

# Understanding Polyolefin Processes: Fact 3

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## How does a catalyst particle look like after 0.x seconds?

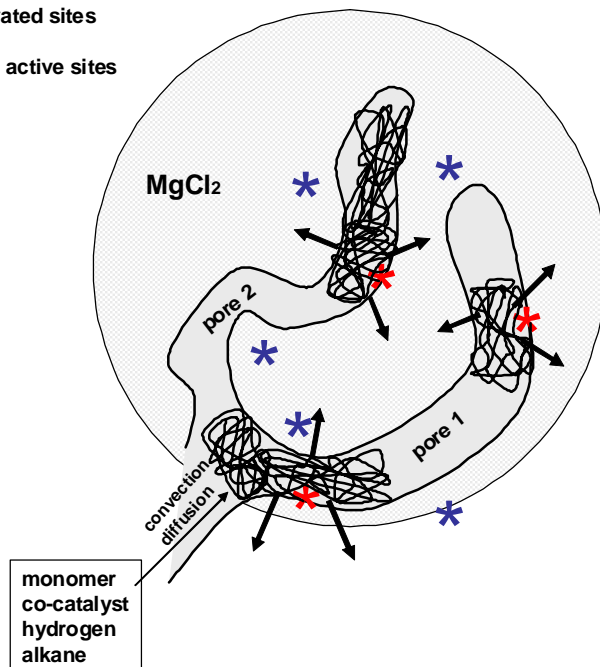
After injection of the catalyst, see also “fact 2”, all components from the bulk flow into the pores of the particle. The polymerization starts at the pre-activated sites and the polymer produced is filling the pores. One big polymer molecule easily reaches the size of an average pore diameter (20 nm). Therefore, only a few polymers are required to generate growth stress, indicated by the arrows in the figure below:

### Two pores with 3 pre-activated sites and 5 potentially active sites

time = 0.1 s: polymer is filling the pores + local growth stress generation near the active sites

\* pre-activated sites

\* potential active sites

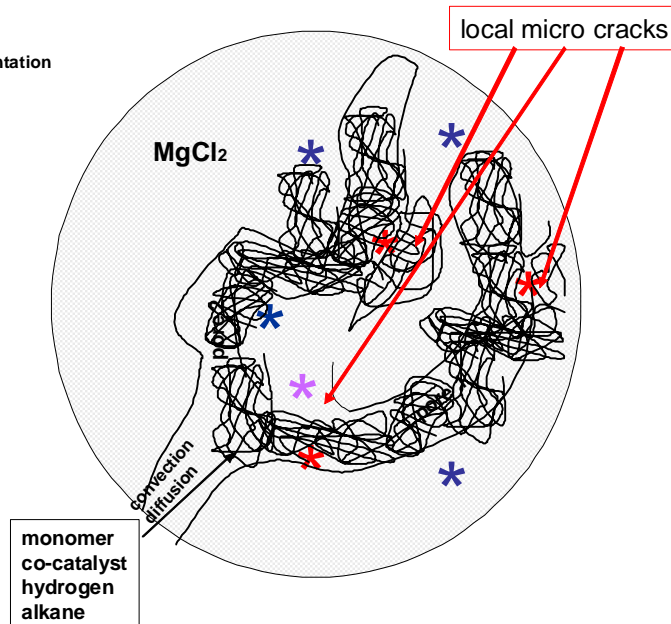


A sufficient number of polymers is formed within parts of a second under industrial conditions, see “fact 4”. These polymers are acting like freezing water in a porous stone, the MgCl<sub>2</sub> carrier starts fragmenting at local positions where the stress reaches a certain critical limit. The MgCl<sub>2</sub> carrier consists usually of primary crystals of about 1 μm diameter and is quite brittle – not to compare with the particle at yields >> 1 g polymer /g catalyst, which is (depending on conditions) much more ductile and does not fragment so easily. At this moment, after 0.1 second, the polymer forms the distributed phase and the MgCl<sub>2</sub> is still the continuous phase that starts fragmenting:

**Two partially cracked pores with 3 activated +1 new + 4 potentially active sites**

time = 0.2 s: particle fragments locally if local stress is higher than the critical; new sites generation starts; new sites start converting to active sites by co-catalyst

- \* pre-activated sites
- \* potential active sites
- \* new sites generated by fragmentation



The local cracks generate new surface converting „potential active sites“ into „new sites“ that are not yet active – they need to be activated by co-catalyst. This activation depends on transport conditions – it is easier in slurry than in gas phase<sup>1</sup>.

Five major effects result from this early – stage fragmentation:

1. the activity is increasing with the increasing number of active sites
2. all active sites are covered by their own polymers produced – this should decrease their activity
3. the cracks are filled with freshly produced polymers – the particle starts growing
4. porosity and pore size are changing
5. the particle starts overheating, see “fact 5”; more in gas phase, less in slurry

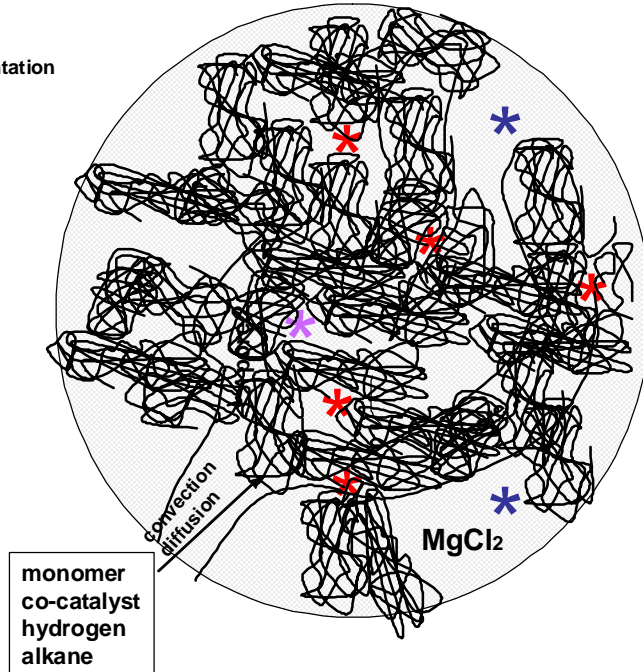
Soon afterwards, the “crack-filling growth” of the particle leads to a phase conversion: at yields > 1L polymer / 1 L catalyst the polymer phase becomes the continuous phase in which the  $MgCl_2$  fragments are distributed – this can happen after 0.2 seconds: a catalyst activity of 36 kg polymer per gram catalyst and hour produces 10 grams polymer per second!

The phase change is shown in the following figure:

<sup>1</sup> common co-catalysts like TEA and TIBA are liquids showing a very low vapor pressure under ,normal industrial’ conditions – surface diffusion is required to bring the co-catalyst to the new sites in gas phase polymerizations

**Part of a polymer particle with 5 activated + 1 new + 2 potentially active sites**  
time = 0.5 s: catalyst fragmentation proceeds; increasing activity and growth stress  
MgCl<sub>2</sub> fragments are distributed within the freshly produced polyolefin (yield > 1)

-  pre- activated sites
-  potential active sites
-  new sites generated by fragmentation



All transport (and other ) properties change when the polymer becomes the continuous phase – this is a very critical stage in terms of particle disintegration that can lead to one of the dominating industrial problems: fines generation, see “fact 6”.