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# Striking different behavior in the activation of $\alpha$ -olefins by homogeneous and heterogenized catalysts based on $\eta^5$ -cyclopentadienyl nickel derivatives

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## Abstract

Homogeneous  $\eta^5$ -cyclopentadienyl nickel catalysts have been applied to ethylene oligomerization. Their activity, enhanced by the presence of  $\text{Al}(\text{OEt})\text{Et}_2$  as co-catalyst, resulted the highest up to now reported for this type of complexes. The same catalytic systems were also able to oligomerize propylene as well as ethylene/propylene mixtures. In particular propylene was converted into branched dimers, mostly 2,3-dimethylbutenes. Heterogenization of the above system, carried out by anchoring the nickel derivative to a styrene/divinylbenzene resin properly functionalized with the cyclopentadienyl group, caused a drastic change of the selectivity of the process, ethylene polymerization to HDPE taking place instead of oligomerization.

**Keywords:** Nickel catalysts; Oligomerization; Polymerization; Polymer support; Heterogenized catalysts

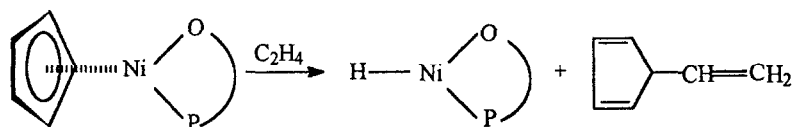
## 1. Introduction

Oligomerization of  $\alpha$ -olefins promoted by nickel catalysts has attracted a great deal of interest in the last few years and several homogeneous and heterogenized systems have been

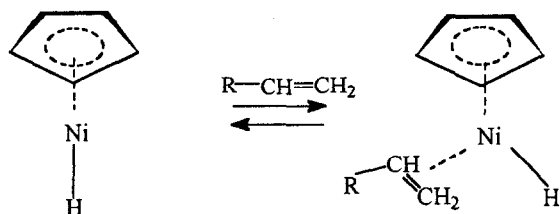
proposed [1–3]. However, only few examples dealing with homogeneous  $\eta^5$ -cyclopentadienyl nickel catalysts have been reported and only for ethylene oligomerization [4–9].

The results up to now reported suggest that, when a chelating hybrid P,O ligand is present, the cyclopentadienyl group is displaced from the above catalysts to give a hydride species with a vacant coordination site, the sole responsible of the catalytic performances [7–9] (Eq. (1)):

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In contrast, our attention has been devoted to those complexes where the cyclopentadienyl ligand should remain bonded to the nickel atom during the catalytic cycle. For these systems, starting from different nickel derivatives, the same  $\eta^5$ -cyclopentadienyl nickel hydride moiety has been proposed as the active species, responsible for  $\alpha$ -olefins oligomerization [5,6] (Eq. (2)).



However, only few data about their catalytic activity towards ethylene oligomerization have been reported; moreover, when the same catalysts have been heterogenized on  $\text{SiO}_2/\text{Al}_2\text{O}_3$

and on sulfidized  $\text{SiO}_2/\text{Al}_2\text{O}_3$ , poor activity and doubtful stability were obtained [10,11].

Therefore, in the present paper we report a novel approach for the obtainment in situ of  $\eta^5$ -cyclopentadienyl nickel catalysts, by direct oxidative addition of cyclopentadiene to  $\text{Ni}(\text{COD})_2$  (COD = 1,5-cyclooctadiene) and their use, in the presence of  $\text{Al}(\text{OEt})\text{Et}_2$  as co-catalyst, in the oligomerization not only of ethylene but also of propylene and ethylene/propylene mixtures.

The same catalyst has been heterogenized directly reacting  $\text{Ni}(\text{COD})_2$  with a styrene/divinylbenzene resin functionalized with the cyclopentadienyl group and its activity checked in the presence of ethylene.

## 2. Experimental

All manipulations were carried out under argon in Schlenk-type vessels, using anhydrous

Table 1  
Ethylene oligomerization in the presence of the homogeneous catalyst (III) <sup>a</sup>

Run	$\text{Ni}(\text{COD})_2$ (mmol)	$\text{AlEt}_2(\text{OEt})$ (mmol)	CpH (mmol)	Time (h)	$T$ (°C)	$P_{\text{C}_2\text{H}_4}$ (MPa)	TF <sup>b</sup>
Blank	–	0.50	0.50	4	130	5	–
Blank	0.26	0.26	–	4	130	5	–
1	0.52	–	0.63	4	110	5	2.2
2	0.57	0.57	0.68	4	110	5	29
3	0.53	0.53	0.64	4	70	5	8.7
4	0.3	0.3	0.35	4	100	5	15.8
5	0.57	0.57	0.68	4	120	5	35.4
6	0.3	0.3	0.36	4	130	5	37
7	0.31	0.31	0.36	4	150	5	78
8	0.26	0.26	0.31	4	180	5	1.7
9	0.25	1.0	0.30	4	150	5	94
10	0.48	0.48	1.18	4	150	5	88
11	0.38	0.38	0.9	1	150	7	232
12	0.28	0.28	0.66	4	150	7	144

<sup>a</sup> Solvent: toluene, 20 ml.

<sup>b</sup> Turnover frequency: g oligomers/(g Ni h).

Table 2

Propylene oligomerization and ethylene/propylene co-oligomerization with complex (III) <sup>a</sup>

Run	Ni(COD) <sub>2</sub> (mmol)	AlEt <sub>2</sub> (OEt) (mmol)	CpH (mmol)	Time (h)	T (°C)	P <sub>C<sub>3</sub>H<sub>4</sub></sub> (MPa)	P <sub>C<sub>3</sub>H<sub>6</sub></sub> (MPa)	TF <sup>b</sup>
13	0.29	0.29	0.73	4	130	–	0.8	24.3
14	0.20	0.20	0.51	4	150	–	0.8	37.8
15	0.34	0.34	0.85	4	130	1	0.8	29.2
16	0.19	0.19	0.47	4	150	1	0.8	50.0

<sup>a</sup> Solvent: toluene, 20 ml.<sup>b</sup> Turnover frequency: g oligomers/(g Ni h).

air-free reagents and solvents, and transfers were performed in an argon-filled glove box.

### 2.1. Preparation of the homogeneous catalyst

The oxidative addition of cyclopentadiene (CPH) to Ni(COD)<sub>2</sub> was carried out at 0°C in benzene or toluene and the quick formation of η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Ni(C<sub>8</sub>H<sub>13</sub>) (I) was ascertained by <sup>1</sup>H-NMR, according to Barnett [12].

The resulting red solution was transferred into an autoclave, pressurized with the alkene and heated up to the reaction temperature. Reaction conditions for different runs are reported in Tables 1 and 2.

### 2.2. Preparation of the heterogenized catalysts

A crosslinked (8%) styrene/divinylbenzene resin (kindly supplied by Dow Chemical) was chloromethylated (1.33 mmol of Cl/g of beads) and successively functionalized with the cyclopentadiene moiety by reaction with sodium

cyclopentadienide in THF according to the method reported by Bonds et al. [13]. The resulting polymer resin contained residual 0.17 mmol of Cl/g as determined by elemental analysis. The content of cyclopentadiene moiety was therefore determined by difference between Cl contents before and after reaction with sodium cyclopentadienide, thus giving 1.16 mmol C<sub>5</sub>H<sub>5</sub>/g (corresponding to a 87.2% reaction yield and a 12.9% functionalization extent of the styrene rings).

Particular attention was devoted to the careful elimination of residual chlorine from unreacted –CH<sub>2</sub>Cl groups by treatment with excess methyllithium and reprotonation with ethanol. Indeed, the complete disappearance of these groups appeared necessary because of their possible competitive oxidative addition to Ni(COD)<sub>2</sub>, thus implying a complete deactivation.

The functionalized polymer, suspended in toluene, was reacted at 0°C for 2 h with Ni(COD)<sub>2</sub>, to give the heterogenized red com-

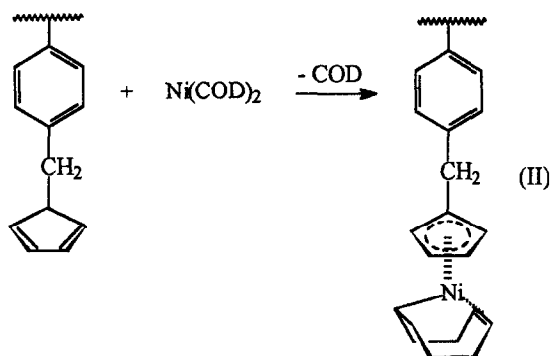
Table 3

Ethylene polymerization with the heterogenized nickel catalyst (II) <sup>a</sup>

Run	Ni(COD) <sub>2</sub> (mmol)	AlEt <sub>2</sub> (OEt) (mmol)	PST-Cp (mmol)	T (°C)	P <sub>C<sub>2</sub>H<sub>4</sub></sub> (MPa)	TF <sup>b</sup>	Mn (M <sub>w</sub> /M <sub>n</sub> )
17	0.7	0.7	1.5	70	5	3.7	
18	0.7	0.7	1.5	90	5	12.2	11 600 (40)
19	cat. recycled from run 18	0.7		90	5	11.9	10 780 (42)
20	0.5	0.5	1.2	110	5	3.4	
21	0.5	0.5	1.2	130	5	–	

<sup>a</sup> Solvent: toluene 20 ml; time: 4 h.<sup>b</sup> Turnover frequency: g polymer/(g Ni h).

plex (II), analogously to that observed in homogeneous phase (Eq. (3)):



Its formation was ascertained by  $^1\text{H-NMR}$  spectroscopy carried out on the reaction product swollen into fresh  $\text{C}_6\text{D}_6$  after washing with the same solvent. Indeed, the appearance of a strong absorption at 5.5 ppm revealed the presence of the cyclopentadienyl ligand  $\eta^5$ -bonded to nickel.

The heterogeneous complex (II), suspended in fresh toluene, was transferred into an autoclave pressurized with ethylene and heated up to the reaction temperature (Table 3).

### 2.3. Apparatus and procedure

Catalytic batch experiments were performed in a 125 ml stainless-steel rocking autoclave heated in an oil bath. Ethylene and propylene were charged at room temperature. Solid polymers were separated from the solvent and liquid oligomers by vacuum distillation.

### 2.4. Analysis

Ethylene oligomers analysis and polymers characterization were performed as previously reported [14] using GC,  $^1\text{H-}$  and  $^{13}\text{C-NMR}$ , FT-IR, and GPC techniques.

Propylene oligomers were subjected to hydrogenation over a Pd/C catalyst (5% Pd on charcoal) under hydrogen (7 MPa) at 120°C for

6 h and then analyzed by GC on a Hewlett Packard 5890 chromatograph (equipped with HP PONA 50 m capillary column) using a HP 3396 integrator.

IR spectra of the catalytic solution were carried out at 100°C under pressure (1 MPa) using a high pressure 0.1 mm KBr cell on a Perkin Elmer 1750 FTIR spectrophotometer.

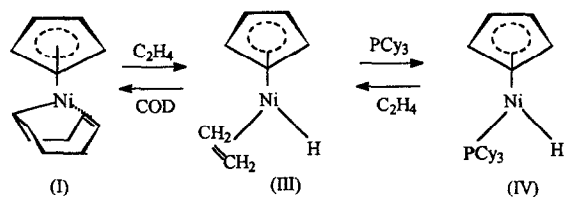
## 3. Results and discussion

### 3.1. Ethylene and propylene oligomerization with homogeneous catalysts

When the red solution of  $\eta^5\text{-C}_5\text{H}_5\text{Ni}(\text{C}_8\text{H}_{13})$  (I) was transferred into the autoclave and heated at 100°C under ethylene pressure ( $P > 0.8$  MPa) the ethylene-assisted elimination of the  $\sigma, \pi$ -cyclooctenyl ligand as 1,5-cyclooctadiene was ascertained by GC.

The contemporary formation of a hydride complex, which until now we have been unable to isolate, was confirmed by an FT-IR spectrum carried out under ethylene pressure (1 MPa) at 100°C.

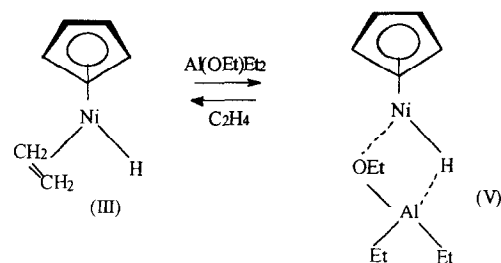
Indeed, the appearance of a strong band at  $1910\text{ cm}^{-1}$  ( $\nu_{\text{Ni-H}}$ ) was ascertained. This nickel hydride, in our opinion responsible for the catalytic activity, was formed and stabilized only in the presence of the olefin and therefore the contemporary presence of an  $\eta^2$ -alkene ligand can thus be supposed (Structure III) (Eq. (4)).



By addition to the solution of tricyclohexylphosphine the (tricyclohexylphosphine)

( $\eta^5$ -cyclopentadienyl)nickel hydride (IV) was formed and characterized [15], thus substantially confirming the above structure (III).

The homogeneous catalyst (III) was active in ethylene oligomerization to linear  $\alpha$ -olefins (linearity in the C<sub>6</sub> fraction > 90%) (Table 1). Its activity was enhanced in the presence of Al(OEt)Et<sub>2</sub> as co-catalyst, as already observed for  $\eta^5$ -cyclopentadienyl nickel systems [5]. The promoting effect of the aluminum co-catalyst could be related to its coordination to the nickel center to give V, thus favoring the formation and the stabilization of the hydride complex (Eq. (5)).



An increase of the catalytic activity was observed raising the reaction temperature up to 150°C, although deactivation of the catalytic system took place at higher temperatures (run 8).

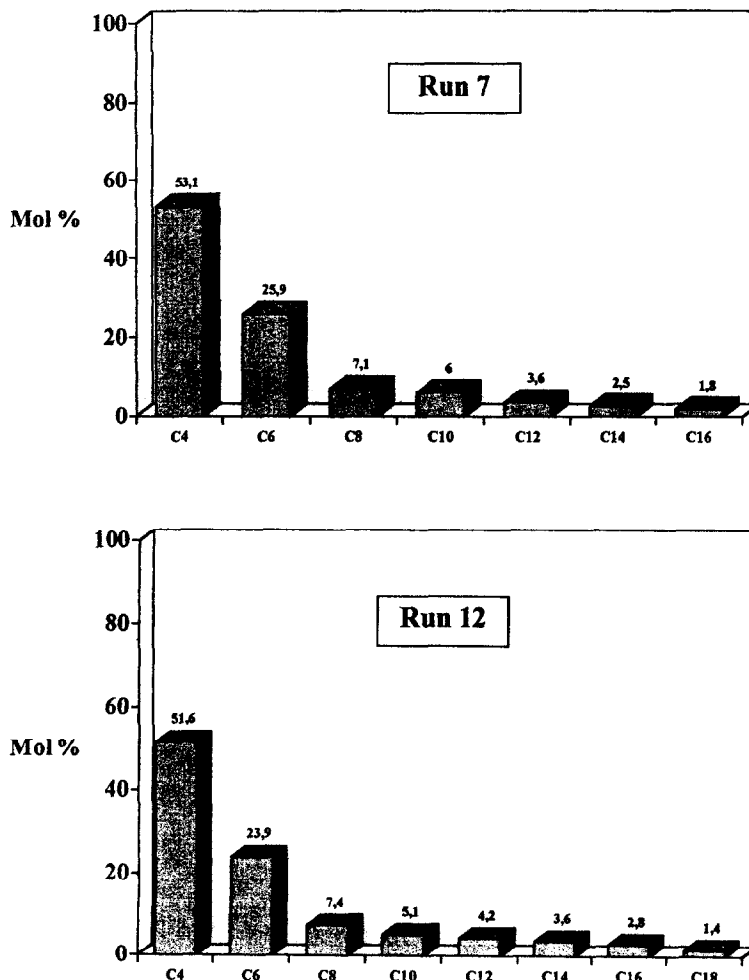


Fig. 1. Ethylene oligomerization (run 7 and run 12): distribution of reaction products.

The distribution of the reaction products in a typical example (run 7) is shown in Fig. 1. The butenes content in the oligomers mixture exceeded 50%, and appreciable amounts of hexenes (25%) and octenes (7%) were also formed.

An increase of the activity was also attained (Table 1) by increasing the Al/Ni ratio (compare run 9 with run 7) and the cyclopentadiene/Ni ratio (compare run 10 with run 7).

A more marked effect on the catalytic activity was observed by raising ethylene pressure, analogously to that observed for other nickel catalytic systems [16]. The formation of higher

oligomers ( $C_{18}$ ) was ascertained working at 7 MPa (Fig. 1, compare run 12 with run 7).

It is worth noting that the achieved turnover frequencies values (232 g of oligomers/g Ni in one h) resulted the highest up to now reported for homogeneous nickel systems having the cyclopentadienyl group  $\eta^5$ -bonded to the metal during the catalytic process.

The same systems resulted also able to oligomerize propylene under mild conditions (Table 2). As shown in Fig. 2 (run 14) hexenes largely prevail among the reaction products and the branched dimers were preferentially formed, mostly 2,3-dimethylbutenes.

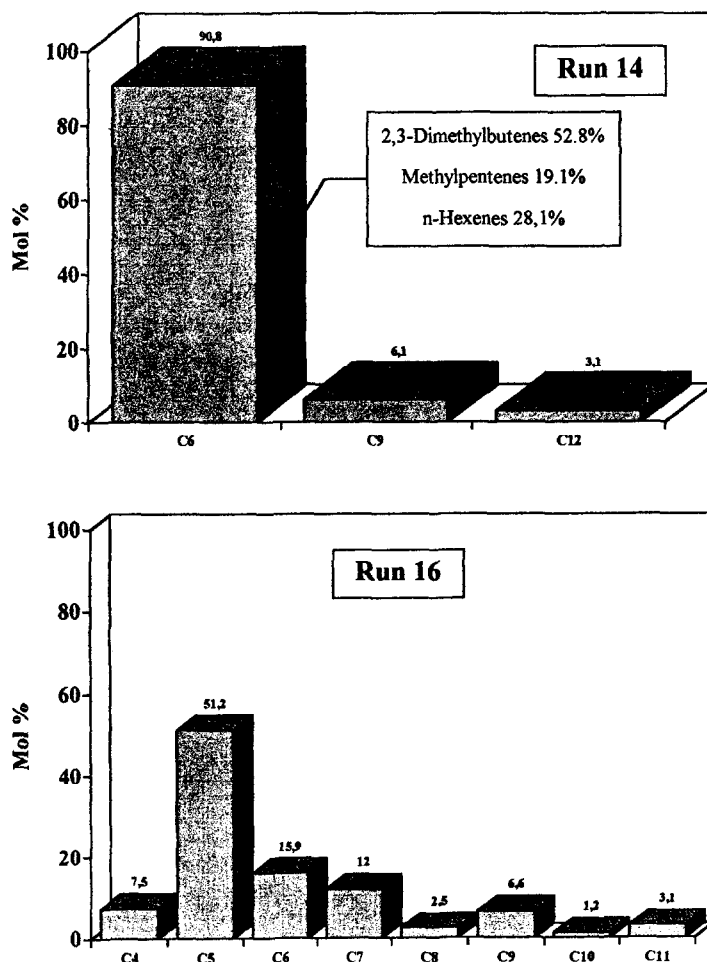


Fig. 2. Propylene oligomerization (run 14) and ethylene/propylene co-oligomerization (run 16): distribution of reaction products.

The activity in the co-oligomerization of ethylene/propylene mixtures was also tested; mainly products with an odd number of carbon atoms were formed (Fig. 2, run 16) and C<sub>5</sub> content reached 50%, methylbutenes largely prevailing (> 85%).

### 3.2. Ethylene polymerization with the heterogenized catalyst (II)

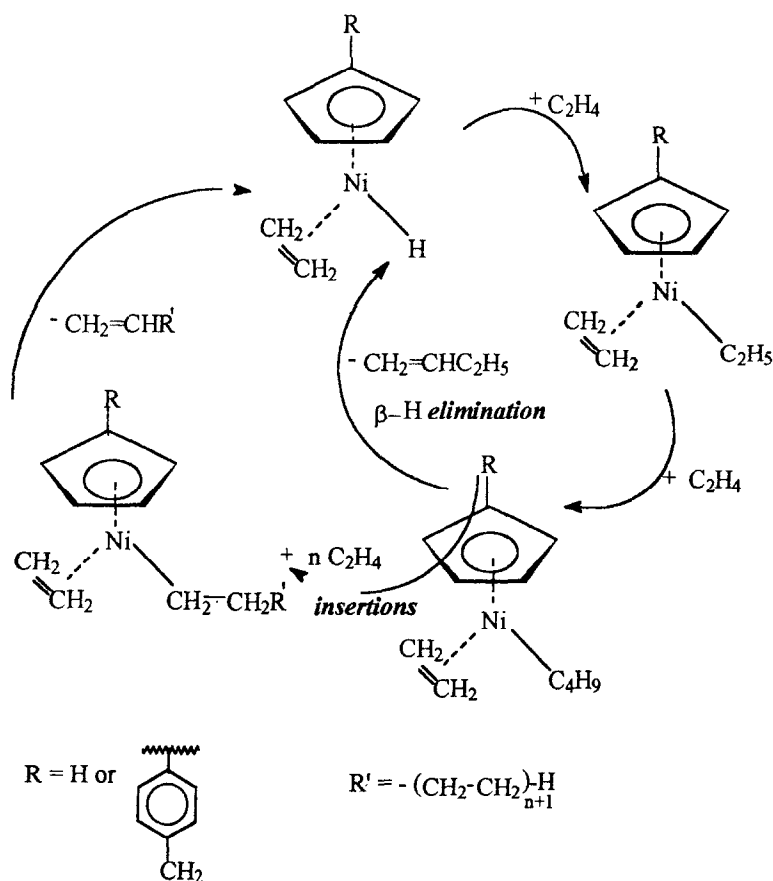
The heterogenized system (II) was tested in ethylene activation analogously to homogeneous one (Table 3). It deactivated at lower temperatures with respect to the homogeneous counterpart, at 130°C being completely decomposed.

The heterogenization caused a very drastic change of the selectivity of the process. Indeed,

high density polyethylene (0.96 g/ml) was exclusively obtained instead of oligomers.

An analogous modification of the selectivity was previously observed by us after the heterogenization of the chelate P,O nickel complexes used in the SHOP oligomerization process. In fact, the heterogenization largely favored the propagation steps (olefin insertion with respect to  $\beta$ -hydrogen elimination), thus giving exclusively HDPE with replica of the support morphology [14,17].

The red beads of catalyst, recovered under ethylene atmosphere from the reaction mixture and washed with fresh toluene, were recycled in a second batch run, showing (Table 3) unchanged activity (compare run 18 with run 19). These results seem to indicate that no nickel release occurs at 90°C and suggest that the



Scheme 1. Catalytic mechanism for ethylene oligomerization/polymerization.

cyclopentadienyl ligand remains tightly bonded to the nickel atom during the catalytic cycle.

Polydispersity indexes, determined by GPC, were very high ( $M_w/M_n$ : 40), probably due to the great steric dishomogeneity of the active centers differently located on and inside the polymeric matrix.

### 3.3. Discussion

The ( $\eta^5$ -cyclopentadienyl)( $\eta^2$ -alkene)nickel hydride, formed under reaction conditions, can be supposed responsible for olefin activation according to Scheme 1.

When  $R = H$ , i.e. in the case of the homogeneous complex, the  $\beta$ -elimination route [18] is favored and butenes and hexenes are mostly formed.

The steric hindrance around the nickel center drastically changes when  $R$  is the polymeric chain of the heterogenized catalyst. As already observed [14,17] the presence of the polymeric chain greatly favors the olefin insertion (propagation step) leading to HDPE with respect to the  $\beta$ -H extraction responsible for oligomers formation. In fact the olefin insertion into nickel-alkyl bond, involving a less hindered intermediate with respect to  $\beta$ -hydrogen elimination which requires the liberation of a coordination vacant site from the intermediate, is favored in the presence of the bulky polymeric ligand [2].

### 4. Conclusions

On the basis of the obtained results the following conclusive remarks can be drawn: homogeneous  $\eta^5$ -nickel cyclopentadienyl catalysts, obtained in situ by oxidative addition of cyclopentadiene to  $Ni(COD)_2$ , displayed high activity in the oligomerization of ethylene and also of propylene and ethylene/propylene mixtures.

Heterogenization of the above catalysts caused a lowering of the activity and a dramatic

change of the selectivity: production of HDPE was observed.

This effect can be related to the presence of the bulky polymeric ligand which favors insertion and propagation steps leading to polyethylene.

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