

Research Article

Optimal Catalyst and Cocatalyst Precontacting in Industrial Ethylene Copolymerization Processes

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In industrial-scale catalytic olefin copolymerization processes, catalyst and cocatalyst precontacting before being introduced in the polymerization reactor is of profound significance in terms of catalyst kinetics and morphology control. The precontacting process takes place under either well-mixing (e.g., static mixers) or plug-flow (e.g., pipes) conditions. The scope of this work is to study the influence of mixing on catalyst/cocatalyst precontacting for a heterogeneous Ziegler-Natta catalyst system under different polymerization conditions. Slurry ethylene homopolymerization and ethylene copolymerization experiments with 1-butene are performed in a 0.5 L reactor. In addition, the effect of several key parameters (e.g., precontacting time, and ethylene/hydrogen concentration) on catalyst activity is analyzed. Moreover, a comprehensive mass transfer model is employed to provide insight on the mass transfer process and support the experimental findings. The model is capable of assessing the external and internal mass transfer limitations during catalyst/cocatalyst precontacting process. It is shown that catalyst/cocatalyst precontacting is very important for the catalyst activation as well as for the overall catalyst kinetic behavior. The study reveals that there is an optimum precontacting time before and after which the catalyst activity decreases, while this optimum time depends on the precontacting mixing conditions.

1. Introduction

Polyolefins account for about one-third of the plastics production, with heterogeneous Ziegler-Natta (Z-N) based catalysts dominating the polyolefin production [1]. Since the first Z-N polymerization in 1953 by Karl Ziegler and his research team, there is a constant progress in catalyst design to increase the catalyst activity, micro structure control and powder morphology [2]. Especially with the use of different heterogeneous support materials such as MgCl_2 and SiO_2 , Z-N catalysts have made a huge leap forward. The actual 4th-generation catalyst systems show a polymer yield up to $100 \text{ Kg}_{\text{pol}}/\text{g}_{\text{cat}}$ for olefin polymerization [2, 3]. With increasing activity, less catalyst is required for achieving the same amount of polymer produced in a polymerization reactor. This leads to fewer catalyst residuals in the product and additionally reduces the cost share of the catalyst [3].

Beside the catalyst design, there are various possibilities to enhance the catalyst activity and improve the associated polymer properties in a polymerization process. The catalyst activation prior to the main polymerization process plays an important role towards reaching the maximum potential of a catalyst system in terms of productivity. It has been shown that pretreatment of the catalyst can increase the activity of the catalyst system [4–6]. Prepolymerization is already a wide explored field for catalyst tuning/optimization and morphology control [7, 8]. Under milder conditions compared to the main polymerization process, small size prepolymer particles are formed (i.e., 20–120 μm). There are various methodologies to carry out the prepolymerization step (e.g., under isothermal conditions at low temperatures, following a temperature gradient during heating up to the desired polymerization temperature, using different monomer/hydrogen molar ratios or even using different

monomers) [7, 8]. Therefore, the prepolymerization step can have a strong impact on the fragmentation behavior of the catalyst particles and it also lessens the risk of particle overheating which can result in activity reduction and reactor fouling. The prepolymerized polymer is commonly produced in a separate reactor before the main polymerization reactor (i.e., prepolymerizer). In industry this concept has already been widely adopted and implemented in different multistage processes (e.g., Unipol, Spherilene, and Borstar®) [9, 10].

An additional way to influence the activity profile of a Z-N catalyst is to precontact the catalyst with the cocatalyst. In general, the catalyst/cocatalyst precontacting process depends on the catalyst type, precontacting time, temperature, and mixing efficiency. In some catalyst systems, precontacting of catalyst and cocatalyst before entering the polymerization reactor is beneficial for increasing the catalyst activity and yield, increasing bulk density and producing polymer powder with better morphology [11, 12].

The active substances of the catalyst system usually consist of TiCl_X based components and an aluminum alkyl. Out of these two components an active site is formed (i.e., catalyst active site), which is the polymerization loci [2]. The formation of the active sites has a major influence on the catalyst productivity. Depending on the operating conditions (e.g., solvent, temperature, and comonomer) some time for the interaction of catalyst components is required in order to generate active sites [5, 13]. This is of even higher importance for heterogeneous Z-N systems as a large number of different active sites types are generated, which heavily effect the polymerization [13–15]. The oxidation state of the titanium is of paramount importance because of its influence on catalyst activity. For ethylene homo-polymerization both Ti^{3+} and Ti^{2+} are active; however Ti^{2+} is inferior in terms of catalyst activity. Reducing the oxidation state of titanium to Ti^{2+} leads to a decrease in catalyst activity of up to 80% [16]. This factor becomes even more important when higher α -olefins are involved in the polymerization process, since only Ti^{3+} is active for polymerization [13, 16].

For the catalyst activation numerous different cocatalysts (i.e., aluminum alkyls) like triethylaluminum (TEA), triisobutylaluminum (TIBA), trioctylaluminum (TOA), or isoprenylaluminum (IPRA) can be used [12, 17]. Depending on the structure of the cocatalyst, the catalyst activation time varies, affecting the polymerization rate. According to Nooijen [12] the catalyst activation process is mass transfer-dependent, as the catalyst activity drops with increasing molecular weight of the cocatalyst.

The longer the catalyst/cocatalyst contact time, the longer the time for the aluminum alkyl to diffuse into the catalyst particles, resulting in deeper species penetration depth, which leads to more homogeneous distribution of cocatalyst species inside the catalyst particle and increased concentration of the generated active sites. The penetration depth has a direct effect on the catalyst particle fragmentation; consequently, the catalyst activity can be influenced. Further investigations by Di Martino et al. [5, 18] support the hypothesis of mass transfer limitations during precontacting. The concentration of cocatalyst inside the catalyst particle will

increase by increasing contact time. However, the longer the contact times are, the more the reduction of the catalyst sites from Ti^{+3} to Ti^{+2} will take place. Thus, an optimal contact time is required in the precontacting process to ensure the maximum activity capability of the catalyst.

Depending on mixing conditions during catalyst/cocatalyst precontacting process, external mass transfer limitations may be manifested. That is, the rate of cocatalyst molecules transfer from the liquid phase to the solid catalyst particles becomes the limiting step. In the past 30 years, various correlations have been proposed in the open literature for the calculation of liquid-solid components mass transfer coefficients for spherical particles in a flowing liquid medium [19–24]. However, depending on the selected mass transfer correlations, the estimated values of liquid/solid film mass transfer coefficients for small size particles (i.e., $<50 \mu\text{m}$) and low Reynolds numbers can vary from the real values by several orders of magnitude [25]. In the present study, the external film mass transfer coefficient for the cocatalyst component in a two-phase liquid/solid system was estimated by employing a correlation proposed by Kittilsen et al. [24]. Subsequently, the value of the external film mass transfer coefficient, k_{ext} , was used to estimate the molecular species concentration at the solid particle surface in a non-well-mixed system following the developments of Kanellopoulos et al. [26, 27]. According to these studies, the cocatalyst concentration at the catalyst particle surface exhibits exponential dependence with respect to the system energy dissipation rate which in turn depends on the energy input (i.e., stirring speed), solids concentration, and the physical (i.e., density, viscosity) and the transport properties (i.e., components diffusion coefficient in the liquid phase) of the liquid/solid system.

Reassuring optimal catalyst/cocatalyst precontacting times using different mixing conditions (reflecting various mixing equipment used in the industry) is of profound importance for large scale polymerization plants, since mixing phenomena as well as mass transfer limitations are manifested to a larger extent compared to small-scale polymerization units [10]. So far, precontacting and its influence on olefin polymerization have only been a minor topic in most investigations. In literature the awareness of the precontacting effect is shown, but only few investigations have put the main focus on the influence of precontacting and the effect of mixing and mass transfer phenomena on the precontacting process. To extend and enhance the knowledge on precontacting effects, this work considers an in-depth, industrially oriented investigation on catalyst/cocatalyst precontacting for a heterogeneous Z-N system and its effect on catalyst behavior. It also provides a practical qualitative and quantitative guidance on the effect of mixing conditions during catalyst and cocatalyst precontacting on the catalyst activity profile in polymerization processes. It should be highlighted that possible chemical changes of the catalyst system during its precontacting with the cocatalyst (e.g., formation of different active site types, population of active sites, and valence states of the active metal species) are beyond the scope of the present study.

In the present study, an experimental investigation was conducted to assess the precontacting effect for slurry

ethylene homo- and copolymerizations with 1-butene under varying mixing conditions for a selected catalyst/cocatalyst molar concentration ratio (i.e., Al/Ti equal to 140 mol/mol) that corresponds to the one employed in large scale slurry-phase loop polymerization reactors. In order to get an insight of the cocatalyst external and internal mass transfer into the catalyst particles, a comprehensive dynamic mass transfer model was employed.

2. Experimental Section

To great extent, modern industrial polymerization plants operate under multistage process configuration. In these processes the catalyst preparation and pretreatment steps usually take place in a separate reactor unit, where the operating conditions (e.g., solvent, temperature, and pressure) can be different compared to the polymerization reactor conditions [9, 28]. The purpose of this study is to carry out the small-scale polymerization experiments under conditions which would be as close as possible to the industrial process.

2.1. Chemicals. Regarding the experimental study, a commercial 4th-generation Z-N catalyst system was provided by Borealis Polymers Oy. The catalyst consists of TiCl_4 supported on MgCl_2 with a mean particle size of $10 \mu\text{m}$. Triethylaluminum (TEA) (Sigma-Aldrich, 93%) has been used as cocatalyst. Liquid propane (Gerling Holz & Co., 99.5%) has been used as solvent. The other respective gases and liquids that had been used are ethylene (Linde, 5.0), hydrogen (Linde 5.0), nitrogen (Linde 5.0), heptane (Donauchem, isomeric mixture 89/95), and 1-butene (Linde, 2.5). All chemicals except the catalyst components were purified with oxidizing/reducing catalyst columns before usage for the polymerization experiments to remove all components which act as catalyst poisons as described in literature [29, 30].

2.2. Experimental Configuration and Procedure. The polymerization experiments have been performed in a 0.5 L multipurpose reactor system in slurry. The experimental configuration is shown in Figure 1. The reactor was filled with 330 mL of propane via the balanced tank. In the case of copolymerization, the comonomer (i.e., 1-butene) was fed together with the solvent. Then, the reactor was heated up to the desired polymerization temperature (i.e., 85°C), hydrogen was fed in the reactor, the reactor was pressurized with ethylene up to 45 bar and, finally, the catalyst/cocatalyst mixture was injected in the reactor. The selected polymerization time was equal to 1 h in all experiments, since it was intended to mimic the mean residence time of the large scale slurry-phase loop reactors employed in Borstar process (i.e., from 30 mins to 60 mins). Moreover, the molar ratio of hydrogen to ethylene was 0.1 mol/kmol, while the comonomer/monomer molar ratio was equal to 10 mol/kmol. The produced polymer powder was dried in vacuum and the net weight was determined.

Regarding the preparation of catalyst system, 5 mg of catalyst and 3 mmol L^{-1} of TEAL (i.e., Al/Ti equal to 140 mol/mol) were precontacted in a glass vial containing 5 mL

of heptane at room temperature. After setting the desired precontacting time (i.e., varying between 0 and 8 min) under well-mixing or static conditions (i.e., stirring speed ranging from 0 to 300 rpm) the catalyst system was injected in the reactor.

During the polymerization experiments the temperature and pressure were monitored and controlled by in-house LabView software on the computer. The reactor pressure was kept constant at ± 0.1 bar from the set point pressure and the reactor was operated at isoperibolic conditions. The jacket temperature was kept constant during the polymerization. As a result, from the exothermic polymerization reaction the reactor temperature was slightly raising, which was directly related to the polymerization rate or catalyst activity, R_p , ($\text{Kg}_{\text{PE}} \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$). Additionally, R_p was determined based on the net weight of the formed polymer powder.

3. Modelling of Internal and External Mass Transfer Limitations of Alkylaluminum Components in Z-N Catalyst Particles

Usually, in a Z-N olefin polymerization slurry-phase process, the catalyst and the cocatalyst (e.g., triethylaluminum, TEAL) components are precontacted in order to increase the catalyst activity as well as to reassure a controllable catalyst fragmentation during the early stages of the polymerization. Thus, in a precontacting vessel two phases can coexist, namely, a liquid phase consisting of diluent, monomer(s), hydrogen, and the dissolved cocatalyst and a solid phase consisting of the catalyst and the sorbed quantities of cocatalyst, monomer(s), hydrogen, and diluent. In Figure 2, the external and internal resistances to the mass transfer of cocatalyst molecules from the liquid phase to the catalyst particle are depicted. As can be seen, the cocatalyst molecules are dissolved to the continuous liquid phase at a concentration equal to $M_{\text{Coc},b}$ (see Figure 2). Subsequently, the dissolved cocatalyst molecules are transferred to the external catalyst particle surface, through the liquid boundary layer surrounding the catalyst particle, where $M_{\text{Coc},s}$ is the dissolved cocatalyst concentration at the external particle surface. $M_{\text{Coc},p}$ denotes the surface concentration of the cocatalyst absorbed species in the solid phase at $r = R$; see Figure 2.

Consequently, in order to calculate the mass transfer rates of the cocatalyst molecules from the liquid phase to the solid catalyst phase in a slurry-phase precontacting vessel, the solubility of the cocatalyst in the different phases present in the slurry process (i.e., liquid and catalyst) should be known. In the present study, those thermodynamic properties have been measured by performing in-house sorption measurements (see Table 1). Moreover, the liquid-solid film mass transfer coefficient, k_{ext} , needs to be calculated from available correlations.

To assess the external and internal mass transfer limitations of the cocatalyst component during its precontacting with a Z-N spherical catalyst particle, the dynamic sorption model developed by Kanellopoulos et al. [26, 27] was employed. The full model description along with its equations and details are presented elsewhere [26, 27]. Let us assume

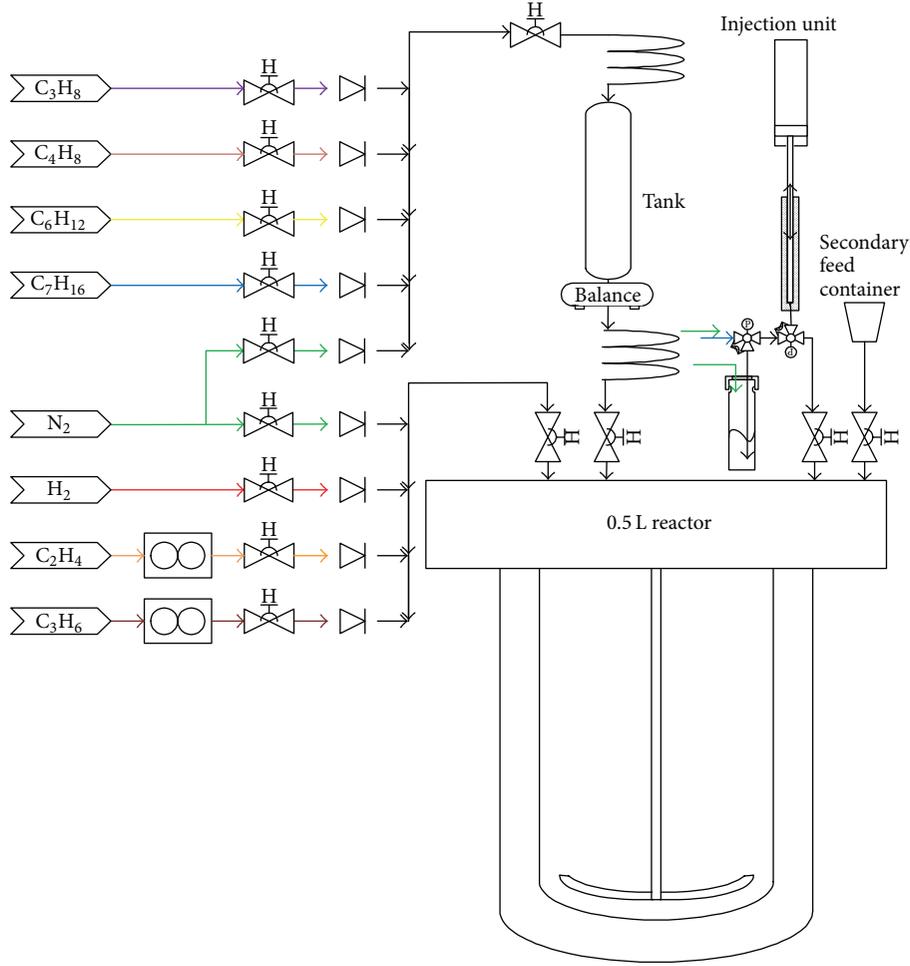


FIGURE 1: Schematic drawing of the 0.5 L polymerization system.

TABLE 1: Operating conditions and main physical, thermodynamic, and transport properties.

Parameter/property	Value
Temperature, T	25°C
Overall pressure, P	1 bar
Catalyst density, ρ_{cat}	1.8 Kg/m ³
Mean catalyst diameter, D_{cat}	10 μm
Catalyst porosity, ε_p	0.2
External mass transfer coefficient, k_{ext}	0.018 1/s*
Overall TEAL diffusion coefficient in catalyst particle, D_i^C [26, 27]	$3.4 \cdot 10^{-7}$ cm ² /s
Cocatalyst thermodynamic concentration in the solid phase, $C_{i,\text{eq}}$	0.0185 gr/gr _{cat}
Cocatalyst thermodynamic concentration in the liquid phase, $C_{i,\text{eq}}^l$	0.0240 gr/gr _{liq}

*: equivalent value of $k_{\text{ext}} = 0.00225$ m/s.

that a porous solid particle of radius R is exposed at time $t = 0$ to a liquid environment. Assuming that the initial cocatalyst concentration value at the catalyst particle is equal to zero

(i.e., $M_i(0, x) = 0$), the following dimensionless dynamic mass balance equation accounting for the diffusion of the cocatalyst molecules from the liquid bulk phase to the catalyst particle can be obtained:

$$\frac{\partial Y_i}{\partial t} = \frac{1}{R^2} \left[R\dot{R}z + \frac{2D_i^C}{z} \frac{\partial D_i^C}{\partial z} \right] \frac{\partial Y_i}{\partial z} + \frac{D_i^C}{R^2} \frac{\partial^2 Y_i}{\partial z^2}. \quad (1)$$

Initial condition is as follows:

$$Y_i = 0 \quad \text{at } t = 0. \quad (2)$$

Boundary conditions are as follows:

$$\frac{\partial Y_i}{\partial z} = 0 \quad \text{at } z = 0, \quad (3)$$

$$Y_i = 1 - e^{-k_{\text{ext}} t} \quad \text{at } z = 1, t > 0. \quad (4)$$

In the above equations, $Y_i(t, z)$ (i.e., $Y_i(t, z) = M_i(t, x)/M_{i,\text{eq}}$) and $z(t)$ (i.e., $z(t) = r/R(t)$) denote dimensionless concentration and space variables, respectively. In addition, D_i^C and M_i are the diffusion coefficient and the concentration of the cocatalyst at time t and $M_{i,\text{eq}}$ is the thermodynamic

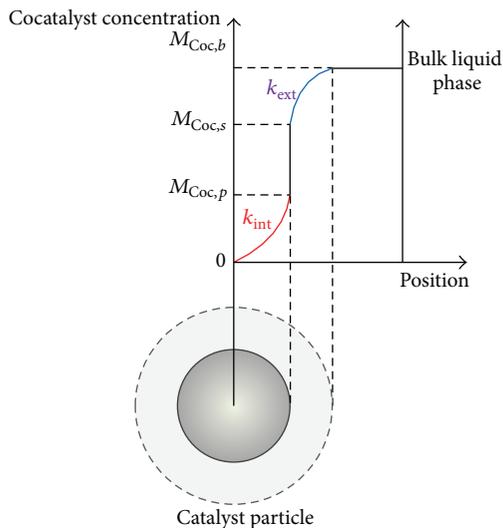


FIGURE 2: External (blue line) and internal (red line) mass transfer resistances, at the catalyst particle level.

maximum concentration of the cocatalyst in the solid catalyst phase (see Table 1). The external liquid/solid film mass transfer coefficient was calculated using the boundary condition described in (4) [26, 27]. In case of poor mixing conditions (i.e., no stirring during catalyst and cocatalyst precontacting), k_{ext} attains low values (i.e., $1.8 \cdot 10^{-2}$ 1/s), while under intensive mixing conditions, k_{ext} reaches order of magnitude higher values (i.e., $k_{\text{ext}} > 1.0$ 1/s). It has to be pointed out that the following equation is employed to calculate the value of k_{ext} taking into account the energy dissipation rate as well as all the physical and transport properties of the liquid medium [24, 26, 27]:

$$k_{\text{ext}} = 0.4 \cdot (\varepsilon \cdot \nu)^{0.25} \cdot \text{Sc}^{-0.5}, \quad (5)$$

where ε is the average energy dissipation defined as $\varepsilon = P_W/V_l \rho_l$, where P_W is the power input by the stirrer. V_l and ρ_l are the volume and the density of the liquid phase, respectively. In addition, $\text{Sc} = (\nu/D_l)$ is the dimensionless Schmidt number. It should be pointed out that the diffusion coefficient of the cocatalyst molecules in the liquid phase, D_l , was calculated via the Wilke-Chang method which, in principle, is based on a calculation of the hydrodynamic forces acting on the “spherical” solute when moving in the solvent [31]. It can be easily shown that the total mass of sorbed species at time t , $m_i(t)$, will be given by the following integral:

$$m_i(t) = m_{i,\text{eq}} \int_0^1 Y_i(z) dz, \quad (6)$$

where $m_{i,\text{eq}}$ is the total mass of the sorbed cocatalyst at equilibrium.

It should be mentioned that for the studied system (i.e., triethylaluminum sorption in Z-N catalyst particle) and the selected operating conditions (i.e., temperature and pressure) the effect of particle swelling due to the components sorption can be assumed as negligible. Moreover, the

density of the catalyst/cocatalyst mixture is approximately constant during the whole sorption process, since only a relatively small amount of cocatalyst is sorbed into the solid catalyst phase (i.e., smaller than 0.02% w/w). Therefore, the variation of the particle radius, $\dot{R}(t) = (dR(t)/dt)$, caused by solid particle swelling, is not considered in (1) [26, 27]. Moreover, the degree of swelling caused by the sorption of triethylaluminum in the catalyst solid phase was estimated by employing a fundamental thermodynamic model (i.e., Sanchez Lacombe EOS) and it was found to be below 5% in terms of catalyst particle volume change [32, 33].

The above dynamic diffusion model consists of a stiff nonlinear partial differential equation (1) and a number of initial and boundary conditions (2)–(4). In the present study, the partial differential equation was solved by the global orthogonal collocation method. Specifically, the partial differential equation was first discretized with respect to the spatial coordinate, z , at selected collocation points, while the unknown variable, Y_i , was approximated by a Lagrange interpolation polynomial [26, 27]. The resulting differential equations were then integrated using the Petzold-Gear method. The operating conditions and the main physical, thermodynamic, and transport properties used in the simulations are shown in Table 1.

4. Results and Discussion

The effect of catalyst/cocatalyst precontacting time under well-mixing conditions and different ethylene partial pressures on the catalyst activity was experimentally investigated (see Table 2, experimental series (1.1) to (1.4)). It can be seen that precontacting has a positive effect on the catalyst activity, irrespectively of the ethylene partial pressure. It should be pointed out that the average increase of the catalyst activity due to precontacting was 12%.

The effect of mixing conditions on the optimal precontacting time was also assessed. Polymerization experiments were performed under stirring (i.e., 300 rpm) and nonstirring, to simulate the well-mixing and nonmixing (plug-flow) conditions. The design of the polymerization experiments was determined by considering the mixing conditions and the precontacting time. It has to be noticed that in those experiments the precontacting time was steadily increased until a plateau in catalyst activity was reached. Figure 3 illustrates the effect of precontacting time on the dynamic evolution of polymerization rate (catalyst activity).

According to Figure 3, the catalyst activity increases until it reaches a maximum value (i.e., $R_p = 5.80 \text{ Kg}_{\text{PE}} \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$) after 1 minute of precontacting. It was also observed that the catalyst activity decreases for longer precontacting times. This can be explained by the fact that for increased precontacting times, a fraction of the potential catalyst sites are deactivated due to catalyst reduction, so the concentration of the actual active catalyst sites decreases.

It is clear from Figure 3 that the dynamic evolution of the catalyst activity follows two stages. The first stage (i.e., $t = 0$ min to $t = 20$ min) is related to the catalyst activation and during that stage the catalyst activity shows a sharp increase

TABLE 2: Polymerization conditions and activities.

Exp. series	p_{C_2} /bar	p_{H_2} /bar	Stirring/—	t_{pre} /min	C_4/C_2 /mol kmol ⁻¹	C_6/C_2 /mol kmol ⁻¹	$R_p/Kg_{PE} g_{cat}^{-1} h^{-1}$	σ /%	Relative R_p /%
(1.1)	2	0.2	Yes	0.5	—	—	3.30	3	—
(1.2)	2	0.2	Yes	1	—	—	3.70	3	12
(1.3)	3	0.3	Yes	0.5	—	—	4.32	3	—
(1.4)	3	0.3	Yes	1	—	—	4.85	3	12
(1.5)	3	0.3	Yes	2	—	—	4.34	3	0
(1.6)	3	0.3	No	0	—	—	3.26	2	—
(1.7)	3	0.3	No	2	—	—	3.78	4	16
(1.8)	3	0.3	No	4	—	—	2.93	6	-10
(1.9)	3	0.3	No	8	—	—	2.36	4	-28
(1.10)	3	0.3	Yes	0.5	100	—	4.38	1	—
(1.11)	3	0.3	Yes	2	100	—	5.20	6	19
(1.12)	3	0.3	Yes	4	100	—	4.14	2	-5.5
(1.13)	3	0.3	Yes	8	100	—	3.63	2	-17

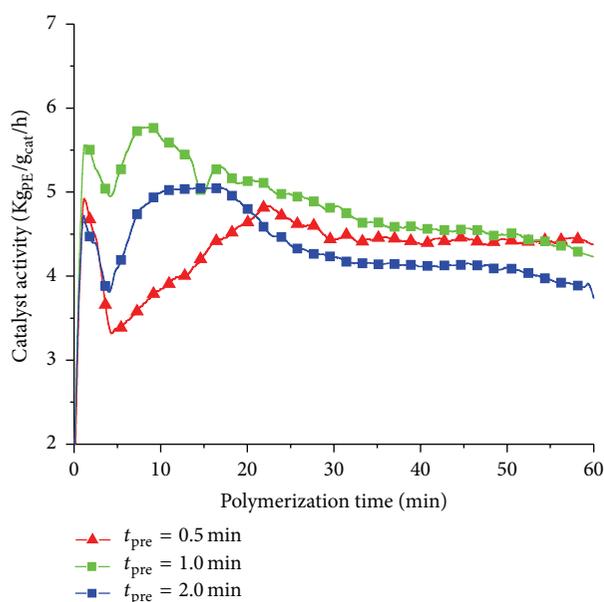


FIGURE 3: Dynamic evolution of catalyst activity for different precontacting times under well-mixing conditions (homopolymerization case).

reaching a maximum point. In the second stage (i.e., $t = 20$ min to $t = 60$ min), the catalyst activity profile reaches a plateau value with a slight negative linear slope, depending on the catalyst deactivation kinetics.

When comparing our results with experiments of Dafaribesheli [4] and Di Martino et al. [5] on precontacting with heterogeneous Z-N system in slurry-phase, similar results are obtained despite the fact that different solvents were used (i.e., hexane and heptane, resp.). Han-Adebekun and Ray [13], studied the effect of long precontacting times in a gas-phase olefin polymerization system. They observed that the polymerization activity decreases when longer precontacting times are applied. Additionally, it should be pointed out that the polymerization rate profile obtained from the present

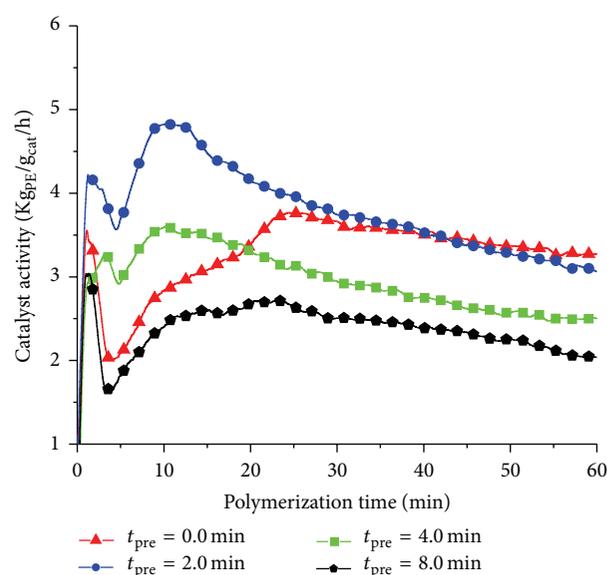


FIGURE 4: Dynamic evolution of catalyst activity for different precontacting times, under nonmixing conditions (homopolymerization case).

study is similar to the one reported by Han-Adebekun and Ray [13] with only difference of the faster increase and decrease of the catalyst activity.

Figure 4 illustrates the effect of catalyst/cocatalyst precontacting time on catalyst activity under nonmixing conditions (i.e., stirring is off during precontacting). As can be seen, the optimum precontacting time without stirring conditions was achieved after longer time (i.e., 2 min) compared to the precontacting under well-mixing conditions (i.e., 1 min). On the other hand, for precontacting times longer than the optimum value the catalyst activity decreases. This is in full accordance with the previous published results and literature findings [4, 5, 13].

To explain the precontacting effect on the catalyst activity, the nature of the cocatalyst (i.e., TEAL) has to be considered.

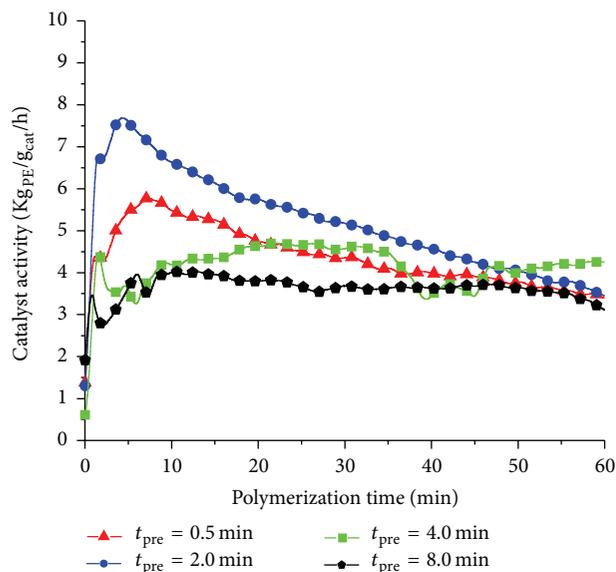


FIGURE 5: Dynamic evolution of catalyst activity for different precontacting times, in copolymerizations with 1-butene under well-mixing conditions.

On one hand, it is an essential component which activates the potential active sites; however, it also acts as deactivating agent [13, 15, 16]. The optimum precontacting time depends on the active sites formation [22] (i.e., titanium reduction from Ti^{+4} to Ti^{+3} and Ti^{+2}) and on cocatalyst external and internal mass transfer limitations [5]. Catalyst activity is strongly influenced by titanium oxidation state; particularly the decrease of activity for longer than the optimal precontacting time can be attributed to an overreduction of the titanium [13, 16].

The precontacting effect was also experimentally investigated for ethylene copolymerization with 1-butene. It was found that the precontacting effect when 1-butene is used as a comonomer follows the same trend as in homopolymerization (see Figure 5). It can be noticed that in all copolymerization runs the catalyst activity is higher compared to the corresponding homopolymerization ones. This can be explained by the well-known cosolubility effect according to which both the solubility and diffusivity of ethylene in a multicomponent mixture (i.e., ethylene, comonomer, and polymer) are increased compared to the corresponding binary system (i.e., ethylene, polymer) under the same operating conditions [34, 35]. Furthermore, higher α -olefins primarily activate titanium to Ti^{3+} (i.e., leading to higher polymerization rate) with less reduction to Ti^{2+} [16].

Based on the data of Figure 5, the average catalyst activity corresponding to the optimal precontacting time (i.e., $t_{pre} = 2$ min) is about 30% higher compared to the case of very short precontacting (i.e., $t_{pre} = 0.5$ min). The increase of the catalyst activity in the presence of 1-butene is even higher compared to homopolymerizations (see Figure 3). In line with previous results there is an activity decrease of 40% for longer precontacting times (i.e., $t_{pre} = 8$ min), compared to optimal precontacting case.

In Table 2 all the experimental results carried out in this study are summarized. In addition relative differences in catalyst activity, R_p , between the precontacting and short- or/and nonprecontacting experiments are presented. The reproducibility of the experiments is given as standard deviation σ of the average value of three repeated polymerizations.

The dynamic mass transfer model described in Section 3 was employed to simulate the effect of external and internal mass transfer limitations of the cocatalyst molecules during their sorption into a Z-N spherical catalyst particle. The dynamic evolution of the cocatalyst sorption rate in a single catalyst particle will depend on the significance of the external particle mass transfer resistances. Figure 6 shows the dynamic evolution of the cocatalyst sorption rate during its contact with the Z-N catalyst under well-mixing (i.e., no external mass transfer limitations) and nonmixing conditions (i.e., external mass transfer limitations). All other operating conditions ($P = 1$ bar and $T = 25^\circ C$) as well as the molar feed composition were kept the same for both cases. As can be seen from the results of Figure 6, under nonmixing conditions, the cocatalyst concentration in the catalyst particle reaches its steady-state (i.e., thermodynamic) value after 3 minutes due to significant external mass transfer limitations (i.e., cocatalyst is transferred from the liquid phase to the solids catalyst particles). That is, the rate of cocatalyst transfer from the bulk liquid phase to the catalyst surface becomes the limiting step in the sorption process (see Figure 7). According to Figure 7, it is apparent that, due to the external mass transfer limitations, the cocatalyst concentration reaches its thermodynamically predicted value (i.e., 0.0185 g/g_{cat}) in longer time compared to the case where the external mass transfer limitations were negligible (i.e., well-mixing conditions). It is also important to notice that in that case no significant internal mass transfer limitations are observed during the dynamic sorption of cocatalyst in the catalyst particles (see Figure 7). On the other hand, when well-mixing conditions have been considered, the time required for the cocatalyst molecules to be sorbed into the solids catalyst particles is substantially shorter (i.e., 10 s), compared to the case where nonmixing conditions were employed (i.e., 180 s).

This is clearly supported by the results of Figure 8 where one can see that the cocatalyst (i.e., TEAL) concentration reaches its final value in a very short time (i.e., 10 s). It should be also pointed out that the concentration of the cocatalyst at the surface of the catalyst particle reaches its thermodynamic value almost from the beginning of the sorption process due to the absence of the external mass transfer resistances (i.e., well-mixing conditions).

5. Conclusion

In the present study a theoretical and experimental investigation of catalyst/cocatalyst precontacting in a Z-N olefin polymerization was performed. A selection of an optimum precontacting time can increase the activity of the studied Z-N catalyst by 10–20% depending on the type of polymerization. In case of long precontacting times, a considerable decrease in

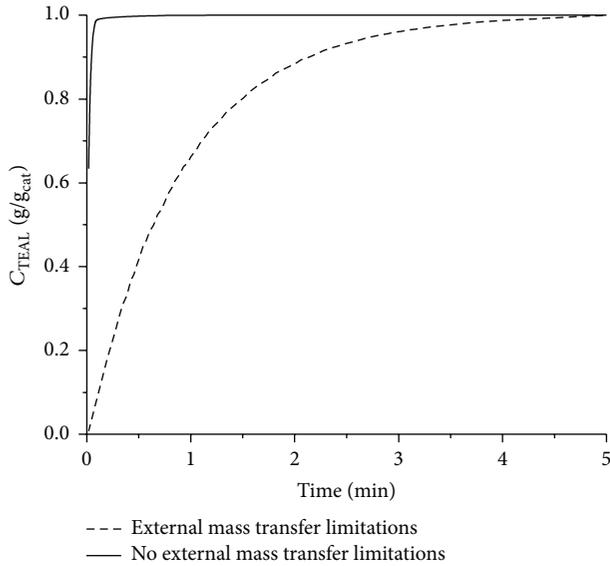


FIGURE 6: Predicted dynamic sorption curves in a catalyst particle for the cocatalyst/catalyst system under well-mixing (i.e., no external mass transfer limitations) and nonmixing conditions (i.e., external mass transfer limitations).

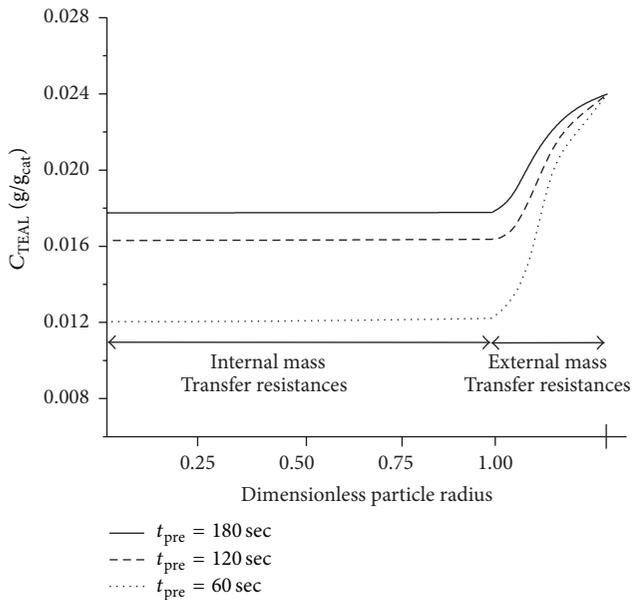


FIGURE 7: External and internal cocatalyst mass transfer limitations in a single catalyst particle under nonmixing conditions.

catalyst activity was observed due to the generation of inferior active sites. In addition, it was found that under well-mixing conditions the optimum precontacting time is shorter compared to nonmixing conditions while the maximum catalyst activity is higher. Overall the catalyst/cocatalyst precontacting process has an effect on the kinetic behavior (i.e., dynamic evolution of catalyst activity). A dynamic mass transfer model was utilized to enhance the understanding of cocatalyst mass transfer inside the catalyst solid phase, considering the internal and external mass transfer limitations related to the

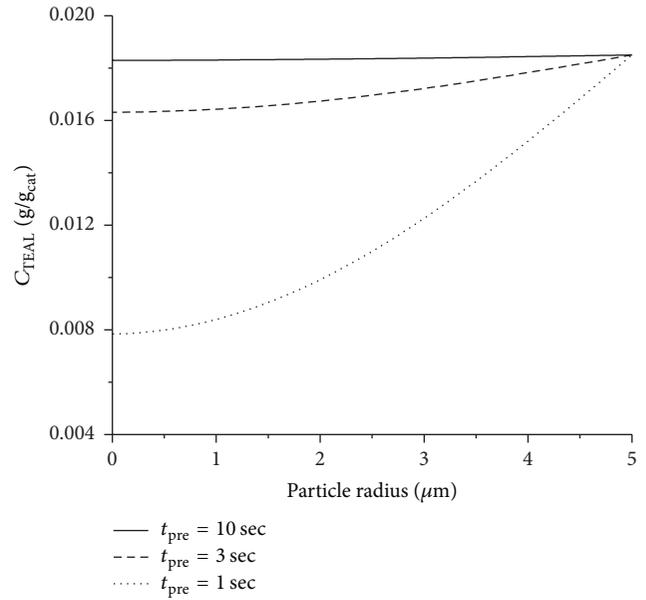


FIGURE 8: Dynamic evolution of the cocatalyst spatial concentration profiles in the catalyst particles under well-mixing conditions.

mixing process. In case of nonmixing conditions (i.e., lack of stirring), where the external mass transfer limitations are manifested, long precontacting times are required in order to reach the thermodynamic concentration of cocatalyst in the solid catalyst phase. This is in full alignment with the long precontacting times required to reach the maximum catalyst activity as concluded by the experimental study. The outcome of the present study provides insight on the effect of process conditions (i.e., mixing effects during catalyst-cocatalyst precontacting process) on catalyst activity profile, thus, facilitating the selection of proper conditions in polymerization processes.

Notation

- C_i : Cocatalyst concentration in solid catalyst phase (Kg/Kg_{cat})
- $C_{i,eq}$: Equilibrium cocatalyst concentration in solid catalyst phase (Kg/Kg_{cat})
- $C_{i,eq}^l$: Equilibrium cocatalyst concentration in liquid phase (Kg/Kg_{liq})
- D_i^C : Cocatalyst diffusion coefficient in solid catalyst phase (m^2/s)
- D_l : Cocatalyst diffusion coefficient in the liquid phase (m^2/s)
- k_{ext} : External film mass transfer coefficient (m/s)
- M_i : Cocatalyst concentration in solid catalyst phase (Kg/m^3)
- $M_{i,eq}$: Equilibrium cocatalyst concentration in solid catalyst phase (Kg/m^3)
- m_i : Mass of the cocatalyst in solid catalyst phase (Kg)

- $m_{i,eq}$: Equilibrium mass of the cocatalyst in solid catalyst phase (Kg)
 P : Overall pressure (bar)
 P_W : Power input by the stirrer (W)
 p_{H_2} : Hydrogen partial pressure (bar)
 p_{C_2} : Ethylene partial pressure (bar)
 R : Catalyst particle radius (m)
 R_p : Polymerization rate or catalyst activity ($Kg_{PE}/g_{cat}/h$)
 r : Radial position inside the catalyst particle (m)
 Sc : Dimensionless Schmidt number ($Sc = \nu/D_l$)
 T : Temperature ($^{\circ}C$)
 t : Time (s)
 t_{pre} : Precontacting time (min)
 V_l : Volume of the liquid phase (m^3)
 Y_i : Cocatalyst concentration at the particle level (dimensionless)
 z : Position inside the particle (dimensionless).

Greek Letters

- ϵ : Average energy dissipation ($J/Kg/s$)
 ϵ_p : Catalyst porosity (volume fraction)
 ν : Kinematic viscosity (m^2/s)
 ρ_{cat} : Density of the catalyst (Kg/m^3)
 ρ_l : Density of the liquid phase (Kg/m^3)
 σ : Standard deviation (%).

Abbreviations

- C_2 : Ethylene
 C_4 : 1-Butene
 C_2/H_2 : Molar ratio of ethylene to hydrogen (mol/kmol)
 C_4/C_2 : Molar ratio of 1-butene to ethylene (mol/kmol)
 H_2 : Hydrogen
 PE : Polyethylene
 rpm : Revolutions per minute (min^{-1})
 TEA : Triethylaluminum
 $TIBA$: Triisobutylaluminum
 TOA : Trioctylaluminum
 $IPRA$: Isoprenylaluminum
 $Z-N$: Ziegler-Natta.

Competing Interests

The authors would like to declare that there are no competing interests regarding the publication of this paper.

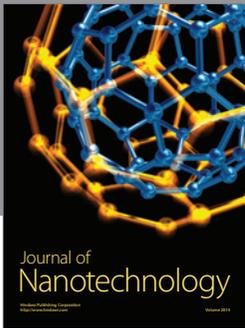
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