DIETHYL ETHER SORPTION ON TITANIUM TRICHLORIDE AND ITS CORRELATION WITH CATALYTIC ACTIVITY IN THE POLYMERIZATION OF PROPENE

Luboš Pololáník, Jiří Mejzlík, Oldřich Hamřík and Jan Blatný

Chemopetrol, Research Institute of Macromolecular Chemistry, 656 49 Brno

Dedicated to Academician O. Wichterle on the occasion of his 70th birthday.

A series of samples exhibiting different catalytic activity and sorption properties was obtained by grinding two basic types of titanium trichloride ($TiCl_3.1/3\ AlCl_3$ and $TiCl_3$). The samples with co-crystallized $AlCl_3$ can sorb, under otherwise identical conditions, by an order of magnitude more diethyl ether than those of pure $TiCl_3$. The amount of sorbed ether increases with its partial pressure and decreases when elevating the temperature of sorption. There is a correlation between the quantity of ether sorbed on $TiCl_3$ and the catalytic activity of the latter in the propene polymerization. This correlation is, however, different for both examined catalyst types.

The ability of systems containing titanium chloride and organoaluminium cocatalyst to catalyze the polymerization of α-olefines is closely connected with the catalyst surface properties. Apart form a more usual surface characterization based on the determination of polymerization active centres some authors have attempted to find a relation between the polymerization activity of $TiCl_3$ catalyst and the acidity of its surface[1-6]. With the exception of Kanetaka[3] all authors determined the catalyst acidity by titration with an organic base employing suitable colour indicators. Kanetaka adsorbed triethylamine on the surface of $TiCl_3$–organoaluminium catalyst and followed the time dependence of the weight changes *in vacuo*. The weight loss during first hour of desorption was considered as being the amount of amine physically adsorbed. The non-released amine was, according to this author, chemisorbed and it was related to the acidity. The acidity values defined in this way were in all cases enormously high. The highest molar ratio of organic base/$TiCl_3$ reached the value as high as ∼ 3. It is our opinion that at such ratios the amount of base cannot characterize the acidity of $TiCl_3$ surface.

In this work we have attempted to characterize the acidity of $TiCl_3$ by sorbing on its surface a weak organic base under relatively mild conditions and to find a correlation between the sorption properties of $TiCl_3$ and its catalytic activity in propene polymerization. Two types of catalyst ($TiCl_3$ and $TiCl_3.1/3\ AlCl_3$) activated to a varying degree by grinding have been examined.

EXPERIMENTAL

Materials. The following titanium trichloride catalysts were employed: TAC 141 (Toho Titanium) mixed crystals $TiCl_3.1/3$ $AlCl_3$, ground; $TiCl_3$-A (Toyo Stauffer) mixed crystals $TiCl_3$. $.1/3$ $AlCl_3$, non-ground; $TiCl_3$-AO (Stauffer) mixed crystals $TiCl_3.1/3$ $AlCl_3$, non-ground; $TiCl_3$—H (Toyo Stauffer) pure $TiCl_3$, non-ground.

Diethyl ether containing less than 10 ppm of water and ethanol was used as an organic base.

Methods. All manipulations with catalysts and auxiliary materials were carried out in a strictly inert medium. The samples of $TiCl_3$—A and $TiCl_3$—H were ground to a different degree in a Molinex ball-mill, volume 0·75 l, 1 200 rpm, water-cooled jacket.

The sorption of ether on $TiCl_3$ was measured on a quartz spring-balance at various temperatures and partial pressures of ether employing the method of isothermal gravimetry[7].

The polymerization activity of $TiCl_3$ was evaluated in the propene polymerization carried out in a 3 l reactor and it was expressed in grams of polymer produced per hour by one gram of $TiCl_3$ catalyst. The conditions of polymerization were as follows: solvent n-hexane; temperature 70°C; propene pressure 1·1 MPa; time of polymerization 2 hours; catalyst $AlEt_2Cl$–$TiCl_3$–diglyme (molar ratio 1·35 : 1 : 0·013); amount of $TiCl_3$ used — c. 1 mmol. Molecular weight of polymer was controlled by the addition of hydrogen (420 ml as the last component before the admission of monomer).

RESULTS AND DISCUSSION

The intense dry grinding of basic catalysts $TiCl_3$—A and $TiCl_3$—H, resp. resulted in a series of samples possessing a varying catalytic activity (Fig. 1) as well as different sorption properties. Figs 2a,b show typical kinetic sorption and desorption curves measured at 30°C using diethyl ether as a sorbate at various pressures and H_{240} and A_{240} catalysts. Sample A_{240} is capable of sorbing by an order of magnitude more ether than sample H_{240}, both catalysts being however approximately equally active in propene polymerization. At low ether pressures ($\sim 1\cdot 3$ kPa) a sorp-
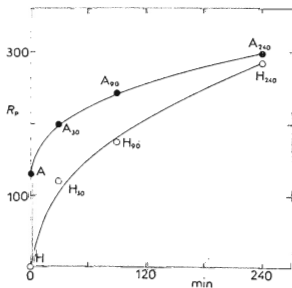

FIG. 1

Dependence of titanium trichloride polymerization activity, R_p (expressed as $g_{pp} \cdot g_{cat}^{-1} \cdot h^{-1}$), on the time of grinding

tion equilibrium was reached in the case of pure $TiCl_3$. When mixed crystals are examined a genuine sorption equilibrium is not attained since, as illustrated in Fig. 2 c the weight changes of $TiCl_3.1/3 \ AlCl_3$ at low ether pressures $(\sim 0.12 \ kPa)$ are likely to stem from several processes: 1) fast sorption of ether on catalyst surface; 2) reactions of ether with available molecules of $TiCl_3$ and $AlCl_3$; 3) slow release of products of sorption or of a chemical reaction from the solid phase. The latter effect was not
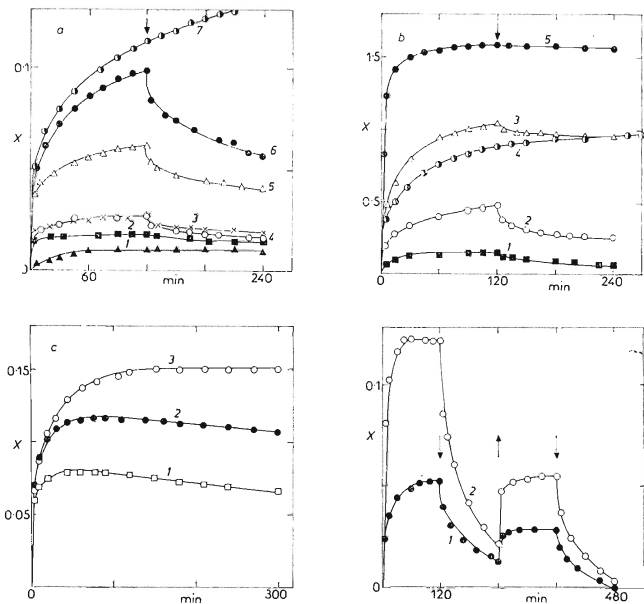

Fig. 2

Time dependence of diethyl ether sorption on $TiCl_3$ at 30°C and various pressures of diethyl ether (X represents the sorbed amount of diethyl ether in mol per mol $TiCl_3$). ↓ Onset of evacuation a) Sample H_{240}, diethyl ether pressures (kPa): 1 0.07, 2 0.12, 3 0.8, 4 1.3, 5 6.7, 6 26.7, 7 26.7 (without evacuation). b) Sample A_{240}, diethyl ether pressures (kPa): 1 0.12, 2 1.3, 3 6.7, 4 6.7 (without evacuation), 5 26.7. c) Diethyl ether pressure 0.12 kPa, samples: 1 A_{30}, 2 A_{90}, 3 A_{240}. d) Diethyl ether pressure 0.12 kPa, ↑ onset of sorption, samples: 1 TAC 141, 2 A_{90}

observed in pure $TiCl_3$ and it is therefore necessary to consider it as being specific for $AlCl_3$ containing systems. If the products of interaction between diethyl ether and $AlCl_3$ are removed by evacuation then in a subsequent repeated sorption the total amount of the sorbed ether is lower (Fig. 2*d*).

In this connection it is worth noting that the sorption of diethyl ether on $TiCl_3$.$.1/3 AlCl_3$ is not a reversible process. The desorption product is probably an $AlCl_3$.$.n Et_2O$ complex, since aluminium was found to be present in the desorption products. The exact composition of desorption products is not known. Thus the time dependence of the weight loss during evacuation should be expressed in weight units. The molar ratio $Et_2O/TiCl_3$ used in our case was preferred for the sake of simplification. This conclusion is further corroborated by the sorption–desorption characteristics measured at higher temperature.

At partial pressures of ether exceeding the value of $0·12$ kPa, the amount of sorbed ether on mixed crystals steadily increases with time (Fig. 2*b*). This probably reflects the process of ether penetration into the crystal lattice of $TiCl_3.1/3 AlCl_3$ at locations of high incidence of co-crystallizing $AlCl_3$. This hypothesis was supported by the sorption experiments with mixed crystals at ether pressure $26·7$ kPa. Under these conditions the sorption of ether was accompanied by the collaps of the catalyst crystal lattice and the catalyst exhibited an amorphous character after the end of sorption period. The dominant role of $AlCl_3$ in this process is evident from the fact that pure $TiCl_3$ exhibits a similar but far less pronounced sorption pattern at considerably higher ether pressures (Fig. 2*a*). The main problem in the case of experiments at higher pressures of ether is too high a rate of sorption which increases the temperature of sample in such a way that the isothermal conditions are no longer preserved. This of course makes the quantitative evaluation very difficult. A preliminary calculation of the heat transfer have shown[8] that at ether pressure of $26·7$ kPa the sample in a given experimental arrangement may be overheated for a short periods of time by as much as $30°C$. Under these conditions the $AlCl_3$.$.n Et_2O$ complexes are already melting (m.p. of $AlCl_3.Et_2O$ was reported[9] to be $35°C$) and the penetration of ether into the crystal lattice of mixed crystals is likely to be significantly enhanced.

It is to be expected that the increasing concentration of diethyl ether in the "solid" phase will change the molar ratio of ether in the complexes. As the enormous sorption ability of mixed crystals is due to the presence of $AlCl_3$ the possibility of formation of $AlCl_3.n Et_2O$ type complexes ($n \geqq 4$) has to be also considered, namely at high pressures of ether ($26·7$ kPa) (see Fig. 2*b*). The existence of such complexes may seem improbable although the explanation suggesting that a solution of ether or that a complex wih lower ether concentration is involved cannot account for the observed behaviour. If such solution were formed the ether would be easily removed by evacuation. The course of $TiCl_3.1/3 AlCl_3$ evacuation as shown in Fig. 2*b* indicates that the fraction of desorbed components decreases when increasing the partial

pressure of ether. This may be accounted for by admitting a higher volatility of $AlCl_3$. $.n\ Et_2O$ complexes with smaller n that are formed at low ether pressures.

The desorption pattern after the $TiCl_3/Et_2O$ interaction at 30°C differs from that found after the interaction of $TiCl_3.1/3\ AlCl_3-Et_2O$. In the former case no titanium could be detected in the desorption products, thus the weight losses during evacuation (Fig. 2a) could be exclusively assigned to the desorption of ether.

At elevated temperature the amount of sorbed ether decreases in the case of both catalyst types (Fig. 3). The volatilization of $AlCl_3.n\ Et_2O$ complexes is particularly pronounced in mixed crystals and will be significant already during the sorption period. A side reaction leading to the formation of trace amounts of ethyl chloride could be detected but its extent could not influence the balance of ether in the system (roughly 0.01 mol per mol of the sorbed ether). A comparison of two samples of mixed crystals (A_{90} and A_{240}) shows that the more active catalyst (A_{240}) contains the $AlCl_3.n\ Et_2O$ complexes of lower volatility. This is consistent with the desorption pattern found at 30°C (compare Figs. 2b,c,d).

Fig. 3 also shows that the sorption equilibrium of pure $TiCl_3$ at 70°C (similarly as at 30°C) is established fairly quickly. It can be observed however that the weight of the sample after the desorption period is slightly lower than the initial one. This observation is indicative of a certain volatility of the $TiCl_3.n\ Et_2O$ complexes at higher temperatures.

It was a purpose of all experiments presented above to select suitable sorption conditions for defining the relationship between the polymerization activity of $TiCl_3$ and its ability to sorb an organic base on the surface. We intended to find such conditions under which all $TiCl_3$ surface centres were occupied by diethyl ether.

The analysis of results indicates that the $TiCl_3$ sorption ability cannot be assessed at higher temperatures because of the volatility of $AlCl_3.n\ Et_2O$ complexes under
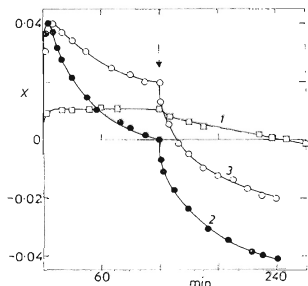

FIG. 3

Time dependence of diethyl ether sorption on $TiCl_3$ at 70°C (X represents the sorbed amount of diethyl ether in mol per mol $TiCl_3$). Diethyl ether pressure 0.12 kPa. ↓ onset of evacuation, samples: 1 H_{240}, 2 A_{90}, 3 A_{240}

these conditions. Thus a correct determination of the sorption equilibrium on $TiCl_3$.
.1/3 $AlCl_3$ mixed crystals is precluded. At low sorption temperature (30°C) it may be
expected (judging from the adsorption isotherm) that in the case of pure $TiCl_3$ all
surface centres will be occupied by diethyl ether at its partial pressure around 1·3 kPa.
In the case of mixed crystals, however, the selection of a suitable sorption pressure
is more difficult. The sorption equilibrium is virtually established within a realistic
period of time only at pressures below 0·12 kPa. This pressure is also an approximate
limit above which isothermal conditions of sorption are no longer guaranteed. Thus,
if the properties of both $TiCl_3$ types are to be compared at identical conditions then
the partial pressure of ether 0·12 kPa and temperature 30°C seem to be the most
suitable compromise. Under these conditions a good correlation between the poly-
merization activity of pure $TiCl_3$ and its sorption ability was observed (Fig. 4).
The amount of sorbed ether is in a satisfactory agreement with the number of poly-
merization active centres as found by the kinetic analysis of propene polymerization
(sample H_{240} sorbs $1·8 . 10^{-2}$ mol Et_2O per mol $TiCl_3$ while $2·3 . 10^{-2}$ mol of active
centres per mol $TiCl_3$ was found[10] by the polymerization test).

$TiCl_3$.1/3 $AlCl_3$ can sorb much more ether under comparable conditions. Thus
even at mild conditions the sorption process seems to proceed not only on $TiCl_3$
active centres but also on $AlCl_3$ structures whose number is by an order of magnitude
higher. The relation between the polymerization activity in this case is not unequi-
vocal. The samples of industrial origin (AO, A, TAC 141) exhibit almost a propor-
tionality between the activity and sorption properties of the surface. The samples
A_{30}, A_{90}, A_{240}, which were prepared by grinding the sample A in a ball mill, sorb
considerable more ether, the polymerization activity being however the same as in pre-
vious cases. This is accounted for by an unusually high mechanical strain under
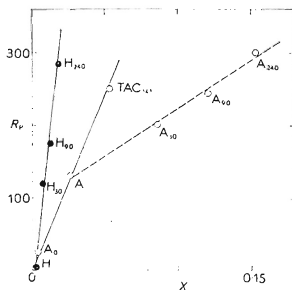our conditions of catalyst grinding. It seems likely that in this way surface defects

FIG. 4
Relationship between the amount of sorbed
diethyl ether, X (mol Et_2O/mol $TiCl_3$).
on $TiCl_3$ surface after reaching equilibrium
and the polymerization activity of $TiCl_3$
catalyst, R_p ($g_{pp} g_{cat}^{-1} h^{-1}$)

are created whose acidity is sufficient to exhibit sorption phenomenon in the presence of an organic base but which are not adequate to act as potentially active centres in polymerization.

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