

The Influence of Various Reaction Parameters on the Performance of (α -Diimine)nickel(II) Catalysts in Ethylene Oligomerization Reactions

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ABSTRACT: Modified (α -diimine)nickel(II) catalysts are suitable for ethylene oligomerization reactions. Due to the mechanism ("chain running"), the formation of double-bond isomers and branched olefins can be observed. The obtained oligomer mixtures show a Schulz–Flory distribution. Increasing ethylene pressure favors the selectivity of α -olefin formation. The same effect can be observed when Lewis bases like thiophene or furane are added to the oligomer-

ization reaction mixture. These results can be related to an interaction of the additives with the catalytic active species during the oligomerization process. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1356–1361, 2003

Key words: (α -diimine)nickel(II) catalysts; oligomerization; α -olefins; oligomerization conditions; Lewis bases; additives

INTRODUCTION

Nickel catalysts that are suitable to oligomerize ethylene to give short chain olefins have been known for 30 years.^{1–14} Some of them found application in the Shell Higher Olefin Process (SHOP).^{15–20} In the 1990s Brookhart et al. discovered the catalytic potential of (α -diimine)nickel(II) complexes (Fig. 1).^{21–30}

These types of complexes were first described by Tom Dieck and Svoboda.^{31–34} Identical or closely related catalyst systems have been reported by other research groups.^{35–40}

The catalytic properties of these (α -diimine)nickel(II) complexes after activation with methylalumoxane (MAO) is explained with the so-called chain running mechanism and depend on the structure of the catalyst precursor (Scheme 1).^{21–30,41,43}

This mechanism gives reasons for the formation of linear and branched polymers and short-chain oligomers as well as isomers of olefins in the ethylene polymerization reaction.

Here, we report a method on how to suppress the formation of isomers of the short-chain olefins by increasing the ethylene pressure in the oligomerization reaction or by adding Lewis bases to the reaction mixture.

EXPERIMENTAL

All preparations were performed under purified argon atmosphere using the standard Schlenk technique to prevent traces of air or moisture (BTS catalyst, molecular sieves). All solvents were purchased in technical grade and purified by distillation over Na/K alloy under argon atmosphere. The catalyst precursor **A** was synthesized according to the literature.⁴⁴

Mass spectroscopy (MS) spectra were recorded with a Varian MAT CH7 mass spectrometer (direct inlet system, electron impact ionization 70 eV). In addition, a Hewlett Packard 5917A mass spectrometer was routinely used to record MS spectra and in combination with a Hewlett Packard Series II 5890 gas chromatograph to record GC/MS spectra.

Gas chromatograms were recorded using a Perkin-Elmer Auto System gas chromatograph with flame ionization detector (FID) and helium as carrier gas (1 mL/min).

Temperature program:

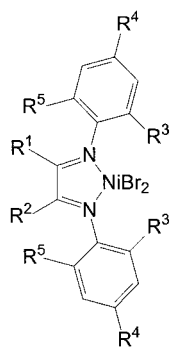
Starting phase: 3 min at 50°C
Heating phase: 5°C/min (15 min)
Plateau phase: 310°C (15 min)

Methylaluminoxane (MAO) was supplied by Witco GmbH, Bergkamen (Germany), as 30% solution in toluene (average molecular weight 1100 g/mol, aluminium content: 13.1%, 3.5% as trimethylaluminum).

Activation of the homogeneous catalysts with MAO

An amount of 10 mg of the corresponding complex was suspended in toluene and activated with an ex-

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R^1, R^2, R^3, R^4, R^5 = different aliphatic or aromatic substituents or H

Figure 1 (α -Diimine)nickel(II) catalyst precursor.

cess of MAO (Al/Ni = 1000/1). The activated catalyst was used for ethylene oligomerization within 30 min.

Polymerization of ethylene

The activated complex was added to a 1 L metal autoclave (Büchi), filled with 250 mL *n*-pentane containing the corresponding additive (2 equivalents per

1 equivalent nickel). The polymerizations were performed under an ethylene pressure of 10, 20, or 30 bar (99.98% ethylene, dried over aluminium oxide) and at a temperature of 60°C. After a period of 1 h, the autoclave was cooled to room temperature and the pressure was reduced. The polymerization mixture was filtered, the remaining polymer was washed with half concentrated hydrochloric acid, dried *in vacuo*, and weighed. After removing *n*-pentane by distillation over a Vigreux column, the obtained oligomers were analyzed by GC.

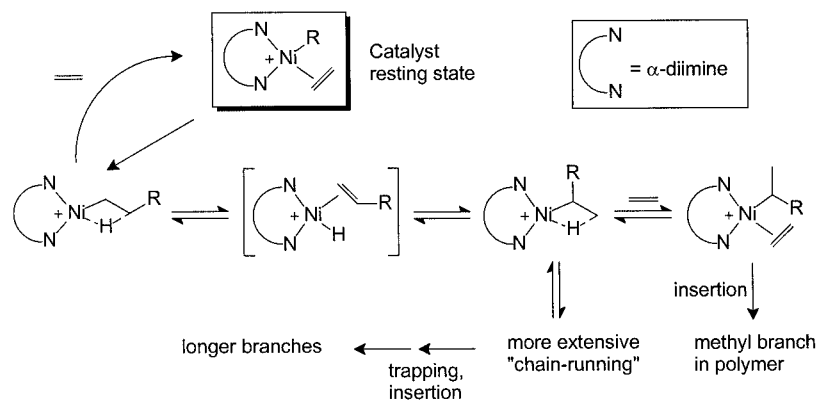
RESULTS AND DISCUSSION

Oligomerization of ethylene

For the oligomerization reactions dibromo[*N,N'*-(1,2-ethanediyldiene)bis[4-fluoro-benzeneamine- κ N]]-nickel (A) and the corresponding complexes with fluorine in the *meta*- and *ortho* position of the aryl moiety were used as catalyst precursors (Fig. 2).⁴⁴

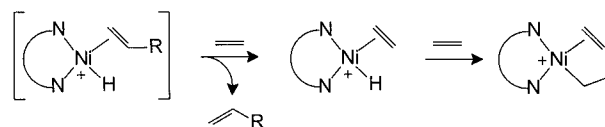
Complexes A–C were activated with MAO (30 wt % in toluene) and tested for homogeneous ethylene oligomerization. The toluene was removed *in vacuo* and

A. Propagation and Isomerization:

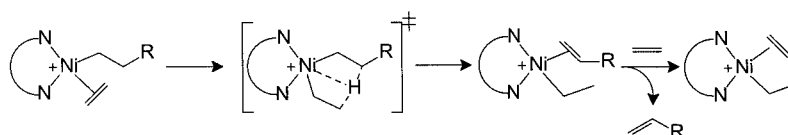


Chain Transfer:

(1) Associative displacement:



(2) Concerted β -H transfer to bound monomer:



Scheme 1 Chain running mechanism.^{21–30, 41–43}

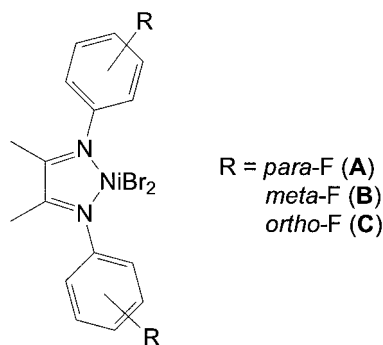


Figure 2 Structure of the catalyst precursors A–C.

the solid catalysts were suspended in pentane and used for slurry oligomerization reactions.

A series of experiments at different ethylene pressures (10–30 bar) was carried out. The results are listed in Table I.

For the separation of the oligomers and the polymers, the oligomerization mixture was filtered and the remaining polymer was washed with half concentrated hydrochloric acid in order to remove MAO. Then the polymer was dried *in vacuo* and weighed. The pentane of the oligomer solution was removed by distillation over a Vigreux column and the oligomers were analyzed by gas chromatography (GC). Based on the GC analyses of the oligomer mixtures, it is possible to calculate the Schulz–Flory constant α for the distribution of the oligomer fractions.^{45–48} For this calculation, the area integrals of the oligomer fractions with a carbon number from 10 to 30 were used. Due to the formation of isomers of the olefins and polymers, the values of α imply a statistical error. The classification for oligomers and polymers was the solubility of the products in pentane. Mass spectrometric analyses suggested a molecular weight of ca. 1000 g/mol as the borderline. In all cases, the amount and the purity of the produced polymer was too low for further analy-

ses. Due to that procedure, the amount of produced butene could not be determined.

A/MAO produced at 10 bar an oligomer mixture that consisted of olefins with an even carbon number from 6 to 40 and their possible isomers. A selectivity for the formation of α -olefins could not be observed (Fig. 3).

In order to quantify the selectivity for the formation of α -olefins, the share of 1-octene of all 16 octene isomers was determined. At 10 bar ethylene pressure, the 1-octene share was only 7.6 mol %.

Comparing the oligomerization results for the catalysts A/MAO, B/MAO, and C/MAO, it becomes obvious that the activities and the selectivities for the formation of α -olefins are a function of the catalyst structures and the electronegativities of the substituents. Similar effects have been found earlier and can be related to interactions of the substituents with the axial coordination sites at the nickel atom and the electron density at the catalytic center.^{22,41,44} Nevertheless, the significant increase of the amount of produced α -olefins by changing the position of the fluorine substituent is remarkable (Fig. 4).

Taking into consideration that the fluorine substituent is not very bulky and the monosubstitution of the aryl rings allows the existence of *syn* and *anti* conformations in the case of B/MAO and C/MAO, the observed effect is bigger than expected.

In addition, the catalytic properties of A/MAO were studied under different polymerization conditions. A closer look at these results reveals that despite an increasing ethylene pressure, the activities were slightly decreasing. This can be caused by mass transport effects that hinder the diffusion of the monomer to the catalytic active centers. In addition, an increase of the obtained polymer share can be observed.

Overall, there is a significant effect of higher ethylene pressure on the selectivity for the formation of

TABLE I
Results of the Homogeneous Ethylene Oligomerization Experiments^a

Catalyst precursor	<i>p</i> (bar)	Activity ^b	TOF ^c	Polymer share (wt %)	α ^d	1-Octene ^e
A	10	1843	69113	<1	0.68	7.6
A	20	1543	57863	8.3	0.68	60.8
A	30	1473	55238	8.6	0.74	74.7
B	10	499	18713	0.7	0.66	26.4
C	10	939	35213	<1	0.65	47.7

^a Reaction conditions: activation with 30 wt % methylaluminoxane in toluene (Al/Ni = 1000/1), oligomerization in 250 mL pentane, 60°C, 1 L autoclave, 60 min.

^b The activities [g(prod.)/mmol (Ni) · h] were calculated from the total consumption of ethylene (1.0 L ethylene = 1.2 g product).

^c TOF [mol(C₂H₄)/mol(Kat.) h] = *turn over frequency*.

^d $\alpha = k_B/(k_B + k_C)$ = rate of propagation/(rate of propagation + rate of chain transfer) = Schulz–Flory constant.

^e 1-Octene share (mol %) of all octene isomers.

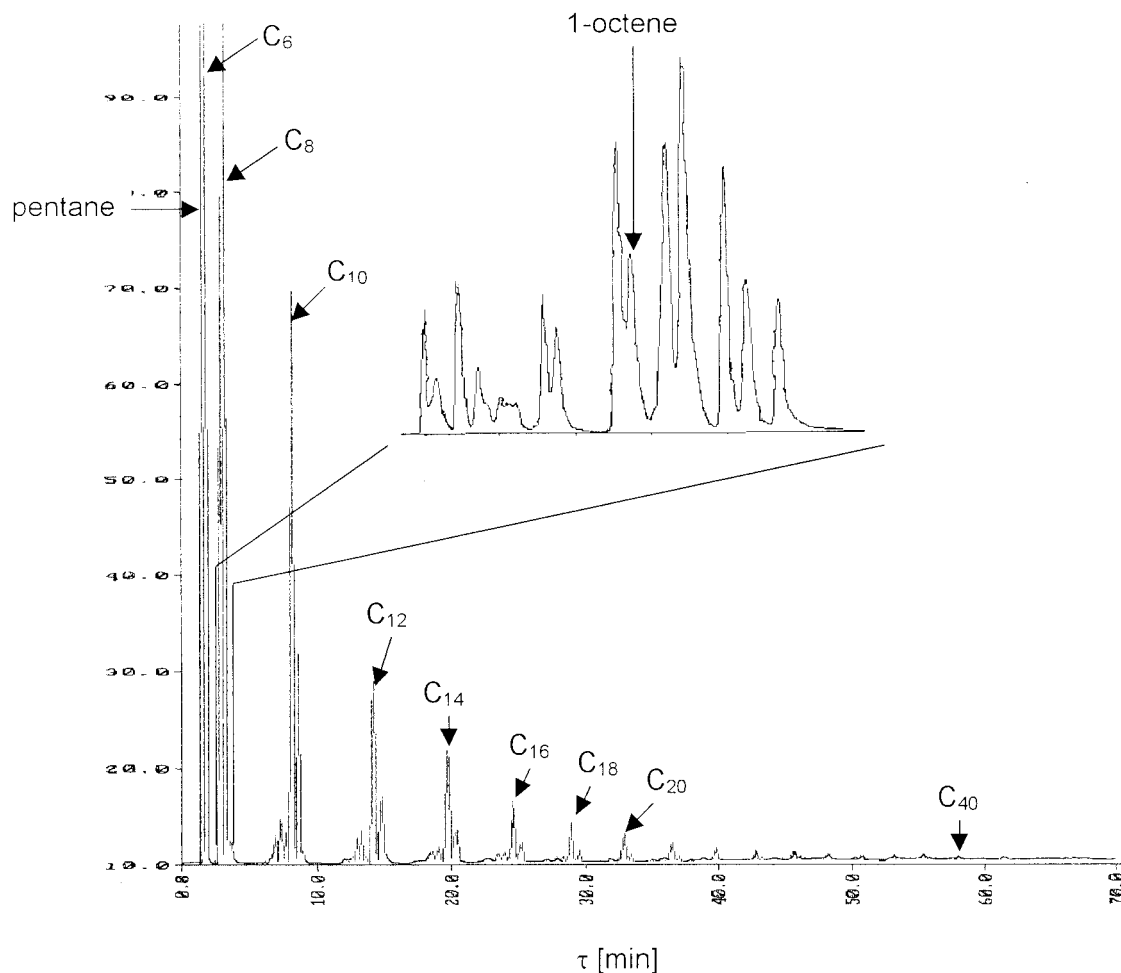


Figure 3 GC analysis of the oligomer mixture obtained with A/MAO at 10 bar ethylene pressure.

α -olefins. This share could be increased nearly ten times to 74.7 mol % at 30 bar ethylene pressure (Fig. 5).

However, the total amount of the produced octenes remained the same. Therefore, the distribution of the olefins was nearly constant, as indicated by comparing the Schulz–Flory constants.^{45–48}

Similar results were also reported by Brookhart et al.^{21–30} They also described the formation of α -olefins and linear polyethylenes at higher ethylene pressures. This behavior can be explained with an associative

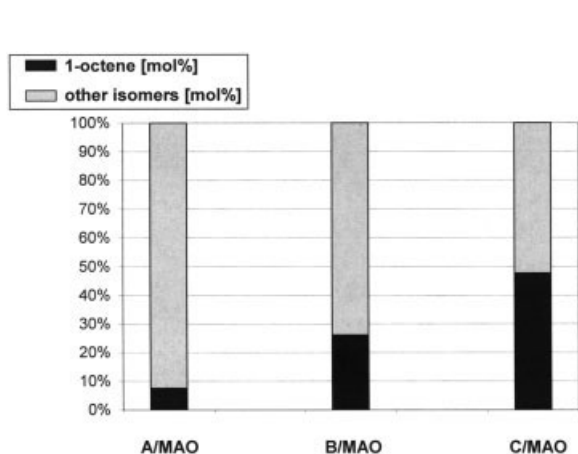


Figure 4 Amount of produced 1-octene by A/MAO, B/MAO, and C/MAO.

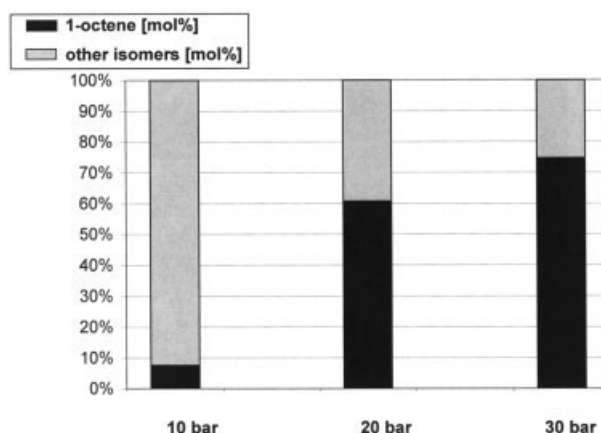


Figure 5 Dependency of the formation of 1-octene on the ethylene pressure; reaction conditions: 60°C, 250 mL pentane, MAO (Al/Ni = 1000/1), 1 h.

TABLE II
Results of the Homogeneous Ethylene Oligomerization with A/MAO and Different Reaction Additives^a

Additive	Activity ^b	TOF ^c	Polymer share (wt %)	α^d	1-Octene ^e
C ₄ H ₂ O ₃ ^f	739	27713	<1	0.73	12.7
Pyridine	739	27713	<1	0.73	15.1
Furane	763	28613	<1	0.71	33.9
Thiophene	1180	44250	<1	0.73	76.1
Cyclooctene	605	22688	<1	0.69	67.6
—	1843	69113	<1	0.68	7.6

^a reaction conditions: activation with 30 wt % methylaluminoxane in toluene (Al/Ni = 1000/1), oligomerization in 250 mL pentane, 60°C, 1 L autoclave, 60 min, 10 bar.

^b The activities [g(prod.)/mmol (Ni) h] were calculated from the total consumption of ethylene (1.0 L ethylene = 1.2 g product).

^c TOF [mol(C₂H₄)/mol(Kat.) · h] = *turn over frequency*.

^d $\alpha = k_B/(k_B + k_C)$ = rate of propagation/(rate of propagation + rate of chain transfer) = Schulz-Flory constant.

^e 1-octene share (mol %) of all octene isomers.

^f C₄H₂O₃ = maleic anhydride.

displacement of the formed α -olefin by an ethylene monomer during the polymerization process before an isomerization of the double bond can take place.

A combination of these two observations, the crucial importance of the axial coordination sites at the metal center that can be easily influenced by substituents at the ligand, and the sensitivity of the catalysts against higher ethylene pressures in the formation of α -olefins leads to the conclusion that chain transfer reactions can only occur if these axial coordination sites are accessible and if the monomer coordination proceeds via the axial positions.

Therefore, additional donor molecules that can block coordination sites at the metal center should

lower the chain transfer rates. Consequently, in further oligomerization experiments two equivalents of an electron donor relative to the amount of catalyst precursor **A** were added to the reaction mixture. The results are summarized in Table II.

Despite the high excess of MAO (Al/additive = 500/1), there is a noticeable influence of the additives on the catalyst performance.

It is evident that in all cases the activity of the catalyst decreases compared to the activity obtained without an additive. For the system **A/MAO/cyclooctene**, the loss of activity is nearly 70%. The reason must be a coordination of these molecules to the active center causing a hindrance of the catalytic process. On

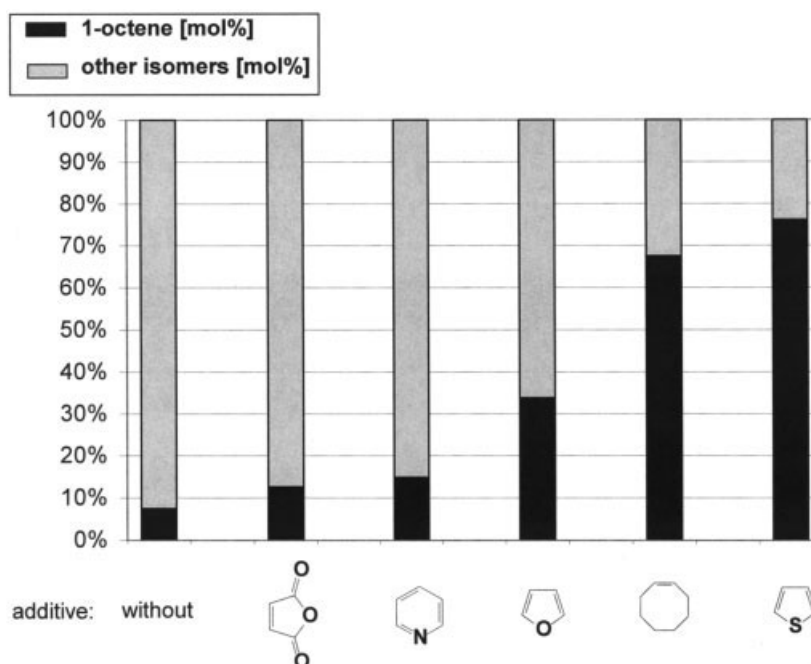


Figure 6 Dependency of the formation of 1-octene on the additive; reaction conditions: 60°C, 250 mL pentane, MAO (Al/Ni = 1000/1), 1 h, 10 bar.

the other hand, this coordination seems to be reversible because none of the systems caused a complete inactivation.

In addition, it could be observed that the presence of donor molecules leads to an increase of selectivity for the formation of α -olefins (Fig. 6).

For **A/MAO/thiophene**, the 1-octene share reached 76.1 mol % and was even higher than the 1-octene share obtained without an additive at 30 bar ethylene pressure.

An explanation for these results can be derived from the "chain running mechanism." In the case of higher ethylene pressures, the formation of α -olefins is favored because the donor molecules support the chain transfer by associative displacement. Here, the additive can replace the formed α -olefin and then can be replaced by the ethylene monomer. In addition, this process does not need high monomer concentrations for the formation of α -olefins. Without an additive, similar selectivities for α -olefins require high ethylene pressures.

CONCLUSION

The selectivities for the formation of α -olefins in the oligomerization of ethylene with (α -diimine)nickel(II) catalysts can be controlled by the catalyst structure and by varying the oligomerization conditions like the ethylene pressure. In addition, we found the possibility to increase the selectivity by adding donor molecules to the oligomerization mixture. The flexible oligomerization pathway following the chain running mechanism allows the manipulation the kinetics of the reaction in order to suppress the isomerization and to favor the associative displacement of formed α -olefins. This associative displacement can be supported either by the monomer itself, if the monomer concentration is big enough, or by donor molecules that are working as mediators for the displacement of the α -olefin for a monomer molecule. The presence of polar compounds containing Lewis basic heteroatoms does not lead to a complete deactivation of the catalysts. Only a loss of activity can be observed caused by a reversible blocking of the active centers.

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