

Effect of Hydrogen on the Ethylene Polymerization Process over Ziegler–Natta Catalysts Supported on $\text{MgCl}_2(\text{THF})_2$.

II. Kinetic Studies

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Received 27 December 1999; revised 17 April, 2000; accepted 27 April 2000

ABSTRACT: This article reports on a study of the effects of hydrogen on the activity of vanadium and titanium catalysts supported on $\text{MgCl}_2(\text{THF})_2$ in ethylene polymerization. It was found that hydrogen did not change the stable nature of the active sites and the polydispersity index of the polyethylene obtained. The propagation rate, expressed as k_p , was found to be independent of the presence and concentration of hydrogen, indicating that this reacting agent does not modify the reactivity of the active sites. However, the presence of hydrogen in the polymerization medium is responsible for partial deactivation of the active sites just before polymerization is initiated. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 361–365, 2001

Key words: ethylene polymerization; vanadium and titanium catalysts; hydrogen; catalyst activity; polymerization kinetic

INTRODUCTION

The use of hydrogen as a chain-transfer agent is the most important commercial method for molecular-weight control in both polyethylene and polypropylene. It is known that the presence of hydrogen in the polymerization medium influences not only the molecular weight of the product but also the activity of the catalyst. The dependence of catalyst productivity on the concentration of hydrogen varies with the nature of the catalyst as well as the monomer. It is generally accepted that hydrogen decreases the polymerization rate of ethylene,^{1–11} but the presence of this agent produces different effects in the polymerization of propylene. Depending on the type of catalyst, the polymerization rate can decrease,

can increase and often does, or can remain unaffected by the presence of hydrogen.¹²

The first part of this article¹³ presents the effects of hydrogen on the molecular weights of polyethylene obtained with vanadium and titanium catalysts supported on $\text{MgCl}_2(\text{THF})_2$. The objective of this work was to study the effect of hydrogen on the activity of these catalysts and the kinetics of ethylene polymerization with a $\text{MgCl}_2(\text{THF})_2\text{-VOCl}_3\text{-Et}_2\text{AlCl}$ catalytic system and to compare this effect with the data reported earlier for polymerization in the absence of hydrogen.¹⁴

EXPERIMENTAL

The materials employed and the catalyst synthesis and ethylene polymerization procedures adopted were specified in our previous articles.¹³

RESULTS AND DISCUSSION

In a number of studies, and in particular in the case of ethylene polymerization, it has been gen-

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Contract grant sponsor: State Committee for Scientific Research of Poland.

Journal of Applied Polymer Science, Vol. 79, 361–365 (2001)
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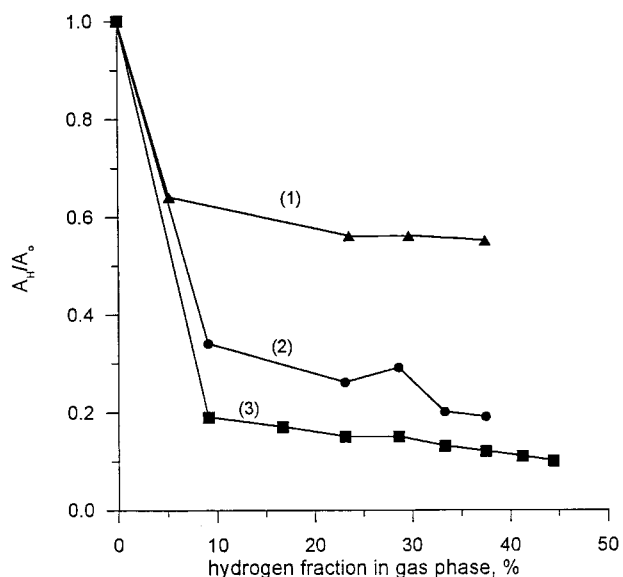


Figure 1 Effect of hydrogen on polymerization activity for catalysts supported on $\text{MgCl}_2(\text{THF})_2$: (1) $\text{MgCl}_2(\text{THF})_2/\text{TiCl}_4/\text{Et}_2\text{AlCl}^a$; (2) $\text{MgCl}_2(\text{THF})_2/\text{VCl}_4/\text{Et}_2\text{AlCl}^b$; (3) $\text{MgCl}_2(\text{THF})_2/\text{VOCl}_3/\text{Et}_2\text{AlCl}^b$. ^aPolymerization conditions: $[\text{TiCl}_4] = 0,135 \times 10^{-3} \text{ mol/dm}^3$, $[\text{Et}_2\text{AlCl}] = 81 \times 10^{-3} \text{ mol/dm}^3$, $p = 0.28 \text{ MPa}$, $T = 50^\circ\text{C}$. ^bPolymerization conditions: $[\text{VOCl}_3] = 0,015 \times 10^{-3} \text{ mol/dm}^3$ or $[\text{VCl}_4] = 0.01 \times 10^{-3} \text{ mol/dm}^3$; $[\text{Et}_2\text{AlCl}] = 25 \times 10^{-3} \text{ mol/dm}^3$, $p = 0.5 \text{ MPa}$, $T = 33^\circ\text{C}$.

erally accepted that catalyst activity decreases with the addition of hydrogen. The same effect was found in the systems currently studied, that is, vanadium (VOCl_3 , VCl_4) and titanium (TiCl_4) catalysts supported on $\text{MgCl}_2(\text{THF})_2$ and activated by Et_2AlCl . The results in Figure 1 show that the reduction in catalyst activity becomes particularly apparent at small hydrogen concentrations in the reaction medium. Comparison of the results presented in Figure 1 with the effect of hydrogen on the molecular weight of polyethylene obtained from these catalytic systems¹³ showed that the effect of hydrogen on the catalytic activity is rather different from its effect on the molecular weight of polyethylene. Other studies^{7,10} found similar situations.^{7,10} Such findings may prove that the reasons are different for both analyzed effects from hydrogen, which has been suggested earlier.⁶

Also the results in Figure 1 show that the influence of hydrogen on catalyst activity is dependent on the type of precatalyst. Unfortunately, the vanadium catalysts proved more susceptible to activity-reducing action from hydrogen than did the corresponding titanium systems.

The nature of the complex effects of hydrogen on catalyst activity has not been clearly explained until now Keii³ suggested that the hydrogen atoms adsorbed dissociatively are active in chain transfer but inactive in polymerization. According to Ross,¹⁵ atomic hydrogen would be responsible for polymerization inhibition. The decreased catalytic activity also may be ascribed to the changed concentration of active sites as a result either of their poisoning by hydrogen or of the change to the inactive form of the transition metal oxidation state.¹¹ The latter seems reasonable, as shown by the data in Figure 1. The depressive effect of hydrogen on catalyst activity is dependent on the type of transition metal compound in the catalytic system, and it increases in the series $\text{TiCl}_4 \ll \text{VOCl}_3 < \text{VCl}_4$. The susceptibility of these compounds to the reduction processes decreases in the same series.¹⁶ On the other hand, consideration should be given to the dissociative adsorption of hydrogen being essentially an oxidative process. Thus, it should increase the oxidation level of the transition metal. This mechanism has been applied to explain the propylene polymerization rate enhancement caused by hydrogen as a result of activation (oxidation) of some highly reduced inactive sites (Ti^{+2} or Ti^{+1}).^{11,17,18} However, this cannot explain the lower catalyst activity in ethylene polymerization in the presence of hydrogen. Moreover, the $\text{MgCl}_2(\text{THF})_2$ -supported catalysts have been found¹⁶ to be very resistant a reduction to lower and inactive levels of oxidation, even with much excess of an organoaluminum cocatalyst. The oxidative adsorption of hydrogen in our systems can be responsible for oxidation of Ti^{+3} or V^{+3} (active in polymerization) to higher (and inactive) levels of oxidation. When hydrogen is removed from the reaction medium, the excess of organoaluminum cocatalyst can reduce the catalyst metal again to a oxidation level that offers catalytic activity. This can explain the reversible effect of hydrogen on the polymerization rate, which has been observed by some researchers.^{7,19} Moreover, the above conclusion seems to have some support from Keii's observation¹⁷ that in the absence of solute alkylaluminum, the effect of hydrogen is irreversible. However, differences found between the hydrogen effect on catalyst productivity and its effect on molecular weight indicate that these effects are independent. Therefore, it can be concluded that the negative effect of hydrogen on the ethylene polymerization process has not yet been completely explained.

Catalyst decay over time is either not affected or slightly retarded by the presence of hydrogen.⁶

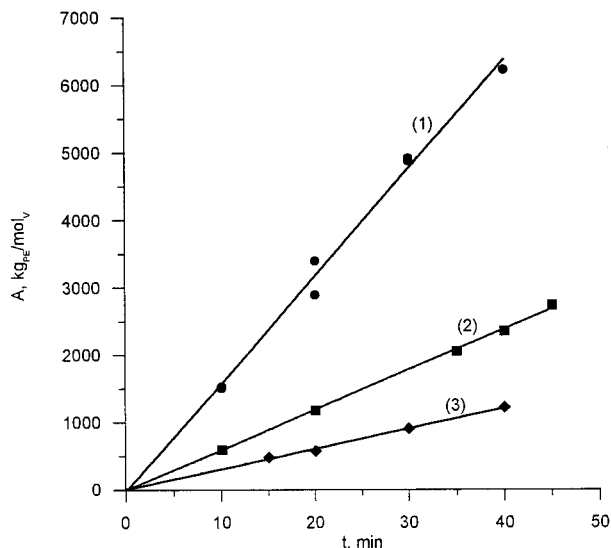


Figure 2 Catalyst activity A in polymerization of ethylene as a function of polymerization time t for the $\text{MgCl}_2(\text{THF})_2/\text{VOCl}_3/\text{Et}_2\text{AlCl}$ catalyst system and different hydrogen shares in gas phase in % (v/v): (1) 0; (2) 16.7; (3) 33.3. Polymerization conditions: $[\text{Et}_2\text{AlCl}] = 25 \times 10^{-5} \text{ mol/dm}^3$, $[\text{VOCl}_3] = 1.5 \times 10^{-5} \text{ mol/dm}^3$, $[\text{C}_2\text{H}_4] = 0.469 \text{ mol/dm}^3$, $T = 33^\circ\text{C}$.

On the other hand, there is a strong enhancement of the decay rate of MgCl_2 -supported catalyst systems containing esters of aromatic acids as external donors when hydrogen is present.¹² The reaction between Ti—H bonds and the carbonyl group of the ester has been suggested as a possible cause.²⁰

Summing up the discussion presented above, various hypotheses can be considered to explain such a negative effect from hydrogen on the activity of catalyst in the ethylene polymerization process:

- active-sites poisoning by hydrogen lead to the lowering of their initial concentration ($[\text{C}_i^*]$),
- changing of the active-sites structure leads to their lower reactivity (lower value, k_p),
- deactivation of active sites by hydrogen in the course of the polymerization process (lower stability of active sites in the presence of hydrogen).

To solving this problem, the effect of hydrogen on the kinetics of ethylene polymerization over the catalyst $\text{MgCl}_2(\text{THF})_2\text{—VOCl}_3\text{—Et}_2\text{AlCl}$ was studied.

Figure 2 presents the dependence of the polymerization yield on the polymerization time for

different hydrogen concentrations in the reaction feed. As can be seen, the activity linearly increases with polymerization time for all conditions investigated. These results indicate that the polymerization rate is constant independent of the presence and concentration of hydrogen. Hence, hydrogen has no effect on the kinetic stability of the investigated vanadium catalyst observed earlier in the polymerization of ethylene without this chain-transfer agent.¹⁴ The same results were obtained earlier for a similar catalytic system containing TiCl_4 supported on $\text{MgCl}_2(\text{THF})_2$.⁸ It appears that the MgCl_2 support, which contains THF as an internal Lewis base, plays a specific role in both the vanadium and titanium systems compared in this study. As was confirmed earlier,¹⁶ such support stabilizes the active sites and prevents their deactivation by reduction to lower and inactive oxidation states, even in the presence of hydrogen.

Moreover, attention should be paid (Fig. 2) to the observed polymerization rate for the use of hydrogen, which is clearly lower from the very beginning of the process compared to the polymer formation rate with no hydrogen present.

As is well known, the polymerization reaction rate can be expressed by the equation:

$$R_p = k_p \cdot [\text{C}_i^*] \cdot [\text{M}] \quad (1)$$

where R_p is the polymerization rate, k_p is the propagation rate constant, $[\text{C}_i^*]$ is the concentration of active sites at time t , and $[\text{M}]$ is the monomer (ethylene) concentration.

Hence, the decreased polymerization rate may be attributed to the changed initial concentration of active sites as a result of their poisoning by hydrogen ($[\text{C}_o^*]$) and/or their changed structure and reactivity (k_p) for the propagation reaction. To look into this problem, the kinetic characteristics for ethylene polymerization at different concentrations of hydrogen and with no hydrogen were investigated, a reasonable inquiry since a much lower molecular weight had been obtained in the presence of hydrogen. The proper value of $\bar{M}_{n,t}$ could be used in this work for the calculation of the number of macromolecules formed in the course of the polymerization process instead of $\bar{M}_{v,t}$, as we had to do in the case of characterizing polymerization with no hydrogen (polyethylene molecular weight of the order of a few million).¹⁴

In the case of polymerization when hydrogen is present, the macromolecule creation rate equals the sum of the transfer reaction rates, both with monomer¹⁴ and with hydrogen¹³:

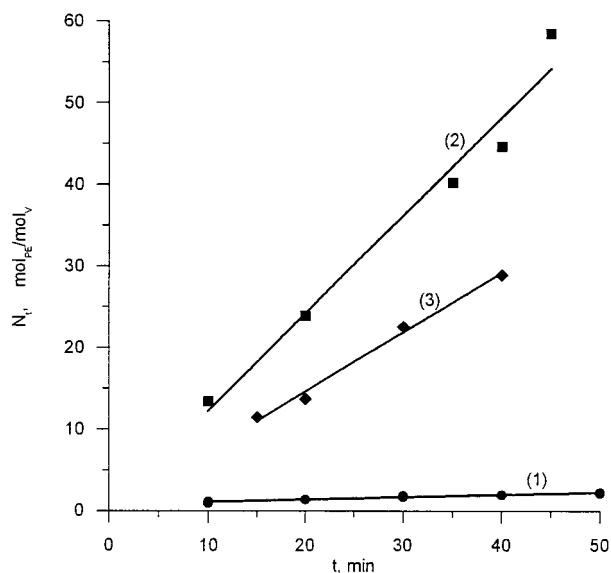


Figure 3 Concentration of macromolecules, N_t , of polyethylene as a function of polymerization time t calculated according to eq. (5). Description of the curves and polymerization conditions are the same as described in Figure 2.

$$dN_t/dt = R_{tr,M} + R_{tr,H} = k_{tr,M} \cdot [C_t^*] \cdot [M] + k_{tr,H} \cdot [C_t^*] \cdot [H_2]^{0.5} \quad (2)$$

After integration, eq. (2) becomes

$$[N_t] - [N_o] = (k_{tr,M} \cdot [C_t^*] \cdot [M] + k_{tr,H} \cdot [C_t^*] \cdot [H_2]^{0.5}) \cdot t \quad (3)$$

where $[N_o]$, $[N_t]$ is the concentration of macromolecules at time $t = 0$ and t , respectively; $R_{tr,M}$, $R_{tr,H}$ is the transfer reaction rate with monomer and hydrogen, respectively; $k_{tr,M}$, $k_{tr,H}$ is the constant of transfer reaction rate with monomer and hydrogen, respectively; and $[H_2]$ is the hydrogen concentration

The concentration of macromolecules after time t can be calculated from the experimental yield and number-average molecular weight of the polymer

$$[N_t] = W_t/M_{n,t} \quad (4)$$

where W_t is the polyethylene yield after time t and $M_{n,t}$ is the number-average molecular weight of polyethylene.

Taking into account that the initial number of macromolecules is equal to the concentration of active sites ($[C^*]$), which remain stable over the polymerization time because of the stability of the catalyst employed, one can obtain

$$W_t/M_{n,t} = [C^*] + (k_{tr,M} \cdot [C_t^*] \cdot [M] + k_{tr,H} \cdot [C_t^*] \cdot [H_2]^{0.5}) \cdot t \quad (5)$$

The corresponding experimental results, presented in Figure 3, show that the number of macromolecules formed in the presence of hydrogen is considerably higher and increases faster than in the case of polymerization without this agent. The analysis of the dependencies presented in Figure 3 may seem somewhat strange when the findings for the two corresponding hydrogen concentrations are compared (less macromolecules formed for a higher hydrogen concentrations). It should be considered, however, that the rate of macromolecule production is also dependent on the active-sites concentration. The reason for this dependence can be found in the concentration difference of various hydrogen concentrations in the process medium.

The coefficients for the linear equations $[N_{n,t}] = A + B \cdot t$ (Table I) can be found on the basis of the data provided in Figure 3. Additionally, as results from eq. (5), the value for A corresponds to the concentration of active sites, while the value

Table I Calculated Results of Ethylene Polymerization over $MgCl_2(THF)_2/VOCl_3/Et_2AlCl$ in Dependence of Hydrogen Concentration

Hydrogen Share in Gas Phase % (v/v)	Results According to eq. (5)			$[C^*]$ (mol/ mol _v)	R_p [kg/(mol _v · min)]	$k_{tr,H}$ [dm ³ /(mol ^{0.5} · s)]	k_p [dm ³ /(mol · s)]
	A	B	r				
0	—	—	—	0.800 ^a	158.1 ^a	0	244.8 ^a
16.7	0.242	1.195	0.985	0.242	58.7	0.606	242.4
33.3	0.092	0.724	0.996	0.092	30.0	0.613	245.2

^a From Reference 14.

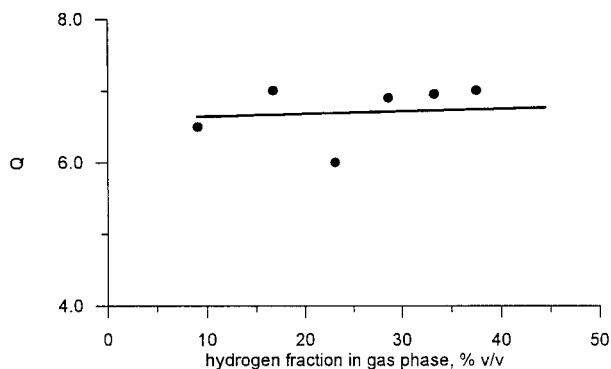


Figure 4 Effect of hydrogen on polydispersity index, Q , of polyethylene obtained over catalyst: $\text{MgCl}_2\text{-(THF)}_2/\text{VOCl}_3/\text{Et}_2\text{AlCl}$. Polymerization conditions are the same as described in Figure 2.

for B enabled the calculation of $k_{tr,H}$ after having considered the known concentrations of the monomer, the hydrogen, and the active sites and the value for $k_{tr,M}$ as determined earlier.¹⁴

The results presented in Table I show that the values for $k_{tr,H}$, as calculated on the basis of two series of tests with different hydrogen calculations, are basically the same, irrespective of the conditions in which they were found. This confirms the values were analyzed properly.

The ratio of the corresponding rate constants for the transfer reaction (with the use of hydrogen) and for the propagation reaction $k_{tr,H}/k_p = 2.5 \cdot 10^{-3}$ were determined in investigations of the effect of hydrogen on the molecular weight of polyethylene with analysis of the polymeric chain-transfer reaction involving that reacting substance.¹³ When the value for $k_{tr,H}$ is known, it is possible to calculate the propagation rate constant, k_p , and to compare it with the value found in the earlier kinetic study on ethylene polymerization without hydrogen. As can be seen from Table I, both these values are virtually the same. This confirms that the nature of active sites is not modified by the presence of hydrogen. Additional evidence for the above statement is that the polydispersity index, Q , for polyethylene is not dependent in practice on the hydrogen concentration of the polymerization feed (Fig. 4).

According to Natta¹⁹ and to Soga and Shiono,²¹ the decrease in the polymerization rate caused by hydrogen is a result of a slow addition of the monomer to the metal-hydrogen bond formed at the step of chain transfer with hydrogen. Contrary to this hypothesis, the results obtained in this work seem to indicate this reaction is fast and does not limit the polymerization rate.

Moreover, the results in Table I show that the introduction of hydrogen into the ethylene polymerization system with vanadium catalyst lowers the concentration of active sites. This negative process increases with an increase of the hydrogen concentration in the polymerization medium and is equivalent to the correspondingly lowered polymerization rate (Table I). These results seem to show that hydrogen deactivates some potentially active sites even before polymerization is initiated, probably via irreversible adsorption on these sites.

This work was financially supported in part by the State Committee for Scientific Research of Poland.

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