



11th International Seminar on Polymer Science and Technology

Iran Polymer and Petrochemical Institute, Tehran, Iran
6-9 October 2014

Bis(imino)pyridyl iron complexes immobilized on MgCl₂ for ethylene polymerization: Effect of polymerization temperatures

Gh. H. Zohuri¹, A. Ghotbi Taheri¹, S.M.M. Mortazavi², S. Ahmadjo*², M. Zahmati³, M. Valieghbal³, D. Jafarifard³

1. Polymerization engineering department, Iran polymer and petrochemical institute (IPPI), P.O. Box 14965/115, Tehran, Iran.
2. Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, Mashhad, Iran
3. Central Laboratory of Jam Petrochemical Co., Assaluyeh, Iran.

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 MgCl₂.EtOH support and utilized in ethylene polymerization using triethylaluminum (TEA) as cocatalyst. Supported catalysts showed higher activities compare 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 MgCl₂ can be a remedy. For a number of MgCl₂-immobilized catalysts, including Ti, V, Cr, Fe, and Ni complexes, activation can be achieved using simple cocatalysts such as AlEt₃ or AliBu₃ [3]. In this work two late transition metal catalysts based on 2,6-bis(imino)pyridine iron(II) were supported on MgCl₂.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 MgCl₂.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 triethylaluminum as co catalyst. The obtained polymers were poured into acidified methanol, collected by filtration, dried, and weighed.

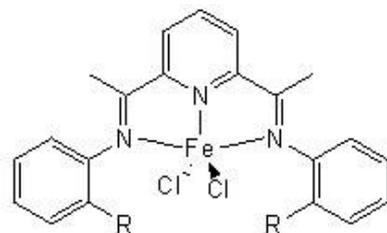
Results and Discussion

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 Table 1. 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.



11th International Seminar on Polymer Science and Technology

Iran Polymer and Petrochemical Institute, Tehran, Iran
6-9 October 2014



A=Me, B=tBu

Figure 1. Structures of the LTM catalysts

Table 1. Activities of homogenous catalysts at different polymerization temperatures.

Polym. Temp. (°C)	Activity Cat A	Activity Cat B
10	1400	550
25	1000	430
50	400	300
65	200	150

Condition: cocatalyst=TEA, Al:Fe=1000, [Fe]= 6×10^{-6} M, Pressure= 6 bar, time= 30 min. solvent=100 ml toluene

The $\text{MgCl}_2/\text{AlEt}_n(\text{OEt})_{3-n}$ supports was modified by reaction of AlR_3 with the $\text{MgCl}_2 \cdot 3\text{EtOH}$ 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 the 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 MgCl_2 . 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.

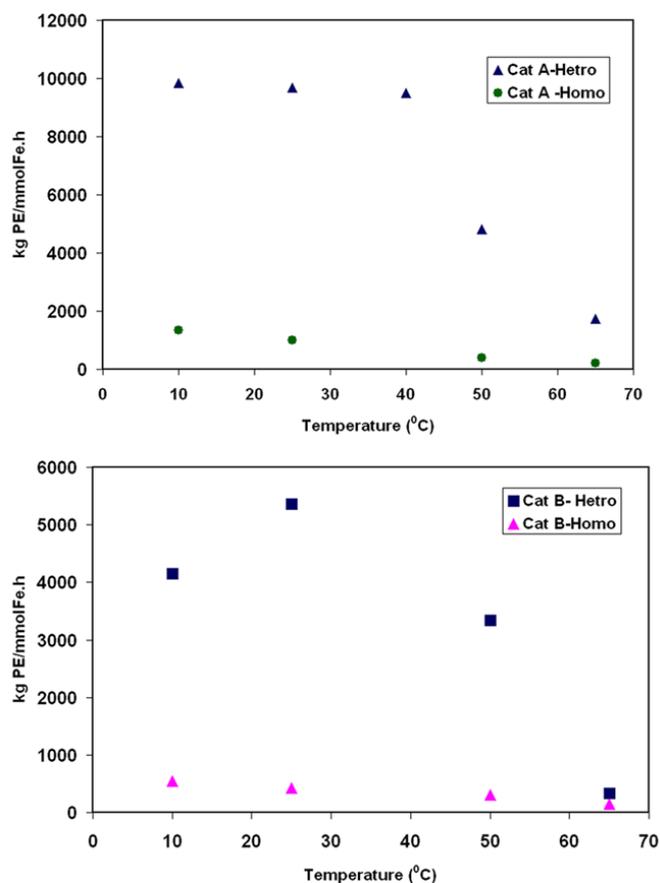


Fig 2. The polymerization results in different polymerization temperatures. Conditions: co catalyst=TEA, Al:Fe=1000, [Fe]= 6×10^{-6} , pressure= 6 bar, time= 30 min. solvent=100 ml toluene

References

1. B.L. Small, M. Brookhart, A.M.A. Bennett, *J. Am. Chem. Soc.* **120**, 4049, 1998.
- 2) G.J.P. Britovsek, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S.J. Mctavish, G.A. Solan, A.J.P. White, D.J. Williams, *Chem. Commun.* **849**, 1998.
- 3) R. Huang, R. Duchateau, C.E. Koning, J.C. Chadwick, *Macromolecules* **41**, 579-590, 2008.
- 4) R. Jamjah, G.H. Zohuri, J. Veazi, S. Ahmadjo, M. Nekoomanesh, M. Pourari, *J. Apply. Polym. Sci.*, **101**, 3829-3834, 2006.