

Hydrogen transfer reactions of supported metallocene catalysts

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Abstract

The evolution of methane from methylaluminumoxane (MAO) solutions is enhanced in the presence of homogeneous metallocenes. This reaction serves as a model for the deactivation of metallocene catalysts. By supporting different metallocenes on a silica/MAO carrier the deactivation reaction by alpha-hydrogen transfer among metallocene active sites and aluminum alkyls can be suppressed. The suppression of alpha-hydrogen transfer is proven for different Al/Zr ratios and by near independence of the polymerization activity on the catalyst aging time, after reaching maximum activity. Aluminum alkyls and MAO leach Cp_2ZrCl_2 from the carrier, the leached metallocene is only active in polymerization if MAO is present. © 1998 Elsevier Science B.V.

Keywords: Supported metallocenes; Hydrogen transfer; Deactivation; Methane evolution; Olefin polymerization; Leaching

1. Introduction

Metallocenes have gained widespread importance as catalysts for the polymerization of olefins due to their high activity and versatility [1–5]. Metallocene catalysts show a single site active center in homogeneous phase and make it possible to tailor the structure of polymers in a precise way.

Great industrial interest has arisen in using them in existing technical processes (drop-in technology) by replacing the conventional heterogeneous catalysts. In this case, the morphology of the obtained polymer has a quality which facilitates polymer processability.

In order to heterogenize metallocenes, they have to be supported on an indifferent carrier

such as silica, aluminum or other inorganic or organic supports [6–10].

The catalyst behavior depends on the carrier and the supporting technique, of which the following are possible:

(1) Initial adsorption of MAO on the carrier with subsequent addition of the metallocene. This method has been used in this work.

(2) Either initial adsorption and immobilization of the metallocene or direct bonding by a spacer to the support surface.

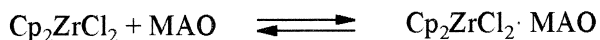
Aluminum alkyls as TIBA (triisobutylaluminum), TEA (triethylaluminum) or TMA (trimethylaluminum) are normally used as cocatalysts in the heterogeneous polymerization of olefins. Great differences were observed in the polymers obtained by supported metallocene catalysts on the one hand and by their homogeneous equivalents on the other. When comparing supported to homogeneous systems the molecular weight of the polymer can be much

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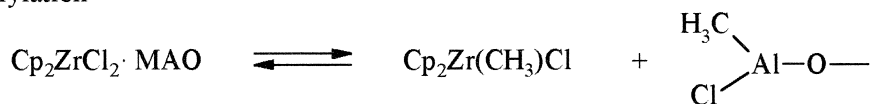
higher than when using the homogeneous catalyst. Under special conditions the microstructure of polypropylene can change even from syndio-

tactic to isotactic [9]. The activity is lower but more stable during long periods. Side reactions were examined to explain these differences.

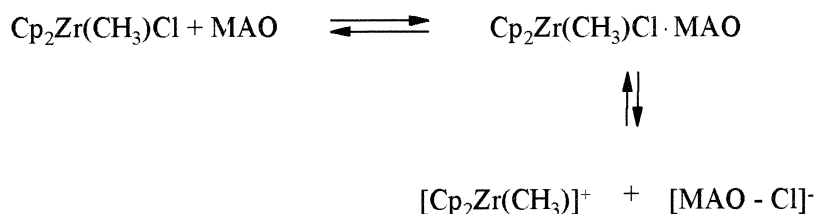
Complexation



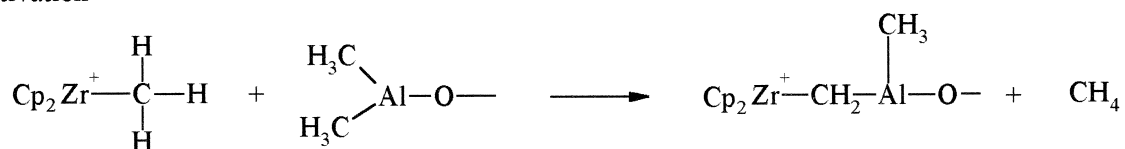
Methylation



Activation



Deactivation



Reactivation

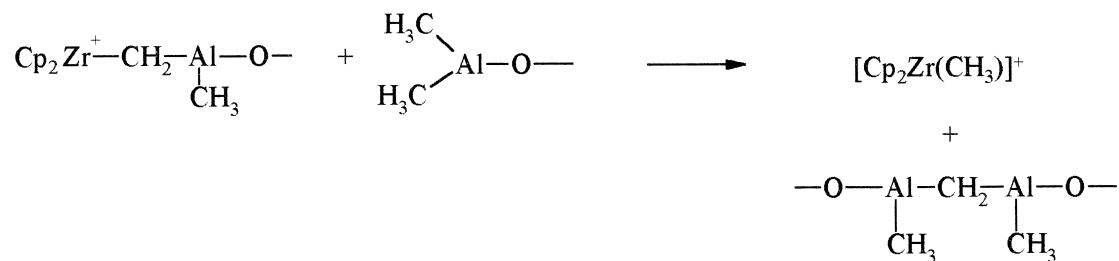


Fig. 1. Reactions of zirconocenes with MAO.

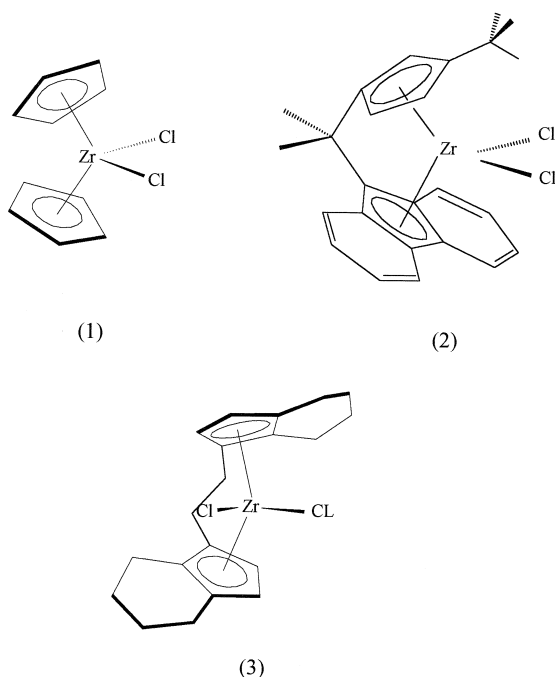


Fig. 2. Used metallocenes: (1) Cp_2ZrCl_2 ; (2) $[\text{Me}_2\text{C}(\text{tert-BuCp})(\text{Flu})]\text{ZrCl}_2$; (3) $[\text{En}(4,5,6,7\text{-H}_4\text{Ind})_2]\text{ZrCl}_2$.

It is known that beside complexation, methylation and activation, alpha-hydrogen transfer between MAO and metallocene occurs as a side reaction (Fig. 1) [11–14].

This side reaction is responsible for the production of methane. Condensation of the metallocene and MAO takes place causing the formation of $\text{Zr-CH}_2\text{-Al}$ or $\text{Zr-CH}_2\text{-Zr}$ structures. Siedle et al. were able to create a dimetallocyclobutane between Cp_2ZrMe^+ and TMA under loss of methane in the gas phase [15]. Half sandwich complexes form clusters by condensation reactions [16]. Metallocene compounds with a $\text{Zr-CH}_2\text{-Zr}$ structure are known to be inactive [17] and a specific cause for the deactivation of metallocene catalysts.

These reactions were studied in detail for the homogeneous $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ system by NMR spectroscopy, polymerization results and measurement of methane evolution [12,18]. In order to catalyse the intermolecular hydrogen transfer, bimetallic reactions are necessary. They could

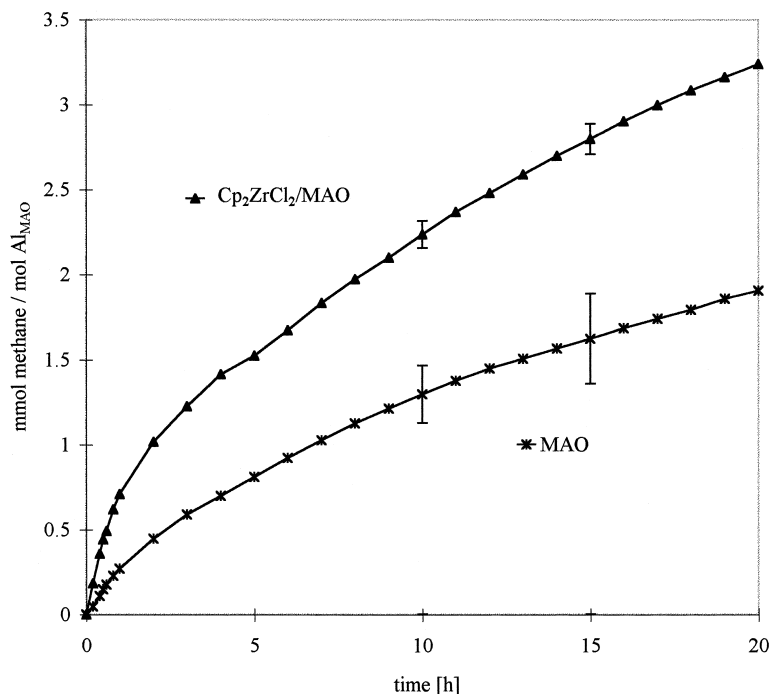


Fig. 3. Comparison of methane evolution of homogeneous Cp_2ZrCl_2 with MAO and MAO alone. Reaction conditions: $T = 10^\circ\text{C}$; $V = 20$ ml; solvent = toluene; $[\text{Cp}_2\text{ZrCl}_2] = 4.5 \times 10^{-3} \text{ mol l}^{-1}$; $[\text{Al}]_{\text{MAO}} = 0.36 \text{ mol l}^{-1}$; $\text{Al}_{\text{MAO}}/\text{Zr} = 80$.

also be responsible for the intramolecular hydrogen reaction and so have an influence on the molecular weight of the produced polyolefins. The question was if the side reaction with hydrogen transfer could be inhibited by supporting the metallocene. Side reactions of supported metallocenes have not yet been investigated, although deactivation reactions are of great interest for the commercial use of these systems. In this paper new results are presented on the stability of supported metallocenes on silica by studying polymerizations and the evolution of methane as a function of the reaction time. These analyses were carried out for three metallocenes with different symmetric structures. Most work was done with (1) Cp_2ZrCl_2 (C_2v), (2) $[\text{Me}_2\text{C}(\text{tert-BuCp})(\text{Flu})]\text{ZrCl}_2$ (C_1) and (3) $[\text{En}(4,5,6,7\text{-H}_4\text{Ind})_2]\text{ZrCl}_2$ (C_2) were also used (Fig. 2).

2. Results and discussion

2.1. Evolution of methane

One way to observe the deactivation reaction shown in Fig. 1 is to follow the evolution of methane by monitoring the pressure as a function of the reaction time. The produced gas was analyzed by gas chromatography to contain more than 98% methane.

The reaction scheme is complicated by the self-condensation of MAO under loss of methane and consequent formation of $\text{Al-CH}_2\text{-Al}$ structures. A series of experiments were performed that contained only MAO in different concentrations (0.36–0.74 mol $\text{Al}_{\text{MAO}}/\text{l}$) in toluene solution. It was shown that the amount of methane evolution per aluminum atom is constant (1.7 mmol methane/mol Al_{MAO} after 20 h reaction time). The methane production is significantly enhanced if dissolved Cp_2ZrCl_2 is present in the reaction system as is seen in Fig. 3. Even after reaction times longer than 110 h the condensation reaction still occurs.

The experiments for heterogeneous systems

were designed to resemble the conditions employed for typical polymerizations and of the homogeneous experiments described above. Methane production is observed when on SiO_2/MAO supported metallocene is stirred in a toluene solution of 0.2 mol/l TMA. In a control experiment the methane evolution of the same amount of SiO_2/MAO precursor is measured under identical conditions and compared to the experiment with metallocene (Fig. 4). No significant difference is observed between the two experiments.

Methane evolution is the same if the supported metallocene is added or not, whereas in the homogeneous case methane evolution is much higher when the metallocene is present (see Fig. 3). In the homogeneous case the metallocene catalyzes methane evolution by α -hydrogen transfer [11,12,18]. By supporting the metallocene this condensation reaction is suppressed.

TMA was chosen as additional aluminum alkyl so that the sole product of condensation is methane and as a common cocatalyst in heterogeneous polymerizations. The use of dissolved MAO is not suitable due to leach phenomena. By comparing Figs. 3 and 4 the higher amount of produced methane is striking. The TMA solution as well as the SiO_2/MAO precursor in toluene cause methane evolution to a higher extent than MAO solution in toluene. The reasons are not clear, perhaps the silica carrier facilitates the methane evolution by electronic reasons or TMA undergoes easier condensation reactions.

The absence of a significant difference between control experiments and experiments with metallocene shows clearly that by supporting the metallocene on silica the α -hydrogen transfer is suppressed. Also no additional methane evolution is observed in all performed experiments with the supported metallocene at $\text{Al}_{\text{TMA}}/\text{Zr}$ molar ratios between 70 and 580 and at temperatures between 0°C and 30°C. Fig. 5 shows that this behavior is the same for all investigated supported catalysts. In comparison

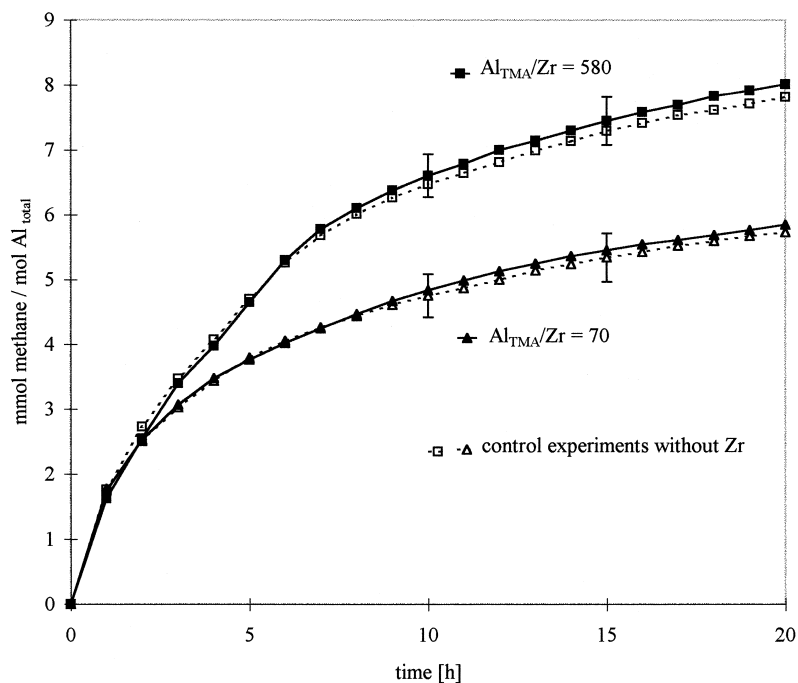


Fig. 4. Comparison of methane evolution of supported $\text{SiO}_2/\text{MAO}/\text{Cp}_2\text{ZrCl}_2$ systems and control experiments with SiO_2/MAO systems at different $\text{Al}_{\text{TMA}}/\text{Zr}$ ratios. Reaction conditions: $T = 10^\circ\text{C}$, $V = 15\text{ml}$; solvent = toluene; $[\text{Al}]_{\text{TMA}} = 0.2\text{ mol l}^{-1}$; $[\text{Cp}_2\text{ZrCl}_2]_{\text{SiO}_2/\text{MAO}} = 3$ or 3.5 mol l^{-1} ; $\text{Al}_{\text{TMA}}/\text{Zr} = 70$ or 580 .

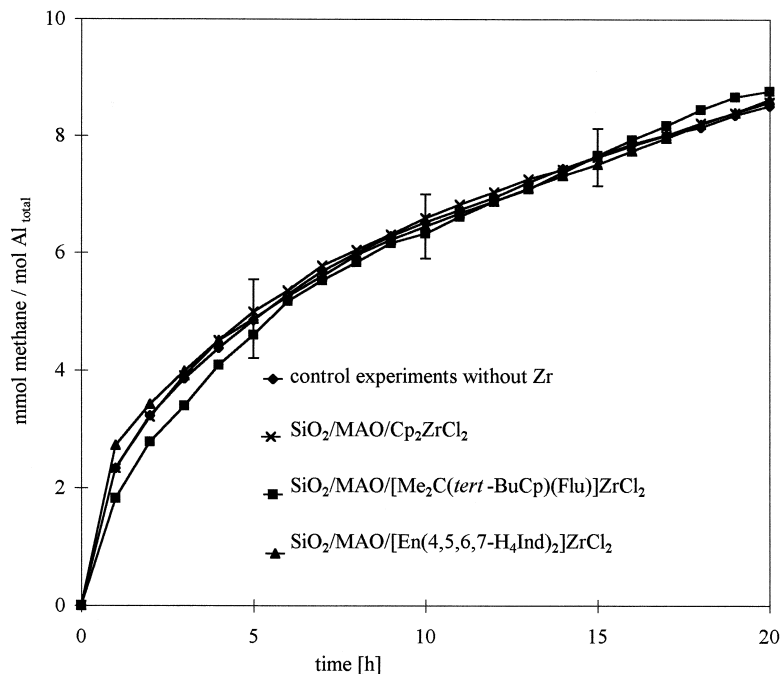


Fig. 5. Methane evolution of different $\text{SiO}_2/\text{MAO}/\text{metallocenes}$ systems and control experiment with SiO_2/MAO systems. Reaction conditions: $T = 30^\circ\text{C}$; $V = 15\text{ ml}$; solvent = toluene; $[\text{Al}]_{\text{TMA}} = 0.2\text{ mol l}^{-1}$; $[\text{metallocene}]_{\text{SiO}_2/\text{MAO}} = 0.8 \times 10^{-3}\text{ mol l}^{-1}$; $\text{Al}_{\text{TMA}}/\text{Zr} = 260$.

to the precursor experiment no difference in the evolution of methane is observed. Regardless of the catalyst symmetry, the α -hydrogen transfer is reduced by supporting the metallocene on the carrier.

2.2. Polymerization results

This significant difference between supported and homogenous catalysts should have an influence on the polymerization activity of ethene after different aging times. In the aging time the supported metallocene can react with a toluene solution of trimethylaluminum without the monomer being present. In homogeneous metallocene catalysis it is known that there is a close relationship between methane evolution, aging time and polymerization activity [18]. After 15 min the activity reaches a maximum value but then decreases quickly to 19% after an aging time of 2.5 h.

The polymerization activity of supported metallocenes for ethene is not as strongly influenced by the length of the aging time as Table 1 clearly shows. For both catalysts (1) and (2) the maximum activity is reached after an aging time of two hours and then remains on nearly the same level for a further 18 h. The activity remains stable during the polymerization.

These results can be interpreted by a slow activation reaction which is already known from homogeneous catalysis. Due to the immobilization of the metallocene, the activation of the supported metallocene is much slower than that of the homogeneous catalyst.

In contrast to the homogeneous system, though, no deactivation is observed during a catalyst aging period of 20 h, during which the activity remains nearly constant. This is in good agreement with the absence of additional methane evolution by the supported metallocene. By supporting the metallocene on silica, the condensation reactions are suppressed by steric or electronic effects. At the moment we cannot distinguish between these two possibilities, further investigation is in progress to solve these questions.

Good agreement is found with a deactivation scheme proposed by Mühlhaupt, in which two active sites form a catalytically inactive complex [19].

2.3. Leaching of Cp_2ZrCl_2

An interesting but not well known aspect of supported metallocenes is the possible leaching of the metallocene during the experiments.

Table 1

Polymerization of ethene with $SiO_2/MAO/Cp_2ZrCl_2$ (1) and $SiO_2/MAO/[Me_2C(tert-BuCp)(Flu)]ZrCl_2$ (2) in dependence on the aging time

Catalyst	Aging time with TMA (h)	Activity (kg PE/(mol Zr h))	T_m (°C)	M_n (kg/mol)	M_w/M_n
1	0	810	138	740	2.1
1	0.25	870	139	740	2.3
1	1	900	138	770	2.5
1	2	1080	138	760	2.5
1	4	1050	138	670	2.3
1	20	1050	140	620	2.4
2	0	275	134	305	2.3
2	0.25	280	135	360	1.9
2	1	385	136	340	2.0
2	2	420	138	340	2.2
2	4	400	137	310	2.0
2	20	395	136	460	2.0

Aging conditions: $T = 30^\circ\text{C}$; $Al_{TMA}/Zr = 230$; $[Al]_{TMA} = 0.01 \text{ mol l}^{-1}$; $[metallocene]_{SiO_2/MAO} = 4.3 \times 10^{-5} \text{ mol l}^{-1}$; $t = 0.5 \text{ h}$; 100 ml toluene. Polymerization conditions: 100 ml toluene; $p_{ethene} = 2 \text{ bar}$; $T = 30^\circ\text{C}$; $[Al]_{TMA} = 0.01 \text{ mol l}^{-1}$; $[metallocene]_{SiO_2/MAO} = 4.3 \times 10^{-5} \text{ mol l}^{-1}$; $t = 0.5 \text{ h}$.

A series of methane evolution experiments employing MAO as aluminum reagent instead of TMA were performed with the supported metallocene. In these experiments a temperature effect was observed. At $T = 10^\circ\text{C}$ no significant increase of methane evolution can be observed in comparison with the control experiment just as when using TMA as reagent. If the temperature is increased up to 30°C , methane evolution is significantly enhanced in the presence of metallocene. A possible reason is the leaching of metallocene from silica, which leads to a partially homogeneous system with increased methane production as described in Fig. 3.

It is found that after stirring supported Cp_2ZrCl_2 in toluene with an aluminum reagent but without any monomer and filtration of the suspension the toluene solution contains a high level of dissolved Cp_2ZrCl_2 under these conditions. The degree of leaching is estimated by comparison of the activity of the homogeneous system with the toluene soluble fraction at a constant amount of MAO in the autoclave and, in a second independent way, by analyzing the supported catalyst by ICP–OES before and after the leaching of the metallocene. Both methods give results in the same magnitude as can be seen in Table 2. For TIBA the difference between the two methods is higher than in the other cases but still in the same magnitude. With TMA about 20% of the supported Cp_2ZrCl_2 is leached, but with MAO nearly

40% is leached. In the ICP–OES measurements it can be seen that the aluminum content of the carrier does not decrease which proves the chemical fixation of MAO on the silica by Al–O–Si structures. The high values for the leached Cp_2ZrCl_2 certainly depend on the use of toluene which is a good solvent for Cp_2ZrCl_2 and the Al/Zr molar ratio. To prevent leaching of metallocenes heptane can be used as solvent [20], but no leaching experiments have been described yet. No polymerization activity for the filtered solution is observed when toluene is used without any aluminum alkyl in the leaching experiment. This means that no zirconium is desorbed from the supported metallocene.

In the presence of only TMA or TIBA the leached metallocene is inactive, but is active in the presence of MAO. The polymerization results are given in Table 2. This shows that it is not sufficient to calculate the leached zirconocene only by the polymerization activity in the absence of MAO, as is written in the literature [21]. As the polymerization conditions are similar to those in homogeneous catalysis, the activity can be seen as a correct estimation of the leaching of the catalyst. The presence of different aluminum alkyls in the polymerization mixture has no large influence on the polymerization activities as shown by Chien [22]. Because the leached metallocene needs to be activated by MAO it is clear that polymerization only takes place on the supported metallocene.

Table 2

Ethene polymerizations with the filtered solution of $\text{SiO}_2/\text{MAO}/\text{Cp}_2\text{ZrCl}_2$ catalyst with MAO, TMA, TIBA or toluene in comparison to the ICP–OES measured zirconium content

Leaching by	Activity (kg PE/(mol Zr h))	Leached amount of Cp_2ZrCl_2		M_w/M_n	M_n (kg/mol)
		polymerization (%)	ICP–OES (%)		
MAO	5 100	37	40	1.8	700
TMA	2 800	21	24	1.7	820
TIBA	3 000	22	32	1.8	620
Toluene ^a	0	0	0	—	—
Homogeneous ^b	13 700			2.0	620

Leaching conditions: $T = 30^\circ\text{C}$; $t = 30$ min; $[\text{Cp}_2\text{ZrCl}_2]_{\text{SiO}_2/\text{MAO}} = 4.3 \times 10^{-5}$ mol l^{-1} ; Al/Zr = 230; toluene = 100 ml. Polymerization conditions: $T = 30^\circ\text{C}$; $t = 15$ min; $p_{\text{ethene}} = 2.5$ bar; additional MAO: 150 mg.

^a $t = 2$ h.

^b $[\text{Cp}_2\text{ZrCl}_2] = 6.25 \times 10^{-6}$ mol l^{-1} .

Therefore it has to be proved in slurry polymerizations, where MAO is used as cocatalyst in the liquid phase, if the high polymerization activity is derived from the supported catalyst or from the leached and activated homogeneous metallocene [23]. By using aluminum trialkyls as cocatalyst leaching is not as important because the leached metallocene is inactive in polymerizations, though the activity is possibly lowered by using aluminum alkyls. Until now it is not clear if the leaching also takes place in the presence of monomers. Further investigation is in progress.

3. Conclusions

It is possible to prevent deactivation reactions of metallocenes by supporting them on silica, thus blocking the α -hydrogen transfer. This effect can also be observed in the long stability of the metallocene in TMA-solutions, in which the activity does not decrease within twenty hours. It explains also that in some cases the molecular weight of the obtained polyolefins is much higher for supported than for homogeneous catalysts, because the β -hydrogen transfer is also suppressed [9].

Depending on the aluminum reagent, between 20 and 40% of the supported Cp_2ZrCl_2 is leached in toluene solutions under formation of a catalytic species that is not active in polymerizations until MAO is added.

4. Experimental section

4.1. Materials

All reaction steps were carried out in an argon atmosphere using Schlenk techniques. Toluene was dried over a sodium/potassium alloy and distilled before use. Ethene was purchased from Linde gas and purified by passing through columns containing mol sieve and the BASF catalyst R 3-11. MAO, TMA and TIBA

were purchased from Witco. The 10% weight solution of MAO in toluene was dried in vacuum at 50°C. SiO_2 from Grace (952) was calcined at 600°C for 6 h and dried in vacuum for 12 h at 80°C.

4.2. Preparation of the supported catalyst

The supported catalyst was prepared according to the literature [24]. In a typical procedure, 4.6 g solid MAO was added to a suspension of 8.3 g SiO_2 in toluene. The mixture was stirred for 1 h at room temperature. The slurry was filtered and washed 2 times with toluene thus obtaining the SiO_2/MAO precursor. A solution of 0.877 mmol of metallocene (1) in toluene was then added to a suspension of the precursor in toluene and stirred for one hour at room temperature. The slurry was filtered, washed with toluene and the supported catalyst was dried in vacuum. The contents of zirconium and aluminum in the supported catalyst were measured by induced coupled plasma-optical emission spectroscopy (ICP-OES). The results for the Zr and Al measurements were as follows: (1) 6.9×10^{-2} and 3.9 (2) 6.8×10^{-2} and 2.9 (3) 7.2×10^{-2} and 2.8 mmol Zr or Al per g catalyst.

4.3. Methane evolution

The methane evolution reactions were performed in a 25 ml glass reactor. Prior to reaction, it was checked if the reactor was adequately sealed, then it was heated at 95°C for 1.5 h and purged with argon 5 times. The reactor was charged with the supported catalyst and cooled to -20°C . A freshly prepared and cooled (-20°C) solution of TMA in toluene was added and the reactor was evacuated. The reaction was started by changing the temperature immediately to the reaction temperature, the methane evolution was monitored by the increasing pressure (EPS 10 and EMV 251 from Edwards). After completion of the reaction a gas sample was taken for analysis in a gas chromatograph.

From the increasing pressure the amount of produced methane was calculated by the ideal gas law with consideration of toluene vapor pressure, solubility of methane in toluene [25] and temperature gradient in the pressure sensor which could not be thermostated.

4.4. Polymerizations

The polymerization reactions were performed in a 1 liter glass autoclave. Prior to polymerization, the autoclave was heated at 95°C for 1.5 h and purged with argon 5 times.

The autoclave was charged successively with toluene, the cocatalyst solution and the supported catalyst. The mixture was allowed to aging for the desired time. The polymerization was started by addition of ethene. The polymerization was terminated by addition of ethanol. The product was washed with Ethanol/HCl, neutralized and dried in vacuum at 60°C. Each polymerization was repeated to ensure reproducibility.

4.5. Analytical methods

Viscosimetry was carried out with an Ubbelohde capillary 0a ($K = 0.005$) at 135°C using decahydronaphthalene as solvent. Molecular weight distributions were determined by gel permeation chromatography in a Waters 150-C instrument (trichlorobenzene, 135°C). The Mark–Houwink constants have been reported in the literature [26]. Differential scanning calorimetry analyses were performed on a Perkin-Elmer DSC-4 instrument (heating rate 20°C min). The gas was analyzed by a Carlo Erba gas chromatograph with $\text{Al}_2\text{O}_3/\text{KCl}$ -Plot-capillary columns and an FID detector. A temperature program between 40 and 200°C was used. To analyze the zirconium content of the supported catalyst, the supported catalyst was treated with HNO_3 (65%), HClO_4 (70%) and HF (30%) in a temperature program between room temperature and 240°C. The aqueous solution was then analyzed in a Perkin

Elmer/6000 Induced Coupled Plasma-Optical Emission Spectrometer with an acquisition station 7500. For zirconium the wave lengths 343.823 and 349.621 nm were analyzed by a calibration concentration of 2.0 mg/l, for aluminum the wave lengths were 308.215 and 394.401 nm by a calibration concentration of 20.0 mg/l.

Acknowledgements

We thank the BMBF for financial support of this work.

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