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About mechanism and model of deactivation of Ziegler–Natta polymerization catalysts

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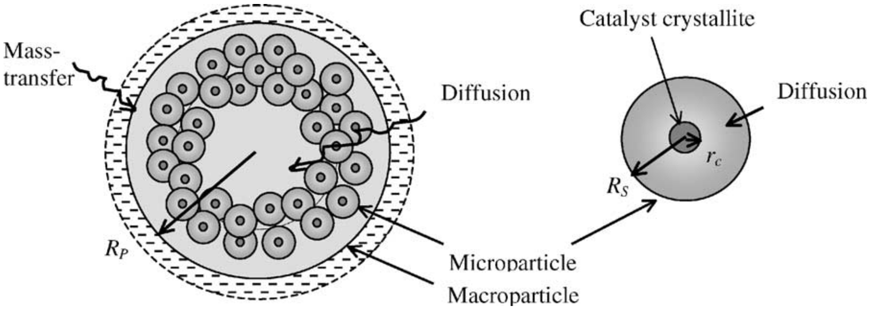
Abstract

A simple model is proposed to examine the possible effect of chlorine mobility in titanium chlorides on the dynamics of polymerization rate. The range of value of Cl^- diffusivity is estimated to be 10^{-17} to 10^{-15} cm^2/s. The model was verified by simulation of experimental data were found in the literature.

Keywords: Ziegler–Natta catalysts; Propylene polymerization; Model of deactivation

Polymerization processes are in unsteady states by their nature, because the reaction rate changes with time. The catalyst has to be a part of the product, since the polymer "grows" on the catalyst surface and capsulate it. Figuratively, growing polymer particle can be imaged as a pomegranate fruit, where the fruit (macroparticle) include grains (microparticles), with seeds (catalyst crystallites):



Such a model of olefins polymerization on Ziegler–Natta catalysts was developed by Ray and coworkers [1–3]. In polymerization, as distinct from other catalytic processes, it is rather difficult (if possible) to separate chemical and physical stages of reaction dynamics. It is determinated by particle growing, as well as by changing of active sites number. The latter happens due to the formation of active sites under the influence of cocatalyst, and their transformation during the reaction. These processes proceed with approximately the same rates, and therefore also cannot be separated. That is why there are not many investigations in literature on deactivation of polymerization catalysts [4]. In most cases, the matter concerns "resultant dynamics" of process within the limits of residence time in reactor. Such an approach is justified because of "one-use" operation of catalyst in polymerization processes, where catalyst deactivation is not a vital problem.

Nevertheless, from the catalyst development and process technology points of view, it is very important to understand the reasons of dynamic behavior, their mechanisms and comparative effect. Decay in rate of polymerization is one of the prominent characteristics of olefins polymerization over Ziegler–Natta catalysts, however, there is still a lack of under-

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Nomenclature

C_m, C_A	concentrations of monomer and alkylaluminum chloride
C_Z, C_V	concentration of potential active centers on surface and in catalyst bulk
D_c	diffusivity of chlorine in catalyst
E	their activation energies
k_A, k_d	constants of catalyst activation and deactivation
r_c, d_c	radius and diameter of catalyst crystallite
R_p, k_p	polymerization rate and its constant

standing of the fundamental mechanism [5]. The experimentally observed decay period usually continues about 1–3 h. Choi and Ray [5] have estimated that the rapid rate increase with particle overheating and diffusion limitation takes place during the very early period of the process (from a few seconds up to 1–5 min), and does not produce the slow decaying reaction rate.

Most authors agree in opinion that the main reason for the observed decrease of catalyst activity is the poisoning by $EtAlCl_2$–ethylaluminum dichloride (EADC), which is the product of interaction of catalyst ($TiCl_3$, $TiCl_4$) with cocatalyst Et_2AlCl (DEAC) and $AlEt_3$ (TEA). For example:

$$TiCl_3 + Et_2AlCl \leftrightarrow TiCl_2\text{–}Et + EtAlCl_2 \tag{1}$$

Yoon and Ray [4] have developed the kinetic model of deactivation based on the poisoning effect of $EtAlCl_2$.

As a result of reaction (1), the gradual elimination of chlorine from the catalyst takes place. Ambrož et al. [6] have drawn attention to this phenomenon as far back as 60th. They found that the course of extraction of Cl^- during the $TiCl_3$ + TEA interaction and the decrease of the catalyst activity are correlated (Fig. 1).

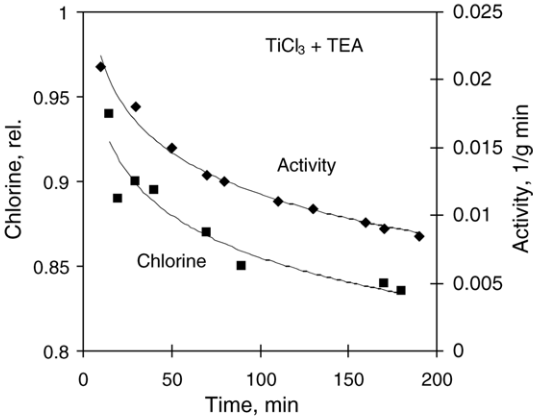


Fig. 1. Course of extraction of Cl^- during $TiCl_3$–$AlEt_3$ interaction and decrease of the catalyst activity during propylene polymerization [6].

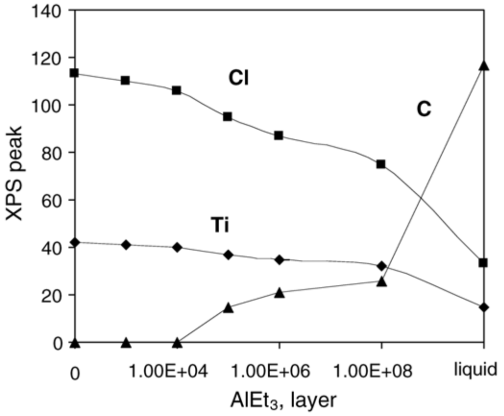


Fig. 2. XPS spectra of a $TiCl_4$ with $AlEt_3$ exposure at 300 K [7].

It was established in [6], that chlorine loss reached 50% of total chlorine in $TiCl_3$, and therefore could not be removed from the surface layers of the catalyst crystal only, but had to “touch” the bulk.

Magni, Malizia and Somorjai [7-9] have investigated the $TiCl_4$–TEA system using the modern technique of “surface science”, such as X-ray photoelectron (XPS) spectroscopy. The reduction and alkylation of the surface $TiCl_4$ have been observed with the formation of $TiCl_2Et$ (Fig. 2). The reaction with liquid TEA for a long time induces the almost complete reduction of the original Ti^{4+} and the formation of surface species of stoichiometry $TiClEt_n$ (n = 1 and/or 2). Additionally, it was found in [8], that in steady state the catalyst consist of a few layers $TiCl_2$ with one monolayer of $TiCl_4$ chemisorbed at the surface.

All these data indicate that the matters can concern the mobility of chlorine in the lattice of $TiCl_3$ or $TiCl_4$, similarly to oxygen mobility in oxides or carbon in carbides. These processes in solid phase are quite slow (formally are similar to diffusion), and can determine the distinctive dynamics of process. In this work, we tried to estimate the parameters of such diffusion and their possible effect on the reaction rate dynamics in propylene polymerization.

1. A simple evaluation

The rate of polymerization is usually expressed as [1–5]:

$$R_\mathrm{p} = k_\mathrm{p} C_\mathrm{z} C_\mathrm{m} \tag{2}$$

Since in reaction (1) EADC is a product of cocatalyst action and is in adsorption equilibrium [4], the rate of deactivation will be proportional to the concentration of DEAC. The compensation of dechlorinated centers one can consider as a diffusion flux in the catalyst crystallite from the bulk to surface:

$$\frac{\mathrm{d}C_\mathrm{Z}}{\mathrm{d}t} = -k_\mathrm{d}^1 C_\mathrm{Z} C_\mathrm{A} + D_\mathrm{c} S \left.\frac{\mathrm{d}C_\mathrm{V}}{\mathrm{d}r}\right|_{r=r_\mathrm{c}} \tag{3}$$

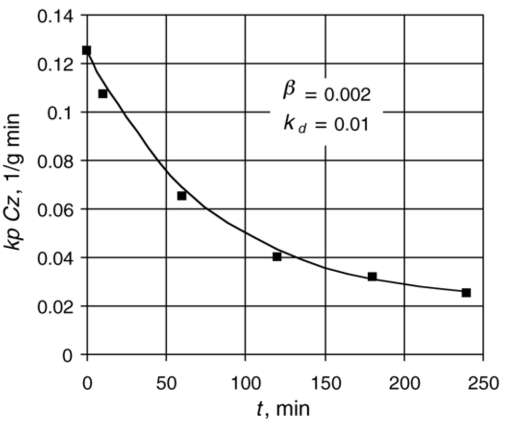


Fig. 3. Variation of polymerization rate ($k_p C_Z$) with time. Points: experiments of [6]; lines: model prediction (Eq. (3)).

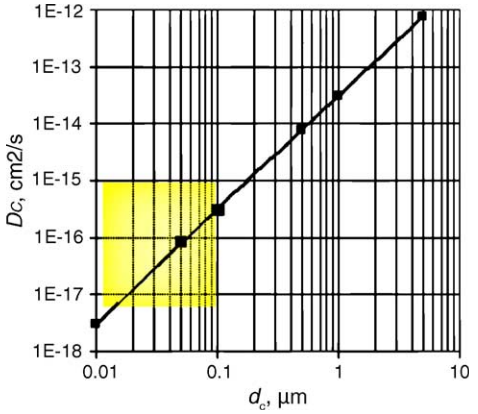


Fig. 4. Correlation of D_c and d_c at $k_d = 0.01$.

Since $C_A \approx$ constant, then $k_d \approx k_d^1 C_A$. The specific surface of crystallite S, depending of their form, can be written as $S = (1.5\text{–}3)/r_c$. The diffusion flux can be approximately expressed as

$$D_c S \left.\frac{dC_V}{dr}\right|_{r=r_c} \approx \beta(\bar{C}_V - C_Z), \quad \beta \approx (1.5\text{–}3)^2 \frac{D_c}{d_c^2} \qquad (4)$$

After substituting these formulas in (3) and its integration, we are able to describe the experimental data of [6] (Fig. 3).

Since β is proportional to D_c/d_c^2, where $d_c = 2r_c$, then a lot of combination of D_c and d_c are probable, presented in Fig. 4. The d_c of industrial catalysts is usually within the values 0.01–0.1 μm (after shattering with the onset of polymerization).

Then the diffusivity $D_c = 10^{-17}$ to 10^{-15} cm^2/s, that is typical for diffusion in solids [10,11].

2. The role of aluminum alkyl chlorides

It is known that the behavior of catalytic systems $TiCl_3$–DEAC and $TiCl_4$–TEA is quite different. It depends mostly on the type of cocatalyst. At the same catalyst ($TiCl_3$), the cocatalyst TEA provides the initial reaction rate 10 times higher than DEAC [4], however after 2 h the reaction rates become practically equal. It was shown by Yoon and Ray [4] that preaging the catalyst with the presence of TEA sharply reduces the reaction rate, but in case of DEAC no significant effect was observed. At the same time, the poisoning effect of EADC takes place on both type of catalytic system that was established in several publications [4,12].

Caunt [12] was probably the first who tried to substantiate the influence of EADC and to analyze the reaction network, which determine its concentration in solution and on the catalyst. The alkylaluminum and alkylaluminum chlorides are known to exist in solution in dimeric form. According to the opinion of Caunt, DEAC and EADC concentrations are presumably controlled by equilibria:

$$Et_4Al_2Cl_2 + Et_2Al_2Cl_4 \leftrightarrow 2Et_3Al_2Cl_3 \qquad (5)$$

Monomeric EADC may be the only entity small enough to be adsorbed on the catalyst. Its concentration is governed by slight dissociation of alkyls:

$$Et_3Al_2Cl_3 \leftrightarrow Et_2AlCl + EtAlCl_2 \qquad (6)$$

In the presence of TEA the inhibitor may be removed by the reaction:

$$Et_3Al + EtAlCl_2 \leftrightarrow 2Et_2AlCl \qquad (7)$$

These reactions (5)–(7) demonstrate that the dynamic equilibrium of species may be achieved in solution, which obviously depends on initial amount of Al, Cl and alkyl groups.

In the presence of catalyst, the equilibrium has to be shifted due to the interaction and adsorption on the surface. When DEAC is used, only a small shift is expected due to the presence of Cl^- in solution. In case of TEA, there is no chlorine in initial solution, and reactions (5)–(7) are not occurring. After bringing TEA and catalyst in contact, several reactions like the following have to start [13]:

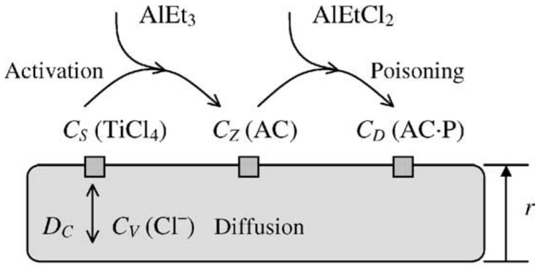
$$\underset{\text{catalyst}}{|Cl_X Ti - Cl} + \underset{\text{cocatalyst}}{Et_3Al} \rightarrow \underset{\text{active center}}{|Cl_X Ti - Et} + Et_2AlCl \qquad (8)$$

The appearance of Et_2AlCl in solution starts up reactions (5)–(7), which should definitely lead to elimination of chlorine from the catalyst, and to the reduction of Ti^{4+} [7,14]. Naturally, the amount of eliminated Cl^- will depend on the $Et_3Al/TiCl_4$ ratio and on the equilibrium of reactions (5)–(7). Therefore no wonder, that the maximum of catalyst activity largely depends on the mole ratio of TEA to $TiCl_4$ [15,16]. Higher activity in the case of TEA in comparing with DEAC [4] is probably related to reaction (7), because the specific activity of active centers is practically the same for different types of catalytic system [13,17].

From the above consideration, we can conclude that the reaction rate dynamics may be controlled by formation and poisoning of active centers, including slow reduction of the catalyst, due to the chlorine mobility in the catalyst bulk. In order to examine such a possibility, more detailed model is necessary.

3. The detail model

In experiments of [6] (Figs. 1 and 3) the reaction rate was not measured during initial 10 min, thus the initial period of rate increasing is not detected and is left out of account in Eq. (3). For the complete simulation of dynamics, it is necessary to write the equation for potential centers in crystallite bulk. Such a model can be presented by the following scheme:



AC – active center, P – poison

The equation for chlorine mobility may have a diffusion form:

$$\frac{\partial C_\mathrm{V}}{\partial t} = D_\mathrm{c}\frac{\partial^2 C_\mathrm{V}}{\partial r^2} \tag{9}$$

with boundaries conditions:

$$r = 0: \quad \frac{\mathrm{d}C_\mathrm{V}}{\mathrm{d}r} = 0, \qquad r = r_\mathrm{c}:$$

$$D_\mathrm{c} S \frac{\mathrm{d}C_\mathrm{V}}{\mathrm{d}r} = -k_\mathrm{A}^1 C_\mathrm{S} C_\mathrm{A} \tag{10}$$

The equation for active centers concentration includes its activation and deactivation stages. Their rates are proportional to activator concentration (C_A), assuming that EADC is in adsorption equilibrium with TEA (or with DEAC):

$$\frac{\mathrm{d}C_\mathrm{Z}}{\mathrm{d}t} = k_\mathrm{A}^1 C_\mathrm{S} C_\mathrm{A} - k_\mathrm{d}^1 C_\mathrm{Z} C_\mathrm{A}, \quad C_\mathrm{S} = C_\mathrm{V}|_{r=r_\mathrm{c}} \tag{11}$$

The solution of (9) at $r = r_\mathrm{c}$ has to be in form:

$$C_\mathrm{S}(t) = C_\mathrm{V}(r_\mathrm{c}, t) = \sum_{n=1}^{\infty} A_n \exp\left(-\frac{\mu_n^2 D_\mathrm{c}}{r_\mathrm{c}^2} t\right) \tag{12}$$

μ_n are roots of characteristic equation $\mathrm{ctg}\,\mu_n = \mu_n D_\mathrm{c}/k_\mathrm{A} r_\mathrm{c}^2$, and $A_n = 2\sin\mu_n \cos\mu_n/(\mu_n + \sin\mu_n \cos\mu_n)$.

Substituting (12) in (11) and integrating we obtain

$$C_\mathrm{Z}(t) = k_\mathrm{A} \sum_{n=1}^{\infty} \frac{A_n}{k_\mathrm{d} - \beta_n}\left[\exp(-\beta_n t) - \exp(-k_\mathrm{d} t)\right],$$

$$\beta_n = \frac{\mu_n^2 D_\mathrm{c}}{r_\mathrm{c}^2} \tag{13}$$

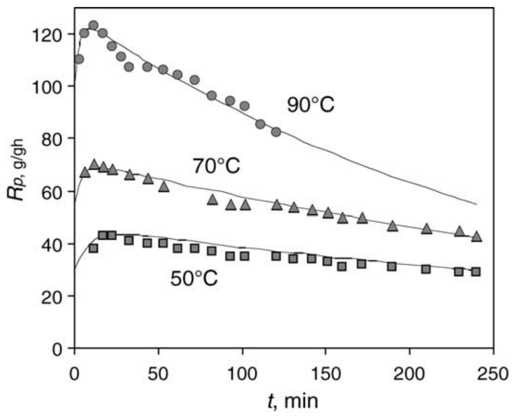


Fig. 5. Dynamics of propylene polymerization rate on catalyst $TiCl_3 + AlEt_2Cl$. Points: experiments of [5]; lines: model prediction (Eqs. (2) and (13)).

Systems (2) and (13) provides the qualitative and quantitative simulation of typical dynamics of polymerization rate [5] (Fig. 5) even with one root of characteristic equation (μ_1). For the catalytic system $TiCl_3$–DEAC, which was studied in [5], the parameters of model have been estimated from least-squares fits of the data, and the following values were found:

$$D_\mathrm{c} = (2\text{–}7) \times 10^{-17}\,\mathrm{cm^2/s\ at}\ d_\mathrm{c} = 0.01\,\mu\mathrm{m}, \quad \text{or}$$

$$D_\mathrm{c} = (2\text{–}7) \times 10^{-15}\,\mathrm{cm^2/s\ at}\ d_\mathrm{c} = 0.1\,\mu\mathrm{m},$$

$$k_\mathrm{A} = k_\mathrm{A}^1 C_\mathrm{A} = 0.04\text{–}0.08\,\mathrm{min^{-1}},$$

$$k_\mathrm{d} = k_\mathrm{d}^1 C_\mathrm{A} = (1.9\text{–}3.5) \times 10^{-3}\,\mathrm{min^{-1}}$$

The corresponding activation energies are presented in Fig. 6: $E_\mathrm{D} \approx 30$; $E_\mathrm{A} \approx 16$; $E_\mathrm{d} \approx 15$ kJ/mol. The activation energy of polymerization was found: $E_\mathrm{p} = 29$–32 kJ/mol.

The estimated diffusivity values are in agreement with rough estimation (Fig. 4) and are typical for ions diffusivity in solids. If the transient regime of polymerization is controlled by such a diffusion, then corresponding characteristic time ($\tau_\mathrm{d} = r_\mathrm{c}^2/D_\mathrm{c}$) is about 1–3 h, that is comparable with the residence time in slurry reactor.

Note that this model does not pretend to a complete description (and especially explanation) of complicated polymerization rate dynamics on Ziegler–Natta catalysts. It is

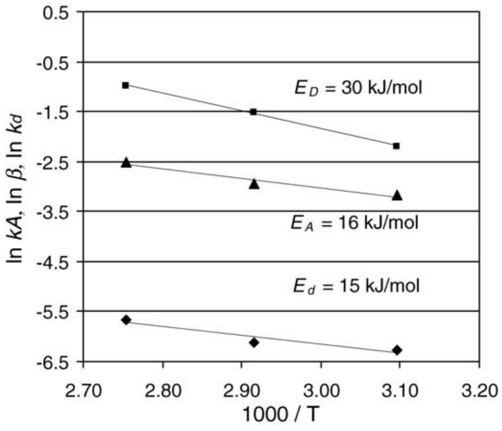


Fig. 6. Activation energies estimated by model.

only intended to draw attention to possible effects of chlorine mobility in titanium chlorides on this dynamics.

References

[1] E.J. Nagel, V.A. Kirillov, W.H. Ray, Ind. Eng. Chem. Prod. Des. Dev. 19 (1980) 372–379.

[2] J.A. Debbling, W.H. Ray, Ind. Eng. Chem. Res. 34 (1995) 3466–3480.

[3] V.B. Skomorokhov, V.A. Zakharov, V.A. Kirillov, Macromol. Chem. Phys. 197 (1996) 1615–1631.

[4] J.-S. Yoon, W.H. Ray, Ind. Eng. Chem. Res. 26 (1987) 415–422.

[5] K.Y. Choi, W.H. Ray, J. Appl. Polym. Sci. 30 (1985) 1065–1081.

[6] J. Ambrož, P. Osecký, J. Mejzlik, O. Hamřik, J. Polym. Sci. Part C 16 (1967) 423–430.

[7] E. Magni, F. Malizia, G.A. Somorjai, Polypropylene—Past, Present and Future: The Challenge Continuous, Montell Italia S.p.A., 1998, pp. 175–203.

[8] E. Magni, G.A. Somorjai, Surf. Sci. 345 (1996) 1–16.

[9] E. Magni, G.A. Somorjai, Surf. Sci. 377 (1997) 824–827.

[10] P. Kofstad, Nonstoichiometry Diffusion and Electrical Conductivity in Binary Metal Oxides, Wiley–Interscience, New York, 1972.

[11] O.Yu. Ovsicer, V.D. Sokolovskii, Catal. Lett. 8 (1991) 379–384; O.Yu. Ovsicer, V.D. Sokolovskii, Catal. Lett. 17 (1993) 239–244.

[12] A.D. Caunt, J. Polym. Sci. Part C 4 (1963) 49–69.

[13] V.A. Zakharov, G.D. Bukatov, Yu.I. Yermakov, Adv. Polym. Sci. 51 (1983) 61–100.

[14] S. Weber, J.C.W. Chien, Y. Hu, in: W. Kaminsky, H. Sinn (Eds.), Transition Metals and Organometallics in Olefin Polymerization, Springer Verlag, Berlin, 1988.

[15] N.G. Gaylord, H.F. Mark, Linear and Stereoregular Addition Polymers: Polymerization with Controlled Propagation, Interscience, New York, London, 1959.

[16] I. Kim, J.H. Kim, S.I. Woo, J. Appl. Polym. Sci. 39 (1990) 837–854.

[17] G.D. Bukatov, V.A. Zakharov, Macromol. Chem. Phys. 202 (2001) 2003–2009.