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Influence of Silica Support Size on the Polymerisation of Ethylene Using a Supported Metallocene Catalyst

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Summary: In the current work, we will focus on the influence of support properties on the activity and molecular weights of polyethylene produced with a metallocene supported on silica treated with MAO. It is demonstrated that relatively small changes in the size of the silica particles have a profound effect on the activity of the growing particles, and that not all particles in a given batch of catalyst behave in the same manner.

Keywords: mass transfer; metallocene; olefin polymerization; supported catalyst; silica properties

Introduction

Due to the strong commercial interest of metallocene catalysts in olefin polymerisation, extensive research has been carried out in this field. The main advantage of metallocene catalysts is that they can, in theory, be used to produce a polymer with a well-defined, narrow molecular weight distribution, i.e. a polydispersity index close to 2.[1,2] Recently, is has been reported that the pore size of supports has a significant effect on the gas-phase polymerisation rates for ethylene homopolymerisation and ethylene/1-hexene copolymerisation over supported (n-BuCp)$_2$ZrCl$_2$-MAO catalysts.[3] Similar effects of support pore size on the activity during slurry polymerisation using supported Cp$_2$ZrCl$_2$-MAO catalysts have also been reported by Sano and coworkers.[4–6] This effect of pore size on catalytic activity suggests that pore size influence the nature of the catalytic sites for supported zirconocene catalyss. This can in part be attributed to the likelihood that the amount of methyaluminoxane (MAO) fixed on the support is highly related to the pore diameter. The same results are observed in the case of polypropylene polymerisation.[7] In the literature, most of the work concerning the influence of support is concentrated on the analysis of the activity and polymer product in terms of molecular weight distribution. Typically, temperature rising elution fractionation (TREF) and crystallisation analysis fractionation (CRYSTAF) were used in order to identify the number of active sites as a function of the different reaction conditions.[8]

Experimental Part

The reactor used in the current work is a 2-L, jacketed metallic reactor, which is insulated with glass wool and equipped with a platform for data acquisition and control of the reaction. A schema of the reactor is found in Figure 1. Water circulating in the jacket is used to control the temperature in the reactor (no water circulates in the cover). A resistance heater placed in the bath warms up the water circulating in the jacket, and during the polymerisation, cold water (with a low flow rate) circulates in the serpentine. This configuration allows us to diminish the inertia of the thermostated bath, and to rapidly decrease the bath temperature during the reaction if necessary.

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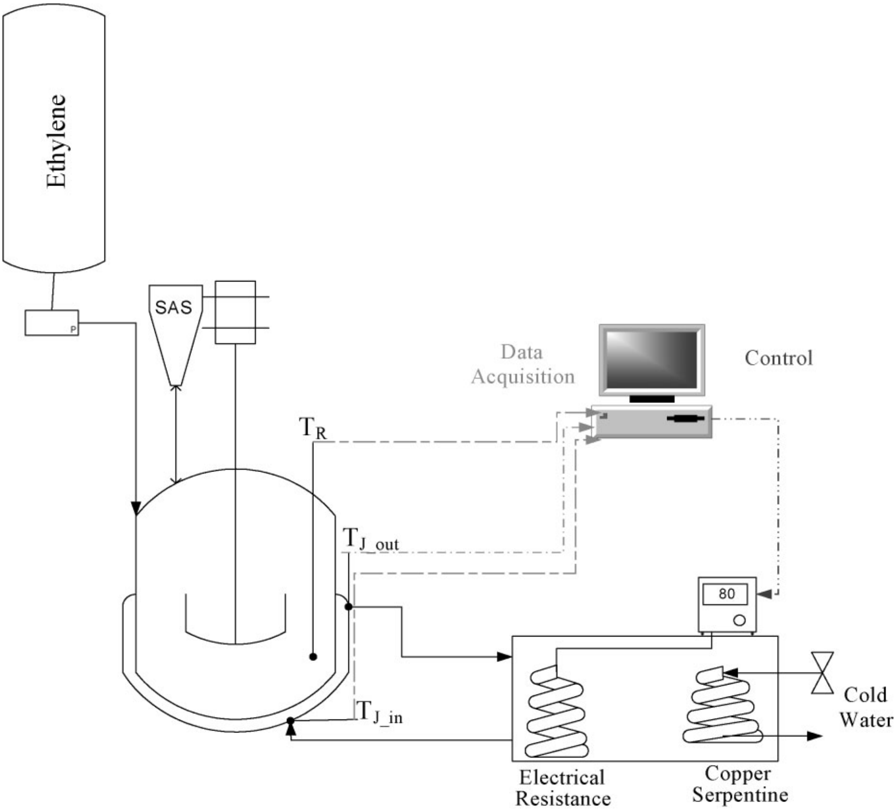

Figure 1.
Schema of the reactor configuration used in this work.

The reactor is equipped with a cartridge for the introduction of the catalyst (c.f. SAS in Figure 1). The monomer is fed from a storage tank connected to the reactor via a regulator that maintains a constant pressure in the reactor with a precision of 0.01 bars. The reactor temperature is measured with a platinium resistance PT100 (precision 0.01 °C). To protect the sensor against aggressive products, it was placed (by the constructor) in a metal tube, serving also as a baffle. Three other platimium resistances, having the same precision, are used to measure the inlet and the outlet temperature of the circulating liquid in the jacket, and the temperature of the monomer entering in the reactor. A thermometer measures the ambient temperature.

The electric signals of all the sensors are sent to a PC through a numerical data acquisition system (HP 34970A) connected to a PC via a RS-232 serial port. This allows us to measure the reaction conditions in-line with a frequency of one measurement per second. It is therefore possible to obtain redundant measurements of the reaction rate: either by monitoring the monomer consumption (ΔP) or by calorimetry.profile by calorimetry.

The commercially available silica was graciously supplied by one of our industrial partners. The catalyst, $EtInd_2ZrCl_2$, is supported on silica treated with MAO. The preparation of the catalyst is largely discussed on the literature, and we followed the method described by Jongsomjit, i.e. the silica was calcined at 450 °C, impregnated with a certain amount of MAO at room temperature, washed with toluene, dried under vacuum and after impregnated with the metallocene[9]. The characteristics of the silica used are given in Table 1.

Table 1.
Characteristic of the silica used for the synthesis of the supports.

Reference	Pore Volume[a] (ml/g)	Specific Surface[a] (m^2/g)	d50 (μm)	Mean Pore Diameter[a] (Å)
Grace_948	1.7	290	58	232

[a]Determined by N_2 porosimetry.

The polymerisations were carried out as follows. After charging the solvent (around 500ml of heptane) and the comonomer (in case of copolymerisation), the reactor temperature and pressure are set up to the polymerisation conditions. A heptane slurry containing a known amount of supported catalyst is contacted with triethylalkylaluminium (TEA; Al/metal = 2000) for a certain time (recorded). This mixture is transferred to the cartridge, and then injected into the reactor with an overpressure of ethylene. The jacket and reactor temperatures as well as the monomer consumption are monitored and polymerisations were carried out during 1h. The polymerisation was stopped by rapid depressurisation and cooling of the reactor. The reaction mixture was washed with ethanol, filtered and dried under vacuum for 2 h.

Results and Discussions

The aim of the work presented here is to look at the influence of the particle size of the support on the kinetics and polymer properties. In the literature, very little work concerning the impact of the catalyst PSD has been reported. Only, Fink et al.[5] investigate the influence of particle diameter of silica/MAO-supported metallocene catalyst during propene polymerisation. They showed that the activity was related to the diameter with a higher activity for the smallest catalyst particles.

Ideally, we should synthesise the catalyst and afterwards separate it in different fractions having a determined size. Thus, all the fractions would have exactly the same pre-treatment condition steps. However, as the catalyst is sensitive to exposure to air, the sieving operation should be realised in a glove box, which was not possible in our laboratory. Therefore we decided to separate the silica and to treat all the different fractions following the same manner. However, we first verified that the catalyst preparation procedure is reproducible. The supported catalyst was made twice using as carrier the silica referenced Grace_948 (c.f. Table 1). The synthesis was performed in two steps, first impregnation of MAO at 85 °C for one hour in toluene, and secondly the tethering of the metallocene complex ($EtInd_2ZrCl_2$) at 30 °C for one hour in toluene. Both catalysts were tested in slurry copolymerisation under the same conditions: temperature = 80 °C, [C2] = 6 wt% in heptane, 1-hexene = 2.44 wt% in heptane, AlTiBA/Zr = 2000 mol/mol and contact time of 10 min. Kinetic profiles and molecular weights of the polymers, shown in Figure 2 and indicate that the synthesis of the catalyst supported on silica treated with methylaluminoxane (MAO) is reproducible to within acceptable limits. Note that in the rest of the text, the abbreviation SMAO refers to a Silica support with MAO as the activator.

Subsequently, the batch of silica was fractionated into three well-defined cuts: 36–45 μm, 45–63 μm, and 80–100 μm. The volume percentage of each fraction is reported in Figure 3. Each fraction, as well as a support based on the entire silica, was used to make a batch of catalyst. The synthesis was performed in two steps: first the dehydroxylated silica was suspended in

Table 2.
Molecular weights of the copolymers with $EtInd_2ZrCl_2$/SMAO.

Reference	Mn	Mw	IP
Grace_948_SMAO_1	36 800	114 900	3.1
Grace_948_SMAO_2	35 000	116 200	3.3

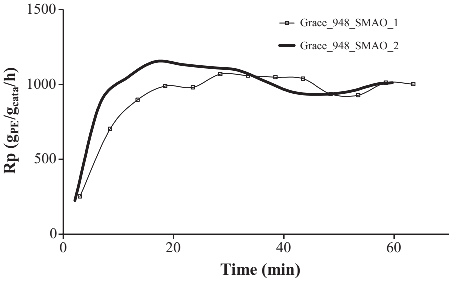

Figure 2.
Kinetic profiles obtained during slurry ethylene/1-hexene copolymerisation with two batches of catalysts supported on SMAO.

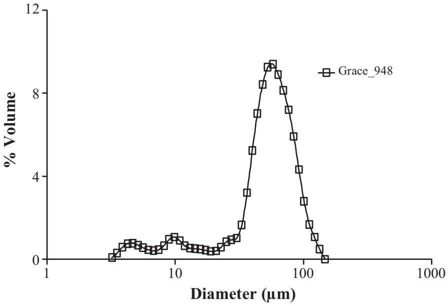

Figure 3.
Particles size distribution of silica before sieving determined by using a Coulter LS230.

toluene and treated with MAO and secondly, the SMAO was suspended in toluene and treated with the metallocene complex. The different catalysts were analysed by Ionisation Coupled Plasma (ICP) in order to determine the aluminum and zirconium concentration. The results are summarized in Table 3.

The chemical composition of the different catalysts synthesised on the different silica fractions are quite similar. Consequently, if the same mass of catalyst is used during the experiments, the same mass concentration of active sites should be theoretically present in the reaction medium. As the SMAO is very sensitive to the air, it was not possible to perform EDX analyses on these catalysts. Consequently, we do not have any certainties concerning the spatial distribution of the elements on and in silica particles.

Table 3.
ICP analysis of the metallocene catalysts supported on the different SMAO.

Size	Grace_948	
	Al (wt%)	Zr (wt%)
Total	13.2	0.39
36–45 μm	12.7	0.39
45–63 μm	12.7	0.35
80–100 μm	12.6	0.34

Slurry copolymerisations were carried out in the calorimetric rector and the reaction conditions were identical for all the experiments, i.e. temperature = 80 °C, [C2] = 6 wt% in heptane, [1-hexene] = 2.44 wt% in heptane, AlTiBA/Zr = 2000 mol/mol, contact time of 10 min.

The kinetic profiles obtained during slurry copolymerisations with the catalyst supported on SMAO are shown in Figure 4. It can be seen that the smallest catalyst particles have a higher activity, and activate/deactivate faster than larger ones. It is also important to note that the global kinetic profile calculated from the weighted sum of the individual rates is close to the rate profile obtained with the support based on the entire silica without fractionation:

$$R_p = \sum_I m_i R_{p,i}$$

The molecular weights are given in Table 1 and it can be seen that the MW are similar for each of the fractions. The rate data suggest that there is some mass transfer resistance occurring here – at least the data are coherent with this interpretation. The fact that the MW do not vary might be taken as evidence that this is not the case, however it should be noted that this type of active site is well-known to show significant chain transfer reactions, so it is likely that the MWD is controlled not by the monomer concentration (at least not with the variations that might be present here) but rather by chain transfer. This would explain why the MW are similar from cut to cut even though the rate of reaction is not. We will return to this point briefly below.

The PSD of the final polymer from the runs shown here is represented in Figure 5.

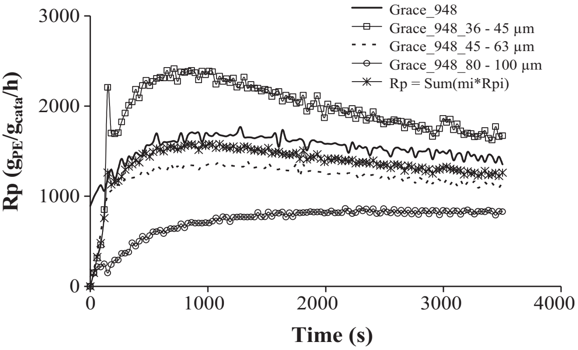

Figure 4.
Kinetic profiles during ethylene/1-hexene copolymerisation with $EtInd_2ZrCl_2$/SMAO as catalysts.

Table 4.
Molecular weights of copolymers obtained with SMAO based on silica Grace_948.

Reference	Average Activity (g/g/h)	Mn	Mw	PDI
Grace_948_SMAO	1500	29 200	149 400	5.1
Grace_948_36–45 µm_SMAO	2200	26 500	127 200	4.8
Grace_948_45–63 µm_ SMAO	1200	28 600	128 700	4.5
Grace_948_80–100 µm_ SMAO	750	27 100	132 800	4.9

They tend to show that when the original catalyst has a well defined PSD, the final polymer has also a well defined PSD; at least under the experimental conditions chosen here (they also serve to prove that the agitation used in this reactor does not impact the PSD). Any fine polymer particles present in the final powder are generated by the smallest particles present in the catalyst. Once again, it is important to keep in mind that these conclusions are valid under the experimental conditions described. If the reaction rate was faster, the fragmentation process would be faster and it could be possible to observe a particle 'explosion' that could generates fines particles.

Let us return to the results in Figure 4. It is tempting to infer from these results that difference in the reaction rate from one cut to the next is due to resistance to monomer transfer to the active sites, which would logically be greater in the larger particles. However, it is important to consider

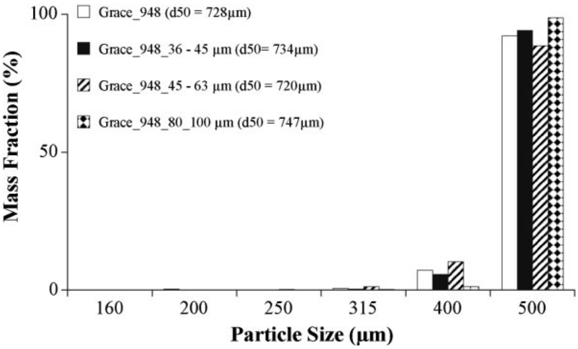

Figure 5.
Particle size distribution of the polymers synthesised with the catalyst based on silica Grace_948.

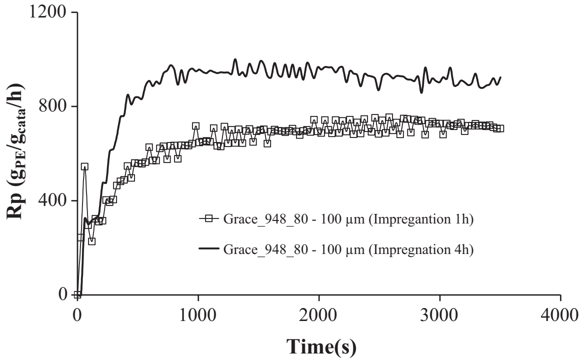

Figure 6.
Kinetic profiles during ethylene/1-hexene copolymerisation with $EtInd_2ZrCl_2$/SMAO as catalysts having experienced different impregnation times.

another type of mass transfer: that of the catalyst and activator during the impregnation phase of the catalyst preparation. During the catalyst preparation the same contact time for the different compounds, i.e. MAO and metallocence complex were used independently of the PSD of the fraction treated. However, the characteristic time for diffusion is four times greater for the larger particles than in the smaller ones, where the characteristic mass transfer time τ is equal to the characteristic length scale for diffusion squared (here the particle radius) divided by the diffusivity (reasonably supposed independent of the particle size as a first approximation). Consequently, to reproduce the same preparation conditions, the contact time for the different steps should be four times longer for the larger fraction than for the smallest one. Based on this, another fraction of larger particles, i.e. 80–100 µm, was impregnated for 4 hours with MAO, followed by an impregnation with the metallocene complex for an additional 4 hours.

This catalyst was compared to the one obtained with the larger fraction treated during one hour, and the rate curve for this longer impregnation time is shown in Figure 6 along with the rate curve for the same cut but with the standard impregnation times. A longer impregnation time seems to provide an observable increase in the activity that cannot be explained by a lack of reproducibility. On the other hand, if we compare the rate curves in Figure 6 with those in Figure 4, it can be seen that increasing the impregnation time does not increase the observed activity to a level commensurate with the smaller particles. This preliminary work indicates that it will be interesting to study more the preparation step of the catalyst.

Conclusion

This study showed that the catalyst particle size has an effect on the polymerisation rate, and that it is possible that both chemical *and* physical differences exist between the larger and smaller particles in a given batch of catalyst. With the catalyst used here, the smaller the catalyst particles are, the higher the yield is for one hour of reaction, and faster the activation/deactivation are. The preliminary test concerning the length of the impregnation time during the SMAO preparation seems to indicate that an increase of time leads to a higher activity but still not equivalent to the one expected. Consequently, some diffusion limits, during the preparation step and/or the polymerisation, can be another explanation for these differences. It would be interesting to investigate more in details this feature.

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