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Polymerization of Propylene with Combined Catalysts of Aluminum Chloride, Sodium Hydride and Titanium Trichloride

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1. Introduction

In 1956 Natta, et al set forth a combination of aluminum trialkyl compounds and titanium chlorides as catalysts for the purpose of producing high molecular polymers from lower olefins, such as ethylene and propylene, at low pressures.

In the present study, the reaction between aluminum chloride and sodium hydride and the behavior of the reaction products in the presence of propylene were observed in anticipation of the formation of aluminum propyl compounds, presumably containing some chlorine atoms, in the intermediate stage of the reaction.

Thus, the aim of this study is to confirm the formation of aluminum propyl compounds from aluminum chloride, sodium hydride and propylene in the early stage of the propylene polymerization.

The authors are of the opinion that high molecular propylene polymers are produced by direct interaction of aluminum propyl compounds with titanium trichloride.

2. Experimental

2.1 Preliminary Experiments under Atmospheric Pressure

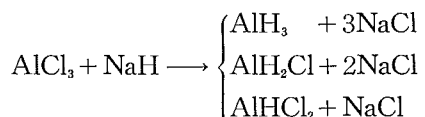
To 250 ml of *n*-heptane contained in a four-necked round bottom flask, 5 gr of sodium hydride and 10 gr of anhydrous aluminum chloride were added under nitrogen atmosphere. Propylene gas was introduced into the flask at a rate of 4 liters per hour under agitation. The temperature of the reaction mixture was gradually raised to 80°C for a certain duration of time. Three hours were required to attain 80°C.

The solid deposit in the reaction products was filtered and examined by the X-ray diffraction method. The X-ray diffraction pattern showed the ex-

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istence of a considerable amount of sodium chloride.

The formation of sodium chloride is considered to suggest the formation of an aluminum alkyl compound in the course of the reaction by the following schema.



2. 2 Experiments under Pressure

1) Experimental Procedure

The pressure experiments were conducted by using an autoclave equipped with a magnetic agitator. The reaction components were charged, together with *n*-heptane used as solvent, into the autoclave under nitrogen atmosphere. The reaction mixture was heated at 80°C for approximately 2 hours to which liquid propylene was added to this mixture. After propylene addition, the temperature of the mixture was elevated to 120°C and maintained at 120°C for several hours.

Some examples of the pressure experiments are shown in the following figure.

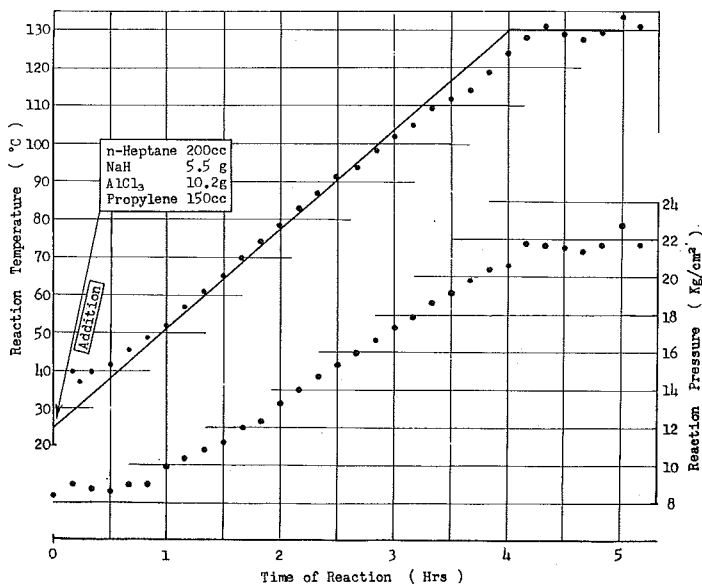


Fig. 1. Procedure of Pressure Experiment (Ex-7)

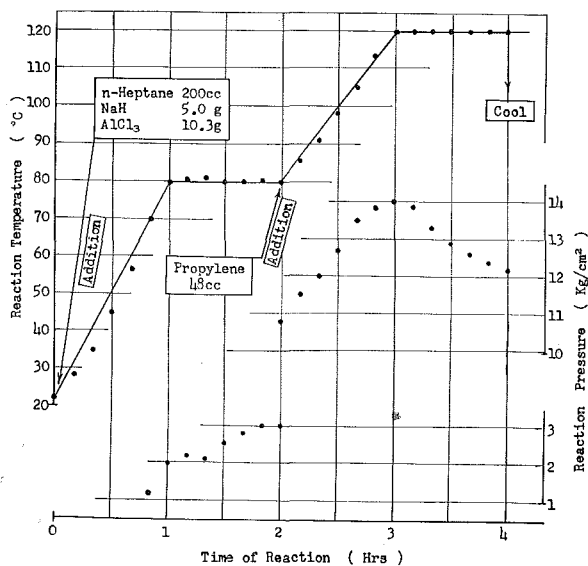


Fig. 2. Procedure of Pressure Experiment (Ex-10)

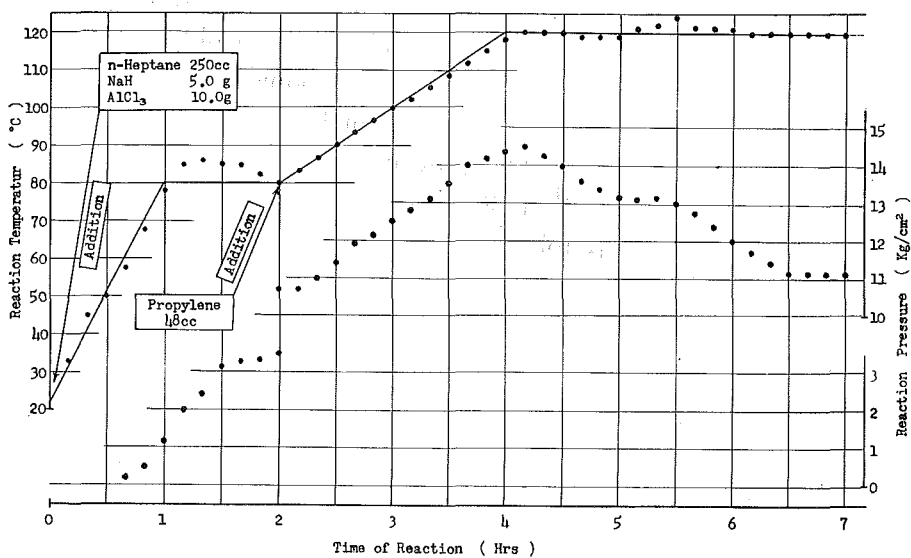


Fig. 3. Procedure of Pressure Experiment (Ex-14)

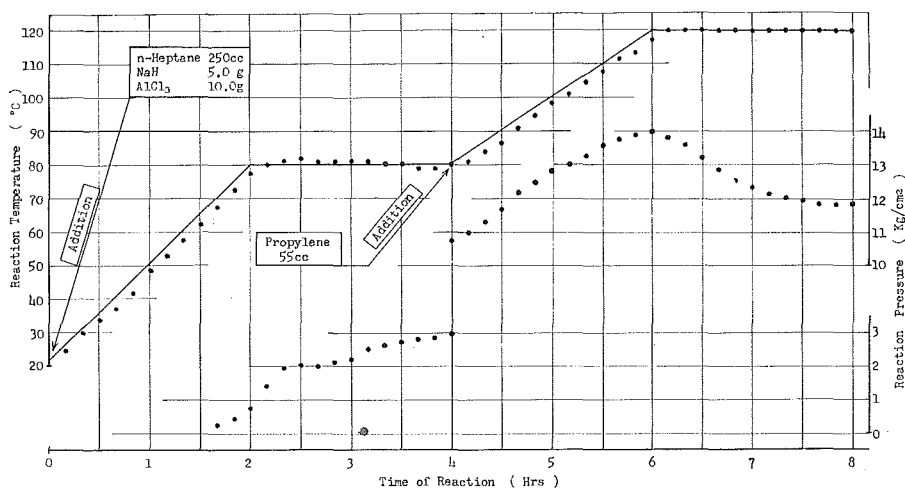


Fig. 4. Procedure of Pressure Experiment (Ex-15)

2) Analysis of the Products

When the reaction was finished, the autoclave was cooled by immersing in cold water. Whereupon, the inner gas was released, measured and analyzed. Of the reaction products, the solid and liquid portion were separated by filtration under nitrogen stream in a dry-box. To the solid portion, octyl alcohol and water were added and the evolved gas was measured and analyzed. The solid residue was finally examined by means of X-ray diffraction method. The liquid portion, in some cases concentrated by driving off a part the solvent *n*-heptane, was also treated with octyl alcohol and water. The gas thus evolved was measured and analyzed. The liquid portion, before and after the alcohol-water addition, was examined under infrared spectrophotometer. All gaseous products were analyzed by means of gas chromatography. For gas analysis, a Shimadzu Model GC-1A gas chromatograph was used. Analytical conditions used were as follows.

- I) For propane and propylene contained gas.
- | | |
|----------------------|---------------------------|
| Column | : Activated alumina 1.5 m |
| Carrier gas | : Hydrogen |
| Carrier gas pressure | : 0.5 kg/cm ² |
| Bridge current | : 175 mA |
| Column temperature | : 120°C |
| Flow rate | : 30 ml/min |

Under these conditions, retention time observed were as follows: nitrogen: 0.8 min, propane: 2.8 min, propylene: 4.1 min, respectively.

II) For hydrogen contained gas

| | |
|----------------------|----------------------------|
| Column | : Molecular sieve 5A 1.5 m |
| Carrier gas | : Nitrogen |
| Carrier gas pressure | : 0.5 kg/cm ² |
| Bridge current | : 145 mA |
| Column temperature | : 25°C |
| Flow rate | : 50 ml/min |

Under these conditions, retention time of hydrogen was 3 min.

The IR spectra of the liquid products were obtained with a Hitachi Model EPI-2 infrared spectrophotometer. The wave number range 4000-400 cm⁻¹ was scanned with NaCl and KBr prisms.

X-ray diffractions of the solid product were obtained with a Rigakudenki Model D-3F X-ray diffractometer. (Target: Cu, Filter: Ni)

3) Experimental Results

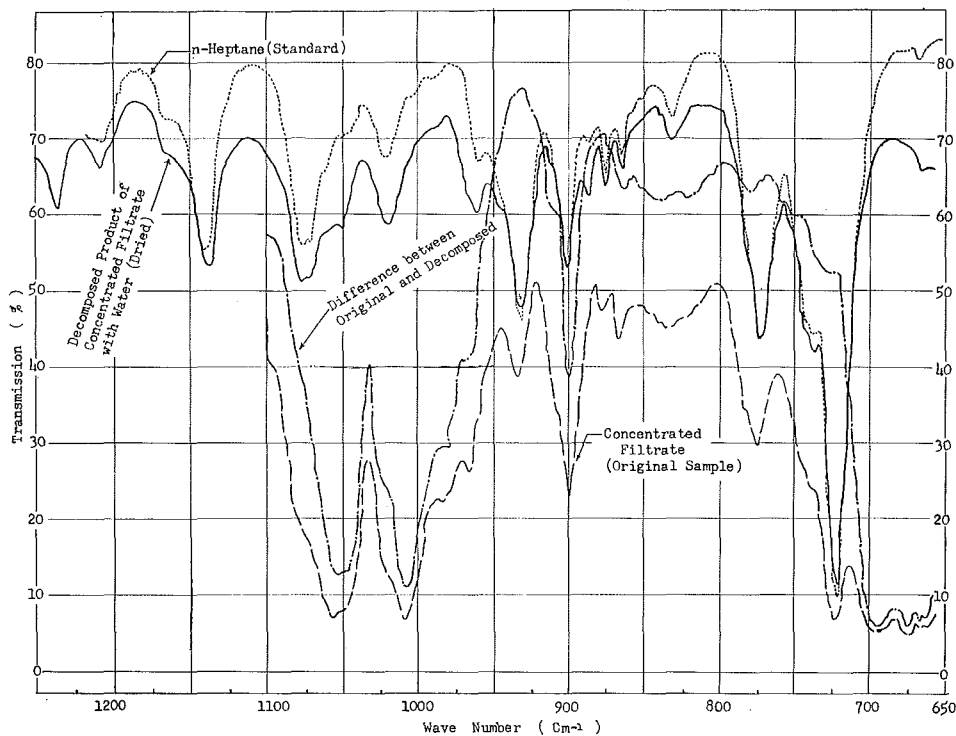


Fig. 5. Infrared Absorption Spectra of the Liquid Portion of the Reaction Product of Ex-10

The gas evolved by alcohol and water addition.

In both the liquid portion and the solid portion of the reaction product, gas evolution was observed, when alcohol and water were added. The evolved gas mainly consisted of hydrogen, nitrogen, propane and propylene. The gas evolution was more remarkable in the solid portion treatment than in the liquid portion treatment. Hydrogen and propane in the evolved gas were considered to be formed by the decomposition of some of the reaction products. The amount of propane evolved in each experiment was ca. 0.6~0.9 liters according to the reaction conditions. The solid residue after alcohol and water addition was a grayish white powder. As a result of scrutinization by means of X-ray diffraction method, it was shown that a large amount of sodium chloride and a small amount of aluminum hydroxide was present.

The infrared absorption spectra of the liquid portion (concentrated) of the reaction products of Ex-10 before and after the alcohol and water addition are shown in the following figure together with that of normal heptane.

3. Discussion of the Results

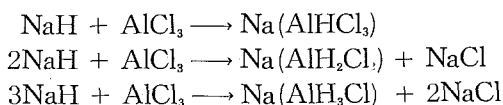
As shown in Fig. 5 in the infrared absorption spectrum of the liquid portion (containing solvent *n*-heptane) of the Ex-10 reaction products, high intensity absorption bands were observed at 1055 cm^{-1} , 1010 cm^{-1} , 720 cm^{-1} , 695 cm^{-1} and 675 cm^{-1} , whereas all these characteristic absorption bands vanished in the spectrum of the liquid products treated with alcohol and water. And the spectrum of the latter was very similar to that of *n*-heptane. Hence, the absorption bands at 1055 cm^{-1} , 1010 cm^{-1} , 720 cm^{-1} , 695 cm^{-1} and 675 cm^{-1} are characteristic of the products which are relatively unstable and are decomposed by alcohol and water to produce propane.

According to Groenwege's spectroscopic study on $\text{Al}_2(\text{CH}_3)_2\text{Cl}_4$ and $\text{Al}_2(\text{CH}_3)_4\text{Cl}_2$, (Groenwege et al., Z. Phys. Chem., **18**, 147 (1958)) the absorption bands at 694 cm^{-1} and 720 cm^{-1} are characteristics of Al-C bond. The authors considered that the absorption bands at 720 cm^{-1} , 695 cm^{-1} and 675 cm^{-1} in the spectrum of the Ex-10 reaction products are characteristic of the Al-C bond. In other words, the reaction products contained aluminum propyl compounds. The absorption bands at 1055 cm^{-1} and 1010 cm^{-1} may be related to other organo-aluminum compounds, such as $\text{Al}(\text{OR})_3$. On the other hand when alcohol and water were added to the heptane-insoluble reaction products, vigorous propane evolution was also observed.

This fact suggested the existence of some aluminum propyl compounds which are difficult to dissolve in *n*-heptane.

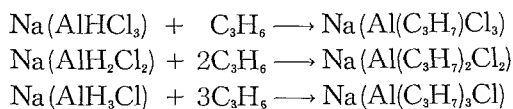
Based on the above-mentioned experimental results, the authors propose the following mechanism for the reaction between aluminum chloride and sodium hydride.

First, aluminum chloride reacts with sodium hydride stepwisely as follows :



The temperature range of 50~80°C favors these reactions. Thus, propylene is introduced and the temperature of the reaction mixture is gradually raised to 120°C and maintained at 120°C for several hours.

Under these conditions, the following reactions occur .



These three complex products are difficult to dissolve in *n*-heptane and are unstable over 130°C.

A part of the complex products decomposes by cooling as follows

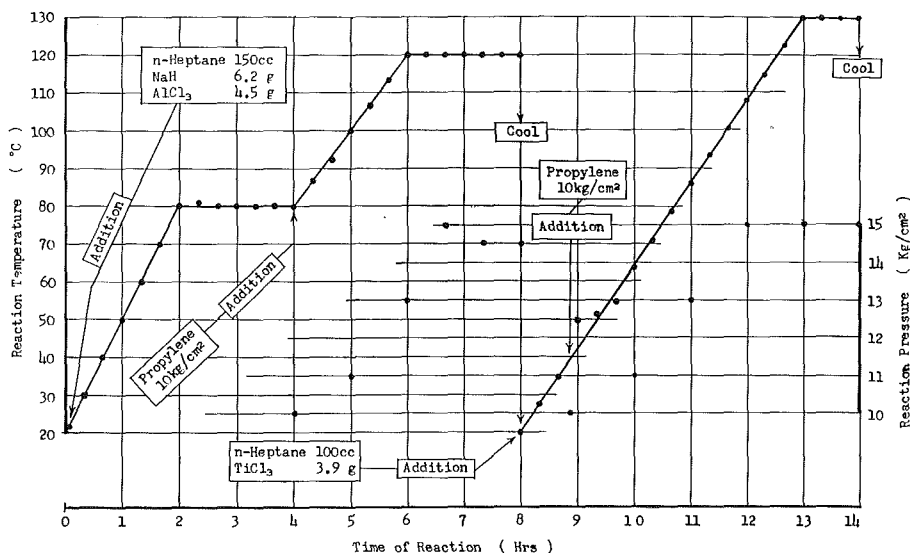
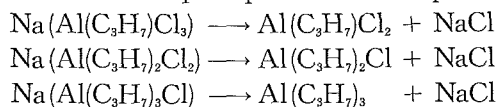


Fig. 6. Experimental Procedure of Pressure Polymerization of Propylene in the presence of NaH-AlCl₃-TiCl₃ Catalyst

Aluminum tripropyl and aluminum propyl chlorides are soluble in *n*-heptane. Hence, the propane-splitting substances, when decomposed with alcohol and water, in the *n*-heptane solution of the reaction products are $\text{Al}(\text{C}_3\text{H}_7)\text{Cl}_2$, $\text{Al}(\text{C}_3\text{H}_7)_2\text{Cl}$ and $\text{Al}(\text{C}_3\text{H}_7)_3$ and those in the solid products are $\text{Na}(\text{Al}(\text{C}_3\text{H}_7)\text{Cl}_3)$, $\text{Na}(\text{Al}(\text{C}_3\text{H}_7)_2\text{Cl}_2)$ and $\text{Na}(\text{Al}(\text{C}_3\text{H}_7)_3\text{Cl})$.

The authors are of the opinion that these aluminum alkyl compounds are the most important intermediates in the propylene polymerization in the course of producing high molecular polypropylene.

From this standpoint, the authors conducted a polymerization experiment under the conditions as shown in Fig. 6.

As clearly observed in Fig. 6, the experiment was conducted in two stages. In the first stage, the reaction conditions were so controlled as to favor the aluminum propyl compounds formation from aluminum chloride, sodium hydride and propylene. In the second stage, additional propylene and titanium trichloride were added to the first stage reaction products and the whole reaction mixture was gradually heated to 130°C.

In course of the heating, polymerization of propylene proceeded remarkably and the motion of the magnetic agitator of the reaction vessel stopped owing to the enormous formation of solid polymer, when the reaction temperature approached the vicinity of 130°C.

Although the exact yield of the solid polymer could not be calculated owing to the incomplete reaction, it might be said that solid polypropylene was produced in very good yield.