Mn doping of the Ziegler–Natta PP catalyst support material

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Abstract

Preliminary tests have shown that if $MnCl_2$ is used as a support material a polypropylene with a low molecular weight is produced. The activity of these catalysts is low. A low molecular fraction increases, however, the gloss of moulded products. As a molecular fraction with short chain length also acts as a lubricant in the polymer this short chain material would be an advantage if it is produced simultaneously with the normal high molecular weight polypropylene. This ability to influence the molecular weight distribution of the product was the reason why $MnCl_2$ was chosen as a doping salt in the $MgCl_2$ support material. The effect of Mn doping on the $MgCl_2$ support material has been investigated. The following conclusions have been drawn from this investigation: (i) Very good morphology is achieved if the $MnCl_2$ concentration is below 30%. At higher doping concentrations the result is poor morphology. (ii) Large catalyst particles were produced. The particles were of great mechanical strength, leading to the formation of large polymer particles with a very narrow PSD. No fines were produced partly due to agglomerization. This advantage was achieved only if the $MnCl_2$ concentration was below 30%. (iii) Optimum Mn doping concentration was 10 mol%. Using this doping concentration activity increased 25% (100% if kg PP/g Ti units are used). No loss in isotacticity. At higher Mn concentrations activity decreased linearly. The molecular weight distribution was effected. A broader MWD was achieved. The greatest effect was achieved with a Mn concentration of 10 mol%. The polydispercity increased from the standard value of 3 to 7. At higher Mn concentrations the MWD decreased steadily. Low molecular weight polypropene can be produced by using pure $MnCl_2$ as support material. (iv) The pore size distribution is effected by the Mn doping. A large portion of pores between 1 and 3 microns are produced. In standard polypropylene the largest fraction is to be found between 10 and 100 microns.

Keywords: Magnesium dichloride; Manganese dichloride; Supported catalysts; Ziegler–Natta catalysis; Propylene; Polymerization

1. Introduction

1.1. Ziegler–Natta catalysts give narrow MWD

The Ziegler–Natta catalyst, used in polypropylene polymerization, gives a material with a narrow molecular weight distribution. [1] This material is good for all injection moulding purposes. However there are several applications where a broader molecular weight distribution is needed. Especially when a greater melt strength is necessary a wider span of chain lengths would be an advantage. [2]

1.2. Uniform active sites result in uniform material

The high yield polypropylene catalyst is produced in a synthesis that consists of a long row of washings. In this washing process the catalyst is purified from all catalyst waste material produced

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in the initial reactions. In the efforts to create an as active catalyst as possible this purification system has been improved as much as possible. Due to this process the active sites in the catalyst are becoming quite uniform in nature. All divergating active sites are lost in the washing stage. When these catalysts are used an equally uniform polymer material is produced. This uniformity shows up as a narrow molecular weight distribution.

1.3. Differentiation in the nature of active sites

Because a broader spectrum of molecular weight is needed in several polypropylene applications a catalyst with different kinds of active sites has been tried to create. By creating a variety in the nature of the sites a corresponding variety of chain lengths in the polymer material could be produced. This could be possible by doping the $MgCl_2$ support material with another metal halide that would go into the crystal lattice and cause disorder in the otherwise homogeneous crystal lattice. This could in turn cause disorder in the set up of active sites. In this work $MnCl_2$ has been used as a doping salt in the support material.

1.4. $MnCl_2$: a salt resembling $MgCl_2$

Manganese dichloride was chosen as doping salt because it has a X-ray diffraction pattern that resembles that of $MgCl_2$. $MgCl_2$ has one distinct peak at 15° indicating the height of the crystal, two intermediate peaks at 30° and 35° and one significant peak at 50° reflecting the width of the crystal. [3,4] $MnCl_2$ has an X-ray diffraction pattern with four main peaks showing up in a close neighbourhood to the $MgCl_2$ peaks. There is one peak indicating the hight at 14° two intermediate peaks at 28° and 35° and a final peak at 48°. [5] This resemblance between the X-ray patterns indicates a good possibility for these salts to mix on a molecular level.

1.5. Preliminary test results

Preliminary tests had shown that $MnCl_2$, when used alone as a support material gives a polypro-pylene material with a low molecular weight. Activity showed to be low. A low molecular fraction however increases the gloss of moulded products. As a molecular fraction of low chain length also acts as a lubricant in the polymer this short chained material would be an advantage if it is produced simultaneously with the normal high molecular weight polypropylene. This ability to influence the molecular weight distribution of the product was the second reason why $MnCl_2$ was chosen as a doping salt in the $MgCl_2$ support material.

2. Experimental

The investigation was divided into four main parts. First the preparation of the support materials, second the catalyst synthesis, third the test polymerizations and last the characterization of the achieved polymer batches.

2.1. Preparation of the support materials

A series of five support materials was produced where the mangane content was successively increasing. The molar fraction of Mn in the support materials were 3, 10, 30 and 60%. In addition to this a support material consisting only of $MnCl_2$ was also produced for comparison. A standard $MgCl_2$ based support material was taken as reference material.

2.2. Morphology by the emulsion method

Portions of 1 to 30 g of the appropriate salts were suspended at room temperature in 600 ml of silicon oil in a reactor. Mixing was continued for half an hour to create equilibrium conditions. After this 56 ml of dry ethanol was added drop by drop and the temperature gradually increased to 40°C. Again, the solution was allowed to reach equilibrium after which the temperature was increased to between 123°C and 132°C. Ethanol was added, as much as was needed, to bring the salt mixture to melt. Vigorous mixing was used to

create an even distribution of the melt droplets in the silicon oil. When an clear salt melt was achieved the hot silicon oil slurry was siphoned through a teflon tube into a reactor containing one liter of cold heptane (− 30°C). The molten droplets of the metal salt mixture solidified in this cold solution. To remove the silicon oil the solids were washed three times with 600 ml of heptane. Finally the support material was dried in vacuum.

2.3. Catalyst synthesis

0.1 mol of the mixed salts of $MgCl_2$ and $MnCl_2$ was suspended in inert conditions in 150 ml of heptane and the suspension was mixed for half an hour. The suspension was cooled down to − 15°C. 300 ml of cold $TiCl_4$ was added and the temperature slowly increased to + 20°C. 5.3 ml of the internal donor (DIBP) was added to the reaction solution. The temperature was increased according to the temperature gradient up to the boiling point of the solution. After the boiling point of the reaction solution had been reached the normal catalyst synthesis recipe was followed.

2.4. Characterization of the catalysts

Of special interest was to follow the composition of the catalyst. Accordingly all the components in the catalysts were measured. Of interest was also to see if Mn caused changes in the crystal structure of the support material. X-ray diffraction patterns where therefore taken from all the catalysts. In addition to this the ratio of complexated internal donor in respect to the total amount of metal in the catalyst was studied.

2.5. Test polymerization

All the catalysts were test polymerized using our standard polymerizing conditions. A 2 l bench reactor was used. Between 20 and 30 mg of catalyst was used in the test polymerization. This amount was mixed with 620 ml of triethylaluminum and 200 ml of a 25% solution of CMMS external donor in 30 ml of heptane. The polym-

erizations were carried out at + 70°C and at 10 bar propene monomer pressure. The partial pressure of hydrogen during the polymerization was 0.2 bar. The polymerization was maintained for three hours. The activity was measured on the basis of the polymerization yield. The soluble part of the polymer was measured by evaporating a measured portion of the polymerization solution.

2.6. Characterization of the polymer batches

Bulk density and the particle size distribution was measured from all polymer lots. Isotacticity was measured by heptane elution and the isotactic index measured using the data from the evaporation residue measurements. Melt index was measured at 230°C using a 2.16 kg weight. To follow the effect of the salt mixing on the polydispersity the molecular weight distribution was measured from all the polymer batches. To investigate the suitability of the material for unpelletized antioxidant treatment the surface area and the pore size distribution were measured.

3. Results and discussion

3.1. Preparation of the support materials

When preparing the support materials it showed that the $MnCl_2$ had a lower solubility in ethanol than $MgCl_2$. In certain mixtures ethanol had to be added to bring the salt into a molten stage. About the double amount of ethanol had to be added to bring mixtures with over 10 mol% Mn to melt in the hot silicon oil. In Table 1 the resulting Mg and Mn concentrations found in the support material are shown.

3.2. Morphology of the support material

As more Mn was added to the salt mixture the mass was more and more difficult to bring into a molten stage. This also made the molten material more viscous. As identical mixing conditions were used in the silicon solution the more viscous

Table 1
Calculated chemical composition of the support material compared to the concentrations found in the product

mol% Mn	% Mn found in		% Mg found in	
calculated	support	product	support	product
0	0.0	0.0	10.4	100.0
3	0.8	3.1	10.4	96.9
10	1.6	10.0	6.5	90.1
30	6.8	29.2	7.3	70.8
60	14.3	57.9	4.6	42.1
100	28.8	100.0	0.0	0.0

Fig. 1. Morphology of the $MgCl_2 \cdot EtOH$ support material doped 3% $MnCl_2$.

Fig. 2. Morphology of the $MgCl_2 \cdot EtOH$ support material doped with 10% $MnCl_2$.

the melt was the larger the particles became. This increase in particle diameter continued up to a Mn content of 30%. After that, the molten droplets could not reach a spherical form any longer. This change in the particle morphology is shown in

Figs. 1-3. In the first picture the morphology of the 3% Mn doped material is shown.

This material resembles the normal $MgCl_2$ support material morphology with a mean diameter of 50 microns. The next picture shows the enlarged particles produced by the 30% Mn doped material and the last picture the collapsed crystalline material produced out of pure $MnCl_2$. The mean particle sizes are listed in Table 2. In Table 2 is also listed the general nature of the morphology together with the colour appearance of the support material.

3.3. The catalyst synthesis

The catalyst synthesis was carried out without any difficulties. The only significant difference

Fig. 3. Morphology of the $MnCl_2 \cdot EtOH$ support material.

Table 2
The mean particle diameter of the support material as a function of the mol % Mn in the $MgCl_2$ together with the colour and the morphology of the material

mol% Mn in support	Diameter (microns)	Colour [a]	Morphology [b]
0	50	W	S
3	50	SG	S
10	200	SG	A
30	300	LT	S
60	50	T	G
100	5	GR	C

[a] W = white; SG = slightly green; LT = light turquoise; T = turquoise.
[b] S = spherical; A = agglomerated mass; G = granular; C = crystalline.

Table 3
The chemical composition of the Mn-doped catalysts

mol% Mn added	Mg (%)	Mn (%)	Ti (%)	Cl (%)
0	16.0	0.0	4.4	56.0
3	16.8	1.2	2.9	56.2
30	11.1	6.0	2.6	53.3
60	5.7	18.6	3.2	49.1
100	0.1	36.3	.3	55.0

Table 4
Comparison between the amount of added Mn and what was found in the support material and the catalyst

mol% Mn added to support	mol% Mn found in the support	mol% Mn found in the catalyst
0	0.0	0.0
3	3.1	3.1
10	10.0	9.9
30	29.2	19.2
60	57.9	58.6
100	100.0	99.1

Table 5
The donor concentrations found in the Mn doped catalyst

mol% Mn added	% DIBP	mol% DIBP	mol% Mn + Mg	Ratio D/Mn + Mg
0	23.0	0.083	0.71	0.12
3	22.2	0.080	0.71	0.11
10	12.5	0.045	0.70	0.06
30	15.5	0.056	0.57	0.10
60	18.9	0.068	0.58	0.12
100	0.4	0.001	0.67	0.00

compared to normal catalyst synthesis was in the colour appearance of the reaction solution. The chemical composition of the catalysts was measured. The results from these measurements are listed in Table 3.

The results show that the relation between $MgCl_2$ and $MnCl_2$ closely follows the expected values. Here the mol% Mn is shown as a function of the added value. Both the support material as well as the catalysts had Mn concentrations that almost totally correlated to the expected values. These results show that $MnCl_2$ can be added to a $MgCl_2$ salt–ethanol mixture just by melting together the two salts.

3.4. The Ti content

No significant change in the ability of the support material to tie up Ti in the crystal structure could be detected due to an increasing amount of Mn in the $MgCl_2$ salt. After an initial drop when going from undoped material to the first doped catalyst (3 mol%) from 4.4 to a level of 3% a stable level was reached.

3.5. The donor concentration

The donor concentration was also followed by measuring the DIBP amount in the catalyst. This is because it was uncertain that Mn could tie up the internal donor to the same extent as Mg. Of special interest was to see if the mixture of the two salts could preserve the normal donor/support material ratio during the synthesis. In Table 4 and Table 5 these ratios are calculated and listed. The results showed a drastic drop in the ability to tie up the internal donor in the intermediate regions of the salt mixture. Thus only 50% of the original amount of donor could be tied up in a 10% Mn doped catalyst. The complexing ability showed a symmetrical behaviour around this intermediate level. The 60% $MnCl_2$ material could again tie up as much internal donor as the pure $MgCl_2$.

3.6. The MgCl_2 crystal dimensions

X-ray patterns were taken from all the catalyst batches to trace the influence of the $MnCl_2$ doping. It showed that concentration up to 30% of Mn could be used without having any change in the $MgCl_2$ X-ray pattern. A normal amorphous $MgCl_2$ pattern was achieved in these concentration with a small sign of the height of the crystal at 15° and with a clear peak at 50° $MgCl_2$ indicating the width of the crystal. At higher Mn concentrations the $MnCl_2$ X-ray pattern took to giving a more crystalline structure. The dimensions for the $MgCl_2$ crystals could be calculated just up to a level of 30% Mn.

Table 6
The activity of the Mn doped catalysts

mol% Mn added	Activity kg PP/g cat	Activity kg PP/g Ti
0	14.3	325
3	14.1	486
10	20.0	606
30	12.8	492
60	8.4	262
100	1.0	43

3.7. Activity

All the catalysts were test polymerized according to the standard conditions. In Table 6 the polymerization results are listed. Activity is here expressed in both kg PP/g cat and kg PP/g Ti units. The results are also shown graphically in Fig. 4. The Mn doping showed to cause an drastic effect on the activity of the catalysts. A 3% Mn doping gave almost the same result as an undoped catalyst if only looking on kg PP/g cat. units but caused already a 25% increase in activity expressed in kg PP/g Ti units. The activity increase effect was most pronounced when using the 10% Mn doped material. Here activities of 20 kg PP/g cat could be reached. If kg PP/g Ti units are used the activity increase is of the order of 100%. When going to higher doping concentration there is an almost linear drop in activity due to the increasing Mn concentration. When using pure $MnCl_2$ as substitute for $MgCl_2$ only 10% of the original activity could be detected.

3.8. Isotacticity

The results showed that the isotacticity stayed on a stable high level even at very high Mn doping concentrations. Only at concentrations above 60 mol% Mn there was a drastic drop in the isotacticity. When using pure $MnCl_2$ as support material the isotactic index went down to 70%. At lower doping concentration, below 60%, the isotactic index varied only slightly being between 97 and 98%.

3.9. The particle size distribution

The polypropylene material achieved by the Mn doped catalysts gave very little fines as long as the doping % was below 30%. Compared to the undoped catalyst the 3% Mn catalyst gives almost no polymer particles with a diameter smaller than 1 mm. The 30% doped catalyst gives an even better result. In opposition to this the 10% doped catalyst gave somewhat controversial results. A few additional tests would be of value here.

3.10. Bulk density

The bulk density results showed a decreasing tendency with increasing Mn doping content. The reason for this drop in bulk density originated from two sources. First, the increase of particle size and simultaneously the decrease in fines causes automatically the bulk density to decrease. Later on when the heavily doped catalyst was used the weak mechanical properties of this catalyst caused the polymer particles to collapse and thereby create a poor morphology with low bulk density.
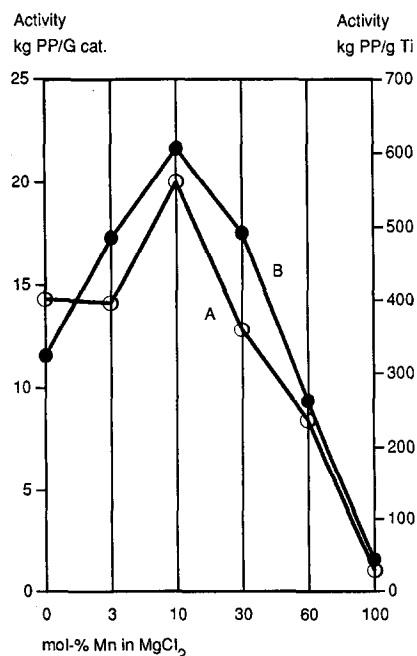

Fig. 4. The activity of the Mn doped Ziegler–Natta catalysts. Curve (A) as kg PP/g cat units and curve (B) as kg PP/g Ti units.

Table 7
The molecular weight distribution of the polymer batches produced with the Mn doped catalysts

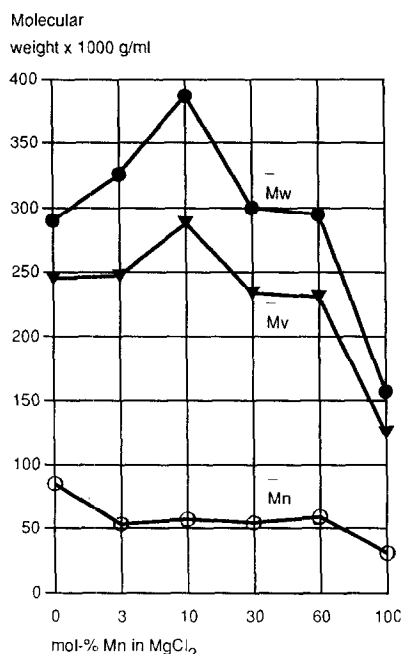| mol% Mn	M_n	M_w	M_v	D
0	85900	28600	242000	3.3
	83200	297000	248000	3.6
3	52900	328000	247000	6.2
	53700	324000	244000	6.0
10	57100	382000	285000	6.7
	56400	392000	288000	7.0
30	53600	298000	229000	5.6
	53600	306000	237000	5.7
60	59400	297000	233000	5.0
	58900	292000	228000	5.0
100	31200	154000	123000	4.9
	30600	161000	121000	5.3

Fig. 5. The molecular weight figures for the polymer batches as a function of the mol% Mn in the catalyst support material.

3.11. Melt index

The melt index results from the polymer batches were all around 10 except in the last polymer batch, that due to the low isotacticity had a high melt index. The results showed that $MnCl_2$ doping does not influence much on the hydrogen sensitivity of the catalyst.

3.12. Molecular weight distribution

The molecular weight distribution was of special interest in this investigation as the original idea was to create a differentiation of the active sites in the catalyst and thereby a differentiation of the polymer material produced. The produced analytical results are listed in Table 7.

As can be seen from Fig. 5 there is a clear broadening both upwards and downwards in the molecular weight for the material produced with a catalyst containing 10 mol % Mn. At higher doping concentrations there is a constant decrease in the molecular weight. The low molecular weights achieved with a pure $MnCl_2$ catalyst explains the low isotacticity and the high melt index of this material. Fig. 6 shows the comparing molecular distribution for the standard undoped material and the doped material produced with a 10% Mn doped catalyst.

3.13. The pore size distribution

The investigation showed also that the Mn doping of the support material caused a significant change in the pore size distribution. This result can best be seen from Fig. 7 that shows the pore size distribution curve for the material produced with a 30% doped catalyst. Here, a distinct change in the distribution curve can be detected. Many more pores are to be found at the region of 1 to 3 microns than in the two other samples.
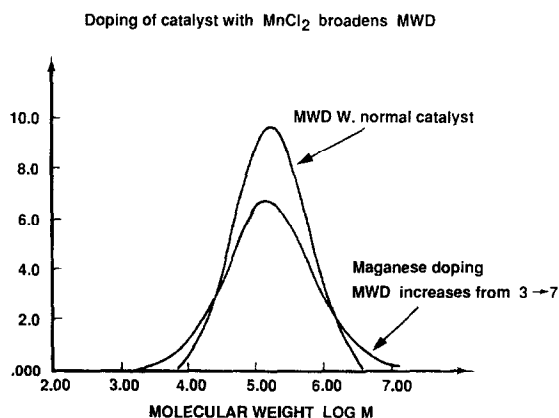

Fig. 6. Comparison of the MWD of PP produced with a normal catalyst and PP produced with a Mn doped catalyst.
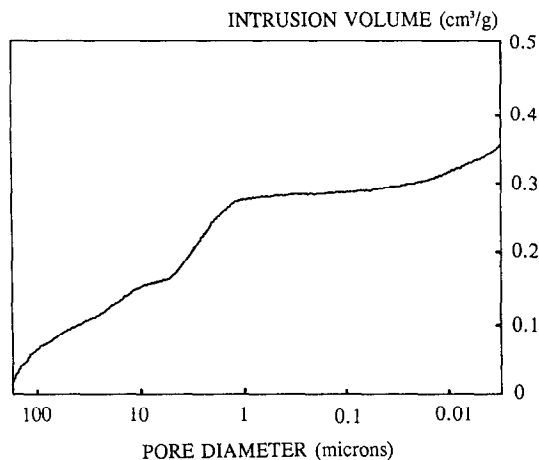
INTRUSION VOLUME (cm³/g)

Fig. 7. Pore size distribution of polypropene produced by a 30% Mn doped NC-1 catalyst.

3.14. Stoichiometry of the catalyst components

The results showed that the greatest influence on the activity of the catalyst could be achieved at a doping ratio of Mn/Mg of 0.1. This corresponds to the earlier results that defines the most optimal ratios of both Ti and donor to Mg as 0.1. The results showed also that the donor content is dropping to 50% of its original value when using the most active Mn/Mg mixing ratio. This gives indications that Mn is to be found close to the active sites in this most active mixture, either complexed to the active Mg atom or by acting as an active site itself. The crystal dimensions also points in this direction as a 6 nm wide crystal should be composed of about 100–120 molecules and having 12 corner positions. This configuration also indicates a possibility of a complexing ratio of 0.1.

4. Conclusions

In this investigation the effect of Mn doping in the MgCl₂ support material has been investigated. The following conclusions can be drawn from this investigation:

1. $MnCl_2$ can easily be melted into a hot $MgCl_2$ ethanol mixture. The $MnCl_2$ does not influence the shape of the catalyst X-ray pattern if present at concentrations below 30%.

2. Very good morphology is achieved when preparing the support material if the $MnCl_2$ concentration is below 30%. At higher doping concentrations poor morphology is the result.

3. Large catalyst particles where produced. The particles were of great mechanical strength, leading to the formation of large polymer particles with a very narrow PSD. No fines were produced. This advantage was achieved only if the $MnCl_2$ concentration was below 30%.

4. Optimum Mn doping concentration was 10 mol %. Using this doping concentration activity increased 25% (100% if kg PP/g Ti units are used) with no loss in isotacticity. At higher Mn concentrations activity decreased linearly.

5. The molecular weight distribution was effected. A broadening of the MWD was achieved. The greatest effect was achieved with a Mn concentration of 10 mol%. The polydispercity increased from the standard value of 3 to 7. At higher Mn concentrations the MWD decreased steadily. Low molecular weight polypropene can be produced by using pure $MnCl_2$ as support material.

6. The pore size distribution is effected by the Mn doping. A large portion of pores between 1 and 3 microns are produced. In standard polypropylene the largest fraction is to be found between 10 and 100 microns.

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