Modification of MgCl$_2$-supported Ziegler-Natta catalyst with Lewis acids for ethylene polymerization

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Abstract – Comparison of MgCl$_2$/AlCl$_3$/DEAC/TiCl$_4$-type supported catalysts by varying the amount of AlCl$_3$ was investigated and used in ethylene polymerization having triethylaluminum (TEA) as a cocatalyst. The effect of AlCl$_3$-doped MgCl$_2$ support showed slightly higher activity than the MgCl$_2$-supported catalyst. The highest catalytic activity at MgCl$_2$/AlCl$_3$ ratio is equal 85 : 15. The addition of AlCl$_3$ causes markedly increase of crystallinity of polymer confirmed by SEM and DSC. The particle morphology of the polymers and catalysts are almost similar after adding AlCl$_3$.

Keyword: Ziegler-Natta catalyst; Polyethylene; MgCl$_2$; AlCl$_3$; TEA
1. Introduction

Polyethylene (PE) has very important roles in polymeric material industry because it has many useful properties, such as low weight, abrasion resistance, corrosion resistance, high impact resistance and superior flexibility. It is well known that appropriate application of polyethylene must depend on its properties. Therefore, the catalyst plays a part of important role to improve its properties.

At present, Ziegler-Natta (ZN) catalyst is studied widely because of its high activity and cheap cost, and controllable morphology of polymer. However, the ZN catalysts can be improved in different ways, such as changing internal electron donors, external electron donors and/or several combinations of both. Modification of MgCl₂ support is one of choices to improve performance of catalyst.

Recently, research articles have shown that doping a suitable amount of Lewis acids in MgCl₂ support causes effective way to improve their catalyst properties. An ZN catalysts modified by doped MgCl₂ with MnCl₂ was prepared by Garoff and Leimonen [1] and with ZnCl₂ that was prepared by Fregonese and Bresadola [2]. Then, Zhiqiang Fan et al. [3-7] investigated Ti catalysts supported on MgCl₂ doped with NaCl and used for 1-hexene and propylene polymerizations. Results showed that NaCl influenced the active center distribution (ACD) of 1-hexene polymerization, influenced a narrower MWD of poly (1-hexene) and broader MWD for polypropylene. Moreover, the preparation of supports can be performed via many methods, such as precipitation, where the supports are dissolved in EtOH and solvent at high temperature, then cool down for precipitation of support. For the ball-milling method, the supports are grounded in the solvent and etc.

In this work, AlCl₃ was chosen as dopant of MgCl₂ support by varying the amount of AlCl₃. It was prepared by the coprecipitation method. Experimentally, MgCl₂/AlCl₃•nEtOH were mixed and reacted with diethyl aluminum (DEAC) via the OH group in MgCl₂/AlCl₃•nEtOH adduct. A series of MgCl₂/AlCl₃/DEAC/TiCl₄-type supported catalysts were prepared and used in ethylene polymerization. The effects of AlCl₃ dosage on the catalyst activity and the crystalline structures of catalyst will be discussed.

2. Materials and experimental

2.1 Materials

Ethylene gas (99.9%) was devoted from National Petrochemical Co., Ltd. Thailand and argon (99.999%) was purchased from Thai Industrial Gas Public Co., Ltd. MgCl₂ anhydrous, AlEt₃ (TEA), diethyl aluminum chloride (DEAC) and AlCl₃ anhydrous were donated from Siam Cement Group Chemical. TiCl₄ was purchased from Sigma-Aldrich Inc. n-Heptane(95%) was purchased from RCI Labscan Ltd. and was purified by refluxing over Na/benzophenone and distilled under Ar atmosphere prior to use. Absolute Ethanol was purchased from MERCK Ltd.

All operations were carried out under an inert atmosphere of argon using a glove box and standard Schlenk technique.

2.2 Experimental

2.2.1 Catalysts preparation

The catalyst was synthesized in a 4-necked 500-ml Schlenk flask that was equipped with a condenser and overhead stirrer. Anhydrous MgCl₂ and/or AlCl₃ were added into the flask containing the AlCl₃ wt% of 0, 5 and 15 under an argon atmosphere glove box. Then Alcohol and DEAC was added into the flask. Finally, TiCl₄ was injected into the flask under stirring. Thereafter the catalyst powder was vacuum dried and stored in a glass bottle under argon.

2.2.2 Ethylene polymerization

The ethylene polymerization was carried out with 2 liters autoclave reactor, Buchii polycylave, connected with the lines available with argon, hydrogen and ethylene gases and also the hexane feed line. The reactor and all the connected feed lines were cleared humid and oxygen first by evacuation with the vacuum pump for 20 minutes, and then followed by purging with the argon gas and evacuation for 10 times for ensuring. The hexane was filled with 1 liter and heated to 80°C. The TEA (Al/Ti molar ratio = 100) was injected into the reactor subsequence by the stirred catalyst. In this condition of presence of hydrogen, the reactor was pressurized with 1 bar of argon followed by pressurizing with hydrogen gas to 3.5 bars and finally pressurizing with ethylene gas to 8 bars and feed the ethylene gas continuously until 2h polymerization was stopped. Then polymer was dried at room temperature overnight and measured the polymer weight.

2.2.3 Characterization

X-ray diffraction (XRD) was used to identify the crystal structure of polymer. The morphologies of the catalysts and polymers were observed by scanning electron microscopy (SEM) (Model JSM-5800LV). Melting temperatures of polymers was determined using differential scanning calorimetry (DSC) (Model Perkin-Elmer DSC7). The Titanium contents of the catalysts were measured by inductively coupled plasma (ICP).

<table>
<thead>
<tr>
<th>Table 1 Ti contents of the catalysts</th>
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<tr>
<td>catalyst</td>
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</tr>
<tr>
<td>A</td>
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<tr>
<td>B</td>
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<tr>
<td>C</td>
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</table>

a Weight percentage found in catalysts. 
b Weight percentage found from AlCl₃/(AlCl₃+MgCl₂).

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3. Results and discussion

3.1 Ti contents of catalysts

The Ti contents found in the catalysts are shown in Table 1. It can be seen that Ti content is not be trended, because these catalysts cannot control Ti content. From the results, it reveals that Ti content of the catalyst C has the highest value, perhaps the amount of MgCl₂/AlCl₃ ratio at 85 : 15 are appropriate with the modification of surface structure of catalyst.

3.2 Ethylene polymerization

The Activity of ethylene polymerization catalyzed by MgCl₂ doped with AlCl₃ catalysts are shown in Fig.2. It can be seen that the catalyst modified with AlCl₃ has markedly increased catalyst activity than the unmodified catalyst. The small amount of AlCl₃ can be change to higher catalytic activity and when increasing the amount of AlCl₃, it still tends to exhibit higher catalytic activity until MgCl₂/AlCl₃ ratio is equal 85 : 15 that is the highest catalyst activity. This means that AlCl₃ has an important role for active support of titanium tetrachloride when using with magnesium chloride support.

3.3 XRD analysis of polyethylene

XRD patterns of the polyethylene are shown in Fig.2, the profile of polyethylene from catalyst A to catalyst C are similar, but it can be observed that at 2θ = 20-25⁰, the polymer from catalyst A has the lowest peak and tends to sharper peak when increasing amount of AlCl₃. This means that AlCl₃ leads to more crystallinity of the polyethylene.

3.4 differential scanning calorimetry (DSC)

Melting temperature (Tₘ) and crystallinity (Xₑ) of polyethylene are shown in Table 2. It can be seen that adding AlCl₃ leads to markedly increased crystallinity as seen from XRD patterns of polyethylene as aforementioned. The higher amount of AlCl₃ has no effect to crystallinity. The polyethylenes that produce from the catalyst modified with AlCl₃ and unmodified with AlCl₃ have no effect on the melting temperature.

3.5 scanning electron microscopy (SEM)

The particle morphology of catalyst and polyethylene polymer are shown in Fig. 3 and 4, respectively. From Fig.3, it can be observed that there is almost no difference particle morphology of polymer when changing catalysts. The particle morphology of catalyst can be also observed from the Fig.4 indicating almost no difference in shape and surface when changing amount of AlCl₃.

Table 2 Crystallinity and melting temperature of polyethylene analyzed by differential scanning calorimetry (DSC)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>%Xₑ</th>
<th>Tₘ(°C)</th>
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<tbody>
<tr>
<td>A</td>
<td>40.8</td>
<td>134.4</td>
</tr>
<tr>
<td>B</td>
<td>58.9</td>
<td>134.6</td>
</tr>
<tr>
<td>C</td>
<td>55.8</td>
<td>134.5</td>
</tr>
</tbody>
</table>

* Polymer A, B and C synthesized by catalyst A, B and C, respectively.

Fig.2 XRD pattern of ethylene polymer

4. Conclusion

The effect of AlCl₃-doped MgCl₂ support showed slightly higher activity than the MgCl₂-supported catalyst. It exhibits the highest catalytic activity at MgCl₂/AlCl₃ ratio is equal 85 : 15. From XRD patterns and crystallinity (Xₑ), it confirms that the addition of AlCl₃ causes higher crystallinity of polymer. When increasing the amount of AlCl₃ doped in catalyst, there is almost no difference in shape and structure as observed by SEM. In the same way, the particle morphology of the polymers is almost no difference when changing amount of AlCl₃ in the support.

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5. acknowledgment

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References