

CHEMISTRY

Chairman: KENNETH E. COOK, Anderson College
ROBERT E. DAVIS, Purdue University, was elected chairman for 1966

Metal-Metal Halide Reaction Products as Low Pressure Olefin Polymerization Catalysts

T. J. MIRANDA, The O'Brien Corporation, South Bend, Indiana
G. F. D'ALELIO, University of Notre Dame, Notre Dame, Indiana

Introduction

The polymerization of olefins, particularly ethylene, propylene, and isoprene was shown to yield variations in polymer structure depending upon the composition of the Ziegler catalyst (6). Of particular interest was the fact that polyethylene could be prepared from catalysts having cationic character although prepared from organo metals.

The results obtained previously indicate that pseudo-cationic systems containing no organo-metal may be useful catalysts for polymerizing ethylene and that solid polyethylene might be obtained instead of the usual oils.

In the experiments reported in the previous paper (6), organo-metals were present in the polymerization system. This was demonstrated by separating the solid phase of the Ziegler catalyst from the liquid which contained the soluble organo-metals. Neither component has catalytic activity, but when recombined performed normally.

To evaluate the possibility that pseudo-cationic systems could initiate olefin polymerization, a number of metal-metal halide reaction products were evaluated. Typical metals are sodium, magnesium, aluminum, titanium, iron, nickel, and cobalt. Typical metal halides are titanium tetrachloride, titanium trichloride, titanium dichloride, and zirconium tetrachloride.

Experimental Preparation of Catalysts

Method A

The metal and the metal halide were placed into a small flask fitted with a reflux condenser and a nitrogen inlet. The liquid phase usually consisted of the metal halide although, in some cases, inert solvents were also employed as a liquid medium. After refluxing for twelve to sixty hours, the catalyst was transferred to the polymerization vessel and pressured with ethylene to 500-1000 psi at temperatures ranging from room temperature to 200°. In some cases, the excess metal halide was removed by distillation or extracted by hydrocarbons.

Method B

To eliminate the difficulties encountered in washing, a furnace was constructed as shown in Figure 1.

A nitrogen stream swept $TiCl_4$ vapor over hot metals while subliming out volatile halides.

Method C

To demonstrate the ease of preparation of the new catalyst systems used in the course of this research, and to utilize the advantages resulting from decreased particle size and increased surface area, ball-milling was used as effective method for the preparation of catalysts directly from the metal and metal halide.

Method D

This method consisted in preparing the catalyst *in situ* by introducing the metal-metal halide and solvent into the polymerization vessel directly and allowing the catalyst reaction to occur in the vessel, followed by polymerization in the same unit.

Method E

In this method, catalysts were prepared by disproportionation. The metal halide can be rendered active either by heating or by grinding in a ballmill.

Polymerization

Ethylene

Titanium Dichloride (Method D). Titanium dichloride, 1.0 grams, in 50 ml of redistilled dry n-heptane was charged to a stainless steel bomb and pressured with ethylene at 500 psi at 150° for 12 hours. Upon cooling and venting, a trace of white powder whose infrared spectrum was that of low molecular weight polyethylene was obtained.

Method E

When 7.45 grams of titanium dichloride was ballmilled in xylene and the polymerization carried out under the same conditions, the bomb became plugged with solid polyethylene. During grinding, TiCl_2 disproportionates to titanium and titanium tetrachloride (1).

Titanium Trichloride (Method D). The attempted polymerization of ethylene using the same conditions for TiCl_2 , yielded no polymer.

Titanium Mono-Oxide (Method D). When titanium mono-oxide was used under the conditions described for TiCl_2 , only a trace of polyethylene was obtained.

Titanium Mono-Oxide and Sodium (Method D). A catalyst prepared by reacting sodium (1 ml of a 50% dispersion) and 6.8 grams of titanium mono-oxide under the same conditions, yielded only a trace of polyethylene.

Titanium Metal (Method D). No solid polymer was obtained when 25 grams of titanium metal was used alone under the conditions described for TiCl_2 although, a trace of low melting wax was obtained by evaporating toluene which was used as a dispersing medium.

Titanium and Titanium Tetrachloride (Method A). Titanium, 8.65 grams (180 mgatom) was refluxed with 10 ml (91.1 mmoles) of titanium tetrachloride for 12 hours. The reaction product was washed several times with dry toluene and the toluene distilled off. The washed reaction

product in 80 ml of freshly distilled dry toluene was charged to the bomb pressured to 850 psi with ethylene and heated to 175°C for 20 hours. The yield of solid polyethylene was 100.95 grams.

Titanium and Titanium Tetrachloride (Method E). To compare the reactivity of the previous catalyst as related to method of preparation, 8.65 grams (180 mgatom) of titanium and 10 ml (91.1 mmoles) of titanium tetrachloride were ballmilled for 60 hours and charged to a bomb containing 80 ml of redistilled dry toluene. Ethylene was pressured to 500 psi and the bomb heated to 125°C for 18 hours. As a result, 14.4 grams of solid polyethylene was obtained.

Titanium and Titanium Tetrachloride (Method B). Titanium (10 grams) was heated to 450°C in a furnace (Figure 1) while passing a nitrogen stream containing TiCl_4 vapor through the metal for five hours. Upon cooling, the reaction product was charged to the bomb containing 80 ml dry redistilled toluene, pressured to 500 psi with ethylene and heated to 125°C for 16 hours. Upon cooling, 50 grams of solid polyethylene was obtained.

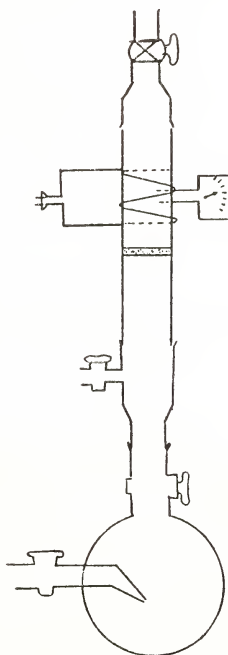


Figure 1

Titanium and Titanium Tetrachloride (Method B). The previous experiment was repeated except that no solvent was used for the polymerization. Upon opening the bomb, polyethylene was observed which had grown directly from the gas phase onto the catalyst surface. Upon extraction with boiling xylene, 2.1 grams of polyethylene was obtained (3).

Aluminum and Titanium Tetrachloride (Method A). Aluminum (10 grams) and 10 ml of titanium tetrachloride was refluxed for 12 hours in chlorobenzene at 111°C. Ethylene was then passed through the mixture at 0.5 liters/minute for 5 hours at atmospheric pressure. From this reaction, 8.0 grams of solid polyethylene was obtained.

Aluminum and Titanium Trichloride (Method C). Aluminum metal, 0.5 grams, and 2.0 grams of titanium trichloride were ballmilled for 8 days. The dry pyrophoric catalyst, 0.5 grams, was transferred to the bomb in a dry box sealed, pressured with ethylene at 500 psi and heated to 100° for 19 hours. On cooling, 0.2 grams of solid polyethylene was obtained which had grown directly on the catalyst surface.

Other examples are given in Table I through Table IX.

Propylene

Aluminum and Titanium Tetrachloride (Method B). Ten grams of aluminum metal were heated for 5 hours in a furnace (Figure 1) while passing a nitrogen stream containing TiCl_4 vapor over the metal. The reaction product was then cooled and transferred to the bomb containing 80 ml redistilled dry n-heptane. Propylene was pressured to 140 psi and the bomb heated to 75° for 48 hours. As a result, 10.5 grams of solid polypropylene was obtained.

Titanium and Titanium Tetrachloride (Method D). Titanium, 8.65 grams and 10 ml of titanium tetrachloride reaction product were charged to the bomb containing 80 ml redistilled dry heptane. The bomb was heated to 60° and pressured with propylene at 100 psi and the reaction carried out for 36 hours; 13.4 grams of solid polypropylene was obtained.

Several other examples are given in Table VIII.

Isoprene

A number of representative metal-metal halide reaction products were evaluated as catalysts for the polymerization of isoprene and the data is summarized in Table IX. In this case, only resinous cationic-type polyisoprene were obtained.

Discussion

Metal of Group I did not yield active catalyst when reacted with the metal halides shown in Table I. The reaction of sodium and titanium tetrachloride proceeds rapidly forming a black solid mixed with sodium chloride. This catalyst was inactive but when ground in a ballmill, became active by disproportionation. This has been recently repeated by Machida who prepared the catalyst by Method C (4) and by Matlack and Breslow (5).

Catalysts prepared from Group II metals and the titanium halides did not yield solid polymers. Washing excess titanium halide from the solid catalyst did not enhance catalyst activity.

Of the Group III metals, the catalyst derived from boron and TiCl_4 was inactive under the experimental conditions tried, while all the catalysts prepared from aluminum and titanium and zirconium halides

were active except potassium hexachlorotitanate. Aluminum-aluminum chloride reaction product was subsequently shown to be active when ballmilled (2).

Unlike aluminum, titanium reacted with potassium hexachlorotitanate (Table IV) to produce an active catalyst. The titanium-titanium halide systems are of the same order of activity of the aluminum-titanium halide system. Of particular interest is the catalyst produced by the vapor phase reaction of titanium and butyl chloride.

Catalysts produced from elements of Group V and VI were not very active under the conditions studied, while those from the elements of Group VII, particularly when chlorinated, produced high yields of polymer.

In Group VIII iron, cobalt, and nickel reduced titanium and zirconium halides to active catalyst; iron being the poorest reducing metal for titanium tetrachloride.

Conclusion

The results obtained in these studies clearly indicate that organo metals are not required to prepare active olefin polymerization catalysts. The catalysts described in this paper may be prepared by several methods and from readily available chemicals.

That the nature of the catalyst is cationic in character was shown by the products obtained from propylene and isoprene. Polypropylene and polyisoprene were similar to those obtained with Ziegler catalysts when the catalyst component ratio was high in Lewis Acid.

Titanium was more effective than aluminum in preparing an active catalyst from K_2TiCl_6 . At atmospheric pressure, aluminum produced a more active catalyst with $TiCl_4$ than did titanium.

The presence of excess metal halide reduces the yield of solid polymer. This was demonstrated by extracting with hydrocarbon or subliming excess metal halides during catalyst preparation. When this operation was performed, higher yield of polymers were obtained.

Literature Cited

1. D'ALELIO, G. F., and H. J. WHITE, JR. 1958. Unpublished results.
2. D'ALELIO, G. F., and T. J. MIRANDA. 1959. Unpublished results.
3. D'ALELIO, G. F., and T. J. MIRANDA. 1965. *J. Polymer Sci.* **A3**:3675.
4. MACHIDA, K. K., TAKAHASHI, and H. Ikegami. 1964. Brit. Patent 967,073. Cited in *C. A.* **63**:3071 (1965).
5. MATLACK, A. S., and D. S. BRESLOW. 1965. *J. Polymer Sci.* **A3**:2853.
6. MIRANDA, T. J., and G. F. D'ALELIO. 1965. Variations of polymer structure with catalyst composition in Ziegler type polymerizations. *Proc. Ind. Acad. Sci.* **75**:81.

TABLE I
Ethylene Polymerization Catalysts Prepared Using Group I Elements

Catalyst Components	Method of Preparation	Solvent	Polymerization Conditions	Product Obtained
Na + TiCl ₄	A	Toluene	60°; 12 hrs.	Trace of polymer
Na + TiCl ₄	A	Chlorobenzene	80°; 6 hrs.	None
Cs + VCl ₃	D	Toluene	125°; 500 psi 12 hours	None

TABLE II
Ethylene Polymerization Catalysts Prepared Using Group II Elements

Catalyst Components	Method of Preparation	Solvent	Polymerization Conditions	Product Obtained
Mg + TiCl ₄	D	Toluene	125° 1 atm; 18 hrs.	Oil
Mg + TiCl ₄	C	Toluene	125° 500 psi; 20 hrs.	None
Zn + TiCl ₄	A	Toluene	60° 1 atm; 24 hrs.	Oil
Zn + TiCl ₄	C	Toluene	100° 500 psi; 18 hrs.	Oil
Zn + TiCl ₄	B	Xylene	175° 500 psi; 26 hrs.	Viscous oil
Zn + TiCl ₃	C	Xylene	100° 500 psi; 72 hrs.	Oil
Zn + TiCl ₄ + AlCl ₃	A	Toluene	60° 1 atm; 18 hrs.	Oil and wax
Hg + TiCl ₄	C	Toluene	125° 500 psi; 24 hrs.	Oil
Hg + TiCl ₃	A	Toluene	125° 500 psi; 6 hrs.	Viscous oil

TABLE III
Ethylene Polymerization Catalysts Prepared Using Group II Elements

Catalyst Components	Method of Preparation	Solvent	Polymerization Conditions	Product Obtained
B + TiCl ₄	A	Toluene	111° 1 atm; 12 hrs.	None
Al + TiCl ₄	A	Toluene	111° 1 atm; 7 hrs.	Oil
Al + TiCl ₄	A	Chlorobenzene	111° 1 atm; 5 hrs.	8.0 g. solid
Al + TiCl ₄	B	Toluene	125° 850 psi; 16 hrs.	71.6 g. solid
Al + TiCl ₄	C	None*	125° 1000 psi; 72 hrs.	1.2 g. solid
Al + TiCl ₃	C	Toluene	125° 500 psi; 18 hrs.	54.8 g. solid
Al + TiCl ₃	C	Toluene	100° 500 psi; 18 hrs.	49.7 g. solid
Al + AlCl ₃	C	Toluene	50° 1 atm; 3 hrs.	None
Al + Ti + AlCl ₃	C	Toluene	100° 500 psi; 4 hrs.	14.0 g. solid
Al + AlCl ₃ + TiCl ₄	C	Toluene	100° 500 psi; 4 hrs.	94.7 g. solid
Al + ZrCl ₄	C	Toluene	100° 500 psi; 12 hrs.	4.6 g. solid
Al + K ₂ TiCl ₆	C	Heptane	100° 500 psi; 12 hrs.	None
Al + TiCl ₃ **	C	Toluene	175° 1100 psi; 16 hrs.	20.0 g. solid

* This catalyst was placed into the dry bomb and the monomer was polymerized directly on the surface from the gas phase.

** TiCl₃ was obtained from the reaction of Na and TiCl₄ in chlorobenzene. This experiment proves that sodium does reduce TiCl₄ to TiCl₃ and probably explains the reason for the inactivity of the Na-TiCl₄ system.

The catalysts prepared using aluminum and titanium halides by ball-milling were the most active and the easiest to prepare. The formation of bimetal complexes may be responsible for the high activity of the catalysts.

TABLE IV

Ethylene Polymerization Catalysts Prepared Using Group IV Elements

Catalyst Components	Method of Preparation	Solvent	Polymerization Conditions	Product Obtained
Ti + TiCl ₄	C	Toluene	125° 500 psi; 18 hrs.	14.4 g. solid
Ti + TiCl ₄	B	None*	125° 500 psi; 20 hrs.	2.1 g. solid
Ti + TiCl ₄ + BuCl**	B	Toluene	100° 500 psi; 14 hrs.	20.0 g. solid
Ti + BuCl	B	Toluene	125° 500 psi; 18 hrs.	1.9 g. solid
Ti + SbCl ₅	A	Toluene	111° 1 atm; 6 hrs.	Oil
Ti + SbCl ₅	B	Toluene	150° 250 psi; 12 hrs.	2.1 g. solid
Ti + TiCl ₂	C	Toluene	125° 500 psi; 24 hrs.	None
Ti + TiCl ₃	C	Toluene	125° 500 psi; 96 hrs.	59.3 g. solid
Ti—Al + TiCl ₄ ***	B	Toluene	125° 1000 psi; 12 hrs.	30.0 g. solid
Ti + K ₂ TiCl ₆	B	Xylene	170° 1000 psi; 20 hrs.	1.1 g. solid
Ti + AlCl ₃	B	Toluene	125° 500 psi; 20 hrs.	10.0 g. solid
Ti + AlCl ₃	C	Toluene	125° 500 psi; 18 hrs.	6.7 g. solid
Ti + ZrCl ₄	C	Toluene	130° 500 psi; 19 hrs.	3.5 g. solid

* This catalyst was placed into the dry bomb and the monomer was polymerized directly on the surface from the gas phase.

** One ml. of n-butyl chloride added to the solvent.

*** Ti—Al alloy of the approximate composition 55% Ti and 40-45% Al.

TABLE V

Ethylene Polymerization Catalysts Prepared Using Group V and VI Elements

Catalyst Components	Method of Preparation	Solvent	Polymerization Conditions	Product Obtained
Cr. + TiCl ₄	A	Toluene	145° 600 psi; 16 hrs.	0.1 g. solid
Sb + AlCl ₃	C	Heptane	100° 500 psi; 48 hrs.	Oil

TABLE VI

Ethylene Polymerization Catalysts Prepared Using Group VII Elements

Catalyst Components	Method of Preparation	Solvent	Polymerization Conditions	Product Obtained
Ti + Cl ₂ *	B	Toluene	150° 600 psi; 12 hrs.	90.0 g. solid
Ti + I ₂	C	Toluene	100° 500 psi; 12 hrs.	5.0 g. solid

* Halogenation of the metal was not complete and free metal exists in these catalysts.

TABLE VII
Ethylene Polymerization Catalysts Prepared Using Group VIII Elements

Catalyst Components	Method of Preparation	Solvent	Polymerization Conditions	Product Obtained
Fe + TiCl ₄	A	Toluene	125° 500 psi; 48 hrs.	0.5 g. solid
Fe + TiCl ₄	B	Toluene	100° 1 atm; 3 hrs.	Oils
Fe + TiCl ₄	C	Toluene	125° 850 psi; 18 hrs.	Oils
Fe + TiCl ₂	C	Toluene	125° 500 psi; 24 hrs.	11.0 g. solid
Fe + K ₂ TiCl ₆	B	Toluene	80° 1 atm; 5 hrs.	Oils
Fe + ZrCl ₄	C	Toluene	125° 500 psi; 24 hrs.	Oils
Ni + TiCl ₄	C	Toluene	125° 500 psi; 48 hrs.	20.8 g. solid
Co + TiCl ₄	C	Toluene	125° 500 psi; 48 hrs.	7.8 g. solid

TABLE VIII
Propylene Polymerization Catalysts

Catalyst Components	Method of Preparation	Solvent	Polymerization Conditions	Product Obtained
Na + TiCl ₄	B	Heptane	75° 140 psi; 12 hrs.	Oil
Hg + TiCl ₄	B	Xylene	100° 240 psi; 12 hrs.	Oil
Al + TiCl ₄	D	Toluene	111° 1 atm; 12 hrs.	Oil
Al + TiCl ₄	B	Toluene	115° 160 psi; 24 hrs.	Oil
Al + TiCl ₄	B	Toluene	75° 140 psi; 16 hrs.	Trace solid
Al + TiCl ₄	B	Heptane	75° 140 psi; 48 hrs.	10.5 g. solid
Al + TiCl ₄	C	Heptane	100° 190 psi; 20 hrs.	52.8 g. solid
Al + AlCl ₃ + TiCl ₄	C	Toluene	25° 170 psi; 12 hrs.	0.9 g. solid + oil
Ti + TiCl ₄	D	Toluene	175° 220 psi; 24 hrs.	Oil
Ti + TiCl ₄	B	Heptane	75° 140 psi; 72 hrs.	15.0 g. solid
Ti + TiCl ₄	D	Heptane	60° 100 psi; 36 hrs.	13.4 g. solid

TABLE IX
Isoprene Polymerization Catalysts

Catalyst Components	Method of Preparation	Solvent	Polymerization Conditions	Product Obtained
Al + TiCl ₄	A	Toluene	25°; 5 hrs.	Resin
Ti + TiCl ₄	B	Heptane	60°; 24 hrs.	Resin
Ti + TiCl ₃	C	Toluene	40°; 12 hrs.	Short rubber