

## Theoretical and empirical investigation on Ni-based catalyst structures for olefin polymerization

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### Introduction

Theoretical and practical studies on the most class of polymerization catalysts have been carried out [1-3]. However, among these investigations, the relation between the structure and properties of the complexes are still studying. Theoretical studies along with the practical experiment are needed to predict the behavior of complex or confirm the results and possible interactions [4,5].

The effects of electron withdrawing group on the catalyst behavior have been investigated. Based on this, electronegative groups such as Cl, Br, CF<sub>3</sub> and NO<sub>2</sub> on meta and para caused an increasing in catalyst activity and molecular weight of produced polymer [6-9]. Presence of electron donating groups on para position leads to higher stability and longer lifetime of active center and producing higher Mw of polymer. This observation probably is attributed to stabilization of transition state including electrophile-unsaturated alkyl (agostic interaction). However, electronegative groups conducting a deplete in catalyst lifetime and polymer molecular weight through the increasing in instability of active center and higher rate of chain transfer reactions [10].

Altogether, steric and electronic effects of aryl substituents are two critical factors which can modify the metal center environment through accelerating or suppressing the polymerization reactions. Herein, we investigated the theoretical parameters such as chemical hardness ( $\eta$ ), electronic chemical potential ( $\mu$ ), global electrophilicity index ( $\omega$ ), electron density around the metal center, electronic and thermal energies to reveal and to confirm the fact that how the structure have impacts on the polymerization media.

### Materials and Methods

The ligands and complexes were synthesized according to our reported work [3]. The polymerization of 1-hexene (monomer purified prior to use) was carried out in a round bottom flask which was conducted under schlenk system before and during the injections. The monomer (10 ml) was injected to the flask which was contained 6 ml of solvent (toluene). Afterward, the desired amount of co-catalyst and catalyst were introduced to the flask, respectively. The solution was stirred over a distinct time. The poly (1-hexene) was precipitated and purified by acidic methanol (5%).

### Results and Discussion

As the experimental results showed the higher activity of the catalyst A bearing isopropyl substituents on *ortho* positions and acenaphthene group on the backbone, catalysts B and C with differences in the backbone and substituents exhibited lower productivities, respectively. This results along with some reasons also can be observed in some other literature, however, we studied on the theoretical and topological parameters, deeply. In addition to the level of energy in the catalyst structure, there are some parameters in relation

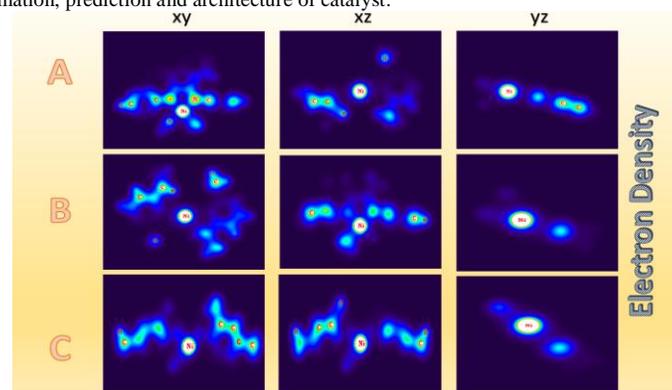
with the activity. To clarify, as higher Mulliken charge on the metal center is good for monomer uptake, but less shielding effects of the active center can cause to deactivation. The results are listed in table 1. Higher shielding of axial sites, electron density, chemical hardness and lower HF energy and weaker electrophilicity index indicated characteristics of an effective catalyst in polymerization of olefin.

**Table 1. Theoretical parameters of catalysts A, B and C.**

Catalyst	Mulliken charge on Ni	$\eta$ or Band gap (eV)	$-\mu$	$\omega$
A	1.099	0.108	0.281	0.366
B	1.346	0.111	0.288	0.372
C	1.282	0.104	0.288	0.398

### Significance

Make a connection between the theoretical parameters and experimental results for confirmation, prediction and architecture of catalyst.



**Figure 1.** distribution of electron density around the nickel center in xy, xz and yz planes.

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