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Simple and Strong Dative Attachment of α-Diimine Nickel (II) Catalysts on Supports for Ethylene Polymerization with Controlled Morphology

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Abstract

In this article, preparation of novel spherical $MgCl_2$ supported α-diimine nickel (II) catalysts for ethylene polymerization in slurry phase is reported. α-Diimine ligands were synthesized by condensation reaction of 2, 6-disubstituted alkyls or aryls anilines and Ace naphthoquinone Which have hydroxyl functionality in their para-position. Hydroxyl functionalized α-diimine attached strongly on to the spherical $MgCl_2$ support surface by dative bonding. No linker was needed to attach the complexes onto the support surface and the amount of loaded Nickel was controllable to improve morphology and especially bulk density of polymer powder. A significant reduction in catalysts activity has happened when homogeneous catalysts were supported onto silica but this reduction was decreased when they were supported onto thermally treated spherical $MgCl_2$. As homogeneous bis(*N*,*N′*-(4-(3-hydroxyl-propyl)-2,6-di[(4-*tert*-butyl-phenyl)-phenyl) amino] Ace naphthoquinone Nickel dibromide(d) showed the highest activity among other evaluated homogeneous catalysts, its $MgCl_2$ supported catalyst (d/S-$MgCl_2$) has shown the highest activity among $MgCl_2$ supported catalysts too. These $MgCl_2$ supported catalysts were pre-polymerized in presence of ethylene monomer in the mild polymerization condition to yield a pre-polymerized catalyst with polymer/catalyst weight ratio equal to six. Ethylene polymerization was carried out to make spherical particles of polyethylene without reactor fouling by these pre-polymerized catalysts. Clearly, it is shown in SEM images that the spherical morphology of $MgCl_2$ support is replicated in the produced polymer. The molecular weight and molecular weight distribution of produced polymer with $MgCl_2$ supported catalysts were higher than those produced by homogeneous catalysts.

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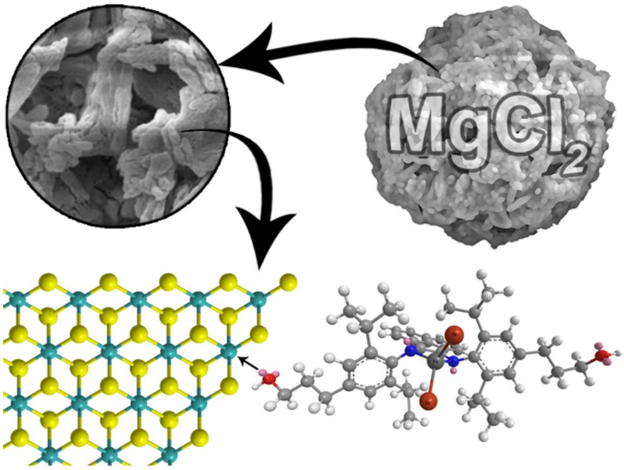
Graphic Abstract

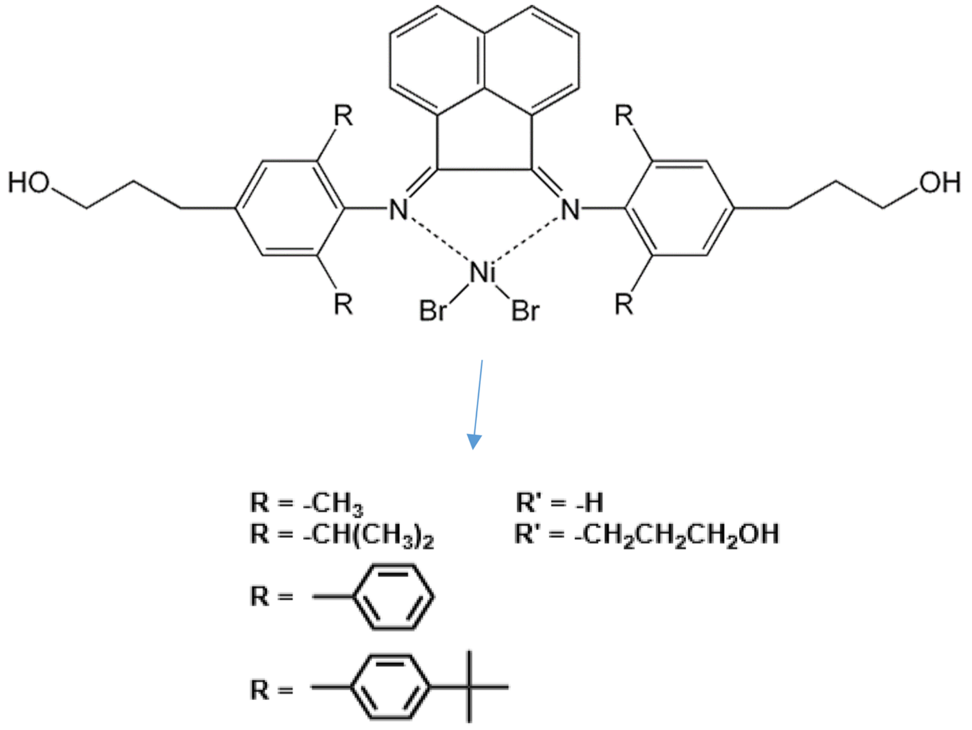
α–Diimine nickel (II) complexes have hydroxy functionality where produce strong dative bonding onto spherical $MgCl_2$. This bonding is strong enough that these catalysts are suitable for slurry polymerization of ethylene without reactor fouling due to catalyst leaching from support. The chemical structure of $MgCl_2$ leads to high active supported catalysts. The molecular weight and polydispersity index of produced polymrers using these supported catalysts are higher than those produced by equivalent homogeneous catalysts and are controllable by selection of appropriate ligand for used α–diimine nickel (II) complex or hydrogen concentration in ethylene polymerization.



Keywords Supported catalysts · Ni diimine · Ethylene polymerization

1 Introduction

Since the discovery of late transition metal catalysts for olefins polymerization by Brookhart, these kinds of catalysts have been interested due to their unique and potential ability to chain walking and produce tailored branch polyethylene from ethylene alone. Despite their versatile advantages, one major drawback to the commercialization of Brookhart catalysts is their rapid and quantitative deactivation in the presence of hydrogen, which is unavoidable for molecular weight control in technical polymerization processes. Recently, Rigger and coworkers reported new polychromatic, highly active and hydrogen-stable Ni(II) complexes [1, 2]. On the other hand, these new late transition metal catalysts have to support a suitable carrier if they want to apply in industrial processes [3–5]. Many different procedures were introduced for preparing supported catalyst using silica, $MgCl_2$ or $SiO_2/MgCl_2$ supports. Silica supports and silica/magnesium chloride supports are commonly used as appropriate supports for Ziegler–Natta and Metallocene catalysts [4, 6, 7] and recent late transition metal catalysts [8, 9]. In some articles, late transition metal catalysts were impregnated on the surface of support physically [10]. In polymerization condition, leaching of catalyst from support is one of the limitations of physically supported late transition metal catalysts [11–14]. This event leads to (1) agglomeration of polyethylene on the reactor wall and stirrer, which decreases heat removing rate and (2) a significant decrease in catalyst activity. Covalently attaching of active centers on the support is a common approach to overcome these obstacles so that researchers used chemically treated supports with aluminum alkyl derivatives to make covalently link betwe`en support and α-diimine Ni(II) catalysts [11–15]. These covalently attached supported catalysts were shown good performances in gas and slurry phase polymerization [16, 17]. Homogenous and appropriate fragmentation of supported catalysts in polymerization process led to the reduction of fine particles portion in produced polymer but the morphology of produced polymer by these supported catalysts was not as good as that produced by spherical $MgCl_2$ supported catalysts [18]. In another procedure, α-diamine Ni(II) complexes were reacted with MAO which then was added to the slurry of support in a solvent [19–22]. These procedures have been mostly used for catalysts. The obtained data showed that supported late transition metal catalysts by these methods would have low activity [4, 6, 23]. To overcome this disadvantage, several research groups reported new methods to attach α-diimine Ni(II) complexes onto $MgCl_2$ support surface covalently [24–27]. These supported catalysts were prepared by reaction of α-diimine Ni(II) complexes containing hydroxyl or amino functionality and SiO_2 which were pretreated with aluminum alkyl derivatives [28, 29]. The most efficient support that has created a revolution in Ziegler–Natta catalysts for ethylene polymerization is $MgCl_2$ and morphology of polymer particles has been one of the most important issues in the polymerization of ethylene. Several different procedures were employed to prepare $MgCl_2$ support to enhance Ziegler–Natta catalysts performance and polymer morphology. Yiyoung et al. [3] and Severn et al. [18] used $MgCl_2$ as support for late transition metal catalysts. Soars and coworkers crystallized $MgCl_2$ from $MgCl_2$/heavy alcohol adducts by reaction with alkyl aluminum and then supported α-diimine Ni(II) complexes through an amino functionality onto the support. Covalently bonded α-diimine catalysts to the support surface prevented leaching of catalysts during ethylene polymerization in slurry phase. Their results showed that $MgCl_2$ supported α-diimine catalysts have higher activity compared to SiO_2 supported catalysts, for the same α-diimine catalysts. In another procedure, Chadwick and coworkers supported α-diimine Ni(II) complexes on $MgCl_2$ by a simple procedure [30, 31]. In this procedure, spherical $MgCl_2$/ethanol adduct was reacted with aluminum alkyls to produce spherical support of composition $MgCl_2$·0.24Al (Et) 2.3(OEt) 0.7. Immobilization of α-diimine Ni(II) catalysts with methyl and isopropyl substituents in the Orth positions of the aryl rings on $MgCl_2$ led to an increase in ethylene polymerization rate compared to those reported for catalysts prepared using silica support. The molecular weight distribution of produced polyethylene by this immobilized catalyst was narrow [32, 33]. The data show that this preparation procedure, conserve single-site characterization of these supported catalysts. In this work, a simple and efficient procedure is introduced for heterogenization of α-diimine Ni(II) catalysts on $MgCl_2$ support with spherical morphology and good mechanical properties. Spherical $MgCl_2$·nEtOH was prepared using the presented method in previous articles [34, 35]. Spherical $MgCl_2$ support was thermally treated to decrease alcohol content and increase the surface area and mechanical properties of the support. The dealcoholized spherical $MgCl_2$·nEtOH was directly used as a support for α-diimine Ni(II) catalysts (Fig. 1) that have hydroxyl functionality in para-position of their aryl rings. The hydroxyl groups were attached to the support without any chemical treatment of the surface. In addition, the influence of ligand structure and the type of support on the polyethylene properties and polymer particle morphology were evaluated with electron microscopy experiments. The most important perspective has been the synthesis of the hydroxy functionalized steric bulky α-diimine ligand with 4-butyl phenyl substituents to improve catalyst activity in presence of hydrogen as well as its thermal stability and The molecular weight and molecular weight distribution of produced polymer with $MgCl_2$ supported catalysts were higher than those produced by homogeneous catalysts.



R in **a**) Methyl, **b**) iso-Propyl, **c**) Phenyl and **d**) 4-tert-Butylphenyl

Fig. 1 α-Diimine nickel (II) catalysts

2 Experimental

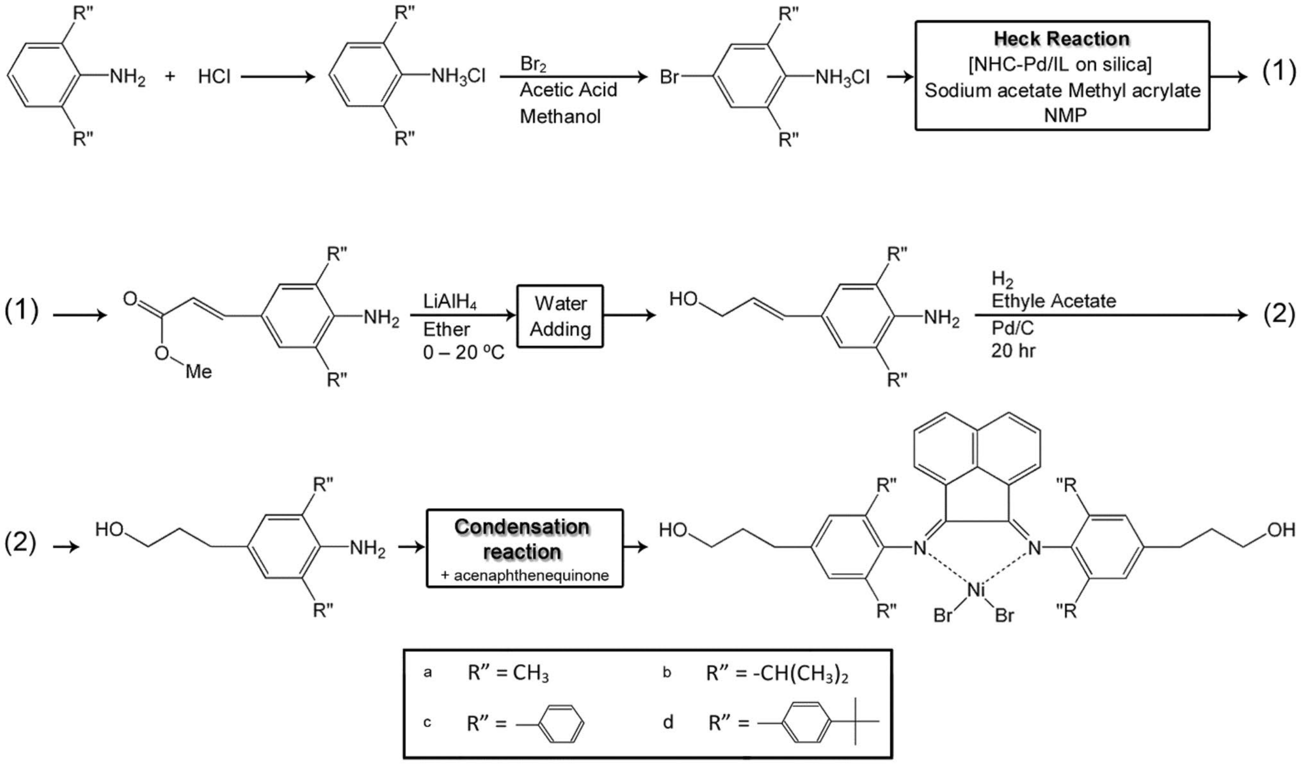
2.1 Materials and Methods

The water content of solvents and reagents should be lower than 5 ppm. Reagents were added to the reaction vessels under a nitrogen blanket. The nitrogen was dried by passing through the columns of molecular sieve 13XA with an average pore diameter 3–4 Å. Syntheses of oxygen and water sensitive materials were carried out under dried nitrogen by dried glassware. The water content of methylene dichloride (CH_2Cl_2) and the other solvent like diethyl ether, hexane and toluene were reduced to an acceptable amount. The synthesized compound and sensitive material were manipulated in a nitrogen-filled glovebox at ambient temperature. Aniline, 2,6-diisopropylaniline, 2,6-dimethylaniline, nickel bromide acenaphthenequinone, lithium aluminium hydride, palladium acetate, tri-ethyl amine, methyl acrylate, 10% palladium on activated carbon, bromine, and acetic acid were purchased from Merck Chemical Co. Silica gel (mesh 300–425) and Anhydrous magnesium chloride were purchased from Grace Davison and Aldrich Co. respectively. Hexane (was used after passing over molecular sieves (4 Å) and Na), hydrogen and polymerization grade ethylene were obtained from Bandar Imam Petrochemical Co, from HDPE unit. 2,6-diphenylaniline, 2,6-di(4-*tert*-butyl phenyl)aniline, N-heterocyclic carbon palladium complex, Ionic liquid matrix immobilized on silica and α-diimine complexes and intermediate materials for the synthesis of a to d were synthesized [26].

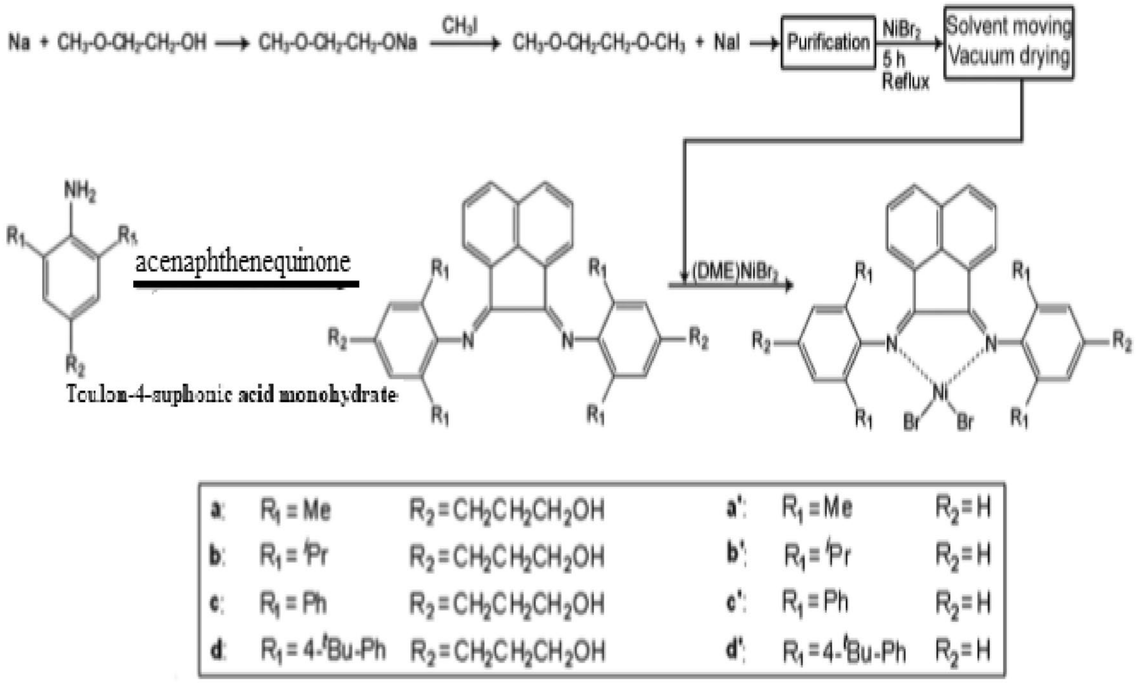
3 Results and Discussion

3.1 Ligands and Complexes Synthesis

2,6-Dimethyl and diisopropyl anilines were purchased and used directly. 2,6-Diphenyl-substituted anilines were synthesized in agreement with literature procedure reported by Reiger et al. [1]. Based on the procedure, the bromination, Grignard and Suzuki cross coupling reactions by palladium catalyst can be performed to produce 2,6-disubstituted anilines. A modified procedure was used to functionalize these anilines with a hydroxyl group in their *para* position (Scheme 1). In this method, anilines were functionalized by Heck reaction with methyl acrylate in the presence of supported recoverable palladium catalyst. α-Diimine were synthesized by condensation reaction of the functionalized anilines with acenaphthenequinone in presence of para-toluene sulfonic acid as a catalyst. the α-diimine nickel (II) catalysts



Scheme 1 Ligands synthesis procedure



Scheme 2 Synthetic route of α-diimine precatalyst

with hydroxy functionality were synthesized in two steps: in the first step, α-diimine ligands were synthesized by reaction of 2,6-disubstituted anilines (a–d) and acenaphthenequinone and in the second step, the produced α-diimines ligands were reacted with(NiBr$_2$(DME)) in dichloromethane (Scheme 2).

3.2 Heterogenization of α-Diimine Nickel (II) Complexes on Spherical MgCl$_2$ Support

These supported catalysts were prepared by reaction of hydroxyl functionality of α-diimine Ni(II) complexes with spherical MgCl$_2$ particles without any linker α-diimine Ni(II) catalysts was dissolved in CH$_2$Cl$_2$ to make a clear

Fig. 2 Proposed complexes of MgCl$_2$ and α-diimine nickel (II) catalysts

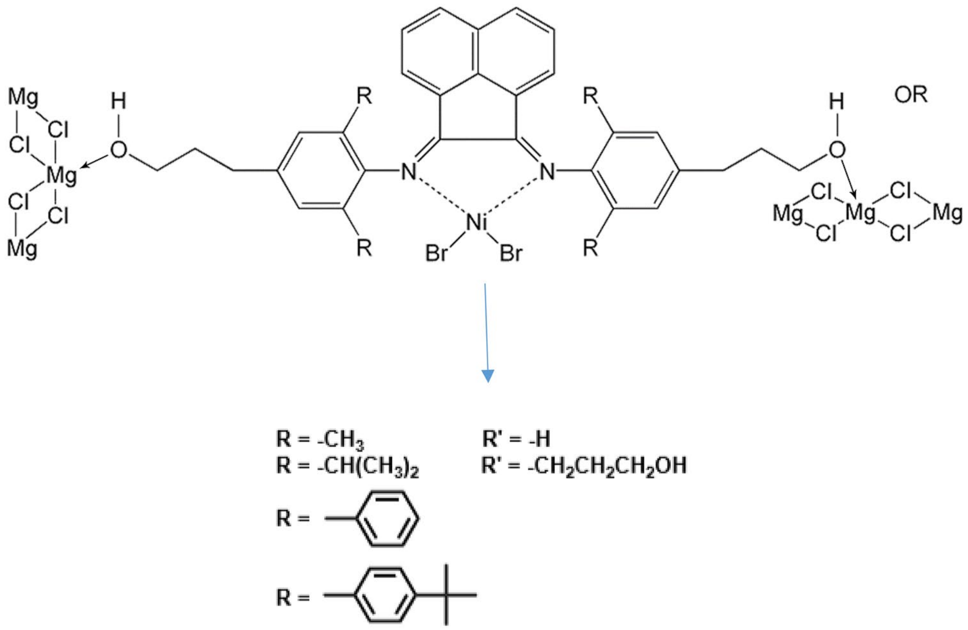


Table 1 Elemental analysis of spherical $MgCl_2$ supported α-diimine nickel (II) catalysts

Catalyst type	Mg[a]	Cl[b]	Loaded Ni[a]	Ethanol[c]
a	16.4	48.8	0.89	22.2
b	16.1	47.8	0.92	20.3
c	15.8	45.5	0.85	19.8
d	14.9	43.8	0.78	19.5
d′	n.d	n.d	2.23	n.d

[a] Determined by atomic absorption

[b] Determined by titration

[c] Determined by GC

solution. Then thermally treated spherical $MgCl_2$ was dispersed in the solution and mixed gently every 15 min. the solution color gradually disappeared. The slurry was filtered and spherical catalyst was dried in vacuum at room temperature. The attachment of α-diimine Ni(II) catalyst on $MgCl_2$ surface via hydroxyl functionality is shown in Fig. 2. The Ni content in supported catalysts was determined by elemental analysis and reported in Table 1.

3.3 Slurry Phase Ethylene Polymerization

The slurry phase ethylene polymerizations were carried out in a one-litter stainless steel Buchi reactor in 750 mL dried hexane. Polymerization of ethylene using unsupported and supported catalysts were carried out in the same condition to compare their performances. The ethyl aluminum sesquichloride was used as an efficient co-catalyst and the selected Al/Ni mole ratio was equal to 300. The reaction time was one hour and the polymerizations were carried out in 45 °C controlled by a high flow rate circulator. To obtain polymer particles with better morphology, the perpolymerization step was carried out in a mild reaction condition before the main polymerization step. The prepolymerization was performed in 10 °C temperature reaction and ethylene partial pressure of 0.2 bar. A mass flow controller measured and controlled the flow rate of ethylene to the prepolymerization reaction. The weight ratio of polymer to the supported

Table 2 Ethylene polymerization results with homogeneous, $MgCl_2/SiO_2$ bisupported and spherical $MgCl_2$ supported α-diimine nickel (II) catalysts

Run	Catalyst	Activity[a]	Temp (°C)	Yield[b]	Mw × 10c^{3} [c]	PDI[d]	T_m (°C)
1	a	12,600	45	29.0	52.0	1.69	128
2	b	17,440	45	43.6	247.5	2.85	116
3	c	25,040	45	62.6	1093	2.72	127
4	d	30,080	45	75.2	3700	2.74	126.5
5	a/Si-Mg	13,000	45	32.5	175.8	5.78	128
6	b/Si-Mg	11,120	45	27.8	384.6	6.23	127
7	c/Si-Mg	18,800	45	47.0	3680	7.02	127.5
8	d/Si-Mg	21,120	45	52.8	4200	7.52	128
9	a/S-Mg	14,200	45	35.5	146	7.23	129
10	b/S-Mg	12,480	45	31.2	517.6	6.38	128
11	c/S-Mg	24,760	45	61.9	1246	8.30	128
12	d/S-Mg	25,680	45	64.2	3952	7.04	129
13	d/S-Mg*	20,800	45	52.0	2779	7.5	129
14	a	15,120	30	37.8	n.d	n.d	128
15	a	8450	60	16.9	n.d	n.d	110
16	b	22,600	30	56.5	n.d	n.d	128.5
17	b	9320	60	23.3	n.d	n.d	74.8
18	c	16,000	30	40.0	n.d	n.d	128
19	c	18,600	60	46.5	n.d	n.d	127.5
20	d	35,080	30	87.7	n.d	n.d	129
21	d	23,360	60	58.4	n.d	n.d	128

Polymerization conditions: homogenous and heterogeneous catalyst 2.5 μmol, cocatalyst: EASC (Al/Ni = 300), nickel loaded in supported catalyst: < 1 wt% and*: 2.23 wt% in Run 13, solvent hexane, ethylene pressure 10 bars, time 60 min

[a] Activity in kg PE/(mol Ni × h)

[b] Yield in gram

[c] Molecular weight in g/mol

[d] Polydispersity index (M_w/M_n), Run 5–8 [26]

catalyst was about 6. The prepolymerized catalyst was dried and diluted in dried hexane. The amount of injected prepolymerized catalyst to the reactor was determined based on concentration of Ni in reactor. Polymerization of ethylene using homogeneous, $SiO_2/MgCl_2$ bisupported and spherical $MgCl_2$ supported α-diimine nickel (II) catalysts were performed. The results of polymerizations are shown in Table 2.

The results showed that, synthesized α-diimine nickel (II) catalysts by *tert*-butyl phenyl substitutes in ortho positions of aryl ring have the highest activity among other catalysts. The data show that the activity of homogenous catalysts significantly depends on the polymerization temperature. The stability of active centers is decreased in higher temperature and this phenomenon is significant for homogeneous α-diimine nickel (II) catalysts with ligands bearing lower steric hindrance. The catalyst activity is decreased when homogeneous catalysts are supported. Exceptional results in Table 2 (run 5 and 9) show that supporting of catalyst **a** with methyl substituents in their ortho-aryl positions increases thermal stability of active centers. This thermal stability leads to increased insertion and decreased β-hydride elimination reactions. Reduction in activity is significant when $SiO_2/MgCl_2$ bisupport is used, but the activity reduction for spherical $MgCl_2$ supported α-diimine nickel catalysts is lower. In supported catalysts, the α-diimine nickel (II) complexes with hydroxyl functionality are strongly attached to the magnesium atoms of $SiO_2/MgCl_2$ and spherical $MgCl_2$ surface. These supported catalysts exhibit high activity and are desirable for ethylene polymerization in industrial processes. Polyispersity index (PDI) of produced polyethylene with homogenous catalyst is about 3, but the supporting of these catalysts increased PDI of the produced polymers in the same polymerization condition. On the other hand, molecular weight of produced polymer by the supported catalyst is higher than homogeneous catalysts. It can be explained by reduced chain termination and increased chain propagation rate of active centers in supported catalysts. Immobilization of α-diimine catalysts on the surface of support reduces the space around the active metal centers and as reported by Rieger and Gibson et al. [33, 34] it might decrease chain transfer rates. Increase in molecular weight of produced polymer by spherical $MgCl_2$ supported catalysts is larger than the polymer produced by $SiO_2/MgCl_2$ bisupported catalysts. It can be related to the acidic nature of $MgCl_2$ support and the electronical effect on the chain propagation rate of active centers. Ethylene polymerization using **d** onto spherical $MgCl_2$ were carried out in different temperature (Table 3). The results show that, the activity of this supported catalyst increases when the reaction temperature is increased from 45 to 60 °C. More increase in reaction temperature has inverse effect on activity due to instability of active centers in α-diimine complexes at high temperature. The molecular weight of produced polymer by homogeneous and supported catalyst was increased using

Table 4 Effect of hydrogen partial pressure on molecular weight of produced polymer by d/S-Mg

Run	H_2 (bar)	Yield[a]	Activity[b]	$Mw \times 10^{3}$ [c]	PDI[d]
1	0	72	28,800	3260	11.5
2	0.5	70	28,000	2220	10.8
3	1.0	67.5	27,000	765.2	11.3
4	2.0	67	26,800	553	9.2
5	3.0	66.7	26,680	360	8.7

Polymerization conditions: heterogeneous catalyst 2.5 µmol, cocatalyst: EASC (Al/Ni = 300), nickel loaded in supported catalyst: < 1 wt%, solvent hexane, ethylene pressure 10 bars, time 60 min, temp: 60 °C

[a] Yield in gram

[b] Activity in kg PE/(mol Ni × h)

[c] Molecular weight in g/mol

[d] Polydispersity index (M_w/M_n)

Table 3 Effect of temperature on performance of Spherical $MgCl_2$ supported α-diimine nickel (II) catalysts

Run	Catalyst	Temp (°C)	Yield[a]	Activity[b]	$Mw \times 10^{3}$ [c]	PDI[d]
1	a/S-Mg	30	31.5	12,600	201	7.0
2	a/S-Mg	60	22.6	10,720	84	8.3
3	b/S-Mg	30	23.5	9400	662	6.2
4	b/S-Mg	60	29.3	11,720	370	7.4
5	d/S-Mg	30	48.7	19,480	n.d	n.d
6	d/S-Mg	60	72.0	28,800	3260	7.5
7	d/S-Mg	80	35.5	14,200	860.8	6.8

Polymerization conditions: heterogeneous catalyst 2.5 µmol, cocatalyst: EASC (Al/Ni = 300), nickel loaded in supported catalyst: < 1 wt%, solvent hexane, ethylene pressure 10 bars, time 60 min

[a] Yield in gram

[b] Activity in kg PE/(mol Ni × h)

[c] Molecular weight in g/mol

[d] Polydispersity index (M_w/M_n)

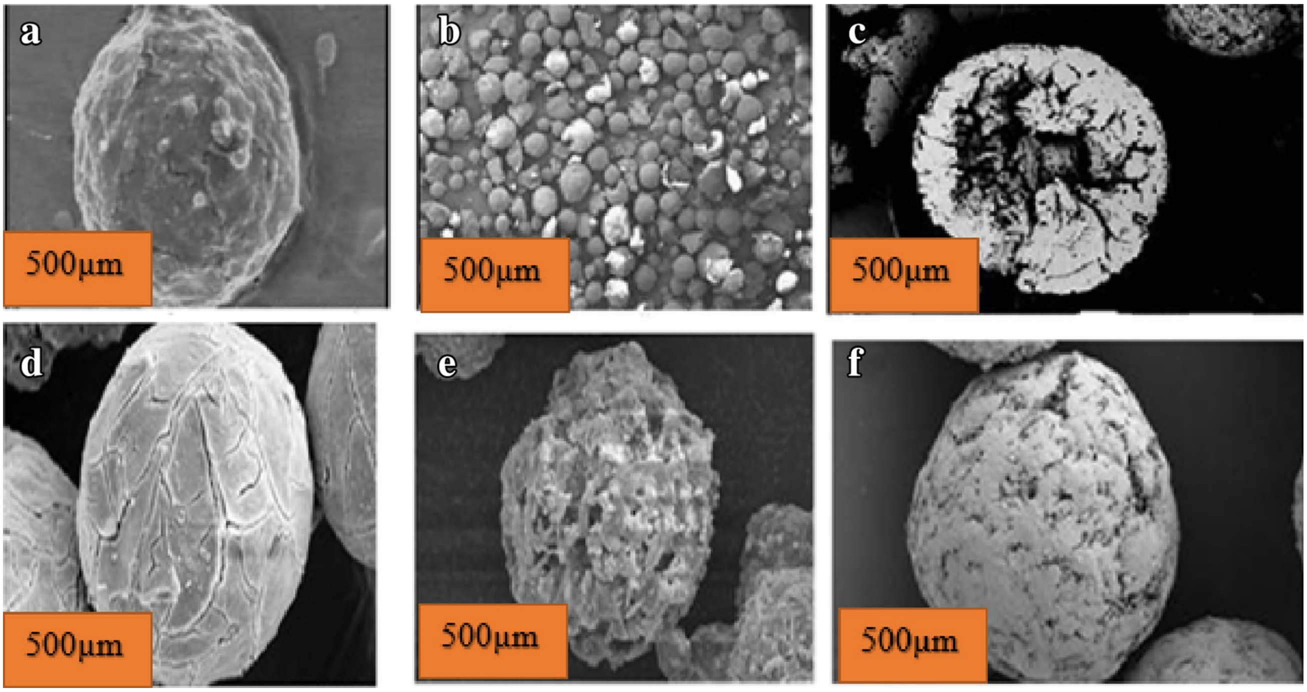


Fig. 3 SEM image of **a** bisupported catalyst **d**/Si-Mg, **b** produced polymer by bisupported catalyst **d**/Si-Mg in 45 °C, **c** Cross section a particle shown in b with 2000-fold magnification, **d** spherical $MgCl_2$ support, **e** heat treated Spherical $MgCl_2$ support, **f** produced polymer by **d**/s-Mg supported catalyst onto spherical $MgCl_2$

more bulky ligands. It seems that, bulkier ligands increase chain propagation or reduced chain termination rates [2]. Homogeneous and supported catalyst, **d** which carries bulky 2,6-di(4-*tert*-butyl phenyl) aryl has shown good activity to produce polyethylene with high molecular weight. In Table 4, the hydrogen response of supported **d** onto spherical $MgCl_2$ was shown. The molecular weight of polymers was decreased by increasing the partial pressure of hydrogen without any sharp decrease in catalyst activity.

3.4 Catalyst and Polymer Particle Morphology

The SEM images in Fig. 3 show an irregular shape of polymer particles with low bulk density using catalysts SiO_2/$MgCl_2$ and spherical $MgCl_2$ supported catalysts surface and regular shape and their related produced polymer particles. It is shown that polymer morphology is not sufficient for polymer processing and it has motivated researchers to attach these catalysts specially SiO_2/$MgCl_2$ and spherical $MgCl_2$ supported catalysts and their related produced polymer particles by covalent bonds onto supports to produce polymer particles with desirable morphology. The SEM images of the polymers showed regular morphology and agglomeration of the polymers on reactor wall and agitator. The SEM micrographs show that the morphology of spherical $MgCl_2$ supported catalyst was replicated into the final polymer particles. Strongly attachment of α-diimine nickel (II) complexes onto the $MgCl_2$ support led to free-flowing polymer particles and the reactor fouling was not observed during ethylene polymerization.

4 Conclusion

α-Diimine nickel (II) complexes were synthesized using different anilines with methyl, isopropyl, phenyl and *tert*-butyl phenyl substitutes in their ortho positions and hydroxyl functionality in their *para* position. These complexes were supported on SiO_2/$MgCl_2$ bisupport and thermally treated spherical $MgCl_2$ support. Supporting of homogeneous α-diimine nickel (II) complexes reduced the catalyst activity. The reduction in activity for bisupported catalyst was significant but it was low or negligible when spherical $MgCl_2$ was used as catalyst support. The supported α-diimine complex on spherical $MgCl_2$ that was prepared from aniline with *tert*-butyl phenyl substitutes showed the highest activity among the examined catalysts. According to the results, this catalyst is desirable for industrial ethylene polymerization processes and has a good hydrogen response for controlling molecular weight. The produced polymer by this supported catalyst had high molecular weight and melting point temperature. The SEM micrographs show that the morphology of spherical $MgCl_2$

supported catalyst was replicated into the final polymer particles. Strongly attachment of α-diimine nickel (II) complexes onto the $MgCl_2$ support led to free-flowing polymer particles and the reactor fouling was not observed during ethylene polymerization.

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