Locating the active sites of metallocene catalysts supported on acid-treated montmorillonite

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ABSTRACT

In this study, we investigated the location of the active sites of montmorillonite-supported metallocene catalysts used for propylene polymerization. X-ray fluorescence, Hammett titration, and scanning transmission electron microscopy/energy-dispersive X-ray spectroscopy revealed that the gradual leaching of Al atoms from the borders of the platelets to their centers and acid site formation occurred when montmorillonite was subjected to an acid treatment. X-ray diffraction and transmission electron microscopy analyses indicated that the metallocene complex was activated only on the borders of the acid-treated montmorillonite platelets. The most plausible explanation for this phenomenon is that the metallocene complex is activated by the acid sites formed on the borders of the platelets by the acid treatment of montmorillonite.

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1. Introduction

Metallocene catalysts have been studied widely for use in olefin polymerization since Kaminsky et al. reported that methylaluminoxane (MAO) is an effective cocatalyst for metallocene activation [1]. In particular, significant efforts have been devoted to developing more effective cocatalysts. To this end, MAO [2] has been modified, and various boron compounds such as boranes and borates [3] have been developed. Mitsubishi Chemical Corporation (MCC) has developed unique clay minerals that can act as specific support materials for activating metallocenes in the absence of additional compounds [4,5].

With respect to the activation mechanism, MAO is a difficult compound to study, given that it exhibits multiple and complex structures [6–9]. The activation performance of a material depends strongly on the synthesis procedure used and on its storage conditions. Therefore, being able to identify which chemical species in a MAO mixture is capable of activation is essential. Coevoet et al. investigated the reaction of zirconocene dichloride with MAO using ultraviolet-visible spectroscopy and found that the reaction mode depended on the ratio of MAO and the complex [10]. In the case of an Al/Zr ratio lower than 30, only a monomethyl complex was obtained. For all other cases, the monomethyl complex was converted into a cationic species of zirconocene monomethyl. Wieser et al. studied the acidity of various MAO species [11]. They found that two types of MAO species exhibit different acidities. MAO_A is a stronger Lewis acid than is MAO_B and is capable of releasing cation species more readily. In the cases where MAO is used in a high enough amount, the proportion of MAO_A becomes higher.

In case of clay minerals, three active species have been proposed to explain metallocene activation: MAO [12], anchored aluminum compounds [13–15], and the acid sites of the clay minerals [16]. Novokshonova et al. reported that MAO prepared on clay minerals shows the same fragmentation profiles during temperature-programmed desorption mass spectrometry as does dry MAO and that it acts as a cocatalyst in the system [12]. Because their research objective was to develop immobilized MAO compounds, they intentionally used clay minerals that contained water of constitution for the partial hydrolysis of alkylaluminum compounds such as trimethylaluminum (TMA). On the other hand, Jeong et al. reported that the products formed during the partial hydrolysis of TMA with acidic montmorillonite (MMT) are capable of activating metallocenes for ethylene polymerization; this was the case even though the MMT was dehydrated before being placed in contact with TMA [13]. They concluded that dehydrated MMT contains only reactive OH groups and an insignificant

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amount of water for forming MAO. In addition, because the surface species formed by the reaction of the OH group and TMA did not exhibit any activity, they did not consider MAO to be an active species.

The first generation of MCC clay mineral technology was a hydrolysis technique similar to Novokshonova's method [4]. However, MCC changed their strategy from a wet system-based one to a dry system-based one [5], owing to the difficulty in achieving further improvements. In the latter case, Takahashi et al. reported the acid sites of a clay-mineral-activated metallocene dialkyl when used for ethylene polymerization in the absence of organoaluminum compounds [16]. Their findings were supported by those of Sano's study on the aluminated siliceous material AlMCM-41 [17]. The Lewis acid sites on AlMCM-41 caused the activation of the metallocene when it was used for propylene polymerization in the absence of organoaluminum compounds. While there is some debate regarding the active species in the clay mineral catalyst system, we believe that an acidic system is necessary in all cases.

In addition, the location of the active sites in the clay mineral system remains the subject of discussion. Because clay minerals typically have a layered structure, the doping of chemicals into the gap between adjacent layers (i.e., intercalation) is a common technique for tailoring their properties. Therefore, a few researchers believe that the active sites are formed in the interlayer region. Kurokawa et al. reported that ethylene is polymerized by intercalated active metallocene molecules after the peeling of the individual layers of the metallocene catalyst system when it is supported on Mg^{2+}-treated mica [18]. On the other hand, the acid treatment of natural clay minerals in water is essential for metallocene activation [19]. Thus, it is highly probable that the active sites are located on the surfaces of the clay mineral particles, which are primarily modified by the acid treatment [20]. It is, therefore, critical to correctly identify the location of the active sites in order to elucidate the catalyst system and to improve its performance, as the two proposed locations mentioned above are completely different.

With this goal in mind, we performed analytical studies to determine the location of the active sites; this was done by investigating the chemical and structural changes induced in the clay minerals after the chemical treatment and the polymerization process. We selected a propylene polymerization catalyst consisting of chemically treated MMT and a specific complex developed by Japan Polychem Corporation as a typical example [21].

2. Experimental

2.1. Materials

Kunipia F (KF) (a commercial product purchased from Kunimine Industry Co., Ltd.) was used as the raw material for MMT. *rac*-Dimethylsilylene bis[1,1-{2-methyl-4-(4-chlorophenyl)-4-hydroazulenyl}]zirconium dichloride (Azu-Zr) was prepared according to the procedure listed in its patent application and used as the metallocene complex for the catalyst for propylene polymerization [21]. The structure of the Azu-Zr metallocene and the assignments of its ^{1}H NMR chemical shifts are shown in Fig. 1. We wish Fig.1 is reduced half current size(single column width).

Industrial grade heptane and toluene were purified using molecular sieves (4A) and were subjected to dry nitrogen bubbling before use. Triisobutylaluminum (TiBA) diluted in heptane as solvent (Tosoh Finechem Corporation) was used as purchased without further purification. Sulfuric acid (H_2SO_4), anthraquinone, 2-benzalacetophenone, and 2,6-dimethylpyridine (purchased from Wako Pure Chemicals Industry Ltd.) were also used as purchased without further purification.
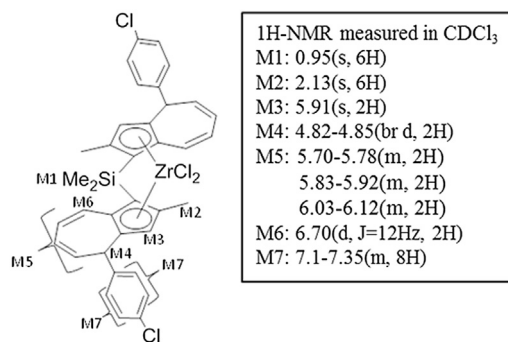

^{1}H-NMR measured in CDCl$_3$
M1: 0.95(s, 6H)
M2: 2.13(s, 6H)
M3: 5.91(s, 2H)
M4: 4.82-4.85(br d, 2H)
M5: 5.70-5.78(m, 2H)
    5.83-5.92(m, 2H)
    6.03-6.12(m, 2H)
M6: 6.70(d, J=12Hz, 2H)
M7: 7.1-7.35(m, 8H)

Fig. 1. Structure and 1H NMR chemical shifts of the Azu-Zr metallocene.

2.2. Synthesis of catalysts

2.2.1. Sulfuric acid treatment of Kunipia F

A 2 L separable four-necked flask, to which a mechanical agitation unit, a water condenser, and a thermometer were connected, was used for the treatment. Distilled water (850 mL) and concentrated H_2SO_4 (250 g) were added to the flask and heated to 90 °C using an oil bath. Kunipia F (150 g) was added to the acid solution to start the treatment. The concentration of H_2SO_4 in the reaction mixture was 20 wt%. After 2 h, the solid formed was collected by filtration and repeatedly washed with cold distilled water until the pH of the slurry was not lower than 4. The obtained cake of the clay mineral was dried in an oven at 120 °C overnight. The agglomerated portion of the dried powder was removed, and the remaining powder was dried under vacuum at 200 °C for 2 h; this sample was labeled as KF(1). KF(2) and KF(3) were prepared in a similar manner; the only difference was that the reaction times were 5 and 8 h, respectively.

2.2.2. TiBA treatment of acid-treated MMT

All the operations were performed in dry N_2 using standard Schlenk techniques. Into a three-necked flask (1 L) equipped with a mechanical agitation unit, 20 g of KF(2) and 73 mL of dry heptane were introduced. To the resulting dispersion, a heptane solution of TiBA (50 mmol) was added, and the mixture was stirred at 25 °C for 1 h. The supernatant liquid was removed by decantation, and the solid material was washed twice with 900 mL of heptane. Then, the solid material was dried by vacuum evaporation at 40 °C. The obtained sample, labeled as KF(4), was stored in a dry N_2 atmosphere.

2.2.3. Synthesis of supported metallocene catalyst

All the operations were performed in a dry N_2 atmosphere using standard Schlenk techniques. Into a three-necked flask (100 mL) equipped with a stirrer, 0.7 g of KF(2) and 5 mL of heptane were introduced. Then, the heptane solution of TiBA (1.66 mmol) was added to the flask, and the mixture was stirred at 25 °C for 1 h. The supernatant liquid was removed by decantation, and the solid material was washed twice with 90 mL of heptane. Next, the heptane solution of TiBA (112 μmol) and a heptane solution of Azu-Zr (28 μmol) were introduced. The mixture was stirred at room temperature for 1 h. After the supernatant liquid had been removed by decantation, the solid material was washed twice with 90 mL of heptane. Then, the solid material was dried by vacuum evaporation at 40 °C. This yielded the supported metallocene catalyst (KF(5)).

2.2.4. Synthesis of catalyst sample containing tiny amount of polypropylene

All the operations were performed in a dry N_2 atmosphere using standard Schlenk techniques. In a three-necked flask (1 L) equipped with a mechanical agitation unit, 12 g of KF(2) was suspended in