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Advances in supported metallocene catalysis

Summary — A kinetic, active centre, and morphological analysis has been carried out on the polymerization of ethylene and propylene in hydrocarbon, aromatic and chloroaromatic media using selected homogeneous and silica supported metallocene catalysts activated by methylaluminoxane (MAO). A number of procedures for supporting selected model zirconocene compounds (biscyclopentadienylzirconium dichloride and ethylenebisindenylzirconium dichloride) on different types of silica have been investigated. It is established that the overall activities and kinetic behaviour of these supported catalysts are strongly affected by the procedure used for the catalyst preparation. In general supported metallocene catalysts were shown to have lower activities and also lower numbers of propagating active centers than did the corresponding soluble catalyst systems. MAO pretreated silica catalysts were shown by SEM studies to produce polymer with good morphology and the results obtained indicated that silica fragmentation producing microreactor behaviour could be obtained in these polymerizing catalyst systems.

Key words: metallocene catalyst, methylaluminoxane, SiO_2 as support, catalyst preparation, cocatalyst activity, polymerization of ethylene and propylene.

The discovery of an effective cocatalyst, methylaluminoxane (MAO) by Kaminsky, Sinn and coworkers [1], which when used with metallocene compounds such as biscyclopentadienylzirconium dichloride can produce soluble catalyst systems of very high activities for the polymerization of ethylene, propylene and other α-olefins, has created enormous interest amongst both industrial and academic research workers. Additionally, the discovery of soluble chiral C_2-symmetry metallocenes by Ewen [2] and by Kaminsky, Brintzinger and coworkers [3] together with the development of new types of MAO-free cocatalyst systems [4—6] have added further to the considerable interest in these polymerization systems. Nevertheless in recent years, mainly because of industrial considerations, there has been an increasing focus on the development of supported metallocene catalyst systems as a means of exploiting their real commercial potential. Supported metallocene catalysts offer a number of potential and realizable advantages. Whilst polymerizations carried out in toluene or hydrocarbon media using soluble systems yield polymers of poor morphology, appropriately supported metallocene catalysts can be used to produce polymers of more regular morphology [7—10]. Furthermore the use of supported catalysts allows the use of lower MAO/metallocene ratios [11], the production of polymer of increased molecular weight [11], and can also achieve enchanced stereochemical and regiochemical control in α-olefin polymerization [12].

A large number of publications describing the preparation of supported metallocene catalysts have appeared in the scientific and patent literature and it is possible to identify at least four types of supported metallocene catalysts systems.

TYPES OF CATALYSTS

Support/metallocene type catalysts

Such catalysts are formed by the direct reaction of a metallocene with a support such as dried silica. In this method the dry support, calcinated to a specific temperature, is reacted with a metallocene dissolved in a solvent such as toluene, then filtered and washed. This method has been used by a number of workers including Kaminsky and Renner [11], Chien and He [13] and Soga *et al.* [14]. A variant of this method is the use of a spacer unit linking the metallocene to a group on the support surface [15—17].

Support/metallocene/MAO type catalysts

These catalysts are formed by first reacting a support with a metallocene followed by treatment with MAO. Kaminsky and Renner [11] prepared a $SiO_2/En(Ind)_2ZrCl_2/MAO$ catalyst using this method and reported that such catalysts can be used to polymerize propylene without the addition of further MAO. Such catalysts are sometimes described as being single-phase catalysts.

Support/MAO/metallocene type catalysts

To prepare these catalysts the support is first pretreated with a small amount of MAO. After filtration and washing with toluene the MAO modified support is then further treated with a solution of a metallocene [11, 14].

Support/MAO/metallocene/MAO type catalysts

Such catalysts were first reported by Janiak and Rieger [18] and their preparation involves the deposition of a sandwich type layer, MAO/metallocene/MAO, on a silica support. When used to polymerize ethylene, these supported catalysts show high activity even at low Al : Zr ratios.

EXPERIMENTAL

Materials

EP10, a granular type of silica, was kindly provided by Crosfields, Warrington, UK and had a surface area of 269 $m^2 \cdot g^{-1}$, a pore diameter of 269 Å, a pore volume of 1.8 $cm^3 \cdot g^{-1}$ and a median particle size of 100 μm.

MS3040, a spherical type of silica, was kindly provided by the PQ Corporation, Conshohocken, USA, and had a surface area of 460 $m^2 \cdot g^{-1}$, a pore diameter of 130 Å, a pore volume of 3.0 $cm^3 \cdot g^{-1}$ and a median particle size of 45 μm.

MS3030, a spherical type of silica, was kindly provided by the PQ Corporation, Conshohocken, USA, and had a surface area of 315 $m^2 \cdot g^{-1}$, a pore diameter of 194 Å, a pore volume of 3.1 $cm^3 \cdot g^{-1}$ and a median particle size of 82 μm.

Dehydration

Approximately 10 g of silica was placed in a glass ampule and dehydrated under vacuum at the selected temperature. The silica was then allowed to cool to room temperature under continuous evacuation after which the ampule was filled with dry nitrogen and transferred to a dry box.

Preparation of supported catalysts

Some details of catalyst preparation procedures have been published elsewhere [8, 19]. Further details will appear in forthcoming publications. Analytical data for the catalysts which were studied are listed in Table 1.

Table 1. **Analytical data of supported catalysis**

Ethylene polymerization catalysts				
Code	Catalyst type	Type of silica	% Zr (w/w)	% Al (w/w)
MM-1	SiO_2/Cp_2ZrCl_2	EP10	2.50	—
S2-2	SiO_2/Cp_2ZrCl_2	MS-3040	2.20	—
S2-3	SiO_2/Cp_2ZrCl_2	MS-3040	1.30	—
MS-1	$SiO_2/MAO/Cp_2ZrCl_2$	MS-3040	1.70	13.3
MS-2	$SiO_2/MAO/Cp_2ZrCl_2$	MS-3040	0.30	13.4
MS-3	$SiO_2/MAO/Cp_2ZrCl_2/MAO$	MS-3040	1.70	14.3
MS-6	$SiO_2/MAO/Cp_2ZrCl_2$	MS-3040	0.35	14.1
MS-12*)	$SiO_2/MAO/\{MAO + Cp_2ZrCl_2\}$	MS-3040	0.24	7.4
MS-30	$SiO_2/MAO/Cp_2ZrCl_2$	MS-3040	2.20	4.4
EP26C	$SiO_2/MAO/Et(Ind)_2ZrCl_2$	EP10	0.18	8.8
EP46A	$SiO_2/Et(Ind)_2ZrCl_2$	EP10	1.53	—
EP46B	$SiO_2/Et(Ind)_2ZrCl_2/MAO$	EP10	0.96	7.7
EP46C	$SiO_2/MAO/Et(Ind)_2ZrCl_2$	EP10	0.44	7.4
EP46D	$SiO_2/MAO/Et(Ind)_2ZrCl_2/MAO$	EP10	0.40	9.0
MS26C	$SiO_2/MAO/Et(Ind)_2ZrCl_2$	MS-3040	0.40	4.0
MS46C	$SiO_2/MAO/Et(Ind)_2ZrCl_2$	MS-3040	0.39	8.3

*) Vacuum pore method.

Polymerization procedure

Polymerizations were carried out either at 1 atm pressure using a specially constructed 0.50 dm^3 double-walled glass reactor or at 6 atm in a 1 dm^3 Büchi reactor. In both cases the monomer uptake per unit of time and the instantaneous polymerization rate was recorded as a function of the polymerization time by use of an electronic measuring and recording system developed at UMIST. Details of the polymerization procedure have been described elsewhere [7, 8].

Determination of active centre concentrations

Active centre concentration determinations were carried out using a tritiated alcohol technique. Details concerning the use of this procedure have been described in previous publications [20, 21].

RESULTS

This paper reports part of a comparative investigation into the essential characteristic of some model soluble and supported metallocene catalyst systems when used along with MAO as cocatalyst for the polymerization of ethylene and propylene. More detailed results for some earlier polymerizations have been published elsewhere [7, 8, 19, 22—24].

Effects of preparation procedures on catalyst activities

Effects of temperature of dehydration

The temperature of dehydration, affecting the concentration of surface hydroxyl and siloxane groups, has a significant effect on the activities of silica supported metallocene catalysts used for this study.

Thus for the polymerization of ethylene using SiO_2/Cp_2ZrCl_2—MAO catalysts (**S2-2** and **S2-3**) prepared using MS 3040 silica, dehydrated at 260°C and 460°C respectively, the use of a lower dehydration temperature, *i.e.*, 260°C, favours the formation of a more active catalyst, as is shown in Fig. 1.

The same behaviour is observed for the polymerization of propylene when using the catalyst system $SiO_2/MAO/Et(Ind)_2ZrCl_2$—MAO, as is evident from an inspection of Table 2.

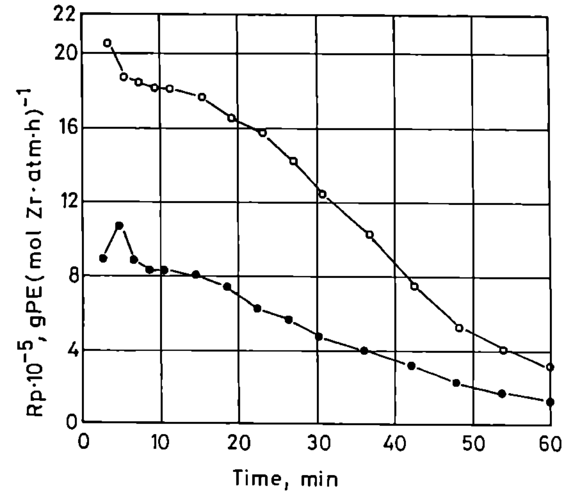


Fig. 1. Effect of dehydration temperature of silica on the rate-time profiles for the polymerization of ethylene using supported catalysts S2-2 (o) and S2-3 (•) (obtained from MS 3040); dehydration temperature for S2-2 = 260°C, dehydration temperature for S2-3 = 460°C; volume of toluene = 250 cm³, ethylene pressure = 1 atm, temperature = 60°C, polymerization time = 1 h; [Zr] = 2.258 · 10⁻⁵ mol · dm⁻³; [Al]/[Zr] = 1735

In this case the higher activities arise because a higher value of Rp_{max} is reached more quickly for dehydration at 260°C, *i.e.*, not only is the length of the settling period reduced but a higher Rp_{max} value is attained, as can be seen from an examination of Fig. 2.

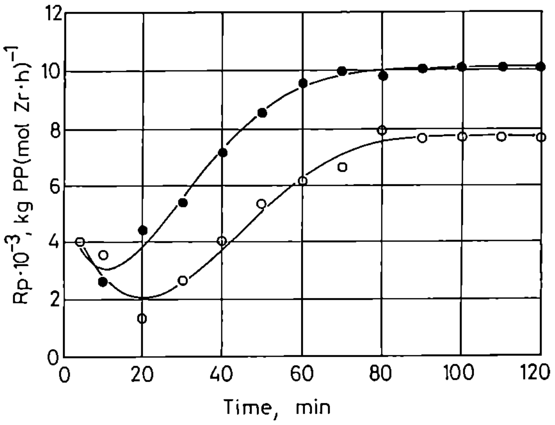


Fig. 2. Effect of dehydration temperature of silica on the rate-time profiles for the polymerization of propylene using supported $SiO_2/MAO/Et(Ind)_2ZrCl_2$—MAO catalysts systems; volume of toluene = 300 cm³, propylene pressure = 6 atm, temperature = 60°C, polymerization time = 2 h; $[Al]_{external}$ = 0.030 mol · dm⁻³; [Al]/[Zr] = 4000; • — EP26C (silica EP10 calcined at 260°C); o — EP46C (silica EP10 calcined at 460°C)

These results suggest that a certain optimum concentration of hydroxyl groups, controlled by the dehydration temperature, is needed to anchor the necessary layer of adsorbed MAO on the surface of the silica.

Effects of order of reaction of catalyst components during catalyst preparation procedures

It is now well established that the order of reaction of silica, metallocene and MAO affects the kinetic behaviour and activity of supported metallocene catalysts.

The results of a series of propylene polymerizations

Table 2. Effect of dehydration temperature of the silica on the activities of supported $SiO_2/MAO/Et(Ind)_2ZrCl_2$—MAO catalyst systems for the polymerization of propylene

Supported catalyst	Type of silica	Dehydration temperature of the silica, °C	$[Al]_{external}$, mol · dm⁻³	Al/Zr	Yield, g	$Rp_{av} \cdot 10^{-3}$ kg PP (mol Zr · h)⁻¹	$Rp_{max} \cdot 10^{-3}$ kg PP (mol Zr · h)⁻¹
EP26C	EP10	260	0.030	4000	37	8.40	10
EP46C	EP10	460	0.030	4000	25	5.70	8.0
MS26C	MS3040	260	0.030	4000	35	8.60	12
MS46C	MS3040	460	0.030	4000	1.3	0.03	1.8

Catalyst **EP26C**: Al content = 8.8% w/w, Zr content = 0.18% w/w; catalyst **EP46C**: Al content = 7.4% w/w, Zr content = 0.44% w/w; catalyst **MS26C**: Al content = 4.0% w/w, Zr content = 0.40% w/w; catalyst **MS46C**: Al content = 8.3% w/w, Zr content = 0.39% w/w. Polymerization conditions: volume of toluene = 300 cm³; polymerization pressure = 6 bar; polym. time = 2 hour; polym. temperature = 60°C.

Table 3. Comparative activities of supported $SiO_2/Et(Ind)_2ZrCl_2$, $SiO_2/Et(Ind)_2ZrCl_2/MAO$, $SiO_2/MAO/Et(Ind)_2ZrCl_2$ and $SiO_2/MAO/Et(Ind)_2ZrCl_2/MAO$—MAO catalyst systems for the polymerization of propylene

Supported catalyst	Catalyst type	$[Al]_{external}$, $mol \cdot dm^{-3}$	Al/Zr	Yield, g	$Rp_{av} \cdot 10^{-3}$ kg PP $(mol\ Zr \cdot h)^{-1}$	$Rp_{max} \cdot 10^{-3}$ kg PP $(mol\ Zr \cdot h)^{-1}$
EP46A	$SiO_2/Et(Ind)_2ZrCl_2$	0.030	110	1.2	0.017	0.21
EP46B	$SiO_2/Et(Ind)_2ZrCl_2/MAO$	0.030	120	1.0	0.016	0.20
EP46C	$SiO_2/MAO/Et(Ind)_2ZrCl_2$	0.009	230	9.2	0.390	1.20
		0.030	4000	25.0	5.700	8.00
EP46D	$SiO_2/MAO/Et(Ind)_2ZrCl_2/MAO$	0.040	4000	1.1	0.390	3.90

Catalyst **EP46A**: Zr content = 1.53% w/w; catalyst **EP46B**: Al content = 7.7% w/w, Zr content = 0.96% w/w; catalyst **EP46C**: Al content = 7.4% w/w, Zr content = 0.44% w/w; catalyst **EP46D**: Al content = 9.0% w/w, Zr content = 0.40% w/w. Polymerization conditions: toluene; polymerization pressure = 6 bar; polymerization temperature = 60°C.

using $SiO_2/Et(Ind)_2ZrCl_2$, $SiO_2/Et(Ind)_2ZrCl_2/MAO$, $SiO_2/MAO/Et(Ind)_2ZrCl_2$ and $SiO_2/MAO/Et(Ind)_2ZrCl_2/$ $/MAO$ supported catalysts containing similar zirconium contents are shown in Table 3.

It is apparent that catalysts of the type $SiO_2/MAO/Et(Ind)_2ZrCl_2$ have higher activities when used under these conditions. A comparison of the appropriate rate-time profiles provides an explanation for these results. Figure 3 shows rate-time profiles the catalyst systems $SiO_2/Et(Ind)_2ZrCl_2$—MAO and $SiO_2/Et(Ind)_2ZrCl_2/MAO$—MAO.

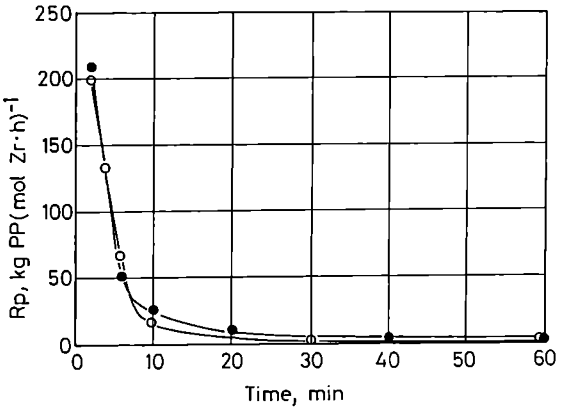


*Fig. 3. Rate-time profiles for the polymerization of propylene using the catalyst systems $SiO_2/Et(Ind)_2ZrCl_2$ (EP46A)—MAO (•) and $SiO_2/Et(Ind)_2ZrCl_2$ (EP46B)—MAO (o); volume of toluene = 250 cm^3, propylene pressure = 6 atm, temperature = 60°C, polymerization time = 1 h; **EP46A**: [Zr] = $2.7 \cdot 10^{-4}$ mol · dm^{-3}, [Al]/[Zr] = 110; **EP46B**: [Zr] = $2.5 \cdot 10^{-4}$ mol · dm^{-3}, [Al]/[Zr] = 120*

The instantaneous rates of polymerization decrease rapidly during the first 10—15 min of polymerization and these catalysts quickly become deactivated.

On the other hand, catalyst systems of the type $SiO_2/MAO/Et(Ind)_2ZrCl_2$—MAO show much more stable rate-time profiles and consequently show much higher activities. Typical rate-time plots for catalysts of this type have been shown in Fig. 2.

Further studies were carried out on the so-called "sandwich-type" supported catalysts, initially reported by Janiak and Rieger [18]. However, research on our group indicated that catalytic activity is affected by both the aluminium and zirconocene contents in the supported catalysts. Therefore, it is more reasonable to compare the activities of catalysts only when they contain similar amounts of both aluminium and zirconium. Catalysts $SiO_2/MAO/Cp_2ZrCl_2$ (**MS-1**) and $SiO_2/MAO/Cp_2ZrCl_2/MAO$ (**MS-3**) were prepared specifically for this purpose and used for ethylene polymerization. The results obtained are shown in Fig. 4. It is evident from an inspection of Fig. 4 that the catalyst system $SiO_2/MAO/Cp_2ZrCl_2$—MAO has a higher activity than the $SiO_2/MAO/Cp_2ZrCl_2/MAO$—MAO system when used under similar polymerization conditions.

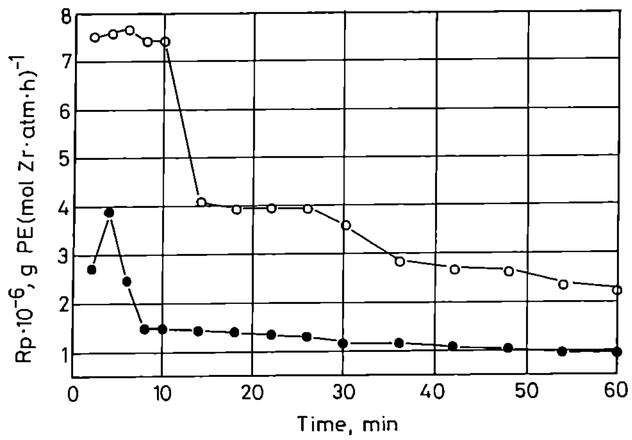


Fig. 4. Comparative rate-time profiles for the polymerization of ethylene using the silica supported catalysts MS-1 (o) and MS-3 (•); volume of toluene = 250 cm^3, ethylene pressure = 1 atm, temperature = 70°C, polymerization time = 1 h; [Zr] = $1.93 \cdot 10^{-5}$ mol · dm^{-3}; [Al]/[Zr] = 2757

Effects of precontacting supported catalysts with MAO

The effects of precontacting a supported metallocene catalyst with MAO at room temperature before introduction into the polymerization reactor were studied.

The precontacting was carried out by mixing the supported catalyst and MAO in a flask for the desired period of time in a nitrogen atmosphere. The mixture was stirred during this procedure. Results for two types of supported catalysts, *i.e.*, $SiO_2/MAO/Cp_2ZrCl_2$ (**MS-6**) and $SiO_2/MAO/Cp_2ZrCl_2/MAO$ (**MS-3**) are shown in Figs. 5—8.

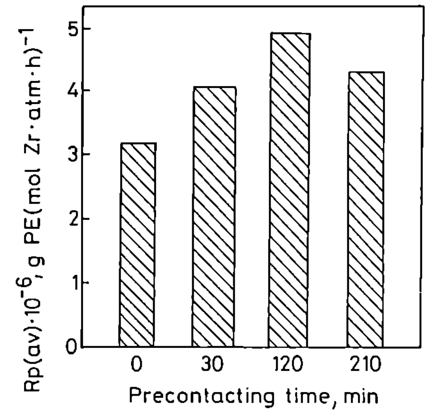


Fig. 5. Effect of different times of precontacting the MS-6 catalyst with MAO on the average rate of polymerization of ethylene; volume of toluene = 250 cm^3, ethylene pressure = 1 atm, temperature = 70°C, polymerization time = 1 h; [Zr] = 1.93 · 10^{-5} mol · dm^{-3}; [Al]/[Zr] = 2757

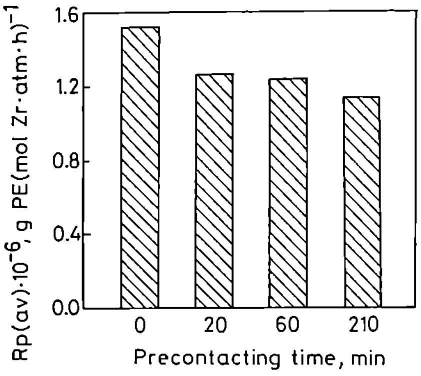


Fig. 6. Effect of different times of precontacting the MS-3 catalyst with MAO on the average rate of polymerization of ethylene; volume of toluene = 250 cm^3, ethylene pressure = 1 atm, temperature = 70°C, polymerization time = 1 h; [Zr] = 2.99 · 10^{-5} mol · dm^{-3}; [Al]/[Zr] = 1780

For the **MS-6** catalyst the procedure of precontacting resulted in an increase in the catalyst activity in the range of precontacting time investigated, as shown in Fig. 5. It is also clear from Fig. 5 that there is an optimum precontacting time for obtaining the highest catalyst activity. The optimum precontacting times for different catalysts were different. However, for the **MS-3** catalyst, the procedure of precontacting caused a decrease in catalyst activity compared to the case without the precontacting procedure, and the longer the precontacting time, the greater the decrease in catalyst activity, as can be seen from Fig. 6.

Comparative rate-time profiles for ethylene polymerizations with and without the procedure of precontacting using the **MS-6** and **MS-3** catalysts are presented in Figs. 7 and 8, respectively. These rate-time profiles show clearly in kinetic terms why the **MS-6** catalyst is more active than the **MS-3** catalyst. As shown in Fig. 7, the procedure of precontacting resulted in a high polymerization rate plateau in the rate-time profiles for the polymerizations using the **MS-6** catalyst. However, when using the **MS-3** catalyst, the rates of polymerization decreased more sharply with time as the contact time increased.

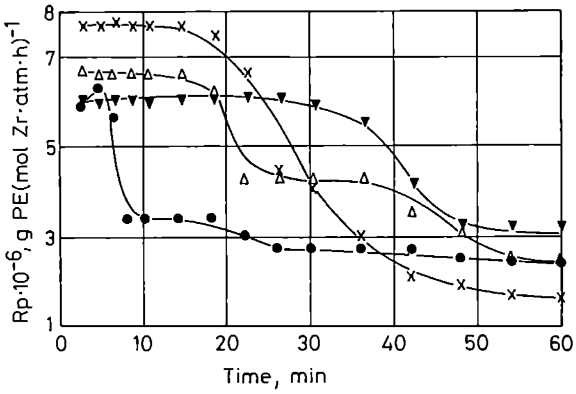


Fig. 7. Rate-time profiles for the polymerization of ethylene using the MS-6 catalyst system for different precontacting times with MAO; volume of toluene = 250 cm^3, ethylene pressure = 1 atm, temperature = 70°C, polymerization time = 1 h; [Zr] = 1.93 · 10^{-5} mol · dm^{-3}, [Al]/[Zr] = 2757; precontacting time: • — 0, △ — 30 min, ▼ — 2 h, x — 3.5 h

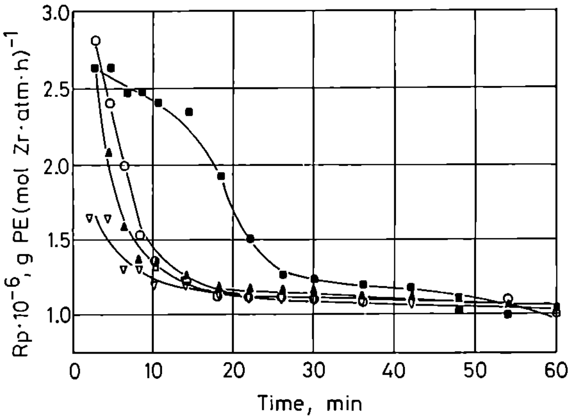


Fig. 8. Rate-time profiles for the polymerization of ethylene using the MS-3 catalyst system for different precontacting times with MAO; volume of toluene = 250 cm^3, ethylene pressure = 1 atm, temperature = 70°C, polymerization time = 1 h; [Zr] = 2.99 · 10^{-5} mol · dm^{-3}, [Al]/[Zr] = 1780; precontacting time: ■ — 0, ○ — 20 min, ▲ — 1 h, x — 3.5 h

Activity and rate-time behaviour

The kinetic behaviour of many silica supported catalyst systems in terms of rate-time profiles can be very complex and may be similar to or different from their homogeneous analogues depending on their method of preparation and the conditions of polymerization.

For ethylene polymerization the rate-time profiles obtained using homogeneous (*e.g.*, Cp_2ZrCl_2—MAO) and supported (*e.g.*, SiO_2/Cp_2ZrCl_2—MAO) catalyst systems show many similarities. Typical rate-time plots are shown in Fig. 9.

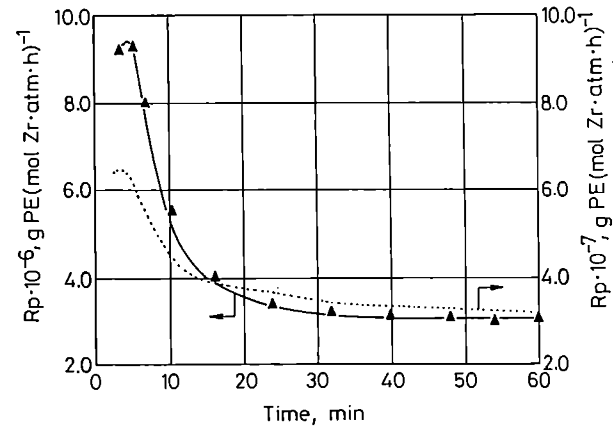


Fig. 9. Comparative rate-time profiles for the polymerization of ethylene using the homogeneous (...) and supported catalysts (▲); volume of toluene = 250 cm^3, ethylene pressure = 1 atm, temperature = 70°C, polymerization time = 1 h; homogeneous catalyst system (Cp_2ZrCl_2—MAO): [Zr] = 1.00 · 10^{-6} mol · dm^{-3}; [Al]/[Zr] = 35 000; supported catalyst system (MM1—MAO): [Zr] = 1.0 · 10^{-5} mol · dm^{-3}; [Al]/[Zr] = 3500

It is evident from Fig. 9 that the instantaneous rates of polymerization for both types of catalyst systems reach maximum values within 3—5 min of the start of the polymerization, then decrease sharply and finally show values which decrease much more gently. However, all catalyst systems do not behave in exactly the same manner as is evident from an inspection of Fig. 8.

The similarity between the shapes of the rate-time profiles for ethylene polymerization as found for the homogeneous catalyst system Cp_2ZrCl_2—MAO and the supported **MM-1** catalyst system (of the type SiO_2/Cp_2ZrCl_2—MAO) is striking and would seem to indicate some similarity in the environment of the active centers in both systems leading to similar rate-time behaviours. The high zirconium loading in the **MM-1** catalyst system (Zr = 2.5%) may play some part in this situation since all the zirconium atoms may not be as firmly bound to the silica surface as might have been expected.

However, in the polymerization of propylene using a somewhat similar SiO_2/metallocene—MAO catalyst system (**EP46A**) the rate-time behaviour was quite different (*cf.*, Fig. 3), but here the monomer, the metallocene and the zirconium loading were all different.

For propylene polymerization using the catalyst system $SiO_2/MAO/Et(Ind)_2ZrCl_2$—MAO the rate-time profiles were generally of a characteristic shape (*cf.*, Fig. 2) showing an initial settling period during which the rate decreased with polymerization time before increasing to reach a stable value which was then maintained for up to 2 h polymerization time. The significance of these plots will be discussed later.

Effects of variation of MAO concentration on ethylene polymerization

The effects of variation of MAO concentration were investigated for a number of supported metallocene catalyst systems.

It is evident that both the average rate and the maximum rate of polymerization increase initially with an increase in the concentration of external MAO (reported as the molar ratio [Al]/[Zr]). However, the average rate tends towards a limiting value when high ratios of [Al]/[Zr] are used. Results and reasons for this behaviour have been detailed in an earlier paper [22].

Effects of polymerization medium

The effect of polymerization medium on the activity and kinetics of ethylene polymerization was studied using a number of catalysts. Typical results for the catalyst system $SiO_2/MAO/Cp_2ZrCl_2$—MAO are reported in this paper for polymerizations in toluene, EC180 (pentamethylheptane) and mixtures of toluene and EC180. Typical plots of *Rp vs.* % toluene in the diluent are shown in Fig. 10.

Figure 11 shows plots of *Rp vs.* time for ethylene polymerization in toluene and in toluene/*o*-dichlorobenze-

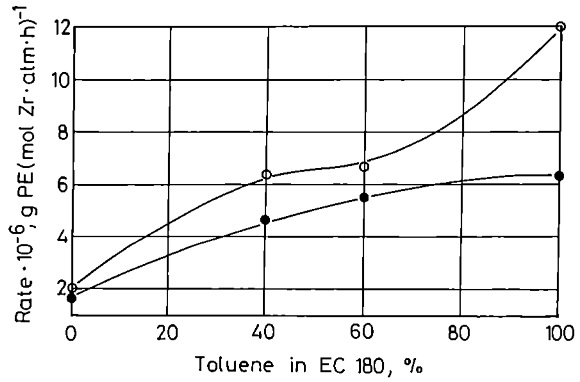


Fig. 10. Effect of the polymerization medium on the average and maximum rates of ethylene polymerization using the MS2—MAO catalysts system; volume of toluene = 250 cm^3, ethylene pressure = 1 atm, temperature = 70°C, polymerization time = 1 h; [Zr] = 1.10 · 10^{-5} mol · dm^{-3}; [Al]/[Zr] = 4842; • — Rp_{av}, ○ — Rp_{max}

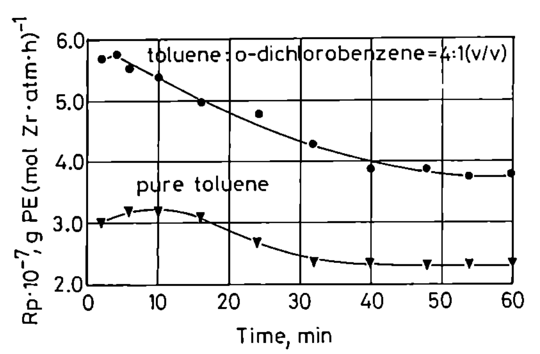


Fig. 11. Effect of the polymerization medium on the rate-time profiles for the polymerization of the ethylene using the catalysts system Cp_2ZrCl_2—MAO; volume of toluene = 250 cm^3, ethylene pressure = 1 atm, temperature = 70°C, polymerization time = 1 h; [Zr] = 1.00 · 10^{-6} mol · dm^{-3}; [Al]/[Zr] = 35 000; ● — toluene : o-dichlorobenzene = 4:1 (v/v); ▼ — pure toluene

ne (4:1 v/v) using the homogeneous catalyst system Cp_2ZrCl_2—MAO.

It is evident that the nature of the polymerization medium can have a significant effect on the activity of the metallocene catalyst system, the more polar the medium the higher the polymerization activity. A possible reason for this behaviour has been suggested in an earlier paper [19].

For supported catalyst systems the effect is not limited only to activity since the nature of the polymerization medium also affects the stability of the catalyst system, the more active systems (in more polar solvents) being less stable, as is shown in Fig. 12.

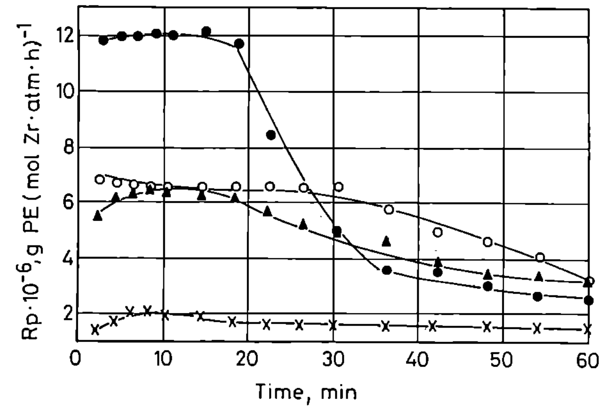


Fig. 12. Rate-time profiles for polymerization in different media for ethylene polymerizations using the MS2—MAO catalyst system; media used: ● — 100% toluene, o — 60% toluene, ▲ — 40% toluene, x — 100% EC 180

Active centre determination

Active centre determinations were carried out on the supported catalyst system SiO_2/Cp_2ZrCl_2—MAO for ethylene polymerization using a tritiated alcohol technique. Typical results are listed in Table 4 for both non-precontacted and precontacted catalysts.

Table 4. Active centre concentration values for the catalyst system: SiO_2/Cp_2ZrCl_2 (MM1) for ethylene polymerization

Non precontacted catalyst	Precontacted catalyst
$C_0^* = 0.091$ mol (mol Zr)$^{-1}$	$C_0^* = 0.68$ mol (mol Zr)$^{-1}$

Polymerization conditions: 70°C, 0.25 dm^3 toluene. Kinetic isotope factor: 2.6. Al : Zr molar ratio 2700:1. Precontact time: 100 min at 22°C

Supported catalysts in general show lower values of active centre concentrations (C_0^*), especially under conditions where the catalyst is not precontacted with MAO. Precontacting a supported catalyst with MAO produces an increase in C_0^*, although the value obtained is still lower than that for the homogeneous catalyst system. The lower activities shown by silica supported catalyst systems result from lower numbers of propagating centres.

Leaching

Research in our group has shown that a significant amount of leaching can take place in the presence of MAO when a supported metallocene catalyst is used in slurry polymerizations [8, 19]. The liquid fraction of the slurry obtained from the supported catalyst system, SiO_2/Cp_2ZrCl_2—MAO could catalyze ethylene polymerization [19]. In the present study the leaching of zirconium from the silica supported catalysts, $SiO_2/MAO/Cp_2ZrCl_2$ (prepared using the slurry method), and $SiO_2/MAO(MAO + Cp_2ZrCl_2)$ (prepared using the vacuum pore fill method) was investigated and the results are shown in Table 5.

From the results shown in Table 5 it is clear that significant leaching of zirconium takes place in the presence of MAO. Furthermore the yield of polymer obtained using the liquid fraction of the catalyst slurry increased significantly with increase in the concentration of MAO (reported as the molar ratio of [Al]/[Zr]).

Table 5. Leaching results for ethylene polymerization

No. of group	Catalyst	Ratio of [Al]/[Zr]	Precontacting time, h	Yield, g		Y_L/Y_{L+S} %
				Y_L*)	Y_{L+S}**)	
1	MS-30	2000	0.5	0.82	5.27	15.6
	MS-12	2000	0.5	0.66	5.44	12.1
2	MS-30	1000	0.5	0.31	2.83	11.0
	MS-30	2000	0.5	0.82	5.27	15.6
	MS-30	3000	0.5	2.37	11.80	20.0
3	MS-30	2000	0.5	0.82	5.27	15.6
	MS-30	2000	1.0	0.79	4.95	16.0
	MS-30	2000	1.5	0.88	4.71	18.7

*) The yield obtained using the liquid fraction of the catalyst slurry.
**) The yield obtained using the catalyst slurry.
Polymerization conditions for those using the catalyst slurry: [Zr] = 1.2 · 10^{-5} mol · dm^{-3}; temperature = 70°C; pressure = 1 atm; time = 1 h.

Morphology

Scanning electron microscopy was used to study the morphology both of supported catalysts and of the corresponding polymer particles which were produced.

Although the morphologies of the polymers produced in ethylene polymerization using supported metallocene catalysts were improved significantly compared to that produced using a homogeneous metallocene system, when polymers of a fibrous nature were formed [7], replication of catalyst morphology *per se* was not apparent in the final polymer when using these supported catalysts under the conditions employed for this investigation.

DISCUSSION

The kinetic and rate-time behaviour of supported metallocene catalysts is complex since it arises from a series of concurrent and consecutive reactions including:

— diffusion of MAO to potential centres;

— alkylation and ion pair formation;

— initial diffusion and complexation of monomer with active centres;

— chain initiation and propagation;

— formation and precipitation of solid polymer;

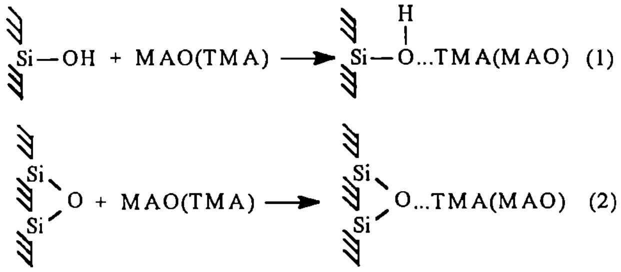
— deactivation of active centres;

— continued diffusion of monomer to active centres;

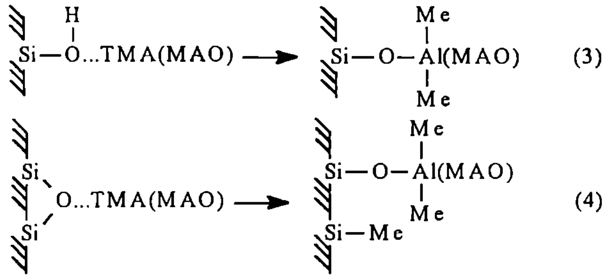
— morphology of growing polymer support particles.

Additional complications which affect the behaviour of supported metallocene catalysts include: uncertainty concerning the nature of the bonding of the metallocene molecules to the support surface; uncertainty concerning the degree of support fragmentation and catalyst particle replication — and arising from this uncertainty uncertainty concerning the degree of encapsulation of the catalyst/support particles, especially in ethylene polymerization.

The interaction of MAO with a silica surface can be regarded as a two stage reaction. Firstly, adsorption of MAO onto the hydroxyl groups and siloxane rings can take place. Since the MAO used for the present study contains 25—30% trimethylaluminium these reactions can be written as:



Secondly, reaction between the adsorbed TMA (MAO) and the hydroxyl and siloxane rings can occur:



The occurrence of leaching by MAO has been clearly demonstrated in the present study and has been reported previously [8, 19]. The significance of these results is that they seem to indicate that more than one type of

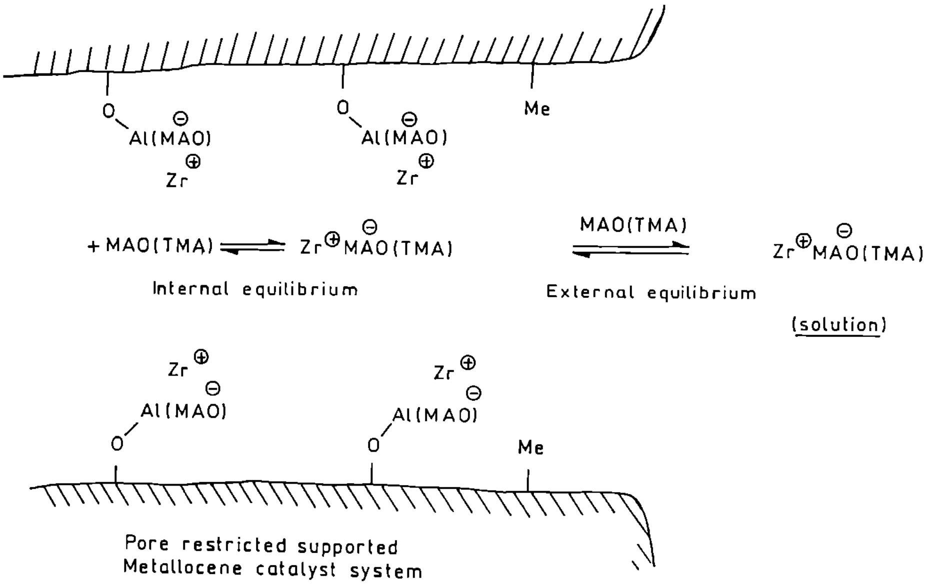


Fig. 13. Schematic representation of leaching when using SiO_2*/MAO/metallocene—MAO catalyst systems*

zirconium species may be present on the silica surface, and that in any case much of the zirconium is only loosely attached. Thus when a metallocene is reacted with MAO-treated silica adsorption followed by further chemical reaction can take place as detailed above. However, a concurrent reaction may be precipitation of the metallocene or a metallocene product in some more insoluble form within the pore structure of the silica, resulting in the formation of more than one type of species.

Formation of a Zr^+— C zirconium cation is then believed to take place and the resulting charged zirconium species may then be regarded as "free" to float within the confines of the negatively charged surface within the pore structure producing a "pore restricted ion pair metallocene catalyst", as is shown in Fig. 13.

The distinctive kinetic features of silica supported metallocene ethylene polymerizations as reported in this paper are believed to arise from initial encapsulation and/or aggregation of sticky polymer coated catalyst particles in the early stages of the polymerization reaction. High initial rates of polymerization followed by much lower rates can result in polymer encapsulation of catalyst particles before catalyst/support fragmentation can take place to any extent. The "true" rate of polymerization is not then observed. The concurrent reactions of catalyst deactivation must also be considered.

In propylene polymerization by SiO_2/MAO/$Et(Ind)_2ZrCl_2$—MAO catalyst systems due to the lower reactivity of propylene, more controlled support fragmentation can take place during the initial stages of polymerization and catalyst support replication can result provided mild conditions of polymerization are used [8 and *c.f.*, 10], depending on the conditions of polymerization. The kinetic behaviour in terms of rate-time profiles can be understood as arising from a sequence of reactions as is shown in Fig. 14. Provided suitable polymerization conditions are established expanding microreactor behaviour can be obtained leading to catalyst particle replication.

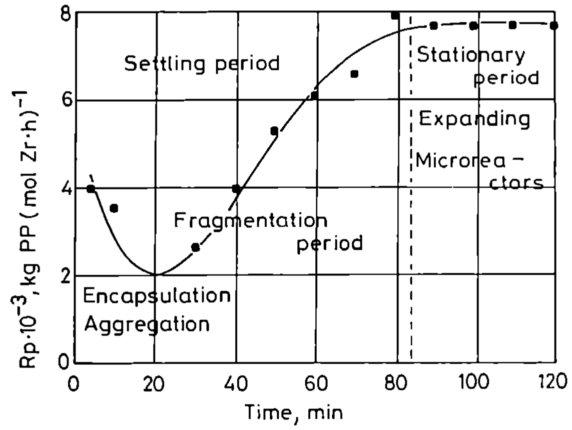


Fig. 14. Explanation of rate-time behaviour of propylene polymerization when using SiO_2/MAO/metallocene—MAO catalyst systems

REFERENCES

1. Sinn H., Kaminsky W., Vollmer H. J., Woldt R.: *Angew. Chem.* 1980, **92**, 396.
2. Ewen J. A.: *J. Am. Chem. Soc.* 1984, **106**, 6355.
3. Kaminsky W., Külper K., Brintzinger H. H., Wild F. R. W. P.: *Angew. Chem. Int. Ed. Engl.* 1985, **24**, 507.
4. Jordan R. F., Dasher W. E., Echols S. F.: *J. Am. Chem. Soc.* 1986, **108**, 1718.
5. Hlatky G. G., Turner H. W., Eckman R. R.: *J. Am. Chem. Soc.* 1989, **111**, 2728.
6. Yang X., Stern C. L., Marks T. J.: *Organometallics* 1991, **10**, 840.
7. Tait P. J. T., Monteiro M. G. K.: "MetCon '95", May 17—19, Houston 1995.
8. Tait P. J. T., Ediati R.: "Metalorganic Catalysts for Synthesis and Polymerization" (ed. Kaminsky W.), Springer, Berlin 1999, p. 307.
9. Steinmetz B., Tesche B., Przybyla C., Zechlin J., Fink G.: *Acta Polymer* 1997, **48**, 392.
10. Bonini F., Fraaije V., Fink G.: *J. Polym. Sci., Part A: Polym. Chem.* 1995, **33**, 2393.
11. Kaminsky W., Renner F.: *Makromol. Chem., Rapid Commun.* 1993, **14**, 239.
12. Sacchi M. C., Zucchi D., Tritto I., Locatelli P., Dall'Occo T.: *Makromol. Rapid Commun.* 1995, **16**, 581.
13. Chien J. C. W., He D.: *J. Polym. Sci., Part A: Polym. Chem.* 1991, **29**, 1603.
14. Soga K., Kim H. J., Shiono T.: *Macromol. Chem. Phys.* 1994, **195**, 3347.
15. *USA pat.* 5 202 398 (1993).
16. Muñoz-Escalona A., Méndez L., Sancho J., Laguente P., Peba B., Michiels W., Hidalgo G., Martinez-Nubez M. F.: "Metallorganic Catalysts for Synthesis" (ed. Kaminsky W.), Springer, Berlin 1999, p. 381.
17. Booth B. L., Ofunne G. C., Stacey C., Tait P. J. T.: *Organomet. Chem.* 1986, **315**, 143.
18. Janiak C., Rieger B.: *Angew. Makromol. Chem.* 1994, **215**, 47.
19. Tait P. J. T., Monteiro M. G. K., Yang M., Richardson J. L.: "Met. Con. '96", June 12—13, Houston 1996.
20. Burford D. R., Tait P. J. T.: *Polymer* 1972, **13**, 315.
21. Tait P. J. T.: "Transition Metal Catalyzed Polymerizations" (ed. Quirk R. P.), Harwood Academic Publ., New York 1983, p. 115.
22. Tait P. J. T., Abozeid A. I., Paghaleh A. S.: "Metallocenes '95", Internat. Congress on Metallocene Polymers, 26—27 April, Brussels 1995, p. 89.
23. Tait P. J. T.: "Developments in Catalysts Support Technology", The Catalyst Group, Spring House, PA, 1996, p. 99.
24. Tait P. J. T., Ediati R.: "MetCon '97", June, 4—5 1997.