Accepted Manuscript

Mechanisms for the effects of fluorine and α -diimine backbone structure on the catalyst behavior and catalyst deactivation in ethylene polymerization by Ni catalysts

S. Ahmadjo, S. Damavandi, G.H. Zohuri, A. Farhadipour, Z. Etemadinia

PII: S0022-328X(17)30134-1

DOI: 10.1016/j.jorganchem.2017.02.043

Reference: JOM 19832

To appear in: Journal of Organometallic Chemistry

Received Date: 22 November 2016

Revised Date: 25 February 2017

Accepted Date: 25 February 2017

Please cite this article as: S. Ahmadjo, S. Damavandi, G.H. Zohuri, A. Farhadipour, Z. Etemadinia, Mechanisms for the effects of fluorine and α -diimine backbone structure on the catalyst behavior and catalyst deactivation in ethylene polymerization by Ni catalysts, *Journal of Organometallic Chemistry* (2017), doi: 10.1016/j.jorganchem.2017.02.043.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.





the man

Mechanisms for the effects of fluorine and α-diimine backbone structure on the catalyst behavior and catalyst deactivation in ethylene polymerization by Ni catalysts

S.Ahmadjo^{*1}, S. Damavandi ^{*2}, G. H. Zohuri², A. Farhadipour², Z.Etemadinia²

Department of Catalyst, Iran Polymer and Petrochemical Institute, Tehran, Iran
 Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, Mashhad, Iran

ABSTRACT

Ethylene polymerizations were carried out via three fluorinated late transition metal (LTM) catalysts activated by methylaluminoxane (MAO) as a co catalyst. The effects of polymerization conditions, the fluorine of ligand and the α -diimine backbone structure on the catalysts performance and polymer properties were studied. Modification of the α -diimine ligand had a notable effect on the catalysts behavior. The catalyst [bis(N,N'-2fluorophenylimino)acenaphthene] nickel(II) dibromide (catalyst 1) showed the highest activity compared to other catalysts used in this study. Moreover, the catalyst 1 produced a polymer with the highest molecular weight, while the catalyst [bis(N,N'-2fluorophenylimino)ethan] nickel(II) dibromide (catalyst 2) produced a polymer with the lowest molecular weight. A mechanism was proposed for the effects of fluorine and α -diimine backbone structure on the catalysts behavior, catalyst deactivation and molecular weight of the polymers obtained. Our mechanistic hypothesis was strongly verified by computational approaches, we used to describe the system. The probable reactive electronic interactions of fluorine substitution were accurately distinguished to explain the influence of the ligand backbone on the molecular weight of the obtained polymer.

Keywords: Late transition metal; Fluorinated nickel catalyst; Ethylene polymerization; Density functional theory (DFT).

^{*} Corresponding authors: S. Ahmadjo, <u>s.ahmadjo@ippi.ac.ir</u> and S.Damavandi, saman_damavandi@yahoo.com

1. Introduction

Based on annual production volume, polyolefins are by far the most important commercial class of synthetic polymers. New polyolefin catalysts technologies synchronized with sophisticated polymerization techniques are promising areas of research. Ziegler-Natta and Philips catalysts both have been exploited commercially over many years. Recently, the study of families of highly active late transition metal catalysts has become one of the most interesting research fields [1-3]. The first effort on this topic involved the nickel-based shell higher olefins process (SHOP) oligomerization catalysts, which were reported by Peuckert et. al.[4]. They showed that modification of the ligand of the catalysts could influence the molecular weight and stereoregularity of polymers [5-9]. Brookhart in 1995 reported the first α -diimine catalysts [10]. These systems showed special properties such as high activities and high molecular weight via retarding the rate of chain transfer reactions [5-11]. There are many papers dealing with ethylene polymerization using nickel α-diimine catalysts [12-19]. Furthermore, Guan investigated the electronic effects of substitutions for a range of Pd-based α -diimine catalysts [3]. He reported that the ligand electronic structure of the catalysts had an important effect on the properties of the polyethylene obtained as well as the catalyst activity. Also, Alt and coworkers studied the electronic influence of the ligand structure on the catalytic properties of halogenated nickel α -diimine catalysts [14].

In the present study, three fluorinated nickel α -diimine catalysts including [bis(N,N'-2-fluorophenylimino)acenaphthene] nickel(II) dibromide (1), [bis(N,N'-2-fluorophenylimino)ethane] nickel(II) dibromide (2), and 1,2-dimethyl [bis(N,N/-2-fluorophenylimino)ethane] nickel(II) dibromide (2), and 1,2-dimethyl [bis(N,N/-2-fluorophenylimino)eth

2

fluorophenylimino)ethane] nickel(II) dibromide (**3**) have been synthesized and used for ethylene polymerization (Scheme 1). The influence of the steric hindrance caused by various substituents on the ligand backbone as well as the electronic interactions induced by introduction of fluorine atom into the aryl groups on the catalyst behavior and polymer properties have been comparatively studied. In addition, theoretical studies have been carried out to find a possible correlation between the catalysts structures and their activities.

(Scheme 1)

2. Experimental

2.1. Materials

Dichloromethane, diethyl ether, methanol, *p*-TsOH and 2-fluoro aniline were supplied by Merck Chemical (Darmstadt, Germany) and were used as received. Toluene and *n*-hexane were obtained by Arak Petrochemical Co (Arak, Iran). The chemicals were prepared from distilling over CaH₂, sodium and benzophenone, respectively. Polymerization grade ethylene (purity 99.9%) was supplied by Iran Polymer Petrochemical Institute (Tehran, Iran). Methylaluminoxane (MAO) (10% solution in toluene), triisobutylaluminm (TIBA) (purity 93%), acenaphthoquinone (purity > 99%), (DME)NiBr₂ and α -diketo compounds were purchased from Sigma Aldrich (Steinheim, Germany).

2.2. Ethylene polymerization

The polymerization was performed as described previously [20], with the use of a stainless steel Buchi reactor size 1 L equipped with an agitator, along with a control system for controlling heat and pressure. The reactor was evacuated and purged with N_2

several times at 110 $^{\circ}$ C for removing impurities. Toluene was added into the polymerization reactor at 25 $^{\circ}$ C and the reactor was saturated with ethylene gas. TIBA and MAO were added into the polymerization reactor as scavenger and co catalyst, respectively. Then, the appropriate amount of catalyst was added into the reactor and the mixture was stirred under ethylene atmosphere at various pressures. After finishing the polymerization reaction, the supply of ethylene gas was stopped and the polymer was washed with acidic ethanol. The polymer was dried in a vacuum oven at 60 $^{\circ}$ C for about 8 h.

2.3. Characterization of catalyst and polyethylene

¹H-NMR spectrum was recorded on a Bruker BRX-100 AVANCE spectrometer. Elemental analysis for CHN was carried out by a CHNO type Thermo Firingan 11112 EA microanalyzer. Differential scanning calorimetry (DSC) (Universal V4IDTA) experiments were used for evaluation of thermal properties of the synthesized polyethylenes at a heating rate of 10 ^oC min⁻¹. The degree of crystallinity of a polyethylene sample can be calculated from the heat of fusion, determined by the differential scanning calorimetry method [21]. The crystallinity percentage of each polyethylene sample was computed form the equation $\Delta H_{f}/\Delta H_{f}^* \times 100$, where ΔH_{f} is the heat of fusion and $\Delta H_{f}^*=69$ cal g⁻¹ is the heat of fusion of 100% crystalline polyethylene. Intrinsic viscosity [η] was measured in decalin at 135 ^oC using an Ubbelohde viscometer. M_v values were calculated through equation [η] = 6.2 × 10⁻⁴ M_v^{0.7} [22].

2.4. Computational details

All computations were carried out by density functional theory (DFT), using Gaussian 09 program [23]. The B3LYP/6-311G level of theory was used to optimize the geometry of molecule. Additionally, the natural bond orbitals (NBO) analysis was carried out using version 3.1 of NBO package [24] included in Gaussian 09 program at the B3LYP level of theory and with the 6-311G basis set.

2.5. General synthesis procedure for the α-diimine ligands

To a solution of respective diketo compound (6.1 mmol) in methanol (20 mL), 2-fluoroaniline (12.2 mmol) and a trace amount of *p*-TsOH were added. The resulting solution was stirred at reflux temperature. The progress of the reaction was monitored by thin layer chromatography (TLC). The precipitate was filtered, washed with *n*-hexane and dried. The obtained solid was recrystallized from ethanol to prepare a pure product. L₁ (86%): ¹H-NMR (CDCl₃): δ 6.80 (dd, 2H), 7.17-7.45 (m, 8H), 7.84 (d, 2H), 7.91 (d, 2H). Anal. Calc. For C₂₄H₁₄N₂F₂: C, 78.25; H, 3.83; N, 7.60 Found: C, 78.34; H, 3.85; N, 7.62.

L₂ (88%): ¹H-NMR (CDCl₃): δ 6.55 (d, 2H, *J*= 7.5 Hz, N=C–H), 6.88 -7.05 (m, 4H, Ar-H), 7.10-7.20 (m, 4H, Ar-H). Anal. Calc. For C₁₄H₁₀N₂F₂: C, 68.85; H, 4.13; N, 11.47; Found: C, 68.70; H, 4.10; N, 11.42.

L₃ (85%): ¹H-NMR (CDCl₃): δ 2.24 (s, 6 H, N=C–CH₃), 6.77-6.96 (m, 5H, Ar-H), 7.20-7.35 (m, 3H, Ar-H). Anal. Calc. For C₁₆H₁₄N₂F₂: C, 70.58; H, 5.18; N, 10.29; Found: C, 70.66; H, 5.23; N, 10.25.

2.6. General procedure for synthesis of the (α-diimine) nickel dibromide catalysts 1-3

Dimethoxyethane nickeldibromide (DME)NiBr₂ (1.2 mmol) and the respective α -diimine ligand (1.2 mmol) were mixed in a flask under an argon atmosphere. CH₂Cl₂ (25 mL) was added to the solid mixture. The produced suspension was stirred for 24 h at room temperature. For purification, the solvent (CH₂Cl₂) was reduced in vacuo and the solid was precipitated by adding pure *n*-hexane. After washing several times until the solvent remained colorless, the product was dried in vacuo. Catalyst was obtained as a brown crystalline powder. The solid was washed with Et₂O and dried in vacuum. NMR characterization was not possible because of the paramagnetic nature of the compounds. Catalyst **1** (80 %; mp: > 300 °C): Anal. Calc. For C₂₄H₁₄Br₂N₂F₂Ni: C, 49.12; H, 2.40; N,

4.77. Found: C,49.18; H,2.44; N, 4.80. EIMS: MS (m/z): 583 (M), 506 (M⁺-Br), 426 (M⁺-2Br), 368 (M⁺-NiBr₂).

Catalyst **2** (77 %; mp: > 300 °C): Anal. Calc. For C₁₄H₁₀Br₂N₂F₂Ni: C, 36.34; H, 2.18; N, 6.05. Found: C, 36.25; H, 2.20; N, 6.09. EIMS: MS (m/z): 459 (M), 380 (M⁺-Br), 302 (M⁺-2Br), 244 (M⁺-NiBr₂).

Catalyst **3** (75 %; mp: > 300 °C): Anal. Calc. For C₁₆H₁₄Br₂N₂F₂Ni: C, 39.16; H, 2.88; N, 5.71. Found: C, 39.11; H, 2.84; N, 5.73. EIMS: MS (m/z): 487 (M), 408 (M⁺-Br), 330 (M⁺-2Br), 272 (M⁺-NiBr₂).

3. Results and discussion

Ethylene polymerizations with the toluene solution of the catalysts were carried out, followed by the addition of MAO and ethylene gas into the polymerization reactor.

The effects of the [Al]:[Ni] molar ratio on the polymerization activities are summarized in Figure 1. As displayed in Figure 1, the catalysts activities are in the order of catalyst 1> catalyst 2> catalyst 3. Since increasing the concentration of MAO may improve the number of the active species in the reaction and also may have contribution in the stabilization of the formed active species [25,26], the polymerization activities progressively increase with the [A1]/[Ni] molar ratio up to [A1]/[Ni] = 1000 and [A1]/[Ni] = 2000 for the catalysts 1 and 2, respectively. Whereas, the activity of the catalyst 3dramatically reduces as the [Al]:[Ni] molar ratio increases. The behavior is directly ascribed to the catalyst structure. In this research, a reasonable mechanism is proposed for the catalyst deactivation. We suggest that the presence of methyl group having α -acidic protons in the α -diimine backbone structure of the catalyst 3, makes the catalyst susceptible to be converted to its enamine tautomer. This indicates that an interaction between the catalyst and co catalyst can be occurred through the coordination of donor N (nitrogen) and Lewis acid Al (aluminium). This interaction leads to methane evolving and production of inactive catalyst species. The deactivation mechanism proposed for the catalyst **3** is shown in Scheme 2. While, due to the lack of CH₃ group in the α -diimine backbone structure, such a tautomerization is not probable for the catalysts 1 and 2. Accordingly, the higher amount of MAO affected the catalyst 3 and reduced its activity.

(Figure 1)

(Scheme 2)

At the monomer pressure of 4 bars, polymerization temperature of 30 0 C and optimum molar ratio of [A1]:[Ni], the catalysts **1-3** yielded polymers with the molecular weights in the order of catalyst **1**> catalyst **3**> catalyst **2** (Table 1). The prepared fluorinated α -dimine Ni-based catalysts **1-3** were found to be able to produce polyethylene with the M_v values of 1.40×10^{5} , 8.85×10^{4} and 1.10×10^{5} , respectively.

Table 1

As it is known, the β -hydride elimination rate directly affects the molecular weight of polymers [27-29]. The introduction of fluorine groups in the *ortho* position of the phenyl groups in the catalyst 1 can effectively suppress the β -hydride elimination through the β -hydrogen of the growing polymer chain (Scheme 3). It inhibits the formation of the olefin hydride complex intermediate that is highly prone to carry out various chain transfer reactions. In spite of the presence of fluorine groups in the ortho position of the aryl rings in the catalysts 2 and 3, the molecular weight of the polymer obtained is lower. In order to justify this discrepancy, we suggested a mechanism which is demonstrated in Scheme 4. As shown, the fluorine groups are more tended to interact with the hydrogen atoms of the imine moiety in the catalyst 2 and of CH_3 group in the catalyst 3 attached to the α -dimine backbone structure. Therefore, in the catalysts 2 and 3, the aryl rings rotate and the fluorine substitutions are in favor of β -hydride elimination, leading to formation of olefin hydride complex intermediate (Scheme 4) which can undergo the probable chain transfer reactions giving rise to decrease of molecular weight of the polymers. Because of more localized positive charge on the protons in the backbone structure of the catalyst 2, the mentioned interaction occurs simply and results in more decrease in molecular weight of the polyethylene.

(Scheme 3)

(Scheme 4)

In this stage, in order to strengthen our propositions and also elaborate the interaction between the fluorine substitutions and the ligand backbone or growing polymer chain, computational study was applied. The calculations were carried out by density functional theory (DFT), using Gaussian 09 program [23]. The program used the B3LYP method of the theory with the 6-311G basis set. Additionally, the natural bond orbitals (NBO) analysis was carried out using version 3.1 of the NBO package [24] included in Gaussian 09 program at the B3LYP level of the theory and with the 6-311G basis set. After full optimization of the catalysts using the B3LYP/6-311G theoretical methods, they exhibited a planar geometry and the bond angles between the two ligands located in the anti-positions were found to be in the range of 168-180⁰ (Schemes 5 to 7).

As shown in Scheme 5, the DFT studies on the optimized active species derived from the catalyst 1 dedicated that the interaction between H-beta of the growing polymer chain and *ortho*- fluorine of the ligand produced higher molecular weight polyethylene by the effective suppression of β -hydrogen transfer reactions to the central metal or incoming monomer (an *ortho*- fluorine atom / β -hydrogen distance = 2.381 Å) (Van der Waals radii of hydrogen atoms and fluorine atom are 1.20 Å and 1.47 Å, respectively).

The optimized structure of the active species derived from the catalyst 2 (Scheme 6) reveals the probable reactive interaction between the fluorine atom substitution of the ligand backbone and the hydrogen atoms of the imine moiety (an *ortho*-fluorine atom / hydrogen atoms of CH=N distance of 2.42 Å versus an *ortho*-fluorine atom / β - hydrogen

distance of 4.95 Å). Additionally, the optimized structure of the active species derived from the catalyst 3 (Scheme 7) supports our hypothesis regarding the occurrence of interaction between the fluorine atom and one hydrogen atom of CH₃ group (an orthofluorine atom / hydrogen atoms distance of 2.47 Å versus an *ortho*- fluorine / β -hydrogen distance of 4.54 Å). The calculated structures depicted in Schemes 5-7 are considerably consistent with those recommended by our mechanistic propositions presented in Schemes 3 and 4. Having strengthened our propositions regarding different reactive interactions between the fluorine atom and β -hydrogen in the catalyst 1 and also between the fluorine and hydrogen atoms or CH_3 in the catalysts 2 and 3, respectively due to the differences in the constitutional structures, the charges on the atoms were estimated. As illustrated in Scheme 8, the amount of the charges on the hydrogen atom of CH=N and the hydrogen atom of CH_3 group on the α -diimine ligand backbone of the active species are in strong accordance with our suggestions regarding higher molecular weight of the polymer obtained by the catalyst 3 in comparison with the catalyst 2. Indeed, more localized positive charge on the hydrogen atom of CH=N (+0.29) comparing with the charge on the hydrogen atom of CH_3 (~ +0.23) improves in the presence of the fluorine atom and leads to formation of lower molecular weight polyethylene. In the other words, the fluorine atom with a lower tendency for electronically interacting with growing polymer chain does not prevent the transferring reaction in the catalyst 2 completely, which, in turn, leads to production of lower molecular weight polyethylene.

(Scheme 5)

(Scheme 6)

(Scheme 7)

(Scheme 8)

The NBO analysis showed that the three complexes had an unpaired electron, so appeared to have paramagnetic property, similar nickel dibromide catalyst exhibiting paramagnetic nature are described by Alt et al [30]. All their five d-orbitals, however, had pair electrons (alpha and beta electrons). As shown in Figures 2-4, the unpaired electrons are located in other molecular orbitals. The electronic properties of the *d*-orbitals of Ni atom are tabulated in Table 2 and their energy diagrams of *d*-orbitals are shown in Figure 5. Among them the d_{xy} -orbital has the lowest energy because it acts as a bonding orbital (bonded to the *p*-orbital of carbon atom) and four other *d*-orbitals act as nonbonding orbitals, and the d_z^2 orbital has the highest energy. In the NBO analysis, the delocalization effects can be identified due to the presence of interaction between some molecular orbitals that act as donor or acceptor. The strengths of these delocalization interactions are estimated by the second order perturbation theory. The second order perturbation stabilization energies, $E^{(2)}$, calculated at the B3LYP/6-311G level for the catalysts 1, 2 and 3, are given in the last column of Table 2. It is common to report the orbital energies, E, in atomic unit (a.u.), and the second order perturbation energies, $E^{(2)}$, in kcal.mol⁻¹. A large stabilization energy E⁽²⁾ value shows higher delocalization effects of the electrons in the *d*-orbitals and their high stabilization, so the d_{xy} which contains a covalent C-C bond, has the lowest second order perturbation stabilization energy.

(Figure 2)

(Figure 3)

(Figure 4)

(Figure 5)

Table 2

Similar to most transition metal-based catalysts, the Ni-based catalysts suffer from the decay of catalytic activity at elevated polymerization temperatures [31, 32]. In the present study, for the polymerization carried out at the optimum value of [Al]:[Ni], the catalysts **1**, **2** and **3** showed the highest polymerization activities at 30, 30 and 20 $^{\circ}$ C, respectively (Figure 6). Incorporation of fluorine atoms into the catalyst structure diminished the catalyst activity in comparison with their analogues having isopropyl substitutions [33. Besides, activity of the catalyst **3**, which has a CH₃ group on the α-diimine backbone structure, is more vulnerable to polymerization temperature. This again strengthens our hypothesis about the deactivation process (Scheme 2).

(Figure 6)

Some properties of the obtained polymer are summarized in Table 1. The degree of crystallinities of the polymers obtained by the catalysts **1-3** at the polymerization temperature of 20 0 C are 44, 38, and 42 %, respectively (Table 1). At low polymerization temperature, because of the interaction between the fluorine atom and the β -hydrogen atom of the polymer chain (Scheme 3), the formation of olefin hydride complex, which is less probable, is in favor of monomer insertion, giving rise to a product with a high crystallinity and melting point. Among the three catalysts, the catalyst **2** produced polyethylene with the lowest crystallinity, which is in accord with our description, i.e. more interaction of the fluorine atom with the protons in the backbone of the structure resulted in formation of the olefin hydride complex which, in turn, led to chain transfer

reactions, short olefin re-insertion and eventually chain walking to furnish branched polymer with low degree of crystallinity. Finally, as can be seen in Table 1, with all the three catalysts, the polymer molecular weight tends to decrease with increasing polymerization temperature.

4. Conclusion

A series of designed fluorinated Ni (II) catalysts bearing various a-diimine backbone structures with different steric bulk were demonstrated to be active in the ethylene polymerizations combined with MAO. The catalyst activity, polymer molecular weight and polymer microstructure could be tuned by modifying the catalyst architecture and by controlling polymerization parameters such as temperature and MAO concentration. Although, all the catalysts had fluorine atom substitution on the aryl rings, the influence of the fluorine atom on the efficiency of each catalyst was different. The mechanism proposed for explaining the effects of fluorine and α -diimine backbone structure on the catalysts behavior, catalyst deactivation and molecular weight of the obtained polymers were confirmed by the calculations made based on the DFT method. The interactions between the fluorine atom and growing chain in the catalyst 1 as well as between the fluorine atom and hydrogen atom and the fluorine atom and CH_3 in the α -dimine moiety, respectively, in the catalysts 2 and 3 were confirmed by DFT studies, and it was found that the interactions could rationalize the effect of electronic interaction on the polymer molecular weight. Our suggested mechanisms for explaining the polymerization behavior of the fluorinated LTM catalysts could make a proper justification about the steric effects provided by α -dimine backbone as well as the electronic effects provided by the fluorine atoms on the aryl rings.

References

- [1] M. Mu, L. Pan, D. Song, Y. Li, Chem. Rev. 115 (2015) 12091–12137.
- [2] S. Ahmadjo, Polym. Adv. Technol. 27 (2016) 1523–1529.
- [3] Z. Guan, Chem. Asian. J. 5 (2010) 1058–1070.
- [4] M. Peuckert, W. Keim, Organometallics 2 (1983) 594-597.
- [5] R. Sandaroos T. Cuenca G.H. Zohuri, S. Damavandi, S. Ahmadjo, Titanium (IV) and nickel (II) catalysts based on anilinotropone ligands, De Souza Gomes, A., (Ed.), In Tech, (2012) 223-244.
- [6] R. Hoff R.T. Mathers, Handbook of transition metal polymerization catalyst, Willy-VCH, (2010).
- [7] B. Rieger, L.S. Baugh, S. Kacker, S. Triegler, Late transition metal polymerization catalysis, Wiley-VCH Verlag GmbH & Co., KGaA, Weinheim (2003).
- [8] D. Takeuchi, Dalton. Trans. 9 (2011) 311-328.
- [9] M. Khoshsefat, G.H. Zohuri, N. Ramezanian, S. Ahmadjo, M. Haghpana, J. Polym. Sci. Polym. Chem. 54 (2016) 3000–3011.
- [10] L.K. Johnson, S. Mecking, M. Brookhart, J. Am. Chem. Soc. 118, (1996) 267-268.
- [11] D.H. Camacho, E.V. Salo, J.W. Ziller, Z. Guan, Angew. Chem. Int. Ed. 34 (2004) 1821-1825.
- [12] M. Khoshsefat, N. Beheshti, G.H. Zohuri, S. Ahmadjo, S. Soleimanzadegan, Polym.Sci. Ser. B. 58 (2016) 1–8.
- [13] B.K. Bahuleyan, U.K. Lee, C.S. Ha, I. I. Kim, Appl. Cat. A. Gen. 351 (2008) 36-44.
- [14] M. Helldorfer, J. Backhaus, H.G. Alt, Inorg. Chim. Acta. 351 (2003) 34-42.
- [15] M. Khoshsefat, S. Ahmadjo S, S.M.M. Mortazavi, G.H. Zohuri, RSC. Adv. 6 (2016) 88625–88632.
- [16] Y.G. Li, L. Pan, Z.J. Zheng, Y.S. Li, J. Mol. Cat. A.Chem. 287 (2008) 57-64.
- [17] J. Azoulay, R. Rojas, A. Serrano, H. Ohtaki, G. Galland, G. Wu, G. Bazan, Angew. Chem. Int. Ed. 48 (2009) 1089-1092.
- [18] J. Li, H. Song, C. Cui, Appl. Organomet. Chem. 24 (2010) 82-85.
- [19] J.A. Rhinehart, N.E. Mitchell, B.K. Long, ACS. Catal. 4 (2014) 2501-2504.

[20] S. Ahmadjo, Polym. Adv. Technol. 27 (2016) 523–152.

[21] J. Justino, A.R. Dias, J. Ascenso, M.M. Marcues, P.J.T. Tait, Polym. Int. 44 (1997) 407-412.

[22] J. Brandrup, E.H. Immergut, Polymer handbook, vol VII: 3rd edn. Wiley, New York, (1989) 1–7.

[23] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J. Montgomery, A. T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O.Yazyev, A.J. Austin, R. Cammi, C. Pomelli ,J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. AlLaham, C.Y. Peng, A. Nanayakkara, M.Challacombe, P.M. W.Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, in: GaussianInc.,Pittsburgh PA,(2003).

[24] E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold, NBO, Version 3.1, (2003).

[25] D.H. Camacho, Z. Guan, Chem. Commun. 46 (2010) 7879-7893.

[26] R. Sandaroos, S. Damavandi, A. Farhadipour. Macromol. Chem. Phys. 211 (2010) 2339-2346.

[27] S.I. Ishii, N. Matsukawa, J. Saito, M. Mitani, H. Tanaka, T. Fujita, Macromol. Rapid. Commun. 24 (2003) 452-456.

[28] G.H. Zohuri, S. Damavandi, R. Sandaroos, S. Ahmadjo, Polym. Bull. 66 (2010) 1051-1062.

[29] S. Damavandi, N. Samadieh, S. Ahmadjo, Z. Etemadinia, G.H. Zohuri, Eur. Polym.J. (64) 2015 118–125.

[30] A. Köppl, H. G. Alt, J. Mol. Cat. A Chem. 154 (2000) 45-53.

[31] P. Ai, L. Chen, Y. Guo, S. Jie, B.G. Li, J. Organomet. Chem. 705 (2012) 51-58.

[32] H. Liu, X. Jia, F. Wang, Q. Dai, B. Wang, J. Bi, C. Zhang, L. Zhao, C. Bai, Y. Hu Y,X. Zhang, Dalton. Trans. 42 (2013) 13723-13732.

[33] F. AlObaidi, Z. Ye, S. Zhu, Polymer 45 (2004) 6823-6829.

Catalyst	Pressure	Temperature	<mark>polymer</mark>	Activity	Crystallinity	T _m	M _v
	(bar)	(°C)	<mark>(gr)</mark>	(g PE/mmol Ni.h)	%	(°C)	
1	2	0	<mark>0.3</mark>	7.9×10^{2}	58	110	2.48×10^{5}
1	2	20	<mark>1.4</mark>	3.9×10^{3}	44	88	2.32×10^{5}
1	2	30	<mark>2.3</mark>	6.6×10 ³		-	8.20×10^4
1	<mark>2</mark>	<mark>50</mark>	<mark>0.2</mark>	6.4×10^{2}	10	<mark>74</mark>	9.80×10^{4}
1	4	30	<mark>3.1</mark>	8.8×10^{3}	-) ′	-	1.40×10^{5}
1	6	30	<mark>4.9</mark>	1.4×10^4	40	118	1.50×10^{5}
2	2	20	<mark>0.7</mark>	2.1×10^{3}	38	88	1.22×10^{4}
2	2	30	<mark>0.8</mark>	2.4×10^{3}	26	85	1.16×10^{4}
2	2	50	<mark>0.5</mark>	1.4×10^{3}	10	77	1.22×10^{4}
2	4	30	<mark>1.3</mark>	3.6×10^{3}	-	-	8.85×10^{4}
2	6	30	<mark>2.7</mark>	7.7×10^{3}	33	90	8.88×10^{4}
3	2	20	<mark>0.8</mark>	2.4×10^{3}	42	102	1.43×10^{5}
3	2	30	<mark>0.7</mark>	2.0×10^{3}	32	100	1.31×10^{5}
3	2	50	<mark>0.3</mark>	8.6×10^{2}	10	90	6.27×10^4
3	4	30	0.3	2.2×10^{3}	-	-	1.10×10^{5}
3	6	30	<mark>1.4</mark>	4.5×10^3	38	116	1.26×10^{5}

Table 1. Characterization of polyethylenes synthesized in this work.

Polymerization conditions: polymerization time= 30 min, [A1]:[Ni]= 1000, [Ni]= 7×10^{-4} mmol, toluene volume= 250 mL.

R CRI

Complay	d orbital	E	Molecular	$\mathbf{E}^{(2)}$
Complex		<mark>(a.u.)</mark>	orbitals type*	(kcal.mol ⁻¹)
	d_z^2	<mark>-0.200</mark>	LP(1)Ni	<mark>0.92</mark>
	d _{yz}	<mark>-0.201</mark>	LP(2)Ni	7.21
1	d_{xz}	<mark>-0.206</mark>	LP(3)Ni	<mark>5.89</mark>
	d_{x}^{2}	<mark>-0.238</mark>	LP(4)Ni	11.63
	d_{xy}	<mark>-0.318</mark>	BD(1)Ni - C	21.05
	d_z^2	<mark>-0.224</mark>	LP(1)Ni	0.82
	d _{yz}	<mark>-0.229</mark>	LP(2)Ni	3.48
<mark>2</mark>	d_{xz}	<mark>-0.233</mark>	LP(3)Ni	<mark>6.37</mark>
	d_{x}^{2}	<mark>-0.262</mark>	LP(4)Ni	<mark>8.69</mark>
	d_{xy}	<mark>-0.317</mark>	<mark>BD(1)Ni - C</mark>	21.87
	d_z^2	<mark>-0.218</mark>	LP(1)Ni	0.87
	d _{yz}	<mark>-0.224</mark>	LP(2)Ni	<mark>3.17</mark>
<mark>3</mark>	d_{xz}	<mark>-0.228</mark>	LP(3)Ni	<mark>5.92</mark>
	d_{x}^{2}	<mark>-0.256</mark>	LP(4)Ni	<mark>8.63</mark>
	d_{xy}	<mark>-0.312</mark>	BD(1)Ni - C	<mark>22.14</mark>

Table 2. Electronic properties of the *d*-orbitals in the complex 1, 2 and 3

* Lp: Lone pair or none bonding, BD: Bonding



Fig. 1. Plots of polymerization activities of the catalysts **1** (**\blacksquare**), **2** (•) and **3** (•) versus [Al]:[Ni] molar ratio. Polymerization temperature = 30 °C, polymerization time= 30 min, monomer pressure= 2 bar, [Ni]= 7×10^{-4} mmol, toluene volume= 250 mL.



Fig.2. Contour diagram of five *d*-orbitals and the molecular orbital with unpaired electron

for the catalyst ${\bf 1}$



Fig.3. Contour diagram of five *d*-orbitals and the molecular orbital with unpaired electron

for the catalyst ${\bf 2}$



Fig.4. Contour diagram of five *d*-orbitals and the molecular orbital with unpaired electron

for compound 3



Fig.5. Energy diagram of five *d*-orbitals in 1, 2 and 3



Fig. 6. Plots of polymerization activities of the catalysts **1** (**\blacksquare**), **2** (•) and **3** (•) versus polymerizations temperature. Polymerization time= 30 min, monomer pressure= 2 bar, [Al]:[Ni]= 1000, [Ni]= 7×10⁻⁴ mmol, toluene volume= 250 mL.



Scheme 1. Structure of the catalysts 1-3 prepared in this work.



Scheme 2. Deactivation mechanism proposed for the catalyst 3.



Scheme 3. Electronic interaction between H- β and *ortho*- fluorine substituted phenyl ring on the N.



Scheme 4. Different effects of fluorine on the catalysts behaviors due to its interaction with the substitution of α -diimine backbone structure.





Scheme 5. DFT-optimized structure of the cationic species derived from the catalyst 1.



Scheme 6. DFT-optimized structure of the cationic species derived from the catalyst 2.



Scheme 7. DFT-optimized structure of the cationic species derived from the catalyst 3.



Scheme 8. Charges of the cationic species derived from the catalysts 2 (up) and 3 (down) calculated by the DFT theory.

- Synthesis of fluorinated nickel α -diimine catalysts based on Ni .
- Comparative ethylene polymerization
- Proposing a mechanism for the catalyst deactivation
- computational study for the interaction between fluorine and the ligand backbone