STUDY OF DIFFERENT MONTMORILLONITES AS “SUPPORT-ACTIVATORS” FOR METALLOCENE-CATALYZED PROPYLENE POLYMERIZATION

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ABSTRACT

Three different kinds of montmorillonites (Benclay SL, Benclay KK, and Kunipia F) were evaluated as “Support-Activators” for metallocene-catalyzed propylene polymerization. The respective clay materials were acid-treated to alter their physico-chemical properties, and used for the preparation of metallocene catalysts. The catalyst systems were subsequently characterized and their efficacy in facilitating the polymerization of propylene was evaluated. It was observed that polymerization activities were specifically influenced by the kind of clay mineral used. Based on our study, the level of catalytic activity is proportionally related to the surface areas of the small-size pores (pore diameter < 6 nm), where strong acid sites are present.

Key words: montmorillonite, metallocene, support activator, propylene polymerization

INTRODUCTION

In our previous work (Tayano et al., 2016a; Tayano et al., 2016b), we reported the characteristics of montmorillonite-based “Support-Activators (S-As)” for metallocene-catalyzed propylene polymerization. It has been confirmed that the metallocene complex is fixed on the edge of the octahedral sheet layers of acid-treated montmorillonite and produces the polypropylene (PP) polymer. Moreover, it has been proposed that the strong acid sites (pKa < −8.2) in the small pores (pore size (Dp) < 6 nm), formed via the acid treatment of Benclay SL (Tayano et al., 2016b), are necessary for the metallocene activation. Here, the prior studies of montmorillonite are briefly outlined to introduce the background of a relatively new and rare application of the clay mineral as a component of olefin polymerization catalyst.

First of all, montmorillonites are natural materials that are mined around the world. As such, their properties such as composition and isomorphous substitution are not necessarily similar (Watanabe, 2009a). There are numerous reports characterizing montmorillonites from various mining districts (e.g., Greece (Christidis et al., 1997), Turkey (Bulent et al., 2013), Ukraine (Belchinkaya et al., 2011), China (Wu and Ming, 2006), Wyoming and Arizona, US and Slovakia (Madejová et al., 1998), India (Kumar et al., 1995; Reddy et al., 2009), and Oklahoma, US (Maeno et al., 1993)), along with their acid-treated materials.

It is known that Al cation extraction from the octahedral sheet of montmorillonite by acid treatment increases both the surface area (SA) and pore volume (PV), and changes the pore size distribution of the clay minerals (Rhodes and Brown, 1992; Rhodes and Brown, 1993; Shinoda et al., 1995a; Shinoda et al., 1995b). Indeed, such behaviors were confirmed in our previous study of Kunipia F (Tayano et al., 2016a). With respect to the extraction rate, Madejová et al. (1998) have pointed out that the metal cation extraction rate from octahedral sheet of montmorillonite is faster when the montmorillonite has a higher isomorphous substitution of metal cations, and the material is finally converted to amorphous Silica upon completing the extraction process.

Other than the aforementioned morphological changes, the formation of acidic sites via Al extraction is also known (Tabernero et al., 2010; Flessner et al., 2001). This behavior is analogous to the formation of acid sites via the de-aluminization of aluminosilicate zeolite (Keii, 1981). The strong acid site formation was also confirmed with Benclay SL (Tayano et al., 2016b).

Another key research area of montmorillonite is its industrial applications (Watanabe, 2009b). In chemistry and other related fields, a number of organic reactions have been studied using acid-treated clay minerals as solid acid catalysts, including the esterification of lauric acid with methanol.

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(Zatta et al., 2013), isopropanol conversion to acetone (Yao and Kawi, 1999), Brønsted acid-catalyzed rearrangement of α-pinene to camphene (Brown and Rhodes 1997), methoxylolation of limonene (Catriñescu et al., 2013), and Friedel–Crafts alkylation of aromatics (Cseri et al., 1995). These are acid-catalyzed reaction systems, in which the acid sites of the clay mineral work directly as the active sites to facilitate the target chemical reaction. With our acid-treated Benclay SL polymerization catalyst, the acid sites in the clay mineral work as a co-catalyst for metallocene activation even though they do not act as direct polymerization active sites.

The effects of acid treatment on the properties of the clay mineral can be summarized as follows: (1) providing the enhancements of PV and SA, (2) inducing the formation of acid sites, and (3) usable the solid acid characteristics for chemical reactions.

As mentioned earlier, the catalyst’s activity is influenced not only by its acid properties, but also the morphological factor of montmorillonite in our acid-treated Benclay SL metalloocene catalyst (Tayano et al., 2016b). This means that the kind of montmorillonite used could potentially change the catalytic performance.

In the present work, Support-Activator properties of two different kinds of montmorillonite, namely Benclay KK and Kunipia F, were investigated and compared with Benclay SL. The fundamental differences of the raw clay materials were first investigated, followed by acid treatment of the clay minerals to prepare the S-As. The S-As were analyzed and tested for propylene polymerization in order to identify the universal factors influencing the catalytic properties of the montmorillonite-based metallocene catalysts.

MATERIALS AND METHODS

Materials

Clay minerals. Benclay KK (a commercial product purchased from Mizusawa Industrial Chemicals, Ltd.) and Kunipia F (a commercial product purchased from Kunimine Industry Co., Ltd.) were used as the raw montmorillonite materials. Benclay KK is a tailor-made granulated powder having a mean particle diameter of 18 μm, which is typically produced using the spray dry method. The raw clay minerals aforementioned were dried at 200 °C for 2 h under vacuum before being used as the catalyst support components.

Metalloocene compounds. rac-(Dimethylsilylene)bis[1,1-(2-methyl-4-(4-chlorophenyl)-4-hydroazulenyl)]zirconium dichloride (Azu-Zr-Cl2) was prepared according to the literature (Sugano et al., 1999) and used as the metallocene complex for the propylene polymerization catalyst. The chemical structures and assignments of 1H-Nuclear Magnetic Resonance (NMR) chemical shifts are shown in Figure 1.

rac-(Dimethylsilylene)bis[indenyl]hafnium dimethyl (Ind-Hf-Me2) was prepared according to patented procedures (Rohmann and Hermann, 1989; Fritze et al., 1998). The chemical structures and the assignments of 1H-NMR chemical shifts are shown in Figure 1.

Other reagents. Industrial grade heptane and toluene were purified using molecular sieves (4A) and underwent dry nitrogen bubbling before use. Japanese Industrial Standards (JIS) special grade concentrated H2SO4 was purchased from Wako Pure Chemicals Industry Ltd. A Hammett titration indicator, dicynmalacetone, (Tokyo Chemical Industry Co., Ltd.) was used as purchased. Other indicators, including 2,4-dinitrotoluene, antraquione, benzalacetophenone, benzeneazodiphenylamine, and methyl red, were purchased from Wako Pure Chemicals Industry Ltd. and used without any further purification. Super dehydrated toluene (Wako Pure Chemicals Industry Ltd.) was used as purchased for the titration with Hammett indicators. 2,6-Dimethylpyridine (Wako Pure Chemicals Industry Ltd.) was used as purchased. Triisobutylaluminum (TIBA) diluted in heptane (Tosoh Finechem Corporation) was also used as purchased without any further purification.

Methods

Acid treatment of clay minerals. A 2-L separable four-necked flask, equipped with a mechanical agitation unit, a water condenser, and a thermometer, was used for the clay mineral’s sulfuric acid treatment. A mixture of 1130 mL of distilled water and 330 g of concentrated sulfuric acid were added to the flask and it was heated to 90 °C in an oil bath. Subsequently, 200 g of non-dried montmorillonite was added to the acid solution and the mixture was agitated. The resulting sulfuric acid concentration in the slurry was 20 wt%. After the stipulated reaction time, the H2SO4-treated solid was collected by filtration and washed with 2000 mL of cold distilled water four times. The solid was then dried at 200 °C for 2 h under vacuum.

Catalyst preparation. A heptane solution of TIBA (2.5 mmol/g-clay mineral) was added to a suspension containing 600 mg of clay mineral in 7.9 mL of heptane. After stirring at room temperature for 1 h, the liquid phase was removed using the cannula technique. The solid was then washed twice with 10 mL of heptane and re-suspended in heptane.
Meanwhile, a solution containing 18 \mu\text{mol} of Azu–Zr–Cl$_2$ and 72 \mu\text{mol} of TIBA in n-heptane was prepared separately. The metallocene solution was added to the solid suspension and the reaction mixture was stirred at room temperature for 30 min. The obtained catalyst was used in the form of a heptane slurry without washing.

**Polymerization.** The propylene bulk polymerization process was conducted using 150 mg of Azu–Zr–Cl$_2$ supported catalyst (described above) at 70°C for 1 h in a 3-L autoclave with 750 g of liquid propylene. TIBA (4 mmol) was added to the reaction mixture as a scavenger. The obtained polypropylene was dried at 70°C for 1 h under atmospheric pressure. Alkyl-aluminum free polymerizations were also conducted using only a large quantity of Ind–Hf–Me$_2$ (3000 \mu\text{mol/g-clay}) combined with 0.16 g of the raw or acid-treated Benclay KK.

**Characterizations of the Support-Activator and catalyst.** Al, Si, Mg, Fe, and Na contents in the clay minerals were determined using X-ray fluorescence (ZNX-100e XRF spectrometer, Rigaku, Ltd., Japan). Zr content in the catalysts was determined using inductively coupled plasma atomic emission spectrometry (ICP-AES) (JY-138U1 trance, Horiba, Ltd., Japan) and the solution was prepared via catalyst decomposition with H$_2$SO$_4$ and HF. The catalysts were washed with heptane and dried under vacuum at room temperature in advance. To obtain the indicative parameters of the materials' surface area (SA) and pore volume (PV), an ordinary N$_2$ adsorption of the Brunauer-Emmett-Teller (BET) analysis was performed with a Quantachrome Autosorb 3B instrument at liquid nitrogen's temperature (77 K) (Thommes et al., 2015). The crystalline structure of the clay minerals was evaluated by X-ray diffraction (XRD, Smartlab diffractometer, Rigaku, Ltd., Japan). The measurement conditions used were as follows: Power = 40 kV and 30 mA, filter = Cu K-beta filter, detector = scintillation counter, scan speed = 0.02°/min, and resolution = 0.02°. Water contents in the clay minerals were determined using a Karl Fischer potentiometric titration method. An instrument, consisting of a moisture vaporizer (VA-21, Mitsubishi Chemical Corporation, Japan) and a moisture detector (Moisture meter CA-07, Mitsubishi Chemical Corporation, Japan), was used. A weighted sample (usually 0.3 to 0.5 g) was heated (200°C) in the vaporizer under a dry nitrogen carrier gas stream (300 mL/min) and fed to the detector section. The titration was performed until the delta of the electric potential difference reached 0.4 \mu\text{g-H}_2\text{O/s.}

Aquamicron AX and CXU (Mitsubishi Chemical Corporation, Japan) were used as the anodic and cathodic electrolysis solvents, respectively. The primary particle size and its distribution were determined using a laser diffraction particle size analyzer (LA-920, Horiba, Ltd., Japan) in a water suspension. The aqueous slurry (5 wt%) was prepared by undergoing a 3 h agitation and it was sonicated for a further 5 min before the measurement was taken. The total amount of acid sites in the clay minerals was evaluated by titration with Hammet indicators of anthraquinone (pKa<−8.2), benzalacetophenone (pKa<−5.6), dicinnamalacetone (pKa<−3.0), benzeneazodicophenylamine (pKa<−1.5), and methyl red (pKa<+4.8), while 2,6-dimethylpyridine was used as a titration agent. The titration procedures were all performed under a nitrogen atmosphere. A small amount of clay minerals (50–100 mg) was weighed and suspended in highly dehydrated toluene. Next, one of the indicators corresponding to the target pKa was added to the suspension. The end point of titration was determined using ultraviolet (UV)-visible (VIS) spectroscopy (PMA-11, Hamamatsu Photonics K.K., Japan) according to a procedure described in the literature (Tayano et al., 2016b).

**Characterizations of polypropylene.** Melting points of the polymers were determined by differential scanning calorimetry (DSC, DSC-6200, Seiko Instruments, Ltd., Japan). The polymer sample was pressed to obtain a sheet with a Mini Test Press MP-SNL (Toyo Seiki, Ltd., Japan) apparatus. The compression was first conducted at 0 MPa for 7 min, followed by 10 MPa for 3 min. After cooling the sheet for 3 min using another press machine (Mini Test Press MP-SC, Toyo Seiki, Ltd., Japan) that operated under 15 MPa of pressure at 30°C, the sheet was cut to obtain 4–6 mg of sample, which was used for DSC measurement. The first melting process was performed by increasing the temperature from 40 to 200°C (heating rate of 100°C/min). After holding the temperature at 200°C for 5 min, the sample was cooled to 40°C at a rate of 10°C/min and held at 40°C for 1 min. The second melting process was performed at a heating rate of 10°C/min up to 200°C and the melting point temperature was then determined. The polymer's molecular weight and its distribution were determined using gel permeation chromatography (GPC, ALC/GPC 150C, Waters). o-Dichlorobenzene was used as the GPC solvent and the measurement was performed at 140°C. The molecular weight of PP was calculated via a universal calibration method based on the retention volume of standard polystyrenes (PS) (Toosoh Corporation, Japan) using the following intrinsic viscosity ([η])-molecular weight (M) relationships.

\[
[\eta]=1.38\times10^{-4}\times M^{0.70} \quad \text{for PS}
\]

\[
[\eta]=1.03\times10^{-4}\times M^{0.78} \quad \text{for PP}
\]

Microstructures of the polymers were determined by $^{13}$C-NMR (Tsitusui et al., 1989). The polymer solutions were prepared in o-dichlorobenzene (as a solvent) and benzene-$d_6$ (as an internal lock) in a 10 mm diameter sample tube. The $^{13}$C-NMR spectra were recorded using a JEOL GSX-400 FT-NMR spectrometer at a 90° pulse angle, a pulse repetition time of 15 s, and 6,000 scans at 130°C.

**RESULTS AND DISCUSSION**

**Comparison of the basic properties of raw montmorillonites**

Table 1 shows the characterization results of the raw Benclay KK and Kunipia F montmorillonites. In addition, the literature data of Benclay SL were also used for comparison (Tayano et al., 2016b). The degree of isomorphous substitution in the octahedral sheets was different for each kind of clay mineral, based on the values of Mg and Fe contents (Watanabe, 2009a). The differences are ascribed to the natural materials themselves. Similar to Benclay SL (Tayano et al., 2016b), the qualitative Hammett titration of Benclay KK and Kunipia F did not show any presence of acidic characteristics.

Figure 2 shows the XRD patterns of Benclay KK and Kunipia F, as well as those from the reference material of Benclay.
SL. All the materials showed a typical montmorillonite structure, with the signals of (001) ($2\theta \approx 7^\circ$), (110) ($2\theta \approx 20^\circ$), and (004) ($2\theta \approx 28^\circ$). It was confirmed that both Benclay SL and Benclay KK contained cristobalite (denoted as “C” in Figure 2) whereas Kunipia F contained quartz (denoted as “Q” in Figure 2) as impurities (Watanabe, 2009a; Elzea and Rice, 1996). It should be noted that the XRD results shown in this study belong to the as supplied clay minerals (i.e., not dried). Therefore, the slightly larger interlayer distance of $d(001)=1.26\text{ nm}$ (calculated from the $2\theta$ value of (001)) indicates the presence of water in the interlayer. Based on a Karl Fischer evaluation of the non-dried Kunipia F, the water content was determined at 16.3 wt%, which was basically comparable to the reported reference values, i.e. 8.9 wt% (Novokshonova et al., 2005) and 14.9 wt% (Camejo-Abreu et al., 2014).

On the other hand, the dried materials contained very little H$_2$O as listed in Table 1. In Figure 3, the expanded XRD patterns show a comparison of the interlayer distances between the non-dried (Figure 3a) and dried materials (Figure 3b). It was confirmed that the (001) reflection for the dried materials shifted to $2\theta=9.1^\circ$ ($d(001)=0.97\text{ nm}$). The peaks around $2\theta=5–6^\circ$ in Figure 3b are attributed to the background diffraction from the Kapton film that was used for the airproof sample holder.

As shown in Table 1, each type of clay mineral showed a very different BET area characteristic. The BET area of Kunipia F was one order smaller than those of Benclay SL and Benclay KK. It is known that the BET measurement of smectite only detects the outer faces’ surface area (i.e., the basal plane and edge) but does not include the interlayer sheets’ surface (Watanabe, 2009c). Therefore, the very small BET area of Kunipia F may suggest a smaller portion of edge compared to Benclay SL or Benclay KK.

To gain a better understanding of the different BET areas, the primary particle sizes of the clay minerals were investigated. Figure 4 shows the primary particle size distributions of the clay minerals as determined in aqueous dispersion. Each clay mineral had a different size. The average particle sizes of Benclay SL and Benclay KK were in the submicron range while that of Kunipia F was in the micron range. It is plausible that small particles tend to have large edge/face proportion as a result of large SA.

Each type of raw montmorillonite showed different properties owing to the distinctive natural materials. As previously reported (Tayano et al., 2016a), the structure’s edge plays a key part in creating the active metallocene species with respect to acid-treated montmorillonites and this seems to correspond to the high reactivity of the edge (Watanabe, 2009d). Therefore,
it is within reason to predict that Kunipia F may produce a relatively poor catalytic performance because of its edge's small SA.

**Changes in montmorillonite property via acid treatment**

To use Benclay KK and Kunipia F as S-As, their acid treatments were performed. Table 2 summarizes materials that were obtained after the acid treatment, along with the reference data of Benclay SL. In general, the H$_2$SO$_4$ treatment of montmorillonite decreased the Al/Si ratio (i.e., increased the ΔAl) as the reaction time increases. Figure 5-a shows the reaction time dependency of the Al cation extraction process from the clay minerals. Kunipia F showed a slightly slower extraction rate in comparison to other montmorillonites. However, the surface areas of the acid-treated materials shown in Figure 5-b were inconsistent with the Al extraction behavior. This may be attributed to a fewer number of edges in Kunipia F, resulting from the low SA and large primary particle size of this particular raw clay mineral.

In all of the raw montmorillonites, the amount of acid sites determined using a titration procedure with Hammett indicators was negligible. However, after the acid treatment, strong acid sites were formed as shown in Figure 5-c. As we have reported previously (Tayano et al., 2016a, b), Al extraction via the acid treatment of montmorillonite occurs at the edge of the layered structure, with strong acid sites appearing at the structure’s edge and the pore size distribution is changed by the formation of small-sized pores. Herein, 2,6-dimethylpyridine adsorption tests were conducted with the acid-treated Kunipia F sample (ΔAl = 28.3%, and the strong acid sites ($pK_a < -8.2$) = 150 µmol/g-clay) in order to characterize the acidic sites’ location in the clay mineral.

Figure 6-a shows the expanded XRD patterns of the acid-treated Kunipia F at the (001) face region. Before the addition of 2,6-dimethylpyridine, the diffraction from (001) appeared at 9.1°, which indicated that the clay interlayer was completely closed. After the addition of 2,6-dimethylpyridine, the intensity of $2\theta = 9.1^\circ$ weakened and a peak at around $2\theta = 7.2^\circ$ was observed. This new peak was assigned as expanded (001), attributed to the intercalation of the 2,6-dimethylpyridine molecules.

Herein, we evaluated the intercalation behavior by observing the change in the (001) diffraction intensity. The relative amount of intercalated clay could be estimated by the intensity ratio $I_{low}/(I_{low}+I_{high})$, where $I_{low}$ and $I_{high}$ are the average

![Fig. 4. Primary particle size distribution of the montmorillonites.](image)

Table 2. Properties of acid-treated montmorillonites.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Reaction time (h)</th>
<th>Al/Si (mol/mol)</th>
<th>ΔAl$^b$ (%)</th>
<th>PV (cm$^3$/g)</th>
<th>SA (m$^2$/g)</th>
<th>$pK_a &lt; -3.0$ (µmol/g)</th>
<th>$pK_a &lt; -5.6$ (µmol/g)</th>
<th>$pK_a &lt; -8.2$ (µmol/g)</th>
<th>H$_2$O (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benclay KK</td>
<td>0</td>
<td>0.319</td>
<td>0.0</td>
<td>0.140</td>
<td>80.8</td>
<td>ND$^b$</td>
<td>ND$^b$</td>
<td>ND$^b$</td>
<td>0.08</td>
</tr>
<tr>
<td>KK-1</td>
<td>0.67</td>
<td>0.276</td>
<td>13.5</td>
<td>0.240</td>
<td>209</td>
<td>430</td>
<td>220</td>
<td>210</td>
<td>---</td>
</tr>
<tr>
<td>KK-2</td>
<td>2.50</td>
<td>0.233</td>
<td>27.0</td>
<td>0.339</td>
<td>287</td>
<td>410</td>
<td>240</td>
<td>180</td>
<td>0.12</td>
</tr>
<tr>
<td>KK-3</td>
<td>5.00</td>
<td>0.156</td>
<td>51.1</td>
<td>0.494</td>
<td>358</td>
<td>500</td>
<td>270</td>
<td>210</td>
<td>---</td>
</tr>
<tr>
<td>Kunipia F</td>
<td>0</td>
<td>0.413</td>
<td>0.0</td>
<td>0.040</td>
<td>7.7</td>
<td>ND$^b$</td>
<td>ND$^b$</td>
<td>ND$^b$</td>
<td>0.05</td>
</tr>
<tr>
<td>F-1</td>
<td>2.00</td>
<td>0.364</td>
<td>11.9</td>
<td>0.193</td>
<td>131</td>
<td>460</td>
<td>260</td>
<td>90</td>
<td>---</td>
</tr>
<tr>
<td>F-2</td>
<td>5.00</td>
<td>0.296</td>
<td>28.3</td>
<td>0.287</td>
<td>176</td>
<td>160</td>
<td>420</td>
<td>150</td>
<td>0.17</td>
</tr>
<tr>
<td>F-3</td>
<td>8.00</td>
<td>0.224</td>
<td>45.8</td>
<td>0.411</td>
<td>204</td>
<td>520</td>
<td>510</td>
<td>160</td>
<td>---</td>
</tr>
<tr>
<td>Benclay SL</td>
<td>0</td>
<td>0.274</td>
<td>0.0</td>
<td>0.209</td>
<td>73.8</td>
<td>ND$^b$</td>
<td>ND$^b$</td>
<td>ND$^b$</td>
<td>0.17</td>
</tr>
<tr>
<td>SL-1</td>
<td>0.52</td>
<td>0.268</td>
<td>2.2</td>
<td>0.259</td>
<td>185</td>
<td>520</td>
<td>230</td>
<td>150</td>
<td>---</td>
</tr>
<tr>
<td>SL-2</td>
<td>1.00</td>
<td>0.233</td>
<td>15.2</td>
<td>0.312</td>
<td>209</td>
<td>240</td>
<td>210</td>
<td>110</td>
<td>---</td>
</tr>
<tr>
<td>SL-3</td>
<td>3.70</td>
<td>0.173</td>
<td>36.8</td>
<td>0.379</td>
<td>248</td>
<td>300</td>
<td>220</td>
<td>110</td>
<td>---</td>
</tr>
<tr>
<td>SL-4</td>
<td>8.00</td>
<td>0.096</td>
<td>65.0</td>
<td>0.535</td>
<td>283</td>
<td>630</td>
<td>300</td>
<td>150</td>
<td>---</td>
</tr>
<tr>
<td>SL-5</td>
<td>16.3</td>
<td>0.054</td>
<td>80.3</td>
<td>0.598</td>
<td>286</td>
<td>700</td>
<td>90</td>
<td>90</td>
<td>---</td>
</tr>
</tbody>
</table>

a) ΔAl is the percentage of Al cation extracted by acid treatment as defined by:

$$\Delta Al = \left(1 - \frac{(Al/Si)_{t}}{(Al/Si)_{0}}\right) \times 100$$

where, (Al/Si)$_0$ and (Al/Si)$_t$ are the Al/Si ratios of the initial (raw) montmorillonite and the acid-treated material for a specific acid treatment reaction time (t), respectively.

b) "ND" in the table indicates "not detected."
intensity (background is subtracted) at 2\(\theta\) = 7.2° and 9.1°, respectively. Figure 6-b illustrates the changing intensity ratio as a function of the added amount of 2,6-dimethylpyridine. With an increasing pyridine amount, the intercalation proceeded monotonically. However, the change in the intensity ratio versus the added pyridine amount was not a linear relationship but showed a sigmoidal growth pattern instead. This indicated that some of the pyridine molecules were trapped on the clay mineral’s surface as opposed to being used for intercalation. Owing to the basicity of pyridine, the acid sites of the clay mineral interacted readily with the base and pyridine adsorption occurred at the strong acid sites. The strong acid sites formed by the acid treatment are presumably located on the outside of the interlayer and possibly at the edge of the acid-treated clay mineral particles (Tayano et al., 2016a).

Based on the acid treatment results of the different montmorillonites, the influence of acid treatment on the clay mineral can be summarized as follows:

1) The Al cation extraction corresponded to prior reports that were mentioned in the introduction.
2) The acid treatment induced an increase in SA and PV.
3) The strong acid sites were located at the edge of the layers (not interlayers), where the structure was disordered by the acid treatment.
4) The differences observed among the various kinds of montmorillonites included the Al extraction rates and the values of SA, which were attributed to the differences in the primary particle size of the raw materials.

Investigation of general S-A characteristics in determining the catalytic activity

Confirmation of acid sites’ metallocene activation capability of acid sites in S-A. As demonstrated in our previous work (Tayano et al., 2016b), acid-treated Benclay SL having strong acid sites (\(pK_a<−8.2\)) are always effective in deriving highly active metallocene catalysts for propylene polymerization. In this work, in order to prove that a strong acid on the acid-treated montmorillonite is essential for the metallocene activation chemistry, we carried out propylene polymerization using an alkyl aluminum-free system according to the experimental procedure that was used for ethylene polymerization (Takahashi et al., 2002). The objective of using the alkyl-aluminum free system test was to confirm the polymerization capability of the catalytic system by excluding the possibilities of methylalumoxane-like contamination. As described in the "MATERIALS AND METHODS" section, a large quantity of Ind-Hf-Me₂ (3000 \(\mu\)mol/g-clay) was introduced into the polymerization reactor for impurity scavenging and 0.16 g of the acid-treated Benclay KK, which contained 0.12 wt% of H₂O (obtained by drying the acid-treated material at 200°C for 2 h) was used as the activator. It is widely known that the active metallocene species for olefin polymerization is the metal–alkyl cation (Chen et al., 2000; Bochmann, 2010; Bryliakov et al., 2007). With respect to the alkyl-aluminum containing catalyst system, it can work as an alkylation reagent for the metal-dichloride metallocene complex. However, in alkyl-aluminum free system, it is impossible to form the metal–alkyl species. Thus, the Ind-Hf-Me₂ dimethyl compound was used as the starting material for this particular polymerization test. As shown in Table 2, the montmorillonite sample had 180 \(\mu\)mol/g-clay of acid sites with a \(pK_a\) strength of <−8.2. Meanwhile, the alkyl-aluminum free system showed 465 g-PP/g-clay h activity.

As a reference, a polymerization process was repeated un-
Montmorillonite-based "Support-Activator" for metallocene-catalyzed propylene polymerization

Montmorillonite-based Support-Activator for metallocene-catalyzed propylene polymerization

under the same aforementioned conditions except for the use of raw Benclay KK (containing 0.07 wt% of H₂O and no acid site was detected by Hammett titration) instead of the acid-treated material. The polymerization activity was 9 g-PP/g-clay h, which was markedly lower in comparison to the acid-treated clay mineral. These results clearly indicated that the acid sites in the clay minerals were able to activate the metallocene complex without involving any alumoxane-like components. Based on an analogous metallocene activation mechanism that was proposed previously (Chen et al., 2000), the strong acid sites in montmorillonite are capable of inducing the methyl anion elimination from the metallocene dimethyl compound to form the active metal-methyl cation species (Nakano et al., 2006).

Relationships between S-A properties and polymerization activity. In this section, the characteristics of the acid-treated montmorillonites were correlated to the catalytic activity of the propylene polymerization reaction. Table 3 summarizes the propylene polymerization activities and the resulting polymer's characterization data. Catalysts prepared from the raw clay minerals of Benclay KK and Kunipia F contained some amounts of Zr but their activities were markedly low. This indicated that the Zr on raw clay mineral was not effectively activated owing to the lack of strong acid sites. The Zr contents and activities of the catalysts prepared using the acid-treated montmorillonites drastically increased in com-

Table 3. Propylene polymerization activities and the resulting polymer's properties, obtained using three different montmorillonite-based support activators.

<table>
<thead>
<tr>
<th>Samples</th>
<th>[Zr] (µmol/g)</th>
<th>Activity (g-PP/g-cat)</th>
<th>Tm (°C)</th>
<th>Mw x10³</th>
<th>Mw/Mn</th>
<th>Stereo regularity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benclay KK</td>
<td>3.1</td>
<td>84</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>KK-1</td>
<td>23.0</td>
<td>1411</td>
<td>150.5</td>
<td>304</td>
<td>2.7</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>KK-2</td>
<td>23.0</td>
<td>1655</td>
<td>150.3</td>
<td>310</td>
<td>3.3</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>KK-3</td>
<td>26.3</td>
<td>2070</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Kunipia F</td>
<td>2.2</td>
<td>1</td>
<td>NA</td>
<td>554</td>
<td>3.2</td>
<td>NA</td>
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<tr>
<td>F-1</td>
<td>8.7</td>
<td>496</td>
<td>150.2</td>
<td>310</td>
<td>3.3</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>F-2</td>
<td>13.2</td>
<td>982</td>
<td>150.2</td>
<td>300</td>
<td>2.6</td>
<td>NA</td>
</tr>
<tr>
<td>F-3</td>
<td>18.8</td>
<td>707</td>
<td>149.4</td>
<td>310</td>
<td>2.9</td>
<td>99.9</td>
</tr>
<tr>
<td>Benclay SL</td>
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<td>29</td>
<td>NA</td>
<td>315</td>
<td>2.8</td>
<td>99.9</td>
</tr>
<tr>
<td>SL-1</td>
<td>18.6</td>
<td>1299</td>
<td>150.7</td>
<td>309</td>
<td>2.7</td>
<td>99.6</td>
</tr>
<tr>
<td>SL-2</td>
<td>NA</td>
<td>1250</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>SL-3</td>
<td>NA</td>
<td>1449</td>
<td>150.4</td>
<td>309</td>
<td>3.3</td>
<td>99.9</td>
</tr>
<tr>
<td>SL-4</td>
<td>21.9</td>
<td>1317</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
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<tr>
<td>SL-5</td>
<td>17.5</td>
<td>852</td>
<td>150.5</td>
<td>296</td>
<td>2.8</td>
<td>996</td>
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<tr>
<td>Control</td>
<td>—</td>
<td>No polymer</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

a) Zr content in catalyst as determined by XRF.
b) Propylene bulk polymerization at 70 °C for 1 h without adding hydrogen.
c) Tm (melting point) as determined by DSC.
d) Mw and MWD as determined by GPC.
e) Stereoregularity as determined by ¹³C-NMR, [mmm] (mol%), 2,1- and 1,3-insertions (mol%).
f) "NA" in the table indicates "not analyzed."
g) Polymerization without montmorillonite-based support activators. Propylene bulk polymerization condition: Azu-Zr-Cl₂= 4.5 µmol, TIBA = 4 mmol, time = 1 h, temperature = 70°C.
These observed behaviors were similar to those of Benclay SL (Tayano et al., 2016b). Therefore, the activity enhancement effect could be attributed to the presence of the strong acid sites, independent of the clay mineral source.

However, the absolute level of activity clearly depended on each kind of clay mineral, appearing in the order of Kunipia F<Benclay SL≤Benclay KK. On the other hand, the properties of the resulting polymers such as melting point, molecular weight, molecular weight distribution, and stereoregularity were equivalent in all three clay minerals. This suggested that the chemical properties of the active metallocene species were not changed by the type of montmorillonite or the degree of acid treatment. In other words, the chemical characteristics of the active zirconocene cation were independent of the montmorillonite species. The different activity levels are a reflection of the different number of the active sites in each kind of montmorillonite. As discussed in our previous work with Benclay SL, the activity levels are influenced not only by the strong acid but also the small-sized pore BET area. In Benclay SL, it has been found that strong acid sites (pK<−8.2) are mainly formed in pores with Dp<8 nm (Tayano et al., 2016b). Nonetheless, for the metallocene activation, stronger acid sites with pK values of<−8.2 are necessary and such sites are typically localized in smaller pores with Dp<6 nm. Applying the same principles used in our previous observation, the polymerization activities of the different montmorillonites were analyzed. Herein, the BET area of the small-size pore (Dp<6 nm) was estimated based on the pore volume distribution by assuming a cylindrical shape pore. The analytical plots are shown in Figure 7. By comparing Figure 6-a and -b, the changes in the catalytic activity (Figure 6-b) showed similar behaviors to the changes in BET area at Dp<6 nm (Figure 7-a). In fact, the catalytic activity increased in proportion to the BET area at Dp<6 nm, as shown in Figure 7-c. The data points from all three kinds of montmorillonites formed a linear line.

Based on the literature (Tayano et al., 2016a, b; Rhodes and Brown, 1992; Rhodes and Brown, 1993; Shinoda et al., 1995a, b; Tabernero et al., 2010; Flessner et al., 2001) and the 2,6-dimethylpyridine adsorption test performed in this study, it was postulated that the strong acid sites are located at where the structure is disordered by the acid treatment of the clay mineral. Since acid treatment induces the formation of small-size pores, strong acid sites are plausibly formed in the small pores. As such, it was concluded that the inside of the small-size pores (containing the strong acid) is potentially the main location where the metallocene complex is supported and activated, independent of the kind of montmorillonite used.

CONCLUSIONS

Three kinds of montmorillonite (Benclay SL, Benclay KK, and Kunipia F) were evaluated as “Support-Activators” in S-A supported metallocene catalyst for propylene polymerization. The raw clay montmorillonites have different composition, purity (clay content), and primary particle size owing to the distinctive natural materials. The physical and chemical modifications of the clay minerals, via acid treatment, were performed to (1) increase their surface area (SA) and pore volume (PV) and (2) promote the formation of strong acid sites (pK<−8.2). Based on the 2,6-dimethylpyridine adsorption tests of the acid-treated Kunipia F, it was postulated that the
acid sites were located at the edge (i.e., not at the interlayer) of the clay mineral’s primary particle. Propylene polymerization activities were dependent on the kind of montmorillonite used. However, it could be concluded that the level of catalytic activity is proportionally related to the SA of the small size pores (DP < 6 nm).

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REFERENCES


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