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Recent Data on the Number of Active Centers and Propagation Rate Constants in Olefin Polymerization with Supported ZN Catalysts

V.A. Zakharov, G.D. Bukatov, A.A. Barabanov*

Boreskov Institute of Catalysis, Novosibirsk, 630090, Russia
E-mail: v.a.zakharov@catalysis.nsk.su

Summary: Data on the number of active centers (Cp) and propagation rate constants (Kp) have been obtained by means of polymerization quenching with ^{14}CO of propylene and ethylene polymerization with supported titanium-magnesium catalysts (TMC) with different composition. In the case of propylene polymerization the Cp and Kp values have been measured separately for isospecific, aspecific and low stereospecific centers. Effects of $MgCl_2$ support, internal and external donors are discussed on the basis of data obtained.

Data on the strong effect of diffusion limitation at ethylene polymerization with number of TMC have been obtained and a set of methods have been used to exclude this effect. Data on Cp and Kp values at ethylene polymerization with low stereospecific and highly stereospecific catalysts are presented.

Keywords: active centers; polyethylene; polypropylene; stereospecificity; Ziegler-Natta polymerization

Introduction

In 1959 Prof. G. Natta published a brilliant survey on the kinetics of stereospecific polymerization of olefines[1]. The author presented systematic data on the kinetics of propylene polymerization with heterogeneous catalyst [$TiCl_3$ + $AlEt_3$] and analyzed the complex process of catalytic polymerization including the reactions of initiation, propagation and chain transfer with active centers which he defined as metalloorganic complexes on the surface of $TiCl_3$. The main parameters determining the catalyst activity are the number of active centers and propagation rate constant. Approaches and concepts formulated in this paper formed the basis for further kinetic studies of catalytic olefin polymerization.

In catalytic olefin polymerization the number of active centers usually accounts for a small part of the content of transition metal in the catalyst and depends on the catalyst preparation procedure, composition and polymerization conditions. Low concentration of active centers,

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their high reactivity and lability and involvement in side reactions hamper the task of evaluation of the active centers number. The method of polymerization inhibition by radioactive CO (^{14}CO)[2,3] and stopped flow method[4-6] are considered as the most efficient for direct determination of the number of active centers (C_p) and propagation rate constant (K_p).

The present work reports the data on Cp and Kp, obtained by the method of polymerization inhibition by ^{14}CO, for the ethylene and propylene polymerization with highly active supported ZN catalysts. The method differs by some peculiarities related to the conditions of polymerization, inhibition by ^{14}CO and subsequent removal of labeled by-products.[7, 8] The presence of hydrogen is a necessary condition for correct calculation of Kp in propylene polymerization, since without hydrogen a part of active centers fall into a dormant state.[8, 9] These details were taken into account in the present work.

Experimental

Microspherical $TiCl_3$ catalyst (26 wt.% of Ti, average particle size of 15μm) is a commercial sample. $TiCl_4/MgCl_2$ catalysts with different Ti content (0.1 and 2.1 wt.% of Ti) have been prepared by adsorbtion of $TiCl_4$ on highly dispersed $MgCl_2$ synthesized according to.[10] $TiCl_4/MgCl_2{\cdot}nD$ catalysts (2.5 wt.% of Ti) have been prepared according to Zakharov et al.[11] [D: dibutylphthalate (DBPh) or 2,2-diisobutyl-1,3-dimethoxypropane (DBDMP)].

The procedures of polymerization, Cp and Kp determination with ^{14}CO have been described by Bukatov et al.[8, 9]

Results and Discussion

1. Propylene polymerization

We have studied the effect of catalyst composition ($MgCl_2$ support, internal and external donors) on Cp and Kp values for propylene polymerization with $MgCl_2$-supported catalysts (titanium-magnesium catalysts - TMC). There are data on the different reactivity of aspecific and isospecific centers at propylene polymerization with TMC.[6,8] We believe it is important to obtain in more detail data on the effect of catalyst composition on the number of AC with different stereospecificity and Kp values for AC with different stereospecificity.

We have performed experiments with quenching of propylene polymerization by ^{14}CO using catalysts with different composition. PP obtained in these experiments have been fractionated to give three fractions:

- fraction soluble in boiling pentane (PP5 fraction – atactic PP)
- fraction soluble in boiling heptane (PP7 fraction – low stereoregular PP)
- fraction insoluble in boiling heptane (IPP fraction – isotactic PP).

Then we have measured Cp and Kp values for these separate fractions obtained from propylene polymerization over all catalysts studied. Data obtained on Cp and Kp values for polymerization in the presence of hydrogen are presented in Table 1. These data allow evaluation of the combined effect of Cp and Kp values on the relative yield of different PP fractions (Y_f) with different stereoregularities. The results obtained for different catalysts are presented in Figure 1 as areas calculated according to simple equation $Y_f = C^f p \times K^f p$ for corresponding fractions (f).

We have done additional polymerizations without hydrogen and we used Kp values, calculated in experiments with hydrogen (Kp^{+H}) and without hydrogen (Kp^{-H}) for estimation of the portion of dormant centers (P_d) formed at polymerization without hydrogen:

$$P_d (\%) = [1 - Kp^{-H} / Kp^{+H}] \times 100 \qquad (1)$$

These data are presented in Table 1.

1.1. Effect of $MgCl_2$ support on Cp and Kp values

Data on Cp and Kp values at propylene polymerization with $TiCl_3$ and supported $TiCl_4/MgCl_2$ catalyst (TMC-1) are presented in Table 1. The supported catalyst has the higher activity and lower stereospecificity. Data on Cp and Kp values allow the following conclusions to be made:

(i) the higher activity of $TiCl_4/MgCl_2$ catalyst in comparison with $TiCl_3$ is determined mainly by a higher total Cp value;

(ii) Kp values for isospecific centers (Kp for IPP fractions) are close for $TiCl_3$ and $TiCl_4/MgCl_2$ catalyst, indicating similar structures of isospecific active centers for both catalysts;

(iii) Kp(PP7) and Kp(PP5) values (low stereospecific and aspecific centers) for supported $TiCl_4/MgCl_2$ catalyst are higher than corresponding constants for $TiCl_3$ catalyst.

Table 1. Data on Cp and Kp values at propylene polymerization over catalysts with different composition (70°C, $AlEt_3$ as cocatalyst, $H_2/C_3H_6=0.15$)

		$TiCl_3$	$TiCl_4/MgCl_2$ (TMC-1)	$TiCl_4/MgCl_2 \cdot nDBPh$ (TMC-2)	$TiCl_4/MgCl_2 \cdot nDBDMP$ (TMC-3)	$TiCl_4/MgCl_2 \cdot nDBPh$ + DCPDMS[3] (TMC-4)
Rp[1], kg/g Ti·h·atm		1.6	16.8	26.0	25.7	37.2
Content of PP fractions, wt.%	PP5	17.1	43	10.6	3.1	1.9
	PP7	10.5	27	14.7	6.9	2.7
	IPP	72.4	30	74.7	90	95.4
Total Cp, mmol/mol Ti		2.34	11.5	23.3	18.4	21.6
Portion of Cp (%) in fractions:	PP5	45	50	41	25	14
	PP7	25	34	25	32	23
	IPP	30	16	34	43	63
Kp (L/mol·s) for fractions:	PP5	250	1230	280	170	220
	PP7	270	1120	660	300	190
	IPP	1580	2590	2480	2820	2560
Portion of dormant sites[2] (P_d,%) for fractions:	PP5	ca.0	53	43	71	85
	PP7	52	63	58	81	68
	IPP	60	47	73	84	72

[1] Polymerization rate at the moment of ^{14}CO addition. [2] At polymerization without hydrogen.
[3] DCPDMS-dicyclopentyldimethoxysilane as an external donor.

It means, probably, that the structures of weakly stereospecific and aspecific centers for $TiCl_4/MgCl_2$ catalyst differ from corresponding centers for $TiCl_3$ catalyst.

So the $MgCl_2$ support increases sharply the total number of AC and affects the structures and reactivity of weakly stereospecific and aspecific centers. The $MgCl_2$ support affects the yield of PP fractions with different stereoregularities via the combined effect of Cp and Kp values (Figure 1): the lower content of IPP fraction for the $TiCl_4/MgCl_2$ catalyst in comparison with $TiCl_3$ is determined by a lower portion of isospecific AC and higher Kp values for PP7 and PP5 fractions.

1.2. Effect of internal donors on Cp and Kp values at polymerization with TMC

Data on effect of internal donors (DBPh and DBDMP in composition of TMC) on Cp and Kp values are presented in Table 1 (catalysts TMC-1, TMC-2 and TMC-3).

Catalysts TMC-2 and TMC-3 with internal donors (ID) have the higher activity, higher total Cp values and higher content of IPP fraction in comparison with TMC-1 catalyst. But the procedures for preparation of TMC-2 and TMC-3 catalysts differ greatly from the procedure for the TMC-1 catalyst. We suppose the total Cp value increases for TMC-2 and TMC-3 catalysts by way of affect on the morphology of catalysts (higher surface area) on the stage of catalyst preparation. The direct and most important effect of ID is the increase of the portion of isospecific centers [Cp(IPP)] from 16% for TMC-1 catalyst up to 34 and 43 % for TMC-2 and TMC-3 catalysts respectively.

Internal donors don't affect Kp values for isospecific centers. There is a rather unexpected effect of ID on Kp values for aspecific and low stereospecific AC: addition of ID into TMC gives a decrease of Kp values for PP7 and PP5 fractions.

Finally we can conclude on the combined effect of Cp and Kp values on the stereospecificity of TMC with internal donors: the yield of IPP fraction increases mainly by way of increase of the portion of isospecific centers and a decrease of Kp values for PP7 and PP5 fractions (Figure 1).

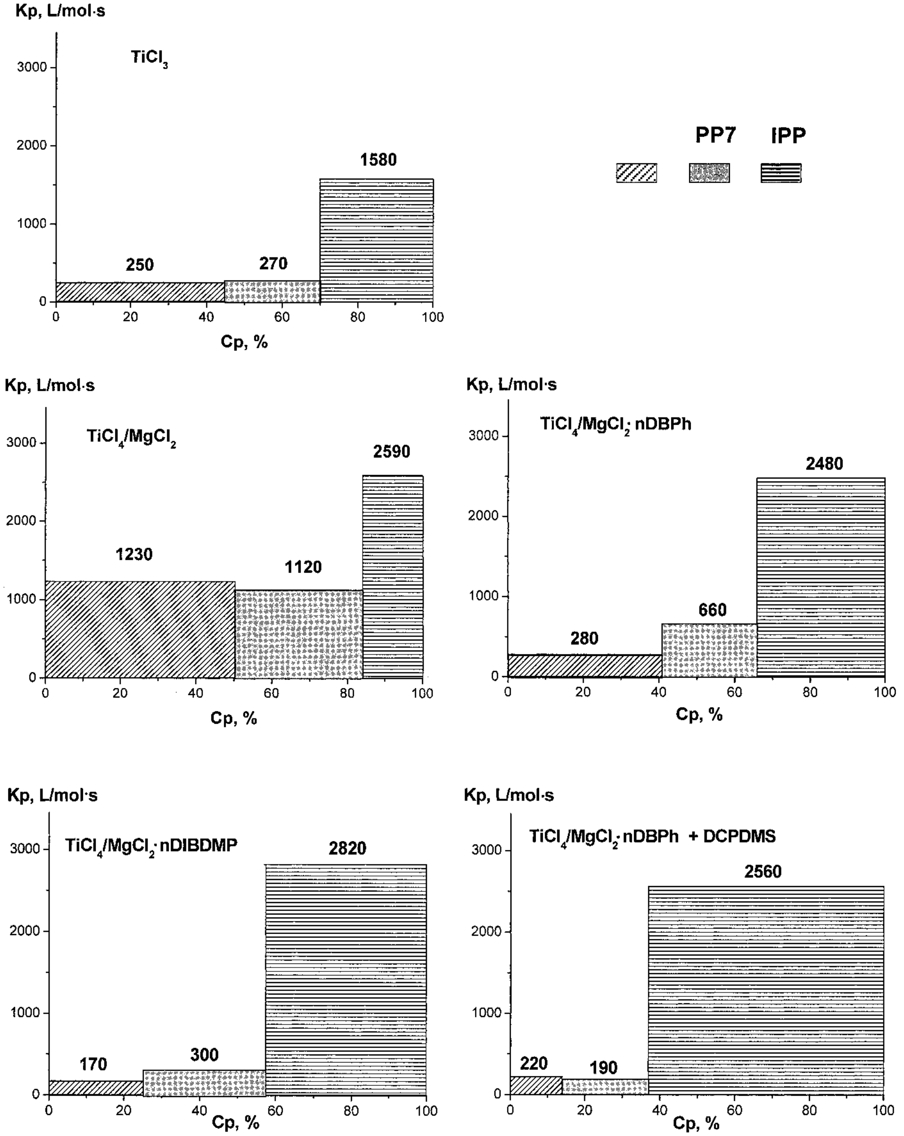

Figure 1. Relative yield of PP fractions with different stereoregularity as combined effect of C_P and K_P values for catalysts with various compositions

1.3. Effect of external donors on Cp and Kp values at polymerization with TMC

Data on the effect of external donor (DCPDMS), added into polymerization with catalyst $TiCl_4/MgCl_2 \cdot nDBPh$ (TMC-2), on Cp and Kp values are presented in Table 1. Addition of ED leads to the increase of activity and stereospecificity. External donor doesn't affect the total Cp value but increases the portion of isospecific centers from 34% up to 63% and decreases the portion of aspecific AC from 41% to 14%. We believe these results evidence the transformation of aspecific centers into isospecific AC by adsorbtion of ED on the catalyst surface.

External donor doesn't affect Kp values for isospecific centers (IPP fraction) but decreases the Kp value for PP7 fraction.

We can conclude on the combined effect of Cp and Kp values on the activity and stereospecificity of TMC with external donor:

(i) activity increases because of the increase of the portion of Cp(IPP) with higher Kp value;

(ii) stereospecificity increases because of the increase of the portion of Cp(IPP) and the decrease of the Kp(PP7) value (Figure 1).

The possible structures of isospecific, low stereospecific and aspecific centers are discussed in literature.[5,6,12]

2. Ethylene polymerization

As we have shown above the isospecific and aspecific centers have different reactivity (Kp values) in propylene polymerization. It is interesting to obtain data on Cp and Kp values at ethylene polymerization using weakly and highly stereospecific catalysts. We have selected for this study the following catalysts:

(1) $TiCl_4/MgCl_2$ catalyst with low content of titanium (0.1wt.% of Ti). This catalyst produces PP with a very low content of IPP fraction (10 wt.%) and contains ca. 95% of weakly strereospecific and aspecific AC.

(2) Catalyst $TiCl_4/MgCl_2 \cdot nDBPh$ + ED (ED: propyltrimethoxysilane). This catalyst produces mainly isotactic PP (96% of IPP fraction) and contains ca. 63% of isospecific AC.

But we have found that TMC with composition $TiCl_4/MgCl_2 \cdot nDBPh$ prepared for stereospecific propylene polymerization according to Ref. [11] have a very low activity in ethylene polymerization. Later we have found that activity of these catalysts at ethylene polymerization depends on porosity of catalysts. As an example data on activity at ethylene and propylene polymerization are shown in Table 2 for two catalyst samples with different porosity. These catalyst samples have a similar high activity in propylene polymerization but their activity differs greatly in ethylene polymerization. Catalyst (II) with higher porosity has much higher activity (Table 2). We propose that diffusion limitation is the possible reason of low activity in ethylene polymerization for catalysts with dense particles (with low porosity).

Table 2. Activity of catalysts $TiCl_4/MgCl_2 \cdot nDBPh$ with different porosity at ethylene and propylene polymerization (70°C, $AlEt_3$ as cocatalyst, PTMS[1])

Catalyst	Porosity	Rp kg PE/g cat·h·atm	Rp kg PP/g cat·h·atm
I	Low	0.13	0.95
II	High	0.73	0.70

[1] PTMS: propyltrimethoxysilane as an ED

The effect of diffusion limitations on the catalyst activity could be evaluated by the analysis of polymerization kinetics with catalysts differing by particle size. It is well known that as the size of catalyst particles increases, the effect of diffusion limitations on the catalyst activity becomes stronger. If polymerization proceeds within diffusion region, the propagation rate and calculated Kp values decrease with increasing catalyst particle size. For slurry polymerization, the effect of catalyst particle size on the Kp value may be estimated based on the analysis of various polymer fractions with different particle size. This approach is based on a replication phenomenon, which involves a close relationship between the catalyst particle size and the final polymer particle size. Table 3 presents the results of two experiments with the catalysts of different compositions. After polymerization inhibition by ^{14}CO, the PE powders obtained in these experiments were sieved into separate fractions and the Cp and Kp values were calculated for each fraction. It is seen that the Kp value for catalyst I depends on particle size and dramatically increases with decreasing particle size. Obviously, the low average Kp value for catalyst I ($2.3 \cdot 10^3$ L/mol·s) is dictated by diffusion restrictions in ethylene polymerization with this catalyst. The calculated Kp value for catalyst II does not depend on particle size, that is, ethylene polymerization on catalyst II proceeds in kinetic region.

An efficient method to diminish or avoid diffusion restrictions consists of a low-temperature prepolymerization at low monomer pressure. We found that the activity of catalyst $TiCl_4/MgCl_2 \cdot nDBPh$ in ethylene polymerization increased sharply after prepolymerization with propylene at 40°C. Table 4 illustrates the effect of prepolymerization on the catalyst activity and calculated Cp and Kp values. It is seen that prepolymerization causes sharp increases in both the activity and the Kp value. It seems reasonable to assume that in this case the calculated Kp ($1.2 \cdot 10^4$ L/mol·s) is close to the real Kp value.

Table 3. Ethylene polymerization over TMC with different composition: effect of particle size on Kp values (70°C, $AlEt_3$ as cocatalyst)

	(I) $TiCl_4/MgCl_2 \cdot nDBPh$ (2.3% Ti)	(II) $TiCl_4/MgCl_2$ (0.1%)
Activity, kg/g cat·h·atm	0.47	0.25
kg/g Ti·h·atm	20	250
Total Cp, mol/mol Ti	0.07	0.18
$Kp \cdot 10^{-3}$, L/mol·s:		
- for total PE	2.4	11.5
- for fraction of 1-2mm*)	1.8	12.0
- for fraction of 0.09-0.25mm*)	8.4	11.3

*) PE powders have been separated by means of sieves on fractions with different particle size

Table 4. Ethylene polymerization over TMC with composition $TiCl_4/MgCl_2 \cdot nDBPh$: effect of prepolymerization on the activity, Cp and Kp values (70°C, $AlEt_3$, DCPDMS as ED)

Exp. No.	Prepolymerization with C_3H_6 at 40°C	Rp kg/g cat·h·atm	Cp mol/mol Ti	Kp L/mol·s
1	-	0.11	0.043	900
2	+	2.3	0.063	12100

Finally we can compare data on Kp values at ethylene polymerization for weakly and highly stereospecific catalysts (Table 5). We can conclude there are no noticeable differences for Kp values in ethylene polymerization on stereospecific and nonstereospecific active centers.

Table 5. Data on Cp and Kp values at ethylene polymerization over TMC with different stereospecificity (70°C, $AlEt_3$)

Catalyst	Content of IPP fraction[1] wt.%	Portion of Cp(IPP)[1] %	Rp kg/g Ti·h·atm	Cp mol/mol Ti	Kp L/mol·s
$TiCl_4/MgCl_2$ (0.1% Ti)	10	5	250	0.18	11500
$TiCl_4/MgCl_2 \cdot nDBPh$ + DCPDMS	96	63	100[2]	0.063	12100

[1] At propylene polymerization
[2] Prepolymerization with propylene at 40°C

Conclusion

In the absence of donors, a $TiCl_4/MgCl_2$ catalyst has a much higher active center content but a lower proportion of isospecific centers than $TiCl_3$ catalyst. Internal and external donors increase the portion of isospecific centers, and decrease Kp values for aspecific and weakly stereospecific centers. Kp values for isospecific centers are higher than for aspecific centers in propylene polymerization with all catalysts studied.

Experimental data on the strong effect of diffusion limitations in ethylene polymerization with a number of TMC have been obtained and a set of methods has been used to exclude this effect. It was found that Kp values at ethylene polymerization on isospecific and nonstereospecific active centers are close.

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