

Optimal catalyst and co-catalyst pre-contacting in industrial ethylene co-polymerization processes

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This poster describes the influence of mixing during pre-contacting of the catalyst and co-catalyst for a heterogeneous Ziegler-Natta (ZN) catalyst system on the overall polymerization activity. It is shown that pre-contacting is very important for the catalyst activation as well as for the catalyst kinetics.

Moreover, a comprehensive mass transfer model is employed to provide insight on the mass transfer process and for support of the experimental findings. The model is capable of assessing external and internal mass transfer limitations during the pre-contacting process.

Experimental:

The experiments have been performed in a 0.5 liter, multi-purpose reactor system in slurry polymerization with propane as solvent. The polymerization reactions have been carried out under constant pressure at a starting temperature of 85°C over a period of 60 minutes.

As co-catalysts different aluminiumalkyls (Tri-ethylaluminium (TEA), Tri-isobutylaluminium (TIBA) and Tri-dodecylaluminium (TDDA) have been used. Pre-contacting time has been varied in the range from zero up to ten minutes, with and without mixing.

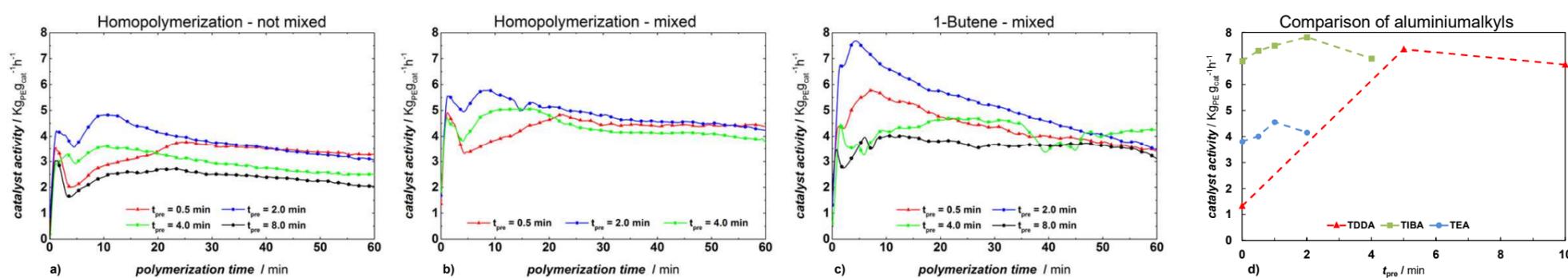


Figure 1a-c: Kinetic profiles of homo-polymerizations under not-/well-mixed conditions (a,b) and co-polymerizations with 1-butene (c) for varying pre-contacting times, using TEA. Figure 1d: Mean catalyst activity using different aluminiumalkyls for homo-polymerizations with varying pre-contacting times.

Model:

For calculation of the mass transfer rates, the thermodynamic properties have been measured by performing in-house sorption measurements. To assess the external and internal mass transfer limitations during pre-contacting, the dynamic sorption model developed by Kanellopoulos et al. [2,3] was employed.

For the studied system (i.e. TEA-sorption in ZN-catalyst particle) and above mentioned conditions the effect of particle swelling can be assumed as negligible, as can be the change in density.

Conclusion:

The study reveals the ideal time for pre-contacting in the experimental setups. The increase in activity seems linear until the maximum is reached. Activity can therefore be increased by up to 20 percent, whereas beyond the optimal pre-contacting time activity decreases significantly (40 percent).

The influence of pre-contacting on the activity of olefin polymerizations with ZN-catalysts highly depends on the used co-monomer respectively the aluminiumalkyl and the mixing conditions applied.

The experimental findings are clearly supported by the model for mixed as well as not mixed conditions.

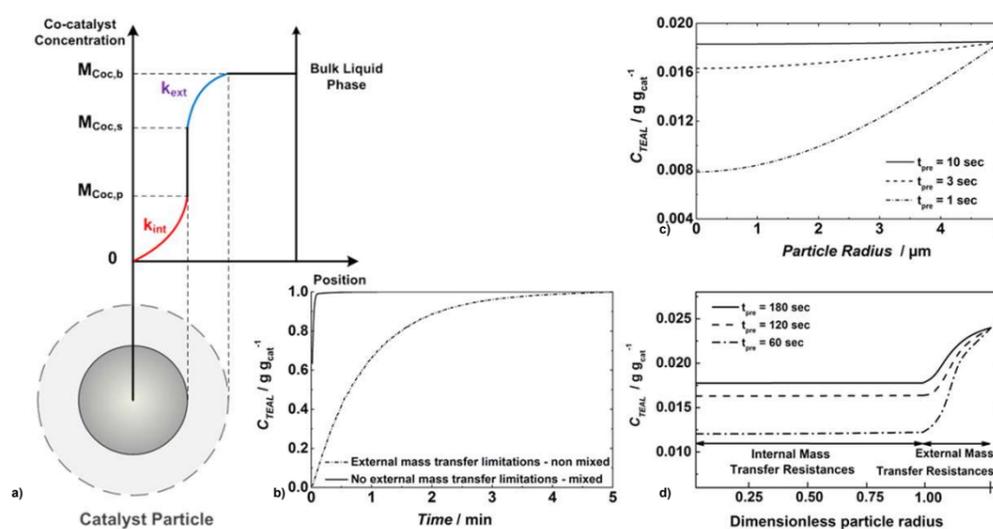


Figure 2a: External and internal mass transfer resistances at the catalyst particle level.

Figure 2b: Predicted dynamic sorption curves in a catalyst particle for the co-catalyst/catalyst system with and without external mass transfer limitations.

Figure 2c: Dynamic evolution of the co-catalyst spatial concentration profiles in the catalyst particles under well-mixed conditions.

Figure 2d: External and internal co-catalyst mass transfer limitations in a single catalyst particle under not-mixed conditions.

References:

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