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Ziegler–Natta catalysts supported on crystalline and amorphous $MgCl_2$/THF complexes

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ABSTRACT

Two $MgCl_2$/THF/$TiCl_4$ (THF = tetrahydrofuran) catalysts were prepared with $MgCl_2$/THF supports having an amorphous (Sup-A) or a molecular compound structure, $[Mg_3Cl_5(THF)_4Bu]_2$ (Bu = *n*-butyl) (Sup-B). Amorphous catalyst A had a normal supported Ziegler–Natta-type structure with low donor and titanium contents (the molar ratios, THF/Mg = 0.14 and Ti/Mg = 0.17), while catalyst B had a molecular type of composition with high donor and titanium contents (the molar ratios, THF/Mg = 0.84 and Ti/Mg = 0.80). Despite the different composition, Cat-A and Cat-B had some structural similarities as evidenced from the powder X-ray diffraction data and nuclear magnetic resonance and infrared spectroscopy results. Polymerization studies showed that these catalysts are highly active in copolymerization of ethylene and 1-butene. Although there were differences in the composition and the structure between the catalysts, they produced almost similar copolymers as indicated by the molecular weight, molecular weight distribution, comonomer content, melting point, and crystallinity of the copolymers.

1. Introduction

Heterogeneous Ziegler–Natta catalysts play a key role in the production of polyolefins [1]. Polypropylene and polyethylene that have numerous applications are examples of polymers that are most often produced with Ziegler–Natta catalysts. These catalysts are usually comprised of $MgCl_2$ support, Lewis bases, $TiCl_4$ active species, and cocatalyst aluminum alkyl [2–5]. One of the key factors in the catalyst preparation is the surface structure of the support. Use of $MgCl_2$ as a support for Ziegler–Natta catalysts was an important breakthrough in the sense of the catalytic activity and polymer properties [6,7]. Even though $MgCl_2$ is often considered merely as a support, its role in the formation of the active centers is crucial and therefore a great attention is paid to the preparation of a suitable $MgCl_2$ support for Ziegler–Natta catalyst [8,9].

Very often $MgCl_2$ is mechanically or chemically transformed into a structurally disordered form i.e. “activated” form or δ-form [10–15], but crystalline $MgCl_2$ can also be used as a support. An example of molecular compounds that are used as supports are $MgCl_2$–ethanol adducts, but other alcohols can also be used. It is to be noted that when contacting these $MgCl_2$–alcohol adducts with $TiCl_4$, alcohol is removed, and typically, the structure changes from a crystalline to an amorphous material possessing a high surface area [16–19]. Other typical molecular compounds that have been used as a support for Ziegler–Natta catalysts are $MgCl_2$/tetrahydrofuran (THF) complexes [20]. $MgCl_2$/THF/$TiCl_4$ catalysts produce polyethylene with a good activity and have a good hydrogen response [21–23]. For activity improvement, the active center distribution can be modified with additives such as $ZnCl_2$ and $SiCl_4$ added to the $MgCl_2$/THF/$TiCl_4$ catalytic system [24]. Also use of vanadium catalysts instead of titanium catalysts can improve the activity and comonomer response in ethylene/α-olefin copolymerization with $MgCl_2$/THF supported Ziegler–Natta catalysts [25,26].

In our previous study [27], the effect of THF on the morphology and the structure of synthesized $MgCl_2$ were studied. It was found that a transition from a fully crystalline to structurally disordered complexes can be controlled by adjusting the amount of THF in the autoclave synthesis of $MgCl_2$. The single crystals obtained had an open dicubane structure, $[Mg_3Cl_5(THF)_4Bu]_2$ (Bu = *n*-butyl), revealing information about THF binding. In this study, the molecular compound $[Mg_3Cl_5(THF)_4Bu]_2$ and an amorphous $MgCl_2$/THF complex are used as supports for preparation of Ti-based Ziegler–Natta catalysts in an autoclave. Compositions and structures of the two catalysts are compared on the basis of chemical analysis, powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), and

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spectroscopic characterization results. The prepared catalysts are found to have high catalytic activity in the copolymerization of ethylene and 1-butene.

2. Experimental

2.1. Materials

Magnesium (Acros Organics) was dried in an oven at 110 °C overnight before use. Iodine was from Merck and used as received. Octane, 1-chlorobutane, and THF were purchased from Sigma–Aldrich and dried with 3 Å molecular sieves before use. $TiCl_4$ (Sigma–Aldrich) was used as received. All support and catalyst synthesis and characterizations were performed under inert gas unless otherwise mentioned.

2.2. Synthesis of supports and catalysts

The support was synthesized as described previously in the literature [27]. Autoclave was packed with Mg (0.5 g, 0.021 mol), few small crystals of iodine, octane (20 mL), 1-chlorobutane (4.6 mL, 0.044 mol), and THF (0.005 or 0.041 mol). The autoclave was heated at 130 °C for 2 h with stirring. The powder was filtered, washed with octane, and transferred into an autoclave with octane (10 mL) and $TiCl_4$ (10 mL). The autoclave was heated at 110 °C for 2 h with stirring. The product was filtered, washed with octane, and dried in vacuum at room temperature.

2.3. Characterization of supports and catalysts

PXRD measurements were performed with a Bruker AXS D8 Advance instrument. For the PXRD measurements, samples were placed on a special steel-made sample holder and protected from contact with air by a Mylar film. The step size was 0.05° and time per step 8 s. SEM measurements were carried out with a Hitachi S-4800 microscope with a voltage of 3 kV in the measurements. The sample was quickly fixed on a tape and immediately moved to the loading chamber of SEM. Solid state ^{13}C cross polarization magic angle spinning (CP/MAS) nuclear magnetic resonance (NMR) spectra were recorded with a Bruker AMX-400 spectrometer with a spinning rate of 4500 Hz, relaxation delay of 4 s, contact time of 3 ms, and number of scans 10,000. Glycine was used as an external reference. Infrared (IR) spectra were measured with a Nicolet Impact 400D with the diffuse reflectance infrared Fourier transform (DRIFT) method. Nitrogen adsorption/desorption was measured at 77 K with an Autosorb iQ2 (Quantachrome instruments) analyzer. Brunauer–Emmett–Teller (BET) surface area was determined from a BET plot at $p/p_0 = 0.05–0.30$ and the total pore volume for pores with diameter less than 42 nm was determined at $p/p_0 = 0.95$.

2.4. Copolymerizations

All polymerizations were conducted in a 3 L stainless steel semi-batch reactor using 1.25 L of propane and triethyl aluminum (TEA) as the co-catalyst. The polymerization procedure was conducted as follows: 1.25 L of propane and the desired amount of 1-butene and hydrogen was added and the contents of the reactor was stirred and heated to the reaction temperature (85 °C). Ethylene was then introduced followed by the co-catalyst and the catalyst and ethylene was fed on demand to maintain the specific pressure for the specific length (1 h) of the polymerization reaction. The reactor was maintained and controlled at the desired reaction temperature throughout the polymerization. Upon completion, the ethylene flow was stopped and the reactor pressure slowly vented off. The reactor was opened and the polymer product was collected and dried in a fume hood overnight. Slurry polymerization conditions: C_2 mol% – 4.8, H_2/C_2 (mol/kmol) – 40, C_4/C_2 (mol/kmol) – 770, Al/Ti (mol/mol) – 15.

Table 1
Synthesized $MgCl_2$/THF and $MgCl_2$/THF/$TiCl_4$ samples and their composition.

Sample	Determined wt%			Molar ratio	
	Mg	THF	Ti	THF/Mg	Ti/Mg
Sup-A[a]	19.7	16.3	–	0.28	–
Sup-B[b]	12.3	44.2	–	1.21	–
Cat-A	17.8	7.6	6.0	0.14	0.17
Cat-B	8.1	20.1	13.0	0.84	0.80

[a] THF/Mg molar ratio in the synthesis of Sup-A was 0.25.
[b] THF/Mg molar ratio in the synthesis of Sup-B was 2.0.

2.5. Characterization of copolymers

Molar mass averages (M_w and M_n) and molar mass distributions (M_w/M_n) of the polymers were determined by gel permeation chromatography according to ISO 16014-4:2003 and ASTM D 6474-99 standards with a Waters GPCV2000 instrument. Two GMHXL-HT columns and one G7000HXL-HT TSK-gel column (Tosoh Bioscience) were used with stabilized 1,2,4-trichlorobenzene as a solvent at 140 °C (flow rate 1 mL/min). Universal calibration was performed with polystyrene standards.

Differential scanning calorimetry (DSC) measurements were performed with a Mettler Toledo DSC823^e instrument. During the measurement a nitrogen gas flow (50 mL/min) was used. The DSC program included three parts: first the sample was heated from 25 to 210 °C, secondly the sample was cooled back to 25 °C, and thirdly the sample was heated again to 210 °C from which data was analyzed with a STARe thermal analysis software. In all steps a heating rate of 10 °C/min was applied and the reported values are an average of three measurements. For the SEM measurements the polymer particles were fixed on a tape and sputtered with a thin layer of gold to reduce charging of the sample surface during the measurements.

3. Results and discussion

3.1. Composition of supports and catalysts

Two Ziegler–Natta catalysts were prepared by using two different types of $MgCl_2$/THF supports (Table 1). Support A (Sup-A) with THF/Mg molar ratio 0.28 has a disordered structure, typical of δ-$MgCl_2$. Support B (Sup-B) with THF/Mg molar ratio 1.21 is a molecular compound with an open dicubane structure, $[Mg_3Cl_5(THF)_4Bu]_2$ (Bu = *n*-butyl), shown in Fig. 1. More detailed information about the supports can be found in our earlier study [27].

Catalyst A (Cat-A) and catalyst B (Cat-B) were prepared by mixing Sup-A and Sup-B with an excess of $TiCl_4$ in an autoclave at 110 °C. According to Table 1, Cat-B has a Ti content over twice as high as that of Cat-A and has a Ti/Mg molar ratio of 0.80, exceptionally high for a Ziegler–Natta catalyst. By comparing the THF/Mg ratios of the supports and the catalysts in Table 1 it is clear that part of THF was removed from the supports when they were brought in contact with $TiCl_4$. The THF/Mg molar ratio 0.14 of Cat-A is only half of the THF/Mg ratio 0.28 of Sup-A. There is also a clear drop in the THF/Mg molar ratio from 1.21 for Sup-B to 0.84 of Cat-B. Due to the notable decrease in the THF content it is likely that the structure of Sup-B has not survived in the reaction with $TiCl_4$.