

## Ethylene Polymerization with Silica-Supported Cr[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>/Alumoxane Catalyst

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**ABSTRACT:** A new silica-supported non-cyclopentadienyl chromium catalyst having high activity for ethylene polymerization is presented. The catalyst was prepared by supporting tris[bis(trimethylsilyl)amido]chromium(III) Cr[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> and alumoxane on silica. The best activity was attained by supporting Cr[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> (0.2 wt%-Cr for silica) on silica calcined at 350°C and next supporting a modified-methylalumoxane (Al/Cr molar ratio = 20). Activity during the slurry-phase polymerization was 75100 g-PE/mmol-Cr-hr at 103°C and 1.4 MPa ethylene partial pressure in isobutane. The obtained polyethylene had a relatively high molecular weight and broad molecular weight distribution (HLMFR = 15.6 g/10 min,  $M_w = 330000$ ,  $M_w/M_n = 33.0$ ). The calcination temperature of silica had significant influence on the catalyst performance. As calcination temperature increased, short branches, mainly *n*-butyl and some ethyl branches, were introduced into the resulting polyethylene. Therefore, poly[ethylene-*co*-(1-hexene)] was obtained from the ethylene monomer alone. This shows two Cr active sites, a polymerization and trimerization site. The relative amount of each site is considered to be determined by the type of silanol groups obtained after calcination.

**KEY WORDS** Tris[bis(trimethylsilyl)amido]chromium(III) / Silica / Alumoxane / Ethylene Polymerization / Poly[ethylene-*co*-(1-hexene)] /

There has been increasing interest in the discovery and development of non-cyclopentadienyl transition metal catalysts using titanium, zirconium, iron, nickel, and palladium for ethylene polymerization.<sup>1-4</sup> As for chromium as a transition metal, cyclopentadienyl complexes are well known for ethylene polymerization.<sup>5-12</sup> Recently, non-cyclopentadienyl chromium catalysts have been reported.<sup>13-22</sup> These homogeneous catalysts have moderate to high activity depending on the ligand structures. We have been exploring non-cyclopentadienyl chromium catalysts because different characteristics could be expected for chromium as a group 6 element from the group 4 elements like titanium and zirconium, the group 8 element like iron and group 10 elements like nickel and palladium. We present a new heterogeneous non-cyclopentadienyl chromium catalyst having high activity for ethylene polymerization with unique features by supporting the tris[bis(trimethylsilyl)amido]chromium(III) complex Cr[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> as a transition metal component and alumoxane as an organometallic component on silica. The characteristics of this catalyst influence polymerization activity and polymer structure (molecular weight, molecular weight distribution, and chain branching). The polymerization mechanism is discussed.

## EXPERIMENTAL

### Materials

Anhydrous chromium(III) chloride CrCl<sub>3</sub> was purchased from Kishida Chemical and used without further purification. Lithium bis(trimethylsilyl)amide (Me<sub>3</sub>Si)<sub>2</sub>NLi was obtained from Aldrich Chemical as a hexane solution and used without further purification. CARiACT P-3 silica (surface area = 708 m<sup>2</sup> g<sup>-1</sup>, pore volume = 1.42 cm<sup>3</sup> g<sup>-1</sup>) was purchased from Fuji Silysia Chemical. Isobutylalumoxane (IBAO) and modified methylalumoxane (MMAO; 30 mol% isobutyl-modified), triethylaluminum (Et<sub>3</sub>Al), triisobutylaluminum (*i*-Bu<sub>3</sub>Al) were purchased from Tosoh Finechem and used without further purification. *n*-Butyllithium was purchased from Wako Pure Chemical Industries as hexane solution and used without further purification. Tetrahydrofuran and hexane were from Wako Pure Chemical Industries and purified by distillation under a nitrogen atmosphere over a sodium/potassium amalgam. Polymerization-grade ethylene and isobutane from Japan Polyolefins were used.

### Synthesis of Tris[bis(trimethylsilyl)amido]chromium(III) Cr[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>

All manipulations were performed under a dry nitrogen atmosphere. Cr[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> was synthesized by

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**Table I.** Comparison between supported and unsupported Cr[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> for ethylene polymerization<sup>a</sup>

Run	Catalyst		Activity g-PE/mmol-Cr-hr	HLMFR g/10 min
	supported or unsupported on silica	(mg)		
1	supported <sup>b</sup>	328.2	58200	3.7
2	unsupported <sup>c</sup>	17.6 <sup>d</sup>	160	64.0

<sup>a</sup>Polymerization temperature, 100°C; ethylene partial pressure, 1.4 MPa; isobutane, 700 mL; polymerization time, 1 h. <sup>b</sup>Cr[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>/IBAO/silica; silica calcination temperature, 400°C; Cr, 0.1 wt%; Al/Cr molar ratio, 120. <sup>c</sup>IBAO added to isobutane solution of Cr[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>; Al/Cr molar ratio, 120. <sup>d</sup>Weight as Cr[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>.

reacting anhydrous CrCl<sub>3</sub> with (Me<sub>3</sub>Si)<sub>2</sub>NLi in tetrahydrofuran and obtained as bright green crystals.<sup>23</sup> The detail procedure of the synthesis and results of elemental analysis and mass spectrum measurement are described in ref 23. The crystals were dissolved and diluted by hexane to prepare the 0.1 M Cr[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> stock solution.

#### Preparation of Catalyst

All manipulations were performed under a dry nitrogen atmosphere. A typical catalyst preparation procedure is as follows. CARiACT P-3 silica was calcined in a quartz tube with fluidizing by dry nitrogen at 350°C for 24 h. Three grams of the silica were placed in a 100 mL round-bottom flask and 35 mL of hexane added. Upon stirring and warming to 40°C, a 1.2 mL hexane solution of Cr[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> was added and stirred (chromium content, 0.2 wt% to silica). The dark-green color of the hexane solution immediately disappeared and the silica turned pale green. After 2 h, a 2.0 mL hexane solution of 1.2 M MMAO (Al/Cr molar ratio = 20) was added. The color of the catalyst did not change. After stirring at 40°C for 2 h, the hexane was removed under reduced pressure until no volatiles appeared. The catalyst was obtained as greenish gray powder.

#### Polymerization Procedure

A typical reaction procedure is as follows. A 1.5 L stainless-steel autoclave equipped with a magnetic stirrer, thermocouple, gas inlet, gas outlet port and heating system was heated to 120°C and continuously flushed with dry nitrogen for 2 h and then cooled to ambient temperature. 100–200 mg of the catalyst were added to the autoclave from a glass ampoule and 700 mL isobutane introduced at ambient temperature. After heating to the polymerization temperature, the autoclave was pressurized at 1.4 MPa of ethylene. The polymerization started immediately by ethylene consumption and the partial pressure of ethylene was maintained throughout the polymerization. After 1 h, the ethylene supply was stopped and the autoclave depressurized using a pressure-relief valve and cooled to ambient temperature. The obtained polymer was dried under reduced

pressure overnight at 110°C.

#### Analysis

High-load melt flow rate (HLMFR) measurements were performed according to JIS K-7210 (1996 version) at 190°C and at a load of 211.82 N.

Density measurements were performed according to JIS K-7112 (1996 version).

Gel permeation chromatography (GPC) measurements were carried out using a Waters 150C model equipped with a Shodex-HT806 M column. The GPC curve was calibrated with standard polystyrene. A solvent, 1,2,4-trichlorobenzene was used as eluent at 135°C.

<sup>13</sup>C NMR measurements were carried out over a JEOL GSX400 spectrometer. 1,2,4-Trichlorobenzene/benzene-*d*<sub>6</sub>/hexamethyldisiloxane (mixing ratio: 30/10/1) was used as the solvent at 120°C. The sample concentration was 0.3 g/3 mL and the pulse repetition time was 2 s.

## RESULTS AND DISCUSSION

#### Effects of Silica as Support

The results of polymerization are shown in Table I (Run 1). High molecular weight polyethylene was obtained with high activity. When polymerization was carried out under the same conditions without the silica as support, activity decreased to nearly 1/400 (Run 2). The silica is essential for the catalyst system and may stabilize the active sites.

#### Effects of Organometallic Component

The results of polymerization with various organometallic components instead of IBAO are shown in Table II. MMAO showed the highest polymerization activity (Run 3). Activity decreased below 1/10 using the trialkylaluminum instead of alumoxanes (Run 4, 5). Alkylolithium showed no polymerization activity at all (Run 6). Alumoxane is an essential component for the catalyst to achieve a high polymerization activity.

#### Effects of Cr Content

The results of polymerization with changing Cr con-

**Table II.** Effects of organometallic component on ethylene polymerization<sup>a</sup>

Run	Organometallic component	Catalyst <sup>b</sup>	Activity		HLMFR
		mg	g-PE/mmol-Cr-hr		g/10 min
3	MMAO	315.0	64000		3.4
1	IBAO	328.2	58200		3.7
4	Et <sub>3</sub> Al	313.1	4160		4.1
5	<i>i</i> -Bu <sub>3</sub> Al	392.8	1350		0.59
6	<i>n</i> -BuLi	360.7	0		—

<sup>a</sup>Polymerization temperature, 100°C; ethylene partial pressure, 1.4 MPa; isobutane, 700 mL; polymerization time, 1 h. <sup>b</sup>Cr[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>/organometallic component/silica; silica calcination temperature, 400°C; Cr, 0.1 wt%; Al/Cr molar ratio, 120.

**Table III.** Effects of chromium content on ethylene polymerization<sup>a</sup>

Run	Cr content	Catalyst <sup>b</sup>	Activity		HLMFR
	wt%	mg	g-PE/g-cat-hr	g-PE/mmol-Cr-hr	g/10 min
7	0.05	579.3	560	58200	0.69
8	0.1	289.2	1010	52500	1.2
9	0.2	229.6	1840	47800	1.1
10	0.4	169.0	1720	22400	2.0

<sup>a</sup>Polymerization temperature, 90°C; ethylene partial pressure, 1.4 MPa; isobutane, 700 mL; polymerization time, 1 h. <sup>b</sup>Cr[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>/IBAO/silica; silica calcination temperature, 400°C; Al/Cr molar ratio, 60.

**Table IV.** Effects of calcination temperature of silica on ethylene polymerization<sup>a</sup>

Run	Calcination temperature of silica	Catalyst <sup>b</sup>	Activity		HLMFR	Density	Ethyl	<i>n</i> -Butyl	$\frac{M_w}{M_n}$ <sup>d</sup>	$M_w/M_n$ <sup>d</sup>
	°C		mg	g-PE/mmol-Cr-hr			g/10 min	branches <sup>c</sup>		
11	200	144.5	45500	4.0	0.9553	0.12	0.28	46.3	41.3	
12	350	106.5	61900	14.2	0.9518	0.19	0.96	31.2	33.4	
13	400	111.5	41900	19.1	0.9453	0.42	3.22	30.6	45.1	
14	500	122.9	23700	19.8	0.9388	0.61	4.46	29.6	64.4	
15	600	198.5	22900	19.3	0.9356	0.86	6.24	29.7	49.3	

<sup>a</sup>Polymerization temperature, 103°C; ethylene partial pressure, 1.4 MPa; isobutane, 700 mL; polymerization time, 1 h. <sup>b</sup>Cr[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>/MMAO/silica; Cr, 0.2 wt%; Al/Cr molar ratio, 60. <sup>c</sup>Determined by <sup>13</sup>C NMR. <sup>d</sup>Determined by GPC.

tent are shown in Table III. Polymerization activity per Cr decreased with increase in the Cr content, but polymerization activity per catalyst increased up to a Cr content of 0.2 wt%. Cr species may adhere to each other at more than 0.2 wt% Cr content and the active sites collapse.

#### Effects of Silica Calcination Temperature

The results of polymerization by changing silica calcination temperature are shown in Table IV. Polymerization activity was maximum at the calcination temperature of 350°C. The molecular weight of polyethylene decreased with increase of calcination temperature.

The main characteristics of the catalyst appeared by changing silica calcination temperature. The density of the polyethylene decreased with increase of silica calcination temperature. Based on <sup>13</sup>C NMR measurements, short branches, mainly *n*-butyl and some ethyl branches, were observed.<sup>24</sup> Upon increasing the silica calcination temperature, *n*-butyl branches per 1000 C

significantly increased versus ethyl branches. Ethyl branches gradually increased with silica calcination temperature. The effect of the silica calcination temperature on the density and number of *n*-butyl branches are shown in Figure 1.

It is considered that the *n*-butyl branches are formed by the copolymerization of ethylene with 1-hexene formed by the trimerization of ethylene. We have reported the ethylene trimerization catalyst by supporting Cr[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> and IBAO on silica with a Cr content of 1.0 wt% and showed high activity for 1-hexene production from ethylene.<sup>25,26</sup> Therefore, poly[ethylene-*co*-(1-hexene)] was obtained from the ethylene monomer alone. The molecular weight distribution ( $M_w/M_n$ ) of the polyethylene was broader than the typical polyethylene produced by the chromium oxide(VI)/silica catalyst (so-called Phillips catalyst) which shows a  $M_w/M_n$  of about 6 to 15.<sup>27</sup>

#### Effects of Al/Cr Molar Ratio

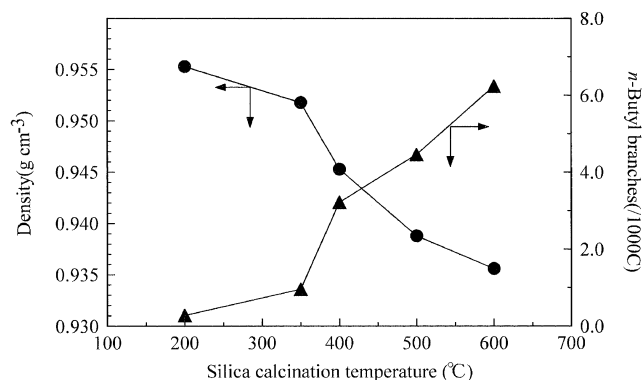
The results of polymerization by changing molar

**Table V.** Effects of Al/Cr molar ratio on ethylene polymerization<sup>a</sup>

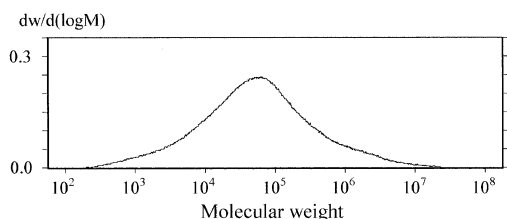
Run	Al/Cr molar ratio	Catalyst <sup>b</sup> mg	Activity g-PE/mmol-Cr-hr	HLMFR g/10 min	Density g cm <sup>-3</sup>	M <sub>w</sub> <sup>c</sup> ×10 <sup>4</sup>	M <sub>w</sub> /M <sub>n</sub> <sup>c</sup>
16	0	150.0	0	—	—	—	—
17	10	143.0	47600	17.3	0.9516	29.0	29.2
18	20	136.5	75100	15.6	0.9548	33.0	32.8
19	30	118.6	73300	14.2	0.9526	31.0	33.5
12	60	106.5	61900	14.2	0.9518	31.2	33.4

<sup>a</sup>Polymerization temperature, 103°C; ethylene partial pressure, 1.4 MPa; isobutane, 700 mL; polymerization time, 1 h.

<sup>b</sup>Cr[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>/MMAO/silica; silica calcination temperature, 350°C; Cr, 0.2 wt%. <sup>c</sup>Determined by GPC.



**Figure 1.** Effects of silica calcination temperature on density and *n*-butyl branch number: Cr[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>/MMAO/silica; Cr, 0.2 wt%; Al/Cr molar ratio, 60; polymerization temperature, 103°C; ethylene partial pressure, 1.4 MPa; isobutane, 700 mL; polymerization time, 1 h.



**Figure 2.** GPC profile of polyethylene (Run 18).

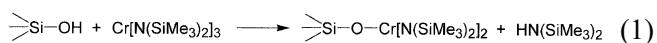
Al/Cr are shown in Table V. Polymerization activity was maximum at Al/Cr of 20. The molecular weight and molecular weight distribution did not significantly change with Al/Cr. GPC of the resulting polyethylene at Al/Cr of 20 (Run 18) is shown in Figure 2, as best activity in the catalyst.

### Polymerization Mechanism

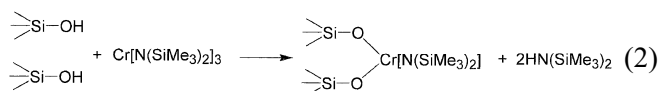
The active site for the ethylene polymerization and active site for the ethylene trimerization independently exist on the silica surface. The amount of each site is influenced by silica calcination temperature.

The silica support plays a key role in our catalyst. Cr species are supported on silica by the reaction between Cr[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> and the surface silanols of the silica. Vicinal silanol, geminal silanol, and isolated silanol are well known for comprising the structure of the surface silanol.<sup>28, 29</sup> The structure of the surface silanol depends

on the silica calcination temperature. From Amor Nait Ajjou *et al.*'s precise analysis of the reaction between the tetraalkylchromium compounds and silica calcined at 200°C and 500°C, it is definite that most silanols are present in the isolated silanol structure over 500°C and most silanols are present in the vicinal silanol structure at 200°C.<sup>30</sup> Therefore, at silica calcination temperature of 600°C, which produces a substantial number of *n*-butyl branches, the reaction between the Cr complex and isolated silanol like that shown below takes place and Cr species may be supported on silica through a Si–O–Cr bond.



At silica calcination temperature of 200°C, which produces some *n*-butyl branches, the reaction between the Cr complex and vicinal silanol like that shown below takes place and the Cr species may be supported on silica through two Si–O–Cr bonds.



Similar surface structures have been proposed by Benham *et al.* with the chromium oxide(VI)/silica catalyst contacted with octakis( $\mu$ -trimethylsilylmethyl)-tetrachromium(II) Cr<sub>4</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>8</sub><sup>31, 32</sup> and by Bade *et al.* with the tris(2-methylallyl)chromium(III)/silica catalyst<sup>33</sup> and *tert*-butyl lithium modified chromium oxide catalyst reduced by carbon monoxide.<sup>34, 35</sup> Their catalysts produce copolymers of ethylene with 1-alkenes from only the ethylene monomer. However, not only *n*-butyl branches but also comparable numbers of ethyl branches are formed, which is different from our catalyst which produces mainly *n*-butyl branches.

At the intermediate calcination temperature, both supported Cr species exist on the silica surface. By reaction with alumoxane, the active site for ethylene trimerization would have been formed from the former type of Cr species and the active site for ethylene polymerization would have been formed from the latter type of Cr species. 1-Hexene produced from the ethylene trimerization site is copolymerized at the ethylene polymerization site. Although activity is low compared to that at 350°C, substantial activity is still shown at

the silica calcination temperature of 600°C. For low Cr content in our case, there may be substantial amounts of the latter type of supported Cr species. At the silica calcination temperature of 200°C, minor numbers of *n*-butyl branches exist. Therefore, a small amount of the former type of Cr supported species is considered to exist.

It is most probable that 1-hexene is produced by a mechanism associated with the chromacyclopentane and chromacycloheptane intermediates, which was proposed by Briggs<sup>36</sup> and supported by Jolly *et al.*,<sup>37</sup> to explain the high selectivity for 1-hexene production by some particular homogeneous Cr catalyst. From the above considerations, the reactivity of the active site with ethylene may be determined by the structure of the Cr species on the surface of the silica.

### CONCLUSIONS

(1) The Cr[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>/alumoxane/silica catalyst showed high activity for ethylene polymerization. Being supported on silica was responsible for the high activity. Polyethylene obtained by the catalyst had a relatively high molecular weight and broad molecular weight distribution.

(2) The calcination temperature of the silica had significant influence on catalyst performance. As the silica calcination temperature increased, short branches were introduced into the polymer chain and the density of the polyethylene decreased. Poly[ethylene-*co*-(1-hexene)] was obtained from the ethylene monomer alone.

(3) The polymerization mechanism including two different Cr active sites, which shows polymerization and trimerization activities, is proposed. The number of each site is determined by silanol group after calcination of the silica.

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