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Ethylene polymerization using nickel α-diimine complex supported on $SiO_2/MgCl_2$ bisupport

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Abstract

Nickel α-diimine complex $[C_6H_5{-}N{=}C(CH_3)C(CH_3){=}N{-}C_6H_5]NiCl_2$ was impregnated on $SiO_2/MgCl_2$ bisupport, and ethylene polymerizations were carried out with alkylaluminum compounds as cocatalyst. Branched polyethylenes were prepared when heptane is used as solvent. Polymerization conditions such as modified method of bisupport, cocatalyst, Al/Ni ratio, temperature and nickel concentration had a pronounced effect on catalytic activity and properties of polyethylenes. The activity of 2.9×10^5 g PE mol Ni h^{-1} was obtained in the presence of $AlEt_2Cl$ as well as the bisupport without $AlEt_3$ modification, Al/Ni ratio 80, nickel concentration 0.12 mmol/l and temperature 14 °C. Branching degree of polyethylenes increased with temperature, and molecular weight, melting point and crystallinity of polyethylenes decreased correspondingly. Polymerization temperature had a pronounced effect on branches distribution of polyethylenes. Content of methyl branch increased sharply with temperature, but long branches dropped quickly.

Keywords: Nickel α-diimine complex; Bisupport; Branched polyethylenes

1. Introduction

Branched polyethylenes have become plastic materials of industrial interest in the recent past because the short-chain or long-chain branches in the polyethylene backbone enhance the mechanical strengths of polyethylene products, such as the stiffness, stress-crack resistance, tensile strength, and most importantly, processability. Therefore, branched polyethylenes have great advantages over more brittle and less easily processable high-density polyethylene (HDPE) [1].

Branched polyethylene is commonly produced by the copolymerization of ethylene with α-olefin comonomers such as 1-butene, 1-hexene, and 1-octene with Ziegler–Natta or metallocene catalysts [2,3]. Moreover, it can be produced with dual-component or dual-site catalyst system. This technique uses a single feed of ethylene and two catalysts operating in the same reactor. One catalyst component oligomerizes ethylene into α-olefins, and the other polymerizes ethylene with the concomitant incorporation of α-olefins formed by the first catalyst component into polyethylene backbone [1,4].

Brookhart has demonstrated that highly branched polyethylenes can be synthesized using homogeneous palladium (II) and nickel (II) catalysts incorporating very bulky chelating diimine ligands [5]. These highly branched polyethylenes are also produced with a single feed of ethylene, without the intermediacy of α-olefins. Polymer branch formation is thought to arise from β-hydrogen abstraction followed by readdition of the resultant coordinated vinyl-ended polymer to the metal hydride, a process that results in the metal migrating or 'walking' along the polymer chain [6,7].

Despite the success of this new approach to the synthesis of branched polyethylenes by homogeneous late transition metal catalysts, the extension of this technique to heterogeneous polymerization catalyst will allow us to implement the late transition metal catalysts in existing industrial processes and to improve the morphology of branched polyethylene. Köppl has demonstrated that branched polyethylenes can be synthesized using three kinds of

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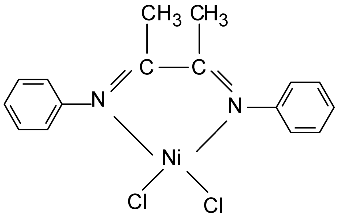


Scheme 1.

diazadiene nickel dibromide complexes supported on modified SiO_2 [8].

In this paper, we report the synthesis of branched polyethylenes by heterogeneous ethylene polymerization with a kind of nickel α-diimine complex (Scheme 1, denoted with the formula of $NiLCl_2$) supported on SiO_2/$MgCl_2$ bisupport, activated by general alkylaluminum compounds. The solvent effect of supported catalyst on ethylene polymerization, influence of polymerization conditions on catalytic activity and properties of polyethylenes, and microstructures of the resulting branched polyethylenes are discussed. In our previous papers, the activity and product character of unsupported, $MgCl_2(THF)_2$ and silica-supported $NiLCl_2$ for ethylene polymerization have been discussed [9–11].

2. Experimental

2.1. Materials

All experiments were performed under nitrogen in Schlenk-type vessels, using anhydrous air-free reagents and solvents. A dichloro(butanedionebis(aniline))nickel complex $[C_6H_5-N=C(CH_3)C(CH_3)=N-C_6H_5]NiCl_2$ ($NiLCl_2$) was synthesized by our group. Diethylaluminum chloride ($AlEt_2Cl$), triethyl aluminum (TEA) and triisobutyl aluminum (TIBA) were taken as 400 g/l solutions in *n*-heptane, respectively. Silica (Grade 955) was calcinated under a nitrogen atmosphere flow at 600 °C for 6 h before use. The other chemicals were purchased commercially and used without further purification.

2.2. Modification of SiO_2 with TEA

Calcinated SiO_2 (3.0 g) was introduced into a glass vessel equipped with a magnetic stirrer, and then 15 ml heptane was added. Eight milliliters of $AlEt_3$ solution of heptane was added to the mixture at 0 °C and stirred for 20 h. The modified SiO_2 was separated by decantation, washed up with heptane and dried under vacuum at 60 °C for 2 h.

2.3. Preparation of three kinds of SiO_2/$MgCl_2$ bisupports

In a typical experiment, 0.5 g of anhydrous $MgCl_2$ was introduced into a glass reactor equipped with a magnetic stirrer, then 20 ml tetrahydrofuran (THF) and 1.5 ml absolute ethanol were added. The mixture was heated to 45 °C and stirred until the $MgCl_2$ was completely dissolved. Calcinated SiO_2 (1.5 g) or modificated SiO_2 by TEA was then rapidly introduced so that it was uniformly dispersed in the solution. After being stirred at 45 °C for 2 h, the agglomerated particles were separated by decanting, washed up with heptane and dried under vacuum at 60 °C for 2 h. Thus, two kinds of SiO_2/$MgCl_2$ bisupports (entries I and II in Table 1) were prepared. The last kind of bisupport (entry III, Table 1) was prepared similarly with the second bisupport (entry II), except for the addition sequence of $AlEt_3$. Eight milliliters $AlEt_3$ solution of heptane was added to the mixture of calcinated SiO_2 and $MgCl_2$, then operated with the same method as Section 2.2 to prepare $AlEt_3$ modified SiO_2/$MgCl_2$ bisupport.

2.4. Preparation of $NiLCl_2$/SiO_2/$MgCl_2$ supported catalysts

To prepare impregnated nickel α-diimine catalysts by the incipient-wetness technique, 0.1 g of $NiLCl_2$ was dissolved in 10 ml of dichloromethane and then added to the above three kinds of SiO_2/$MgCl_2$ bisupports suspended in 15 ml of heptane, respectively. The suspension was stirred at room temperature overnight. After decantation, several washes with the mixture of heptane and dichloromethane (volume ratio = 4/1), and dried under vacuum. The supported nickel α-diimine complex was obtained as solid, yellow particles.

2.5. Ethylene polymerization

The measured amounts of heptane or toluene, and supported catalyst were introduced to a 250 ml glass reactor equipped with a magnetic stirrer. After a solution of a cocatalyst was added, polymerization was carried out under a

Table 1
The effects of modificated method of $MgCl_2$/SiO_2bisupport on catalytic activity and properties of polyethylenes (polymerization conditions are: [Al]/[Ni] = 100; temperature = 14 °C; [Ni]: 0.12–0.14 mmol/l; solvent: heptane; reaction time = 1 h)

Entry	Modificated method	Activity[a]	M_η ($\times 10^{-4}$)	T_m (°C)	X_c[b] (%)	Branches (1000C)
I	None	2.5	3.4	122.7	35.1	17
II	$MgCl_2 + SiO_2(AlEt_3)$	1.7	4.4	122.5	36.5	16
III	$MgCl_2 + SiO_2 + AlEt_3$	1.5	2.8	121.3	36.2	16

[a] 10^5 g PE mol Ni h^{-1}.
[b] Crystallinity.

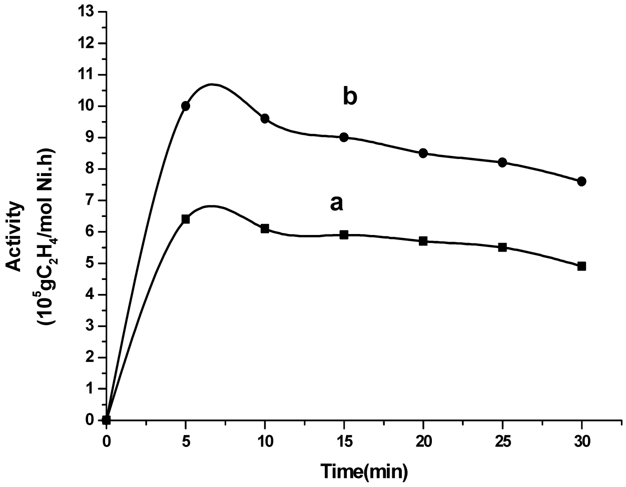


Fig. 1. Kinetic curves of ethylene polymerization in different solvents (polymerization conditions are: [Ni] = 0.50 mmol/l; solvent: (a) toluene; (b) *n*-heptane; co-catalyst: $AlEt_2Cl$; temperature 28 °C; [Al]/[Ni] = 100).

constant ethylene pressure of 106.7 kPa for 1 h at polymerization temperature. The polymerization was terminated by adding acidic ethanol. The precipitated polymers were washed with methanol and dried under vacuum at 60 °C for 6 h. By adding saturated NaOH–ethanol solution, the filtrates of ethylene oligomers were determined by GC–MS analysis.

2.6. Characterization

The Ni content in the supported catalysts was determined by inductively coupled plasma (ICP, IRIS Advantage HR). Ethylene oligomers were analyzed by Finnigan Voyager GC–MS detector.

Properties of polyethylene were determined with the same method used in Ref. [12]. The molecular weight of polyethylene (M_η) was determined by viscosimetric analysis at 135 °C with decahydronaphthalene as solvent. Branching degree of polyethylene was determined by FTIR spectra using a Japanese NICOLET205 FT-IR spectrometer. The heat of fusion (ΔH_f) and melting temperature (T_m) were measured on the samples which had been previously melted and recrystallized with the use of a Perkin–Elmer DSC-7 calorimeter at a heating rate of 10 °C/min. From the ΔH_f, the percent crystallinity $X_c = \Delta H_f(100/286)$ was calculated. ^{13}C NMR analysis of the branched polyethylenes was recorded at 130 °C on a Varian INOVA 500NB NMR spectrometer. The solution was made up in *o*-dichlorobenzene and deuterio-*o*-dichlorobenzene (volume ratio = 3/1) up to 10 wt%. Spectra were taken with a 90° flip angle, an acquisition time of 1 s, and a delay of 15 s.

3. Results and discussion

3.1. Solvent effect of $NiLCl_2/SiO_2/MgCl_2$ supported catalyst

Fig. 1 shows the kinetic curve of ethylene polymerizations catalyzed by $NiLCl_2/SiO_2/MgCl_2$ supported catalyst in different solvents. Both toluene and heptane have similar kinetic curve, as can be seen there are no induction period and slightly decreased catalytic activity with time. However, higher catalytic activity is obtained when heptane is used as solvent instead of toluene. More importantly, only ethylene oligomers are produced in toluene while polyethylene as well as ethylene oligomers can be produced in heptane. GC–MS analyses show ethylene oligomers are mostly C_4–C_{18} olefins. Molecular weight (M_η) of the polyethylene is 21,000, and catalytic activity of polyethylene formation is 43 kg PE mol Ni h^{-1}. Compared to the total amount of ethylene monomer in reaction, the ratio incorporating in the polyethylene backbone is 5.3%.

$NiLCl_2$ can be dissolved in toluene but not dissolved in heptane. When toluene is used as solvent, $NiLCl_2$ can escape from the supported catalyst and dissolve in it. Because $NiLCl_2$ has no bulky backbone substituents or *ortho* substituents, chain transfer then is quite fast relative to chain propagation [7]. Therefore, low molecular weight of ethylene oligomers are produced. When heptane is used as solvent, $NiLCl_2$ will be inclined to remain at the surface of the supported catalyst. It is thought that supports increase steric bulk of $NiLCl_2$, then chain transfer decreases and high molecular weight of polyethylene is produced.

In previous papers, we have discussed the activity and product character of unsupported, $MgCl_2(THF)_2$ and silica-supported $NiLCl_2$ for ethylene polymerization [9–11]. Only ethylene oligomers are obtained when homogeneous $NiLCl_2$ is used to polymerize ethylene in the presence of $AlEt_2Cl$ cocatalyst [9]. However, polyethylenes as well as ethylene oligomers can be achieved when $NiLCl_2$ is supported on $MgCl_2$ $(THF)_2$ or silica. $MgCl_2(THF)_2$ is found to activate the complex of $NiLCl_2$ distinctly, but silica slightly deactivates [10,11]. When heptane is used as solvent, the complex of $NiLCl_2$ which distributes on the surface of $SiO_2/MgCl_2$ bisupport can also be activated by $MgCl_2$ and catalytic activity of ethylene polymerization increases correspondingly.

3.2. Influence of polymerization conditions on catalytic activity and properties of polyethylene

3.2.1. Cocatalyst

As for $NiLCl_2/SiO_2/MgCl_2$ supported catalyst, the effect of cocatalysts ($AlEt_2Cl$, TEA and TIBA) on ethylene polymerization under the conditions of Al/Ni ratio 100 and temperature 14 °C is investigated. It is found that $AlEt_2Cl$ can effectively initiate ethylene to polymerize, but TEA and TIBA cannot initiate at all.

Generally, it is the cationic form of organometallic complexes that is of interest in polymerizations. Reaction of halo complexes with methyl aluminoxanes (MAO) in the presence of ethylene or other olefins is presumed to form cationic, catalytically active species [7]. $AlEt_2Cl$ is also presumed to react with supported nickel α-diimine complex in the presence of ethylene to form similar cationic, catalytically active species while TEA and TIBA probably make the complex of $NiLCl_2$ reduce excessively and cannot form the cationic species (Scheme 2).

3.2.2. TEA treatment of bisupport

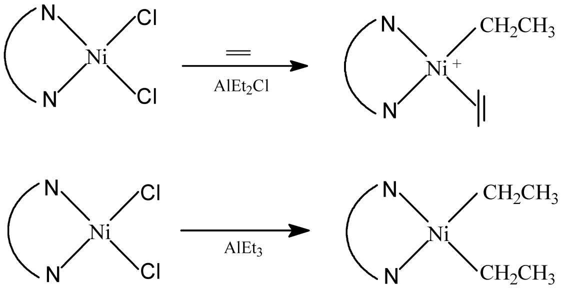
It is well known that if metallocene is directly impregnated on the supports without any modification of their surfaces, the catalytic activity is usually low [13]. In this study, TEA is used as modificator for the $SiO_2/MgCl_2$ bisupport, and the effect of modificated method on catalytic activity is investigated. As shown in Table 1 the activity of 2.5×10^5g PE mol Ni h^{-1} is obtained as the bisupport is not treated with TEA. On the other hand, when TEA is used as modificator, catalytic activity decreases irrespective of the modification method used.

The above result is quite surprising. Although heating SiO_2 in nitrogen flow at temperature as high as 600 °C removes the majority of the surface OH groups, the remaining functional groups still have the capacity to interact with metallocene catalysts and make the deactivation of them [14]. Therefore, the catalytic activity is very low if without any modification on SiO_2. Unlike metallocene catalysts, late transition-metal catalyst of $NiLCl_2$ is much more functional group-tolerant [7]. Therefore, fairly high catalytic activity of ethylene polymerization is still obtained without the modification of TEA. On the contrary, due to the excessive reducing effect mentioned in Section 3.2.1, the existence of TEA can deactivate the complex of $NiLCl_2$.

Modificated method of bisupport has little effect on properties of polyethylene products. Branching degree of polyethylene is about 16 irrespective of the modificated method used, and melting point (T_m) and crystallinity (X_c) also change little.

3.2.3. Al/Ni ratio

Table 2 shows the effects of the Al/Ni on catalytic activity of ethylene polymerization and properties of polyethylenes. Ethylene polymerization cannot proceed at Al/Ni = 20, but is able to proceed as it rises to 40. The activity increases with the increment of Al/Ni ratio, highest activity of 2.9×10^5g PE mol Ni h^{-1} being at Al/Ni = 80, but decreases as Al/Ni ratio increases further.



Scheme 2.

Table 2
The effects of Al/Ni ratio on catalytic activity and properties of polyethylenes (polymerization conditions are: [Ni]:0.11–0.13 mmol/l; temperature = 14 °C; solvent:heptane; reaction time = 1 h)

[Al]/[Ni]	Activity[a]	M_η ($\times 10^{-4}$)	T_m (°C)	X_c (%)	Branches (1000C)
40	1.3	4.4	124.8	40.2	11
60	2.4	3.8	122.7	36.5	16
80	2.9	3.5	122.4	36.2	16
100	2.5	3.4	121.8	35.8	17

[a] 10^5 g PE mol Ni h^{-1}.

It is thought that Al/Ni ratio has a pronounced effect on concentration of cationic nickel α-diimine complex. Too little amount of aluminum reagent cannot completely eliminate the THFs which combine with nickel complex on the surface of bisupport, and hence cannot form the cationic nickel species. The THFs can be eliminated completely as with the increase in Al/Ni ratio and the excessive amount of $AlEt_2Cl$ commences reducing nickel α-diimine complex to form cationic nickel species, and thus initiate ethylene to polymerize. Concentration of cationic nickel species increases with Al/Ni ratio, and reaches the highest point at 80. Further increase in the amount of aluminum reagent will speed up chain transfer on $AlEt_2Cl$, thus decreasing the catalytic activity of polyethylene formation.

Molecular weight of polyethylenes decreases with the Al/Ni. M_η of 44,000 is obtained at Al/Ni = 40 and 34,000 obtained as Al/Ni ratio increases to 100. $AlEt_2Cl$ is regarded as a chain transfer reagent in ethylene polymerization, therefore, chain transfer rate will increase with Al/Ni ratio and thus lead to the decrease in the molecular weight of polyethylenes.

Al/Ni ratio has only a slight effect on branches of polyethylene, it increases from 11 to 17 as Al/Ni ratio increases from 40 to 100. T_m and X_c of polyethylene slightly decrease with the increment in Al/Ni ratio.

3.2.4. Polymerization temperature

The effects of polymerization temperature on ethylene polymerization activities and properties of polyethylenes are shown in Table 3. The activity of 2.5×10^5 g PE mol Ni h^{-1} for polyethylene formation is obtained at 14 °C, and decreases irrespective of the decrease or increase in temperature. Ethylene polymerization rate decreases with the decrease in polymerization temperature. For example, the activity of 5.4×10^5 g C_2H_4 mol Ni h^{-1} is obtained at 0 °C and 18.2×10^5 g C_2H_4 mol Ni h^{-1} at 42 °C. However, chain transfer rates increase with temperature, therefore, usually ethylene oligomers are produced at higher temperatures. The ratio of polyethylene formation at 42 °C is only 2.0%, but increases to 26.9% at 14 °C.

Molecular weight of polyethylenes decreases with temperature. M_η of 46,000 is obtained at 0 °C and 30,000

Table 3
The effects of polymerization temperature on ethylene polymerization activities and properties of polyethylenes (polymerization conditions are: [Al]/[Ni] = 100; [Ni]: 0.11–0.14 mmol/l; solvent: heptane; reaction time = 1 h)

Temperature (°C)	Activity of PE formation[a]	Total activity[b]	Ratio of PE formation (%)	M_η ($\times 10^{-4}$)	T_m (°C)	X_c (%)	Branches (1000C)
0	1.5	5.4	27.8	4.6	124.9	40.0	12
14	2.5	9.3	26.9	3.4	122.5	36.2	17
28	1.3	12.9	10.1	3.2	122.3	22.3	32
42	0.4	18.2	2.0	3.0	122.2	20.2	35

[a] 10^5 g PE mol Ni h^{-1}.
[b] 10^5 g C_2H_4 mol Ni h^{-1}.

obtained as temperature increases to 42 °C. The reason is that chain-transfer rates increase with polymerization temperature.

For nickel α-diimine complex, branching of polyethylene products is thought to produce according to the mechanism of 'chain walking' [7]. As temperature increases, branching degree of polyethylene increases sharply. It increases from 12 to 35 as temperature rises from 0 to 42 °C. This is consistent with higher reaction temperatures favoring unimolecular chain walking relative to bimolecular trapping and insertion, resulting in a more highly branched microstructure [7].

Normally, T_m and X_c are observed to decrease with an increasing branch content of the polymer [1]. This is in agreement with the results shown in Table 3, wherein the decrease in T_m and X_c with the increment in polymerization temperature can be observed. The crystallinity of polyethylene decreases from 40.0 to 20.2% as degree of branching of polyethylene increases from 12 to 35, and melting point also decreases slightly.

3.2.5. Nickel concentration

Table 4 shows the effect of nickel concentration on ethylene polymerization. The activity of polyethylene formation increases with the decrease in nickel concentration. The activity of 2.5×10^5 g PE mol Ni h^{-1} is obtained when nickel concentration is 0.12 mmol/l and 0.4×10^5 g PE mol Ni h^{-1} obtained when it rises to 0.45 mmol/l. The total ethylene polymerization rate decreases slightly with nickel concentration. Therefore, the ratio of polyethylene formation decreases with nickel concentration. It decreases from 26.9 to 5.2% when nickel concentration increases from 0.12 to 0.45 mmol/l.

Under the condition of Al/Ni = 100, concentration of $AlEt_2Cl$ also increases with the increment in nickel concentration. Therefore, chain transfer on $AlEt_2Cl$ will speed up as nickel concentration increases, and thus, ethylene oligomer products are produced usually.

3.3. Microstructures of the resulting branched polyethylenes

The microstuctures of the branched polyethylenes obtained with supported nickel α-diimine catalyst are analyzed by the ^{13}C NMR spectroscopy [15]. Table. 5 shows the effect of different temperatures on branches distribution of polyethylenes. At 0 °C there is no methyl branch incorporated in the polyethylene backbone, but the incorporation of butyl and long branches can be observed in the ^{13}C NMR spectrum. To integrate, it is found that there are 18.2% of butyl branch and 81.8% of long branches at polyethylene backbone. As temperature rises, the methyl branch content increases sharply, yet that of long branches drops quickly. At 42 °C there is 66.7% of methyl branch and 33.3% of butyl branch incorporated in polyethylene backbone, but the incorporation of long branches is not observed.

For nickel α-diimine complexes, polyethylene branch formation is also thought to arise from β-hydrogen abstraction followed by readdition of the resultant coordinated vinyl-ended polymer to the nickel hydride, a process that results in the nickel migrating or 'walking' along the polymer chain [7]. The branched polyethylene products are produced only with a single feed of ethylene, without the intermediacy of α-olefins. The branches do not come from ethylene oligomers even though they are largely distributed in the reaction system. Ethyl branch is hence not present although ethylene oligomerization obeys Schultz–Flory distribution and the mole fraction of 1-butene is the highest [9].

Table 4
The effect of nickel concentration on ethylene polymerization (polymerization conditions are: [Al]/[Ni] = 100; temperature 14 °C; reaction time = 1 h)

[Ni] (mmol/l)	Activity of PE formation[a]	Total activity[b]	Ratios of PE formation (%)
0.12	2.5	9.3	26.9
0.28	1.3	9.0	14.4
0.45	0.4	8.2	5.2

[a] 10^5 g PE mol Ni h^{-1}.
[b] 10^5 g C_2H_4 mol Ni h^{-1}.

Table 5
Branches distribution of polyethylenes obtained with $NiLCl_2/SiO_2/MgCl_2$ supported catalyst on different temperatures (polymerization conditions are: [Al]/[Ni] = 100; [Ni]: 0.11–0.14 mmol/l; reaction time = 1 h)

Temperature (°C)	Branches distribution (%)		
	Methyl	Butyl	Long branches ($n \geq 6$)
0	0	18.2	81.8
14	0.4	47.4	52.2
42	66.7	33.3	0

4. Conclusions

$NiLCl_2/SiO_2/MgCl_2$ supported catalyst shows a remarkable solvent effect on ethylene polymerization. Only ethylene oligomers are produced when toluene was used as the solvent. However, when *n*-heptane is used as the solvent, high molecular weight of polyethylene can be produced and an increased catalytic activity is observed.

Cocatalyst has a great effect on ethylene polymerization. $AlEt_2Cl$ can effectively initiate ethylene to polymerize, but TEA and TIBA cannot initiate at all. When TEA is used as modificator for the bisupport, the catalytic activity decreases irrespective of the modification method used. Other polymerization conditions such as Al/Ni ratio, polymerization temperature and nickel concentration also have a pronounced effect on catalytic activity and properties of polyethylene products. The activity of 2.9×10^5 g PE mol Ni h^{-1} is achieved when Al/Ni ratio is 80, polymerization temperature 14 °C and nickel concentration 0.12 mmol/l. Degree of branching of polyethylenes increases gradually with Al/Ni ratio, but rises sharply with temperature.

The polymerization temperature has a pronounced effect on distribution of branches of polyethylenes. The methyl branch content increases sharply with temperature, however, that of long branches drops quickly.

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