Suppression of Metallocene Catalyst Leaching by the Removal of Free Trimethylaluminum from Methylaluminoxane

Jani P. J. Turunen, Tuula T. Pakkanen

Department of Chemistry, University of Joensuu, P.O. Box 111, FI-80101 Joensuu, Finland

ABSTRACT: The leaching of the catalyst zirconocene dichloride (Cp_2ZrCl_2) from an SBA-15 silica support during ethylene polymerization was studied; severe leaching was observed when commercial methylaluminoxane (MAO) was used as the cocatalyst. However, the removal of free trimethylaluminum (TMA) from an MAO solution with a sterically hindered phenol reduced the catalyst leaching by 97–100%. The results obtained from the leaching experiments with TMA-free MAO suggested that the major reason for catalyst leaching was the free TMA in the commercial MAO solution, not the pure MAO itself. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 4632–4635, 2006

Key words: metallocene catalysts; polyethylene (PE); silicas; supports

INTRODUCTION

Commercial polymerization processes that produce high-density polyethylene or polypropylene with metallocene catalysts require the use of a heterogeneous catalyst; that is, the metallocene is supported on an insoluble carrier, such as silica. The advantages of heterogenization include, for example, diminished reactor fouling, less cocatalyst required, good and uniform polymer morphology, and high polymer density.[1,2] Despite heterogenization, the single-site nature of homogeneous metallocene catalysts is preserved. Problems arise when the metallocene compound desorbs from the support during the polymerization and still works as an active polymerization catalyst; the benefits of heterogeneous polymerization are lost when part of the polymer is produced with an unsupported, homogeneous catalyst. This catalyst leaching is a well-known problem, and the best ways of dealing with it involve attempts to bind the metallocene to the support more effectively. In addition to binding the metallocene compounds to the support through the active metal center or through an ion-pair interaction with a methylaluminoxane (MAO)-pretreated support[2] (the two most common methods of heterogenization), resistance against leaching has been enhanced by the bonding of the metallocene covalently to the support through a functional group of a cyclic ligand or an ansa ligand.[3–5]

Catalyst leaching has been reported to take place especially in the presence of the cocatalyst MAO,[6–8] which, according to Semikolenova and Zakharov,[6] is suspected of destroying the surface metallocene oxy compounds and forming soluble metallocene–MAO complexes.[6] That particular study did not, however, take into account the fact that commercial MAO solutions also contain trimethylaluminum (TMA), the amount of TMA being, for example, 20–35% of the total aluminum content. Kaminsky and coworkers[7,8] showed that alkylaluminums also cause the desorption of metallocenes from silica supports and that the leached metallocene is active only if MAO is present. According to Mulhaupt et al.,[9] the reaction of alkylaluminum compounds with siloxanes results in a cleavage of the Si—O bond, and this explains why metallocenes leach even if they are bound to the silica surface with various bonding mechanisms (ionic or covalent via the metal center, cyclic ligand, or ansa ligand). Thus, one could conclude that even though MAO may also cause catalyst leaching, the free TMA in MAO is at least an important factor in the leaching. Surely other factors also, such as the type of alkylaluminum, the contents of metallocene and MAO on the support, and the method of catalyst preparation, have an influence on the amount of desorbed metallocene. In this study, we supported zirconocene dichloride on mesoporous silica supports with two common immobilization methods and investigated whether the removal of TMA from MAO with 2,6-di-*tert*-butylphe-

Correspondence to: J. P. J. Turunen (jani.p.turunen@joensuu.fi) or T. T. Pakkanen (tuula.pakkanen@joensuu.fi).

nol (^{t}Bu$_2$Ph-OH) reduced catalyst leaching during ethylene polymerization.[10]

EXPERIMENTAL

Materials

Zirconocene dichloride, ^{t}Bu$_2$Ph-OH, and TMA (2.0M solution in toluene) were purchased from Aldrich (Schnelldorf, Germany) and MAO (10% solution in toluene, TMA concentration = 33%) from Crompton GmbH (Bergkamen, Germany). All were used as received. Heptane and toluene (Riedel-de Haën, Seelze, Germany) were dried over 4-Å molecular sieves and distilled with benzophenone and Na under a nitrogen atmosphere.

Catalyst preparation

The catalyst support was mesoporous SBA-15 silica fiber, which was synthesized according to the procedure of Zhao et al.[11] and had an average pore diameter of 55 Å. Catalyst A was prepared by the immobilization of (Cp = .5-C$_5$H$_5$) Cp$_2$ZrCl$_2$ on the silica by adsorption. Toluene was used as a solvent, and the solution was shaken with the silica under nitrogen at 50°C overnight. Catalyst B was prepared by the pretreatment of the silica with an MAO solution before the immobilization of Cp$_2$ZrCl$_2$ in toluene (both were shaken overnight at 50°C). The amount of MAO was selected to correspond to 5 wt % aluminum on the silica and was diluted to ~20 mL of toluene before use. To remove nonbonded metallocene, both catalysts were washed several times with the solvent via shaking for about 10 min at room temperature and were finally dried at 50°C *in vacuo*. The solid catalysts A and B both had a zirconium loading of 1.2 wt %, and catalyst B had, in addition, an aluminum concentration of 4.5 wt % due to the MAO pretreatment.

Ethylene polymerization

A 250-mL stainless steel reactor (Büchi AG, Uster, Switzerland) was used in the polymerization. The catalyst (~30 mg, 4.0 μmol of Zr), MAO solution (Al/Zr = 1000), and 50 mL of heptane were packed in a stainless steel catalyst container in a nitrogen glovebox. Whenever ^{t}Bu$_2$Ph-OH was used, it was mixed with the MAO solution for 3 h before its use. The solution was transferred to the evacuated reactor with a nitrogen overpressure, and after 30 min of total activation at the ambient temperature, the polymerization was started by the introduction of 5 bar of ethylene pressure and stirring (750 rpm). During the polymerization, the partial pressure and temperature (80°C) were kept constant. The reaction was terminated by the venting of the ethylene and then the

addition of ethanol. The product was stirred in an acidic (HCl) ethanol solution for 3–4 h, filtered, washed with ethanol, and dried at room temperature.

Leaching experiments

For the catalyst leaching experiments, the catalyst (~30 mg, 4.0 μmol of Zr), cocatalyst MAO, and 50 mL of heptane were stirred in a 500-mL glass reactor at 80°C under nitrogen for the same time that the polymerization would take. The mixture was then filtered through a glass sinter and a Whatman 0.45-μm syringe filter (Clifton, NJ) in a nitrogen glovebox and was finally transferred into the polymerization reactor for polymerization. No additional MAO was used in the polymerization of the leaching experiment, except in the case of TMA as the cocatalyst (run 5 in Table I).

Characterization

The zirconium contents of the catalysts were determined with a TJA (Offenbach, Germany) IRIS inductively coupled plasma/atomic emission spectroscopy (ICP–AES) instrument. The molar masses of the polymers were determined with a Waters (Milford, MA) Alliance GPCV 2000 gel permeation chromatograph at 140°C with trichlorobenzene as a solvent, and the melting points were determined with a Mettler–Toledo (Zürich, Switzerland) DSC821e differential scanning calorimeter at a scanning rate of 10 K/min. The reaction of free TMA with ^{t}Bu$_2$Ph-OH was observed with a Bruker Instruments (Karlsruhe, Germany) Avance 400-MHz ^{1}H-NMR instrument.

RESULTS AND DISCUSSION

The leaching of a metallocene from a support can be measured by the application of the polymerization conditions without the monomer to the catalyst, the filtration of the solution, and the polymerization with the filtrate as a catalyst. Another way of determining leaching involves measuring the metallocene concentration on the support by ICP–AES both before and after it is mixed with an MAO solution. The mesoporous silica support, however, adsorbs various amounts of the cocatalyst and solvent, which are practically impossible to remove without the risk of decomposing the catalyst, so we prefer polymerization with the filtrate for the determination of the leaching. The determination of the amount of metallocene in the filtrate of the leaching experiments proved to be too difficult to measure because zirconium existed below the level of parts per million, and there was over a 1000-fold excess of aluminum. Thus, the polymer yields and polymerization activities obtained from the polymerizations with the leaching filtrate as a catalyst were used as the measurements for the degree of

TABLE I
Results of the Polymerizations and Leaching Experiments with Catalysts A and B

Run	Catalyst	Catalyst amount (μmol)	Cocatalyst	Type of polymerization[a]	Time (min)	Yield (g of polyethylene)	Activity [kg of polyethylene/ (mol h bar)]	M_w	M_w/M_n	T_m (°C)
1	Homogeneous Cp_2ZrCl_2	2.0	MAO	Normal	5	4.07	4,880	47,800	2.1	135.9
2	A	4.0	MAO	Normal	20	2.61	389	65,400	2.8	135.3
3	A	4.0	MAO	LE	20	0.70	105[c]	41,300	3.2	132.3
4	A	4.0	TMA	Normal	20	0	0	—	—	—
5	A	4.0	TMA[b]	LE, MAO added in polymerization[c]	20	4.17	625[c]	38,800	2.3	136.7
6	B	4.0	MAO	Normal	20	4.43	667	66,000	3.7	134.9
7	B	4.0	MAO	LE	20	8.28	1,250[c]	48,700	3.0	136.5

M_w = weight-average molecular weight; M_n = number-average molecular weight; T_m = melting temperature.
[a] LE = leaching experiment: catalyst and cocatalyst mixed in a glass reactor at 80°C for 20 min before filtration and polymerization. Al/Zr = 1000 in all polymerizations or leaching experiments.
[b] TMA = 4000 μmol; MAO = 4000 μmol.
[c] Calculated according to the amount of Zr in the catalyst before the leaching experiment.

leaching. The activities were calculated according to the original amount of zirconium in the catalyst (4.0 μmol).

The role of TMA in the catalyst leaching was clarified with a few simple polymerizations (runs 2–5 in Table I). As expected, TMA as a cocatalyst alone did not yield any polyethylene (run 4). However, when the leaching experiment was carried out with TMA and MAO was added (Al/Zr = 1000) afterwards to the filtrate, the yield was even higher than that with a normal polymerization with MAO. These polymerizations verified the results of Kaminsky and Strübel,[7] that TMA causes catalyst leaching but does not activate the metallocene for polymerization; MAO is required to obtain the active catalyst for polymerization. In contrast to the results of Kaminsky and Strübel, we used heptane as the solvent instead of toluene, which should have suppressed the leaching because of the lower solubility of Cp_2ZrCl_2 in heptane. Runs 2 and 3 show the degree of leaching for catalyst A, and runs 6 and 7 show the same for catalyst B. Leaching was clearly higher when the metallocene was immobilized on an MAO-pretreated silica support (catalyst B), as expected because of ionic bonding of the metallocene on MAO–SiO_2. The polymer yield from the leaching experiment with catalyst B was even higher than that from a normal polymerization (runs 6 and 7 in Table I). This can be explained by the fact that in a normal polymerization, the amount of the highly active form of the homogeneous metallocene in the reactor increases gradually because of the leaching, but in the polymerization of the leaching experiment, the concentration of the active form is high already in the beginning and remains constant throughout the polymerization. There was some bimodality in the gel permeation chromatography and melting curves of the polymers obtained from the normal polymerizations because of the presence of two kinds of active metallocene species in the reactor, that is, metallocene in homogeneous and heterogeneous media.

To discover whether the removal of free TMA from MAO would reduce leaching, an efficient way of obtaining TMA-free MAO was needed. Although several methods for removing TMA from MAO have been introduced in the literature, including the distillation of TMA from MAO[12] and the synthesis of MAO with nonhydrolytic means,[12,13] we preferred the treatment of MAO with $^tBu_2Ph-OH$, the method used by Busico et al.[10] The sterically hindered OH group of the phenol preferentially reacts with the free TMA, although this happens at a $^tBu_2Ph-OH/TMA$ molar ratio greater than 2 to some extent also with the Al—Me bond of MAO.[10] In our reactions, we used a $^tBu_2Ph-OH/TMA$ molar ratio of 1.5, which, according to our ^1H-NMR measurements, was considered to be sufficient. $^tBu_2Ph-OH$ was allowed to react with the MAO solution for 3 h at room temperature before its use.

The addition of phenol to MAO reduced the activities of homogeneous Cp_2ZrCl_2 (run 1 in Table I and run 8 in Table II) and heterogeneous catalyst A (runs 2 and 9), whereas the activity of catalyst B remained about the same (runs 6 and 11). However, and most importantly, in the case of the heterogeneous catalysts, the metallocene leaching was dramatically reduced; according to the yields of the polymerizations with the filtrates of the leaching experiments, in the case of catalyst A, no leaching at all was observed, and in the case of catalyst B, leaching was reduced by 97%! These results indicate that pure (or TMA-free) MAO has far less of a role in the metallocene leaching than previously suggested[6] and that the major reason for leaching is the free TMA in MAO.

TABLE II
Results of the Polymerizations with TMA-Free MAO

Run	Catalyst	Catalyst amount (μmol)	Type of polymerization[a]	Time (min)	Yield (g of polyethylene)	Activity [kg of polyethyle/ (mol h bar)]	M_w	M_w/M_n	T_m (°C)
8	Homogeneous Cp$_2$ZrCl$_2$	3.0	Normal	5	4.41	3,530	80,100	2.3	138.1
9	A	4.0	Normal	20	0.44	66	176,000	2.3	141.7
10	A	4.0	LE	20	0	0	—	—	—
11	B	4.0	Normal	20	4.61	693	152,000	2.3	142.3
12	B	4.0	LE	20	0.27	40[b]	115,000	2.2	138.1

M_w = weight-average molecular weight; M_n = number-average molecular weight; T_m = melting temperature.
[a] LE = leaching experiment: catalyst and cocatalyst mixed in a glass reactor at 80°C for 20 min before filtration and polymerization. Al/Zr = 1000 in all polymerizations or leaching experiments.
[b] Calculated according to the amount of Zr in the catalyst before the leaching experiment.

The aforementioned conclusions are explained not only by differences in the polymerization activities but also by differences in the physical properties of the polymerization products (Tables I and II). First, the polydispersities of the polymers are different. Because of leaching, heterogeneous polymerizations without phenol addition yield polyethylenes with higher polydispersities (3.2–3.7), whereas polyethylenes obtained with phenol and MAO have polydispersities close to those obtained from homogeneous polymerizations (2.3 and 2.1–2.3, respectively). This indicates that there is an active metallocene only in one type of medium (heterogeneous).

Second, the same phenomenon can be seen in the molar masses of the polyethylenes. The molar masses from the leaching experiments are, naturally, about the same magnitude as those from the homogeneous polymerizations because the leached catalyst is in a homogeneous medium. Heterogeneous catalysts yield polyethylene with a higher molar mass. Because TMA acts as a chain-transfer agent, molar masses obtained with TMA-free MAO are higher than those obtained with normal, commercial MAO. One can, however, compare the relative molar masses of heterogeneous and homogeneous polymerizations. Without the addition of phenol, the heterogeneous catalysts yield polyethylene with a weight-average molecular weight about 1.4 times higher than that of homogeneous Cp$_2$ZrCl$_2$, but the addition of phenol increases the factor to 1.9–2.2. This also proves that when phenol is used, less leaching (or no leaching at all) occurs, and more of the polymerization occurs inside the silica support. The melting temperatures of all the products follow the same trend as the molar masses.

CONCLUSIONS

According to our leaching experiments with TMA, MAO, and ^{t}Bu$_2$Ph-OH/MAO, the major reason for the catalyst leaching during the polymerization is the free TMA in MAO, not the MAO itself. By removing free TMA from the commercial MAO effectively, for example, with a sterically hindered phenol, one can obtain a cocatalyst with no or only minor catalyst leaching. The removal of TMA from MAO is a much more convenient and effective way of suppressing the catalyst leaching and ensuring the truly heterogeneous nature of the polymerization than, for example, the preparation of a metallocene that is bonded onto the support through its functional ligands.

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