Bis(imino)pyridyl iron complexes immobilized on MgCl$_2$ for ethylene polymerization: Effect of polymerization temperatures

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Abstract

Two late transition metal catalyst based on 2,6-bis(imino)pyridine iron(II) were synthesized and used in ethylene polymerization. The selected catalysts involved one with methyl substituent (A) and the other with t-butyl substituent (B) at the ortho position of the aryl rings. Both catalysts were immobilized on MgCl$_2$.EtOH support and utilized in ethylene polymerization using triethylaluminium (TEA) as cocatalyst. Supported catalysts showed higher activities compared to their homogenous counterparts.

Keywords: Late transition metal, polyethylene, supported catalyst, polymerization.

Introduction

In 1998, Brookhart [1] and Gibson [2] independently described olefin polymerization and oligomerization catalyzed by the well-known class of compounds, diimino pyridine complexes of iron and cobalt, the late transition metal catalyst for polymerization of olefin, with an activator such as methylaluminoxane (MAO). Unfortunately, homogeneous catalysts resulted fouling of the reactor in slurry process. Immobilization of the catalysts through supporting on suitable carriers such as silica or MgCl$_2$ can be a remedy. For a number of MgCl$_2$-immobilized catalysts, including Ti, V, Cr, Fe, and Ni complexes, activation can be achieved using simple cocatalysts such as AlEt$_3$ or AlBu$_3$ [3]. In this work two late transition metal catalysts based on 2,6-bis(imino)pyridine iron(II) were supported on MgCl$_2$.nEtOH. The effects of polymerization temperatures on activity of the catalysts in the homogenous and heterogeneous state were investigated.

Experimental

Material

The materials preparation and solvents purification was according literature [4]. Catalysts in the homogenous state were prepared by mixing the LTM catalysts with 2 ml toluene. Catalysts in the heterogeneous state were prepared by mixing the LTM catalyst with modified MgCl$_2$.EtOH in toluene.

Ethylene polymerization

Polymerization reactions were performed in a 200 mL steel reactor equipped with controlling systems for temperature, stirring speed, and reaction pressure. The reactor was fully dried before polymerization. The system was saturated with a continuous flow of ethylene under atmospheric pressure. Then, it was filled with an appropriate amount of toluene and triethylaluminium as cocatalyst. The obtained polymers were poured into acidified methanol, collected by filtration, dried, and weighed.

Results and Discussion

The structures of late transition metal catalyst are shown in Figure 1. The results of polymerization with homogenous LTM catalysts that used TEA as the cocatalyst in the different polymerization temperatures are shown in Table1. As can be seen Catalyst A possesses higher activity in polymerization of ethylene compared to Catalyst B, which can be related to the bulkier structure of Catalyst B.
The MgCl₂/AlEt₃(OEt)₃ supports was modified by reaction of AlR₃ with the MgCl₂·3EtOH adduct, and subsequently used for immobilization of both LTM catalysts. The catalytic activities of two supported LTM catalyst by changing the polymerization temperatures in the homogeneous and heterogeneous states are compared in Figure 2. As can be seen both of catalyst in the heterogeneous state showed higher activities compared to the homogeneous states, however the activities of Catalyst A were higher than the corresponding values for Catalyst B in both homogeneous and heterogeneous polymerization conditions.

**Conclusion**

Late transition metal catalysts based on 2,6-bis(imino)pyridine iron(II) were synthesis and supported on MgCl₂. Ethylene polymerization was carried out using supported catalysts. The activity of the supported catalyst was better than that of the homogeneous one when TEA was used as the cocatalyst. Catalyst A showed higher activities both in homogeneous and heterogeneous states compared to Catalyst B.

**Fig 2.** The polymerization results in different polymerization temperatures. Conditions: co catalyst=TEA, Al:Fe=1000, [Fe]=6x10⁻⁶ M, Pressure=6 bar, time=30 min. solvent=100 ml toluene

**References**