

Novel Clay-Mineral-Supported Metallocene Catalysts for Olefin Polymerization

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Introduction

Since the discovery of metallocene-methylalumoxane (MAO) catalyst system by Sinn and Kaminsky many efforts to develop the improved co-catalyst have been reported¹. One of the objects to study is reducing the catalyst cost due to the expensive co-catalyst. Even though MAO is good co-catalyst for metallocene, it tends to be expensive due to high cost of raw materials, such as trimethyl aluminum (TMA). Moreover, large excess of MAO is normally needed to achieve the high catalyst activity. Mitsubishi Chemical Corporation and Japan Polychem Corporation (JPC) found that several clay minerals were capable of activating metallocene complex without using MAO.²⁻⁴ As clay-minerals also work for an excellent catalyst support by themselves, we call it "Support-Activator". In 2001 JPC started to commercialize metallocene-based propylene random copolymer "WINTEC[®]" which showed very low melting point, by using this catalyst system⁵. In this paper, we report the features of clay-mineral "Support-Activator" and the studies of activation of this catalyst system.^{6,7}

Features of clay-mineral "Support-Activator"

Structural and chemical features of clay minerals

Clay minerals are selected out by paying attention to the features as follows:

- Acidic site and basic field.
- Exchangeable interlayer-cation.
- Layered structure.
- Cleavability.

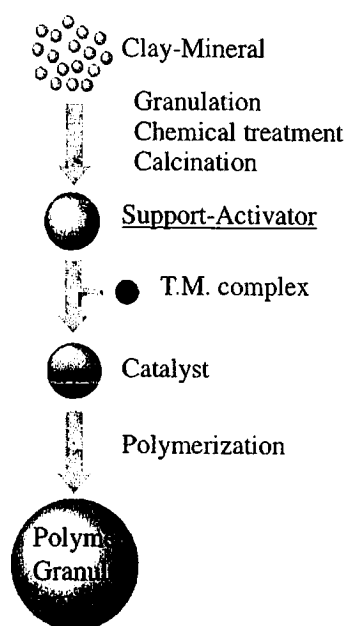
At the beginning of investigation several clay minerals were evaluated as the co-catalyst of metallocene catalyst for olefin polymerization. These results showed clay minerals were capable of working as co-catalyst and clay mineral with the higher acidity tended to show higher activities. By modifying the acidity of the clay minerals with various approaches extremely high active

co-catalyst system named "Support-Activator" has been developed.

Performance of clay-mineral "Support-Activator"

Performances of "Support-Activator" are summarized as follows:

- High activity and low residue.
- Polymer powder of good morphology.
- Non-hazardous and stable under air and heat.
- Low catalyst and product cost.
- Capable of activating "post" metallocenes and others.



Scheme 1. Preparation and use of clay-mineral supported catalyst

Typical "Support-Activator" is prepared as shown in scheme 1. The choice of clay mineral species and chemical treatments are the important factors to control the features as an activator. Chemical treatment also enables the control of catalyst

reactivity and polymer properties such as molecular weight distribution, comonomer distribution, and branching. Polymer powder morphology has been controlled by the granulation step from the clay mineral fine particles.⁴

Activation of clay-mineral-supported catalyst system

We have reported that the essential factor of activation of metallocene by clay-mineral is its acidity.^{6,7} In this paper the catalyst system composed of acid treated montmorillonite with high acidity ($pK_a < -8.2$) and $rac\text{-Me}_2\text{Si}(2\text{-Me-4-Ph-1-Ind})_2\text{ZrCl}_2$ (PID) has been studied by UV-vis spectroscopy in solid state for the purpose of investigating the activation mechanism. Main peak at 540nm shifted to longer wave length by contacting with acid treated montmorillonite as shown in Figure 1. This change was assigned to the formation of cationic metallocene species, by the analog of the UV spectra with reaction mixture of the corresponding dimethyl complex (PIDM) and tris(pentafluorophenyl)boron (B-1) or tetrakis(pentafluorophenyl)borate compound (B-2) in solution as shown in Figure 2. And the prediction by Quantum chemical calculation analysis also supports this speculation. The UV-vis spectral shift has been retarded by the pretreatment of montmorillonite with 2,6-dimethylpyridine (DMP) to the amount of 0.2mmol/g-montmorillonite before contacting with metallocene and most of the metallocene remained neutral. These suggest that strong acidity of montmorillonite might have the role of producing the cationic species. We will also discuss the correlation between the catalyst activity and the change of UV-vis spectroscopy.

References

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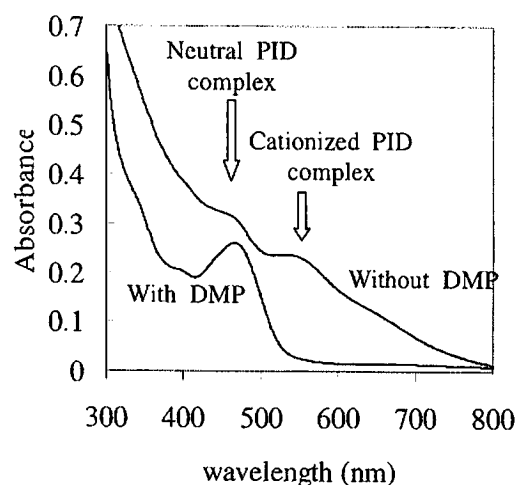


Figure 1. Solid-state UV-vis spectra of the clay mineral supported catalysts with and without DMP

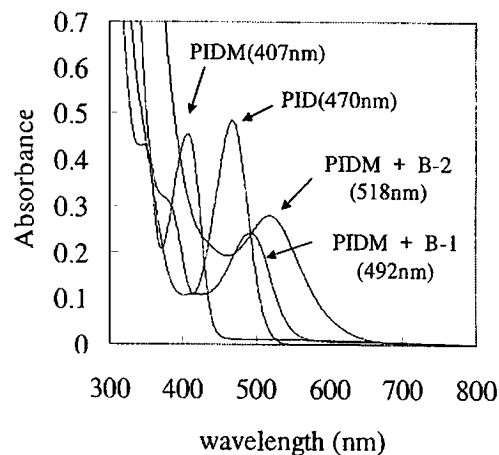


Figure 2. Solution-state UV-vis spectra of Metallocene complexes and mixtures with metallocene dimethyl and boron compounds