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Toshimitsu Suzuki[a]; Shun-Ichi Izuka[a]; Shigeki Kondo[a]; Yoshinobu Takegami[a]
[a] Department of Hydrocarbon Chemistry, Faculty of Engineering Kyoto University, Kyoto, Japan

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Polymerization of Olefins by a Ziegler Catalyst Supported on Poly(ethylene-co-Vinyl Alcohol)

TOSHIMITSU SUZUKI, SHUN-ICHI IZUKA, SHIGEKI KONDO, and
YOSHINOBU TAKEGAMI

Department of Hydrocarbon Chemistry
Faculty of Engineering
Kyoto University
Kyoto, 606, Japan

ABSTRACT

The polymerization and catalytic behavior of a Ziegler type catalyst supported on poly(ethylene-co-vinyl alcohol) (EVA) were investigated. The rate of ethylene polymerization by a catalyst prepared from titanium tetrachloride supported on EVA (vinyl alcohol 18 mole %) and triethylaluminum ($AlEt_3$) is much higher than that of an n-butoxytitanium trichloride (BTT)–$AlEt_3$ catalyst. The polymer-supported catalyst has prolonged high activity during polymerization compared with the BTT–$AlEt_3$ catalyst. The stabilization of the catalyst seems to depend on its slower reduction by alkylaluminum compounds, due to steric hindrance by bulky polymer ligands. Polypropylene prepared by the polymer supported Ziegler catalyst is essentially atactic, and it differs little from that prepared with a BTT–$AlEt_3$ catalyst. Vinyl chloride was also polymerized by this catalyst. The catalytic activity was, however, very small.

INTRODUCTION

Recently several investigations on supported Ziegler-type catalysts on metal oxide surfaces have been reported [1, 2]. Some such catalysts showed higher activity and prolonged catalyst life compared with conventional Ziegler catalysts. Ballard [3, 4] reported catalysts consisting of transition metal alkyls, such as tetrabenzylzirconium, supported on alumina or silica. In these catalysts, hydroxy groups on metal oxide surfaces react with transition metal alkyls to give several types of metal–O–transition metal bonds, depending on the reaction conditions. These types of catalysts are called colloidal catalysts, and they show remarkably high activity for ethylene polymerization compared with soluble transition metal alkyls [3, 4].

The number of active centers contained in conventional Ziegler type catalysts is reported to be of the order of a few percent of the transition metal component [5-8].

In view of this, we thought it of interest to support transition metals uniformly. We have developed a Ziegler type catalyst supported on an organic functional polymer. As a polymer support, a commercially available ethylene–vinyl alcohol copolymer (EVA) was employed, and titanium tetrachloride was reacted with the polymer. This yielded a polymer-supported titanium chloride catalyst which was further treated with alkylaluminum compounds. Ethylene, propylene, and vinyl chloride were employed as monomers.

Catalysts, based on titanium or vanadium supported on organic polymers are described in a patent issued by Solvay and Co. [9]. In the patent, highly active catalysts for ethylene polymerization were reported to be prepared by reacting titanium tetrachloride or vanadium chloride with an ethylene–vinyl alcohol copolymer or vinyl chloride–vinyl alcohol copolymer. However, to our knowledge at present, the catalytic behavior of this type of catalyst was not reported precisely. To compare with the effect of the polymer-supported catalyst, catalysts derived from n-butoxytitanium trichloride and di-n-butoxytitanium dichloride were also investigated.

EXPERIMENTAL

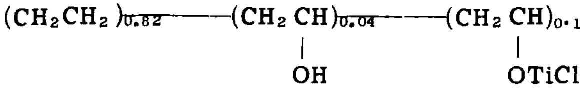
Saponification of Ethylene–Vinyl Acetate Copolymers

A 3-g sample of a commercial ethylene–vinyl acetate copolymer (VAc 18 mole % or 10 mole %) was dissolved in 40 ml of toluene at 60° C. To this solution, 10 ml of a solution of sodium methoxide in toluene, which was freshly prepared from sodium metal and methanol, was added. After stirring 2 hr at 60° C, a small portion of the reaction mixture was analyzed by infrared spectroscopy to confirm 100% hydrolysis. The reaction mixture was poured into a large amount of methanol. The ethylene–vinyl alcohol copolymer separated as a fine precipitate and was neutralized with acetic acid. The copolymer was washed with methanol, filtered off, and dried under vacuum at 40° C. The yield of the copolymer was 2.3 g (94%).

Preparation of Polymer-Supported Transition Metal

A three-necked flask equipped with a reflux condenser, self-sealing rubber cap, and a gas inlet connected to an argon line, was flushed with argon. A 0.6 g sample of the copolymer was suspended in 30 ml of dry n-heptane and freshly distilled titanium tetrachloride (0.89 ml, 7.9 mmole) was added to the suspension. Under a gentle stream of argon, the reaction mixture was stirred for 1 hr at room temperature. The reaction mixture was heated to 50-60° C for 12 hr (or refluxed at the boiling point of n-heptane). The suspension of the reaction mixture was filtered off under an argon atomosphere and washed with dry n-heptane. Polymer-supported titanium, thus obtained, was dried in vacuo and stored in glass ampoules under argon.

Elemental analyses showed C, 45.59%; H, 7.64%, Ti, 15.93%. Provided that each hydroxy group in the copolymer reacts with one molecule of titanium tetrachloride, this compound has the structure I, where the calculation was based



$$(CH_2CH_2)_{0.82}\text{---}\underset{\displaystyle OH}{\underset{|}{(CH_2CH)_{0.04}}}\text{---}\underset{\displaystyle OTiCl_3}{\underset{|}{(CH_2CH)_{0.14}}}$$

I

Reaction of vanadium tetrachloride with EVA was carried out in a similar manner. Elemental analyses (C, 28.1%; H, 7.20%; and V, 21.4%) indicate that the vanadium content of this compound is higher than that expected from the assumption considered in the case of titanium tetrachloride. An attempt to react vanadyl chloride with EVA was unsuccessful. In this case, a suspension of EVA in an aliphatic hydrocarbon changes to a homogeneous solution after addition of vanadyl chloride. n-Butoxytitanium trichloride (BTT) and di-n-butoxytitanium dichloride (DBT) were synthesized by the methods reported in the literature [10].

Polymerization Procedure

A 200-ml three-necked flask was fitted with a magnetic stirrer and connected to lines for argon, vacuum, and to a gas buret of ethylene. The flask was flushed with argon, catalyst was introduced, and the flask was evacuated. To this flask, 30 ml of n-heptane was added, and ethylene was introduced. A certain amount of alkylaluminum was introduced, after the gas buret reading became constant. The rate of polymerization was followed by the reading of the gas buret. Polymerization was stopped by the addition of 2-propanol containing small amount of hydrochloric acid. Polymer was precipitated in a large amount of 2-propanol washed with methanol, and dried in vacuo.

The other monomers were polymerized in a 100-ml pressure bottle.

Infrared spectra were recorded on a Hitachi model 215 spectrometer. 200 MHz NMR spectra were measured on a Varian HR 220 instrument. Approximately 4-6 % (w/v) polymer solutions in o-dichlorobenzene were employed with tetramethylsilane as an internal reference at 120°C.

RESULTS AND DISCUSSION

Polymerization of Ethylene

The results of polymerization of ethylene with the use of polymer-supported catalysts and BTT catalyst are compared in Table 1. In general, the rate of polymerization by the polymer-supported Ziegler catalyst is at least five to ten times that of BTT catalyst at the initial stage of polymerization. Polymerization rate was expressed as milliliters of ethylene absorbed per milligram-atom of titanium per minute. At late stages of the polymerization (after a reaction time of about 60 min), the differences in the activity between the two types of catalysts reach fifty to one (compare No. 4 and No. 9).

As shown in Fig. 1, the catalytic activity of the BTT–$AlEt_3$ system decreases with increasing reaction time, while the rate behavior of the polymer-supported Ziegler catalyst has two distinct features. At the initial stage, the rate of polymerization increases gradually and reaches a steady state. An increase in the rate of polymerization during the initial stage is often observed in the course of polymerizations of propylene with titanium trichloride–alkylaluminum catalysts [5]. The rate behavior of the BTT–$AlEt_2Cl$ system is different from that with both of the catalysts and polymerization proceeds at an

TABLE 1. Polymerization of Ethylene With Polymer-Supported and Butoxytitanium Chloride Ziegler Catalysts

Run	Ti (mg atom)	Al/Ti	Temp (°C)	Time (hr)	Activity (ml ethylene absorbed/min-mg atom Ti)[b]		Yield (g)
					Initial	60 min	
1[c,d]	0.28	2.2	30	3.0	43.8	9.0	1.28
2[c,d]	0.35	2.0	40	4.0	42.9	9.8	1.06
3[d,e]	0.62	2.0	40	3.5	8.5		0.41
4[d,f]	0.24	2.0	40	1.33	30.4	124.6	2.16
5[f,g]	0.22	2.0	40	0.90	58.0	158.5	2.10
6[f,g]	0.29	2.0	40	0.80	80.9	107.1	2.08
7[g,h]	0.94	1.0	40	1.50	26.5	19.1	1.95
8[d,h]	1.05	1.0	40	1.00	37.8	9.7	1.11
9[d,i]	2.30	2.0	40	1.00	7.2	3.0	0.92
10[g,i]	0.72	2.0	40	1.10	36.8	48.8	2.86
11[d,j]	3.01	2.0	40	4.00	1.3	0.6	0.24

[a] Solvent, n-heptane, 40 ml; ethylene partial pressure, 660 Torr.

[b] Initial: calculated from absorption of ethylene at first 5 min; 60 min: calculated from absorption of ethylene at 55-60 min.

[c] Catalyst was prepared in refluxing heptane.

[d] $AlEt_3$ as cocatalyst.

[e] Catalyst prepared from 10 mole % vinyl alcohol copolymer.

[f] Catalyst was prepared at 50-60°C.

[g] $AlEt_2Cl$ as cocatalyst No. 5-7, and No. 10.

[h] VCl_4 was reacted with EVA (18 mole % vinyl alcohol).

[i] BTT as catalyst.

[j] BTD as catalyst.

almost constant rate. Polymer-supported vanadium tetrachloride combined with $AlEt_3$ or $AlEt_2Cl$ also showed catalyst deactivation at the initial stage of polymerization.

Activation of catalyst during polymerization is attributed to the development of fresh surfaces of the transition metal compound by

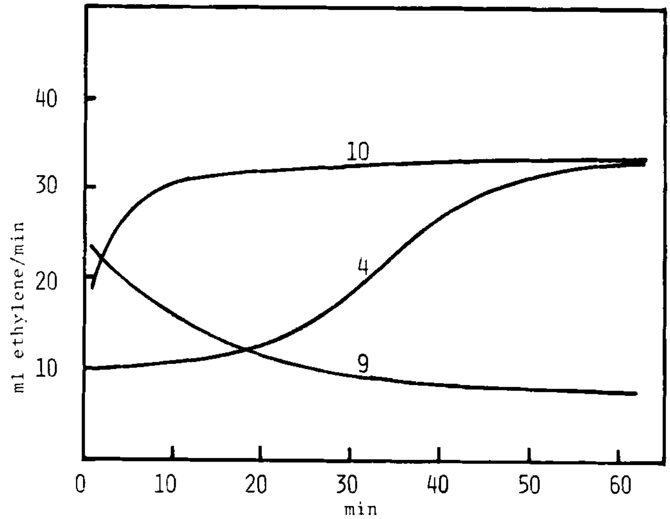


FIG. 1. Rate of ethylene absorption vs. polymerization time. Numerals indicate experimental number in Table 1.

mechanical cracking of titanium trichloride [5-8]. In this polymer-supported catalyst, the transition metal not exposed on the surface of the polymer support will gradually be activated by alkylaluminum due to slower diffusion of alkylaluminum into the polymer particles. A steady-state rate of polymerization may be attained due to slower reduction of titanium which has bulky polymer ligand. Most of the titanium moiety bound to EVA samples used in this study, are separated by at least two ethylene units. This may produce a good dispersion of titanium along the polymer chain. The aggregation of active centers will be interrupted by the bulky polymer chain. In this manner, the higher activity and stability of polymer-supported catalyst may be explained.

Vanadium–alkyl bonds are considered to be less stable compared with titanium–alkyl bonds [11]. Therefore the catalytic activity of vanadium tetrachloride supported on EVA decreases during polymerization.

The reducing ability of $AlEt_2Cl$ is smaller than that of $AlEt_3$. Accordingly, the catalytic activity of BTT-$AlEt_2Cl$ catalyst is constant throughout polymerization.

When DBT is used with $AlEt_3$, the rate of polymerization was smaller than that of the BTT–$AlEt_3$ system. In addition, the yield of solid polymer is considerably smaller than that calculated from ethylene absorption. Formation of 1-butene was confirmed by gas-chromatographic analysis.

Polyethylene formed by the polymer-supported Ziegler catalyst, is somewhat different from that obtained by the BTT–$AlEt_3$ catalyst or by conventional catalyst systems. The polymer did not melt, even at 200°C, and was not extracted completely by boiling xylene (residue 60-30%). This indicates that polyethylene prepared in this system is grafted to EVA in some manner to give crosslinked polymers. The mechanism of this process is not known at present. However, if we obtain a large amount of polyethylene compared with supported catalyst (in this experiment polyethylene/EVA = 20), the physical properties of the polyethylene obtained are similar to those of a conventional Ziegler polymer.

Polymerization of Propylene

The results are summarized in Table 2. The catalytic activity of the polymer-supported Ziegler catalyst was not remarkably different from the BTT catalyst. The rate of polymerization of propylene at atmospheric pressure is very small.

Polypropylene obtained by using the supported catalyst is apparently

TABLE 2. Polymerization of Propylene[a]

Run	Ti (mg atom)	AlR_3	Al/Ti	Yield (g/g Ti)
1	0.59	$AlEt_3$	2.0	100.0
2	0.97		1.5	97.0
3	0.78		5.0	42.0
4	0.15	$AlEt_2Cl$	4.0	43.0
5[b]	2.60	$AlEt_3$	2.0	11.2
6[b]	1.00	$AlEt_2Cl$	2.0	47.0

[a] At 40°C, 5 hr, 10 ml propylene at -78°C, 30 ml n-heptane.
[b] With BTT as cocatalyst.

TABLE 3. Extraction and Tacticity of Polypropylene[a]

		Dyads		Triads		
Fraction	Wt %	m	r	mm	2mr	rr
Ether-soluble	53.1	0.45	0.55	0.27	0.33	0.40
n-Heptane-soluble	18.9	0.70	0.30	0.64	0.13	0.23
Xylene-soluble	11.9	0.87	0.13	0.85	0.04	0.11
Xylene-insoluble	6.1	Insoluble				

[a] Run 1 in Table 2; dyads measured at 220 MHz and triads measured at 100 MHz.

TABLE 4. Polymerization of Vinyl Chloride[a]

					Dyads		Triads		
Run	Catalyst	Ti (mg atom)	Al/Ti	PVC yield (g/g Ti)	m	r	mm	2mr	rr
1	BTD	5.60	1.5	2.3	0.46	0.54	0.17	0.48	0.35
2	BTT	2.40	2.0	0.1	–	–	–	–	–
3	Polym. Ti	0.23	1.0	4.4	–	–	–	–	–
4	Polym. Ti	0.34	2.0	12.0	0.40	0.60	0.16	0.53	0.32
5	Polym. Ti	0.34	5.0	1.4	–	–	–	–	–

[a] At -78°C; 30 ml n-heptane, 5 ml vinyl chloride; $AlEt_2Cl$, 40°C, 5.0 hr.

different from that obtained by a $TiCl_3$–$AlEt_3$ catalyst. To elucidate the steric structure of the polymer, it was extracted by several solvents. Most of the polymer was extracted by boiling diethyl ether and n-heptane.

Dyad and triad stereosequence distributions were estimated by a 100 MHz and 220 MHz NMR spectroscopy. The most characteristic feature of this polymer is that the heterotactic triad content in all fractions is smaller than the syndiotactic triad content (Table 3). This clearly indicates that it is a stereoblock polymer.

The effect of the polymer support was not remarkable for either catalytic activity or stereosequence distribution. This may be attributed to the fact that the alkoxytitanium chloride–alkyl aluminum catalyst is not a good catalyst for propylene polymerization.

Polymerization of Vinyl Chloride

Some Ziegler type catalysts are reported to be active for vinyl chloride polymerization [12]. Yamazaki, et al. [13, 14] reported that the Lewis acid character of titanium compounds plays an important role for the catalytic activity of Ziegler type catalysts in vinyl chloride polymerizations. Catalysts derived from BTT combined with various alkylaluminum compounds are reported to be inactive for vinyl chloride polymerization [13, 14]. As reported by Yamazaki [13, 14], tetravalent titanium species are active species for vinyl chloride. In such modified Ziegler catalysts BTT is easily reduced to trivalent species to give inactive catalysts. However, titanium trichloride moieties bound to EVA will be reduced slowly by alkylaluminum, to give active species for polymerization of vinyl chloride. The catalytic activity changes with the molar ratio of titanium to $AlEt_2Cl$ and becomes maximum at a molar ratio of two (Table 4). Such a characteristic of this catalyst may well be described by a typical coordinated polymerization mechanism. However, as pointed out by the investigation of vinyl chloride polymerization by $Ti(O\text{-}n\text{-}Bu)_4$–$Al_2Et_3Cl_3$ system [15], polymerization of vinyl chloride proceeds by a free-radical mechanism in the presence of transition metal catalyst. The NMR study of poly(vinyl chloride) obtained in this system indicates that its stereosequence distribution is essentially the same as that of a conventional polymer. Dyad and triad relations follow Bernouillian statistics. From these results it is difficult to comment on the mechanism of polymerization.

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