Activation of Cp_2ZrCl_2 using common alkylaluminum supported on clay materials for ethylene polymerization

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Introduction

A metallocene catalyst precursor can be activated by aluminoxanes, especially methylaluminoxane(MAO). MAO was the product of the partial hydrolysis of trimethylaluminum(TMA) with water and much large excess amount of MAO was needed. Novokshonova[1] et.al. synthesized the aluminoxane on zeolite by partial hydrolysis of TMA with inside zeolite water and then forms the heterogenized complexes with Cp_2ZrCl_2. Using these catalysts they carried out the ethylene polymerization without addition of free MAO. Suga[2] and Weiss et. al.[3] could polymerize the ethylene over Cp_2ZrCl_2 using montmorillonite by partial hydrolysis of aluminumalkyl without addition of MAO.

In this works, we prepared the fixed organoaluminum compounds as the product of TMA partial hydrolysis with water in clays and was used to ethylene polymerization. The effects of the water and acidity of the clay were investigated in the polymerization on clay/TMA-Cp_2ZrCl_2 systems.

Results and Discussion

The TMA was reacted with montmorillonite K-10(MMTK-10) in toluene, and then this slurry was used to polymerize ethylene over Cp_2ZrCl_2 without introduction of the free MAO as shown in Table 1. The Cp_2ZrCl_2 impregnated on the TMA treated hydrated MMTK-10 shows higher activity than that of dehydrated MMTK-10 at the same Al/Zr ratio. It may be due to larger amount of the aluminum compounds impregnated on the hydrated MMTK-10 than that of dehydrated MMTK-10. Also, high activity in hydrated MMTK-10 was due to smaller amount of free TMA than that of dehydrated one. Without regard to the presence of water in the clay, these showed catalytic activity for ethylene polymerization.

In order to survey the role of the water in the montmorillonite, we investigated the other type of montmorillonite such as Kunipia. The Kunipia was reacted with TMA in toluene, and then this slurry was used to polymerize the ethylene. But, as shown in Table 2, it did not show the catalytic activity for the ethylene polymerization even though it contained 10% of the water over Cp_2ZrCl_2. On the contrary, when MAO was impregnated on Kunipia, the Cp_2ZrCl_2 impregnated on it showed the catalytic activity for ethylene polymerization. When it was acidified by inorganic material such as $ZrOCl_2$, the acidity of the kunipia was changed to pH 1.2 from pH 10.0. The partial hydrolysis of TMA with acidified kunipia with $ZrOCl_2$ was conducted in

toluene, and this slurry was used to polymerize the ethylene over Cp_2ZrCl_2. It showed the high catalytic activity unlike using the unmodified kunipia as shown in Table 2.
So, if the MAO was synthesized by partial hydrolysis of TMA with water on the kunipia and impregnated on it, the Cp_2ZrCl_2 should show the catalytic activity for the ethylene polymerization using this treated clay material. Therefore, we did not convinced that the MAO was synthesized in the kunipia as a result of partial hydrolysis of TMA with water.
The organic aluminum compounds have been prepared on surface of the clay by reaction of partial hydrolysis of trimethylaluminum with hydroxyl group, where is surface of clay such as acidic montmorillonite K-10 and basic kunipia. Without regard to the presence of water in the clay, the Cp_2ZrCl_2 impregnated on modified montmorillonite by TMA showed catalytic activity for ethylene polymerization when acidic montmorillonite K-10 was used, while in case of basic kunipia it did not show the catalytic activity for ethylene polymerization.

Table 1. Effect of dehydration of montmorillonite on ethylene polymerization

MMTK-10	Zr (μmol)	Al[a)]/Zr ratio	Al[b)]/Zr (TMA)	Activity	Mυ (g/mol)	Tm (℃)
Hydrated	20	300	150	519	274,533	135.4
Dehydrated	20	300	220	217	307,028	134.5

Activity: kg-PE/mol-Zr.hr.atm
Polymerization Conditions: Clay: 1g, Temp.: 50℃, Pressure: 3.4atm, Time: 1hr
(a) Total aluminum injected to the reactor with the form of clay slurry
(b) Al as TMA

Table 2. The relationship between pH of the clay and catalytic activity.

	Kunipia/ TMA	$ZrOCl_2$/Kunipia/TMA	Kunipia/ MAO	MMTK-10/ TMA
pH	10.0	1.2	-	3.2
Activity	Trace	2,300	125	1,000

Activity: kg-PE/mol-Zr.hr.atm
Polymerization Conditions: Temp:50℃, Pressure:1atm, Time:1hr, Clay:0.5g

References

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