



Indirect synthesis of Bis-2PhIndZrCl₂ Metallocene catalyst used for ethylene polymerization

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Abstract

Bis(2-PhInd)ZrCl₂ was simply synthesized indirect via the intermediating bis(2-PhInd)ZrMe₂ compound from 2-Phenylindene and four equivalents of MeLi. The final product was achieved by use of halogenating agent (HCl). This method although requires two equivalents MeLi more but it still has some advantages. The bis(2-PhInd)ZrCl₂ is obtained in higher yield compared to the classic method, easier to purify and free from LiCl, since LiCl can be removed efficiently by filtration from the more soluble dimethyl complex. Effect of cocatalyst concentration on homopolymerization of ethylene was investigated. Activity of the catalyst was increased with Al/Zr up to 2333 then decreased with further Al concentration.

Keywords: Metallocene catalyst – Synthesis – Bis(2Ph-Ind)ZrCl₂ –Ethylene polymerization

Introduction

As one of the olefin polymerization catalysts metallocene have been at the center of the attention in the past decade and their importance reflected by series of reviews on the topic [1,2]. Single site catalysts have more advantages than multi site catalysts (Ziegler-Natta). The major advantage of these group catalysts is that they can tailor the molecular architecture of polymer by subtle changes in ligand structure. The comonomer incorporation and its distribution are more excellent and uniform in comparison to multi site catalysts [3,4]. The most serious steps in synthesis of these catalysts are purification and preparation steps. In this work the produced catalyst was used for ethylene polymerization.

Experimental

Material

All operations were carried out in dry nitrogen. MeLi and HCl solution in Et₂O were purchased from Acros. 2-Phenylindene and MAO (10% wt solution in toluene) were prepared from Aldrich. Toluene and Et₂O were purchased from Luba (India) and all of them were refluxed and distilled over drying agent before use.

Polymerization

Ethylene polymerization was performed in 450 ml toluene in a 1 liter Buchi reactor that connected to constant temperature circulator. Toluene was introduced into the reactor and saturated with 1 atm ethylene at the required temperature. The polymerization components were added in the following orders; MAO and the catalyst solution. After 1 h reaction, the polymer was poured into an excess amount of methanol, filtered and dried.

Result & Discussion

The growth in application of metallocene catalysts led to improvement of the catalyst synthesis procedure. The schematic of indirect method was shown in Figure 1. The ligand was reacted by two equivalents MeLi and then reacted by MtCl₄. The final product was obtained by use of halogenating agent to replace the chloride group in place of methyl group. In this method the final product was provided simply and quantitatively.

Catalyst Synthesis (Indirect method)

MeLi (12 ml of a 1.6 M solution) was added over a period of about 5 min at room temperature to 2-Phenylindene (1.24 gr) dissolved in 30 ml Et₂O. During the addition gas evolution was observed. The

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mixture was stirred for 40 min and then it was added at once to $ZrCl_4$ (5 mmol, 1.17 gr) dispersed in toluene (30 ml). The suspension was stirred for 90 min at room temperature. The product was filtered. The filtrate was treated at room temperature with HCl (5 mmol) and stirred 60 min; during the addition gas evolution was observed. The final product was obtained by removing the solvent under reduced pressure.

Ethylene polymerization

Cocatalyst concentration

The influence of the cocatalyst concentration on the activity of the catalyst is shown in Table 1. Activity of the catalyst was increased with Al/Zr up to 2333 then decreased with further Al concentration. The excess MAO probably shifted the reaction equilibrium toward generation of the inactive species. This phenomenon might be attributed to excessive complexation of MAO with active centers. Therefore, the vacant coordination positions at these active centers become unavailable for monomer complexation[5,6].

Conclusion

The indirect method used for preparation of bis(2-PhInd)ZrCl₂. The indirect method has some advantages: simple and more quantitative, the product in the final step has volatile by product (CH₄) and free from LiCl.

The bis(2-PhInd)ZrCl₂ catalyst showed high activity in ethylene polymerization. The evaluation of ethylene polymerization with this catalyst demonstrated that the activity of catalyst severely is depended on cocatalyst concentration.

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Table 1 Effect of Cocatalyst on ethylene polymerization.

Al/Zr	Activity ^a	Tm
833	467	135.23
1250	3567	139.35
1667	5733	139.16
2333	6433	138.97
3000	4767	138.93
3667	3667	135.71

Conditions: Pt= 2 bar, temp= 60 °C, toluene= 450 ml, [cat]= 3.0*10⁻⁶ mol Zr,

a) Activity: kg Polymer/ mol Zr.hr.

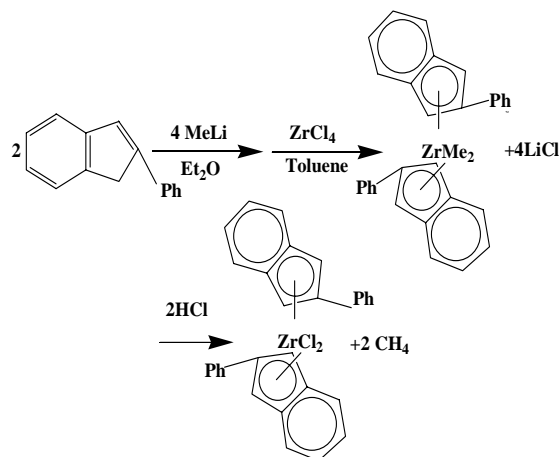


Figure 1 Schematic of indirect method.