

Bridge effect on dinuclear α -diimine Ni-based catalysts for polymerization of ethylene

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Introduction

The main purposes of the multinuclear catalyst synthesis are superior activity and selectivity [1]. In the field of multinuclear catalysts for polymerization of olefins, many papers have been reported. In some cases, a unique polymer with a distinct microstructure and narrow polydispersity has resulted [2,3]. However, in the most cases, a broad to bimodal molecular weight distribution has been observed [4,5]. The phenomenon which is called cooperative effect completely depends on the structure of the catalyst including the nature of active sites, the distance between them and the presence of weakly basic substituents such as hydrogen, phenyl and so on [1].

By considering all these factors, it should be noticed that the origin of results can be different. The higher or lower activity of multinuclear catalysts in comparison to mononuclears can be attributed to the presence of adjacent metal center or the backbone structure which all these effects can interpret as steric and electronic effects. Each structural parameter has impact on these effects.

Herein, we investigated the effect of nature and length of spacer between two nickel center in the dinuclear α -diimine based catalysts. The catalyst behavior and resulted polymer in the presence of these complexes using MMAO were investigated.

Materials and Methods

The ligands and complexes were synthesized according to our reported work [6]. Toluene was refluxed and distilled over sodium wire before use and kept over 4A/13X activated molecular sieves. The polymerization was conducted in a 200-mL stainless steel Bucci reactor, using toluene as the solvent. Reactor was saturated with ethylene to the desired total pressure and reaction proceeded for 30 min, under mixing at 800 rpm. Ethylene consumption was compensated using a mass flow meter to keep the total pressure constant. Finally, the reactor was evacuated and the product was washed with acidic methanol and vacuum dried.

Results and Discussion

As it can be observed in the kinetic profile of ethylene polymerization (Figure 1) using the dinuclear catalysts in presence of MMAO as cocatalyst, effect of the bridge structure and backbone of the ligands are very striking. Based on the results, higher electronic effects and electron density on the metal center which can stabilize the catalyst leads to higher activity and stability of the complexes. However, this effect along with some possible interactions such as deactivation and less shielding of axial sites around the active center revealed an opposite impact on the catalyst performance. This behavior was observed for dinuclear polymethylene bridged catalysts. However, by increasing the methylene groups on the bridge activity increased due to less negative effect and higher stability [7]. The nature of the bridge also

exhibited high impact on the kinetics of the polymerization. The catalyst bearing aromatic rings on the bridge between the centers showed higher productivity in comparison to catalysts with the linear aliphatic linker. Moreover, presence of the two phenyl rings caused greater activity than one [8]. The result is due to the higher electronic effects of electron rich rings between the centers. In addition, it is proved that the presence of bulky groups such as acenaphthene in the backbone structure in term of steric, electronic and structural impact on the active site which can block the equatorial situations of the metal center and open the axial situations can lead to increasing of the catalyst activity [9].

Significance

By considering the background of multinuclear catalysts in the olefin polymerization, they have a duty to produce polyolefins (homopolymers and copolymers) with higher performance, significant microstructure and properties.

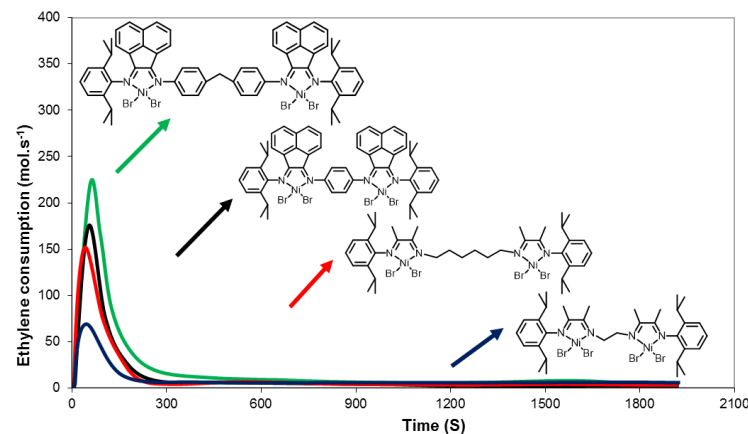


Figure 1. Kinetic profile of ethylene polymerization using different dinuclear catalysts in presence of MMAO.

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