Catalytic Dimerization of Propene with a Bis(salicylaldiminato)Nickel(II) Catalyst using 2,4,6-Trichlorophenol for Isomerization Reactions

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Abstract

A bis(salicylaldiminato)nickel(II) catalyst was used for dimerization reactions of propene. The catalyst precursor was activated with a triethylaluminum/aluminum trichloride mixture in the presence of phosphines and 2,4,6-trichlorophenol. The influence of the various components on the catalytic activity and product distribution is shown. Keywords: Dimerization of propene; Bis(salicylaldiminato)Nickel(II) complex; 2,4,6-Trichlorophenol; Isomerization.

Introduction

Bis(salicylaldiminato)nickel complexes have been widely employed as catalysts for olefin oligomerization and polymerization reactions [1-13]. Both linear α-olefins or (bi)cyclic olefins like norbornene can be applied as monomers. For industrial applications, catalysts for the selective dimerization or oligomerization of ethylene or propene are extremely attractive, since the resulting dimers or oligomers (C6-C15) are of considerable interest as fuel additives. The catalytic dimerization of propene can proceed in two different ways: at the C1-atom or at the C2-atom. After the termination of the reaction, eight different primary reaction products are possible. Furthermore, the option of isomerization reactions is given offering the possibility of the formation of four additional products (Scheme 1) [14-17].

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Depending on the desired reaction products, there are different goals like the production of linear hexenes as co-monomers for the production of Low Density Polyethylene (LDPE) [18-20]. Nowadays, when the gasoline prices are quite high, the petrochemical industry focuses on the production of branched products as additives for gasoline. Especially 2,3-dimethyl-1-butene impresses with a high octane number (RON (2,3-DMB-1) = 101.3) and low RVP (Reid Vapour Pressure) [21-26]. 2,3-Dimethyl-2-butene is a hexene isomer that is formed by isomerization of the primary reaction product.

Additives in catalytic propene oligomerization reactions can have tremendous effects on both product compositions and isomerization behavior. In 1966, Wilke described a catalyst system containing a $\pi$-allylnickel complex in combination with a tertiary phosphine and a Lewis acid like aluminum trichloride [27] producing mainly propene dimers (80-85 %). The branching factor strongly depended on the nature of the applied phosphine compound. Ewers [28] reduced nickel acetylacetonate with alkylaluminum chlorides resulting in somewhat higher catalytic activities compared to the Wilke system, but the percentage of the desired dimethylbutenes was low (< 5%). Eberhardt and Griffin [29] postulated that the aluminum compound must have two attributes: alkylation potential and Lewis acidity. Tolman [30] and Olivier [19] emphasized
the steric effects of the employed phosphine compounds on the product compositions. Bulky phosphines like tricyclohexylphosphine gave the best results in dimerization reactions. In 1993, Sato et al presented a catalyst system containing nickel naphthenate, triethylaluminum, and a tertiary phosphine which mainly produced 2,3-DMB-1 and 2,3-DMB-2 [31,32]. The addition of a chlorinated phenol derivative selectively lead to isomerization reactions of the produced dimers (selectivity to 2,3-DMB-2: 85%). A similar system was applied by Nomura et al who used sulfonic acids or dialkylsulfates instead of chlorinated phenols [3,4].

An improved concept to increase the selectivity of oligomerization catalysts includes the so-called “ligand-tailoring” that is based on structure-property relationships. In 2000 and 2001, Carlini et al. developed (β-dithioacetylacetonato)nickel complexes and (β-diketonato)nickel complexes with high selectivities to dimers (80-85 %), especially to 2,3-dimethylbutenes (up to 60 % of the dimer fraction) [22,33-36]. A further increase of the dimer fraction was reported by Lu when (β-diketiminato)nickel complexes or poly(salen) stabilized nickel complexes were applied while the observed selectivities to dimethylbutenes reached 50 % (salen-type complexes) and 65 % (β-diketiminato complexes) [23,37]. The group of Lu also investigated the dimerization properties of bis(salicylaldiminato)nickel complexes which also turned out to be highly efficient catalysts [7].

Based on the work of Sato, Nomura, and Lu, propene dimerization reactions were performed with a selected bis(salicylaldiminate)nickel catalyst in the presence of 2,4,6-trichlorophenol as an isomerization agent.

Materials and methods

All experimental work was routinely carried out using Schlenk technique. Dried and purified argon was used as inert gas. Toluene and pentane were purified by distillation over Na/K alloy. Deuterated solvents such as chloroform-d1 were dried over molecular sieves (3 Å).

NMR-spectroscopy

NMR studies were performed with a Bruker ARX 250 instrument. All samples were measured at 25 °C. CDCl3 was used as solvent. The chemical shifts (δ) in the 1H-NMR spectra refer to the residual proton signal of the solvent (δ = 7.24 ppm for chloroform) and in the 13C-NMR spectra to the solvent signal (δ = 77.0 ppm for chloroform-d1).

Mass spectrometry

MS spectra were recorded with a VARIAN MAT CH 7 mass spectrometer (direct inlet system, electron impact ionization, 70 eV).
Gas chromatography

For analysis of the dimerization products a gas chromatograph Agilent 6890 N was used. Argon was applied as carrier gas. A 30 m HP-5 (5 % phenyl methyl siloxane) column (film 1.5 µm, diameter 0.53 mm) was used. The flow was 150 ml/min (split 50:1). The temperature program included:

Starting phase: 6 min (35 °C)
Heating phase: 2 °C/min (10 min), then 20 °C/min (10 min)
Plateau phase: 20 min. (250 °C)

Synthesis of N-isopropylsalicylaldimine

To a solution of 25 mmol salicylaldehyde diluted in toluene, 27.5 mmol of isopropylamine were added. A small amount of p-toluenesulfonic acid was used as catalyst. The solution was heated for 4 h in a Dean Stark apparatus. Afterwards, the solution was washed with 100 ml water. The organic phase was separated and the solvent was removed with a rotary evaporator to yield the title compound as a yellow oil.

$^1$H NMR: 13.70 (s, 1H, OH), 8.29 (s, 1H, N=CH), 7.30-7.14 (m, 2H, Ar-H), 6.97 (d, 1H, Ar-H), 6.87 (t, 1H, Ar-H), 3.50 (sept, 1H, isopropyl), 1.27 (d, 6H, isopropyl).

$^{13}$C NMR: 161.9 (CH, N=CH), 161.1 (Cq, OH), 131.7, 130.9 (2- Ar-CH), 118.7 (Cq) 118.2, 116.7 (Ar-CH), 59.8 (CH, isopropyl), 24.0 (CH₃, isopropyl).

MS: 163 (M+, 100); 148 (M+Me, 63); 120 (M-isopropyl, 58).

Synthesis of the bis(salicylaldiminato)nickel complex

The ligand precursor was dissolved in 150 ml ethanol and 0.5 eq of nickel acetate as added. The mixture was heated up to 95 °C for 2 h. Afterwards, the solvent was removed in vacuo and the complex was washed with pentane several times. The nickel complex resulted as a light green powder with a yield of 90 %.

MS: 382 (M⁺, 37); 221 (M+H – ligand, 15), 162 (ligand, 100).

Elemental analysis: Calc.: C 62.70; H 6.31; N 7.31; Found: C 62.61; H 6.25; N 7.22.

General procedure for the activation of the complexes

An amount of 20 mg of the complex was suspended in 10 ml toluene. The calculated amount of phosphine was added afterwards. The mixture was activated with AlCl₃/AlEt₃. Finally, the appropriate amount of 2,4,6-trichlorophenol was added carefully.

Dimerization of propene in pressure Schlenk tubes

The activated catalyst precursor was transferred to a pressure Schlenk tube that was evacuated and cooled with liquid nitrogen. Liquid propene (100 ml) was sucked into the tube. After 1 h the reaction was terminated by releasing the pressure. The reaction products were hydrolyzed with diluted hydrochloric acid. The product mixtures were analyzed by GC.
Results and discussion

Synthesis of the bis(salicylaldiminato)nickel(II) complex

The ligand precursor was synthesized by a condensation reaction of salicylaldehyde with isopropylamine \[^{[38]}\]. The product was reacted with 0.5 equivalents of nickel acetate to give the bis(salicylaldiminato)nickel(II) complex (Scheme 2) \[^{[39,40]}\].

\[
\text{Catalytic dimerization reactions}
\]

The synthesized nickel complex was activated with a mixture of triethylaluminum/aluminum trichloride in the presence of triphenylphosphine or tri(n-butyl)phosphine as additive.

The experiments were carried out with different amounts of aluminum compounds without and with 2,4,6-trichlorophenol (TCP). All results are given in Table 1.

Scheme 2: Synthesis of the bis(phenoxyimine) Ni(II) complex used for catalytic dimerization reactions of propene.
Table 1: Results of the catalytic dimerization reactions of propene with bis(salicylaldiminato)nickel catalyst at room temperature. The percentages of the propylene dimers were calculated from the GC integrals. The GC signals of 2,3-dimethyl-1-butene and cis-4-methyl-2-pentene overlap, the same was observed for 2-methyl-2-pentene and trans-2-hexene.

<table>
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<th>TCP [eq]</th>
<th>Activity [g(oligomer)/mol(cat.)*h]</th>
<th>C₆ [%]</th>
<th>4-MP-1 [%]</th>
<th>DMB-1 t-4-MP-2 [%]</th>
<th>t-2-Hex [%]</th>
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<td>5.7</td>
<td>13.4</td>
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</table>

DMB-1: 2,3-dimethyl-1-butene; 4-MP-1: 4-methyl-1-pentene; t-4-MP-2: trans-4-methyl-2-pentene; 2-MP-1: 2-methyl-1-pentene; t-2-Hex: trans-2-hexene; 2-MP-2: 2-methyl-2-pentene; cis-2-Hex: cis-2-hexene; DMB-2: 2,3-dimethyl-2-butene.
The addition of 150 equivs. of 2,4,6-trichlorophenol to one equivalent of the bis(salicylaldiminato)nickel(II) complex (run 3) led to a decrease of the catalytic activity and selectivity to dimeric products compared to the TCP free system (run 1) (Figure 1).

![Activity and Selectivity](image)

**Figure 1**: Influence of 2,4,6-trichlorophenol on the catalytic activity (left) and selectivity to produce hexenes (right).

An interesting influence of trichlorophenol on the product distribution was observed. Without TCP (run 1), only 0.4 % of 2,3-dimethyl-2-butene (DMB-2) was formed. The use of 2,4,6-trichlorophenol (run 3) gave an increase to 43.3 %, formed by isomerization reactions. Other potential isomerization products like 2-methyl-2-pentene were hardly produced.

![Product Distribution](image)

**Figure 2**: Product distribution without (run 1) and with 2,4,6-trichlorophenol (run 3).

This behavior can be explained by the way of insertion. The addition of propene to the nickel center (with the C1- or C2-atom) is defined by the quotient \( p \) \[^1\] in the first insertion step, where

\[^1\] Reference or explanation needed.
\[ p = \frac{\% \text{ (2-methylpentenes + n-hexenes)}}{\% \text{ (4-methyl-1 and -2-pentene + 2,3-dimethylbutenes)}} \]

while the quotient \( q \) \(^{[1]} \) expresses the average of C-1 or C-2-insertion in the second step:

\[ q = \frac{\% \text{ (2-methylpentenes + 2,3-dimethylbutenes)}}{\% \text{ (4-methyl-1 and -2-pentene + n-hexenes)}} \]

According to run 3, \( p \) gives a ratio of 14.5:85.5 in the first insertion step. This means that mainly products were formed resulting from C2-insertions in the first reaction step. The probability of a C1-insertion was only about 14%.

The ratio of C1- and C2-insertion of the second reaction step was 61.6:38.4 corresponding to a slightly preferred C1 insertion in the second step. Therefore, the formed TCP-Al-species seems to influence only the first part of the reaction.

Changes of the aluminum/nickel ratio (applying 3 equivs. PBu\(_3\) and 150 equivs. TCP; runs 9, 11, 12, 13 in Table 1) lead to the following observations (see Figure 3):

The highest catalytic activity was observed with an aluminum/nickel ratio of 400. Higher ratios led to decreasing activities. A larger amount of aluminum compounds also showed a negative effect on the selectivities for hexenes. An influence on the product distributions was not observed.

![Figure 3](image)

**Figure 3:** Influence of the Al/Ni ratio on the catalytic activity (3 PBu\(_3\), 150 TCP; runs 9, 11, 12, 13 in Table 1).

The application of a larger amount of TCP had a negative influence on the catalytic activity of the catalyst (co-catalyst: Al/Ni = 400; 3 equivs. PBu\(_3\); runs 11, 14, 15, 16 in Table 1; Figure 4). The percentage of the produced dimers was at first
constant (about 91 %) and then dropped to 79 % when 400 equivs. of TCP were added.

![Bar chart showing activity vs. TCP equivalents](chart)

**Figure 4:** Influence of the amount of 2,4,6-trichlorophenol on the catalytic activity (co-catalyst: Al/Ni = 400; 3 equivs. PbBu₃; runs 11, 14, 15, 16 in Table 1).

The product distribution was clearly influenced by the use of different amounts of TCP. With increasing amounts of TCP, larger concentrations of 4-MP-1 and DMB-2 were observed. These products are formed by a C2-insertion in the first reaction step of the dimerization process. As shown before, 2,4,6-trichlorophenol influences mainly the direction of the first reaction part. The quotient p depends on the TCP-amount as indicated in the following table.

**Table 2:** Influence of TCP on the p value.

<table>
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<th>Run</th>
<th>TCP</th>
<th>p</th>
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<tr>
<td>11</td>
<td>150</td>
<td>44.9 : 55.1</td>
</tr>
<tr>
<td>15</td>
<td>300</td>
<td>25.4 : 74.6</td>
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</table>

2,4,6-Trichlorophenol is a component of the catalyst system that is on the one hand able to shift the dimerization process to products formed by C2-insertions and that has on the other hand the ability to act as isomerization catalyst.

For comparison purposes, additional dimerization/oligomerization runs were performed using different activators (runs 17-21) [11,12]. Good catalytic activities were observed with methylaluminoxane (MAO) as the cocatalyst, but the products mainly consisted of internal hexenes and methylpentenes (runs 17, 18). However, the desired 2,3-dimethylbutenes were determined to less than 10 %. According to Eberhardt and Griffin [29], the system was not active when triethylaluminum was employed as the
cocatalyst due to its insufficient Lewis acidity (run 19). Higher oligomers and no dimers were obtained when aluminum trichloride was applied (run 20) while little amount of dimers were produced with diethylaluminum chloride as cocatalyst (run 21). For all these comparative examples, the obtained amounts of the desired branched dimers 2,3-DMB-1 and 2,3-DMB-2 are extremely low. These results indicate the positive effect of the additive 2,4,6-trichlorophenol.

Conclusion

Propylene was dimerized with a bis(salicylaldiminato)nickel complex in combination with aluminum trichloride/triethylaluminum and phosphine compounds as additives. Further addition of a chlorinated phenol derivative lead to isomerization of the produced propylene dimers. In many cases, the selectivities towards hexenes exceeded 90%. Within the hexene fraction, the selectivity towards the desired 2,3-dimethyl-2-butene could be distinctively increased compared to the phenol-free catalytic systems.

Acknowledgements

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References