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Multilateral characterization for industrial Ziegler–Natta catalysts toward elucidation of structure–performance relationship

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ABSTRACT

High-performance Ziegler–Natta catalysts with ill-defined structural hierarchy were studied over multi-length scales. In this study, multilateral characterization was performed to address quantitative structure–performance relationships in ethylene/1-hexene copolymerization with $Mg(OEt)_2$-based Ziegler–Natta catalysts. Macroscopic characteristics of the catalysts (e.g., particle size and meso- and macropore volumes) were greatly affected by structures of $Mg(OEt)_2$ precursor particles, while microscopic characteristics (e.g., micropore volume and chemical composition) were hardly influenced. Ethylene/1-hexene copolymerization results suggested the significance of monomer diffusion: The activity was enhanced for smaller catalyst particles, while the 1-hexene incorporation was improved with larger meso- and macropore volumes.

1. Introduction

"Multi-components" and "structural hierarchy" are the key issues to realize multifunctional and performant heterogeneous catalysts. The word, multi-components, represents that active components, support materials, modifiers, and cocatalysts in a system play different roles, while "structural hierarchy" dictates the significance of the structural design over multi-length scales. The most illuminative example, the three-way catalyst [1,2] for automotive catalytic converters typically consists of cordierite honeycomb support, whose structure is optimized to enhance the contact efficiency without penalizing airflow resistance, and a few-micron-thick washcoats deposited on the support. The washcoat consists of BaO-stabilized porous γ-Al_2O_3 as a carrier, CeO_2 (/ZrO_2) as an attenuator for the oscillation of the air-to-fuel ratio, and nano-sized noble metal or metal alloy (Pt/Pd/Rh) as active catalytic materials [1,3,4]. These multifunctional catalysts have been invented and developed mainly in an empirical manner from viewpoints of performance optimization in terms of activity, selectivity catalytic lifetime, and so on. In most of cases, roles of each component and impacts of each structural factor on the whole catalytic performance are roughly or qualitatively understood, while it is still challenging to embody quantitative structure–performance relationships (SPR) [5–7]. The difficulty comes from several reasons: A catalyst performance is usually affected by several chemical and structural factors in a complicated way, while to vary one of these factors without changing the other factors is not easy in usual preparation procedures [8,9]. Furthermore, prepared catalysts contain different extents of chemical and structural heterogeneity over multi-length scales, making it extremely demanding to parameterize all factors that affect a catalytic performance [4,10].

The heterogeneous Ziegler–Natta catalyst for industrial olefin polymerization is a representative example of such catalysts. Manufacturing high-quality polymer products under efficient plant operation generally requires for a catalyst to simultaneously fulfill various performances such as high activity at an elevated temperature, (extremely) high selectivity, an appropriate kinetic profile, uniform particle sizes with spherical morphology, high hydrogen response for the polymer molecular weight control, and so on [11–13]. While there is a huge variety of preparation routes empirically established in terms of performance optimization [14], Ziegler–Natta catalysts at the level of industry generally possess the following structural features.

(1) Pro-catalysts consist of $TiCl_4$ and a Lewis basic compound co-supported on activated $MgCl_2$ support, where the Lewis base called as internal donor is a key component to drastically improve the catalyst stereospecificity as well as to activate the $MgCl_2$ support during preparation [13,15–17].
(2) Catalyst macroparticles possess spherical morphology with narrow particle size distributions typically between 10 μm and 100 μm. They are made by hierarchical agglomeration of primary structural units of $TiCl_4$/internal donor/$MgCl_2$, whose dimensions are believed to be around 1–10 nm [18,19].

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(3) The said hierarchical agglomeration leads to the formation of a range of porosity from micro to macropores, whose distributions and shapes are sensitively affected by employed preparation methods and conditions [20]. In Ziegler–Natta olefin polymerization, polymer initially formed in accessible pores build up mechanical stresses inside catalyst particles to trigger particle fragmentation (called the pore-breakage process), in which fresh catalyst surfaces which are originally hidden in inaccessible pores are continuously exposed. These processes enable industrial catalysts to retain stable polymerization activity over hours. In this way, inner structures of catalyst macroparticles significantly affect the fragmentation process [21,22] and the kinetic behavior during polymerization [12].

Roughly speaking, the first structural feature at the atomic scale is mainly related to the primary structure and polydispersity of produced polymer through the performance of active sites [14,23], while the latter two at larger scales from nm to μm mainly affect the kinetic profile of a catalyst and the resultant polymer particle morphology through fragmentation and replication phenomena during polymerization [11,24,25]. However, from a quantitative viewpoint, all these issues are believed to more or less exert influence on each said performance.

Though several research studies have been undertaken with the aim to understand relationships between catalyst structures and performances in Ziegler–Natta olefin polymerization, quantitative structure–performance relationships have not yet been reached. One of the main drawbacks in the previous studies can be attributed to the absence of multilateral characterization: They determined only one or a few structural parameter(s) of catalyst samples such as the crystalline disorder of $MgCl_2$ [26], surface area [27], total pore volume [12,28], and average pore size [12], without considering other parameters which also affect a targeted performance. Characterization and parameterization of the structures of Ziegler–Natta catalysts are actually not trivial in terms of the complexity and heterogeneity in chemical and physical structures as well as of their extreme sensitivity to moisture. Nevertheless, reliable quantitative structure–performance relationships are not to be acquired without parameterizing catalyst structures as precisely as possible with various characterization methods.

Based on these backgrounds, we have set as our primary objective to first establish and apply multilateral characterization for structures of Ziegler–Natta catalysts. Four catalysts were prepared based on the chemical conversion of $Mg(OEt)_2$ precursor, which is one of the most commonly employed preparation routes in industry due to superior activity and copolymerization ability of resultant catalysts. They were subjected to a variety of characterization methods in order to achieve structural parameterization over multi-length scales such as electron microscopy, N_2 adsorption/desorption, Hg intrusion, UV/vis spectroscopy, and gas chromatography. We also examined impacts of the determined structural parameters on the ethylene/1-hexene copolymerization ability of the catalysts.

2. Experimental

2.1. Materials

Anhydrous $MgCl_2$, triethylaluminium (TEA), and four kinds of poreless Mg particles (termed Mg A–D) were donated from Toho Titanium Co., Ltd., Tosoh Finechem Corporation and Yuki Gousei Kogyo Co., Ltd., respectively. The morphologies of Mg A,C are flake-like, while those of Mg B,D are spherical (Fig. 1). Characterization results of the Mg particles are shown in Table 1. The size of Mg particles becomes smaller in the order of A → C → B → D.

Ethanol (purity >99.5%) was dried over 3A molecular sieve with N_2 bubbling. Heptane (purity >99.5%), toluene (purity >99.5%) and di-*n*-butylphthalate (DBP) (purity >98%) were dried over 4A molecular sieve with N_2 bubbling. Cyclohexylmethyldimethoxysilane (CMDMS) was purified by distillation under reduced pressure. Ethylene of research grade donated by Sumitomo Chemical Co., Ltd. was used as delivered.

2.2. $Mg(OEt)_2$ synthesis

$Mg(OEt)_2$ was synthesized based on a patent [29] with several modifications. 0.25 g of $MgCl_2$ (as an initiator) and 31.7 mL of dehydrated ethanol were introduced into a 500 mL jacket-type separable flask equipped with a mechanical stirrer rotating at 180 rpm under N_2 atmosphere. After the dissolution of $MgCl_2$ at 75 °C, 2.5 g of Mg and 31.7 mL of ethanol were introduced. 2.5 g of Mg and 31.7 mL of ethanol were again added 10 min after the reaction was initiated by $MgCl_2$. Thereafter, 2.5 g of Mg and 31.7 mL of ethanol were added repeatedly 4 times every 10 min, followed by aging at 75 °C for 2 h. Finally, the temperature was decreased to 40 °C, and the product was washed with ethanol. In this study, four kinds of $Mg(OEt)_2$ particles (MGE A–D) were synthesized from Mg A–D under the same conditions.

2.3. Catalyst preparation

The preparation of Ziegler–Natta catalysts from $Mg(OEt)_2$ was conducted again based on a patent [30] with several modifications. 10 g of $Mg(OEt)_2$ and 140 mL of toluene were charged in a 300 mL 3-neck flask equipped with a mechanical stirrer rotating at 180 rpm under N_2 atmosphere. 20 mL of $TiCl_4$ was added dropwise, while the temperature of the suspension was kept within 0–5 °C. Thereafter, the temperature was first elevated to 90 °C to add 3.0 mL of DBP, and then, it was brought to 110 °C. The reaction slurry was continuously stirred at 110 °C for 2 h. Subsequently, the reaction product was washed with toluene twice at 90 °C and further treated with 20 mL $TiCl_4$ at 90 °C for 2 h. After that, the product was washed with *n*-heptane 7 times to get the final catalyst. Four kinds of Ziegler–Natta catalysts (Cat A–D) were obtained from MGE A–D under the same conditions.

2.4. Polymerization

Ethylene/1-hexene copolymerization was performed in a 1 L autoclave equipped with a mechanical stirrer rotating at 350 rpm. 407 mL of *n*-heptane was introduced into the reactor. TEA ([Al] = 10 mmol/L), CMDMS (Al/E × D = 10) and 93 ml of 1-hexene (corresponding to 0.75 mol) were introduced into the reactor, and the solution was saturated with 0.5 MPa of ethylene at 50 °C. A catalyst ([Ti] = 0.005 mmol/L) was fed into the reactor by a bomb injection technique to initiate the polymerization. The polymerization was conducted for 30 min with a continuous supply of ethylene gas at 0.5 MPa. The polymer was recovered by pouring the reaction slurry into mixture of acetone and methanol kept at 0 °C and subsequent filtration.

2.5. Characterization

2.5.1. Scanning electron microscopy

Particle morphological characteristics of $Mg(OEt)_2$ and catalyst particles were studied with scanning electron microscopy (SEM, Hitachi S-4100) operated at an accelerating voltage of 20 kV. Before the measurements, particles were subjected to Pt sputtering for 100 s. To quantify observed particle morphology, SEM images