

Controllable Formation of MgCl_2 -based Spherical Catalyst Support Precursors *via* Composites of Liquid Inorganics and Polymers

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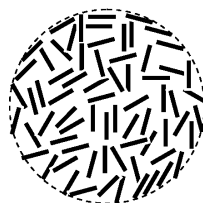
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Anhydrous MgCl_2 was reacted with 2 equiv. of ethanol to generate the $\text{MgCl}_2(\text{EtOH})_2$ adduct **1**. An appropriate amount of higher alcohol having a long carbon chain, such as 1-decanol, was anchored on the surface of a part of adduct **1** to give a mixture of MgCl_2 adducts having an internal surfactant. A multifunctional polymer/oligomer, *e. g.* poly(ethylene glycol)-200 (PEG-200), was introduced into this system yielding a composite of liquid inorganics and polymers (CLIP). Under the regulation of the internal surfactant and the multifunctional polymer, this composite was melted and dispersed in an inert hydrocarbon solvent under vigorous agitation at elevated temperatures followed by fast cooling to generate a MgCl_2 -based spherical catalyst support precursor. SEM pictures show that this support precursor has a narrow particle size distribution, and its surface structure is an intricate combination of smaller MgCl_2 -based crystallites.

Key words: Magnesium Dichloride, Alcohol Adducts, Surfactants, Composites, Supports

Introduction

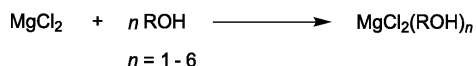
It is well known that in the presence of appropriate electron donors, the combination of Group IV or V transition metal halides with active magnesium dichloride-based supports, activated by an organoaluminum compound, can catalyze α -olefin polymerizations or copolymerizations to generate polymers with high activity and high stereo- and regioselectivity. The active magnesium dichloride can be dispersed on inorganic carriers such as silica or aluminum oxide having controlled shape. The components can simply be mixed with each other or spray-dried [1]. However, it is preferred to refrain from using such inorganic fillers and form support materials from active magnesium dichloride in the presence of a suitable electron donor thus having uniform morphological properties and increased catalytic activity [2]. According to the recently established “replication and particle growth mechanism”, polymer particles duplicate the morphology (shape and texture) of the catalyst particles during the process of polymerization [3–5]. Active catalysts having a uniform morphology will generate polymer particles with desirable bulk density, regular shape and narrow particle size distribution, which consequently leads to a high reactor throughput and good flowabil-



Scheme 1. Model of ideal highly active δ - MgCl_2 -based catalyst support.

ity of the polymer products. Although the exact growing model of polymer particles on catalytically active centers is still under disputation, it is assumed that the ideal catalyst is of spherical shape and composed of smaller primary crystallites (Scheme 1) [6]. These primary particle-containing spherulites are mechanically strong enough to withstand the loading of active species on their surface; at the same time they easily break during polymerization and generate aggregates of fragments that are loosely contacted with each other with polyolefins as a “cement”. Such behavior allows a fast transfer of monomer into the bulk of each catalyst particle and as a result, catalytic efficiency is greatly increased.

Recently, Gower *et al.* have introduced the concept of a polymer induced liquid precursor (PILP) trying to clarify the recrystallization of inorganic materials in the presence of polymers [7, 8], which is an impor-

Scheme 2. Formation of MgCl₂-alcohol adducts.

tant process to form nano-scaled crystallites of calcium phosphate in collagen fibrils of animal bones. It is believed that a bone's stiffness and toughness are the result of such a unique structure. In the light of PILP theory, it would be interesting and meaningful to regulate the formation of MgCl₂ crystallite-based Ziegler-Natta catalyst support precursors by using multifunctional polymers or oligomers.

According to previous arts, active MgCl₂-based supports can be prepared *via* the formation of alcohol adducts (Scheme 2), such as MgCl₂-ethanol adducts [9, 10]. These adducts were melted in an inert hydrocarbon solvent under vigorous agitation to give spherical droplets [11]. Such spherical droplets were normally stabilized with an additionally added surfactant (external surfactant) and were quickly solidified to give a support precursor by fast cooling [12]. It was also assumed that a magnetic or an electromagnetic field might affect the formation of the support precursor [13]. The subsequent experiential evaporation of alcohol inside the support precursor is supposed to generate a suitable inner structure and appropriate porosity for the desired use. This method of producing a catalyst support is widely accepted for industrial use; however, the addition of an additional external surfactant followed by the experiential evaporation of the alcohol inside the precursor is not effective to narrow the particle size distribution or to adjust the inner structure of the generated catalyst support particles. In this paper, a novel approach to MgCl₂-based spherical support precursors *via* composites of liquid inorganics and polymers (CLIP) is described.

Experimental Section

Materials and analytical methods

All reagents and solvents were purchased from Acros Organics with the exception of anhydrous MgCl₂ and paraffin from Merck KGaA. Anhydrous MgCl₂ was stored in a glove-box before use. Ethanol was distilled out from a magnesium (turnings)/iodine drying system and was stored over molecular sieve (4 Å). *n*-Heptane was dried using activated aluminum oxide (neutral) and stored over molecular sieve (4 Å). Other liquid reagents and solvents were taken directly from a solvent purification system (SPS) from MBraun. All the preparations were performed under the protection by argon. Particle samples were observed and images were recorded

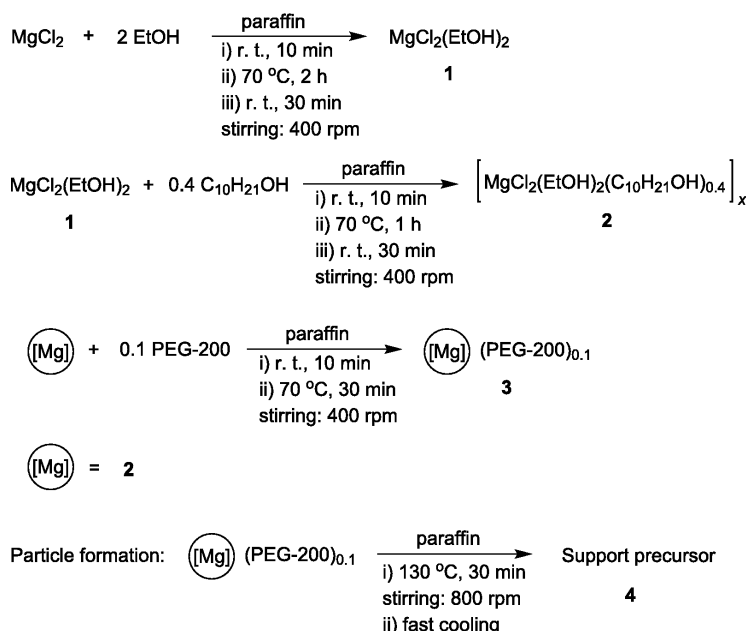
by using a Hitachi Tabletop Scanning Electron Microscope (TM-1000). The particle size distribution was determined as follows: By using IMAGEJ, SEM-images of the particles were preprocessed with a thresholding algorithm, and the area of each particle's projection was measured. By using OPENOFFICE.ORG CALC, the obtained 444 values were then converted to circle-equivalent diameters, and the distribution density $q_1(x)$ was calculated.

Preparation of support precursor 4

Anhydrous MgCl₂ (5.0 g, 52 mmol) was added into a steel autoclave equipped with a magnetically coupled blade stirrer, to which was charged paraffin (250 mL). The suspension was stirred at a speed of 400 rpm. Dry ethanol (4.9 g, 106 mmol) was added to the suspension dropwise at r. t. The mixture was stirred at r. t. for 10 min followed by heating to 70 °C for 2 h. Then the mixture was allowed to cool down to r. t. under mechanical agitation. 1-Decanol (3.3 g, 21 mmol) was added to the slurry of the adduct MgCl₂(EtOH)₂ (**1**) in paraffin, and the mixture was stirred at 70 °C for 1 h followed by cooling down to r. t. to give **2**. PEG-200 (1.1 g, 5.9 mmol) was added to the generated suspension of MgCl₂ adducts in paraffin at r. t., and the suspension was heated to 70 °C and was continuously stirred for 30 min to give **3**. Then the mixture was heated to 130 °C with a stirring speed of 800 rpm for another 30 min. The resulting emulsion of molten MgCl₂-alcohol adducts in paraffin was poured into a 2 L Schlenk flask containing *ca.* 1 L of pre-cooled *n*-heptane (−30 to −20 °C) which was under agitation at a speed of 400 rpm. The formed particles were allowed to settle down, and the upper turbid solution was decanted. The produced MgCl₂-based spherical particles were washed three times with *n*-pentane (total: 300 mL) followed by drying under vacuum. 6.8 g of support precursor was collected. PSD: $d_{\text{max}} = 58 \mu\text{m}$, $d_{50} = 58 \mu\text{m}$.

Preparation of support precursor 5

Adduct **1** was prepared as outlined in the preparation of support precursor **4** in a Schlenk tube with a magnetic stirring bar (5.2 mmol MgCl₂, 15 mL paraffin, 10.3 mmol ethanol). 1-Decanol (0.83 g, 5.2 mmol) was added to the slurry of adduct MgCl₂(EtOH)₂ (**1**) in paraffin, and the mixture was stirred at 70 °C for 1 h followed by heating to 130 °C with a stirring speed of 800 rpm for another 30 min. The resulting emulsion of molten MgCl₂-alcohol adducts in paraffin was quickly cooled to −78 °C, and the whole system was frozen as a result. The cold mixture was allowed to warm up to r. t. The product was allowed to settle, and the upper turbid solution was decanted. The produced MgCl₂-based chunks were washed five times with *n*-pentane (total: 50 mL) followed by drying under vacuum. 1.60 g (yield: 89 %) of support precursor was collected.

Scheme 3. Formation of support precursor **4** with CLIP with an internal surfactant.

Preparation of support precursor **7**

Adduct **1** was prepared as outlined in the preparation of support precursor **4** in a Schlenk tube with a magnetic stirring bar (5.2 mmol MgCl₂, 15 mL paraffin, 10.3 mmol ethanol). PEG-200 (0.34 g, 1.8 mmol) was added to the slurry of adduct MgCl₂(EtOH)₂ (**1**) in paraffin at r. t. The suspension was heated to 70 °C and was continuously stirred for 30 min to give **6**. Then the mixture was heated to 130 °C with a stirring speed of 800 rpm for another 45 min. The resulting emulsion of molten MgCl₂-alcohol adducts in paraffin was cooled quickly down to −78 °C, and the whole system was frozen as a result. The cold mixture was allowed to warm up to r. t. The product was allowed to settle, and the upper turbid solution was decanted. The produced MgCl₂-based chunks were washed five times with *n*-pentane (total: 50 mL) followed by drying under vacuum. 1.09 g (yield: 83 %) of support precursor was collected.

Preparation of support precursor **9**

Adduct **1** was prepared as outlined in the preparation of support precursor **4** in a Schlenk tube with a magnetic stirring bar (5.2 mmol MgCl₂, 15 mL paraffin, 10.3 mmol ethanol). 1-Decanol (0.25 g, 1.57 mmol) was added to the slurry of adduct MgCl₂(EtOH)₂ (**1**) in paraffin, and the mixture was stirred at 70 °C for 30 min followed by cooling to r. t. PEG-200 (0.22 g, 1.18 mmol) was added to the generated suspension of MgCl₂ adducts in paraffin at r. t. The suspension was heated to 70 °C and was continuously stirred for 30 min to give **8**. Then the mixture was heated to 125 °C with a stirring speed of 800 rpm for another 30 min. The re-

sulting emulsion of molten MgCl₂-alcohol adducts in paraffin was quickly cooled to 0 °C. The cold mixture was allowed to warm up to r. t. The product was allowed to settle, and the upper turbid solution was decanted. The produced MgCl₂-based particles were washed five times with *n*-pentane (total: 50 mL) followed by drying under vacuum. 0.90 g of support precursor was collected.

Results and Discussion

Formation of support precursor **4** via CLIP with an internal surfactant

A steel autoclave was chosen for the reactions. As opposed to glass containers, the alcohol and MgCl₂ adducts don't stick to the metal walls. Furthermore, its double mantle design and magnetically coupled stirrer offered effective temperature control and agitation force in a closed environment. Additionally, the bottom valve of the autoclave allowed a quick release of the reactants for their fast solidification in a precooled anhydrous hydrocarbon solvent. The autoclave was kept closed during the experiment. It was only opened at a top-mounted valve during the addition of further reagents protected by a counter current of argon.

Anhydrous MgCl₂ was suspended in paraffin in an autoclave under mechanical stirring, and 2 equiv. of ethanol was added (Scheme 3). The reaction mixture was stirred at r. t. until no more heat was evolved. In order to form the adduct MgCl₂(EtOH)₂ (**1**) stoichiomet-

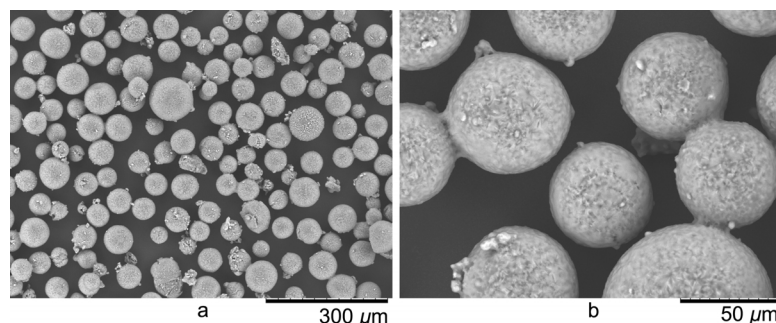
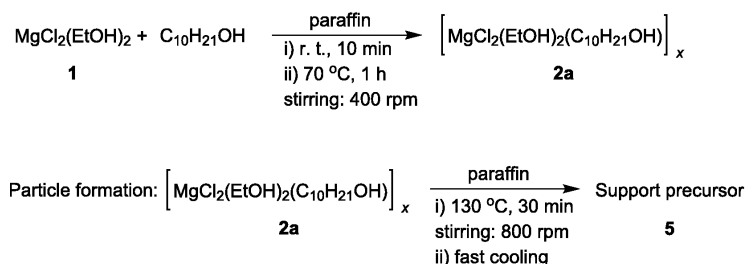


Fig. 1. SEM pictures of spherical support precursor **4**.



Scheme 4. Formation of support precursor **5** from 1-decanol.

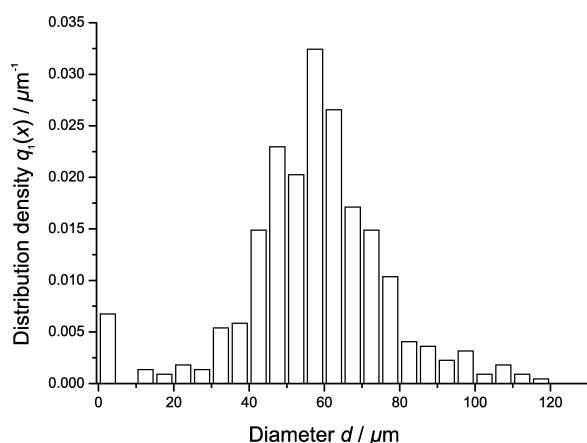


Fig. 2. Particle size distribution of support precursor **4**.

rically, agitation of the white suspension was continued at an elevated temperature followed again by stirring at r. t.

0.4 Equiv. of 1-decanol was introduced into the system at r. t., and stirring of the white suspension was continued. The agitated system was then heated to 70 °C followed by cooling to r. t. to generate a non-stoichiometric network of adducts **1** and MgCl₂-(EtOH)₂(C₁₀H₂₁OH) (**2**). In this system, adduct **2**, having a long carbon chain, served as an internal surfactant to assist spherical particle formation.

0.1 Equiv. of PEG-200 was added into the above mixture at r. t., which led to an aggregation of the

MgCl₂ particles inside. The produced mixture of MgCl₂ adducts (**1**, **2** and **3**) in paraffin was stirred at elevated temperature and was finally melted at 130 °C under vigorous mechanical agitation. The mechanical stirring dispersed the molten MgCl₂ adducts into droplets in paraffin, which were quickly poured into a large amount of precooled *n*-heptane in a Schlenk flask. Liquid droplets of MgCl₂ adducts were frozen to form spherical particles with $d_{\text{max}} = 58 \mu\text{m}$ and $d_{50} = 58 \mu\text{m}$ according to scanning electronic microscopy (SEM) measurements (Fig. 1) and a corresponding statistical particle-size-distribution analysis (Fig. 2). These spherical particles having small sub-particles inside show a complex surface structure, which suggests a high surface area and porosity after dealcoholation. According to the amount of starting material, a “yield” of 48 % can be determined. The weight loss can be attributed to the structural changes of the mixture at elevated temperatures at which ethanol can evaporate. This evaporation is accompanied by an increase of the melting point of the adduct mixture thus leading to a desirable faster solidification.

Formation of support precursor **5** from 1-decanol

In order to investigate the different functions of 1-decanol and PEG-200 in the above described process, the formation of MgCl₂-based support precursors was also performed with changed parameters. The SEM pictures are shown in Fig. 3a–d.

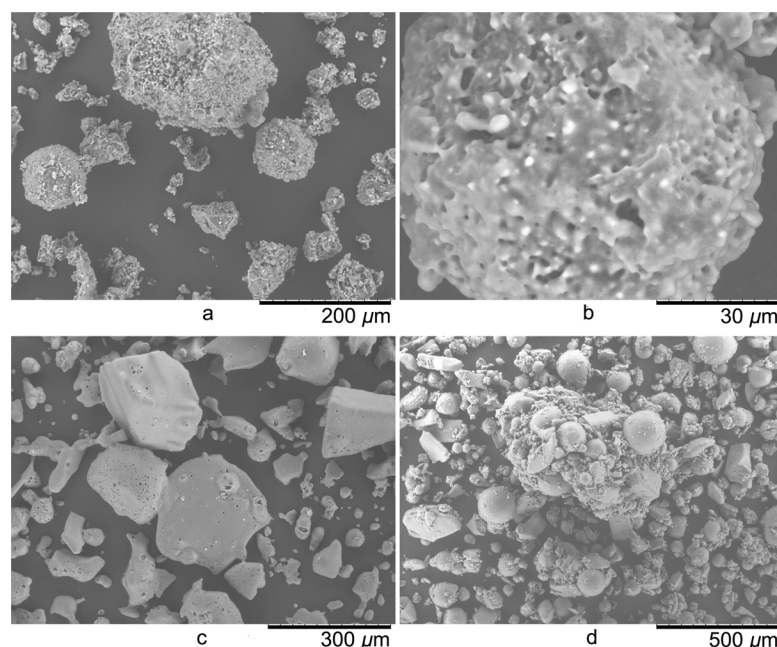
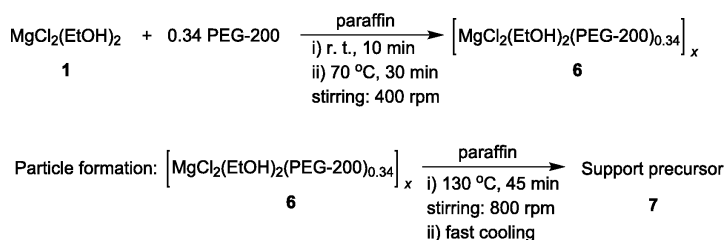


Fig. 3. SEM pictures of (a) support precursor **5** formed from 1-decanol; (b) magnified support precursor **5** formed from 1-decanol; (c) support precursor **7** formed from PEG-200; (d) support precursor **9** formed from 1-decanol/PEG-200 in another ratio.



Scheme 5. Formation of support precursor **7** from PEG-200.

Particles in Fig. 3a–b were produced by reacting the adduct $\text{MgCl}_2(\text{EtOH})_2$ (**1**) with 1 equiv. of 1-decanol in paraffin (Scheme 4). The Figures clearly show that a lot of chunks having irregular shape were formed. However, a close look suggests that these chunks are composed of small sub-particles in a size below several micrometers (Fig. 3b). These small particles aggregate without control and are sensitive to moisture in the air.

Formation of support precursor **7** from PEG-200

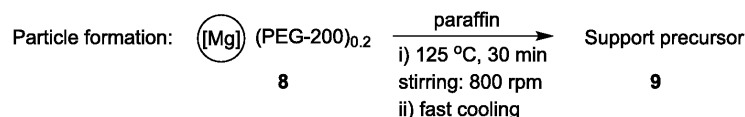
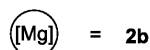
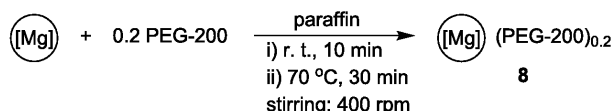
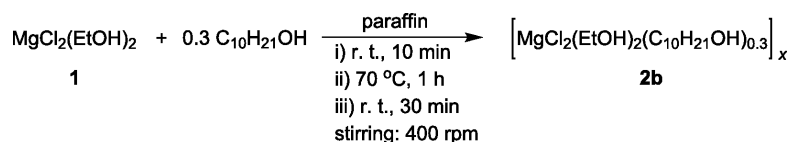
When the adduct $\text{MgCl}_2(\text{EtOH})_2$ (**1**) was reacted with 0.34 equiv. of PEG-200 in paraffin (Scheme 5), irregular chunks were produced almost exclusively (Fig. 3c). These chunks show a smooth surface structure in comparison with the chunks generated by using only 1-decanol and seem not to consist of small sub-particles. Such a phenomenon is consistent with the stronger coordinating ability of PEG-200 to MgCl_2

as opposed to that of 1-decanol due to the existence of multi electron-donors in the backbone of PEG-200.

Formation of support precursor **9** from 1-decanol / PEG-200 in another ratio

The results of stepwise reactions between the adduct $\text{MgCl}_2(\text{EtOH})_2$ (**1**) and 0.3 equiv. of 1-decanol and 0.2 equiv. of PEG-200 (Scheme 6) have shown that a mixture of spherical particles and irregular chunks are formed (Fig. 3d).

According to the SEM picture, some of these particles and chunks contain no obvious sub-particles, which is different from the result generated by the procedure in Scheme 3. This is probably due to the use of an excessive amount of PEG-200 in the former, which eliminates the chance of sub-particle formation. As outlined in the discussion of the formation of support precursor **4**, a “yield” (62%) can be calculated.



Scheme 6. Formation of support precursor **9** from 1-decanol/PEG-200 in another ratio.

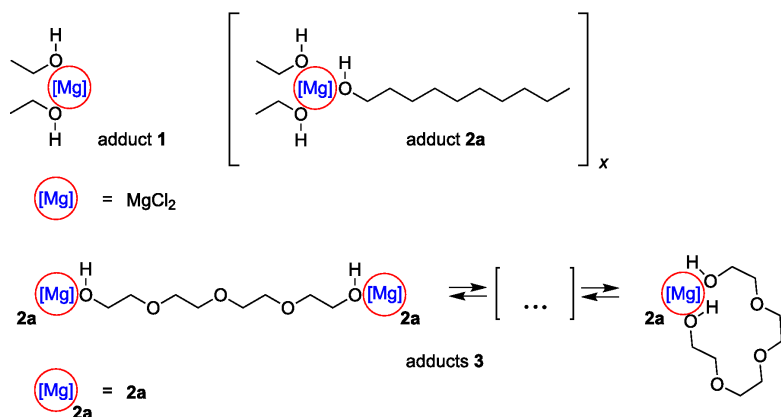


Fig. 4. Possible structures of adducts **1**, **2** and **3** formed in Scheme 3.

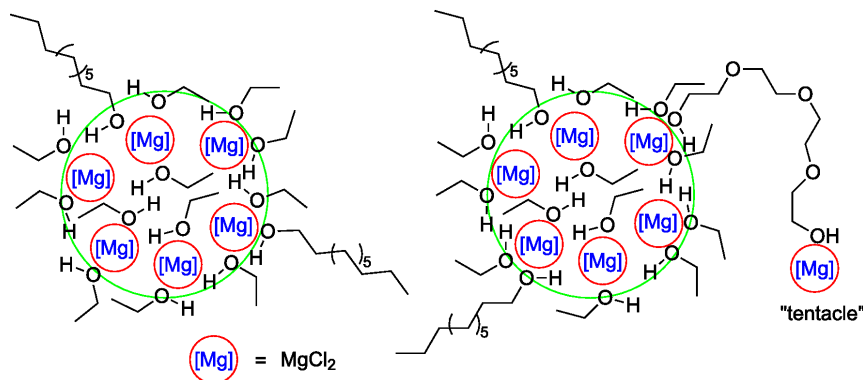


Fig. 5. Supposed structures of primary spherical composites.

Supposed mechanism of support precursor formation

Based on the above experiments, a mechanism is proposed for the spherical particle formation. In the inert solvent paraffin, anhydrous MgCl₂ reacted with ethanol and 1-decanol successively; as a result, a

non-stoichiometric network of adducts MgCl₂(EtOH)₂ (**1**) and MgCl₂(EtOH)₂(C₁₀H₂₁OH) (**2**) was produced (Fig. 4). A part of the adducts **1** and **2** further reacted with PEG-200 giving a mixture **3**, which contains a series of adducts in an equilibrium because of the complicated coordination behavior of PEG-200.

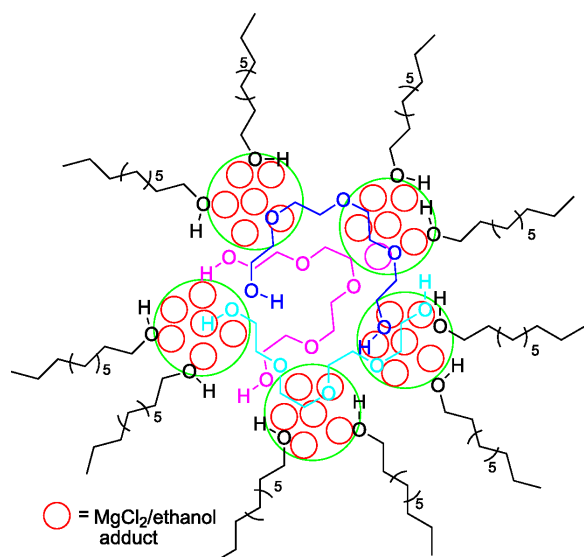


Fig. 6. Supposed structures of the final spherical support precursor.

During the increase of temperature under vigorous mechanical agitation, the mixture of **1**, **2** and **3** (or part of this mixture) was melted and dispersed, which led to the formation of primary spherical composites (Fig. 5). Such primary composites were stabilized in the hydrocarbon solvent paraffin by the long carbon chain anchored on adduct **2**. Inside these composites, there were mainly aggregates of the hydrophilic adduct **1** which prefers to stay away from the non-polar solvent paraffin.

The chain of PEG-200, having both hydrophilic oxygen atoms and hydrophobic ethylene moieties, can either penetrate through some composites or attach to the surface of these composites and behave as a “tentacle”. Such a “tentacle” has a strong ability to grasp other primary composites to form the final spherical composite (Fig. 6).

Upon rapid heat dissipation, the shape of these final composites was frozen, and MgCl_2 -based spherical catalyst support precursors were generated.

Conclusion

A novel and highly promising method to generate MgCl_2 -based spherical catalyst support precursors via a composite of liquid inorganics and polymers/oligomers is presented. A higher alcohol (1-decanol), having a long carbon chain, was anchored on the surface of MgCl_2 adduct particles which were formed by pre-treatment of MgCl_2 with ethanol to lower the manipulation temperature. During the temperature increase under strong agitation, this internal surfactant-containing mixture was melted, dispersed and stabilized as small spherical primary composites. Under the regulation of PEG-200 (like a “cement”) final spherical composites were formed as a catalyst support precursor with a narrow particle size distribution and a complex surface and inner structure. Two important properties of catalyst supports, particle size distribution and porosity, can be adjusted by selectively using different higher alcohols and multifunctional polymers/copolymers. However, the alcohols have to be removed prior to the application of such composites as a support for Ziegler-Natta polymerization catalysts: During the catalyst synthesis – upon impregnation with late transition metal halides such as TiCl_4 – the OH functionalities would compete for the desired coordination sites on the MgCl_2 surface and form non-catalytic moieties. Further investigations in this field including the generation of polymerization catalysts from CLIP-precursors are in progress.

Acknowledgement

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