Polymer Bulletin 1, 665–670 (1979)

Polymer Bulletin

Polymerization of Propylene over Titanium Exchanged Y-Zeolite

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Summary

It was found that isotactic polymerization of propylene took place over titanium ion-exchanged Y-zeolite without organometallic compounds. The results obtained have led to the conclusions that Ti^{4+} species as well as Ti^{3+} species are active for the polymerization and that neither Ti-alkyl bonds nor Cl ligands are necessarily essential for polymerization of propylene.

Introduction

Recently one-component catalysts, being simpler in composition, have extremely been investigated in the polymerization of α-olefins (BOOR 1967, CLARK 1969, BALLARD 1973, KAROL 1976, YERMAKOV 1976). More recently the present authors have found that titanium ion-exchanged Y-zeolite (Ti-Y) catalyst initiates isotactic polymerization of propylene without any additives. The catalyst is apparently simplest in composition among one-component catalysts reported so far. This paper reports the preparative method of the catalyst as well as the brief results of the polymerization.

Experimental

Materials Research grade $TiCl_3$, $Ti(SO_4)_2 \cdot 4H_2O$ and $Ti_2(SO_4)_3 \cdot 8H_2O$ were commercially obtained from Takachiho Chemical Co. and Yoneyama Yakuhin Kogyo Co. $TiCl_2$ was obtained from Toho TiTanium Co. and purified by evacuating at 600 °C for 6 h. Research grade propylene and n-heptane (from Takachiho Chemical Co.) were purified according to the same procedures reported earlier (SOGA et al. 1977). Nitrogen of ultra high purity (from Nihon Sanso Co., 99.9989 % purity) was further purified by passing through the molecular sieve 3A column cooled at -196 °C.

Preparation of the catalysts. Ti-Y catalysts

0170-0839/79/0001/0665/$01.20

were prepared by the conventional ion exchange of Na form of Y-zeolite (Linde SK-40) with Ti^{3+} or Ti^{4+} : Na-Y was immersed in an aqueous solution of $Ti_2(SO_4)_3 \cdot 8H_2O$ (or $TiCl_3$) or $Ti(SO_4)_2 \cdot 4H_2O$ at room temperature, filtered and then washed thoroughly with water. These catalysts were used for the polymerization after being evacuated at 100 to 600 °C for 3 h. The silica supported $TiCl_2$ catalyst was prepared as follows : To a solution of $TiCl_2$ in pure ethanol was added a measured amount of silica (from Fuji-Devison Co.) which had been evacuated at 300 °C for 4 h. After raising the temperature to the boiling point, the reaction was allowed to continue for 7 h with vigorous stirring. Then the precipitate was filtered under a nitrogen atmosphere, washed adequately with pure ethanol and evacuated at 150 °C or 250 °C for 3 h.

Polymerization procedures. In a 100 ml stainless steel reactor equipped with a magnetic stirrer were placed the measured amounts of the catalyst and n-heptane under a nitrogen atmosphere. The reactor was cooled by liquid nitrogen, degassed i. vac. and then 0.3 mol of purified propylene was introduced. The polymerization was terminated by adding plenty of a dilute hydrochloric acid solution in methanol. The polymer produced was extracted by hot o-dichlorobenzene, precipitated by adding plenty of methanol and dried i. vac. at room temperature.

Analytical procedures. The amounts of titanium contained in the catalysts were determined by atomic absorption spectrophotometry (Shimadzu AA-6105). The ESR spectrum was taken in a pyrex glass tube of 3 mm diameter at -196 °C on a JEOL JES-PE-IX ESR Spectrometer with 100 kc/sec field modulation. 1,1-Diphenyl-2-picrylhydrazyl (DPPH) and Mn^{2+} doped on MgO were used to determine the concentration of Ti^{3+} and the g-value, respectively. The intrinsic viscosity of the polymer was measured at 135 °C in decaline and the molecular weight was calculated by the following equation (KINSINGER 1957).

$$[\eta] = 1.07 \times 10^{-4} [\bar{M}w]^{0.80}$$

The isotacticity of the polymer was determined by the method of LUONGO (1960) with IR, from 995 and 974 cm^{-1} bands.

Results and Discussion

The Ti-Y catalyst prepared from $Ti_2(SO_4)_3 \cdot 8H_2O$ or $TiCl_3$ displayed an anisotropic spectrum with a g-value of 1.945 and a line width of 35 Oe at -196 °C, which can be attributed to Ti^{3+} ions in Y-zeolite (ONO et al. 1974). As can be seen in Table 1, the concentration of Ti^{3+} ions decreased to a certain degree with an increase in the evacuation temperature. The color of the catalyst also changed gradually from dark violet to pale violet. It may therefore be considered that Ti^{3+} ions are partly oxidized by the residual H_2O to form TiO_2 upon heating. On the other hand, the Ti-Y catalyst (white color) prepared from $Ti(SO_4)_2 \cdot 4H_2O$ did not show any ESR signal even after it had been evacuated at 600 °C for 3 h, which indicates that titanium exists as Ti^{4+} in Y-zeolite. X-ray analysis confirmed that the structure of the Y-zeolite remained unchanged by the evacuation at 500 °C.

Polymerization of propylene was conducted at 65 °C for 45 h by using about 1.0 g of each catalyst without any additives. In Table 1 are shown the polymerization results together with the analytical data of the catalysts.

It should be noted that isotactic polymerization of propylene did take place over these Ti-Y catalysts. These results strongly imply that neither Ti-alkyl bonds nor Cl ligands are necessarily essential for isotactic polymerization of propylene. The low activity of these catalysts may be attributed to the small pore diameter of the Y-zeolite (ca. 10 Å) as reported previously (SOGA et al. 1974, in press). It may also be considered that the decrease in the activity over the catalysts evacuated at lower temperatures is mainly attributed to the water in the zeolite cage. It has already been reported that many transition metal cation exchanged catalysts promote the oligomerization of olefins (JONES et al. 1967, RIEKERT 1970, YASHIMA et al. 1972, YASHIMA et al. 1973, YASHIMA et al. 1975) and that Cr-Y catalyst initiates the polymerization of ethylene (YASHIMA et al. 1977). However, no report can be seen on the isotactic polymerization of propylene over transition metal cation exchanged catalysts. The data in Table 1 also suggest that Ti^{4+} ions also initiate the polymerization in addition to Ti^{3+} ions.

We have recently studied the polymerization of propylene in the absence of any activator by using a γ-alumina-supported $TiCl_4$ catalyst after activation under evacuation at 100-800 °C for 6 h. It has been found that the polymerization activity increases in proportion to the concentration of the Ti^{3+} species (g=1.942) by increasing the evacuating temperature. The correlation between the activity and the concentration of the Ti^{3+} species has led to the conclusion that the titanium consisting active species for the polymerization is Ti^{3+} (SOGA et al. in press).

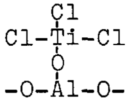
The present result that Ti^{4+} ions are also active conflicts with this conclusion. However, it may easily be considered that the Ti^{4+} species  $\begin{array}{c} Cl \\ | \\ Cl-Ti-Cl \\ | \\ O \\ | \\ -O-Al-O- \end{array}$ (SOGA

TABLE I

Results of Propylene Polymerization over Ti-Y catalysts[a)]

Catalyst	Evacuating Temp. (°C)	Polymer Yield (mg/g-cat.)	Ti supported[b)] (matom/g-cat.)	Conc. of Ti^{3+} [c)] (matom/g-cat.)	$\bar{M}w$[d)] ($x10^4$)	I.I.[e)] (%)
Y-$TiCl_3$	100	0	1.2	-	-	-
"	200	trace	-	0.63	-	-
"	250	28	1.3	0.58	13	61
"	300	27	0.97	-	11	63
"	400	30	1.2	0.37	-	53
"	450	21	-	0.22	-	-
"	500	23	1.1	-	18	-
"	500	2955[f)]	1.1	-	-	-
Y-$Ti_2(SO_4)_3$	250	37	1.1	0.76	-	66
"	450	19	0.99	0.32	-	63
Y-$Ti(SO_4)_2$	250	2.8	0.61	0	-	-
"	350	4.0	-	0	-	-
"	450	3.7	-	0	-	-
"	600	4.0	0.56	0	-	54
$TiCl_2$ on SiO_2	150	0	0.24	0	-	-
"	250	~0	0.32	0	-	-

a) Polymerization was conducted at 65 °C for 45 h by using 1.0 g of each catalyst, 5 ml of n-heptane and 0.3 mol of propylene in a 100 ml stainless steel reactor.

b) Determined by atomic absorption spectrophotometry.

c) Calculated from ESR spectrum with a g-value of 1.945.

d) Molecular weight of polymer (KINSINGER 1957).

e) Isotacticity index of polymer (LUONGO 1960).

f) Polymerization of ethylene was conducted at 65 °C for 16 h by using 1.0 g of catalyst, 5 ml of n-heptane and 0.2 mol of ethylene in the same reactor.

et al. in press) in the γ-alumina-supported catalyst is surrounded with three large Cl ligands whereas the Ti^{4+} ions in the present system is free from such ligands. In the other words, propylene can easily be coordinated with the Ti^{4+} ions in the present system whereas it can hardly be coordinated with the Ti^{4+} species in the γ-alumina-supported catalyst. This may be the main reason why Ti^{4+} ions are also active in the present system.

Then a silica-supported $TiCl_2$ catalyst (dard grey) was prepared and the polymerization of propylene was conducted over it to check whether Ti^{2+} species are also active or not. (It seems very difficult to prepare Ti^{2+}-Y catalyst). The catalyst did neither show any ESR signal nor activity for the polymerization as shown in Table 1. These results are consistent with the previous result that Ti^{2+} species are inactive for the polymerization (SOGA et al. in press).

The conclusion reached can be expressed as follows. Both Ti^{3+} and Ti^{4+} species are active and neither Ti-alkyl bonds nor Cl ligands are necessarily essential for isotactic polymerization of propylene.

Acknowledgment

The authors would like to express their gratitude to Associate Professors Yoshio Ono and Takeshi Yashima of Tokyo Institute of Technology for their valuable advice.

References

BOOR, J. : Macromol. Rev. 2, 115 (1967)
CLARK, A. : Catal. Rev. 3, 145 (1969)
BALLARD, D. G. H. : Adv. Catal. 23, 267 (1973)
KAROL, F. J. : "Encyclopedia of Polymer Science and Technology" Supp. Vol. 1. Ed. by MARK, H. F. Interscience Publishers, New York, 1976
YERMAKOV, Yu. I. : Adv. Catal. 24, 173 (1976)
ONO, Y., K. SUZUKI and T. KEII : J. Phys. Chem. 78, 218 (1974)
SOGA, K., K. HYAKKOKU and S. IKEDA : J. Polym. Sci., Polym. Chem. Ed. in press
JONES, D. G., C. HILL and P. S. LANDIS : U. S. Pat., 3,325,465 (1967)
RIEKERT, L : J. Catal. 19, 8 (1970)
YASHIMA, T., M. EBISAWA and N. HARA : Chem. Letters, 1972, 473
YASHIMA, T., M. EBISAWA, Y. USHIDA and N. HARA : 3 rd Intern. Conf. Molecular Sieves, Preprint, Nol 165, p.418 (1973)
YASHIMA, T., Y. USHIDA, M. EBISAWA and N. HARA : J. Catal. 36, 320 (1975)
YASHIMA, T., J. NAGATA, Y. SHIMAZAKI and N. HARA : ACS Symp. Ser., 40, 626 (1977)

SOGA, K., K. IZUMI, M. TERANO and S. IKEDA : Makromol. Chem. in press
KINSINGER, J. B. : Paper presented at the 132 Meeting, A. C. S. New York, Sept. 1957
LUONGO, J. P. : J. Appl. Polym. Sci. 3, 302 (1960)

Received July 28, 1979