A kinetic study of propylene dimerization by binuclear nickel–ylide complexes in presence of diethylaluminium chloride as cocatalyst

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Abstract

The propylene dimerization by catalytic systems consisting of binuclear nickel–ylide complexes 1 (linked by alkyl chain) or 2 (linked by benzene) and diethylaluminium chloride was studied. Very high activities were encountered for both catalytic systems. Thus for complexes 1 and 2 maximum activities of 46.7 kg dimers/(g-Ni h) and 34 kg dimers/(g-Ni h) were observed, respectively. The composition of the dimers obtained was studied on the basis of propylene and nickel concentration and Ni:Al ratio. A kinetic analysis for complex 1 was carried out showing first order dependence on catalyst and second order dependence on propylene.

1. Introduction

Nickel based catalysts have been broadly used in chemical technology during the past several decades [1]. The discovery of the 'nickel effect' as well as the investigations on the influence of transition metals in ethylene oligomerization led to the development of Ziegler–Natta catalysts [2].

A number of publications, for example [3–6] are dedicated to the use of nickel complexes generated by interaction of nickel salts with organoaluminium compounds. The activity, selectivity and stability of such catalytic systems can be modified by a manner referred in the literature as 'ligand tailoring'.

Nickel–ylide complexes are well known as ethylene oligomerization/polymerization catalysts [7–18]. On the other hand the binuclear nickel–ylide complexes (BINYC), studied by Tomov and Kurtev [19,20] are more active oligomerization/polymerization catalysts compared to the mononuclear ones. Data about the use of nickel–ylides/organoaluminium compounds as catalysts in ethylene oligomerization are scarce in the literature [21–24]. Data are generally missing for propylene dimerization. However Keim [11] has been reported a case of propylene dimerization by unicomponent mononuclear nickel–ylide catalyst, in which very high selectivity towards 4-methyl-1-pentene

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was obtained. That is why it was of importance to study the binuclear nickel–ylide complexes in presence of diethylaluminium chloride as propylene dimerization catalysts.
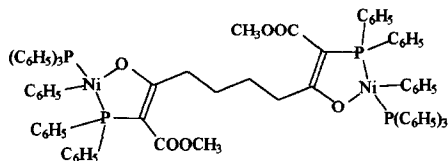
In the present work the propylene dimerization by binuclear nickel–ylide complexes/diethylaluminium chloride as well as the kinetics of propylene dimerization in presence of BINYC $1/Al(C_2H_5)_2Cl$ are described (Fig. 1).

2. Experimental

2.1. Materials
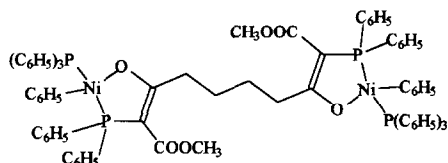
All manipulations were carried out in an inert atmosphere (argon) using standard techniques. Toluene was stored over sodium and then freshly distilled under argon. Diethylaluminium chloride (Schering, Germany) was used as a 25% (w/w) solution in toluene. The binuclear nickel–ylide complexes 1 and 2 were prepared according to [19]. Propylene (99,96%, Neftochim Plc. Bulgaria) was used without further purification. GC analysis of the propylene dimerization products were performed using a Sigma 2000 gas chromatograph, equipped with a flame-ionisation detector. Data handling was provided by the Chromatographics 2 Data System (Perkin Elmer). Permaphase DMS (dimethylsilicone) fused-silica capillary columns (50 m × 0.25 mm i.d.; two columns in series connected with butt connector) used in our work

were from Perkin Elmer. The analysis temperature was 313 K.

2.2. Propylene dimerization

The propylene dimerization was carried out in a 200 ml thermostatted magnetic stirred batch glass reactor (Fisher–Porter), equipped with magnetic stirring bar. Before every experiment the reactor was cleaned and kept under vacuum at 383 K for 2 h. When cooled under argon it was filled with BINYC suspended in 20 ml toluene and then charged with liquid propylene until a 80 ml volume was reached. After disconnection from propylene device 0.25–2 ml 25% solution of diethylaluminium chloride in toluene was injected in reactor via syringe. The reaction was terminated by adding of 2% sodium carbonate in water into the reactor. Solution of sodium carbonate was used to prevent further olefin isomerization by the products of active complex decomposition (e.g. HCl). The unreacted propylene was vented at 273 K and the reaction mixture was distilled in the range 318–348 K. CG analysis samples were withdrawn immediately after the propylene release.

2.3. Kinetic procedure
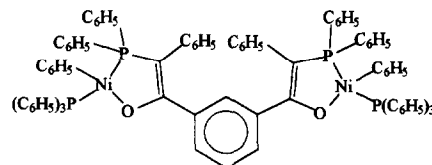
The experiments were conducted in an isothermal magnetically stirred semibatch glass reactor, which was carefully flushed with dry, oxygen-free argon prior to each run by succes-
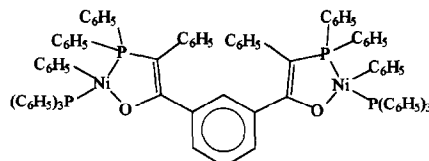

Fig. 1. Structures of the binuclear nickel–ylide complexes.

sive evacuation, argon back-fill cycles. The reactor was connected to a system with a thermostatted volumetric gas balloon. After this it was charged with an appropriate amount of BINYC 1, suspended in 20 ml of toluene. Propylene was fed into the reactor in such a manner that a constant pressure of propylene was held in the apparatus. The reaction was initiated by adding the toluene solution of diethylaluminium chloride. A number of runs were performed at 273 K, 283 K and 293 K, and concentrations of BINYC 1 in the range of 0.10×10^{-3} to 0.35×10^{-3} mol l^{-1}. In all experiments the reaction proceeded in the kinetic region. The propylene consumption–time curves for a series of initial substrate concentrations were derived by periodically reading the volume of the gas, consumed from the gas balloon. These are equivalent to concentration–time curves obtained in a batch reactor, under the same conditions, because the total volume of the reaction mixture did not change significantly during the course of the reaction. The differential method and especially the method of initial rates of data analysis was employed to evaluate the reaction order and specific reaction rates.

3. Results and discussion

3.1. Propylene dimerization by BINYCs 1 and 2 in presence of diethylaluminium chloride

Propylene dimerization in presence of BINYCs 1 and 2, and diethylaluminium chloride was carried out in liquid phase with vary of catalyst concentration, ratio Ni:Al, temperature and the reaction time. The results from a number of runs are listed in Tables 1 and 2. The data for the propylene conversion are obtained by termination of the reaction at different times. In all experiments mainly dimers were obtained. The content of the higher oligomers was less than 5%.

Both catalytic systems are characterized by

an inductive period of 2 to 4 min. The reaction was performed at Ni:Al ratios from 1:5 to 1:250. The catalytic systems were inactive at Ni:Al ratios lower than 1:5. As a result it was found that the catalytic activity increased with increase of the Ni:Al ratio.

The propylene dimers can be attributed to primary products and products from $C_6^=$ isomerization [3] (Scheme 1). The degree of isomerization of the primary products as well as the product selectivity depends on the propylene conversion and practically does not change with the Al:Ni ratio. As the catalytic systems possess very high activity all experiments were performed at BINYC concentration from 0.07×10^{-3} to 0.34×10^{-3} mol l^{-1}.

As shown in Table 1 there no yields were obtained for 2-methyl-2-pentene and 2,3-dimethyl-2-butene (isomerization products) at lower propylene conversion (run 2). It is obvious that at such conversion the product distribution is closer to that corresponding to the primary products. Therefore, it may be used for calculation of the quotients p and q [3], which represent the direction of the addition of propylene ($Ni \rightarrow C_1$ and $Ni \rightarrow C_2$) for the first and second insertion steps, respectively. Thus for the catalytic system consisting of BINYC-1 and diethylaluminium chloride p and q amount to 42.8/57.2 and 8.9/91.1 respectively.

The propylene dimerization was studied at a number of different Al:Ni ratios. In general the composition of the propylene dimers is less dependent on these values, except for trans-4-methyl-2-pentene, whose content increases with

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$$p = \frac{\%(2\text{-methyl-1-pentene} + 1\text{- and 2-hexene}}{\%(4\text{-methyl-1- and 2-pentene} + 2,3\text{-dimethylbutenes})}$$

$$= \frac{\%Ni \rightarrow C_1}{\%Ni \rightarrow C_2}$$

$$q = \frac{\%(2\text{-methyl-1-pentene} + 2,3,\text{-dimethylbutenes})}{\%(4\text{-methyl-1- and 2-pentene} + 1\text{- and 2-hexene})}$$

$$= \frac{\%Ni \rightarrow C_1}{\%Ni \rightarrow C_2}$$

Table 1
Reaction conditions and composition of the dimers obtained in propylene dimerization by BINYC-1 in presence of diethylaluminium chloride

No. [a]	$C_{cat} \times 10^3$ mol×l^{-1}	Ni:Al ratio	Propylene conversion, %	4-M-1-P	2,3-DM-1-B cis-4-M-2-P	trans-4-M-2-P	2-M-1-P 1-H	cis-3-H	trans-3-H	trans-2-H	cis-2-H	2-M-2-P
				Composition of propylene dimers [b,c], % (w/w)								
1	0.07	1:250	85	1.3	6.2	39.4	10.6	2.9	10.7	15.2	5.5	8.2
1a	0.07	1:250	90	0.9	6.5	39.6	10.1	2.6	9.9	16.1	4.0	10.3
2	0.14	1:250	4	3.6	8.7	44.9	8.9	1.0	2.1	14.2	16.6	–
3	0.34	1:12	95	0.8	7.9	26.8	14.1	3.0	9.9	19.7	11.2	6.6
4	0.34	1:25	97	0.8	7.5	28.9	13.2	3.5	9.4	19.3	11.3	6.1
4a	0.34	1:25	95	0.5	6.9	29.1	13.7	3.3	9.5	20.0	10.0	7.0
5	0.34	1:50	30	0.8	5.1	30.5	12.6	3.4	8.6	19.7	13.1	6.2

[a] Runs 1a and 4a were carried out at 283 K.

[b] 4-M-1-P = 4-methyl-1-pentene; 2,3-DM-1-B = 2,3-dimethyl-1-butene; 4-M-2-P = 4-methyl-2-pentene; 2-M-1-P = 2-methyl-1-pentene; 1-H = 1-hexene; 3-H-hexene; 2-H = 2-hexene; 2-M-2-P = 2-methyl-2-pentene.

[c] 2,3-Dimethyl-2-butene is not obtained in the propylene dimerization by the catalytic system studied.

Table 2
Reaction conditions and composition of the dimers obtained in propylene dimerization by BINYC-2 in presence of diethylaluminium chloride

No [a]	$C_{cat} \times 10^3$ mol $\times$ l^{-1}	Ni:Al ratio	Propylene conversion, %	Composition of propylene dimers [b,c], % (w/w)								
				4-M-1-P	2,3-DM-1-B / cis-4-M-2-P	trans-4-M-2-P	2-M-1-P / 1-H	cis-3-H	trans-3-H	trans-2-H	cis-2-H	2-M-2-P
1	0.08	1:50	2.5	1.2	14.9	27.4	8.1	2.0	8.5	17.2	17.0	3.7
2	0.08	1:100	40	0.8	7.9	28.8	9.7	1.1	13.4	18.3	10.9	9.1
3	0.08	1:250	25	1.6	10.4	31.6	9.9	1.5	11.3	14.2	13.8	5.7
3a	0.08	1:250	27	1.2	12.4	30.1	9.6	2.0	12.2	13.5	12.8	6.2
4	0.14	1:250	65	0.7	9.0	32.7	9.8	2.8	9.2	20.4	6.9	8.5
5	0.26	1:250	52	0.9	8.5	28.5	13.3	3.1	9.5	18.8	11.1	6.3
5a	0.26	1:250	50	0.5	7.2	26.1	12.2	3.6	10.2	17.5	13.9	8.8

[a] Runs 3a and 5a were carried out at 283 K.
[b] 4-M-1-P = 4-methyl-1-pentene; 2,3-DM-1-B = 2,3-dimethyl-1-butene; 4-M-2-P = 4-methyl-2-pentene; 2-M-1-P = 2-methyl-1-pentene; 1-H = 1-hexene; 3-H = 3-hexene; 2-H = 2-hexene; 2-M-2-P = 2-methyl-2-pentene.
[c] 2,3-Dimethyl-2-butene is not obtained in the propylene dimerization by the catalytic system studied.

the Ni:Al ratio. The concentration of diethylaluminium chloride however, influence upon the activity of the catalytic system. It rises from 12.7 kg dimers/(g-Ni h) at Ni:Al = 1:50 to 46.7 kg dimers/(g-Ni h) at Ni:Al = 1:250. It was assumed that the rise of catalytic activity with increase of the Al:Ni ratio is due to the ability of diethylaluminium chloride to take part in some reversible steps of the active species formation.

The change of the reaction temperature also does not significantly influence the composition of the dimers.

Table 2 presents data for the composition of the dimers obtained in propylene dimerization by the BINYC-2/diethylaluminium chloride catalytic system. Similar to the data obtained from BINYC-1 in this case the highest content was observed for *trans*-4-methyl-2-pentene. However, it does not change significantly with the Ni:Al ratio. The activity of this catalytic system amounts to 12 kg dimers/(g-Ni h) at

Ni:Al = 1:50 and 34 kg dimers/(g-Ni h) at Ni:Al = 1:250. The higher activity of BINYC-1 compared to that obtained for BINYC-2 is probably due to the presence of the stronger electron-withdrawing CO_2CH_3 groups in its molecule.

3.2. Kinetics of propylene dimerization by BINYC-1 and diethylaluminium chloride

Kinetic studies on the propylene dimerization in presence of nickel based Ziegler–Natta type catalytic systems are described in several works [25–29]. The experimental kinetic data analysis is complicated by the presence of an induction period (ca. 1–2 min). On the other hand the reaction rate is dependent on the concentration of the reaction products as well as the type of the solvent used. That is why the maximum rates after the induction period were employed for the next calculations. These were obtained by numerical differentiation of the kinetic curves
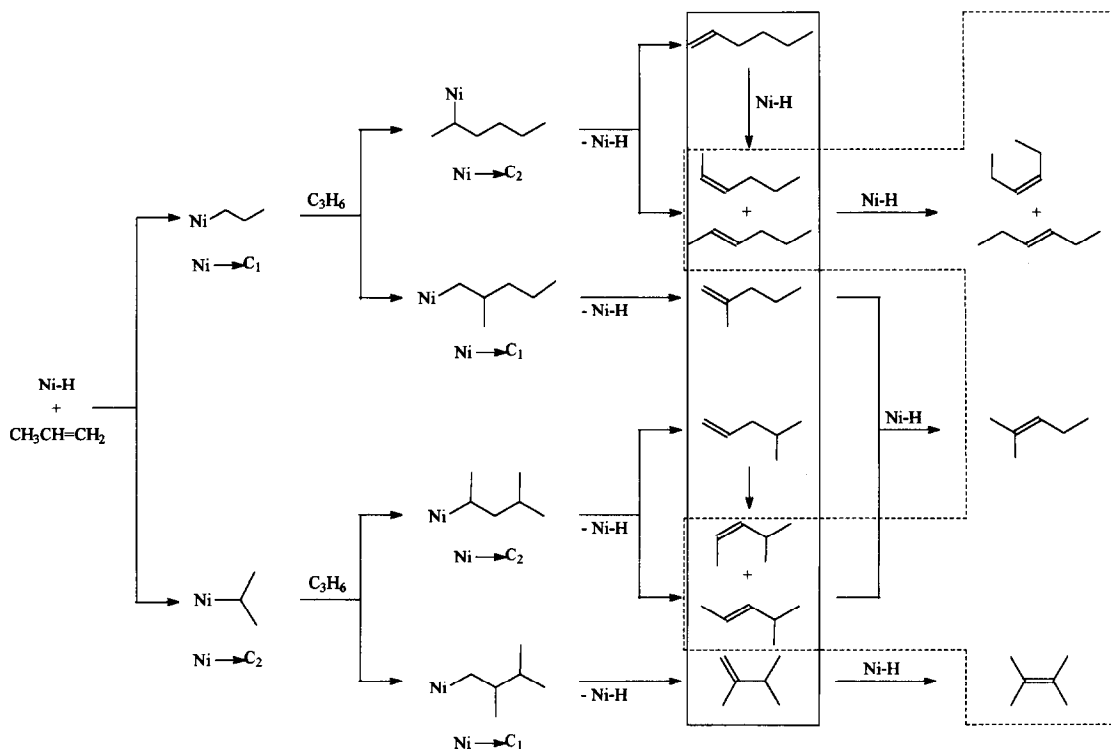
Scheme 1. The dimers obtained in propylene dimerization. (——) Dimerization products; (- - -) isomerization products.

Fig. 2. Plot of log r vs. log[C_3H_6].
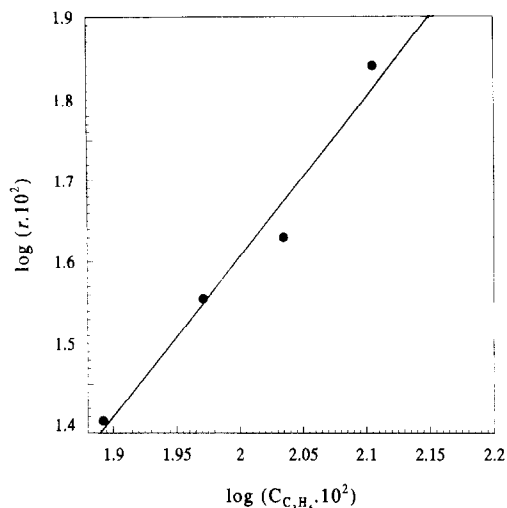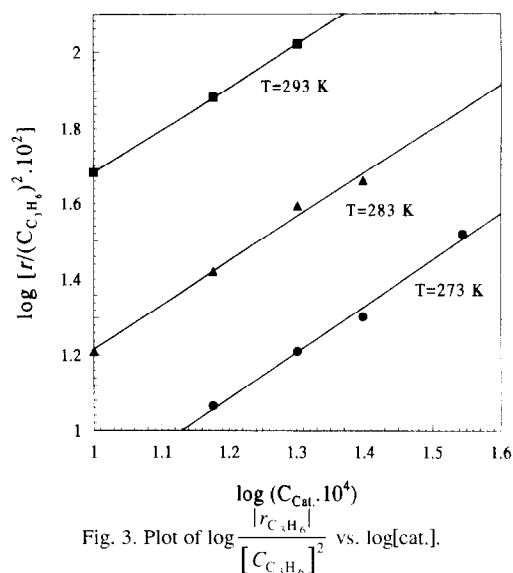
Fig. 3. Plot of log $\dfrac{|r_{C_3H_6}|}{\left[C_{C_3H_6}\right]^2}$ vs. log[cat.].

of propylene consumption. In order to check the reproducibility of the data, four series of rate measurements were made using four catalyst solutions prepared separately.

3.2.1. Rate law

3.2.1.1. Dependence on propylene concentration.
Initial rates were measured with varying the propylene concentrations from 0.78 to 1.27 mol l^{-1} at a nickel concentration of 0.20 mmol l^{-1} and 283 K. A plot of log r vs. log[C_3H_6] indicates that the rate under such conditions is

second order with respect to the propylene concentration (Fig. 2).

3.2.1.2. Dependence on catalyst concentration.
The effect of the catalyst concentration was examined by varying the nickel concentration from 0.15 mmol l^{-1} to 0.35 mmol l^{-1} at temperatures of 273, 283 and 293 K. A plot of log $\dfrac{|r_{C_3H_6}|}{\left[C_{C_3H_6}\right]^2}$ vs. log[cat.] indicates that the rate is first order with respect to the nickel concentration (Fig. 3).

Table 3
Kinetic data for propylene dimerization by BINYC-1 and diethylaluminium chloride

T K	$C_{cat} \geq \times 10^4$ mol l^{-1}	$|r_{C_3H_6}|$ mol l^{-1} min^{-1}	$C_{C_3H_6}$ mol l^{-1}	$\frac{|r_{C_3H_6}|}{[C_{C_3H_6}]^2}$ l mol^{-1} min^{-1}	k_{obs} l^2 mol^{-2} min^{-1}	$t_{sk,obs}$	TON s^{-1}
273	1.5	0.1209	0.9604	0.1161	5128.6	± 1.3	13.43
	2.0	0.1687	0.9604	0.1620			14.05
	2.5	0.1925	0.9604	0.2004			12.83
	3.5	0.3169	0.9604	0.3299			15.09
283	1.0	0.0986	0.6084	0.1621	7413.0	± 1.3	16.43
	1.5	0.1600	0.6084	0.2630			17.77
	2.0	0.2540	0.6084	0.3917			16.93
	2.5	0.2964	0.6084	0.4571			19.76
293	1.0	0.1454	0.3025	0.4808	14791.0	± 1.0	24.23
	1.5	0.2308	0.3025	0.7629			25.64
	2.0	0.3167	0.3025	1.0471			26.39

From the above results, the experimental rate law is:

$$r = k_{obs}[\text{cat.}][C_3H_6]^2$$

where [cat.] and $[C_3H_6]$ are the concentrations of BINYC-1 and propylene used, respectively.

3.2.1.3. Kinetic parameters. The effect of temperature on the rate was examined at temperatures ranging from 273 to 293 K in order to obtain kinetic parameters. The rate constant, shown in Table 3, give a linear Arrhenius plot and is summarized by the equation: $k_{obs} = 2.44 \times 10^{10} \exp(-35060/RT)$ mol^{-2} l^2 min^{-1}. From a value of E_a of 35.06 kJ mol^{-1} and the specific rate constant at 283 K were calculated: $\Delta S^{\#} = -53.99$ J mol^{-1} K^{-1} and $\Delta H^{\#} = 32.71$ kJ mol^{-1}.

Acknowledgements

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