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Low pressure ethylene oligomerization with a nickel-P^O complex

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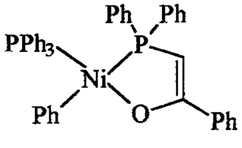
Summary

The oligomerization of ethylene catalyzed by nickel-P^O complexes at room temperature and low pressure (5 to 30 bar) yields butenes, hexenes and octenes. The molecular weight distribution can be manipulated by variation of ethylene pressure and by addition of triphenylphosphine. An unexpected linear dependence between the growing factor β of the Schulz-Flory type distribution and the pressure has been observed. The equation: $\beta = 6.2\ (PPh_3/Ni)^{1.2} - [0{,}17\ P(PPh_3/Ni)^{1.2}]$ allows to predict the composition of the α-olefins formed under different reaction conditions.

Introduction

A variety of nickel chelate complexes has been shown as very active in ethylene oligomerization with remarkable selectivities for linear terminal olefins (1,2). For example, Keim's nickel-P^O complexes (2) have been used by Shell in the SHOP process, one of the largest applications of the homogeneous catalysis by a transition metal (3).

The catalytic behavior of model complexes of type **1** has been already described in detail for batch reactions at rather high ethylene pressures (4).



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It has been demonstrated that nickel-P^O hydride complexes are the catalytically active species in olefin oligomerization, with step-grow carbon-carbon bond formation by 1~2 shift and chain termination by β-hydrogen elimination (5). In such a process a Schulz-Flory type distribution is obtained (6):

$$x_p = \frac{\beta}{(1+\beta)^p} \qquad (1)$$

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Where p is the degree of polymerization, x_p the fraction of polymerized olefin, and β the quotient of growth and displacement reaction rates that determines the shape of the molecular weight distribution.

Interest in the production of linear low-molecular-weight α-olefins to be used as co-monomers in the synthesis of low-density-linear-polyethylene (LDLPE) stimulated us to study the use of **1** as catalyst for ethylene oligomerization at low pressure (continuos feed) and low temperature.

Experimental

General procedures

All manipulations were performed using standard Schlenk techniques under dry argon. Solvents were distilled over desiccants immediately before use. The $[Ni(Ph_2PCHCOPh)(Ph)(PPh_3)]$ complex was prepared by reaction of (benzoylmethylene) triphenylphosphine, triphenylphosphine and bis(cycloocta-1,5-diene)nickel in toluene, as described (4b) giving 64% yield of complex **1**.

Catalytic experiments

The catalyst solution was prepared in a Schlenk tube and brought into a stainless steel double walled 100 mL autoclave. Ethylene was continuously introduced at the desired pressure and the temperature controlled by an external circulation bath. The reaction products, mainly low-molecular-weight olefins, were analyzed by gas chromatography on a HP5890 instrument using a 50m long silicon OV101 capillary column (id. 0.25 mm, film tickness 0.3μm); working at 30°C (7 min) and then heated at 10°C/min until 170°C (where it remained for 20 min).

Results and Discussion

Ethylene is oligomerized in contact with nickel-P^O catalysts under very mild reaction conditions, i.e. between 5 and 30 bar and from ambient to 70°C. As shown in Table 1, ethylene oligomerization in contact with **1** is remarkably selective to α-olefins in the C_4 to C_{10} range.

Table 1. Ethylene oligomerization with nickel-P^O complexes **1**

Run	P (bar)	Temp. (°C)	Time (h)	P/Ni	Turnover (h^{-1})	Selectivity (wt %)								β_{obs}	β_{calc}
						C_4	α-C_4	C_6	α-C_6	C_8	α-C_8	C_{10+}	α-C_{10}		
1	5	50	6.0	2	41	89	95	11	47	-	-	-	-	11.9	12.4
2	10	50	6.0	2	78	83	97	15	84	2	83	-	-	9.9	10.4
3	20	50	6.0	2	107	78	99	17	95	4	90	1	88	5.8	6.5
4	30	50	6.0	2	293	63	>99	24	98	9	95	4	90	2.9	2.7
5	30	50	6.0	2	22	61	>99	25	97	9	94	5	90	2.7	2.7
6	30	70	6.0	2	55	77	96	15	>70	5	>70	2	>65	3.7	2.7
7	30	50	2.5	1	160	43	88	20	79	12	79	9	79	0.9	1.1
8	30	50	6.0	1	135	41	87	22	74	13	74	9	72	1.0	1.1
9	30	50	6.0	3	111	77	>99	18	>98	4	>90	1	>90	5.4	4.5

As expected, low ethylene pressure causes the production of light olefins (entries 1 to 4), with the corresponding β quotient ranging from 2.9 to 11.9 on changing the ethylene pressure from 30 bar until 5 bar (7). This behavior is expected in a step-grow process where higher ethylene concentrations in solution give larger growth rates and a corresponding enhancement of heavier oligomerization products. It should be mentioned that at low ethylene concentrations the α-olefins content decreases (entries 1 and 2).

The catalyst system is active at 30°C, but with turnover rates of only 22 h^{-1} (entry 5) and shows a dramatic enhancement at 50°C, with a turnover rate of 293 h^{-1} (entry 4). At 70°C the system shows a turnover rate of 55 h^{-1} (entry 6) in a typical catalyst deactivation process. In fact, in this case, a partial decomposition of the complex has been observed at the end of the reaction.

Time has little effect on catalyst behavior under continuous ethylene feed up to 50°C. A slight catalyst deactivation and almost constant selectivity between 2.5 and 6h (entries 7 and 8) have been observed.

The phosphine to nickel ratio (PPh_3/Ni) has a remarkable effect on the system's selectivity. Higher PPh_3/Ni ratios lead to higher β values, i. e. an enhancement of the low-molecular-weight C_4 fraction from 41% to 63% and 77% on changing the PPh_3/Ni ratio from 1 to 2 and 3, respectively (entries 8, 4 and 9). As expected (3), the use of phosphines for the tailoring of the molecular weight distribution is effective and maintains the high content in α-olefins, which is larger than 98% in the C_6 fraction and 90% in $C_{10}+$ fractions with a PPh_3/Ni ratio = 3 (entry 9).

Continuous feeding of ethylene allows to investigate the validity of the Michaelis-Menten-type mechanism proposed by Keim and co-workers (8). A Lineweaver-Burk rate-law (equation 2) is expected from this mechanism:

$$\frac{1}{v} = \frac{K_m}{[\text{Ethylene}]}\frac{1}{v_{max}} + \frac{1}{v_{max}} \tag{2}$$

where v is the reaction rate, K_m is the Michaelis-Menten constant, [Ethylene] the ethylene concentration in the liquid phase and v_{max} the maximum reaction rate.

The application of the Lineweaver-Burk equation to our system gives a maximum rate of 1.8 s^{-1} in agreement with Keim's results for batch systems (8), taking into account that both results have imprecisions resulting from the low values of 1/turnover and that a higher rate is expected from continuos feeding compared to batch reactions.

From a Michaelis-Menten mechanism we can expect a linear dependence between β and 1/P (where P is ethylene pressure), a dependence that was observed under batch conditions only at higher pressures of ethylene (> 30 bar) (4a). Our results, however, do not show the 1/P dependence and we find a linear dependence between β and the pressure up to 30 bar of ethylene (Figure 1). Unexpectedly, we have also observed a linear dependence between the logarithm of β and the logarithm of the PPh_3/Ni ratio (Figure 2).

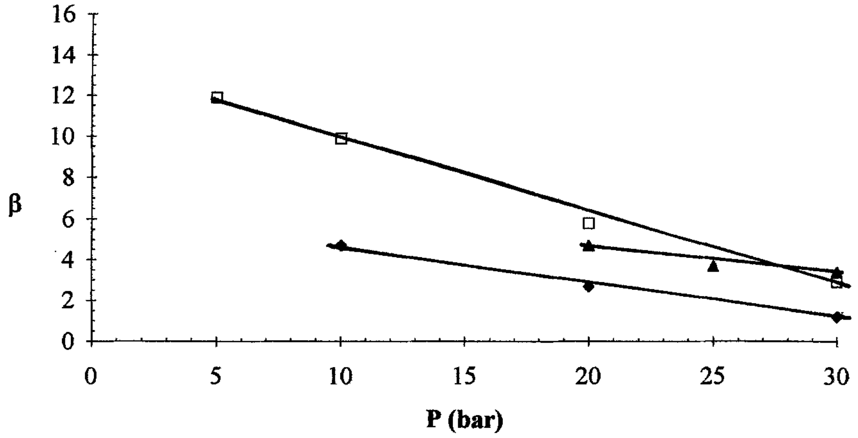


Figure 1. β *versus* pressure for the oligomerization of ethylene with 1.0 (◆), 1.5 (▲) and 2.0 (□) PPh_3/Ni ratio.

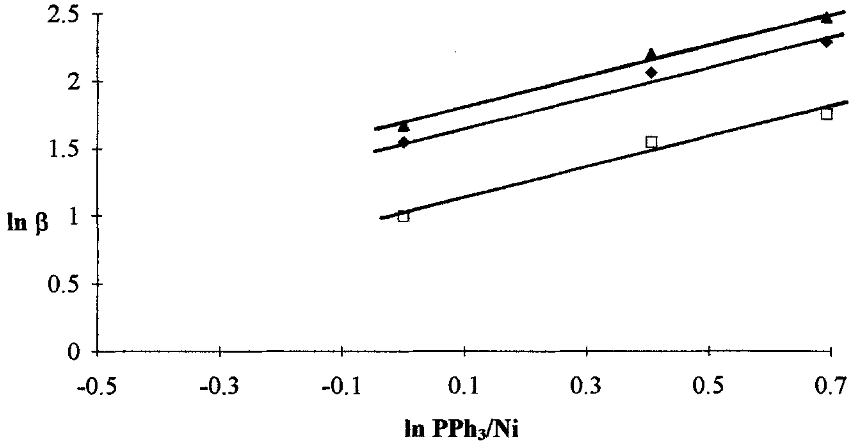


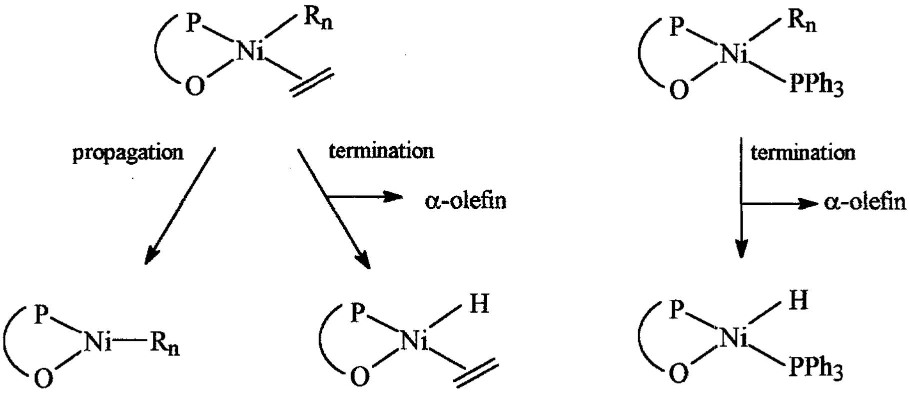
Figure 2. ln β *versus* ln PPh_3/Ni ratio for the oligomerization of ethylene with 5 (□), 10 (◆) and 20 (▲) bar ethylene pressure.

The combination of these dependencies provides equation 3:

$$\beta = 6.2\ (PPh_3/Ni)^{1.2} - [0{,}17\ P(PPh_3/Ni)^{1.2}] \qquad (3)$$

The application of equation 3 to catalytic runs under various reaction conditions described in Table 1 permits to predict β in very good agreement with the experimental values, assuming 10% relative error (compare the last two columns of Table 1).

Under these conditions a linear dependence between β and 1/P has not been observed.We find that the first term depends only on the phosphine/nickel ratio and the second term on both the phosphine/nickel ratio as well as the ethylene pressure (or ethylene concentration in the liquid phase). This kind of dependence suggest the existence of (at least) two basic types of active species which can be represented as shown in Scheme 1. One active species involves a phosphine-nickel-hydride (or alkyl) complex and the other an ethylene-nickel-hydride (or alkyl) complex.



Scheme 1

The ethylene-nickel-alkyl complex leads by insertion of coordinated ethylene into the metal carbon bond to growth products (chain propagation) or to termination by β-hydride elimination. The first reaction is probably more important since the increase of ethylene pressure leads to a decrease in the low-molecular-weight olefins fraction and in the absence of triphenylphosphine we observe only higher olefins formation. On the orther hand, the phosphine-nickel-alkyl complex do not contain a vacant coordination site for olefin coordination and subsequent chain propagation. For this complex the most probable reaction is the β-elimination. The increase of triphenylphosphine in this system leads to an enhancement of the low-molecular-weight olefins fraction. At low ethylene pressure we observe a decrease in the α-olefins content. This can be explained by a competition between ethylene (at low concentration) and olefins formed by it. The reduced coordination ability of the produced olefins in comparison with ethylene or triphenylphosphine explains the high selectivity to α-olefins at higher olefin and phosphine concentrations.

To conclude, this work shows that the oligomerization of ethylene can be performed under very mild conditions and continuous feeding to form low-molecular-weight α-olefins. Under these conditions a maximum rate of 1.8 s^{-1} was obtained and we have demonstrated that it is possible to control product formation by ethylene pressure and phosphine content using a single equation. It is worthwhile to mention that the behavior of the nickel catalyst under these conditions is not the same as has been observed at high ethylene pressures and batch conditions.

Acknowledgments

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