Chimia 55 (2001) 231–233
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ISSN 0009–4293

New Method for Online Observation of Growing Polyolefin Particles

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Abstract: In classical experimental research work on catalytic olefin polymerization, kinetics and powder properties are always determined as an average value over a large number of polymer particles. When studying the properties of the polymer, the powder has to be evacuated from the reactor system. This evacuation step will often change the properties to be measured.

Here, a method for direct observation of growing polymer particles is shown. To allow individual observation of a number of growing polymer particles in a catalytic gas phase polymerization, a polymerization cell was built with a transparent lid. The cell was placed in a microscopic video system in such a way that the particles could be observed during reaction and pictures of the particles were stored with a preset time interval.

Using a 4th generation Ziegler-Natta catalyst at 40 °C and a propylene pressure of 8 bar, polymerizations were carried out in the presence of hydrogen. It was shown that reaction kinetics can be derived from these experiments, not only average values for larger number of particles, but also kinetics for individual particles. It is shown that kinetic results can be obtained in a reproducible way, and thus it is well possible to kinetically characterize a catalyst in gas phase polymerization using this method.

As the current lid is not only transparent to visible light, but also to infrared light, an infrared camera can be applied to measure surface temperatures of the growing polymer particles. This can be of large help in development of single particle models. One can also think about different applications and extensions. New analysis method could be applied to the same principle, for example Raman spectroscopy or X-ray tomography. Next to that, currently a stirrer is being implemented to introduce convective cooling of the particles and one can also think about application of other media than gas phase, like the slurry phase.

Keywords: Experimental tools · Microscopic observation · Olefin polymerization

Introduction

Over the past 30 years, a lot of effort on the modeling of single particles in the catalytic olefin polymerization has been reported. The relatively slow development of the models and their poor ability in the prediction of single particle behavior related to larger scale reactor conditions are clear indications that introduction of detailed experimental verification for the models is inevitable. In this work a polymerization cell is shown that can be used in direct observation of the growing polymer particles during the reaction. A similar method was first developed by Reichert's group for the polymerization of butadiene at lower pressures [1][2] and was also described by Kaneko [3] and already mentioned earlier [4][5]. Some of the (im-) possibilities of our present system are explored in this work.

Experimental – Chemicals

The catalyst used in the current investigation is a commercially available Ziegler-Natta catalyst of the fourth generation [6], with $TiCl_4$ on a $MgCl_2$ support. As co-catalyst and external electron donor tri-ethyl aluminum (TEA) and di-cyclo pentyl di-methoxy silane were used. Hexane was used to suspend the catalyst and all used gases were of 'Pro Analysi'- and 5.0-quality respectively and further purified by beds of molecular sieves and reduced Cu-catalyst.

Experimental – Set-up

The micro-reactor setup used here consists basically of two parts. The first part is the polymerization cell in which the polymerization reactions are carried out. The second part is the connected observation system. These two parts are schematically shown in Fig. 1.

Polymerization Cell

The polymerization reaction is carried out in a 6 ml stainless steel polymerization cell (1) that has a transparent lid (2) to allow particle observation. The lid is mounted tight with a metal ring (3) to permit pressures up to 40 bar without leaking. Pre-activated catalyst particles (4) are distributed on the glass support disk (5). The polymerization cell is placed in a thermostatic jacket (6) to ensure a constant temperature in the cell. A thermocouple located in the gas phase direct-

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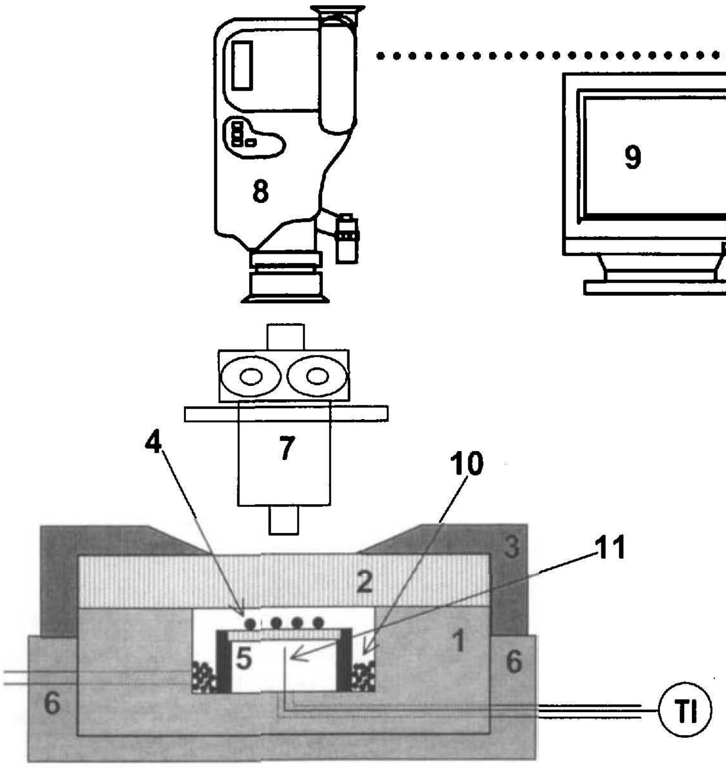

Fig. 1. Schematic representation of the set-up used. The polymerization cell is placed underneath a digital camera using a microscope. A frame-grabbing PC saves pictures of the digital camera. (Numbers are explained in text.)

ly underneath the support disk (11), measures gas temperature in the cell.

System for Optical Observation

In the observation system, a Pieper FK 7512-IQ digital camera (8) is connected to the Carl Zeiss Axiotech Vario 25 HD microscope (7). Next to the internal light source of the microscope a second, external light source is used to obtain good contrast of the polymer particles on their background. The digital camera is connected to a frame grabbing PC (9) with imaging software. With a preset frequency images of the polymer particles are saved.

Experimental – Preparation of the Catalyst

The catalyst is prepared in a glovebox under nitrogen atmosphere. Hexane, a 4 mg/g TEA-solution in hexane and a 2 mg/g D-donor solution in hexane are added to the catalyst to activate it. The suspension is shaken for 15 min at r.t. and subsequently the liquid is removed from the catalyst. The catalyst is washed with fresh hexane once and dried quickly at room temperature. An activated, dry, free flowing catalyst powder is obtained.

The dry catalyst is dispersed on a glass support disk, in such a way that the observable area of the optical microscope will contain about ten catalyst particles. In the polymerization cell, a small amount of polyethylene powder is put, that was treated with a TEA-solution in hexane (10). The activated polymer powder will scavenge impurities from the incoming gas, but due to the low vapor pressure of the alkyl, it will barely show co-catalytic activity. The reaction cell is closed, moved out of the glovebox and brought to reaction conditions at the set-up.

Experimental – Polymerization Procedure

The cell is placed in the jacket to be brought to reaction temperature. The frame grabber is started and introducing the process gas, propylene and hydrogen, into the nitrogen filled reactor starts the polymerization reaction. Typically the reaction is continued for 20 min.

Results and Discussion

With the digital camera, every 10 sec a 2-dimensional image of the growing polymer particles is obtained. After the experiment, imaging software of ImageC is used to determine in every picture, the size of the 2D representation of all the present catalyst/polymer particles. This is an important step in the data processing. Due to spherical aberration and background blurring, the boundary of the particle is often not clear to recognize. In every picture, an 'intensity threshold' has to be determined that indicates if a pixel belongs to the particle or to the background. The cover of the polymerization cell strongly influences the scattering of the light coming from the polymer particles. To reduce these effects the thickness of the lid should be as small as possible. By using sapphire the thickness of the lid was reduced from 8 to 2.5 mm, without changing the maximum allowable pressure of the cell, which is 40 bar.

After determination of the 2D surface area of every particle, the 3D volumes of the particles can be calculated, assuming a spherical shape for the particles. The increase of the particle volume is then transformed into a polymerization reaction rate, using the density and porosity of the polymer. With this calculation, the images of the growing polymer particles can be calculated to a reaction rate versus time curve, as shown in Fig. 2. It shows the growth rate of four different particles in the same experiment. Scattering of the reaction rate is caused by difficulties in the determination of the 2D surface area, and does not reflect a real changing reaction rate. An error in determination of the 2D area (d^2) is intensified in the calculation of the volume (d^3). The growth rates of the different particles are shown not to

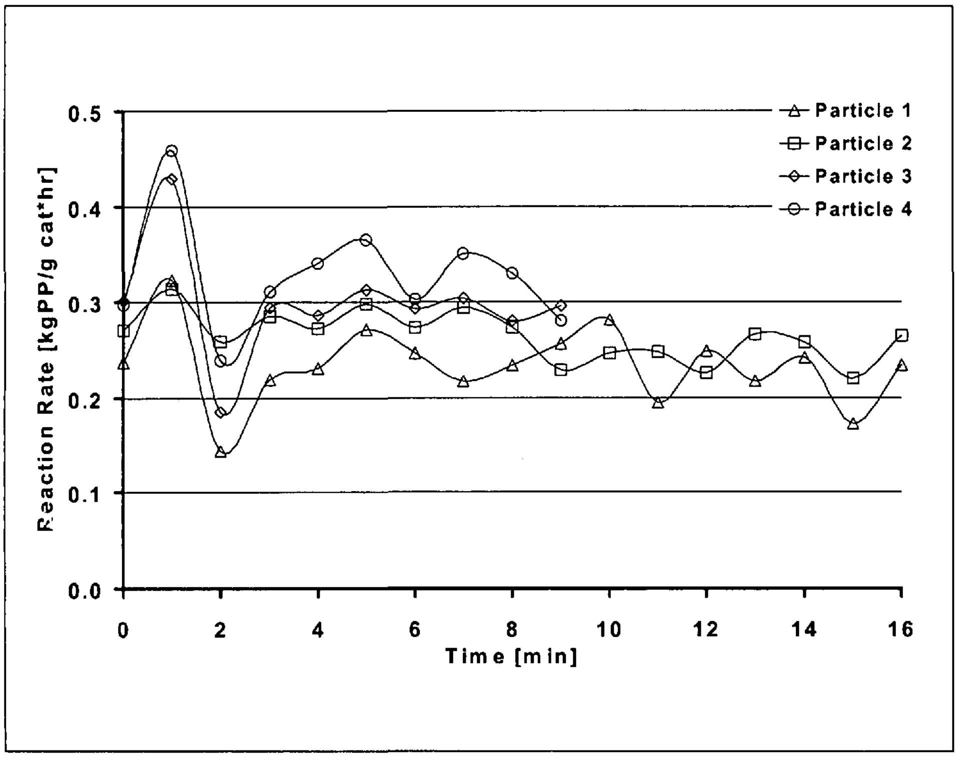

Fig. 2. Reaction rate over time, calculated from the surface of the 2D representation of four different polymer particles in the same experiment. Reactor gas consisted of 8.3 bar propylene, 0.5 bar hydrogen and 1.1 bar nitrogen and reactor temperature was 40 °C.

be equal, but remain between certain boundaries. In all polymerization experiments worked out with this method this scattering of rates of the particles has been found. In future work, the reaction rate of the particle can for example be related to its initial particle size.

When reaction rates obtained with this method are compared to typical reaction rates for this catalyst in liquid phase bulk polymerization – 5 kg/g*h at 40 °C in presence of H_2 – after a correction is made for the difference in monomer concentration at the active site as suggested by Meier [7], reaction rates are about 50% lower than expected. There are a few explanations for this difference, of which one is the recipe used. As a dry catalyst powder is needed in this reactor, the catalyst is activated and dried; no additional co-catalyst or donor is available for the catalyst after the activation. In the case of a liquid phase polymerization, donor and co-catalyst are dissolved in the liquid phase and a possible deficiency can be replenished.

Because of the fact that the method shows individual particles, and allows comparing the different individual particles during the polymerization, the method is very well suited to study effects that can not be studied in conventional systems. It is for example well possible to study the shape replication and shape development of the growing particles. Existing kinetic methods only allow comparing the initial and final particle size distribution and from this it is hard to draw firm conclusions on, for example, the distribution of active material on the support. Our method would produce such future data in the investigation of the relation between initial size of the catalytic particle and the polymerization rate of this particle. These examples show that this method can add much to existing experimental methods.

Of course the application of this idea is not limited to the use of an optical camera system. In the near future we will report on the application of an infrared camera for measuring surface temperatures of the particles, but one can also think about the use of Raman spectroscopy, X-ray tomography and other analytical methods.

Acknowledgements

The authors wish to acknowledge Gert Banis, Fred ter Borg, Karst van Bree and Geert Monnink for their technical assistance on the realization of the reactor set-up. Ronald Capel, Frank de Nobel and Petra Meulman are recognized for their efforts in the experimental work.

Received: December 18, 2000

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