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Heat Transfer and Nascent Polymerisation of Olefins on Supported Catalysts

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Summary: An improved gas phase reactor system has been designed and tested in order to study heat transfer in gas phase olefin polymerisation on supported catalysts. It is shown that temperature rise in a fixed bed configuration is highly dependent on the flow rate of gas, with higher outlet gas temperatures being observed at higher flow rates. In addition it is shown that the shape of the rate curve is dependent on the initial conditions of the reaction, suggesting that the mechanism of particle fragmentation depends to a certain extent on the start-up of the reaction.

Keywords: fragmentation; heat transfer; nascent polymerisation; olefin polymerisation; supported catalysts

Introduction

Polyolefins – polymers based on polyethylene (PE) and polypropylene (PP) – represent the largest family of polymers in the world in terms of volume, with annual production over 100 million tonnes[1] - 80% of which is made on supported catalysts. Advances in R&D over the course of the last few years help polyolefins to steadily replace other, more expensive, less environmentally-benign engineering thermoplastics and traditional materials. This progress in the control of the microstructure of macromolecules has allowed producers to offer a wider range of properties to their customers than previously. However, part of the attractiveness of polyolefins comes from the fact that they are outwardly simple molecules – composed only of carbon and hydrogen. While this confers environmental and cost benefits, it makes it difficult to propose an ever-wider range of properties. One of the ways this can be done is by the manipulation of the structure of the catalyst and its support during the preparation stage, or by correctly "growing" the polymer in the reactor environment. This requires us to have total mastery of the complex issues that govern polymer production on supported catalysts, as well as specialised reactors and tools.

The catalysts used for this type of polymerisation are chemically and physically complex structures. The active site upon which the polymer chains grow is most commonly obtained from a metal chloride (e.g. $TiCl_4$) in the case of Ziegler-Natta catalysts, a metal oxide (CrO_x) in the case of Phillips catalysts, or a metallocene catalyst (metal linked to one or two cyclopentadienal rings). The precursors are deposited on a highly porous solid support (typically $MgCl_2$ for ZN catalysts, or silica for the others), and the supported catalyst is often activated by the addition of a cocatalyst (e.g. alkyl alumina). The challenges currently faced by polymer and catalyst producers include:

- **Complex interactions** between the support and the precursors that lead to different active polymerization sites.
- **Modification of the chemical structure** *in situ*. E.g. exposure to monomer alters the behaviour of the active sites. Such changes are less well established in other catalytic systems. Also, local overheating

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can cause the catalyst to deactivate in unforeseen ways.
- **Rapid morphological changes** of the particle structure. It appears that the morphology of the particle is fixed within the first seconds of the reaction.
- **Highly "non-linear", dynamic kinetics**. It is not feasible to extrapolate the behaviour of the reaction at one bar to more realistic conditions (10–30 bars). We need to have reactors that run under such conditions, and that allow us to recover the particles.

Advances have been made in the study of olefin polymerisation catalysts, and modelling efforts have been made that help us to more clearly see the complex relationship between reaction conditions and the evolution of product morphology.[2–7] Nevertheless, the complexity of the catalytic system is responsible for the fact that there are a number of lacunae in our knowledge of how they function. This means that it is necessary (perhaps more so than ever with the current state of the petrochemicals market) to make fundamental progress in understanding how the polymerisation reaction is controlled, how we can design catalysts that can satisfy material demands (wider range of better defined properties), and what is influenced by different operating conditions (morphology, high yields, simplicity of use). The study of these complex issues is currently hampered by some important shortcomings that include a lack of well-adapted experimental equipment needed to understand the complex changes taking place. The chemical nature of the catalyst, as well as the morphology of the particles can be fixed with a few seconds, even fractions of seconds.

At the risk of over generalising, until very recently most of what we know about the evolution of particle morphology comes from either microscopy studies of particles formed after a certain period of time (several grams of polymer per gram of catalyst at best under industrial conditions), or "idealised" conditions. These latter experiments can be subdivided into two groups: (i) very controlled conditions (low T, P) to get low reaction rates.[8] This has the obvious disadvantage of producing particles in a manner different from that in a real process; (ii) idealised supports (e.g. silica wafers).[9,10] These experiments are very interesting in the sense that we can learn a great deal about the way in which nascent polymer chains are formed. The obvious disadvantage is the lack of realistic particle morphologies.

In an earlier work, we presented a high pressure gas phase reactor with residence times as short as 0.1 seconds[11] to look at the initial instants of the reaction, and to provide a partial solution to some of these difficulties. This early version of the fixed bed gas phase system worked reasonably well for higher pressures, but the set up did not allow for controlled flow rates, and problems with the initial design meant that there were difficulties associated with back flow at low pressures.

In the current text we present a new improved version of the gas phase reactor, and some preliminary results that show that the initial rate of polymerisation on silica and $MgCl_2$ – supported catalysts seem to be controlled (at least partially) by particle fragmentation, but this phenomena is different at different reaction conditions.

Experimental Part

Ethylene with minimum purity of 99.5% was purchased from Air Liquide (France). Triethylaluminum (TEA) was obtained from Witco (Germany). Argon from Air Liquide (France) with minimum purity of 99.5%, was used to keep the reaction environment free of oxygen. Silica particles were treated with TEA; vacuum dried at 150 °C and kept under argon atmosphere at room temperature. Unless stated otherwise, all reagents were used as received, without additional purification.

Two different catalysts were used in this study: A proprietary metallocene (M1) supported on silica, and a commercial

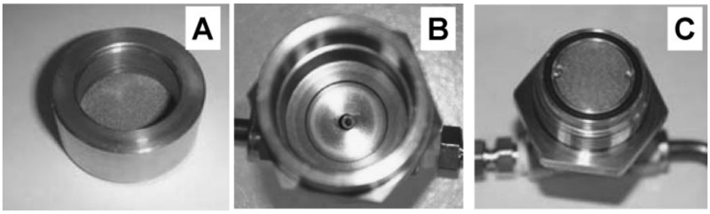

Figure 1.
Interior view of the high pressure fixed bed reactor used for olefin polymerisations. (A) Reactor Cartridge, (B) interior views of the reactor chamber, and (C) frittered metal filter for sealing the reactor.

Ziegler-Natta catalyst (Z1; $TiCl_4/MgCl_2$). Contractual agreements preclude further information on the preparation and composition of the catalyst M1. Z1 has a titanium content 2.6 wt.-%.

The reactor developed in this study consists of a metal chamber closed with a frittered metal cartridge, and can be seen in Figure 1. The chamber (A) is filled with a mixture of silice (usually treated with TEA) and catalyst (1–6% catalyst w/w) inserted into chamber (B), and then closed with the frittered metal lid (C). Gas enters through the hole in the bottom of (b), and leaves through a similar hole at the back of the filter (C). The entire assembly is then plunged into a water bath to ensure constant inlet gas and jacket wall temperatures (c.f. Figure 2). Thermocouples at the inlet and outlet of the reactor allow us to record the temperature rise of the gas phase as it flows through the bed. Temperature measurements are received each 0.5 sec by a data acquisition unit (Hewlett Packard 34970A) and are treated in a computer using the program Agilent BenchLink Data Loger. The filling operations are performed in a glove box to avoid contamination of the contents.

In order to control the reaction time, the system is equipped with two miniature solenoid valves (ASCO Joucomatic, France). These valves allow the entry of the gas or not. They are controlled by a logic controller (Crouzet Millenium II+, France) which allows us to program the injection time automatically or manually. A pressure transmitter (SCAIME ATM, France) was used to monitor the reactor pressure. And a metering valve is installed for chose the flow rate of the gas. The experimental procedure was as follows:

- After purging the feed lines the reactor was attached to the system and the thermocouples were connected to the data acquisition unit.
- Argon is injected through the feed lines and the reactor until the reactor temperature remains constant and equal to the temperature of the heating bath.

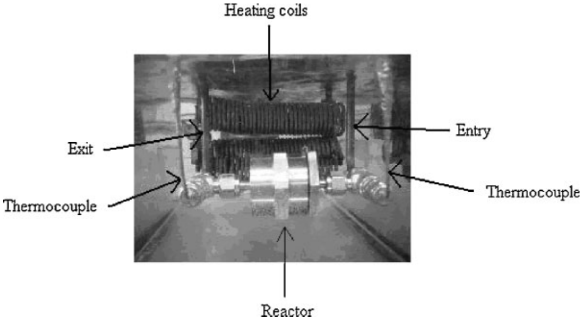

Figure 2.
View of the reactor assembly *in situ* in the thermostatted water bath.

- The argon feed valve is closed, the metering valve on the ethylene feed line was set to the desired level, the solenoid valves on the feed line were set at the desired level, and the pressure of the ethylene feed was also set.
- The solenoid is programmed to open for a given time.
- The reactor is then degassed rapidly to remove any residual monomer, thereby stopping the reaction.

Productivities are measured by weighing the reactor before and after the polymerisation step (after a drying period to ensure that there is no residual water on the reactor assembly of course).

Results and Discussion

Effect of Flow Rate

Different ethylene flow rates were tested to determine the influence of relative gas particle velocities: 5, 8, 16 cm^3s^{-1} (STP). The results of a standard series of runs at 80 °C, 13 bars of ethylene using 6% of catalyst M1 in silica are shown in Figure 3, where we can see the temperature of the outlet gas stream as a function of reaction time. It can be seen here that the higher the flow rate, the higher the outlet gas temperature is. This might at first seem to be counter intuitive as the higher flow rate will correspond to a shorter residence time for the gas phase in the reactor, thereby giving it less time to heat up. However it appears that a number of conflicting factors are at play here. First of all, the increased flow rate corresponds to a higher linear velocity, and thus a higher Reynolds number. Therefore one obtains a much more favourable gas-particle heat transfer coefficient at 16 cm^3s^{-1} than at 8 cm^3s^{-1}. It is therefore probable that the higher flow rate gives us a much better indication of the surface temperature of the polymer particles than does the lower flow rate. Of course, a more in-depth modelling study would be extremely useful in determining the different temperature gradients in the reactor (particle-gas in particular).

This conclusion is further supported by the graph of productivity (g polymer per g catalyst) as a function of flow rate in Figure 4. Here we can see that the higher the flow rate, the lower the productivity for the 75 seconds of reaction. If the temperature rise in Figure 3 was caused by a higher rate of reaction (perhaps due to a lower conversion of monomer and therefore a more uniform and higher concentration along the bed), then one would expect the productivities to be higher. In fact this is the

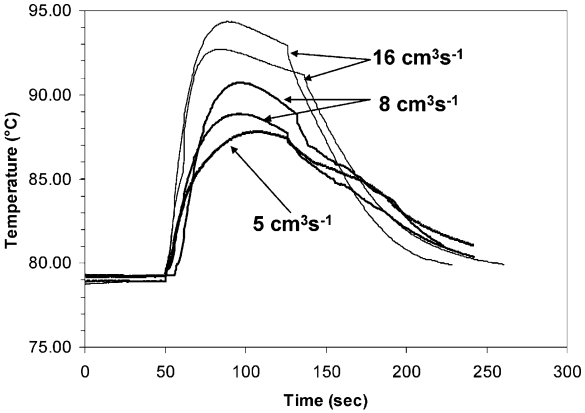

Figure 3.
Temperature rise over fixed bed of catalyst/silica for 13 bars of ethylene, 80 °C and different ethylene flow rates (STP). The sharp breakpoint in the curves at approximately 125–150 seconds corresponds to the point where the reactors were degassed.

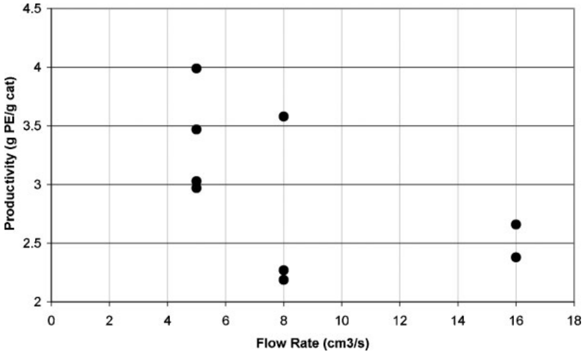

Figure 4.
Productivities for the different flowrates shown in Figure 3.

opposite of what is observed, with the lowest productivities corresponding to the higher flow rates. This in turn implies that the particles were probably hotter at the lower flow rates than they were at the higher ones, and therefore polymerised faster.

Nevertheless, this result shows that by controlling the flow rate this tool will allow us to explore a wide range of heat transfer conditions while maintaining important process parameters such as the overall pressure (and gas phase composition in more complex systems) constant.

Since the higher flow rate seemed to give the most clearly measurable ΔT (N.B. in the rest of the paper, ΔT will refer to the inlet-outlet temperature difference), we chose to use 16 cm^3s^{-1} (STP) as the ethylene flow rate in the remainder of the experiments.

In a different series of experiments using catalyst M1, the reaction conditions were changed from 13 bars and 80 °C (“normal” conditions) to 1 bar and 30 °C (“mild” conditions), and the reactor system was used to look at the initial seconds of polymerisation. The results can be found in Figure 5. Here we see the temperature rise between the inlet and outlet gas temperatures for the two conditions.

If one compares the initial slope of all three curves, it can be seen that the rate of temperature increase (which is directly proportional to the reaction rate) is similar for all three runs. This implies that at the start of the reaction the rate is the same in all cases. However, if one examines the curves for the “mild” runs, it is clear that after a short time, there is a “plateau” that lasts for approximately 5 to 6 seconds, and then the reaction begins to accelerate once again. The most likely explanation for this plateau is the one offered by Knocke

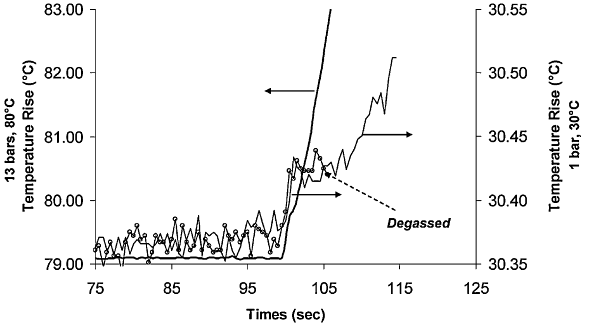

Figure 5.
Temperature rise at the reactor outlet for “mild” and “normal” reaction conditions using catalyst M1.

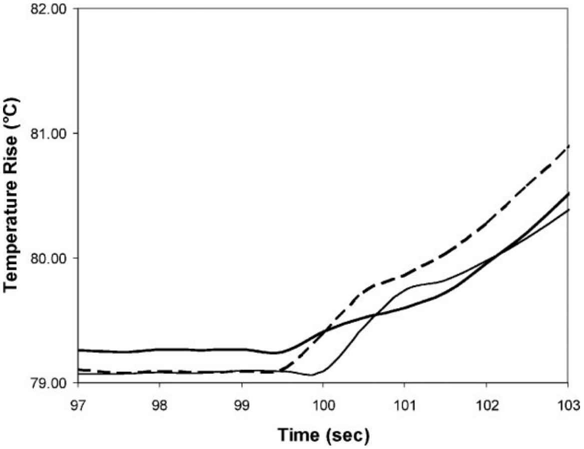

Figure 6.
Temperature rise at the reactor outlet for repeat runs under "normal" reaction conditions using catalyst M1. It is clear that a small change of slope is still observed.

et al.[8]. These authors investigated polymerisation on silica-supported metallocenes, and saw plateaux much like the ones in Figure 5 under the vapour pressure of liquid propylene at 50 °C. Under such mild conditions the authors used electron microscopy to identify the formation of a "crown" of polymer in the outer layers of the particle. They claimed that this crown blocked the mass transfer of monomer to the interior of the particle for a certain time – the time necessary for polymer to build up at a slower rate – needed to cause this outer layer to fragment. Once this occurs the polymerisation begins at its expected rate. This explanation is probably acceptable for the silica-supported catalyst used here under mild conditions, and can account for the curves for the "mild" experiments. However, it is quite clear that no such behaviour is seen for the "normal" conditions, where the rate increases rapidly, and with no visible interruption or plateau formation in the run shown here. In this instance, there is a very small break in the curve after 5 seconds which lasts for less than a second. It is entirely possible that this change of slope can be attributed to measurement noise, however examination of the curves just following the injection of ethylene for replicate "normal" runs seen in Figure 6 shows that this short change of slope is present for each reaction at approximately the same moment. This tends to suggest that fragmentation might slow the reaction down under more violent conditions for a very short time. If this is the case, then this result shows that the rate of fragmentation is controlled to a certain extent by the rate of reaction. More work needs to be done on this point to allow us to draw a more definite conclusion, but the

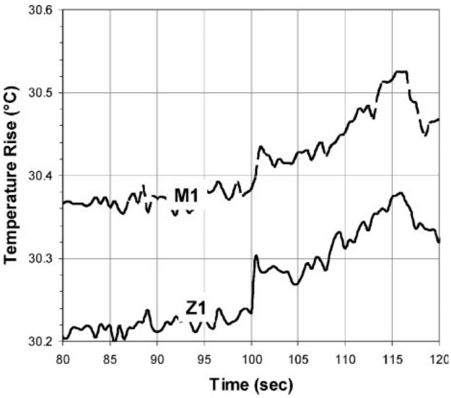

Figure 7.
Temperature rise at the reactor outlet for "mild" reaction conditions using catalyst M1 (see Figure 5) and Z1. Injection of ethylene was at 100 seconds in both cases.

evidence available at the current time supports this hypothesis.

A comparison of the temperature rise during the initial moments of polymerisation on catalyst M1 and catalyst Z1 is shown in Figure 7. It can be seen that under the "mild" reaction conditions used in these runs the plateau that we have attributed to the fragmentation step is very similar in duration and amplitude for the two different supports. This is not necessarily expected as current opinion often holds that catalyst fragmentation is more rapid for Ziegler catalysts on $MgCl_2$ than for silica-supported catalysts. However it is very important to underline that this result is for one specific set of very mild conditions, and significantly more experiments need to be done before a general conclusion can be drawn on this point.

Conclusions

We have presented a gas phase reactor for the investigation of heat transfer effects during the initial stages of the polymerisation of olefins on supported catalysts. It has been shown that this reactor can be used to examine the rate of heat generation under different conditions, including conditions approaching those used in industrial production. Coupled with a detailed modelling study, this type of tool will be able to provide experimental evidence of heat transfer effects and particle over-heating under different conditions.

It is hopefully clear that this novel research tool will allow us to study what appears to be one of the most critical parts of an olefin polymerisation reaction, and to obtain direct measurements of the heat rise – again a piece of information that until now has not really been studied directly. As a proof of this claim, we have used this tool in a way suggesting that the rate of reaction has a very strong influence on the rate of fragmentation. However much more work needs to be done on these different points in order to exploit the potential of this important tool.

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