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| Author(s) | TANABE, Kozo; WATANABE, Yoshihisa |
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ACIDITY AND ACID STRENGTH OF TITANIUM TRICHLORIDE AND OF TITANIUM TRICHLORIDE-TRIETHYL ALUMINUM

By

Kozo TANABE and Yoshihisa WATANABE*

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Abstract

Surface acidity and acid strength of titanium trichloride and of titanium trichloride-triethyl aluminum were measured by a modification of the method used by WALLING, TAMELE, JOHNSON or BENESI. It has been found that the acid sites having different acid strengths exist on the surface of titanium trichloride and its total acidity is anomalously large compared to those of silica-alumina and nickel sulfate *etc.* There have been also found remarkable changes of the acidity and acid strength on heat-treatment in vacuum. Titanium trichloride in the presence of triethyl aluminum has also shown a great acidity at the acid strength equal to or lower than $H_0 = +3.3$, which is about the same as that of titanium trichloride alone at the same acid strength. It is pointed out that the observed acidic property of titanium trichloride correlates with its catalytic activity for the propylene polymerization to low polymer and that the acceleration of the polymerization of propylene to high polymer by the addition of traces of organic basic compounds might be interpreted as being due to the change of the acidic property of the titanium trichloride-triethyl aluminum catalyst.

Introduction

Titanium trichloride-triethyl aluminum is well-known as the NATTA-ZIEGLER catalyst for the polymerization of propylene. From the fact that the solid surfaces of various metal chlorides show strong acidic property¹⁾, it is anticipated that the catalyst or titanium trichloride will also show acidic property on the surface. We, therefore, attempted to measure the acidity together with the acid strength.

A number of methods for determining acidity and acid strength of solid surfaces have been reported recently²⁾. Among those, the most suitable one for the present study seems to be the method developed by TAMELE³⁾, JOHNSON⁴⁾ and BENESI⁵⁾, which involves the titration of solid acid in benzene with an organic base, using suitable indicators^{6,7)} to determine the end-point, because

*) K. T.; The Research Institute for Catalysis, Hokkaido University, Sapporo, Y. W.; Mizonokuchi Research Laboratory, Mitsubishi Petrochemical Company Ltd., Kawasaki.

titanium trichloride is suspended in non-polar solvent under the reaction conditions of propylene polymerization. Since it is difficult, however, in the case of titanium trichloride, strongly colored with violet, to observe the color changes of the indicators on the solid surface, the above method requires a modification. We employed a method involving titration of colored solid mixed with white one of known acidity, which was suggested once before by JOHNSON⁴⁾.

Experimental

Materials and Reagents :—Four kinds of titanium trichlorides used are all Stauffer Chemical's products; *i. e.*, AR, HR, ARA and HRA. The AR is the titanium trichloride which is said to have been reduced by aluminum metal and the HR is the one reduced by hydrogen. The ARA or HRA is the activated AR or HR respectively. Triethyl aluminum of specific gravity 0.835 was supplied from the Mitsubishi Petrochemical Co. as *n*-heptane solutions. This was used by diluting with dry benzene. Silica-alumina used as a standard white solid acid was prepared by the method described by HARA *et al.*⁸⁾ and dried at 500°C. The indicators used in the present study are as follows: an extra pure reagent grade methyl red, the product of the Kanto Chemical Co., Inc., with $pK_a = +4.8^9)$, a guaranteed reagent grade benzene-azo- α -naphthylamine, the product of the Tokyo Chemical Industry Co., Ltd., with $pK_a = +4.0^7)$, a guaranteed reagent grade *p*-dimethylaminoazobenzene (Kanto Chemical Co.) with $pK_a = +3.3^6)$ and a guaranteed reagent grade benzeneazodiphenylamine (Tokyo Chemical Industry) with $pK_a = +1.5^7)$. The benzene (Kanto Chemical Co., guaranteed reagent) used was further purified by drying over sodium followed by distillation.

Heat-treatment of Titanium Trichloride :—To examine the effect of pre-heating of titanium trichloride on its acidic property, three kinds of heat-treatment have been employed to minimize the effect of moisture or oxygen in atmosphere on the chlorides. 1). The sample was transferred

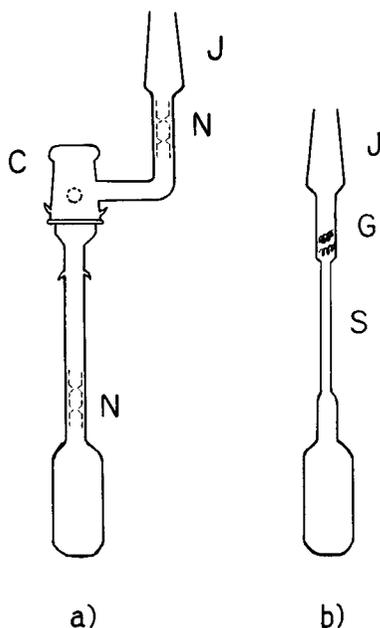


Fig. 1. Sample tubes for heat-treatment.

J; joint, C; stopcock,
N; narrow path, G; glass wool,
S; striction.

to a tube shown in Fig. 1. a) in a dry box through which dry nitrogen is passed. After closing stopcock, the tube was taken out from the dry box, connected to a vacuum line and evacuated to 10^{-5} mmHg. The sample was then heated by an electric furnace for 15 minutes at a desired temperature. After closing the stopcock, the tube was disconnected from the vacuum line and the sample was transferred into a weighing bottle with a ground glass stopper in the dry box. The weighed sample was put into an Erlenmeyer flask with a ground glass stopper which contains dry benzene and the acidity was measured as described in the next section. 2). The sample was heated in vacuum similarly as above by using a tube shown in Fig. 1. b). In this case the tube was disconnected by sealing off the striction from the vacuum line. 3). The method without using dry box is also employed, where the sample suspended in benzene was transferred to the tube of Fig. 1. b) and then heated in vacuum after evaporating benzene. The three methods mentioned above showed no appreciable difference on the result of acidity measurement.

Measurement of Acidity and Acid Strength:—Acidity of titanium trichloride was determined by subtracting the known acidity of silica-alumina from the acidity of a sample of titanium trichloride mixed with a suitable amount of silica-alumina. The acidity of silica-alumina or the sample was measured by titrating each solid suspended in benzene with a benzene solution of *n*-butylamine, using various indicators according to the procedure described originally by Tamele⁹⁾. The endpoint of the titration was determined by the color change of an indicator which can be noted on the white surface of mixed silica-alumina. Since titanium trichloride goes to the bottom of the flask immediately after shaking the mixture, but silica-alumina is floating for a while, the observation of the color change is not difficult. The sharpest color change has been observed for the mixture with the composition of 0.05~0.02 g. titanium trichloride and *ca.* 0.2g. silica-alumina. It becomes difficult to observe the color change with the amount of titanium trichloride beyond 0.15 g., even if that of silica-alumina is increased in the same proportion as mentioned above. Of course, the accuracy falls off if the relative amount of silica-alumina to titanium trichloride is increased.

Acid strength of colored solid can be determined similarly with the aid of white solid acid by using indicators having various pK_a values as reported by WALLING⁹⁾ and BENESI⁷⁾. The principle is the following. If the acidity of titanium trichloride is measured to be zero by use of a certain indicator, the acid strength is higher than the H_0 corresponding to pK_a of the indicator used. If titanium trichloride shows some acidity with a certain indicator, the acid strength is equal to or lower than the H_0 corresponding to pK_a of that

indicator.

Evidence for that the Observed Acidity and Acid Strength are not due to Impurities such as Hydrogen Chloride or Other Volatile Acids:—Since titanium trichloride is quite unstable in the presence of air and reacts rapidly with moisture in the atmosphere to form hydrogen chloride, one may suspect that the observed acidity is due to the presence of hydrogen chloride, although the sample was avoided to expose in air as practically as possible. It is also plausible that the observed acidity may be due to any volatile acid impurities included in the sample. In most cases of the present work, however, indicators dissolved in benzene phase showed the color of their basic form. This indicates that the observed acidity is not due to hydrogen chloride, because hydrogen chloride is soluble in benzene and if it exists, the solvent shows the color of the conjugate acids of indicators. In some experiments, actually solvent showed the color of acidic form of indicator (red when *p*-dimethylamino-azobenzene is used). Since the color, however, disappeared on the addition of one drop of 0.1 *N* *n*-butylamine, the amount corresponds to only 0.003 mmoles of acid which is negligible in the present work.

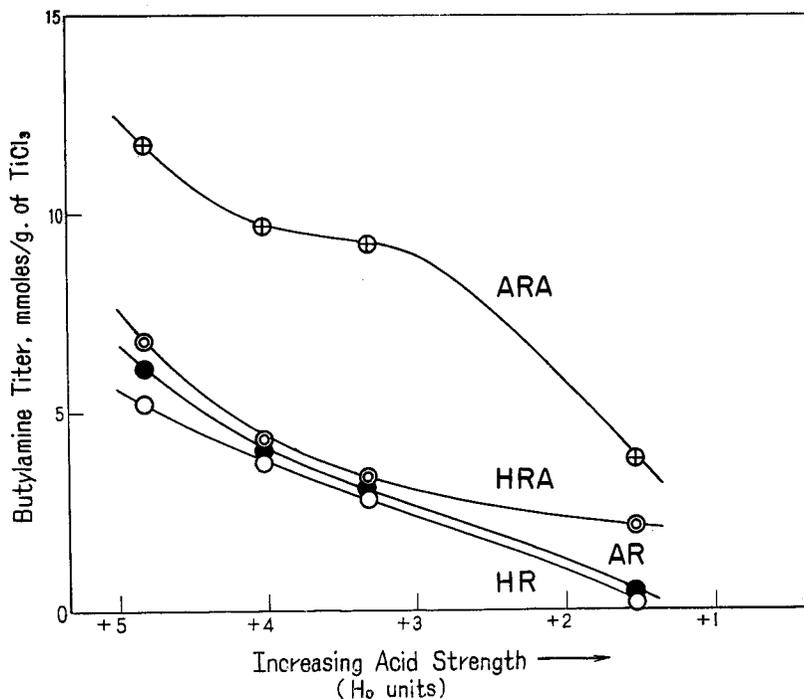


Fig. 2. Butylamine titers vs. acid strength for $TiCl_3$ without heat-treatment.

Another evidence is provided by the fact that the acidity of titanium trichloride is in general increased with increase of temperature of heat-treatment in vacuum as shown in Fig. 5. If the acidity is due to hydrogen chloride or other volatile acidic impurities included in the solid, the acidity must decrease on heating in contradiction to the observed results.

Results

Acidity and Acid Strength of Titanium Trichloride:—The *n*-butylamine titers (acidity by definition) plotted against acid strength in Figs. 2~4 are cumulative; *i.e.*, they are measures of the number of acid sites (in mmoles/g.) having an H_0 equal to or lower than the pK_a value of the indicator used. (It should be remembered that as H_0 decreases, the acid strength of the surface increases.)

The actual amount of surface acid in a given H_0 range is given by the difference between *n*-butylamine titers using the two indicators bracketing that

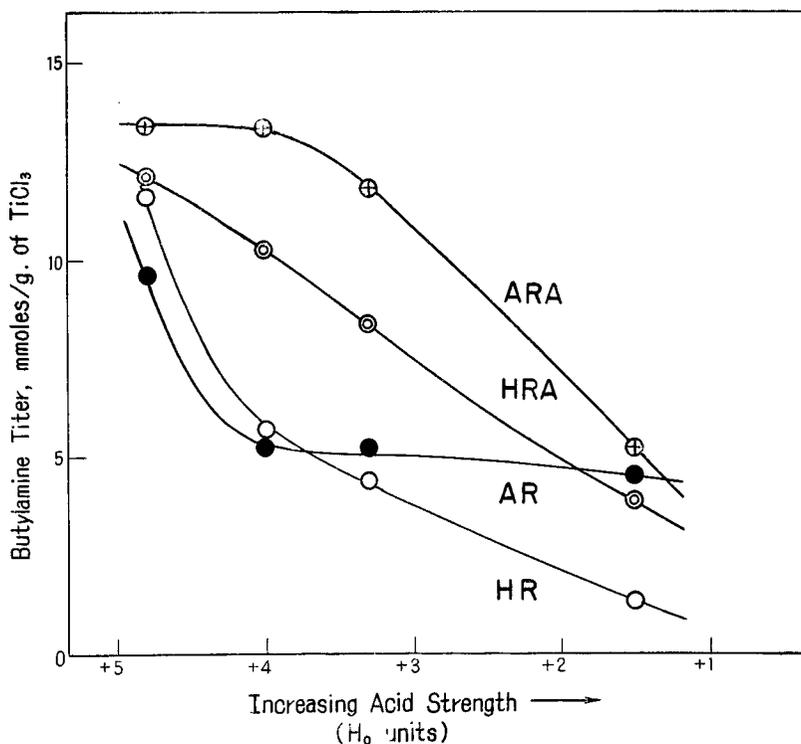


Fig. 3. Butylamine titers vs. acid strength for $TiCl_3$ heated at $200^\circ C$.

H_0 range. It is seen in Fig. 2 that the acid strengths of ARA and HRA types of titanium trichloride is stronger than $H_0 = +1.5$ and that the total acidity (the acidity having acid strength equal to or lower than $H_0 = +4.8$) of ARA is largest, while even those of the other three types are surprisingly large as discussed later. The acidity having acid strength between $H_0 = +3.3$ and $+1.5$ is smallest in HRA and largest in ARA.

Acidity and acid strength of titanium trichloride when preheated in vacuum at 200°C or 300°C for 15 minutes are shown in Fig. 3 or 4 respectively. Acidity of all types of titanium trichloride is increased remarkably by heat-treatment at 200°C. The increase in the acidity of AR whose acid strength is equal to or lower than $H_0 = +1.5$ is most remarkable. The acidities of ARA and AR having acid strength equal to or lower than $H_0 = +1.5$ are further increased by heat-treatment at 300°C, whereas those of HRA and HR are considerably decreased.

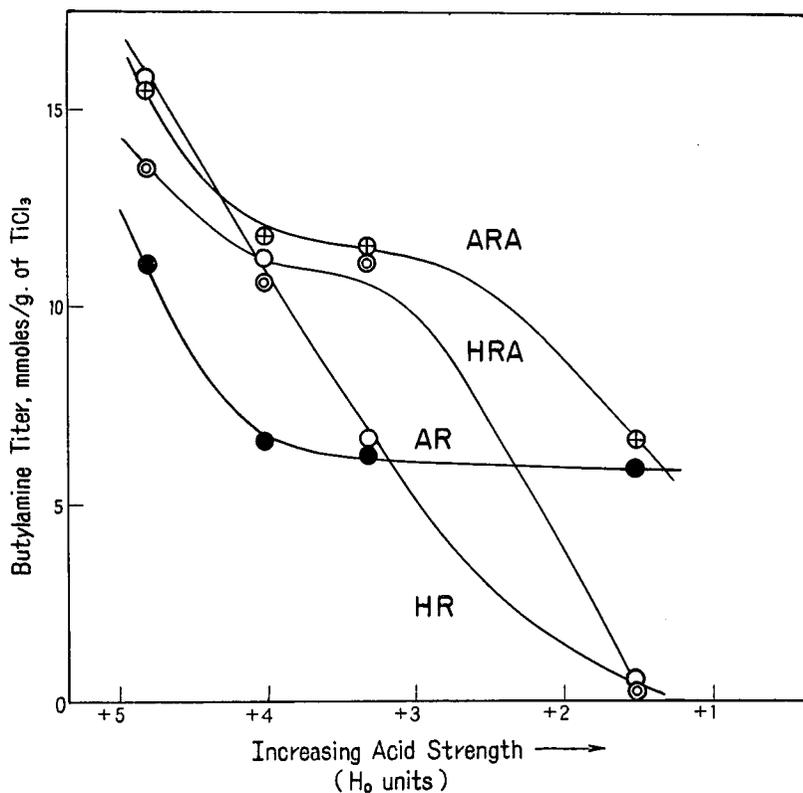


Fig. 4. Butylamine titers vs. acid strength for $TiCl_3$ heated at 300°C.

In order to see more easily the effect of heat-treatment on the acidity, the total acidity is plotted against the heating temperature in Fig. 5. As seen in the figure, the acidity is increased with increasing temperature of heat-treatment in each case of ARA, HRA, HR and AR.

Acidic Property of Titanium Trichloride-Triethyl Aluminum:—In order to test the acidity of this catalyst or the change of acidic property of titanium trichloride on the addition of triethyl aluminum, the following four measurements were made by using 0.1 *N* *n*-butylamine as titrating base and *p*-dimethylamino-azobenzene as an indicator. The ratio of titanium trichloride to triethyl aluminum was the same as that of the catalyst employed by NATTA and PASQUON¹⁰) for propylene polymerization; *i.e.*, $TiCl_3 : Al(C_2H_5)_3 = 1 : 3.5$ (mole ratio), $[Al(C_2H_5)_3] = 0.023$ mole/l, volume of solvent = 20 ml. Type ARA of $TiCl_3$ was used in this experiment. The results are given in Table 1.

Let us consider first the change of the acidity of $SiO_2 \cdot Al_2O_3$ on the addition of $Al(C_2H_5)_3$. The change is given by 0.75 mmoles/g. (from No. 2)—0.45

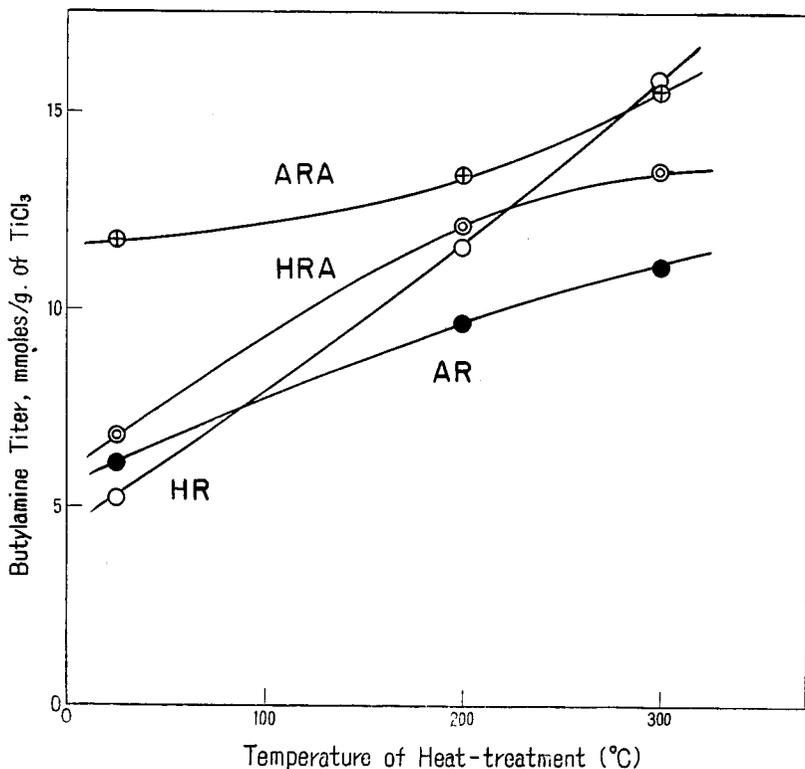


Fig. 5. Effect of heat-treatment on butylamine titers for $TiCl_3$.

TABLE 1.

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|--------|--|
| No. 1. | Acidity of $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$: —The <i>n</i> -butylamine titers required for 0.2013 g. $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 = 0.90$ ml. Hence, the acidity of $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 = 0.45$ mmoles/g. |
| No. 2. | Acidity of $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 + \text{Al}(\text{C}_2\text{H}_5)_3$: —The <i>n</i> -butylamine titers required for 0.2026 g. $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 + \text{Al}(\text{C}_2\text{H}_5)_3 = 1.52$ ml. Hence, the acidity of $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 + \text{Al}(\text{C}_2\text{H}_5)_3 = 0.75$ mmoles/g. |
| No. 3. | Acidity of TiCl_3: —The <i>n</i> -butylamine titers required for 0.0156 g. $\text{TiCl}_3 + 0.2011$ g. $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 = 2.24$ ml. By subtracting the acidity of $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ measured in No. 1, the acidity of $\text{TiCl}_3 = 8.7$ mmoles/g. |
| No. 4. | Acidity of $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 + \text{Al}(\text{C}_2\text{H}_5)_3 + \text{TiCl}_3$: —The <i>n</i> -butylamine titers required for 0.2010 g. $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 + \text{Al}(\text{C}_2\text{H}_5)_3 + 0.0159$ g. $\text{TiCl}_3 = 2.62$ ml. Hence, the acidity of this mixture = 0.26 mmoles. |

mmoles/g. (from No. 1) = 0.30 mmoles/g. The acidity of $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ increases by 0.30 mmoles/g. Next the *n*-butylamine titers which will be required for 0.0159 g. $\text{TiCl}_3 + \text{Al}(\text{C}_2\text{H}_5)_3$ is calculated to be 0.11 mmoles by subtracting the *n*-butylamine titers ($0.75 \text{ mmoles/g.} \times 0.2010 \text{ g.} = 0.15 \text{ mmoles}$) required for 0.2010 g. $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 + \text{Al}(\text{C}_2\text{H}_5)_3$ from 0.26 mmoles of No. 4. The acidity per gram of TiCl_3 is thus estimated to be $0.11 \text{ mmoles}/0.0159 \text{ g.} = 6.9 \text{ mmoles/g.}$ The difference between this value and that from No. 3, *i.e.*, 8.7 mmoles/g.—6.9 mmoles/g. = 1.8 mmoles/g. is the change of the acidity of TiCl_3 on the addition of $\text{Al}(\text{C}_2\text{H}_5)_3$. Namely, $\text{Al}(\text{C}_2\text{H}_5)_3$ decreases the acidity of TiCl_3 by 20%. It can be said from the above results that the NATTA-ZIEGLER catalyst under the conditions of propylene polymerization has fairly strong acidic property on the surface; *i.e.*, the acidity = 6.9 mmoles/g., the acid strength $H_0 \leq +3.3$.

Discussion and Points to Note

The acidity of titanium trichloride is anomalously large. For example, the acidities of ARA and HR having an acid strength equal to or lower than $H_0 = +4.0$ are about 10 mmoles/g. and 3.8 mmoles/g. respectively. These values are ten to one hundred times as large as those of silica-alumina (0.5 mmoles/g.)¹¹⁾ or nickel sulfate (0.11 mmoles/g.)¹¹⁾. Their acidities per unit surface area (0.44 mmoles/m² for ARA¹²⁾, 2.5 mmoles/m² for HR¹²⁾) are also large compared to 0.01 mmoles/m². of nickel sulfate^{*}). The area which a butylamine molecule would occupy is estimated to be 0.38 Å² for ARA or 0.66 Å² for HR, if one assumes monolayer adsorption. Since a crosssectional area of *n*-butylamine is 20 Å² per molecule¹³⁾, the above figures are obviously too small to assume the monolayer adsorption of *n*-butylamine on the solids. Nevertheless, discussion

*) The surface area of nickel sulfate having 0.11 mmoles/g. of acidity was found to be 11 m²/g. according to the B.E.T. method by the present authors.

is continued in what follows assuming that the *n*-butylamine titers are indicative of at least the relative acidity of four solids presently studied.

The acidities having acid strength equal to or lower than $H_0 = +1.5$ of HR and HRA (both reduced by hydrogen) are increased by heat-treatment at 200°C, but decreased at 300°C, while those of AR and ARA (both reduced by aluminum metal) increase with increasing temperature of heat-treatment. The difference may be due to the effect of heat-treatment on aluminum chloride included in AR and ARA, since the acidity of aluminum chloride increases with increase of heating temperature*).

The acidic property of ARA is very strong compared to that of HRA, AR or HR. This correlates with the pronounced catalytic activity of ARA for the propylene polymerization to low polymer observed by KEII, TAKAGI and KANETAKA¹⁴⁾.

The observed results that titanium trichloride has many acid sites having various acid strength and that titanium trichloride-triethyl aluminum has also strong acidic property may give a good explanation for the results that the addition of the traces of some basic organic compounds accelerates the polymerization of propylene to high polymer¹⁵⁾. It might be considered as one of the possible explanations that the catalytic activity of the NATTA-ZIEGLER catalyst increases when acid sites having strong acid strength are covered by basic compounds.

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