Late Transition Metal Catalyst Based on Cobalt for Polymerization of Ethylene

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Abstract

The catalyst of [2,6-diacethylpyridinebis(2,6-diisopropylphenylimine)]cobalt(II) dichloride was prepared and used for polymerization of ethylene. The highest activity of the catalyst was obtained at reaction temperature 30 $^\circ$C. the activity decreased with increasing temperature. At the temperature higher than 50 $^\circ$C not only a sharp decrease in the activity was observed but also an oily polyethylene product was obtained. The ($\overline{MV}$), the melting point and the crystallinity of the resulting polymer at the monomer pressure of 1 bar and polymerization temperature of 20 $^\circ$C were 1.2×10^5, 133 $^\circ$C and 67% respectively. Heterogeneous polymerization of ethylene using the catalyst and the MAO/SiO$_2$ improved morphology of the resulting polymer.

Keywords: olefin Polymerization, ethylene polymerization, late transition metal catalyst.

Introduction

Molecular weight of produced polymer is strongly affected with the steric bulky group of o-aryl substitution of catalyst used for its production[1]. The bulkier group substitution (isopropyl) can enhance the activity that has been reported[2,4]. In this study, [2,6-diacethylpyridinebis(2,6-diisopropylphenylimine)] cobalt(II) dichloride as a late transition metal catalyst is prepared. Homougenous and hetrogenous ethylene polymerization was carried out with the prepared catalyst and the effects of the polymerization temperature, cocatalyst/catalyst molar ratio, monomer pressure, polymerization time and hydrogen concentration on the polymerization activity and the viscosity average molecular weight were investigated.

Experimental

Methylaluminoxane (MAO) (10% solution in toluene), triisobutylaluminm (T1BA) (purity 93%), were supplied by Merck Chemical (Darmstadt, Germany). Polymerization grade ethylene (purity 99.9%) was supplied by Iranian Petrochemical Co (Tehran, Iran).

Result and Discussion

polymerization of ethylene was carried out using the prepared catalysts in toluene (Figure1). The polymerization activity was increased linearly with the addition of the [MAO]:[Co] ratio. Due to the oligomeric nature of the MAO, the the catalyst active centers even at very high chemical is not able to deactivate or overreduce concentration[4]. Increasing of the [MAO]:[Co] ratio up to 7500:1 produced some oily polyethylene.The oily polymer which produced could be as a result of chain transfer reactions could occur at very high concentration of MAO which decreased the molecular weight of the resulting polymer.The highest activity of the catalyst was obtained at about 30 $^\circ$C. The catalyst activity was increased with increasing the temperature from 20 $^\circ$C to 30 $^\circ$C following to a sharp decrease at higher temperature (Figure 2). An increase in the the propagation rate constant with increasing the temperature and irreversible deactivation of the active sites at high temperature were reported[6,8]. Higher temperature than 50 $^\circ$C, not only decreased the activity of the catalyst, but also produced completely oily polyethylene that could be as a result of β-hydride elimination which facilitate with increasing the temperature.There is a linear relationship between monomer pressure and activity of catalyst however the fouling was remarkably high at the monomer pressure higher than 3 bars. The behavior is mainly due to high concentration of the monomer close to the catalyst active centres.With increasing of the monomer pressure was decreased the crystallinity of

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the polymer. Crystallinities of polymer was 67.42 and 42% for pressure of 1 and 5 respectively.The maximum activity of the catalyst was observed after 60 min of the polymerization for the reaction carried out at 30 °C. Hydrogen concentration as a chain transfer agent could slightly vary the activity of the catalyst and the viscosity average molecular weight of the polymer obtained. Homogeneous polymerization produced polymer with irregular shape and size with some dusty particles cause fouling of the reactor. Heterogeneous polymerization improved morphology of the polymer particles (Figure 3).

Conclusion

The prepared catalyst of [2,6-diacethylpyridinebis (2,6-diisopropylphenylimine)]cobalt(II)dichloride as an active catalyst for the ethylene polymerization. Higher activity was found at temperature of 30 °C. Polymerization activity was increased with increasing both of the monomer pressure and [MAO]/[Co] ratio, but higher fouling of the reactor was observed. The viscosity average molecular weight of the resulting polymer decreased with increasing of the monomer pressure. Neither the activity of the catalyst nor the viscosity average molecular weight ($\overline{MV}$) of the polymer obtained were affected by the hydrogen concentration. Heterogeneous polymerization decreased the activity of the catalyst, improved morphology of the resulting polymer and eliminated fouling of the polymerization reactor.

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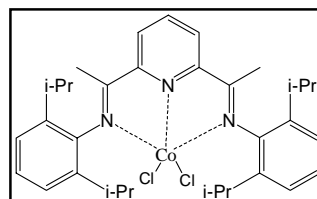7- Moor, EP, *Polypropylene Handbook*, Hanser Publishing, Munich pp **4727-4739** (1996).
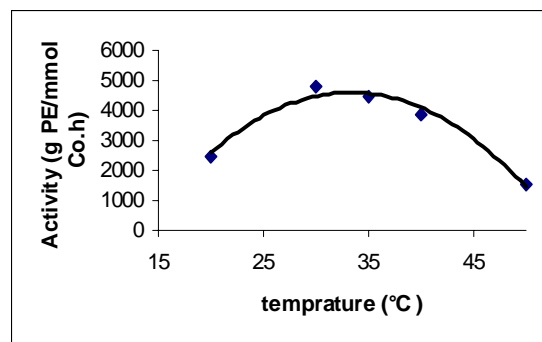
Figure 1 Structures of the catalyst

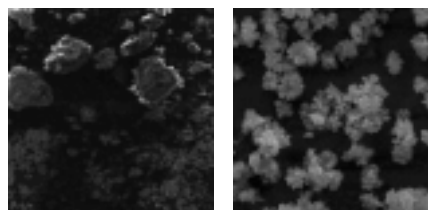**Figure 2. Effect of temperature on the Rp**

Figure 3. SEM micrograph of the polyethylene obtained using homogeneous (left) and heterogeneous (right) polymerization.