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Phenylene spacer between nickel centers in α -diimine binuclear catalysts for ethylene polymerization

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Abstract

To investigate dinuclearity and bridge effects on the catalyst performance and some polyethylene properties, two binuclear and a mononuclear α -diimine Ni(II)-based catalysts were comprised. Diphenyl Bi-Nuclear catalyst (DBNC) with a structure showed the highest activity (1750 g PE/mmolNi. h.) at the same ethylene polymerization condition while the bi-nuclear catalyst (BNC) illustrated moderate activity (1073 g PE/mmolNi. h.) and mono-nuclear catalyst (MNC) with no activity. This observation assigned to synergistic dinuclearity and cooperative effects which increased as the length, flexibility and thermal stability of bridge increased in DBNC (biphenyl methylene spacer). DSC thermograms revealed that polymer resulted using DBNC has insignificant crystallinity degree less than 1% with melting point at 117.2 °C, however, BNC yielded polyethylene with 24.7% crystallinity and $T_m=123.0$ °C. The vinyl content and branching of resulted PE in presence of catalyst DBNC were 21.2 and 101, however, these quantities decreased to 9.1 and 78 for catalyst BNC, respectively.

Keywords: Binuclear α -diimine complex -Catalytic polymerization -Polyethylene -Dinuclearity-Structure-Property relation.

Introduction

The development of polyolefin catalysts especially late transition metal complexes has seen impressive progress due to their unique reactivity patterns and unusual catalytic properties for poly/oligomerization. Considering this significant field of homogeneous single-site catalysts, a sort of cooperative effects involving two or more metal center is possible. These effects can be a reason of achieving more efficient chain propagation to yield novel polymer in structure, tacticity and bimodal/multimodal curves. Homogeneous catalyst systems based on late transition metal catalysts are currently regarded as being one of the interesting research fields in olefin polymerization catalysts [1-5].

Moreover, reasons and mechanisms of the most results from olefin polymerization and copolymerization in presence of multinuclear catalysts are explained suggestively but a huge number of practical and theoretical studies reported cooperation and absence of cooperation between

centers. Among this class of catalysts, sort of center and linkage are main factors in comparison to their mononuclear analogues. Totally, generation of catalyst center and steric, electronic effects and distances between centers can cause a variation in performance and catalyst behavior, producing polyolefin with different microstructure and properties [6-9].

In this work, two binuclear and a mononuclear α -diimine Ni(II)-based late transition metal catalysts were synthesized under controlled condition and used in homo-polymerization of ethylene. dinuclearity and bridge effects of ligand structure on catalyst productivity was investigated.

Experimental

The ligand and complexes (Scheme A) were prepared according to our recently work [10].

Results and Discussion

To investigate dinuclearity and bridge effects on the catalysts performance and some polyethylene

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properties, two binuclear and a mononuclear α -diimine Ni(II)-based catalysts were comprised (Scheme A). Diphenyl bi-Nuclear catalyst (DBNC) with a novel structure showed the highest activity (1750 g PE/mmolNi. h.) at the same ethylene polymerization condition while the bi-nuclear catalyst (BNC) illustrated moderate activity (1073 g PE/mmolNi. h.) and mono-nuclear catalyst (MNC) with no activity. DSC thermograms revealed that polymer resulted using DBNC has insignificant crystallinity degree less than 1% with melting point at 117.2 °C, however, BNC yielded polyethylene with 24.7% crystallinity and $T_m=123.0$ °C. The vinyl content and branching of resulted PE in presence of catalyst DBNC were 21.2 and 101 (in 1000 carbon atom), however, these quantities decreased to 9.1 and 78 for catalyst BNC, respectively.

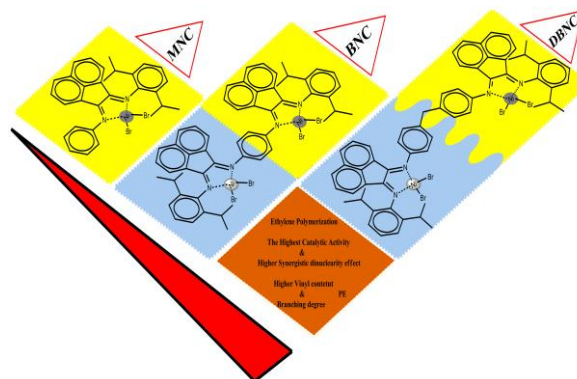
Conclusion

The catalysts productivity assigned to synergistic dinuclearity and cooperative effects which increased as the length, flexibility and thermal stability of bridge increased in DBNC (biphenyl methylene spacer). Besides, higher chain walking and vinyl end chain production along with the reinsertion led to PE with higher and variable amounts of chain branching and less crystallinity degree of PE using catalyst DBNC.

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Scheme A. Representation of the complex structures.