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Siloxene-Supported Catalysts for Ethylene Polymerization

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A new type of Ziegler ethylene polymerization catalyst has been formed using as a support, siloxene, a layer compound with an empirical formula of Si_2H_2O. Siloxene is a reducing compound, and it reacts with excess $TiCl_4$, giving an inactive brown solid with 5.2% Ti and 8.0% Cl. However, when additional $TiCl_4$ is reduced by a metal alkyl and precipitated onto the brown solid, a catalyst with moderate activity is formed. Maximum activity for ethylene polymerization was obtained when the catalyst was pretreated with *n*-butylmagnesium, contained 0.06 g $CaCl_2$/g siloxene, and was run at 80°C with 40–50 ppm of TEA cocatalyst. These catalysts are very active in the initial portion of the reaction, but the activity decreases rapidly over the first 30 min. Their hydrogen response and hexene incorporation is similar to that observed with other Ziegler catalysts. © 1993 Academic Press, Inc.

INTRODUCTION

Siloxene is a layer compound with an empirical formula of Si_2H_2O. It was first prepared by Kautsky in 1921 when he reacted calcium silicide ($CaSi_2$) with alcoholic HCl (*1*). Over the years, there has been some disagreement over the structure of siloxene, and three different possibilities have been proposed:

1. Kautsky *et al.* (*2*) proposed a structure (Fig. 1a) where sheets are formed by six-membered Si rings joined by oxygen atoms. A hydrogen atom, alternating above and below the sheet, is attached to each silicon.
2. Weiss *et al.* (*3*) prepared siloxene crystals and the single-crystal X-ray patterns support the structure shown in Fig. 1b, where a sheet is formed from silicon atoms each containing either a hydrogen or hydroxyl. This structure is also supported by IR analysis that shows hydroxyl groups. However, siloxene was prepared for these analyses by treating $CaSi_2$ with concentrated HCl. This results in a yellow to yellow-green solid, while Kautsky's synthesis gives a gray color. So there is obviously some difference in the compounds formed by these two methods. While the structure in Fig. 2 appears to be what is produced by Weiss' synthesis, it may not be what is produced by Kautsky's synthesis.
3. Wiberg proposed the structure in Fig. 1c where chains of silicon atoms are joined by Si–O–Si linkages to form a sheet. Each silicon bears a hydrogen atom (*2*).

Recent investigations by X-ray photoelectron spectroscopy (*4*) show that siloxene prepared by Kautsky's method contains silicon oxidation states from −1 to +4. The +1 oxidation state accounts for 50% of the silicon. This is in agreement with the structure proposed by Weiss. However, there is also 23% Si^0, 15% Si^{2+} to Si^{4+}, and 12% Si^{1-}. Hirabayashi *et al.* (*5*) suggest that siloxene has the crystalline structure found by Weiss, but there are also a number of imperfections and dangling chains that could account for the other silicon oxidation states. If so, the differences between the yellow-green siloxene from Weiss' synthesis and the gray siloxene from Kautsky's synthesis may simply be due to the number of imperfections in the crystalline structure. This is supported by the reported Si/O ratios in siloxene samples made by the two different meth-

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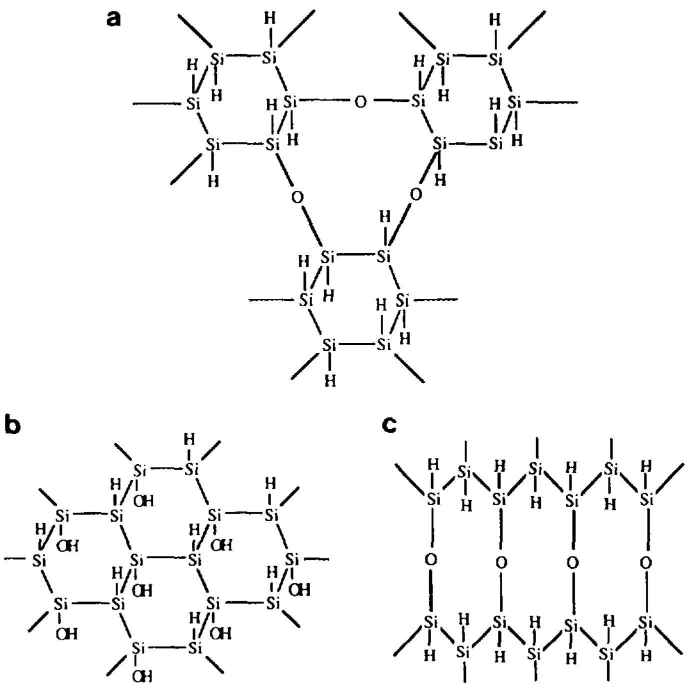

FIG. 1. Siloxene structures proposed by (a) Kautsky *et al.* (*2*), (b) Weiss *et al.* (*3*), and (c) Wiberg (*2*).

ods. Wurzbach (*4*) found Si/O = 1.4 when Kautsky's synthesis was used, while Weiss reported Si/O ratios close to the theoretical value of 2 in siloxene freshly prepared by his method (*3*).

The structure of siloxene gives it some unique and interesting properties. The layers are held together loosely, allowing it to expand and adsorb hydrophobic liquids and gases (*3*). The low silicon oxidation states also make it a good reducing agent. It gives off hydrogen when it reacts with water, and it is reported to reduce Cu^{2+} and Ag^{+} to metallic copper or silver (*3*). It was this reducing ability of siloxene that first led us to try it as a support for Ziegler ethylene polymerization catalysts.

A wide range of supports have been used with Ziegler catalysts, including inert supports such as $MgCl_2$ (*6–9*) and hydroxyl-containing supports such as silica, alumina, Mg(OH)Cl, aluminosilicates, titania, and poly(vinyl alcohol) (*10–14*). By dispersing the titanium centers in an inert support or chemically anchoring them on a hydroxyl-containing support, mutual interactions of the titanium centers are decreased causing a higher percentage of the titanium to be potentially active. This increases the overall catalyst activity (*7*).

Like many of the supports currently used, siloxene has hydroxyl groups that can be used to covalently bind the titanium centers. But the reducing ability of siloxene makes it different from other supports. In most supported catalysts, the Ti is reduced by a metal alkyl after it is put on the support, and the choice of reducing agent can have a significant effect on the properties of the catalyst (*15*, *16*). Since siloxene can serve as both the support and the reducing agent, it may form a new catalyst with properties different from those of other Ziegler catalysts.

The pore structure of siloxene is also different from other commonly used supports. Porous supports must be able to fracture when the pores fill with polymer. Otherwise, the pores will become plugged, cutting off ethylene diffusion to the active sites and killing the reaction (*12*). The loosely held layer structure of siloxene may fracture more easily than other supports, such as silica or alumina, influencing the activity of the catalyst.

EXPERIMENTAL

Materials

All solvents were purged with nitrogen to remove oxygen. Heptane, isobutane, ethylene, acetonitrile, and nitrogen were dried over activated alumina. Calcium chloride was dried at 300°C under nitrogen. A stock solution of $TiCl_4$ in heptane contained 0.02 g Ti/ml. A stock solution of *n*-butylmagnesium in heptane contained 3.5 wt% Mg. Aluminum alkyl solutions in heptane were generally around 15 wt%.

Procedures

The siloxene was prepared under a nitrogen atmosphere by adding 13 g of calcium silicide (Alfa, tech grade) from a powder addition funnel to a stirred mixture of 52 ml of concentrated hydrochloric acid, 250 ml of deionized water, and 1500 ml of isopropanol. Hydrogen evolution was observed, and if the addition was made too rapidly, the temperature was increased. This mixture was stirred at room temperature for 24 hr. At this time, hydrogen evolution had ceased and the slurry had turned from a dark gray to a green-gray color. The reaction mixture was filtered under nitrogen, and the recovered solid was washed with 6 × 200 ml of isopropanol and 6 × 150 ml of anhydrous ethyl ether. It was then dried by passing nitrogen through it, giving 10.08 g (theoretical = 10.03 g) of a gray solid.

In a typical catalyst preparation, siloxene (1 g) and calcium chloride were mixed under nitrogen. Dry acetonitrile (20 ml) was added and the mixture was stirred for 20 min to dissolve the calcium chloride. The acetonitrile was then evaporated, and the siloxene/$CaCl_2$ was dried to a powder at 80–100°C. It was then slurried in 40 ml of dry heptane, and a solution of $TiCl_4$ in heptane was added to give the desired amount of Ti. Upon addition of $TiCl_4$, the slurry immediately turned from gray to brown, and HCl was evolved. This mixture was stirred for 30 min. Then 0.02–0.3 g metal alkyl/g siloxene was added at room temperature. Metal alkyls that were used are triethylaluminum (TEA), *n*-butylmagnesium (*n*-Bu_2Mg), methyl aluminoxane (MAO), and diethylaluminum chloride (DEAC). The reaction mixture immediately turned a darker brown upon addition of the metal alkyl. The solvent was evaporated over a hot water bath, leaving the catalyst as a brown, pyrophoric solid. Catalysts with the highest activity contained 0.06 g $CaCl_2$/g siloxene, 0.10 g Ti/g siloxene, and 0.115 g TEA/g siloxene or 0.29 g *n*-Bu_2Mg/g siloxene.

Polymerizations in the 2.6-liter reactor were performed by a general procedure in which the reactor was first purged with nitrogen at 100°C to remove all moisture and air. The catalyst (0.03–0.08 g) was then charged under an isobutane purge and 1.2 liters of isobutane was added. The reactor was brought up to the reaction temperature, and the desired amount of hydrogen was added. Ethylene was fed to the reactor until the pressure reached 450–500 psig. Then 10–170 ppm (based on isobutane) of TEA or DEAC cocatalyst was added, and ethylene addition was continued until the reactor pressure reached 550 psig. Ethylene was fed to the reactor throughout the polymerization to keep the pressure constant. A typical run lasted 30 min.

In the 1-gal. reactor, the TEA (0.5 ml of 15 wt%) and catalyst (0.03–0.14 g) were charged to the reactor under an isobutane purge. Then 2 liters of isobutane was added, and the reactor was heated to the reaction temperature. The hydrogen was added from a 2.2-liter charge vessel, and 15 g of 1-hexene was pressured into the reactor with ethylene. The ethylene valve was left open for the remainder of the reaction, with the pressure regulator set to keep the total reactor pressure at the chosen value. Reaction time was 1 hr.

Titanium, calcium, and sodium were analyzed by X-ray fluorescence using a Siemens SRS-200 X-ray spectrometer. A weighed sample was exposed to air overnight before being fused in potassium pyrosulfate for analysis. The measured values were corrected using the weight of the sample before and after air exposure.

Analysis of chlorine could not be done by the above procedure because chlorine was lost upon exposure to air. Therefore, a Philips 1480 X-ray spectrometer, equipped with a complex calibration technique covering the 60 most common elements, was used to perform a semiquantitative analysis (+15%) directly on the unfused catalyst powder. The sample was weighed and placed in the sample holder under nitrogen. It was quickly transferred from the glove box to the instrument to prevent air from entering the sample holder.

Particle size analyses were performed on a Microtrac FRA particle size analyzer.

RESULTS AND DISCUSSION

Siloxene

Early results in this work indicated that the siloxene prepared by Kautsky's method gave slightly higher activities than when it was prepared by Weiss' method. So all of the siloxene discussed in this paper was prepared by reacting calcium silicide with a mixture of hydrochloric acid, water, and isopropanol. After washing with isopropanol and ethyl ether, a gray, pyrophoric solid was recovered.

The particle size distribution of the siloxene was broad, ranging from 1 to 700 μm in diameter. However, more than 70% of the particles were between 1 and 20 μm, and the mean particle diameter was 8 μm. The surface area and pore volume were 406 m^2/g and 0.335 cm^3/g by nitrogen adsorption. The pore size distribution is shown in Fig. 2.

The low pore volume of siloxene makes it different from most supports used with Ziegler catalysts. As discussed above, a support must be friable enough to be broken apart by the pressure exerted by the growing polyethylene (PE) chains. With supports such as silica or alumina, a pore volume of 0.335 cm^3/g would not be high enough to produce an active catalyst *(12)*. But since siloxene is made of layers that easily expand, it is possible to make an active catalyst even at this low pore volume.

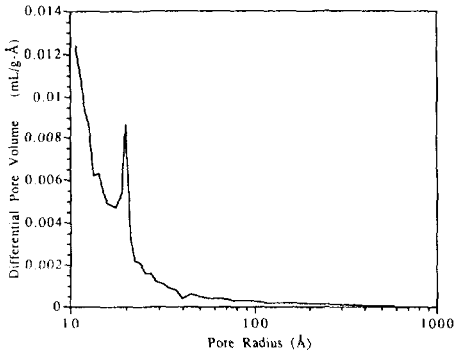

FIG. 2. Nitrogen pore size distribution of siloxene.

Reaction of Siloxene and Titanium Tetrachloride

When the siloxene was slurried in heptane and reacted with $TiCl_4$, it immediately turned brown and HCl was evolved. This suggests that the Ti(IV) was reduced to Ti(III). However, when enough $TiCl_4$ was added to give 7.5% total Ti and the excess $TiCl_4$ was washed away, 5.2% Ti and 8.0% Cl were found by X-ray fluorescence. This corresponds to a Cl/Ti molar ratio of 2.1. The catalyst also contained 0.72% Ca and 0.51% Na. Assuming that these are in the form of the chloride salts, formed as byproducts in the siloxene synthesis, an average of only 1.7 chlorines are directly bonded to each titanium. This low Cl/Ti ratio could be due to a number of things:

1. The chlorine analysis is semiquantitative and may be off to a certain extent. However, this method normally gives results

within 15% of the actual value, and these values are 30–45% lower than expected.

2. Since the sample holder must be punctured and then quickly placed in the instrument, the sample may have picked up some air, resulting in a loss of HCl and the low Cl content.

3. Siloxene may reduce Ti below the 3 + state.

4. $TiCl_n$ may become covalently bonded to the surface rather than simply adsorbed.

Polymerization Results in the 2.6-liter Reactor

When the catalyst with the excess $TiCl_4$ removed was used for ethylene homopolymerization, it gave <100 g PE/g catalyst in a 30-min reaction. To form a high activity catalyst, the excess $TiCl_4$ was not removed, but TEA was added to precipitate it as $TiCl_3$. This increased the productivity to 2200 g PE/g catalyst in 30 min. Apparently, the catalyst activity is due to reduction and precipitation of the excess $TiCl_4$ onto the siloxene/$TiCl_4$ reaction product, rather than to the direct reaction of $TiCl_4$ with siloxene. Therefore, essentially all of the activity comes from only 30% of the titanium. This is possibly because the $TiCl_4$ that reacts directly with siloxene is overreduced as indicated by the X-ray fluorescence analysis described above.

If reaction of the $TiCl_4$ with siloxene does not produce an active catalyst, a question remains of whether the siloxene has any effect on the catalyst. To answer this, a siloxene-containing catalyst was compared to an unsupported catalyst, formed by simply reacting $TiCl_4$ and TEA, and to a silica-supported catalyst that was prepared by the same method as the siloxene catalyst except Davison 952 silica, calcined at 600°C, was used as the support. The siloxene-containing catalyst had higher activity (29000 g PE/g Ti in a 30-min reaction) than the unsupported catalyst (16900 g PE/g Ti) or the silica-supported catalyst (7800 g PE/g Ti). The presence of siloxene also changed the rate profile of the polymerization reaction. The siloxene-containing catalyst started off very fast and then the activity dropped rapidly over the first 30 min of the reaction (Fig. 3). After this, the activity leveled off, but the rate was so low that in a 1-hr period, virtually all the polymer present was formed during the first 30 min of reaction. With the unsupported catalyst, the reaction rate increased over the first 20 min of the reaction and then began to decrease. The silica-supported and unsupported catalysts if a longer of reaction, but it increased throughout the reaction. So its activity would have been more competitive with the siloxene-supported and unsupported ctalysts if a longer reaction time had been used. The obvious differences in these three catalysts show that the use of siloxene as a support has an effect on the catalyst properties.

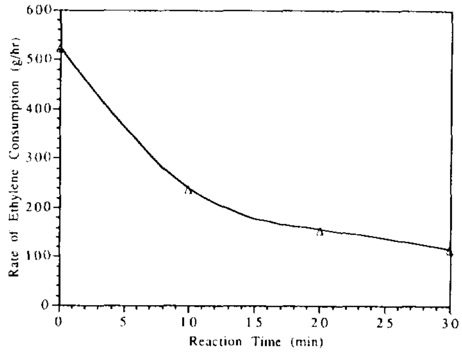

FIG. 3. Rate profile of a siloxene-supported catalyst.

$TiCl_4$ seems to be required to give significant activity. When titanium ethoxide ($Ti(OEt)_4$) was added to siloxene, no color change from gray to brown was observed. The resulting catalyst polymerized ethylene when the Al/Ti ratio in the reactor was approximately 3, but it had only 20% of the activity observed when $TiCl_4$ was used. Even when it was treated with TEA and then washed with a $TiCl_4$ solution in heptane, a procedure commonly used to increase activity, only a trace of polymer was formed. In both cases, the amount of ethylene consumed was equal to the amount of polymer formed, indicating that no ethylene dimerization was occurring (*17*). These results suggest that even though the reaction between siloxene and $TiCl_4$ does not produce an active catalyst, it may be necessary to chemically change the siloxene surface and make it a good catalyst support.

Methyl aluminoxane, diethylaluminum chloride, and *n*-butylmagnesium were also used to reduce the excess $TiCl_4$ during catalyst preparation. MAO and DEAC gave lower activity than TEA. But a significant increase in activity was observed when *n*-Bu_2Mg was used (6771 g PE/g catalyst in 30 min compared to 1814 g/g with TEA pretreatment). Addition of *n*-Bu_2Mg to the siloxene before reacting it with $TiCl_4$ resulted in an additional 50% increase in activity. This increase in activity upon addition of *n*-Bu_2Mg is well known and has been attributed to an increase in the number of active sites and to stabilization of the titanium centers from deactivation processes (*7*, *15*, *16*).

On the TEA-pretreated catalyst, the maximum activity was obtained when 40–50 ppm of TEA was added to the reactor (Fig. 4). DEAC can also be used as a cocatalyst, but it gives slightly lower activity than TEA.

During our initial experiments with ethylene polymerization, the results were not reproducible. We found a correlation between the amount of residual $CaCl_2$ in the siloxene and the activity. By increasing the number of washes used during the siloxene preparation to remove excess $CaCl_2$, the activity became consistent from batch to batch. But as shown in Fig. 5, 0.06 g $CaCl_2$/g siloxene must be put back into the siloxene to achieve the maximum activity. The role of the $CaCl_2$ is possibly either to increase the interlayer distance of the siloxene or to react with the siloxene surface in some way. Other salts will need to be studied to determine its exact role.

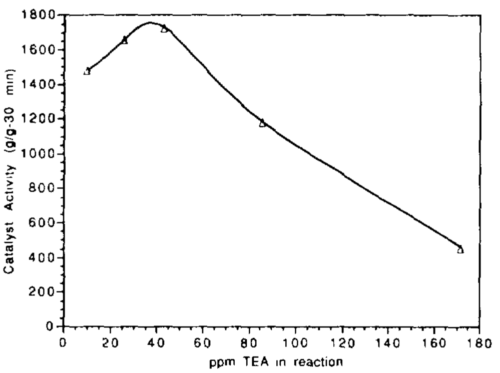

FIG. 4. Effect of TEA cocatalyst on catalyst activity. The catalyst contained 0.1 g Ti/g siloxene, 0.06 g calcium chloride/g siloxene, and 0.023 g TEA/g siloxene. Polymerizations were run at 95°C with 50 psi hydrogen on the reactor.

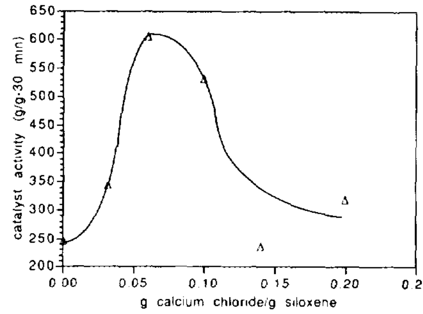

FIG. 5. Effect of calcium chloride on catalyst activity. All catalysts contained 0.1 g Ti/g siloxene and 0.115 g TEA/g siloxene. Polymerizations were run at 95°C with 50 psi hydrogen and 170 ppm of TEA.

Polymerization Results in the 1-gal Reactor

Some more detailed experiments were also performed in a 1-gal. autoclave. The reaction conditions were chosen so that the reactor temperature could be varied while holding the concentrations in solution relatively constant (Table 1). However, the calculated ethylene and hydrogen concentrations may be off by as much as 15 and 30%, respectively. Therefore, care must be taken in analyzing this data. For example, the variations in MI with each catalyst may be caused by the actual hydrogen concentrations being slightly different from the calculated values.

The TEA-pretreated catalyst had very low activity under these conditions. With

TABLE 1

Results from Polymerizations in 1-gal Reactor[a]

Metal alkyl[b]	Reaction temp. (°C)	Hydrogen (psi)	Ethylene (psi)	Activity (g/g-hr)	MI (g/10 min)	HLMI (g/10 min)	Density[c] (g/ml)	Bulk density (lb/ft^3)	Ti[d] (ppm)	Cl[e] (ppm)
n-Bu$_2$Mg	60	115	58	780	0.99	44.4	0.9594	7.3	82	170
n-Bu$_2$Mg	70	70	63	906	1.25	51.7	0.9597	7.5	70	155
n-Bu$_2$Mg	80	45	67	1357	0.66	25.2	0.9562	8.2	51	125
n-Bu$_2$Mg	90	28	70	1330	0.76	26.8	0.9548	9.9	53	95
n-Bu$_2$Mg	100	16	72	1137	0.42	13.2	0.9518	11.1	63	145
TEA	60	115	58	130	0.23	15.0	0.9621	4.4	433	800
TEA	80	45	67	159	0.07	4.6	0.9546	4.6	405	455
TEA	90	28	70	31	—	—	—	—	—	—

[a] Reaction conditions were adjusted so that the calculated concentrations in solution remained essentially the same for each run at [H$_2$] is 0.04 *M* and [C$_2$H$_4$] is 0.4 *M*. Only the reaction temperature was varied.

[b] Metal alkyl used for catalyst pretreatment.

[c] Each reaction contained 15 g of 1-hexene comonomer.

[d] Amount of titanium in the polyethylene produced.

[e] Amount of chlorine in the polyethylene produced.

the n-Bu$_2$Mg pretreated catalyst, a maximum activity of 1360 g/g catalyst-hr or 19600 g/g Ti-hr was observed at 80°C. The lower activities in the 1-gal. reactor, as compared to the 2.6-liter reactor, are mostly due to a large reduction in the ethylene concentration. However, we also found during reactions in the 2.6-liter reactor that 5 wt% 1-hexene, based on isobutane, causes up to a 25% reduction in the catalyst activity. So the presence of 1-hexene in these reactions may also be decreasing the catalyst activity.

As normally observed with Ziegler catalysts, the polyethylene molecular weight decreases when hydrogen is added to the reactor. This is shown in Table 2 by the increase in HLMI as the hydrogen pressure is increased. The n-Bu$_2$Mg-pretreated catalysts produce polyethylene with slightly lower molecular weight than that produced by

TABLE 2

Hydrogen Response of Siloxene-Supported Catalysts

H$_2$ (psi)	HLMI (TEA pretreatment)[a]	HLMI (n-Bu$_2$Mg pretreatment)[b]
0	0	—
50	0.4	4.4
100	1.4	81.3

[a] The catalyst contained 0.1 g Ti/g siloxene, 0.065 g CaCl$_2$/g siloxene, and 0.115 g TEA/g siloxene. Polymerizations were run in the 2.6-liter reactor at 80°C with 40 ppm of TEA.

[b] The catalyst contained 0.1 g Ti/g siloxene, 0.07 g CaCl$_2$/g siloxene, 0.06 g n-Bu$_2$Mg/g siloxene, and 0.115 g TEA/g siloxene. Polymerizations were run in the 2.6-liter reactor at 95°C with 170 ppm of TEA.

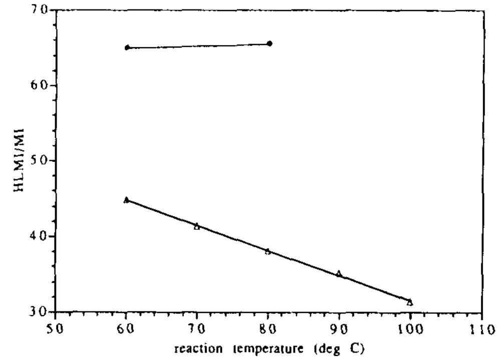

FIG. 6. Effect of reaction temperature on polymer shear response (HLMI/MI). (●) TEA pretreated catalyst; (△) n-butylmagnesium pretreated catalyst.

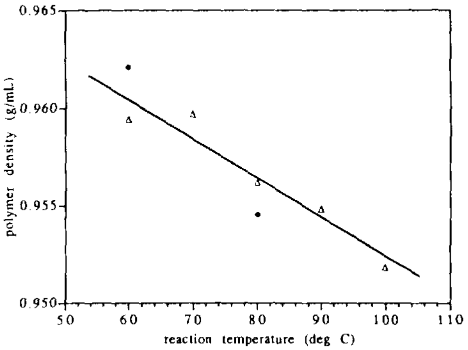

FIG. 7. Effect of reaction temperature on hexene comonomer incorporation. (●) TEA pretreated catalyst; (△) *n*-butylmagnesium pretreated catalyst.

TEA-pretreated catalysts (Table 1), due to enhanced chain transfer processes (*7*).

When the catalyst is *n*-Bu_2Mg pretreated, the shear response (HLMI/MI) appears to decrease as the reaction temperature is increased (Fig. 6). This dependence of shear response on reactor temperature is not normally seen, and it implies that the molecular weight distribution is narrowing as the reaction temperature increases. Each active site in a catalyst can be slightly different from other active sites, depending on the ligands attached to it, whether it is covalently bonded to the support, etc. It is this dispersity of active sites that normally controls the molecular weight distribution. Therefore the decrease in shear response suggests that the range of active sites is becoming less disperse at high reaction temperatures. This could be due to some sites losing activity at high reaction temperatures. But if this is the cause, shear response should be dependent on catalyst activity, which does not appear to be the case. Therefore, there must be some other change occurring in the distribution of active sites at high reaction temperatures. With the TEA-pretreated catalyst, the shear response is broader, as expected (*7*), and appears to be independent of reaction temperature.

Under these conditions, the hexene comonomer incorporation is similar to that observed with other Ziegler catalysts. There is almost no hexene incorporation at 60°C. As the reaction temperature is increased, hexene incorporation increases slightly, until the polymer density decreases to 0.952 g/cm^2 at 100°C (Fig. 7).

CONCLUSIONS

The use of siloxene as a support has a definite effect on the catalyst properties. However, from these results we cannot say what exact role the siloxene is playing. More needs to be known about how the siloxene is affected by $TiCl_4$, *n*-Bu_2Mg, and $CaCl_2$.

There are two points in the synthesis where changes may give further increases in the activity: (1) The amount and type of metal alkyl used for pretreatment needs to be studied more closely and (2) salts other than $CaCl_2$ should be added. The $CaCl_2$ has a major influence on the activity, but we have not looked at any other salts to see if they might increase the activity even more.

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