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Bottom-Up Synthesis of Multi-Grained Ziegler–Natta Catalyst Based on MgO/MgCl₂/TiCl₄ Core–Shell Catalyst

Tomohiro Ikeda, Toru Wada , Yusuke Bando, Patchanee Chammingkwan and Toshiaki Taniike *

Graduate School of Advanced Science and Technology, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi 923-1292, Ishikawa, Japan; s1820401@jaist.ac.jp (T.I.); toruwada@jaist.ac.jp (T.W.); s1540015@jaist.ac.jp (Y.B.); chamming@jaist.ac.jp (P.C.)

* Correspondence: taniike@jaist.ac.jp

Abstract: Morphology control plays a major role in the design of solid catalysts. Since the heterogeneous Ziegler–Natta catalyst (ZNC) is based on the in situ synthesis of MgCl₂ support in a top-down manner, the individual control of the exterior and the interior structure of the catalyst macro-particles is challenging. In this study, we successfully prepared a ZNC with a multi-grain interior structure by the spray-drying of MgO nanoparticles, inspired by the fact that the MgO/MgCl₂/TiCl₄ core–shell catalyst can maintain the morphology of the raw MgO nanoparticles. This catalyst is the first example of the bottom-up preparation of MgCl₂-supported ZNC. Here, we report its basic preparation method, characterization results, and performance in the homo-polymerization of ethylene and propylene, and copolymerization with 1-hexene.

Keywords: heterogeneous catalysts; Ziegler–Natta catalysts; polymerization; co-polymerization; ethylene; propylene; 1-hexene; spray-drying; nanoparticles

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1. Introduction

Morphology influences the performance of solid catalysts through the diffusion of reactants and heat. Particle morphology influences the performance of solid catalysts, as it dictates the mass transport and heat transfer phenomena during catalysis. This is often found in catalyzed gas-phase polymer production, where the gaseous monomer is converted to a solid polymer by the active sites distributed throughout a catalyst macroparticle. Thus, it is essential to obtain spherical catalyst macroparticles with sufficient strength to prevent the formation of fine particles during the reaction [1]. In fact, such a stringent requirement of particle morphology is unique to solid catalysts employed for polymer production at the industrial scale.

Heterogeneous Ziegler–Natta catalysts (ZNCs) are widely used in the synthesis of polyolefins (polyethylene (PE), polypropylene (PP), and relevant copolymers, etc.). In ZNCs, Ti species (mostly TiCl₄) adsorbed on MgCl₂ support form active species by contacting with an alkylaluminum reagent. The catalyst before being activated is called a pre-catalyst. The mainstream preparation method is based on a top-down approach of the chlorination of spherical Mg precursors (representatively, MgCl₂ alcohol adduct and Mg(OEt)₂), which results in effective pre-catalysts, from the viewpoint of performance and morphology control. Regardless of the types of raw materials, such a top-down method produces a pre-catalyst with spherical macroparticles of micro-meter size and qualitatively similar interior structures. There are various sizes of pores within a macroparticle, originating from the hierarchical aggregation of primary catalyst particles. These primary particles are made of TiCl₄ adsorbed on lateral surfaces of MgCl₂ nanocrystals with a lateral dimension of about 5–10 nm and a thickness of 1–2 nm [2]. This interior structure of a macroparticle, on the basis of the aggregation of primary particles, is referred to as the multi-grain structure. The multi-grain structure and its function have been studied both experimentally and theoretically [3–5]. It has been revealed that the size and distribution

of pores affect the diffusion of reagents, and thus the proportion of polymers grown on the outer surface of the catalyst particles and inner surfaces of the pores formed in the early stages of polymerization. In the subsequent stages of polymerization, the growing polymer inside the pores induces the fragmentation of the catalyst macroparticle by the hydraulic power, exposing fresh Ti species. Continuation of the polymer growth and the fragmentation processes cause the synthesized polymer particles to mimic the morphology of the catalyst macroparticle (so-called replica effect) [6–8]. Therefore, the multi-grain structure of catalyst particles nicely explains the fact that immediately after the start of the polymerization reaction, the catalyst activity is small, but gradually increases as polymerization proceeds, and, finally, remains high for a relatively long period of time (build-up-type kinetics). Such polymerization kinetics is feasible as the multi-grain structure helps to avoid undesirable phenomena, such as atomization, due to crushing of the catalyst/polymer particles by rapid reaction and deactivation, due to localized heating. On the other hand, a method to control the multi-grain structure has not been established yet. Even though a few model catalysts with primary particles made of fused silica or polystyrene were employed to investigate the role of the particle interior structure in diffusion and polymer particle growth, such catalysts hardly represent the industrially applied ZNCs. Therefore, to study the multi-grain structure of ZNCs, the bottom-up development of a catalyst with $\text{TiCl}_4/\text{MgCl}_2$ as the primary particle is interesting and important in its own right.

Previously, we have developed a $\text{TiCl}_4/\text{MgCl}_2/\text{MgO}$ core-shell catalyst by treating MgO nanoparticles with TiCl_4 . In this catalyst, only the surface of the MgO particles was converted into a $\text{MgCl}_2/\text{TiCl}_4$ catalyst overlayer, while the center remained as MgO . Because the catalyst overlayer is very thin (1–2 nm), all the Ti species of the catalyst remain exposed from the beginning during the polymerization, and no new active sites are formed, due to fragmentation. In heterogeneous ZN catalysis, due to the transient nature of the catalyst during polymerization, it is difficult to relate the catalytic activity to even the surface area, which is a most basic structural characteristic. Using the $\text{TiCl}_4/\text{MgCl}_2/\text{MgO}$ core-shell catalyst, we demonstrated, for the first time, that the activity of a ZNC is proportional to the BET-specific surface area of its pre-catalyst [9]. The combined advantages of a relatively simple preparation protocol and low Cl content carried over to the final product inspired us to apply the core-shell catalyst to the production of ultra-high-molecular-weight polyethylene (UHMWPE) [10]. Furthermore, by treating the raw MgO nanoparticles with a surfactant (polyoxyethylene alkylamine, PA), the catalyst with a nanometer-sized diameter could be fully dispersed in heptane. The UHMWPE powder synthesized in this way had an extremely small particle size and a lesser degree of entanglement, thus being significantly advantageous for compression molding applications [11,12].

Here, we propose a bottom-up synthesis protocol of a multi-grain catalyst, on the basis of this core-shell catalyst. The spray-drying of MgO nanoparticles gives spherical secondary agglomerated macroparticles, and the subsequent TiCl_4 treating provides a secondary agglomerated catalyst with the core-shell catalyst as primary particles. In this method, the morphology of the primary catalyst particles and the secondary agglomerated macroparticles can be individually modified by the morphology of the raw MgO nanoparticles and the spray-drying conditions, respectively. Therefore, it has the potential to enable us to systematically study the relationship between the multi-grain structure and its catalytic function, which has not been realized so far. In this paper, we report the basic preparation method of the bottom-up multi-grain catalyst, the results of its characterization, and performance evaluation in the homo-polymerization of ethylene, propylene, and their copolymerization with 1-hexene.

2. Results and Discussion

In order to realize catalyst macroparticles with the $\text{MgO}/\text{MgCl}_2/\text{TiCl}_4$ core-shell catalyst as primary particles, spray-drying of MgO nanoparticles ($\text{MgO}50$) was performed, using water as the dispersant. The summary of the screening of the spray-drying conditions is reported in Table S1. Feed rate, atomizing air pressure, feeding slurry concentration,

and blowing rate of hot air to the main chamber were screened within the framework of conditions available for the instrument (see Section 3.2 in the Materials and Methods section for the meaning of the parameters). No noticeable effect of spray-drying conditions on the MgO particle properties was observed, except that the particle morphology and size distribution deteriorated upon lowering the feeding slurry concentration. Thus, considering the results of Table S1, the recommended parameters by the manufacturer were chosen as a standard condition set. The spray-dried particle sample obtained with the standard condition set (S-MgO(H₂O)) exhibited a narrow particle size distribution, with its peak top positioned at around 4 μm (Figure 1A), and the particles appeared in a spherical shape (Figure 1C). On the other hand, in the SEM image with a higher magnification (Figure 1C'), it was found that S-MgO(H₂O) was an aggregate of particles with a plate-like texture that was clearly different in size and morphology from the raw MgO nanoparticles (Figure 1B).

Figure 1. Characterization of S-MgO(H₂O) particles. (A) Particle size distribution, (B) TEM image of the raw MgO nanoparticles (MgO50), (C) SEM image, and (C') its high magnification.

In order to identify the origin of the plate-like texture, the feeding slurry with water as the dispersant before being spray-dried was analyzed. Figure 2A,A' show the SEM images of the dried slurry (MgO50(H₂O)). A large number of plate-like particles, with a lateral dimension of less than 1 μm , was observed, confirming that the plate-like morphology appeared even before spray-drying. The XRD patterns of the raw materials MgO50 and MgO50(H₂O) are shown in Figure 2B. As a matter of course, MgO50 only exhibited diffraction peaks characteristic of MgO, but in MgO50(H₂O), the MgO peaks disappeared, and the peaks that can be attributed to Mg(OH)₂ appeared instead. It is plausible that the hydroxyl radicals generated by ultrasonication reacted with MgO to produce Mg(OH)₂. To avoid this undesirable phenomenon, methanol was used as a dispersant, instead of water, to prepare a feeding slurry (MgO50(MeOH)). The dried feeding slurry showed no plate-like particles in the SEM observation, and no diffraction peak derived from Mg(OH)₂ was observed by XRD (Figure 2B). Due to the difference in the physical properties between the dispersants, it became necessary to screen the spray-drying conditions for methanol as the dispersant (Table S2). Condition 6 in Table S2 was chosen as it resulted in spherical

particles (Figure 2C,C') with a narrower size distribution compared to other investigated conditions. Thus, the obtained sample was named S-MgO. As shown in the XRD pattern of Figure 2B, no Mg(OH)₂-derived peaks were observed in S-MgO. Thus, spherical-shaped secondary agglomerated MgO macroparticles, free from Mg(OH)₂ contamination, could be obtained by using methanol as the dispersant.

Figure 2. Characterization of the MgO feeding slurries and the spray-dried particles. (A) SEM image of dried feeding slurry of MgO/water (MgO50(H₂O)) and (A') its high-magnification SEM image; (B) XRD patterns; (C) SEM image of the spray-dried MgO particles of which dispersion media is methanol (S-MgO) and (C') its high-magnification SEM image.

Three catalyst samples were prepared by the TiCl₄ treatment of raw MgO50 nanoparticles, MgO50 nanoparticles dispersed by the PA surfactant treatment (PA-MgO50), and S-MgO spray-dried spherical macroparticles. These catalysts were named Cat50, PA-Cat50, and S-Cat, respectively. The results of the particle size distribution analysis in *n*-heptane, before and after the TiCl₄ treatment, are shown in Figure 3 and Table 1. MgO50 showed a broad particle size distribution centered at ca. 10 µm, with an RSF value of 1.12. After the TiCl₄ treatment of MgO50, another peak centered around 100 µm appeared, and the RSF value of the resultant catalyst (Cat50) significantly increased to 8.25. This is because the particles that were not well dispersed at the raw material stage probably fused together when its surface converted to a MgCl₂/TiCl₄ catalyst overlayer by TiCl₄ treatment, which further inhibited dispersion. On the other hand, MgO50 treated with a surfactant (PA-MgO50) showed a much narrower particle size distribution (RSF = 0.49), and the average particle size (D_{50} = 0.07 µm) is fairly close to the specification value of 50 nm of MgO50. The surfactant likely diminished the electrostatic interaction among the MgO nanoparticles, thereby enabling high dispersion of the particles in *n*-heptane [11]. Furthermore, the TiCl₄ treatment of PA-MgO50 hardly changed the particle size and distribution for PA-Cat50 (D_{50} = 0.07 µm and RSF = 0.44), assuring that the original dispersion of PA-MgO50 particles in *n*-heptane prevailed after catalyst preparation. In contrast to the primary MgO particles, the secondary agglomerated macroparticles (S-MgO) showed a sharp and narrow particle size distribution without using a surfactant, exemplified by a smaller RSF value of 0.36. Also, both the D_{50} and RSF remained nearly unaffected, even after the TiCl₄ treatment (change in D_{50} = 4.84 to 4.98 µm, and change in RSF = 0.36 to 0.31, respectively). This surfactant-free dispersion was probably due to the decrease in the apparent surface area by aggregation, making the surface forces, such as the electrostatic interaction, less significant. Table 1 also contains the Ti loading of each catalyst sample. The relatively low Ti loading of Cat50 compared to industrial ZNCs (1–3 wt.%) can be attributed to the fact that the size of the primary particles (50 nm) is larger than that of the industrial catalysts (2–10 nm). S-Cat

had a comparable Ti loading to that of Cat50, which supports the fact that the secondary agglomerated macroparticles were successfully obtained while maintaining the properties of the primary particles. On the other hand, the relatively high Ti loading of PA-Cat50 (0.76 wt.%) is due to the coordination of additional TiCl_4 molecules with the ether group of the PA surfactant, as confirmed earlier by FT-IR investigation [11].

Figure 3. Particle size distribution of the three supports before and after TiCl_4 treatment, measured by light scattering experiment using *n*-heptane as the dispersant.

Table 1. Summary of the particle size analysis of the support and catalyst samples.

Sample Name	D_{10} (μm)	D_{50} (μm)	D_{90} (μm)	RSF	BET Surface Area ($\text{m}^2 \text{g}^{-1}$)	Ti Cont. (wt.%)
MgO50	4.48	7.58	13.0	1.12	34.3	
PA-MgO50	0.05	0.07	0.09	0.49		
S-MgO	4.04	4.84	5.77	0.36	24.2	
Cat50	5.02	11.3	98.3	8.25	33.5	0.47
PA-Cat50	0.06	0.07	0.09	0.44	32.6	0.76
S-Cat	4.25	4.98	5.80	0.31	26.6	0.30

Figure 4A shows the N_2 adsorption/desorption isotherm of each support and catalyst sample. MgO50 exhibited almost no slope in the low-pressure region ($p/p_0 > 0.01$) of the adsorption isotherm, followed by a gradual increase in N_2 adsorption up to around $p/p_0 = 0.8$, and a sharp increase up to $p/p_0 = 1$. The absence of adsorption in the low-pressure region and no hysteresis together suggest that micropores ($\varphi < 2 \text{ nm}$) and mesopores ($2 < \varphi < 50 \text{ nm}$) were almost nonexistent in MgO50. The sharp rise in N_2 adsorption in the high-pressure region indicates the presence of macropores originated from the interparticle voids of the aggregated MgO nanoparticles. The BET-specific surface area of MgO50 was $34.3 \text{ m}^2 \text{g}^{-1}$ (Table 1), close to the theoretical surface area ($32.9 \text{ m}^2 \text{g}^{-1}$) determined by assuming the MgO50 particle as a sphere with a diameter of 50 nm and a specific gravity of 3.65 g mL^{-1} . The isotherms of S-MgO were almost overlapped with those of MgO50, and the BET-specific surface area was comparable ($24.2 \text{ m}^2 \text{g}^{-1}$), suggesting that the interior structures of S-MgO correspond to the aggregation of MgO50 nanoparticles. The isotherms of the catalyst samples (Cat50, PA-Cat50, and S-Cat in Figure 4B) were almost identical to each other and their respective supports. Moreover, their BET-specific surface area was also similar to that of the supports, indicating that the morphology of the primary particles was not significantly affected by the TiCl_4 treatment.

Figure 4. N_2 adsorption/desorption isotherms of (A) support and (B) catalyst samples.

The catalytic performance of S-Cat was first evaluated in the homo-polymerization of both ethylene and propylene. To examine the effect of the multi-grain interior structure on the polymerization kinetics, the fully dispersed catalyst PA-Cat50 was used as a reference. The polymerization kinetic curves were drawn using the activity at a polymerization time of 1–60 min (Figure 5 and Table 2). The activity of PA-Cat50 was significantly lower than that of S-Cat (for ethylene, 6–7 times; for propylene, 16–30 times), plausibly due to the deactivation of a fraction of $TiCl_4$ molecules by complexation with the PA surfactant, as described above [11]. On the other hand, they showed similar kinetic curves, i.e., the maximum activity was observed immediately after the polymerization started (1 min), and the activity reduced to half of its maximum value in about 30 min, and remained almost constant until the polymerization was stopped after 60 min. This kind of polymerization behavior is known as decay-type kinetics. Typical ZNCs, in which the exposure of buried Ti species occurs due to the fragmentation of catalyst particles during polymerization, show a build-up-type kinetic curve, i.e., the activity increases with time in the beginning, and remains stable for a prolonged duration. Thus the decay-type kinetics clearly indicates that the exposure of buried Ti species does not occur in the polymerization with both PA-Cat50 and S-Cat, and all Ti species on the catalysts were exposed from the beginning of polymerization. In addition, Figure 5 also suggests that macropores based on the aggregation of primary particles with the diameter of about 50 nm do not affect the diffusion of monomers, and thus do not affect the polymerization kinetics. These results, in turn, strongly support the fact that the presence of micropores and mesopores would be important to control polymerization kinetics.

Figure 5. Polymerization kinetics of (A) ethylene and (B) propylene homo-polymerization with S-Cat and PA-Cat50.

Table 2. Summary of ethylene and propylene polymerization results.

	Polymerization Time (min)								
	1	2	5	10	20	30	40	50	60
	Ethylene polymerization activity (g-PE g-cat ⁻¹ h ⁻¹)								
S-Cat	2809	2249	2139	1599		1539			1051
PA-Cat50	404	352	362	254	237	209			168
	Propylene polymerization activity (g-PP g-cat ⁻¹ h ⁻¹)								
S-Cat	1176	654	237		194	146	129	130	122
PA-Cat50	39	23	15	10	9	5			

The SEM images of the obtained polymer particles are shown in Figure 6. Since the fragmentation of catalyst particles on a typical ZNC occurs within a few seconds to a minute, here, we compare the polymer particles formed at the polymerization time of 1 min (early stage of the polymerization) and 30 min (when the polymer particle is expected to be almost fully grown). Each sample is expressed as xx-yyzz (xx: catalyst name, yy: polymer name, zz: polymerization time in min). It is found that PA-Cat50-PE1 (Figure 6C,C') is completely formless. Extending the polymerization time gave no significant difference in the morphology of the polymer particles made by PA-Cat50 (PA-Cat50-PE30, Figure 6D,D'). This is probably due to the fact that the formation of the polymer diluted the PA surfactant, and, as a result, the catalyst particles could no longer maintain the monodispersity. A similar morphology is observed for the PP particles made by PA-Cat50 (i.e., PA-Cat50-PP1,30: Figure 6G,G',H,H'). On the other hand, the polymer particles synthesized by S-Cat (i.e., S-Cat-PE1,30, S-Cat-PP1,30: Figure 6A,A',B,B',E,E',F,F') mimicked the spherical morphology of the catalyst macroparticles plausibly, due to occurrence of the fragmentation process. In order to confirm the dissociation of MgO nanoparticles during polymerization, the cross-section of polymer particles formed at 1 min polymerization time was observed by SEM-EDX (Figure S1). In both S-Cat-PE1 and S-Cat-PP1, the Mg, Cl, O, Al, and Ti elements were almost uniformly dispersed on the surface of the cross-section, indicating that the MgO/MgCl₂/TiCl₄ core-shell catalyst particles were dissociated from each other at the polymerization time of 1 min. On the other hand, fibril morphology was observed on the surface of the polymer particles produced by S-Cat (Figure 6A',B',F'). This fibrous morphology has hardly been reported for ZN catalysts, but it is probably formed by hydraulic extrusion of the polymer generated inside the pores. The same fibril morphology was observed in PE produced with a MgO/MgCl₂/TiCl₄ core-shell catalyst, without spray-drying [10]. The absence of PE fibrils in PA-Cat50 suggests that the aggregation of primary particles in S-Cat is somehow related to the fibril structure, but the detailed mechanism is still unclear.

The copolymerization with 1-hexene was performed for both ethylene and propylene. The results for S-Cat and PA-Cat50 are summarized in Tables 3 and 4, respectively. The ethylene polymerization performance of Cat50 has already been reported in the previous paper [10]. Since the polymerization is carried out using *n*-heptane as a solvent, low-crystalline components dissolved in the solvent. After the separation of polymer particles, the remaining filtrate was casted into an excess amount of acetone to solidify and collect the low-crystalline component, and the activity was calculated using the sum of the insoluble and soluble polymers. It has long been known that the addition of a small amount of comonomer significantly increases the activity compared to homo-polymerization. This phenomenon is often referred to as the comonomer effect. The mechanism is still under discussion, and various reports have been made, even in recent years. The possible origins proposed so far are (1) a reduction in the barrier effect of the generated polymer [13,14]; (2) activation of dormant sites [15,16]; and (3) enhancement of catalyst fragmentation, to expose Ti species that is not used for homo-polymerization [17–19]. The activity enhancement by comonomer is typically 2–10 times in normal ZNC [17,20].

Figure 6. SEM images of polymer particles obtained with S-Cat and PA-Cat50. The sample name corresponds to the catalyst name and polymerization conditions as xx-yyzz (xx: catalyst name, yy: polymer name, zz: polymerization time in min). PE obtained with S-Cat for (A) 1 min and (B) 30 min. PE obtained with PA-Cat50 for (C) 1 min and (D) 30 min. PP obtained with S-Cat for (E) 1 min and (F) 30 min. PE obtained with PA-Cat50 for (G) 1 min and (H) 30 min. (A'–H') high-magnification images of (A–H).

Table 3. 1-Hexene copolymerization with ethylene.

Catalyst	1-Hexene (mol L ⁻¹)	Polymer Yield (g-pol g-cat ⁻¹)		Activity (g-pol g-cat ⁻¹ h ⁻¹)	Activity (kg-pol mmol-Ti ⁻¹ h ⁻¹)	Comonomer Effect ¹	Hexene Content (mol%) ²	
		Insoluble	Soluble				Insoluble	Soluble
S-Cat	0	803	trace	1607	25		n.a.	n.a.
	0.4	1421	trace	2842	45	1.8	0.01	
	0.8	1618	11.6	3259	52	2.0	0.02	10.0
	1.2	1513	44.1	3115	50	1.9	0.03	
	2.4	1247	384	3262	52	2.0	0.07	15.5
PA-Cat50	0	112	trace	223	3.6		n.a.	n.a.
	0.4	92	trace	184	2.9	0.8	0.01	
	0.8	88	trace	177	2.8	0.8	0.02	
	1.2	103	trace	205	3.3	0.9	0.02	
	2.4	92	trace	183	2.9	0.8	0.07	

¹ Calculated by activity of copolymerization with 1-hexene/activity of homo-polymerization. ² n.a.: not applicable, blanks: not determined, n.d.: not detected.

Table 4. 1-Hexene copolymerization with propylene.

Catalyst	1-Hexene (mol L ⁻¹)	Polymer Yield (g-pol g-cat ⁻¹)		Activity (g-pol g-cat ⁻¹ h ⁻¹)	Activity (kg-pol mol-Ti ⁻¹ h ⁻¹)	Comonomer Effect ¹	Hexene Content (mol%) ²		<i>mmmm</i> of PP Unit (mol%) ²	
		Insoluble	Soluble				Insoluble	Soluble	Insoluble	Soluble
S-Cat	0	38.8	8	94	1496		n.a.	n.a.	79.8	
	0.4	36.7	46	164	2624	1.8	2.7	5.1	84.0	34.7
	0.8	34.1	52	173	2760	1.8				
	1.2	27.5	99	254	4051	2.7				
	2.4	14.8	103	236	3762	2.5	8.1	26.9	84.2	46.2
PA-Cat50	0	1.72	trace	3.4	42		n.a.	n.a.	84.6	
	0.4	2.45	trace	4.9	60	1.4	n.d.		86.8	
	0.8	2.08	trace	4.2	51	1.2				
	1.2	1.30	trace	2.6	32	0.8				
	2.4	1.14	trace	2.3	28	0.7	n.d.		87.7	

¹ Calculated by activity of copolymerization with 1-hexene/activity of homo-polymerization. ² n.a.: not applicable, blanks: not determined, n.d.: not detected.

As shown in Tables 3 and 4, the activity was increased by the presence of 1-hexene in both the ethylene and propylene polymerization using S-Cat. In the case of ethylene, the activity increased about two times, regardless of the amount of 1-hexene, and in copolymerization with propylene, the activity increased about 2.5 to 3 times with increasing the amount of 1-hexene. The content of 1-hexene in the copolymer samples also increased with the increase in 1-hexene in the reaction system. In particular, the 1-hexene content of the heptane-soluble component polymer changed significantly, suggesting that the insertion of 1-hexene into the polymer chain reduced the polymer crystallinity. It is interesting that such a sufficient comonomer effect was observed for S-Cat, even though its catalyst overlayer was fully opened from the beginning, in terms of fragmentation. This suggests that diffusion inhibition by the polymer film (barrier effect) also works at the level of the primary catalyst particles. On the other hand, when PA-Cat50 was used, no comonomer effect was observed for both ethylene and propylene. The 1-hexene content in the copolymer increased slightly with the amount of 1-hexene introduced. In propylene/1-hexene copolymer samples, the incorporation of 1-hexene was not detected. It is considered that 1-hexene was hardly inserted into the polymer, due to the presence of the surfactant, and thus the comonomer effect did not appear.

The content of the *mmmm* sequence of PP, obtained by S-Cat, was 79.8 mol%, which is higher than that of PP obtained by internal/external donor-free MgCl₂-supported ZNC [9]. The removal of the soluble component, and the use of TIBA as a co-catalyst probably contributed to it. The reason why 1-hexene improved the stereoregularity of the insoluble component was thought to be because the crystallinity of the slightly lower stereoregular PP in the insoluble component was decreased by the introduction of 1-hexene and removed as a soluble component. The stereoregularity of the soluble component seems to increase with increasing the amount of 1-hexene, but this is probably because 1-hexene is introduced into the originally highly stereoregular PP, thus increasing the ratio of the soluble component. The stereoregularity of the whole polymer is estimated from the yields of insoluble and soluble components ((Yield_{insol} × *mmmm*_{insol} + Yield_{sol} × *mmmm*_{sol})/(Yield_{insol} + Yield_{sol})): 56.6 mol% for 0.4 mol L⁻¹ and 51.0 mol% for 2.4 mol L⁻¹, which seems consistent with the

trend of the comonomer effect. The fact that the stereoregularity of the PP obtained with PA-Cat50 is slightly higher than that of S-Cat can be attributed to the fact that the surfactant on the surface affects the bulkiness of the vicinity of the active site. The stereoregularity was almost unchanged by introducing 1-hexene, which is consistent with the fact that 1-hexene was hardly incorporated.

3. Materials and Methods

3.1. Materials

MgO nanoparticles with a mean particle size of 50 nm (MgO50), methanol, and titanium tetrachloride (TiCl_4) were purchased from FUJIFILM Wako Pure Chemical Co., Ltd. and used as received. *n*-Heptane (Wako Pure Chemical Co., Ltd., Osaka, Japan) was used after dehydration by passing through a column filled with molecular sieve 4A, followed by N_2 bubbling for 2 h. Ethylene of polymerization grade (Sumitomo Seika Chemicals Co., Ltd., Osaka, Japan) and propylene of polymerization grade (Japan Polypropylene Co., Tokyo, Japan) were used as received. Further, 1-Hexene (purity > 97%, Sigma-Aldrich Co. LLC, St. Louis, MO, USA) was used after dehydration by N_2 bubbling for 2 h in the presence of molecular sieve 4A. Triisobutylaluminum (TIBA) donated by Tosoh Finechem Corp. was used after dilution in heptane (1 mol L^{-1}).

3.2. Spray-Drying of MgO Nanoparticles

A schematic diagram of the spray-drying apparatus is shown in Figure 7 (Tokyo Rikakikai, SD-1010). Pristine MgO nanoparticles (MgO50) were dispersed in water or methanol by means of ultrasonication for 6 h to prepare a feeding slurry. The feeding slurry was introduced into the atomizer by a peristaltic pump and sprayed into the main chamber by compressed air. The sprayed droplets were dried by hot air in the main chamber where extremely large dried particles fell into the separation container, and the rest were carried over to the cyclone. Particles of a certain size were collected as a spray-dried product (denoted as S-MgO50) by centrifugal force, and fine particles were flown out to the exhaust line. The parameters for spray-drying are feeding slurry concentration, feeding rate, inlet temperature, atomization air pressure, and blowing rate.

Figure 7. Schematic diagram of the spray-drying apparatus.

3.3. Catalyst Synthesis

Then, 0.5 g of S-MgO was heated at 130 °C under N₂ flow for 6 h to remove physisorbed water before treating with 30 mL of TiCl₄ at the reflux temperature for 2 h. The obtained product (denoted as S-Cat50) was repetitively washed with heptane and stored as a slurry in heptane under N₂. For the sake of comparison, two reference samples (Cat50 and PA-Cat50) were prepared from non-spray-dried MgO50. For Cat50, the same procedure explained above was exploited except the fact that pristine MgO50 was used instead of S-MgO50. In the case of PA-Cat50, organic modification of MgO50 was performed using polyoxyethylene alkylamine (PA) to assist full dispersion of MgO nanoparticles in heptane prior to chlorination in heptane. The detailed procedure was reported in our previous paper [11].

3.4. Polymerization Test

Ethylene and propylene homo-polymerization were performed in a 1 L stainless steel autoclave equipped with a mechanical stirrer rotating at 500 rpm. After sufficient N₂ replacement, 300 mL of heptane as a solvent was introduced to the reactor and then saturated with 0.5 MPa of ethylene or propylene at 50 °C for 30 min. Following the addition of 2.0 mmol of TIBA as a co-catalyst, ca. Then, 30 mg of a catalyst was introduced to start polymerization. The polymerization was performed at 50 °C for pre-defined time from 1 min to 60 min at the constant pressure of 0.5 MPa.

Copolymerization of ethylene or propylene with 1-hexene was also performed using the same procedure, except a specified amount of 1-hexene was introduced just after the addition of heptane. The concentration of 1-hexene was set as 0.4, 0.8, 1.2 or 2.4 mol L^{−1}, and the total volume of heptane and 1-hexene was set to 300 mL. After 30 min of polymerization, the resultant polymer was filtered and dried in vacuum at 60 °C for 6 h. The heptane-soluble polymer was collected by pouring the filtrate into 1 L of cold acetone. The precipitate was filtered out and dried using the same procedure.

3.5. Characterization

Morphologies of catalyst and polymer particles were observed using scanning electron microscopy (SEM, S-4100, Hitachi, Tokyo, Japan) operated at an accelerating voltage of 20 kV. The elemental distribution of catalyst components in polymer was analyzed on a cross-sectioned polymer particle using energy-dispersive X-ray emission (EDX, JCM-6000PLUS, JEOL Ltd., Tokyo, Japan) operated at an accelerating voltage of 15 kV. The polymer particle was cut by a razor chilled with liquid N₂. Before the SEM and EDX measurements, the sample was subjected to Pt sputtering for 90 s.

Particle characteristics of a support and a catalyst were analyzed by light scattering (Partica LA-950V2, Horiba, Tokyo, Japan) in heptane. The particle size is expressed with D_{10} , D_{50} , and D_{90} , which correspond to the particle size at 10, 50, and 90% of the cumulative volume-base distribution. A relative span factor (RSF) was calculated based on Equation (1), as follows:

$$RSF = \frac{D_{90} - D_{10}}{D_{50}}, \quad (1)$$

XRD measurements were performed using MiniFlex600 (Rigaku Co.) with CuK α radiation at an acceleration voltage of 40 kV and a current of 30 mA in the 2θ range of 3–90° with a scanning speed of 10°/min.

N₂ adsorption and desorption isotherms at 77 K were acquired on a BELSORP-max instrument (Microtrac BEL Corp., Osaka, Japan). Prior to the measurement, 20–50 mg of sample powder was outgassed at 80 °C over 2 h.

The Ti content was determined by UV-vis spectroscopy (V-770, JASCO, Tokyo, Japan). A measured amount of a catalyst was dissolved in HCl/H₂SO₄ solution, and then H₂O₂ was added to form a Ti-peroxo complex that exhibits the absorbance of the ligand metal charge transfer at 410 nm. The Ti content was determined from the peak intensity using a pre-determined standard curve.

The copolymer samples were analyzed by NMR (Bruker 400 MHz) operated at 120 °C. About 40 mg of a copolymer sample was dissolved in 0.2 mL of 1,1,2,2-tetrachloroethane-*d*₂ (internal lock and reference) and 0.5 mL of 1,2,4-trichlorobenzene containing 0.006 wt.% of 2,6-di-*tert*-butyl-4-methylphenol (stabilizer for heat degradation of polymer). The content of 1-hexene in the copolymer samples was determined with ¹³C NMR spectra (the number of scan = 5000). The chemical shift assignments were performed according to the works of Randall [21] and Kissin [22]. The stereoregularity of PP unit (*mmmm*) in the polymers was determined by the methyl peaks in the ¹³C NMR spectrum [23].

4. Conclusions

In summary and conclusion, spherical macroparticles with a narrow particle size distribution were obtained by the spray-drying of MgO nanoparticles (50 nm in diameter), using methanol as a dispersant. The subsequent TiCl₄ treatment allowed us to realize the bottom-up preparation of the multi-grained MgO/MgCl₂/TiCl₄ core-shell catalyst (S-Cat). The catalyst has no micropores and mesopores, but it possesses macropores derived from the interparticle voids among MgO nanoparticles with a diameter of 50 nm. S-Cat showed decay-type kinetic curves in the homo-polymerization of both ethylene and propylene, i.e., the catalyst displayed the highest activity at the early stage of polymerization, and then its activity dropped to a certain level, which remained constant until the polymerization was stopped. These polymerization behaviors were similar to that of a monodispersed MgO/MgCl₂/TiCl₄ core-shell catalyst treated with a surfactant (PA-Cat50), suggesting that macropores never influenced the diffusion of the cocatalyst and the monomer. Thus, all the catalyst overlayers in S-Cat were open for a polymerization reaction from the beginning. These facts, in turn, indicate that the micropores and mesopores are deeply involved in the fragmentation and build-up kinetics. Even when using S-Cat with fully opened surfaces, the degrees of activation (comonomer effect) by introducing 1-hexene in both ethylene and propylene copolymerization were comparable to that of general heterogeneous Ziegler-Natta catalysts. This fact suggests that the diffusion inhibition effect of the polymer layers is effective, even at the level of the primary catalyst particles. As described above, the multi-grained MgO/MgCl₂/TiCl₄ core-shell catalyst was shown to be useful for obtaining insights into the structure-performance relationship of ZNCs, with respect to their interior structures. In the following studies, it is expected that quantitative discussions will be available, by controlling the interior structure by intentionally changing the size of the primary particles, etc., which would give us clearer insights into the structure-performance relationship of MgCl₂-supported ZNCs.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/catal11091092/s1>, Table S1: screening of spray-drying conditions for water dispersant, Table S2: screening of spray-drying conditions for methanol dispersant, Figure S1: SEM-EDX images of cross-section of (A) PE and (B) PP particles obtained with S-Cat in short-time polymerization (1 min).

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