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High-throughput approach for establishing structure-performance relationship in Ziegler-Natta catalyzed olefin polymerization

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Ziegler-Natta

We developed the methodology to improve the throughput in generating a large data set of catalysts for discovering the structure-performance relationship in olefin polymerization. The outcome of the research provides a new technical concept which is useful for catalyst developments in the industry.

In this research, the application of a high-throughput approach using in-house developed parallel reactor systems for the synthesis of Ziegler-Natta catalysts was successfully demonstrated, aiming at unveiling the quantitative structure-performance relationship in olefin polymerization. The developed systems enabled the parallel synthesis of magnesium ethoxide as a support material and catalysts with the excellent reproducibility and particle quality for the first time. The obtained catalysts were parameterized by means of various characterization techniques. Due to the complexity of the catalyst structure, it was found that the performance of the catalyst was hardly explained on the basis of one-to-one relation. On the other hand, the statistical analysis based on the multiple linear regression model reasonably explained the performance with adequate prediction ability.

Catalysis

high-throughput　Ziegler-Natta　Olefin polymerization　Structure-performance

様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９（共通）

１．研究開始当初の背景

In heterogeneous catalysts, superior catalytic performance often arises from catalytic multi-functionalities, where an interplay of multi-phase components and their spatial placement in the hierarchical nature of support are greatly involved. To enable the rational design of these performant materials, a sophisticated understanding of structural features in relation to the catalytic performance is crucial. The heterogeneous Ziegler-Natta catalyst is one of the most important industrial olefin polymerization catalysts that possesses multi-functionalities. It is well-known that the multi-component nature and particle architectures synergistically manipulate the polymerization performance; At the active site scale, Ti species heterogeneously distributed on $MgCl_2$ surfaces are responsible for the activity and polydispersity of produced polymer. Lewis base as an internal donor co-adsorbs with Ti species to modulate the catalytic nature. At the particle scale, the catalyst morphology influences the final polymer morphology through the replicating phenomena. The kinetic profile in polymerization is dependent not only on pore architectures, but also on how the macro-particle is constructed. Monomer polymerizes at accessible pores and induces fragmentation to circumvent mass transfer limitation and to maintain the catalytic activity. In order to establish the structure-performance relationship (SPR) for the realistic Ziegler-Natta catalyst system, a statistical approach has been recently pursued in our group. However, to achieve the quantitative level of SPR, a plenty of samples with a diversity of structural features is essential to avoid a statistical artifact. This is extremely hard to achieve even in an industrial level research due to the exhaustive and time consuming catalyst synthesis process. In this research, the application of a high-throughput approach using an in-house designed parallel reactor system for the synthesis of Ziegler-Natta catalysts is demonstrated for the first time, aiming at unveiling the quantitative SPR by means of combined multilateral characterization and multivariate analysis.

２．研究の目的

To implement the first high-throughput approach for the Ziegler-Natta catalyst synthesis and its application in establishing the quantitative SPR in Ziegler-Natta catalyzed olefin polymerization

３．研究の方法

(1) Synthesis of magnesium ethoxide as a catalyst support

Magnesium ethoxide ($Mg(OEt)_2$) was synthesized from the reaction between Mg metal and ethanol in the presence of halide ions as an initiator. An in-house parallel reactor system was exploited to realize the parallel synthesis of $Mg(OEt)_2$ with 24 times increase in the throughput as compared to a conventional experiment (Fig. 1a). In this reactor system, a glass tube (O.D. = 24 mm) is used as a reactor cell. 24 glass tubes are inserted in an aluminum block placed on top of an electric heater. Stirring of the suspension is achieved via a mechanical stirring. In each cell, two paddles are fixed on a stainless steel shaft where the center of the shaft is drilled to create a 4.0 mm-feeding channel (Fig. 1b). The cover head for multiple reaction cells is fabricated with a gas distribution line that allows each reaction cell to be evacuated or filled with gases. Various condition parameters, such as the particle size of Mg, the type of an initiator, the interval time and addition amount for sequential Mg addition, etc., were varied to obtain $Mg(OEt)_2$ with different particle characteristics. In addition, organic modifiers in the group of alcohol, alkoxy alcohol, mono- and dicarboxylic acids, mono- and diesters were exploited for $Mg(OEt)_2$ particle modulations.

(2) Synthesis of catalysts

A 12-paralell reactor system for the catalyst synthesis was newly developed under the scope of the current project (Fig. 1c). A 50 mL disposable cylindrical glass bottle was used as a reactor. To preserve the morphology of particles while minimizing the space of the system, the suspended magnetic stirring system and polytetrafluoroethylene cap were specially designed to replace a typically used overhead motor stirrer (Fig. 1d). A hollow aluminum block was placed on top of a multi-position magnetic stirrer. The temperature control in the range of -20 ^{o}C and 120 ^{o}C was achieved via an oil medium that circulates through the hollow aluminum block in one direction. Under N_2 atmosphere, 2.0 g of $Mg(OEt)_2$ and 14 mL of toluene were added into the reactor. After cooling down to -10 ^{o}C, 8.0 mL of $TiCl_4$ in toluene (1:1 vol/vol) was dropwise added via a multi-channel peristatic pump. The mixture was heated to 90 ^{o}C, followed by the

addition of 0.55 mL of di-*n*-butylphthalate (DBP) as an internal donor. The temperature was raised to 110 °C and the reaction was kept for 2 hours. The second treatment with $TiCl_4$ was performed under the same condition after washing the solid product twice with toluene. The final product was repetitively washed with toluene and heptane.

(3) Performance evaluation

The performance of the catalyst was evaluated in propylene homopolymerization and ethylene-propylene copolymerization for producing high impact polypropylene copolymer (imPP). For homopolymerization, 300 mL of heptane was introduced into a 1-L reactor, followed by the addition of triethyl aluminum ([Al]=10 mmol/L) and cyclohexylmethyl-dimethoxysilane (CMDMS, Al/CMDMS=10) as a cocatalyst and an external donor, respectively. The solvent was saturated by propylene at 0.5 MPa for 30 minutes. Thereafter, the catalyst was charged into the reactor to initiate polymerization. The reaction was conducted at 50 °C and 0.5 MPa under the stirring speed of 350 rpm for 1 hour before terminating by the addition of acidic ethanol. Thus obtained polymer was filtered, washed with methanol and dried at 60 °C under vacuum for 6 h.

In the case of imPP, two-step polymerization, propylene homopolymerization followed by propylene-ethylene copolymerization, was performed. After 1 h of homopolymerization, the reactor was degassed, followed by the removal of the solvent by a suction pump under N_2 atmosphere. Produced polymer powder was dried under vacuum for 15 minutes at 50 °C. The second stage polymerization was initiated by introducing ethylene and propylene (1:1 ratio) and the copolymerization was conducted at 50 °C and 0.2 MPa for 5 minutes. Finally, resultant polymer was collected and dried under vacuum at 60 °C for 6 hours.
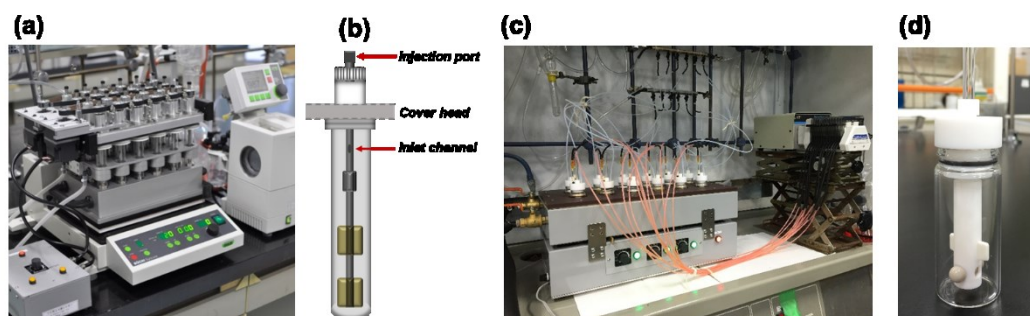

Fig. 1 Reactor systems for parallel syntheses of a,b) $Mg(OEt)_2$ and c,d) catalysts.

４．研究成果

$Mg(OEt)_2$ samples having different particle characteristics were obtained by varying the synthesis condition, and by the introduction of organic modulators. Fig.2a shows a typical morphology of $Mg(OEt)_2$ obtained from a 24-parallel reactor system under the optimized condition. These particles were found to possess the spherical morphology without agglomerates and fine particles. It is noted that the particle quality is fully comparable to a typical glassware experiment with high repeatability. Fig. 2b shows the influence of synthesis parameters on particle characteristics. It can be seen that the variation of condition parameters enabled the control of particle characteristics in a wide range. While the type of the initiator exhibited the largest impact on both of the particle size and its distribution, the change in the Mg amount per addition allowed the fine-tuning of the particle size with a relatively narrow size distribution. The second set of $Mg(OEt)_2$ samples was acquired by the introduction of organic modulators, such as acetic acid, propionic acid, hexanoic acid, diethyl succinate, etc. Differently from changing the synthesis condition, the presence of modulators only at 1.0 mol% with respective to Mg greatly altered the particle size in a boarder range as compared to the previous set of samples without affecting the circularity and relative span factor. With the above two methodologies, a library of $Mg(OEt)_2$ with different particle characteristics was successfully obtained. $Mg(OEt)_2$ samples were converted into catalysts using the established parallel catalyst preparation system. It must be noted that during the catalyzation, the heat generation due to exothermicity of the reaction caused the breakage of $Mg(OEt)_2$ particles that have insufficient particle strength. These samples were majority in the library, but they were excluded from the data set in order to establish the realistic catalyst library in terms of an industrial usage. Fig. 2c shows the example of the successful catalyst prepared from the $Mg(OEt)_2$ sample in Fig. 2a. It can be seen that the morphology of the resultant catalyst

resembled that of original Mg(OEt)$_2$ without the particle breakage or fine generation. The parameterization of catalyst features was acquired by exploiting various characterization techniques. Briefly, the particle characteristics, such as D$_{10}$, D$_{50}$, D$_{90}$, circularity, and RSF, were obtained from the analysis of SEM images using the ImageJ software. The Ti and donor contents were analyzed by UV-vis and ^{1}H NMR, respectively. The pore characteristics were devised from the adsorption branch in N$_2$ adsorption/desorption experiments using the Grand canonical Monte Carlo method (Fig. 2c). The analysis results showed that not only the particle size, but also the chemical compositions and pore characteristics were sensitive to the exploited Mg(OEt)$_2$ samples.

  To establish the structure-performance relationship in olefin polymerization, the catalyst parameters were firstly screened based on the correlation matrix using the Origin software. For parameters expressing the same catalyst feature, if more than one parameter are strongly correlated with the dependent variable, only the strongest correlation is selected as a descriptor. For example, for the group of parameters expressing the particle size, D$_{10}$ possessed the strong collinearity with D$_{50}$ and D$_{90}$ (>0.95), and exhibited the highest correlation coefficient with the activity. Thus only D$_{10}$ was chosen to be a representative for the correlated group. On the other hand, if none of collinearity exists among parameters expressing the same feature, all parameters are treated as independent descriptors. Fig. 2d shows a scatter plot between the actual propylene homopolymerization activity for 26 catalyst samples and the predicted value based on a multiple linear regression model. The best fitted correlation with R^2 = 0.73 was expressed by;

$$Activity = -0.91+0.0041D_{10}+0.64Cir+0.032DBPcont.-0.0440Etcont.-0.0015V_{Micro}+0.0012V_{Total}$$

From the above equation, the activity tends to increase with the particle size and particle circularity. In terms of chemical compositions, the internal donor gives the positive influence on the activity while the presence of the ethoxy group, which arises from the catalyst by-product, exhibits an adverse effect. Finally, a large pore volume is required to promote the activity, especially for the pore size larger than micropores. In the case of imPP, the total copolymer produced in the second stage is expressed with R^2 = 0.69 by;

$$Total copolymer = 0.32 TiCont.- 0.61 DEPCont.- 0.35V_{micro}$$

Till the end, it is important to note that the current project successfully developed and implemented the methodology to improve the throughput for support and catalyst syntheses to realize the generation of a large data set for discovering the SPR in olefin polymerization for the first time. The obtained best fitted regression equations possessed adequate prediction ability in the cross-validation. At the same time, a higher sample number with higher variances would be more profitable to improve the prediction precision.
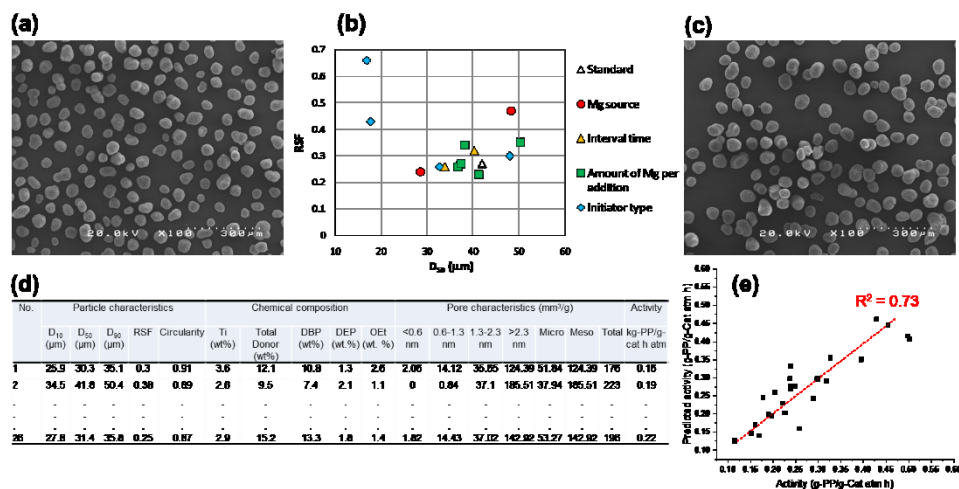

No.	Particle characteristics					Chemical composition					Pore characteristics (mm³/g)						Activity
	D$_{10}$ (μm)	D$_{50}$ (μm)	D$_{90}$ (μm)	RSF	Circularity	Ti (wt%)	Total Donor (wt%)	DBP (wt%)	DEP (wt.%)	OEt (wt. %)	<0.6 nm	0.6-1.3 nm	1.3-2.3 nm	>2.3 nm	Micro	Meso	Total kg-PP/g-cat h atm
1	25.9	30.3	35.1	0.3	0.91	3.6	12.1	10.8	1.3	2.6	2.06	14.12	36.65	124.39	51.84	124.39	176	0.15
2	34.5	41.8	50.4	0.38	0.89	2.8	9.5	7.4	2.1	1.1	0	0.84	37.1	185.51	37.94	185.51	223	0.19
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26	27.8	31.4	35.8	0.25	0.87	2.9	15.2	13.3	1.8	1.4	1.82	14.43	37.02	142.92	53.27	142.92	196	0.22

Fig. 2 a) Morphology of Mg(OEt)$_2$ obtained from the parallel reactor system, b) influence of synthesis parameters on Mg(OEt)$_2$ particle characteristics, c) morphology of a catalyst prepared from Mg(OEt)$_2$ in 2a, d) parameterization of catalyst samples, and d) scatter plot of catalytic performances based on the multiple linear regression model.

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