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Kinetic features of ethylene polymerization over titanium-magnesium Ziegler-Natta catalysts: Effect of monomer concentration on the number of active centers and propagation rate constant

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ABSTRACT

It was found that the observed order of the polymerization rate with respect to ethylene concentration at ethylene polymerization over two titanium-magnesium catalysts of different compositions is significantly higher than 1 (1.6–2.1). The data on the effect of ethylene concentration on the number of active centers (C_P) and the propagation rate constant (k_P) at ethylene polymerization over these catalysts were obtained by method of polymerization quenching with ^{14}CO. An increase in ethylene concentration was found to increase the number of active centers. In some cases the increase of ethylene concentration proceeds to the narrowing of the molecular weight distribution of the resulting polyethylene and an increase in the calculated value of propagation rate constant. These effects were shown to be most pronounced at low ethylene pressure and increased concentration of an activator ($AlEt_3$). Based on the experimental data, we proposed a scheme of reactions to explain the effects of ethylene and AlR_3 concentrations on the number of active centers, the average values of propagation rate constant and molecular weight distribution of polymers produced over these multi-site catalysts.

1. Introduction

Studying the kinetics of olefin polymerization over modern highly active supported titanium-magnesium catalysts (TMC) is an important step towards understanding the mechanism of action of these systems. A number of reviews have been devoted to the analysis of the kinetic features of olefin polymerization over Ziegler-Natta catalysts [1–6]. However, some kinetic findings remain uninterpreted because of the versatility of the catalysts of this type, complex composition of the active component, several types of active centers, and changes they undergo during polymerization. In particular, dependence of the polymerization rate on monomer concentration is a key feature of polymerization. According to the two-stage mechanism of the propagation reaction at catalytic polymerization proposed by Cossee [7], the propagation rate can be linearly dependent on monomer concentration and described by the first-order equation. Indeed, these dependences were observed in a large number of studies devoted to olefin polymerization over different catalysts [1–6]. However, some studies showed that a mixed (between the first and second) order of the polymerization rate with respect to ethylene is observed at low ethylene pressure [8–12].

Several hypotheses have been proposed to interpret this effect. Thus, Ystenes proposed the so-called “trigger” mechanism of the propagation reaction suggesting that an ethylene molecule coordinated on titanium ion at the titanium–polymer bond is inserted when the active center interacts with the second ethylene molecule [13,14]. The features of the “trigger” mechanism were also discussed by other authors [9,15–17].

A number of studies suggested that the observed second order of the polymerization rate with respect to monomer is due to the presence of a slow initiation stage, which occurs when a monomer interacts with the precursor of active centers containing the titanium–alkyl bond [18–20]. Resconi et al. suggested that the centers with different reactivities with respect to monomer may differ in conformation of the growing polymer chain (agostic interactions of β- and γ-hydrogen and titanium atom) [21,22].

The assumptions in the existing literature regarding the reasons for the observed shift in the order of the polymerization rate with respect to monomer (from the first towards the second order) are

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insufficiently substantiated by the experimental data. In this work, we experimentally studied the effect of ethylene concentration on the number of active centers (C_P) and the propagation rate constant (k_P) at ethylene polymerization over modern highly active TMC designed in our laboratory. The data on the effect of ethylene concentration on these kinetic parameters were obtained for the first time; these data provide better supported explanation for the shift in the order of the polymerization rate with respect to monomer from the first towards the second order. When analyzing the data on the effect of ethylene concentration on the calculated k_P value, we additionally used the experimental findings on the effect of ethylene concentration on the molecular weight distribution of the resulting polymer. Based on the experimental data, we proposed a scheme of the reactions occurring upon formation and transformation of active centers at polymerization. This scheme explains the nonlinear dependence of the polymerization rate on monomer concentration and formation of dormant sites, whose number depends on concentration of ethylene and organoaluminum activator.

2. Experimental

2.1. Catalysts

The support of TMC-1 catalyst (S-1) was prepared by interaction of $PhSiCl_3$ with organomagnesium compound $Mg_3Ph_4Cl_2$ dissolved in diisoamyl ether [23]. The support for TMC-2 catalyst (S-2) was synthesized by interaction of the organomagnesium compound $Mg_3Ph_4Cl_2$ solution in dibutyl ether with the mixture of $PhSiCl_3$ and $Si(OEt)_4$ [24]. Support S-2 was additionally treated with a solution of diethylaluminum chloride in heptane at 40 °C and molar ratio Al/Mg = 1.5 and then washed with CCl_4 to convert adsorbed $AlEt_2Cl$ into $AlCl_3$.

The catalyst TMC-1 was synthesized by supporting titanium tetrachloride on magnesium chloride support S-1 at 60 °C and molar ratio $TiCl_4$/Mg = 1. The catalyst TMC-2 was prepared by deposition of calculated amount of titanium tetrachloride on magnesium-containing support S-2 modified by $AlCl_3$. For the catalysts TMC-1 and TMC-2, the titanium content (determined by AES-ICP) was equal to 1.0 and 0.12 wt. %, correspondingly. The obtained catalysts had a spherical shape with the average particle size of 5–6 μm and a narrow particle size distribution.

2.2. Ethylene polymerization

The polymerization runs were performed in a steel 0.5 L reactor. A sealed glass ampoule with suspension of a catalyst in heptane (5–8 mg) was placed into the reactor. The reactor was heated at 80 °C under vacuum for 1.5 h and cooled to 20 °C. Then the reactor was filled with 150 mL of heptane and 2-4 mL of $AlEt_3$ solution in heptane ($[AlEt_3]$ in the reactor was 4.5–9.0 mmol/L). The reaction mixture was heated to the desired temperature (80 °C) and saturated with ethylene (0.5–4.0 bar). The reaction was started by breaking an ampoule with the catalyst. During polymerization, the ethylene pressure was maintained constant through an automatic computer-controlled system for the ethylene feed; the ethylene consumption to the reaction medium was measured a few seconds apart. The temperature in the reactor was permanently measured by a thermocell and kept constant through water-jacket cooling. After a prescribed time, the reactor was vented, and the obtained solid product was separated and then dried under ambient conditions to the constant weight. The polymerization rate was calculated according to ethylene consumption taking into account the weight of the obtained polymer.

2.3. Determination of the number of active centers (C_P) and the propagation rate constant (k_P)

Polymerization quenching by ^{14}CO was used to determine the C_P and k_P values. We used this method earlier to study ethylene and propylene polymerization over traditional Ziegler-Natta catalysts ($TiCl_3/AlEt_3$) [25–27] and supported titanium-magnesium [28–31] catalysts. The detailed description of the method of polymerization quenching by ^{14}CO is given in refs.[32–35] Most studies involving this method were conducted when studying propylene polymerization [28–31,35,36]. There are much fewer data on determining the C_P and k_P values at ethylene polymerization [30,31,37].

The conditions used for polymerization quenching (the amount of ^{14}CO and duration of quenching (τ_{CO})) were the same as those used earlier [28,35] for TMC: $^{14}CO/Ti = 15–20$, $\tau_{CO} = 15$ min. The polymer samples were purified from the labeled by-products by double reprecipitation from undecane using the procedure described in ref. [35].

An Intertechnique SL-4000 scintillation counter was used to measure polymer radioactivity. The number of active centers (C_P) was determined based on radioactivity of PE. The propagation rate constant (k_P) was calculated from Eq. (1)

$$k_P = R \times C_P^{-1} \times [C_2H_4]^{-1} \quad (1)$$

where R is the polymerization rate at the moment of ^{14}CO introduction and $[C_2H_4]$ is the ethylene concentration in heptane, which was calculated using the Henry's constant [38].

2.4. Polymers characterization

GPC measurements were performed using a PL 220 C instrument with RI and DV detectors. Run conditions were as follows: 160 °C; 1,2,4-trichlorobenzene (TCB) was used as a solvent at a flow rate of 1 $cm^3\ min^{-1}$. A set of Olexis-gel columns was employed. Calibration was performed using PS and PE standards with narrow MWD.

Viscosity (η) of the polymers was measured in decalin at 135 °C on an Ubbelohde viscosimeter. The viscosity average molecular weight M_v was calculated according to the Mark–Houwink equation:

$$M_v = \eta \times K^{-1} \times \alpha^{-1}, \quad (2)$$

where the Mark–Hauwink coefficients are $K = 67.7 \times 10^{-5}$ and $\alpha = 0.67$ [39].

3. Results and discussion

3.1. Effect of monomer concentration on the C_P and k_P values and molecular-weight characteristics of the resulting polyethylene

Table 1 list the data on C_P and k_P values for ethylene polymerization at different monomer pressures (in the range of 0.5–4 bar) for TMC-1 and TMC-2 catalysts. Fig. 1 shows the kinetic profile of the polymerization rate in these experiments. Let us mention that TMC-1 and TMC-2 catalysts differ in the way they were prepared, support composition, and content of the active component (titanium). In particular, TMC-2 catalyst contains OEt moieties and has a very low titanium content (0.12 wt. %). This catalyst is characterized by a significantly higher activity per one atom of titanium [40] compared with TMC-1 catalyst and produces polyethylene with a lower molecular weight (compare data on molecular weight of polymers in runs 2 and 6 in Table 1). Having plotted the dependence of the polymerization rate on monomer concentration at the moment of ^{14}CO introduction (when the steady-state rate is achieved) in rectifying coordinates, we determined the order of the polymerization rate with respect to monomer (n value), which is higher than 1 for