

Polymerization Rate Modeling of Ethylene Polymerization with Supported Chromium Oxide Catalysts

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ABSTRACT: Supported chromium oxide catalysts have long been used for the polymerization of ethylene to high-density polyethylene. Unlike Ziegler–Natta catalysts, chromium oxide catalyst systems do not require cocatalysts to obtain high polymerization activity. One of the most distinctive characteristics of the chromium oxide catalyst is the presence of an induction period during the initial period of polymerization. The duration of induction period is dependent on many factors such as catalyst preparation, activation procedures, and polymerization conditions. After the induction period, the polymerization rate increases steadily with reaction time until it reaches a stationary value. Although chromium oxide catalysts have been used for years in industrial processes, there is still a dearth of literature concerning the kinetic modeling of chromium oxide catalyzed

polymerization processes. In this article, a kinetic model is developed for the chromium oxide catalyzed ethylene polymerization in gas and slurry phases. In this model, it is proposed that the reaction byproduct generated by the reduction of hexavalent chromium species to Cr^{2+} by ethylene poisons the active sites. With the desorption of the poison species, the deactivated sites are transformed to active sites to polymerize ethylene. The validity of the proposed model is illustrated by comparing the model calculations with the experimental data obtained from gas phase and liquid slurry polymerization experiments. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2923–2927, 2004

Key words: chromium oxide catalysts; kinetic modeling; polyethylene (PE); polyolefins; gas phase

INTRODUCTION

Supported chromium oxide catalysts, known as the Phillips catalyst, have been used for years to manufacture high-density polyethylene (HDPE) in liquid slurry phase and gas-phase polymerization processes. Although many different types of transition metal catalysts including recently developed metallocenes are used in the polymer industry to produce ethylene polymers, a family of supported chromium oxide catalysts still accounts for about 70% of the world's HDPE production. The three major types of chromium oxide catalyst systems used in industrial polyethylene processes are: (1) chromium oxide supported on silica or other supports such as alumina and AlPO_4 ; (2) organic chromium compounds supported on silica, alumina, and AlPO_4 ; (3) mixed catalyst, in which certain amounts of organic chromium are deposited onto a chromium oxide catalyst.

It is well known that the performance of the supported chromium oxide catalysts is strongly dependent on the methods of their preparation. The catalyst mostly controls the polymer productivity and the key polymer properties such as molecular weight distri-

bution and branching. For example, when an organochromium compound is deposited onto an aluminophosphate support, the catalyst becomes very active but produces the polymers with a bimodal molecular weight distribution.¹

In general, the chromium oxide-based catalyst is prepared by first treating the catalyst at about 200°C to form a surface chromate species. Then, the catalyst is calcined at higher temperature (500–900°C). The silica-supported chromium oxide catalyst is not immediately active for polymerization and it goes through a period in which no noticeable polymerization occurs. This period of near-zero polymerization rate is called the induction period or the nascent period, which can last from a few minutes to over 1 h. The duration of the induction time depends on several factors (e.g., method of catalyst preparation, method of catalyst activation, polymerization conditions). After the induction period, the polymerization rate starts to increase steadily with time until it levels off. Then, the polymerization rate remains nearly constant or declines slightly because of deactivation. This kinetic behavior is quite different from that observed in other olefin polymerization processes with Ziegler–Natta type catalysts and metallocenes. With these nonchromium catalyst systems, the catalytic site activation is almost instantaneous and the polymerization rate quickly increases to a maximum followed by either a rapid or a slow rate decrease attributed to site deacti-

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vation and/or diffusion limited intraparticle monomer mass transfer.

Because the catalyst activation step has a very significant effect on the performance of the catalyst, it is necessary to understand the process of active-site formation. After a chromium compound is deposited onto a fully hydrated wide-pore silica support with surface silanol groups the supported catalyst is calcined at high temperature in oxygen to activate the catalyst.² Chromium oxide is anchored onto the silica surface as a surface chromate or dichromate ester. It is believed that any remaining surface hydroxyl groups may interfere with polymerization if not removed.¹ When the catalyst (Cr^{6+}) is exposed to ethylene, the hexavalent chromium is reduced to a lower valent active species such as divalent chromium with the generation of byproducts such as formaldehyde.³ It is possible that other byproducts such as acetaldehyde can also be produced. The byproduct may coordinate to the chromium until displaced by ethylene. It is thought that the insertion of the first monomer molecule into an active center (Cr^{2+}) (alkylation) might be a rate-controlling step, although the exact mechanism is still not completely understood. The alkylation may not occur, or occur at a very slow rate, when the concentration of reduced Cr^{2+} on the catalyst surface is very low. McDaniel and Welch⁴ report that the polymerization activity of supported chromium oxide catalysts is strongly dependent on the activation temperature, although the induction time is scarcely affected. They also report that polymer molecular weight tends to decrease as higher catalyst calcination temperature is used. Their experimental data show that the more dehydrated catalyst yields a lower molecular weight polymer. It was also suggested that the concentration of active sites on the catalyst is probably not constant. The existence of different types of chromium (VI) active centers with different chain termination activities was also proposed.

Because of the complexity of chemical reactions that occur during the calcination and activation stages, the chromium oxide catalysts are very sensitive to minor variations in catalyst purity, porosity, calcining history, and impurities. Thus, it might be very difficult to develop a kinetic model that can be universally applied to every chromium oxide catalyst system.

Although there has been a large number of publications on the polymerization kinetics, reaction mechanisms, and the nature of chromium species during the polymerization, very little has been published on the quantitative modeling of the polymerization kinetics for the chromium oxide catalyzed ethylene polymerization process. The scarcity of kinetic modeling work for this catalyst system is quite surprising in view of the fact that Ziegler-Natta or metallocene catalyzed ethylene polymerization processes have been extensively studied through kinetic and process

modeling studies and that chromium oxide catalyzed ethylene polymerization is still industrially very important.

In this article, a kinetic model is proposed for a silica supported chromium oxide catalyst for ethylene polymerization where the induction period is present. The main objective is to develop a model capable of predicting the initial induction period and the subsequent polymerization rate phenomena.

KINETIC MODELING

One of the major issues in the kinetic modeling of chromium oxide supported ethylene polymerization is concerned with the modeling of the initial induction period. Several plausible causes for the induction period have been suggested in the literature. For example, the induction period might be caused by the slow reduction of Cr^{6+} by ethylene to a lower-valent active chromium species. The subsequent rate increase was attributed to the slow alkylation step in which the chain propagation begins.¹ Hence, the first task in our kinetic modeling was to devise a kinetic scheme for the prediction of the induction period.

A supported chromium oxide catalyst is typically heat treated at high temperature (e.g., 816°C) for more than 10 h. According to Merryfield et al.,⁵ the induction time becomes shorter with (1) increasing calcining temperature, (2) increasing reaction temperature, and (3) increasing ethylene concentration. It has been reported that formaldehyde is produced as a reaction byproduct when hexavalent chromium is reduced to divalent chromium by ethylene. Merryfield et al.⁵ suggest that the induction time probably corresponds to the time required for the reduction of Cr^{6+} to the lower-valent active species, or perhaps for the desorption of byproducts. McDaniel and Martin⁶ report that duration of the induction period is affected by the type of catalyst poisons (e.g., oxygen, methanol, acetylene, carbon monoxide) and that the concentration of poison that has a visible effect on observed reaction rates is on the order of 1 ppm.

Recently, Embry proposed the multistep catalyst activation process represented by the following kinetic scheme⁷:

Initial catalyst activation by monomer



Site activation by monomer



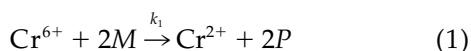
Initiation of polymerization



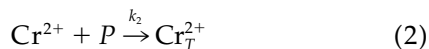
The catalyst activation is assumed to be the rate-controlling step and responsible for induction time.

In the following, we propose a kinetic scheme for ethylene homopolymerization with a supported chromium oxide catalyst. We postulate that Cr⁶⁺ is first reduced to Cr²⁺ by reacting with two ethylene monomers. The reduction reaction generates a poisonous compound such as aldehyde that is adsorbed onto the reduced chromium site. The divalent chromium site adsorbed by the poison (P) is inactive for propagation until the poison is removed by subsequent desorption process (site transformation).

Reduction of hexavalent chromium



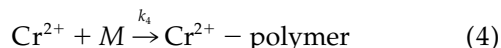
Poisoning of active site



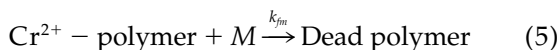
Site transformation



Chain propagation

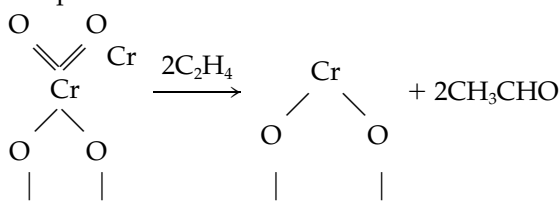


Chain transfer



In the above, the following assumptions are made:

1. Cr²⁺ is the active chromium species and it is formed only in the presence of ethylene. For example:



2. The activated chromium site (Cr²⁺) is quickly poisoned by the adsorption of a poison material generated by the monomer-assisted reduction reaction.
3. Temporarily deactivated or poisoned site (Cr_T²⁺) recovers its full activity through a site transformation reaction. We assume that when the de-

activated site recovers its activity, the desorbed poison species diffuses out quickly from the solid surface. In other words, we assume that the desorbed poison is not adsorbed again.

4. Both vacant Cr²⁺ sites and active propagation site (Cr²⁺-polymer) are subject to poisoning.

With the kinetic scheme shown above, the polymerization rate (*R_p* in g/min) is expressed as

$$R_p = k_4 W_{\text{cat}} [\text{Cr}^{2+}] [M] w_m \quad (6)$$

where *W_{cat}* is the g-catalyst charged into the reactor, *w_m* is the molecular weight of ethylene (g/mol), [M] is the monomer (ethylene) concentration (mol/L), and [Cr²⁺] is the total active chromium site (vacant and occupied) (mol/g-cat). The kinetic modeling equations for the above kinetic scheme take the following form:

$$\frac{d[\text{Cr}^{6+}]}{dt} = -k_1 [\text{Cr}^{6+}] [M]^2 \quad (7)$$

$$\frac{d[\text{Cr}^{2+}]}{dt} = k_1 [\text{Cr}^{6+}] [M]^2 - k_2 [\text{Cr}^{2+}] [P] + k_3 [\text{Cr}_T^{2+}] \quad (8)$$

$$\frac{d[\text{Cr}_T^{2+}]}{dt} = k_2 [\text{Cr}^{2+}] [P] - k_3 [\text{Cr}_T^{2+}] \quad (9)$$

$$\frac{d[P]}{dt} = 2k_1 [\text{Cr}^{6+}] [M]^2 - k_2 [\text{Cr}^{2+}] [P] \quad (10)$$

Initial conditions: at *t* = 0, [Cr⁶⁺] = [Cr⁶⁺]₀, [Cr²⁺] = 0, [Cr_T²⁺] = 0, [P] = 0.

To test the proposed kinetic model, laboratory semi-batch polymerization data were used. Here, the monomer concentration was maintained constant by keeping the ethylene pressure constant in either the semi-batch gas phase or liquid slurry phase polymerization experiments. Then, the ethylene supply rate was equivalent to the rate of polymerization. The polymerization temperature was also constant (isothermal reaction).

RESULTS AND DISCUSSION

As the polymerization rate reaches a stationary rate, it can be expressed as

$$R_{p,ss} = k_4 W_{\text{cat}} [\text{Cr}^{2+}]_{ss} [M] w_m \quad (11)$$

Here, the subscript *ss* refers to the stationary state value. Because the monomer concentration [M] is kept constant in a semibatch polymerization experiment, the propagation rate constant *k₄* can be estimated from eq. (11) if the stationary polymerization rate and the

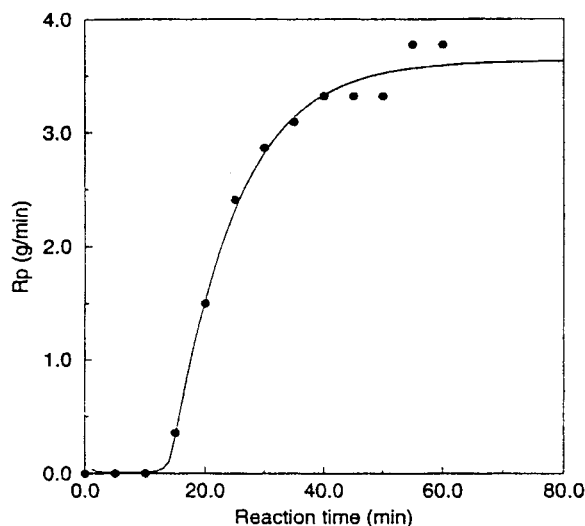


Figure 1 Polymerization rate profiles for gas-phase ethylene polymerization in a semibatch reactor at 100°C (symbols, experimental data; lines, model predictions).

active chromium site concentration ($[\text{Cr}^{2+}]$) are known. However, no actual measurements of the concentrations of chromium sites of different valence state were possible. Therefore, we assume that when the polymerization rate reaches a stationary rate, all of the chromium sites were fully activated or transformed to active Cr^{2+} sites. Also, at constant monomer concentration, we obtain the following from eq. (7):

$$[\text{Cr}^{6+}] = [\text{Cr}^{6+}]_0 \exp(-k_1)[M]^2 t \quad (12)$$

Assuming that $[\text{Cr}^{6+}] = 0.5[\text{Cr}^{6+}]_0$ at $t_{1/2} = 0.5t_{ss}$, we can determine the k_1 value from eq. (12). k_2 and k_3 values are determined by fitting the experimental data.

The experimental data were produced at an industrial laboratory and the specific details of the supported chromium oxide catalyst and the experimental procedure are proprietary. Using the data at 100°C, we

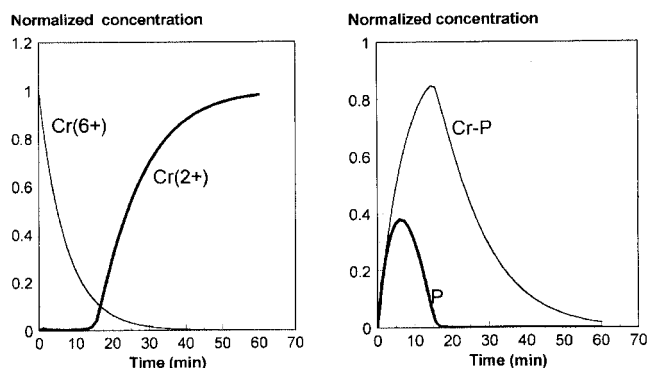


Figure 2 Normalized chromium site concentrations and poison (P) concentration (Cr-P represents the chromium site adsorbed by poison; Cr_T^{2+}).

TABLE I
Semibatch Slurry Polymerization Data

Run number	Polymerization temperature, T (°C)	Ethylene concentration ($[\text{M}]^*$, mol/L)	$R_{p,ss}$ (g/min)	$t_{1/2}$ (min)
S1	80	0.6709	2.5	190
S2	90	0.6275	12.0	145
S3	100	0.5730	17.0	140
S4	105	0.5380	18.0	70

obtained the following rate constant values [normalized by the chain propagation rate constant k_4 (in $\text{L mol}^{-1} \text{min}^{-1}$): $k_1/k_4 = 2.35 \times 10^{-4} \text{ L/mol-min}$, $k_2/k_4 = 27.27$, $k_3/k_4 = 4.55 \times 10^{-6} \text{ mol/L}$. Although individual rate constant values cannot be released because they are proprietary, the above rate constant values show the relative magnitudes of the reaction rate constants of the model.

Figure 1 shows the comparison of the model predictions and the semibatch experimental data of the gas phase ethylene polymerization rate with the supported chromium oxide catalyst. Notice that the model predicts quite well the initial induction period of about 12 min. It should also be pointed out that a little bit of the polymerization reaction occurred during the induction period (i.e., the rate of polymerization is not exactly zero). The model also provides a reasonably accurate prediction of the steadily increasing polymerization rate after the induction period. The concentrations of various chromium species are shown in Figure 2 (calculations), where Cr-P represents the chromium site adsorbed by the poison species (Cr_T^{2+}). It is interesting to notice that the reduction of Cr^{6+} continues even after the induction period is over. The concentration of poisoned chromium site becomes nearly zero as the polymerization rate reaches the stationary value (Fig. 1). The overall polymerization rate profile is very similar to that of the Cr^{2+} profile.

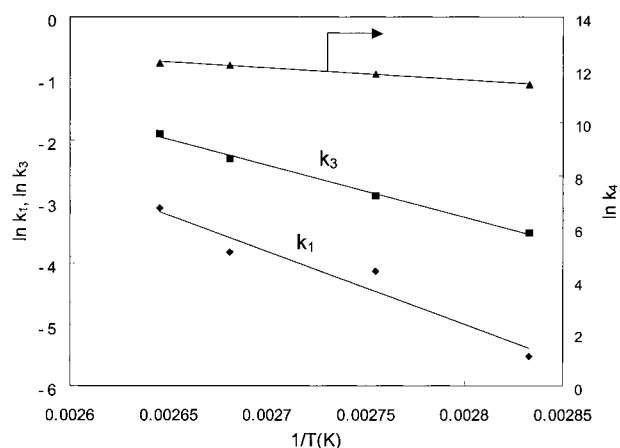


Figure 3 Arrhenius plots of rate constants for liquid slurry polymerization of ethylene.

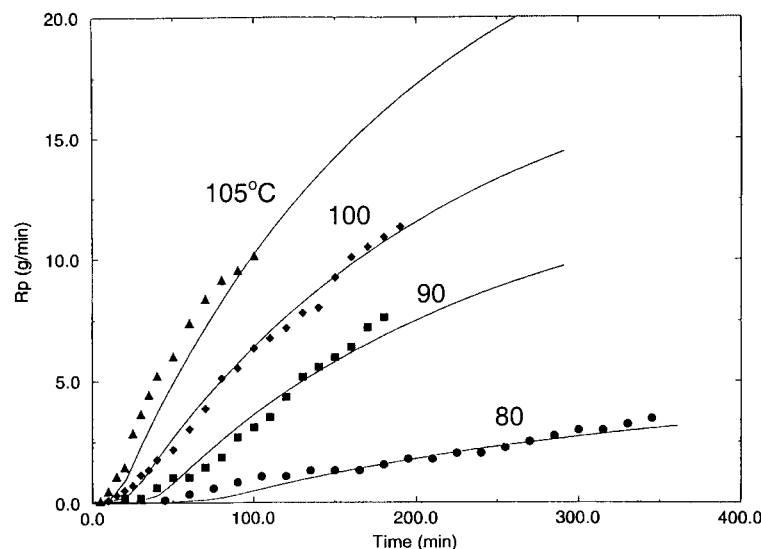


Figure 4 Liquid slurry ethylene polymerization rates at four different temperatures: symbols, data; lines, model calculations.

The slurry phase polymerization experiments were also carried out with the same catalyst used in the gas-phase polymerization experiments. Table I shows the experimental data obtained at four different reaction temperatures. In each experiment, the reaction pressure was kept constant at 27.3 bar and the active site content in the catalyst was 1%. The monomer mole fraction in the liquid phase was kept at 8 mol % and the molar concentration of ethylene was calculated using the Peng–Robinson equation of state. Again, the interfacial and intraparticle mass transfer resistances were assumed negligible. The rate constant values (k_1 – k_4) were estimated using the same method as in the gas-phase polymerization.

Figure 3 shows the Arrhenius plots of the rate constants (k_2 values are not shown because $k_2 = 10k_4$). The activation energies (in kcal/mol) for these rate constants are $E_1 = 9.508$, $E_2 = E_4 = 19.177$, $E_3 = 16.790$. Figure 4 shows the experimentally measured and the model-predicted polymerization rate profiles at 80, 90, 100, and 105°C. Both experimental data and the model calculations show that the induction period becomes shorter at higher polymerization temperatures. Some discrepancies between the model predictions and the experimental data are present but the agreement between the two seems quite reasonable, supporting the validity of the proposed kinetic model for the experimental conditions used in this work.

CONCLUSIONS

In this article, a kinetic model was proposed for the modeling of ethylene homopolymerization catalyzed by supported chromium oxide catalysts that exhibit an initial induction period. It has been assumed that the reaction byproduct generated as the hexavalent chromium species is reduced to Cr^{2+} by ethylene monomer acts as a catalyst poison. During the initial reaction period both the poisoning and the site transformation (conversion to active sites) occur simultaneously. As the concentration of poisoned sites decreases, the polymerization rate starts to increase until it levels off. The proposed model was applied to gas-phase and liquid slurry polymerization data and the agreement between the model predictions and the experimental data was quite satisfactory.

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