



New FI Zr-based Catalyst for Ethylene Polymerization

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Abstract

A new FI Zr-based catalyst of Bis[N-(3,5-dicumylsalicylidene)-naphtylaminato]zirconium(IV) dichloride was found to display a moderate ethylene polymerization activity of 37×10^4 g PE/mmol Zr. h with a viscosity average molecular weight (\overline{M}_V) of 2.8×10^4 using triisobutylaluminum (TIBA) and methylaluminoxane (MAO) as scavenger and cocatalyst respectively. Despite the moderate activity, the catalyst showed a life time longer than the other similar FI catalysts. The naphtyl substituted phenyl ring on the N provided longer durability. The Rate/time profile for the catalyst was almost stable which indicates longer life time of its catalytic activity. The highest activity of the catalyst was obtained at about 30-40 °C, however activity of the catalyst was almost stable with increasing the temperature. Some specification of the obtained polymer was studied.

Keywords: catalytic polymerization, FI catalyst, Zr-based catalys, olefin polymerization, polyethylene.

Introduction

Recently, new classes of metal complex have been studied as precursors for a new generation of olefin polymerization [1,2]. Specially ethylene polymerization catalysts have been developed from phenoxy-imine and diimine ligands [3]. A new FI Zr-based catalyst was prepared and used for ethylene polymerization. Polymerization results showed that the prepared catalyst comprising naphtyl ring on the catalyst structure could increase the thermal stability and durability of the catalyst activity as well. Ethylene polymerization was studied at different conditions. Some specification of the obtained polymer was investigated.

Result and Discussion

Polymerization of ethylene was carried out using the prepared catalyst (Figure 1) at different conditions in toluene. The polymerization activity increased with addition of MAO to a maximum activity of 37×10^4 g PE/(mmol Zr. h) in the range studied. The highest activity of the catalyst was obtained at about 35 °C.

Polymerization activity was slowly rise to a maximum values within 30 min of the reaction time following to decrease of the activity at 35 °C (Figure 2). The behavior may be as a result of the presence of conjugated aromatic system on the catalyst structure could turn it to a suitable acceptor and it is in favor of the monomer insertion which

may survive its activity for longer time. Due to the incorporation of the aromatic conjugation rings the catalyst doesn't show tendency to β -hydride elimination leading to survival of active centers. Polymerization of ethylene using the prepared catalysts was studied in the different [Al]/[Zr] molar ratio. As expected, the activity of catalyst increased with the addition of the [Al]/[Zr] molar ratio. The polymerization results showed that use of a ratio of at least 75000:1 is necessary to produce a reasonable active catalyst system. The influence of polymerization temperature on activity was investigated at the temperature between 25 and 65 °C, while the [Al]/[Zr] molar ratio were kept constant at [Al]/[Zr]=100000:1. Polymerization activities showed maximum values for the catalysts in the range of 35-40 °C. Activity of the catalyst was almost stable with increasing of the temperature and activity wasn't sensitive to the temperature unless

higher than 65 °C which decreased the activity. The decrease in the polymerization activity could be due to the β -hydride elimination reactions that take place at higher temperature[3,4]. Polymerization was carried out at the pressure of 1 to 3 bars. Increasing of the monomer pressure increased the activity of the catalyst in the range studied.

Conclusion

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A new FI Zr-based catalyst was prepared and used for ethylene polymerization. Polymerization results showed that the prepared catalyst comprising naphthyl ring on the catalyst structure could increase the thermal stability and durability of the catalyst activity

as well. We proposed that presence of more aromatic conjugated systems on the catalyst structure makes it fall down the LUMO energy level so that it could perform as a better acceptor for monomer insertion. Ethylene polymerization at different conditions was studied. The highest productivity was obtained at 35-40 °C. Increasing of the monomer pressure increased the activity of the catalyst in the range studied. Viscosity average molecular weight of the obtained polymer was 2.8×10^4 at the monomer pressure of 3 bars, while this value was increased with increasing the monomer pressure.

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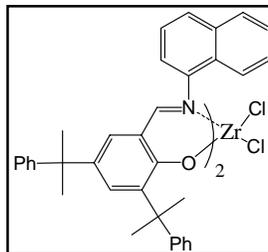


Figure 1. Structure of catalyst.

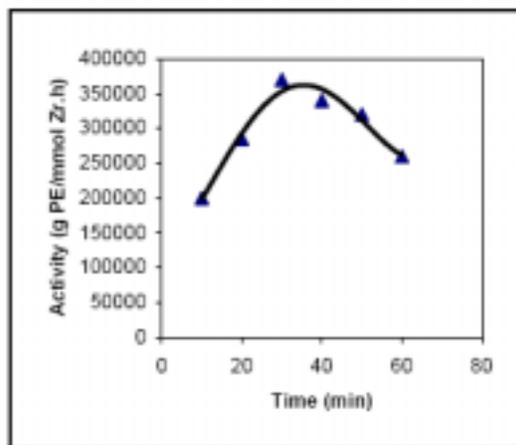


Figure 2. Rp versus time.