A REACTION KINETIC MODEL FOR THE ETHYLENE POLYMERIZATION USING AN HOMOGENEOUS CHROMIUM CATALYSTS

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ABSTRACT

The description of a reaction path often represents the most challenging part in the modelling of chemical reactor. A reliable description is rarely available at priori, and it is well known that reaction kinetics for complex systems, like reactions of polymerization, can not necessarily be derived even if the stoichiometries are known. In order to improve our understanding on the reaction mechanism for the ethylene polymerization over homogeneous chromium catalysts, using P-MAO as a co-catalyst, a model was developed where the polymerization rate can be predicted based on the concentration of ethylene. Additionally, we studied the effect of the reaction temperature.

The experimental data used in this work were obtained in a laboratory scale apparatus that was designed and built with the purpose of performing homogeneous polymerization of ethylene, in the Polymer Laboratory of the Chemical Center of IVIC.

Pursuing the objective of this work, a kinetic model was developed for this kind of reactions taking into account each elemental step of the reaction mechanism, and the balance of available active centers. Values for the kinetic parameters were found by fitting the model to the experimental data. The model was based on the following assumptions: a) Variables related to the catalyst structure are kept constant, b) the insertion of the monomer into the catalyst active sites is not diffusion controlled, c) the catalyst/co-catalyst system is maintained soluble in the solvent medium, d) all reactions reach a pseudo-steady state, and e) the total amount of catalyst is kept constant.

In order to solve the system of equation and to find the unknown constants for the reaction, we used a MATLAB® routine which is a set of three parts. The first part is the reaction kinetic model, and the starting seeds for all unknown parameters. In this part, the reaction rates constants were expressed in the form $k = A * \exp(-E/R/T)$ where the unknown variables were A (pre-exponential factor), T (reaction temperature) and E (activation energy).

The second part is a regression algorithm whose purpose is to find the best set of parameters that fit the experimental results. In order to achieve this goal, an error function was calculated by summing the squared difference between the observed and predicted value, and dividing this value by the number of data points. This error was minimized using a MATLAB® function called "fminsearch", which is an

unconstrained non-linear optimization sub-routine, to find the minimum of a scalar function of several variables, starting at an initial estimate. Finally, the third is the data file where all the experimental data were stored.

Two reaction mechanisms were evaluated. In the first one, it was assumed that the monomer is first coordinated to a metallic active site and afterwards inserted in the metal-carbon bound increasing therefore the polymer chain length (migration). The sequential process of insertion-migration of the monomer led to linear chain polymer growth (chain growing). In the second one, an additional termination reaction (chain transfer) was included to evaluate if this step improve the prediction of the yield in polyethylene. The polymerization mechanism by coordination can be used with catalysts based on late and early transition metal complexes[1].

An expression for the ethylene polymerization rate, using the proposed model, was formulated as a function of the monomer concentration (see equation (1)), and it was validated against experimental values. The specific reaction rate constants for the coordination reaction and for the insertion reactions were evaluated using the mathematical routine above described. Simulation results shoved to produce a satisfactory approach to experimental data with an even distribution of errors.

$$R_p = \frac{k_{\mathrm{c}}\,[E]\,C_T}{1 + \dfrac{k_{\mathrm{trap}}}{k_{\mathrm{ins}}}[E]} \equiv \frac{k_{\mathrm{c}}\,[E]\,C_T}{1 + K\,[E]}; \qquad K = \frac{k_{\mathrm{trap}}}{k_{\mathrm{ins}}} \tag{1}$$

where R_p is the polymerization rate, $[E]$ is ethylene concentration, C_T is the total catalyst site, k_{c} and k_{ins} are the kinetic constants for the trapping and insertion steps respectively.

The resulting kinetic model fit is presented in Figure 1a, in order to show the performance of the proposed model for the polymerization reaction, and the corresponding Arrhenius plot is shown in Figure 1b.
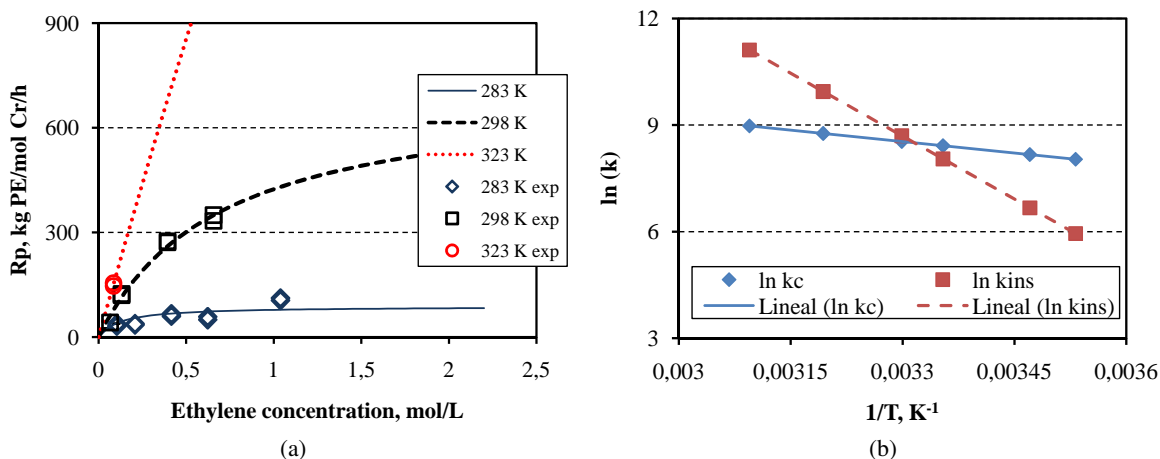

Figure 1: (a) Fit to experimental data at 283 K, 298 K y 323 K. Symbols represent experimental data and lines represent model fit (b) Arrhenius plot for trapping and insertion rate constants.

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