Practical and Theoretical Study on the $\alpha$-Substituent Effect on $\alpha$-Diimine Nickel(II) and Cobalt(II)-Based Catalysts for Polymerization of Ethylene

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Abstract—The Late transition metal catalysts based on Ni(II) and Co(II) were synthesized and their structure and activity in polymerization of ethylene were compared. Methylenealuminoxane (MAO) was used as a co-catalyst. To discover the optimum polymerization conditions, the effect of polymerization temperature, monomer pressure, [Al] : [Ni] molar ratio and time of polymerization were studied. Activity of the catalysts was promoted by increasing of the monomer pressure. The viscosity average molecular weights $M_v$ of the synthesized polymers using 1,2-bis(2,4,6-trimethyl phenyl imino)acenaphthene Nickel(II) dibromide were increased with increasing of the monomer pressure from 1 up to 6 bar which studied. Explicitly, the ortho-substituent has a significant effect on the catalyst behavior. Melting point and crystallinity of the obtained polyethylene using 1,2-bis(2,4,6-trimethyl phenyl imino)acenaphthene Nickel(II) dibromide catalyst were increased with enhancing monomer pressure. The optimum and stable structures were computed and some factors related to the activity were studied. Catalyst 1,2-bis(2,4,6-trimethyl phenyl imino)acenaphthene Nickel(II) dibromide had the highest activity with the highest quantities of dipole moment (18.29 Debye), charge of Mullikan on metal atom (1.48) and Sum of electronic and thermal Energies (−7906.52 e.u.).

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INTRODUCTION

Transition metal catalysis for polymerization of olefins are vital to the plastic industry [1], which are manufactured employing Ziegler–Natta, metallocene and Philips catalysts [2–4]. In addition to metallocene catalysts, another major advancement in the area of olefin polymerization was the discovery of the homogeneous $\alpha$-diimine based late transition metal catalysts (Ni and Pd) in 1995 [5]. Early transition metals, which are applied in polyolefins synthesis are based on Ti, Zr, Cr, and V. These catalysts have oxophilic property, and this lead to be reactive toward water and oxygen [6–10]. The late transition metals (Ru, Co, Rh, Ni, and Pd), however, are much less oxophilic and therefore they may be used even in aqueous systems [11–13]. The late transition metal catalysts systems, therefore, are able to produce highly branched and low molecular weight polymers of ethylene [14].

The first synthesis of branched polyethylene solely from ethylene monomer using a nickel catalyst was reported in 1981 by W. Keim and co-workers, 14 years prior to disclosure of practical catalysts based on Ni $\alpha$-diimine complexes [15]. The nickel $\alpha$-diimine complexes represent an attractive group of such catalysts due to their high polymerization activity [16], lower oxophilicity, easy synthesis and
the fact that they do not need high Al/metal ratios for catalyst activation [17]. Many articles discuss the influence of variables such as polymerization temperature, monomer pressure, catalyst structure and role of bulky substituents on polymerization using α-diimine Ni(II) catalysts [18–20].

The activities and selectivity to reach α-olefins are dependent on the catalyst structure. The steric bulky groups around the metal center of the catalysts are a key to retarding chain transfer reaction to obtain high molecular weight polyethylene. The protective bulky groups of the ortho-substituents above and below the metal active enters was critical to the molecular weight of the resulting ethylene polymerizations [17, 21–23]. There are many striking papers and reviews on the late transition metal, especially on α-diimine Nickel catalysts, which have been published [14, 17, 22–29].

In this work six catalysts, namely Ni(II)- and Co(II)-based late transition metal complexes, were synthesized and characterized. Each group of complexes differs in the methyl substituent positions. The ortho-substituent effect on the catalyst performance in ethylene polymerization was investigated. Moreover, optimization of polymerization condition and comparison between catalysts both practically and theoretical factors related to the catalyst activity were the aims of this work.

EXPERIMENTAL

Materials and Polymer Synthesis

All manipulations of air and/or water sensitive compounds were conducted under argon/nitrogen atmosphere using the standard Schlenk techniques. All the solvents were purified prior to use. Toluene (purity 99.9%) (Iran, Petrochemical Co.) was purified over sodium wire/benzophenone, and used as polymerization solvent. Dichloromethane (purity 96%) (Sigma Aldrich Chemicals, Germany) was purified over calcium hydride powder, and distilled prior to use as a complex synthesis solvent. Polymerization grade ethylene gas (purity 99.9%) (Iran, Petrochemical Co.) was purified through activated silica gel, KOH, and 4 Å/13 X molecular sieves column. 2,4,6-trimethyl-ylaniline, 2,3-dimethylaniline, 3-methylaniline, acenaphtoquinon, Cobalt(II) chloride, Nickel(II) bromide ethylene glycol dimethyl ether complex [(DME)NiBr₂] (purity 97%) and diethyl ether (purity 99.5%) were supplied by Merck Chemical (Darmstadt, Germany) and used in synthesis of ligands and catalysts. Decaline (decacylronaphthalene) (purity 97%) was purchased from Sigma Aldrich Chemicals (Steinheim, Germany). Triisobutylaluminium (purity 93%) (TIBA) was supplied by Sigma Aldrich Chemicals (Steinheim, Germany) which was used in synthesis of methylaluminoxane (MAO) according to the literature [30].

Two kind of polymerization in low and high pressure were employed. The low pressure process was carried out in a 100 mL round bottom flask which was equipped with Schlenk system, vacuum line, ethylene inlet and magnetic stirrer. The high pressure (more than 2 bar) was carried out using a 1 L Buchi bmd-300 type reactor.

Characterization

1H NMR and FTIR spectrums were obtained using Bruker AC-80 and Bruker IF-505 spectrometers, respectively. Elemental analysis was performed on a Thermo Finnigan Flash 1112EA microanalyzer. The viscosity average molecular weight $M_v$ of some polymer samples was determined according to the literature [31]. Intrinsic viscosity $\eta$ was measured in decaline at 133 ± 1°C using an Ubbelohde viscometer. $M_v$ values were calculated through Mark-Houwink $[\eta] = KM_v^\alpha$ equation ($\alpha = 0.7$, $K = 6.2 \times 10^{-4}$) [20]. Differential scanning calorimetry (DSC) (Q100 Perkin Elmer) with a rate of 10 grad/min instrument was used for polymer characterization.

Synthesis of Ligands and Complexes

The general reaction for synthesis of the ligands and catalysts are shown in Scheme.