also proposed.

EXPERIMENTAL

Details of synthesis of $\text{Cr}[\text{CH}(\text{SiMe}_3)_2]_3$ was described in ref 4, preparation of the $\text{Cr}[\text{CH}(\text{SiMe}_3)_2]_3/\text{silica}$ catalyst, polymerization procedure, gel permeation chromatograph (GPC) and ¹³C nuclear

magnetic resonance (¹³C NMR) measurements of the polyethylene were described in ref 1 and density measurements were described in ref 5. $\text{Cr}[\text{CH}(\text{SiMe}_3)_2]_3$ was synthesized by the reaction of CrCl_3 with three equivalents of $\text{Li}[\text{CH}(\text{SiMe}_3)]_2$ and obtained as bright green crystals. The $\text{Cr}[\text{CH}(\text{SiMe}_3)_2]_3/\text{silica}$ catalyst was prepared by calcining Sylopol 952 silica^{6,7} (surface area = 300 m² g⁻¹, pore volume = 1.6 cm³ g⁻¹), which is one of the most representative silica supports used for the Phillips catalyst, at 200 °C and 600 °C followed by supporting $\text{Cr}[\text{CH}(\text{SiMe}_3)_2]_3$ on the calcined silica in a hexane slurry. Slurry-phase polymerization of ethylene using isobutane as a diluent was conducted in a stainless steel autoclave by the catalyst without organoaluminum compounds as cocatalysts or scavengers (ethylene partial pressure, 1.4 MPa; polymerization temperature, 100 °C; polymerization time, 1 h).

RESULTS AND DISCUSSION

Effects of Silica Calcination Temperature and Cr Content

The results of polymerization by changing the Cr content for each silica calcination temperature (200 °C and 600 °C, respectively) are shown in Table I. The effect of the Cr content on the activity per Cr is shown in Figure 1. The activity of the catalyst per Cr with a silica calcination temperature of 200 °C gradually increased up to a Cr content of 2.0 wt%. On the other hand, the activity of the catalyst per Cr with a silica calcination temperature of 600 °C significantly decreased with an increase of Cr content. A slight increase of Cr content

[†]To whom correspondence should be addressed (Fax: +81-44-276-3501, E-mail: takashi.monoi@jpo.co.jp).

Table I. Effects of silica calcination temperature and Cr content on ethylene polymerization^a

Run	Catalyst ^b (mg)	Cr content to silica (wt%)	Activity		Density (g cm ⁻³)	M_n^c ($\times 10^4$)	M_w^c ($\times 10^4$)	M_w/M_n^c
			(g-PE/g-cat-h)	(g-PE/mmol-Cr-h)				
Silica calcination temperature, 200 °C								
1	238.7	0.5	570	5930	0.9578	1.1	40.6	36.9
2	211.1	1.0	1330	6920	0.9548	1.2	34.5	28.8
3	68.1	1.5	2880	9980	0.9533	1.0	33.5	33.5
4	56.5	2.0	4020	10500	0.9505	1.0	32.6	32.6
5	75.2	2.5	3970	8260	0.9471	1.3	31.5	24.2
Silica calcination temperature, 600 °C								
6	223.6	0.1	1210	62900	0.9590	1.5	31.7	21.1
7	188.3	0.2	1510	39300	0.9371	1.0	18.7	18.7
8	174.6	0.22	890	21000	0.9292	0.8	17.5	21.9
9	173.0	0.25	760	15800	0.9241	0.4	12.7	31.8
10	197.5	0.4	600	7800	0.9065	0.4	14.2	35.5

^aPolymerization temperature, 100 °C; ethylene partial pressure, 1.4 MPa; isobutane, 700 mL; polymerization time, 1 h.

^bCr[CH(SiMe₃)₂]₃/silica. ^cDetermined by GPC.

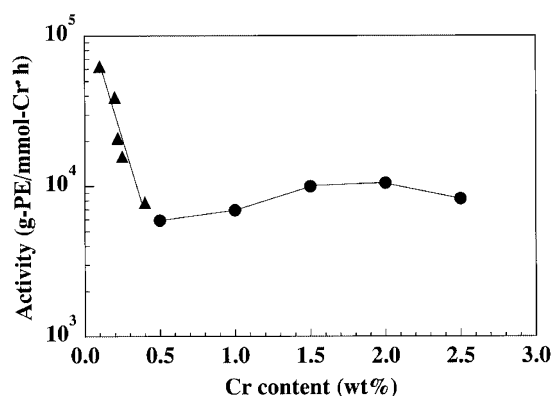


Figure 1. Effect of Cr content on activity per Cr: Cr[CH(SiMe₃)₂]₃/silica; ●, silica calcination temperature = 200 °C; ▲, silica calcination temperature = 600 °C; polymerization temperature, 100 °C; ethylene partial pressure, 1.4 MPa; isobutane, 700 mL; polymerization time, 1 h.

from 0.1 wt% to 0.4 wt% decreased the activity to about 1/10. The results suggest that, with a silica calcination temperature of 600 °C, the active site for polymerization is rather unstable and transforms to another type of species with an increase of Cr content, while the active site for polymerization with a silica calcination temperature of 200 °C is stable and does not change with an increase of Cr content.

The effect of the Cr content on the density of polyethylene is shown in Figure 2. The density of polyethylene with a silica calcination temperature of 200 °C decreased slightly with an increase of Cr content. On the other hand, the density of polyethylene with a silica calcination temperature of 600 °C drastically decreased with an increase of Cr content. A slight increase of Cr content from 0.1 wt% to 0.4 wt% decreased the density from 0.9590 to 0.9065. Such a drastic decrease of density must be a result of the formation of short-chain branching. The ¹³C NMR measurement of the 0.9065 density of polyethylene showed

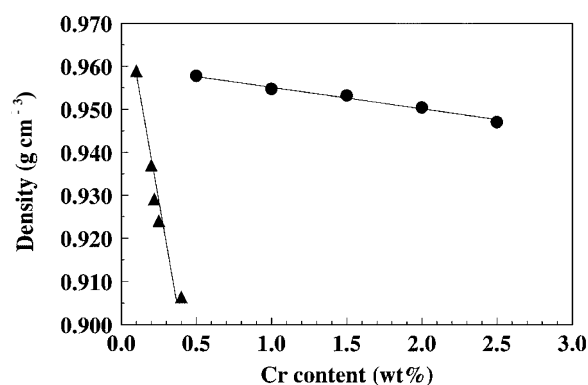


Figure 2. Effect of Cr content on density: Cr[CH(SiMe₃)₂]₃/silica; ●, silica calcination temperature = 200 °C; ▲, silica calcination temperature = 600 °C; polymerization temperature, 100 °C; ethylene partial pressure, 1.4 MPa; isobutane, 700 mL; polymerization time, 1 h.

the presence of 6.0 *n*-butyl branches per 1000 carbons with trace amount of ethyl branches and no detectable amounts of other short-chain branches, in contrast to 0.05 *n*-butyl branches per 1000 carbons in the 0.9590 density of polyethylene. It is considered that the *n*-butyl branches are formed by the copolymerization of ethylene with 1-hexene formed by the trimerization of ethylene, which showed characteristics very similar to the silica-supported Cr[N(SiMe₃)₂]₃/alumoxane catalyst previously reported by us.⁵ Namely, poly[ethylene-*co*-(1-hexene)] was obtained from the ethylene monomer alone. The molecular weight of the polyethylene also decreased significantly with an increase of Cr content, showing that a chain transfer reaction to 1-hexene took place. Considering the fact that the activity per Cr decreased with an increase of Cr content, the results of the *n*-butyl branching formation suggest that the active site for polymerization transforms to the active site for ethylene trimerization and both active sites independently exist on the silica surface. It is considered that a small

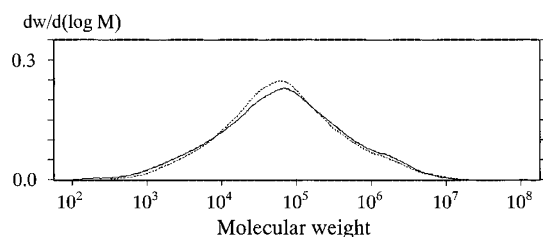


Figure 3. GPC profile of polyethylene: solid line, run 4; dotted line, run 6.

amount of ethylene trimerization is also formed with a silica calcination temperature of 200 °C, although the transformation from the active site of ethylene polymerization to the active site of ethylene trimerization takes place only to a small degree with an increase of Cr content.

The GPC profiles of the polyethylene with a silica calcination temperature of 200 °C and 600 °C respectively are shown in Figure 3 as the best activity of each calcination temperature (run 4, Cr content 2.0 wt%; run 6, Cr content 0.1 wt%). The molecular weight distributions (M_w/M_n) of these polyethylenes are comparatively broad and both are very similar to each other, which suggest that the active sites for polymerization with silica calcination temperatures of 200 °C and 600 °C also resemble each other.

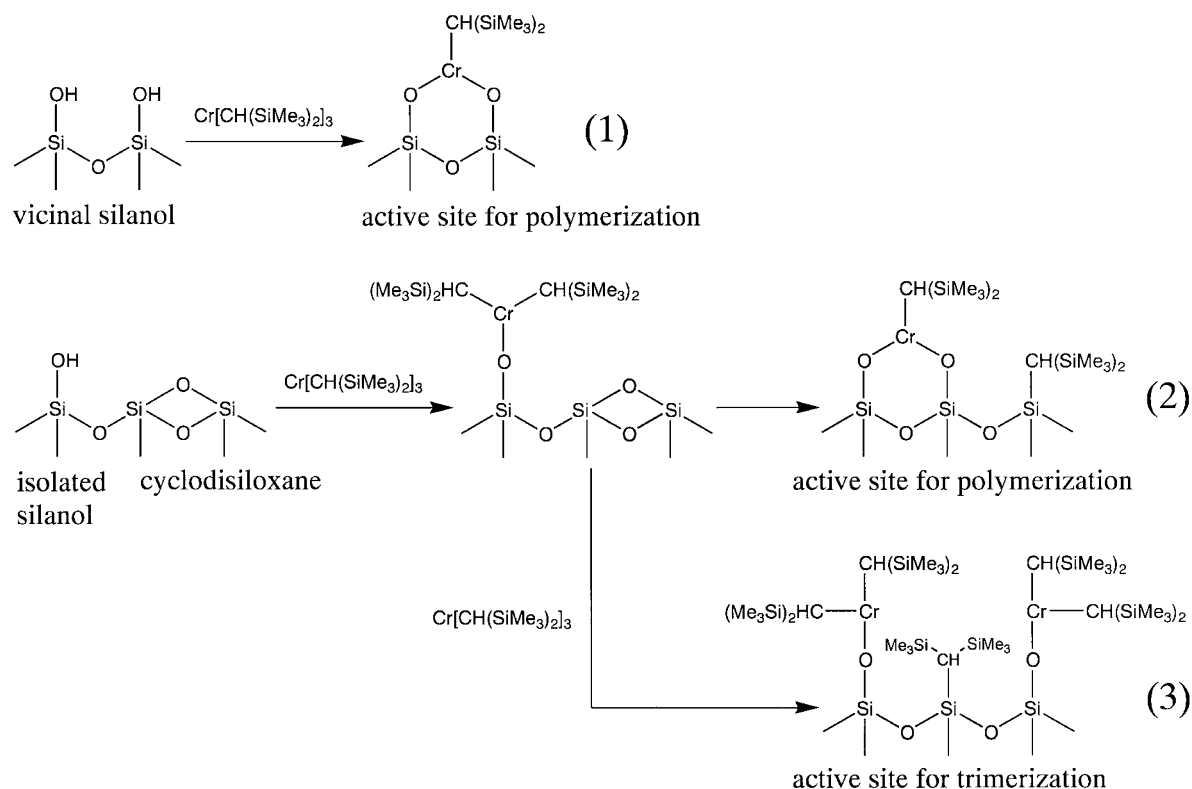
Mechanism for Active Site Formation

The above results show that the silica calcination temperature significantly influences the nature of the active sites which are formed after supporting $\text{Cr}[\text{CH}(\text{SiMe}_3)_2]_3$. Cr species are supported on the silica by the reaction between $\text{Cr}[\text{CH}(\text{SiMe}_3)_2]_3$ and the surface silanols of the calcined silica. Vicinal silanol, geminal silanol, and isolated silanol are well known for comprising the structure of the surface silanol, and that structure depends on the silica calcination temperature.⁸ From Amor Nait Ajjou *et al.*'s precise experiments on silica, it is definite that most silanols are present in the vicinal silanol structure at 200 °C and most silanols are present in the isolated silanol structure over 500 °C.⁹ Moreover, we have determined the amount of silanols by measuring the volume of methane liberated by the reaction between trimethylaluminum and silica ($\text{Si-OH} + \text{Me}_3\text{Al} \rightarrow \text{Si-O-AlMe}_2 + \text{CH}_4$) in a hexane slurry, according to the method by Kratochvila *et al.*¹⁰ The amount of silanols were determined to be 1.96 mmol g^{-1} at a silica calcination temperature of 200 °C and 0.85 mmol g^{-1} at a silica calcination temperature of 600 °C. Even at 2.5 wt% Cr content (0.48 mmol-Cr/g) and a silica calcination temperature of 200 °C (corresponding to run 5), the excess amount of silanol is about 4 times that of the Cr com-

plex. Also, even at 0.4 wt% Cr content (0.077 mmol-Cr/g) and a silica calcination temperature of 600 °C (corresponding to run 10), the excess amount of silanol is about 11 times that of the Cr complex.

Therefore, at a silica calcination temperature of 200 °C, which does not decrease the density of the polyethylene with an increase of Cr content, a reaction between $\text{Cr}[\text{CH}(\text{SiMe}_3)_2]_3$ and vicinal silanol takes place and the Cr species are supported on the silica through two Si-O-Cr bonds,⁹ as illustrated in eq 1 of Scheme 1. Considering the fact that the catalyst does not require organoaluminum compounds as cocatalysts or scavengers, it strongly suggests that this supported structure is the active site for polymerization. From quantum chemical calculations reported by Børve *et al.*,¹¹ this structure, which was referred to as a monoalkylchromium site by them, showed a much lower activation energy for ethylene insertion than other model active sites, like the carbenochromium site, alkenylhydridochromium site, dialkylchromium site, π -allylchromium site and chromacycloalkane site which were previously put forward by many researchers as the active sites for the Phillips catalyst.^{3, 12, 13}

On the other hand, at a silica calcination temperature of 600 °C, which dramatically decreases the density of the polyethylene with an increase of Cr content, a reaction between $\text{Cr}[\text{CH}(\text{SiMe}_3)_2]_3$ and isolated silanol, illustrated in eq 2 of Scheme 1, takes place and the Cr species are supported on the silica through one Si-O-Cr bond.⁹ Furthermore, upon considering the above suggestion that the active sites for polymerization with silica calcination temperatures of 200 °C and 600 °C should resemble each other, this one-legged Cr species may react with a highly strained cyclodisiloxane group⁸ which is formed by thermal dehydroxylation of vicinal silanols ($2\text{Si-OH} \rightarrow \text{Si-O-Si} + \text{H}_2\text{O}$) and the same active site for polymerization may be formed, as illustrated in eq 2 of Scheme 1. With an increase of Cr content, the strained cyclodisiloxane group may react further with $\text{Cr}[\text{CH}(\text{SiMe}_3)_2]_3$ and the one-legged Cr species is formed at the expense of the active site for polymerization illustrated in eq 3 of Scheme 1. Our previous finding,¹⁴ that the ethylene trimerization catalyst ($\text{Cr}[\text{N}(\text{SiMe}_3)_2]_3/\text{isobutylalumoxane/silica}$) produces 1-hexene at a high activity and high selectivity by using silica calcined at 600 °C and our current finding that the density of polyethylene drastically decreased with an increase of Cr content together strongly suggest that this supported structure is the active site for trimerization. Similar surface structure of one-legged and two-legged Cr species in Scheme 1 have been proposed by Bade *et al.* with the tris(2-methylallyl)chromium(III)/silica catalyst.¹⁵



Scheme 1. Proposed mechanism for active site formation.

Finally, because the $\text{Cr}[\text{CH}(\text{SiMe}_3)_2]_3/\text{silica}$ catalyst displayed a very similar performance to that of the Phillips catalyst as we previously reported,¹ the active site for polymerization of the Phillips catalyst, which is still in many confusing controversies, should resemble the active site suggested in eq 1 of Scheme 1. The only difference between the $\text{Cr}[\text{CH}(\text{SiMe}_3)_2]_3/\text{silica}$ catalyst and the Phillips catalyst is that the addition of hydrogen resulted in a decrease of the molecular weight of the polyethylene for the $\text{Cr}[\text{CH}(\text{SiMe}_3)_2]_3/\text{silica}$ catalyst, whereas the molecular weight did not change in the case of the Phillips catalyst. The active site for trimerization present in the $\text{Cr}[\text{CH}(\text{SiMe}_3)_2]_3/\text{silica}$ catalyst may be responsible for the hydrogen response, about which further investigation is now in progress.

REFERENCES

1. H. Ikeda, T. Monoi, and Y. Sasaki, *J. Polym. Sci., Part A: Polym. Chem.*, **41**, 413 (2003).
2. M. P. McDaniel, in "Handbook of Heterogeneous Catalysis", G. Ertl, H. Knözinger, and J. Weitlamp, Eds., VCH, Weinheim, 1997, Vol. 5, chapt. 4, pp 2400–2405.
3. M. P. McDaniel, *Adv. Catal.*, **33**, 47 (1985).
4. H. Ikeda, T. Monoi, K. Ogata, and H. Yasuda, *Macromol. Chem. Phys.*, **202**, 1806 (2001).
5. T. Monoi, H. Ikeda, H. Ohira, and Y. Sasaki, *Polym. J.*, **34**, 461 (2002).
6. R. Merryfield, M. McDaniel, and G. Parks, *J. Catal.*, **77**, 348 (1982).
7. M. P. McDaniel and M. B. Welch, *J. Catal.*, **82**, 98 (1983).
8. C. J. Brinker and G. W. Scherer, in "Sol-Gel Science—The Physics and Chemistry of Sol-Gel Processing—", Academic Press, San Diego, CA., 1990, chapt. 10, pp 617–672.
9. J. Amor Nait Ajjou and S. L. Scott, *Organometallics*, **16**, 86 (1997).
10. J. Kratochvila, Z. Kadlc, A. Kazda, and Z. Salajka, *J. Non-Cryst. Solids*, **143**, 14 (1992).
11. Ø. Espelid and K. J. Børve, *J. Catal.*, **195**, 125 (2000).
12. K. H. Theopold, *Eur. J. Inorg. Chem.*, 15 (1998).
13. K. Matsuura and N. Mikami, "Polyethylene Gijutsu Tokuhon", Kogyo Chosakai Publishing, Co., Ltd., Tokyo, 2001, chapt. 2, pp 81–113.
14. T. Monoi and Y. Sasaki, *J. Mol. Catal. A: Chem.*, **187**, 135 (2002).
15. O.M. Bade, R. Blom, and M. Ystenes, *Organometallics*, **17**, 2524 (1998).