

Oligomerization and co-oligomerization of α -olefins catalyzed by nickel(II) /alkylaluminum systems

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Abstract

This work describes α -olefins oligomerization/co-oligomerization of 1-butene, 1-hexene, 1-octene to linear oligomers (C_8 – C_{16} range) promoted by catalytic systems based on nickel(II) salts/alkylaluminum compounds. Conversion, selectivity (isomerization or oligomerization) and linearity are determined by mass distribution calculation of the substrates (α -olefins) in the products. The best results are obtained with $Ni(acac)_2/AlEt_2OEt$ working at 60°C, Al/Ni ratio between 0.8–1.4 and using toluene as a solvent. Under these conditions, the conversion is higher than 90% giving 40% of oligomerization selectivity. The linearity varies from 65% (C_{16} fraction) to 98% (C_8 fraction).

Keywords: α -olefins; Oligomerization; Nickel; Homogeneous catalysis

1. Introduction

In the past, olefins $< C_{20}$ were normally prepared via oligomerization reactions promoted by acid catalysts which are very efficient in producing branched products [1]. However, linear oligomers are required for many technological purposes, mainly in the synthesis of biodegradable detergents and plasticizers.

There are many examples in the literature of ethene and propene oligomerization catalyzed by transition metal complexes with or without the use of a co-catalyst [2]. Systems based on

nickel complexes have been well studied by Jolly and Wilke [3], Keim (SHOP process) [4–10] and Chauvin (DIMERSOL process) [11,12]. However, the use of higher α -olefins shows a very efficient double bond isomerization producing internal, almost unreactive isomers.

A system prepared by mixtures of $Ni(acac)_2$ and $AlEt_2OEt$ was studied by Jones and Symes [13]. The authors reported high conversion rates for C_3 – C_6 α -olefins giving linear oligomers with 75–85% of linearity. Nevertheless, this system was also very efficient in isomerizing the starting α -olefins.

In a preliminary work, α -olefins in the C_4 – C_8 range were obtained by Ni-phosphorus catalyzed ethene oligomerization [14,15]. In this paper we present our results on 1-butene, 1-hexene and 1-octene oligomerization/co-

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oligomerization catalyzed by nickel(II)/alkylaluminum systems, producing highly linear C_8 – C_{16} internal olefins. Some results on the attempt to optimize the reaction parameters and to elucidate the reaction mechanism are also reported.

2. Experimental

All reactions were carried out under an argon atmosphere. The solvents and cyclohexane (internal standard, Merck) were purified by distillation under argon over metallic sodium. The α -olefins (Aldrich, 98%) were distilled just before use and dried with molecular sieves (Merck, 3 Å). 1-Butene (PPH Company) was condensed just before use.

2.1. Catalytic precursors

Three different nickel(II) complexes were synthesized: $Ni(acac)_2$, $Ni(oct)_2$, $Ni(ste)_2$. The last two complexes were prepared in agreement with a general method for metal soap synthesis [16]. $Ni(acac)_2$ was obtained as reported by Charles and Pawlikowski [17]. All complexes were dehydrated at 60°C in vacuum (10^{-2} mbar) overnight.

2.2. Co-catalysts

Three organoaluminum compounds were tested as co-catalysts: $AlEt_3$ (Alkyls do Brasil), $AlEt_2Cl$ (Alkyls do Brasil), $AlEt_2OEt$ (controlled $AlEt_3$ alcoholysis) were used as toluene solutions. The aluminum content of these solutions was determined by atomic absorption spectrophotometry on a Perkin-Helmer 2380 spectrophotometer equipped with an HGA 400 graphite oven.

2.3. Catalytic reactions

The Ni(II) complexes (0.2 mmol) were suspended in 10 ml of toluene and transferred to a

pressure resistant Schlenk tube under argon. 1-Butene, 1-hexene, 1-octene and the internal standard (cyclohexane, 1 g) were introduced into the reactor cooled at $-50^\circ C$. The total amount of α -olefins added was approximately 100 mmol. The desired amount of a co-catalyst solution (organoaluminum complex) was added via syringe and the reactor closed. The reaction mixture was magnetically stirred and then heated to the reaction temperature ($50^\circ C$) where it was maintained for 6 h. The reaction mixture was then analyzed using an HP-5890 gas chromatograph equipped with a SE-30 capillary column ($l = 23$ m, $\varnothing = 0.25$ mm) and a flame ionization detector.

2.4. Linearity determinations

The linearity of the oligomers was evaluated for completely hydrogenated samples. The hydrogenation was carried out using a Pd/C (Merck, 10% Pd) catalyst and 5 bar of H_2 at $80^\circ C$ for 5 h. After the reaction, the hydrocarbon mixture was analyzed by GC, GC/MS and 1H -NMR spectroscopy (Varian VXR-200). Linear olefins standards (C_6 , C_8 , C_{10} , C_{12} , C_{14} , C_{16} , Aldrich, 98%) were treated in the same way, thus allowing precise linearity assignment of the obtained oligomers. Since branched and linear hydrogenated oligomers present different ratios of the methyl ($-CH_3$) and methylene ($-CH_2-$) protons, the linearity was also determined directly from the 1H -NMR spectra by measuring the methyl/methylene protons integral ratios.

3. Results and discussion

Only the systems based on $Ni(acac)_2$ combined with $AlEt_3$ or $AlEt_2OEt$ showed catalytic activity for α -olefin oligomerization. Experiments using the co-catalyst $AlEt_2Cl$ led only to the substrate isomerization. Precursors such as $Ni(ste)_2$ and $Ni(oct)_2$ combined with $AlEt_3$, $AlEt_2OEt$ or $AlEt_2Cl$, showed high catalytic

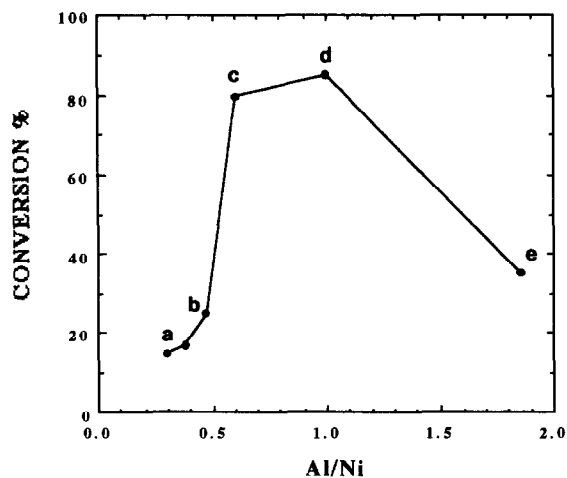


Fig. 1. Catalytic behavior of the system $\text{Ni}(\text{acac})_2 / \text{AlEt}_3$: influence of the Al/Ni ratio on the conversion.

activity to substrate isomerization but no oligomerization products were observed. In the case of $\text{Ni}(\text{acac})_2$, a direct relationship between selectivity in isomerization and the Lewis acidity of the aluminum co-catalysts was observed, suggesting the formation of bimetallic Al–X–Ni active species.

The experiments with the three ligands (stearate, octoate and acetylacetonate) revealed that such ligands direct the selectivity of the catalytic system and, therefore, interact with the nickel and/or aluminum in the catalytically active species.

3.1. Al/Ni ratio influence on the catalytic activity

Many authors have reported the influence of the Al/Ni ratio in Ziegler-Natta type catalytic systems [13,18–21]. In this work, the importance of the Al/Ni ratio was evaluated by a model system consisting of $\text{Ni}(\text{acac})_2 / \text{AlEt}_3$, 1-hexene in toluene at 50°C for 6 h. Fig. 1 shows the variation of the conversion as a function of the Al/Ni ratio. Four individual segments: *ab*, *bc*, *cd* and *de* can be identified. The first segment, *ab*, shows a very low conversion which might be a consequence of a low concentration of active species in the reaction medium.

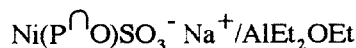
In the second segment, *bc*, a remarkable increase in conversion occurs, as a consequence of little increase in the Al/Ni ratio. This is probably related to the formation of a high concentration of active complex(es). The *cd* interval represents the Al/Ni ratio for which the highest concentration of active species is obtained.

The *de* segment represents a decrease in the concentration of the active species. This might be due to over-alkylation reactions of the nickel complexes leading to inactive metallic nickel species through reductive elimination reactions [22].

3.2. Oligomerization reactions of 1-butene, 1-hexene and 1-octene

The oligomerization of each α -olefin was performed using the $\text{Ni}(\text{acac})_2 / \text{AlEt}_2\text{OEt}$ catalytic system. AlEt_2OEt was chosen as the co-catalyst since it has the lowest isomerization selectivity and showed the same best value for the Al/Ni ratio of approximately 1.

Table 1 shows that oligomerization of 1-hexene and 1-octene leads to a similar product distribution. A high linearity was observed for their dimeric products (dodecenes and hexadecenes, respectively). A high isomerization for both 1-hexene and 1-octene was already observed by Kissin [23,24] employing



The reaction of 1-butene showed oligomerization to dimers, trimers and tetramers as well

Table 1
1-Hexene and 1-octene catalytic oligomerization results^a

Substrate	t.n.	conv%	olig%	iso%	lin%
1-Hexene	237	95	30	70	81
1-Octene	244	98	26	74	76

^a 15 ml of toluene, 50°C, 25 h, Al/Ni = 1. 0.2 mmol of $\text{Ni}(\text{acac})_2$ and AlEt_2OEt , 50 mmol of α -olefin.

Table 2
1-Butene catalytic oligomerization results ^a

Substrate	t.n.	conv%	olig%	iso%	Oligomers					
					dimers		trimers		tetramers	
					%	lin%	%	lin%	%	lin%
1-Butene	347	89	57	43	73	> 98	23	54	4	34

^a Reaction conditions as described for the 1-hexene and 1-octene oligomerization experiments.

as isomerization (Table 2). The isomerization is lower than that observed for 1-hexene or 1-octene (43% compared with 70–74%). The high linearity of the dimeric fraction (> 98%) is also remarkable. It is worth to note the appreciable amount of linear trimers and tetramers, which is not expected in terms of the classical nickel–hydride mechanism [25].

3.3. Co-oligomerization of 1-butene, 1-hexene and 1-octene

In the co-oligomerization experiments different mixtures of α -olefins were employed as shown in Table 3. Considering the hypothesis that α -olefins may stabilize low valence active nickel species, the total substrate concentration was varied. Since 1-butene presents a lower isomerization tendency than 1-hexene or 1-octene, it was employed in excess in all mixtures tested in order to ensure a high concentration of α -olefin.

Since the co-oligomerization reactions can

Table 3
1-Butene (C₄), 1-hexene (C₆) and 1-octene (C₈) catalytic co-oligomerizations results ^a

Parameters	Reactions								
	1/1/1			2/1.5/1			4/2/1		
	C ₄	C ₆	C ₈	C ₄	C ₆	C ₈	C ₄	C ₆	C ₈
conv%	88	91	92	92	92	91	74	77	73
iso%	53	61	66	47	59	62	46	65	61
olig%	48	40	34	53	41	38	54	36	40
t.n.	88	116	104	205	140	90	306	154	71
Σ t.n.	308			435			531		
substrate/Ni	345			470			710		

^a Reaction conditions as employed in the oligomerization experiments (Table 1Table 2).

lead to the formation of the same products originating from the oligomerization of a single α -olefin (for instance, dodecenes can be formed from either 1-hexene dimerization or 1-butene trimerization, as well as by the co-dimerization of 1-butene and 1-octene), the quantification of such reactions requires a weight balance calculation for each α -olefin [26]. The following steps illustrate the weight balance calculation for 1-hexene, allowing the precise determination of the 1-hexene weight in the total weight of dodecenes produced:

$$mC_6(\text{olig}) = mC_6(\text{conv}) - mC_6(\text{iso}) \quad (1)$$

$$mC_6(C_{10}) = nC_{10} \times MC_6 \quad (2)$$

$$mC_6(C_{14}) = nC_{14} \times MC_6 \quad (3)$$

$$C_6(C_{12}) = mC_6(\text{olig}) - [mC_6(C_{10}) + mC_6(C_{14})] \quad (4)$$

where:

$mC_6(\text{olig})$ = grams of 1-hexene converted to oligomers;

$mC_6(\text{conv})$ = total of grams of 1-hexene converted;

$mC_6(\text{iso})$ = grams of 1-hexene converted to isomers

$mC_6(C_{10})$ = grams of 1-hexene converted to decenes;

$mC_6(C_{14})$ = grams of 1-hexene converted to tetradecenes;

$mC_6(C_{12})$ = grams of 1-hexene converted to dodecenes;

nC_{10} = mols of decenes;

nC_{14} = mols of tetradecenes;

MC_6 = molar weight of 1-hexene.

Table 4
Linearity calculated from hydrogenated olefinic oligomers

Oligomers (C_n)	Linearity (%)		
	1/1/1	2/1.5/1	4/2/1
8	> 98	> 98	> 98
10	77	77	81
12	76	77	77
14	69	74	70
16	65	68	62

An important goal of the weight balance is the evaluation of the 1-octene isomerization since internal octenes can also result from the dimerization of 1-butene. Therefore, isomerization ratios can not be directly calculated from the chromatograms but should be determined through the total weight of 1-octene converted and the weight of 1-octene converted to oligomers using a similar calculation as showed above. The results of co-oligomerizations are shown in Table 3.

A very similar conversion was observed for all α -olefins tested. Also, the selectivity (olig% and iso%) seems to be independent of the substrate composition for each α -olefin.

Table 3 shows an increase on the turnover number as the total amount of α -olefins is increased. This shows that the reaction rate depends on the α -olefin concentration. Nevertheless, a maximum seems to be reached between substrate/Ni ratio of 470 and 710 in

agreement with a decrease on the conversion. At this range, the reaction becomes substrate independent and the thermal decomposition reaction the main operating process.

Analogous conclusions were drawn by Chauvin et al. [11] whom established for a similar catalytic system, by kinetic studies, a thermal deactivation behavior depending on the initial catalyst concentration and the reaction time.

3.4. Linearity ratios of the co-oligomerization reactions products

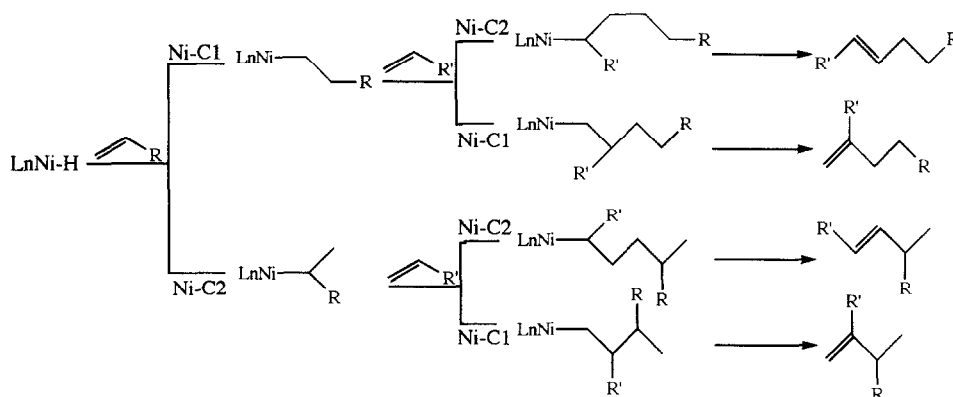
The co-oligomerizations led to olefinic products in the C_8 – C_{16} range with high linearity, as shown in Table 4.

The products obtained by trimerization or higher oligomerization showed lower linearities. This consideration explains the apparent discrepancy verified in the linearity obtained, for example, for the C_{16} fraction prepared by the 1-octene dimerization (76%, Table 1) and that arising from co-oligomerization (62%, Table 4).

Finally, no dependence of the oligomer linearity on the substrate composition is observed.

3.5. Mechanistic considerations

The high linearity observed in the dimeric and co-dimeric products as well as the isomerization activity shown by this catalytic system



Scheme 1.

led to the conclusion that a Ni–H species is responsible for the catalysis [27].

However, the best indication of a Ni–H formation was obtained in the oligomerization reactions of a single α -olefin, where it was possible to identify, by gas chromatography, products with carbon numbers of the α -olefin plus ethyl (major) and two α -olefins plus ethyl (minor). The total amount of such products was always equimolar to the half of the AlEt_2OEt employed. This is in agreement with the formation of a Ni–ethyl moiety from the mono alkylation of $\text{Ni}(\text{acac})_2$ by AlEt_2OEt . A Ni–H species might be derived from a Ni–alkyl through β -elimination [28].

Scheme 1 shows the possible products of a nickel–hydride catalyzed dimerization/co-dimerization. In this scheme, Ni–C1 and Ni–C2 represents the nickel atom attached to the α and β olefinic carbon, respectively, after a insertion/migration reaction between the α -olefin and the $\text{L}_n\text{Ni–H}$ complex. As seen in this scheme, there is only one way to form a linear dimeric product which is represented by the steps Ni–C1 followed by Ni–C2. So, the high linearity observed in the oligomerization products indicates a high regioselectivity of the catalytic system.

The $^1\text{H-NMR}$ spectra of the oligomerization products did not show any signal around 4.7

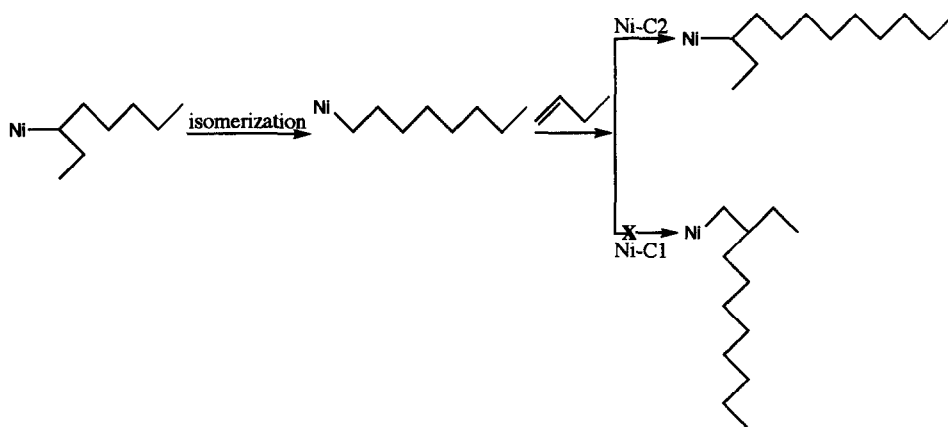
ppm, indicating the absence of vinylidenic products (routes Ni–C1/Ni–C1 and Ni–C2/Ni–C1) but only a broad peak at 5.4 ppm (2H) related to internal olefinic products. This observation confirms the regioselective character of the oligomerization reaction promoted by this catalytic system.

However, a simple metal–hydride mechanism can not explain the linearity presented by the trimers and tetramers. In order to account for these results, three situations must be operating:

- (1) Isomerization of a branched Ni–alkyl to a linear intermediate inside the nickel coordination sphere.
- (2) Coordination of a further substrate molecule.
- (3) β -elimination of the higher linear olefins.

As mentioned above, the coordination of a further substrate molecule must be of the Ni–C2 type in order to produce a linear non-vinylidenic product. Scheme 2 presents the steps described above applied for the trimerization of 1-butene.

The isomerization of Ni–alkyl species or double bond migration induced by nickel is a known process. Shimizu et al. [29] and Endo et al. [30,31] reported crystalline poly-1-butene as the unique product during *cis*-2-butene polymerization experiments using systems based on $\text{TiCl}_3/\text{NiCl}_2/\text{AlEt}_3$. This result was explained



Scheme 2.

in terms of the isomerization of *cis*-2-butene to 1-butene by the nickel atoms and subsequent polymerization by titanium centers. Studying α -olefins polymerization by Ni(0)/PR₃ and Ni(II)/PR₃/AlEt₃ systems, Fink and co-workers also observed products indicating isomerization of Ni-alkyl moieties [32].

The driving force for the isomerization of branched to linear alkyl-nickel compounds would be the steric interactions between the branched alkyl radical with the ligands around the nickel atom. This is consistent with the assumption that ligands and co-catalysts are composing the active species in such form that the nickel atom is placed inside a 'cage' with a restricted entrance. Similar considerations were made by Fink and co-workers explaining the steric effects of the phosphoranes ligands on the selectivity of the nickel catalyzed α -olefins polymerization [32].

4. Conclusion

Studies on the reactivity of different nickel complexes with quelating ligands in the presence of alkylaluminum co-catalysts indicate that both the nickel ligands and the aluminum compound participate in the composition of the active species.

The Ni(acac)₂/AlEt₂OEt catalytic system was found to be very efficient for the oligomerization of higher α -olefins, generating products of high linearity.

The catalytic activity showed a remarkable dependence on the Al/Ni ratio but was almost insensitive to the substrate composition.

The analysis of the oligomerization results led to the proposal of a nickel-hydride mechanism. The linearity observed in trimers and tetramers would be explained by a catalytic isomerization of a branched alkyl dimer or trimer generating a linear alkyl-nickel species in the coordination sphere of the nickel, followed by an insertion of another substrate molecule to form a linear trimer or tetramer.

5. Nomenclature

acac:	acetylacetonate
oct:	octoate
ste:	stearate
conv%:	conversion = mols of converted substrate/mols of initial substrate \times 100%
t.n.:	turnover number = mols of converted substrate/mols of nickel
iso%:	isomerization = mols of isomerization products/mols of converted substrate \times 100%
olig%:	oligomerization = mols of oligomerization products/mols of converted substrate \times 100%
lin%:	linearity = mols of linear products/total mols of products \times 100%
sel%:	selectivity = mols of product/mols of converted substrate \times 100%

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