

Active sites concentration in ethylene homo- and co-polymerization with 1-hexene using the highly active $\text{TiCl}_4/\text{MgH}_2\text{-AlEt}_3$ catalyst system

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Abstract

The determination of active centres concentration, $[\text{C}^*]$, by the ^{14}CO radio-labelling technique in ethylene homopolymerization and copolymerization with 1-hexene using various $\text{TiCl}_4/\text{MgH}_2$ catalysts of different Ti contents and surface areas is discussed. The effects of 1-hexene/ethylene, AlEt_3/Ti mole ratios, the polymerization time and the polymerization temperature on $[\text{C}^*]$ are reported. At the same polymerization conditions the activity in copolymerization is higher; however, $[\text{C}^*]$ in homo- and in copolymerization are found to be more or less the same. For a low Ti-content catalyst, the addition of a small amount of 1-hexene results in a two- to threefold increase in the rate of ethylene consumption relative to a homopolymerization run. Such an increase in the rate of polymerization is not observed for a high Ti-content catalyst. Interestingly, $[\text{C}^*]$ determinations reveal that, for either the low or high Ti-content catalyst, $[\text{C}^*]$ in homo- and in co-polymerization are more or less the same. The effect of the polymerization temperature on $[\text{C}^*]$ for both homo- and co-polymerization is also reported and the activation and propagation energies for the catalytic system under investigation are estimated.

Keywords: Active sites concentration; $[\text{AlEt}_3]$; Copolymerization; Ethylene; 1-Hexene; Homopolyethylene; Polymerization time; Ziegler catalyst

1. Introduction

This paper discusses the effect of Ti content and the surface area of various $\text{TiCl}_4/\text{MgH}_2$ catalysts on the activity and active centres concentration in ethylene homopolymerization [1] and ethylene/1-hexene copolymerization [2]. Furthermore, this article also reports on the influence of the AlEt_3/Ti molar ratio [3], temperature [4] and

polymerization time on the active centres concentration.

In olefin polymerization, it is normally observed that the addition of small amounts of comonomer, e.g., 1-hexene, to an ethylene polymerization system results in an increase in the ethylene consumption rate in comparison to a homopolyethylene run. The reason for this has been interpreted in terms of chemical effects [5,6], e.g., number and type of active sites, or in terms of physical effects [7–9], e.g., catalyst particle fragmentation and diffusion phenomena. Tait et al. [5] have stated that both chemical and phys-

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ical factors may be operating in these catalytic systems, and that no single explanation may be adequate to account for the observed behaviour of a variety of different polymerization systems.

The data in the literature on the effect of the type and the concentration of the alkylaluminium compound on the kinetics of olefin polymerization is difficult to generalize because different materials and catalytic systems have been used [10]. However, it is generally observed that there is a continual increase in the polymerization rate upon increasing the alkylaluminium concentration in the low region. As the alkylaluminium concentration is increased further it is often observed that the polymerization rate decays rapidly which can be explained by adsorption [11,12] and reduction reactions [13,14].

Studies on the effect of varying the reaction temperature on the catalytic activity and on $[C^*]$ in olefin polymerizations are very scarce. This article also discusses our new findings on the variation of $[C^*]$ in ethylene/1-hexene copolymerization compared to $[C^*]$ in ethylene homopolymerization in dependence of the reaction temperature.

2. Experimental

The experimental procedure, materials, catalysts and techniques for active centre determination using the ^{14}C radio-tagging method have been detailed previously [15]. The oxygen-flask method used for the measurement of the polymers radioactivity has been described in ref. [2]. For some homopolymerization runs the values of $[C^*]$ were obtained at an earlier stage of this work and were evaluated using the radioactivity values obtained from the gel method [15], these $[C^*]$ could be slightly higher since, as will be shown, it is found that oxygen-flask method yields slightly higher $[C^*]$. Homo- and co-polymerizations of ethylene with 1-hexene were carried out in a slurry reactor at temperatures in the range 20–80°C and an ethylene pressure of 2 atm. AlEt_3/Ti molar ratios employed were in the range 20–80.

3. Results and discussion

3.1. Effect of the Ti content and catalyst surface area on the activity and $[C^*]$

The variation of the polymerization activity with the titanium content and the surface area for the various $\text{TiCl}_4/\text{MgH}_2$ catalysts used is shown in Fig. 1. By almost doubling the titanium amount on the support, the surface area decreased by a factor of three, whereas the overall polymerization activity was reduced by a factor of about ten. Active centres determinations for the catalysts studied show that the reason for the dramatic reduction in the overall polymerization activity is the sharp reduction in $[C^*]$, Fig. 2, and not to a change in the value of the propagation rate constant, (k_p for these polymerizations varied only in the range 230–300 $1/(\text{mol}\cdot\text{s})$ [1]. Figs. 1 and 2 emphasize without doubt that there exists a direct relationship between four parameters: namely, Ti

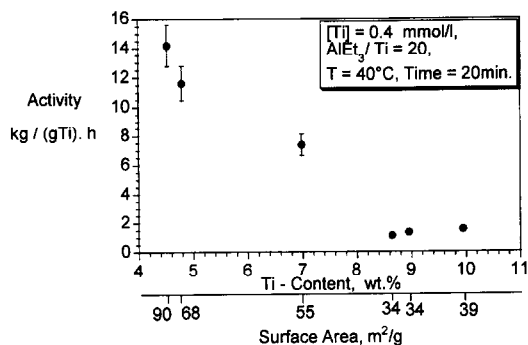


Fig. 1. Variation of the polymerization activity with the Ti content and the surface area of various $\text{TiCl}_4/\text{MgH}_2$ supported catalysts.

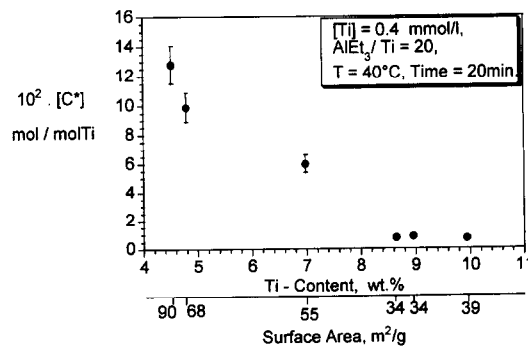


Fig. 2. Variation of $[C^*]$ with the Ti content and the surface area of various $\text{TiCl}_4/\text{MgH}_2$ supported catalysts. $[C^*]$ determined using the gel method. Conditions as in Fig. 1.

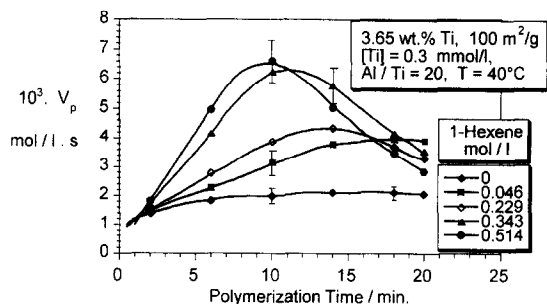


Fig. 3. Rate-time profiles in ethylene homopolymerization and C_2/C_6 copolymerization using the 3.65 wt.% Ti catalyst. The effect of [1-hexene] on the ethylene consumption rate.

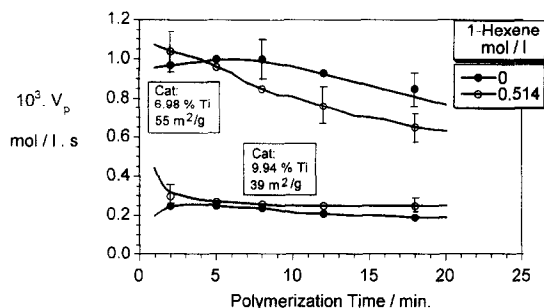


Fig. 4. Rate-time profiles in ethylene homopolymerization and C_2/C_6 copolymerization using the 6.98 or the 9.94 wt.% Ti catalysts. The effect of [1-hexene] on the ethylene consumption rate. Polymerization conditions as in Fig. 3.

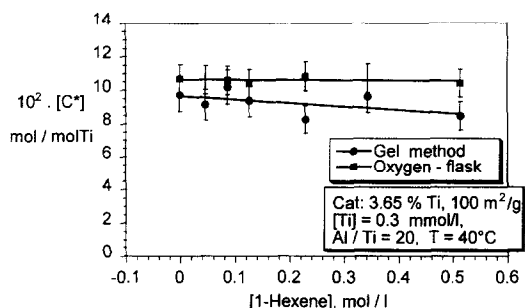


Fig. 5. Variation of $[C^*]$ independence of [1-hexene]. C_2/C_6 copolymerization using the 3.65 wt.% Ti catalyst. $[C^*]$ determined by the gel or the oxygen-flask method.

content, surface area, polymerization activity and active centres concentration. For the $TiCl_4/MgH_2$ catalyst system, it is evident that increasing the titanium content on the support results in reducing the surface area, the polymerization activity and $[C^*]$. It has been emphasized earlier that the reason for the reduction in $[C^*]$ with increasing titanium content is due to decreasing the ethylene homopolymerization centres [2].

3.2. C_2/C_6 copolymerization using various Ti contents and surface areas catalysts

The rate-time profiles obtained for ethylene consumption in homopolymerization and C_2/C_6 copolymerization using a $TiCl_4/MgH_2$ catalyst of 3.65 wt.% Ti, are presented in Fig. 3. At low initial 1-hexene concentration the rate of ethylene consumption is higher than that in homopolymerization and is of an acceleration type. The higher the initial 1-hexene concentration the higher is the initial rate of ethylene consumption; however, the rate-time profile is now characterized by a gradual increase followed by a rapid decay. In comparison to a homopolymerization run, it is apparent that the maximum rate of ethylene consumption in copolymerization increases by a factor of about three at an initial 1-hexene concentration of 0.514 mol/l. In contrast, when using $TiCl_4/MgH_2$ catalysts of more than 6 wt.% Ti, the rate-time profiles, Fig. 4, show that there is no increase in the rate of ethylene consumption as a result of the comonomer addition.

In order to explain the observations in Figs. 3 and 4, $[C^*]$ were determined. Employing the scintillation technique, $[C^*]$ values were initially determined using the radioactivity values using the gel technique [15]. However, it was found out that $[C^*]$ in copolymerization are not higher than in homopolymerization as is shown in Figs. 5 and 6. In order to make sure that the radioactivity values and consequently $[C^*]$ were valid, the oxygen-flask method was used to determine the

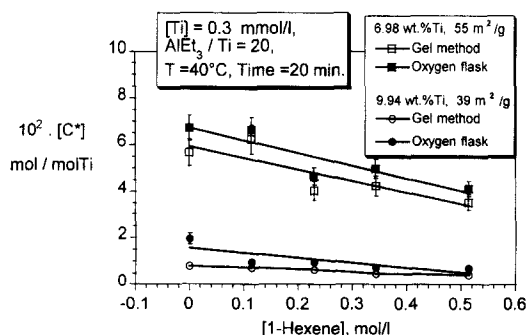


Fig. 6. Variation of $[C^*]$ independence of [1-hexene]. C_2/C_6 copolymerization using the 6.98 or the 9.94 wt.% Ti catalysts. $[C^*]$ determined by the gel or the oxygen-flask method.

radioactivity values [2]. Employing the gel method, the polymer is frozen and ground to a fine powder in liquid N_2 , then about 0.03–0.05 g are mixed with a very viscous scintillation gel. However, using the oxygen-flask method about 0.05 g of the polymer are burned in oxygen and the liberated CO_2 is absorbed in a basic solution. Afterwards, the radioactivity of either the viscous gel or the basic solution are measured using the scintillation counting technique [15].

The results obtained using the gel or the oxygen-flask method are shown in Figs. 5 and 6. Fig. 5. shows a comparison of $[C^*]$ determined using a catalyst of 3.65 wt.% Ti; whereas Fig. 6. shows the variation of $[C^*]$ for higher Ti-content catalysts, 6.98 and 9.94 wt.% Ti. It is clear that the oxygen-flask method gives higher $[C^*]$ when compared to the gel method. This emphasizes that the oxygen-flask method is a better technique for radioactivity measurements because of the more homogeneous scintillation medium in comparison to the gel method whereby a fine polymer powder and a viscous liquid are combined.

The results reported in the present article show distinct phenomena. Firstly, in spite of the differences in the rate of ethylene consumption observed in the homo- and co-polymerization, it is found that whether or not there is an increase in the rate of ethylene consumption as a result of 1-hexene addition, the $[C^*]$ either remain constant or tend to decrease. Secondly, the lower the Ti content on the catalyst surface the higher is the ethylene consumption rate and the higher is the concentration of the ethylene polymerization centres. Furthermore, only with the low Ti-content catalyst is an enhancement in the rate of ethylene consumption observed upon the addition of 1-hexene comonomer.

The reason for this behaviour has been explained in terms of different types of active centres on the various $TiCl_4/MgH_2$ catalysts. It has been emphasized that a low Ti-content $TiCl_4/MgH_2$ catalyst possesses mainly ethylene homopolymerization centres. Upon increasing the Ti content, the number of active centres for ethylene homopolymerization decreases and the polymer-

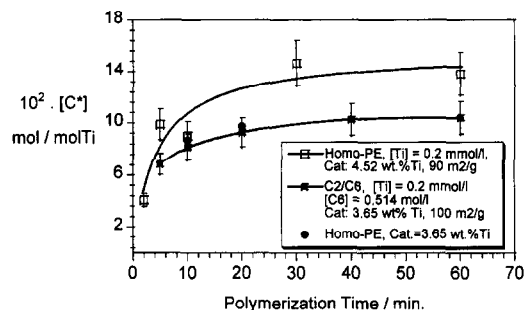


Fig. 7. Effect of varying the polymerization time on $[C^*]$ in homopolymerization and C_2/C_6 copolymerization. $[C^*]$ determined by the gel in homopolymerization and by the oxygen-flask method in C_2/C_6 copolymerization.

ization centres are now more suitable for copolymerization [2].

3.3. Effect of the polymerization time on $[C^*]$

The variation of $[C^*]$ in dependence of the polymerization time in homo- and co-polymerization is shown in Fig. 7. In homopolymerization there seems to be an increase in $[C^*]$ at the very early stage of polymerization, between 2 to 10 min, beyond which $[C^*]$ is more or less constant. In copolymerization, $[C^*]$ varied only between 7 to 10% mol/mol Ti. These results indicate that in homo- and in co-polymerization the concentration of active centres is more or less constant with the polymerization time. Similar observation in propylene homopolymerization has been reported earlier [16]. The decay in the polymerization rate, (e.g., Fig. 3.), with time could be therefore due to the continuous build up of polymer around the active centres thus making it more difficult for ethylene to diffuse to the active polymerization centres. The difference in $[C^*]$ between the homo- and the co-polymerization cases could be due to the use of different $TiCl_4/MgH_2$ catalysts of slightly different Ti contents and surface areas. When the same catalyst is used, $[C^*]$ for a homopolymerization run is basically the same as for a copolymerization run, (Fig. 7. runs performed for 10 min polymerization time using the 3.65 wt.% Ti catalyst). This emphasizes again that for the $TiCl_4/MgH_2$ catalyst system there is no increase

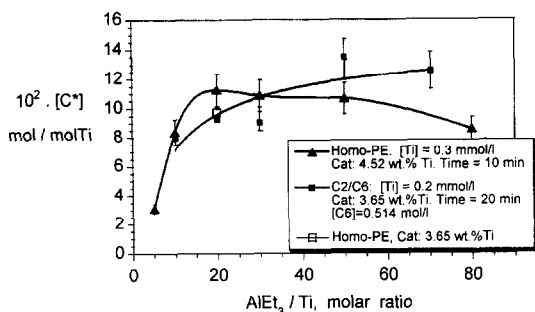


Fig. 8. Effect of varying the $[AlEt_3]$ on $[C^*]$ in homopolymerization and C_2/C_6 copolymerization. $[C^*]$ determined by the gel method in homopolymerization and by the oxygen-flask method in C_2/C_6 copolymerization.

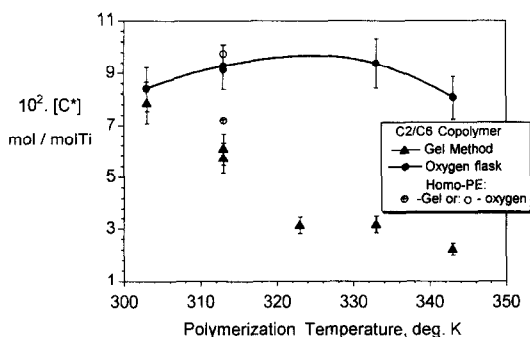


Fig. 9. Effect of varying the polymerization temperature on $[C^*]$ in homopolymerization and C_2/C_6 copolymerization. Gel vs. oxygen-flask method for $[C^*]$ determination. Conditions as in Fig. 10.

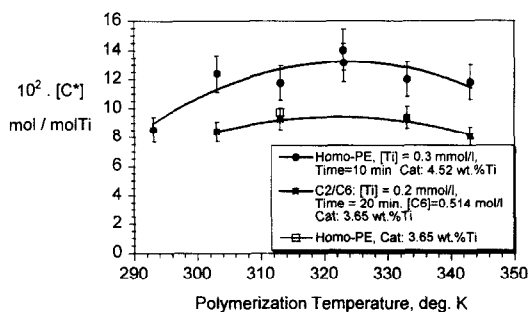


Fig. 10. Effect of varying the polymerization temperature on $[C^*]$ in homopolymerization and C_2/C_6 copolymerization. $[C^*]$ determined by the gel in homopolymerization and by the oxygen-flask method in C_2/C_6 copolymerization.

in $[C^*]$ in copolymerization when compared to a homopolymerization run.

3.4. Effect of the $AlEt_3/Ti$ mole ratio on $[C^*]$

The variation of $[C^*]$ with varying the $AlEt_3/Ti$ mole ratio, in homo- and in co-polymerization, is presented in Fig. 8. The plot of $[C^*]$ against

the $AlEt_3/Ti$ mole ratio in homopolymerization shows an $AlEt_3$ -isotherm type of curve. The concentration of active centres reach more or less a limiting value above an $AlEt_3/Ti$ molar ratio of 20 in homopolymerization and about 50 in the case of copolymerization. This finding confirms the $AlEt_3$ -isotherm type of curve for $[C^*]$ in both the homopolymerization of ethylene and copolymerization with 1-hexene. In copolymerizations, there are two noteworthy observations. Firstly, the maximum number of active centres is generated when the $AlEt_3/Ti$ mole ratio is about 50. Secondly, although there is an increase in the polymerization rate [3], still $[C^*]$ did not increase in copolymerization when compared to a homopolymerization run. In accordance with a previous publication [2], the active centres on the low Ti-content catalyst of 3.65 wt.% Ti are mainly homopolymerization centres. Therefore, the observed increase in the polymerization rate without an increase in $[C^*]$ can be attributed to a diffusion phenomenon. In other words, the incorporation of the 1-hexene molecules in the polymer chain leads to a less crystalline polymer and therefore increases the diffusivity of ethylene to the active centre.

3.5. Effect of temperature on $[C^*]$

The variation of $[C^*]$ in C_2/C_6 copolymerization within the temperature range of 303 to 343 K is shown in Fig. 9. The active centres concentration determined using the oxygen-flask method yields a higher concentration of active centres when compared to the gel method. This confirms again that the oxygen-flask method is a better technique for radioactivity measurements when compared to the gel method. The dependence of $[C^*]$ on temperature in both homo- and co-polymerization of ethylene is shown in Fig. 10. In both cases, the variation in the reactor temperature has little effect on $[C^*]$. The differences in $[C^*]$ between the homopolymerization and the copolymerization cases could be due to the fact that these runs were performed using slightly different catalysts of different Ti contents and surface areas.

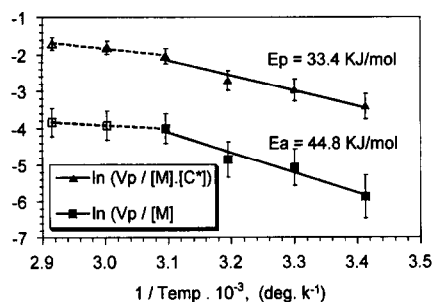


Fig. 11. Arrhenius type of plot for the estimation of the activation and propagation energies in ethylene homopolymerization. Conditions as in Fig. 10.

When the same catalyst is used in homo- and copolymerization, Fig. 10 shows that, at the same temperature 313 K, a homopolymerization run yields basically the same $[C^*]$ as in copolymerization.

The overall activation energy, E_a , and the propagation energy, E_p , were evaluated using an Arrhenius type of plots and using the formula:

$$V_p = k_p [M] \cdot [C^*]$$

whereby

$$k_p = A \cdot e^{-E_a/RT}$$

In the case where the value of $[C^*]$ independence of temperature is not known then Eq. (1) is used to estimate E_a :

$$\ln(V_p/[M]) = -E_a/RT + \ln(A \cdot [C^*]) \quad (1)$$

However, if $[C^*]$ is known then Eq. (2) is employed to estimate E_p :

$$\ln(V_p/([M] \cdot [C^*])) = -E_p/RT + \ln(A) \quad (2)$$

Thus the overall activation, E_a , is obtained from the slope of the plot $\ln(V_p/[M])$ versus $1/T$, as is shown in Fig. 11 (lower line). The plot is observed to consist of two linear parts. This shape of plot has been observed by many workers in this field, e.g., [17]. The break in the line at ≈ 323 K could originate from the destruction of active centres at high polymerization temperatures. The E_a value obtained from the line in the temperature range 293 to 323 is estimated to be about 44.8 kJ/mol. This value is in excellent agreement of previous estimation of E_a for the $TiCl_4/MgH_2$ catalyst, whereby a value of 45 kJ/mol was

reported [18]. In addition, this value is in good agreement with other published values in the literature for olefin polymerizations; for example, Keii et al. [17] and Chien et al. [19] have both reported a value of 50 kJ/mol activation energy in the polymerization of propylene.

Most of the E_a values reported in the literature did not however include the variation of active centres with temperature in the activation energy evaluation. In the present investigation, the propagation energy, E_p , can be evaluated using Eq. (2). This is also shown in Fig. 11 (upper line). The propagation energy estimated from the slope of the linear part (temperature range 293–323 K) gave a value of 33.4 kJ/mol. The difference between E_a (44.8 kJ/mol) and E_p (33.4 kJ/mol) is rather small. This means that for the catalyst system under investigation the temperature dependence of $[C^*]$ is, if at all, very small.

4. Conclusion

The results reported in this article and preceding publications [1,2,18] emphasize that the reason for the substantial increase in the rate of ethylene consumption in copolymerization when a low Ti-content catalyst was used is because the active centres on this type of catalyst are mainly homopolymerization centres. In other words, lowering the crystallinity of the polymer particles as a result of the comonomer incorporation led to faster diffusion of ethylene and to an increase in the rate of ethylene consumption. In contrast, the reason that no rate enhancement in copolymerization was observed when a high Ti-content catalyst was used is because the active centres on this type of catalyst are mainly copolymerization centres. In this case, lowering the crystallinity of the polymer particles did not have an effect on the ethylene consumption rate because the active centres in this case are not suitable for ethylene polymerization. For a particular $TiCl_4/MgH_2$ catalyst of certain Ti content and surface area the results emphasize that the sum of active centres is constant.

For the $\text{TiCl}_4/\text{MgH}_2$ catalyst system in ethylene, homo- and co-polymerization requires an optimal AlEt_3/Ti mole ratio of about 50 to achieve maximum activity and a maximum number of active centres. In homo- and in co-polymerization, the results obtained indicate that the plot of $[C^*]$ against the AlEt_3/Ti mole ratio follows an AlEt_3 -isotherm type of curve. Furthermore, for the catalyst system under investigation the difference between E_a and E_p is 11.4 kJ/mol, (2.7 kcal/mol), this indicate that the temperature dependence of $[C^*]$ is rather small.

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