METAL COMPLEXES IN CATALYTIC CONVERSION OF OLEFINS.
3.* CATALYTIC DIMERIZATION OF ETHYLENE AND PROPYLENE BY $Ni(PPh_3)_n$–$Et_3Al_2Cl_3$ SYSTEM

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The $Ni(PPh_3)_n$–$Et_3Al_2Al_3$ catalytic system was found to be most effective for the dimerization of ethylene and propylene when the ligands Bu_3PO and $(BuO)_2$–$PNEt_2$ were used in the Ni complex. For propylene dimerization in the liquid phase, the yield was 54 kmole/mole Ni·h at 40-55°C. Using mathematical planning methods for the experiments the optimum conditions range for the formation of hexanes was found, in which selectivity for dimerization reached 85-96% at 80-90% conversion.

It has been shown [1] that reduction of $NiCl_2 \cdot 6H_2O$ by the action of $NaBH_4$ in the presence of PPh_3 produces a catalyst which appears to be a mixture of the complexes $Ni(PPh_3)_n$ where n = 2-4: $Ni(PPh_3)_4$, $Ni(PPh_3)_3$ and probably $Ni(PPh_3)_2$. Such a catalyst brought about conversion of C_3-cyclic olefins without an activator [1, 2].

This present work is devoted to an investigation of the catalytic properties of the $Ni(PPh_3)_n$–$Et_3Al_2Cl_3$ system in the dimerization of linear C_2-C_3 olefins and also to a search for the optimum conditions for the production of hexane from liquified propylene.

Ni complexes obtained as in [1] with P-containing ligands of different types exhibited corresponding differences in ethylene dimerization. The greatest activity was exhibited by a catalyst with a PPh_3 ligand (Fig. 1). Although a few of the other ligands increase the selectivity of the process for dimer formation (Table 1), there is a sharp decrease in yield compared to the $Ni(PPh_3)_n$–$Et_3Al_2Cl_3$ (Cat-1) system, which according to [4] is linked to the lower basicity of these ligands compared to PPh_3. The Cat-1 system appears to be the most effective for the liquid phase dimerization of propylene [5].

A mathematical design method for the experiments was used to find the optimum conditions for the process. The process indicators were judged to be the conversion of propylene (y_1, %), catalyst yield (y_2, kmole/mole Ni·h) and selectivity for dimers, trimers, and tetramers (y_3, y_4, y_5, %). The variable parameters of the process were: T, °C (Z_1), concentration of complex C_{Ni} mole/liter (Z_2), molar ratio Al/Ni (Z_3). The process parameters were varied with the ranges: $20 \le Z_1 \le 60$; $1.36 \cdot 10^{-4} \le Z_2 \le 6.79 \cdot 10^{-4}$; $3.3 \le Z_3 \le 83.0$. The dependence of the process indicators on the parameters is approximated by regression equations of the form:

$$y_c = b_0{}^c + \sum_i^3 b_i{}^c x_i + \sum_{ij}^3 b_{ij}{}^c x_i x_j$$

where b^c are coefficients of regression and x_i are dimensionless variables corresponding to the Z_i parameters. Conversion to dimensionless coordinates was achieved by means of the formula $x = (Z_i - Z_i{}^0)/\Delta Z_i$, where $Z_i{}^0$ is a standard value (the middle of the investigated range) and ΔZ_i is the variation increment. The standard values were selected as follows: $Z_1{}^0 = 40$, $Z_2{}^0 = 4.075 \cdot 10^{-4}$, $Z_3{}^0 = 43.2$; variation increments: $\Delta Z_1 = 20$, $\Delta Z_2 = 2.7 \cdot 10^{-4}$, $\Delta Z_3 = 39.85$. The experimental points were selected with respect to an orthogonal second-order plane. The experimental results are presented in Tables 2, 3. A statistical treat-

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*For previous communication, see [1].

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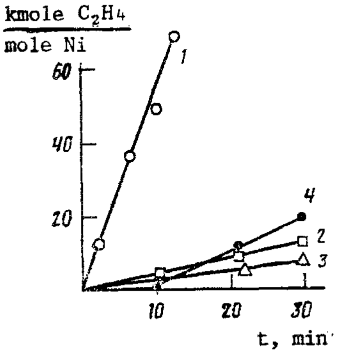

Fig. 1. Effect of P-containing ligand (L) on the activity of the Ni complex obtained by reduction of $NiCl_2 \cdot 6H_2O$ by $NaBH_4$ in the presence of L (activator – $Et_3Al_2Cl_3$; reaction – ethylene dimerization); 1) PPh_3; 2) Bu_3PO; 3) $(BuO)_2 \cdot PNEt_2$; 4) $Ni(CO)_x(PPh_3)y/Al_2O_3$ where $x + y = 4$.

TABLE 1. Effect of Nature of P-containing Ligands (L) on the Selectivity of Propylene Dimerization in the Presence of NiL_n–$Et_3Al_2Cl_3$ Complexes

Expt. number	L	Selectivity of dimerization, %	Expt. number	L	Selectivity of dimerization, %
1	PPh_3	79,1	3	$(BuO)_2PNEt_2$	88,6
2	$Bu_3P{=}O$	79,0	4	$Ni(CO)_x(PPh_3)_y/Al_2O_3$	96,0

ment [6], which included verification of the adequacy of the specifications according to Fisher's criteria and of the significance of the regression coefficients according to Student's criteria, enabled the functions of the process indicators to be represented by the following equations:

$$y_1 = 91.6 + 24.2x_2' + 24.6x_3 + 9.84x_1x_2 + 8.21x_1x_3 - 8.27x_2x_3 - 34.15x_3^2; \quad (1)$$

$$y_2 = 26.8 - 1.51x_1 + 7.83x_2 + 11.1x_3 - 5.14x_1^2 - 3.58x_1x_2 + 3.35x_1x_3 + 8.51x_2^2 - 9.61x_2x_3 - 13.3x_3^2 \quad (2)$$

$$y_3 = 80.5 - 0.93x_1 - 3.72x_2 - 8.24x_3 - 1.61x_1^2 + 0.71x_1x_3 + 8.15x_2^2 \quad (3)$$

Analogous equations were obtained for selectivity of C_9 and C_{12} olefins.

The differences from zero of paired coefficients of interaction of the obtained regressional equations indicated a significant cooperative action of the factors. It was very complicated to estimate this effect during a study of univariate functions. The adequacy of the process description by Eqs. (1) to (3) allowed the experimental results to be analyzed on the basis of these regressional models.

The catalytic yield was found to be dependent on T and the molar ratio (Al/Ni) (Table 2) as in [7]. Such an effect is usually linked with thermal destruction of active centers and "transreduction" of the complexes with subsequent coagulation and the formation of a Ni (0) phase. However, as a rule the optimum temperature did not exceed 30-40°C and more often was in the range −10 to 0°C. Cat-1 was distinguished by exhibiting its maximum efficiency at higher temperatures (40-55°C) which enabled water cooling to be used. The selectivity for dimerization is not very dependent on the reaction temperature. This is characteristic for most nickel systems modified by phosphine [8]. However, an increase in the molar ratio Al/Ni significantly reduces the fraction of C_6-olefins in the catalysis product (Fig. 2a-c). Minimum selectivity for propylene dimer formation was observed at $C_{Ni} \simeq 5 \cdot 10^{-4}$ mole/liter.

The dimer fraction compositions are presented in Table 3. They are typical for systems modified with phosphine [8]. The optimization of the process can be worked out from the regressional equations. Conversion 80-90%, selectivity for dimer 85-96% and yield 35-48 kmoles/mole Ni·h is achieved within the following ranges: $48°C \le T \le 60°C$; $1.36 \cdot 10^{-4} \le C_{Ni} \le 1.52 \cdot 10^{-4}$ mole/liter; and $50 \le Al/Ni \le 65$, and at the same time the model indicates that the catalyst concentration might be lowevered to $0.6 \cdot 10^{-4}$ mole/liter with conservation of the specified process indicators (Fig. 3a).

It should be noted that the Cat-1 yield of 54 kmoles/mole Ni·h is not likely to be a limit: the limitation is linked to the static conditions under which the reaction was conducted. Thus, in some experiments (Table 2) 90% propylene conversion, estimated from the

TABLE 2. Matrix of Planned Experiments and Their Results for Liquid Phase Oligomerization of Propylene in the Presence of Catalytic Systems. Cat-1–$Et_3Al_2Cl_3$ ($C_{C_3H_6}$ = 9.8 moles/liter, τ = 1 h)

Expt. number	T, °C	$C_{Ni}\cdot10^{-4}$, mole/liter	Al/Ni	y_1, %	y_2, kmole C_3H_6/mole Ni·h	y_3, %	Time to reach 90% conversion, min	Initial yield,* kmole C_3H_6/mole Ni·h
1	60	6,79	83,0	93,5	13,6	75,8	30	25,5
2	60	6,79	3,3	50,6	7,3	90,0	–	–
3	60	1,36	83,0	72,9 †	52,9 †	83,2 †	–	–
4	60	1,36	3,3	0,2	0,1	100	–	–
5	20	6,79	83,0	100	14,5	74,1	4	174
6	20	6,79	3,3	93,0	13,5	93,5	40	20
7	20	1,36	83,0	43,1	31,3	81,8 †	–	–
8	20	1,36	3,3	4,3	3,1	100	–	–
9	60	4,07	43,2	93,6	22,6	74,4	30	43
10	20	4,07	43,2	91,1	22,0	82,4	25	52
11	40	6,79	43,2	99,9	14,5	84,9	5	157
12	40	1,36	43,2	79,0	57,4	91,4	–	–
13	40	4,07	83,0	98,9	23,9	73,3	25	52
14	40	4,07	3,3	18,1	4,4	86,2	–	–
15	40	4.07	43.2	99.0	24.0	83.6	15	87

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*Estimated results.

†Average of three experiments.

TABLE 3. Composition of Propylene Dimer Fractions

Expt. number	2,3- DMB-1	4- MP-1	cis-4-MP-2	trans-4-MP-2	H-1+2-MP-1	H-3	trans-H-2	2-MP-2	cis-H-2	2,3-DMB-2
1	0,2	1,4	5,2	31,8	6,2	7,5	18,9	22,8	4,5	1,6
2	0	3,9	7,5	30,3	14,7	6,5	16,0	14,4	6,0	0,7
3	0,2	1,9	5,7	31,7	6,1	5,2	19,5	23,1	5,0	1,7
4	Not determined									
5	0,4	1,1	3,0	27,8	5,0	4,3	16,2	33,0	5,7	3,5
6	0	1,2	4,1	31,9	12,5	5,4	17,4	23,2	3,6	0,7
7	0,2	1,7	6,8	42,6	4,3	6,0	18,2	15,4	3,9	0,9
8	Not determined									
9	0,3	1,4	4,0	28,7	7,6	6,6	17,8	27,3	4,9	2,0
10	0,2	1,4	4,0	30,6	5,8	5,7	15,1	31,2	4,4	1,6
11	0,1	0,8	2,8	25,8	8,6	5,4	16,9	32,7	4,4	2,5
12	0	1,2	3,8	29,0	5,0	6,2	17,4	29,7	4,6	3,1
13	0,4	1,2	3,5	23,0	6,1	6,1	17,8	34,0	4,3	3,6
14	0,2	2,5	6,6	44,1	3,8	3,7	15,1	17,7	4,0	1,7
15	0.4	0.8	2.7	26.8	8.1	5.7	15.8	32.3	4.6	3.1

Note. H = hexene, MP = methylpentene, DMB = dimethylbutene.

pressure decrease in the reaction vessel to 0.10-0.15 MPa, was achieved much more quickly. On the basis of these results calculated values for the initial activity of Cat-1 > 170 kmoles/mole Ni·h were obtained. The only catalytic system comparable, but nevertheless markedly inferior, to Cat-1 in yield for propylene dimerization is nickel salt–trialkylaluminum–isoprene–organophosphorus compound of general formula $R^1R^2R^3P$, $(R_2{}^1N)_nPR_{3-n}{}^2$, or $(R^1O)_nPR_{3-n}{}^2$ (R^{1-3} are the same or different Alk, Ar, cycloalkyl, alkenyl, ArAlk; n = 1-3) – polyhalophenol of general formula X_5C_6OH (X = Hal) [9]. The activity of this system under optimum conditions with the use of $(i\text{-}Pr)_3P$ and chlorobenzene reaches 74 kmoles/mole Ni·h. However, in the case of PPh_3 it is ≤12.5 kmoles/mole Ni·h for propylene.

EXPERIMENTAL

The mixture of triphenylphosphine complexes were obtained as in [1]. Oligomerization of ethylene was carried out in a water-cooled metal reactor of 250 ml capacity fitted with a mechanical stirrer and a valve for removing samples. The reaction temperature was maintained by an ultrathermostat. A weighed portion of the catalyst and then the solvent (~100

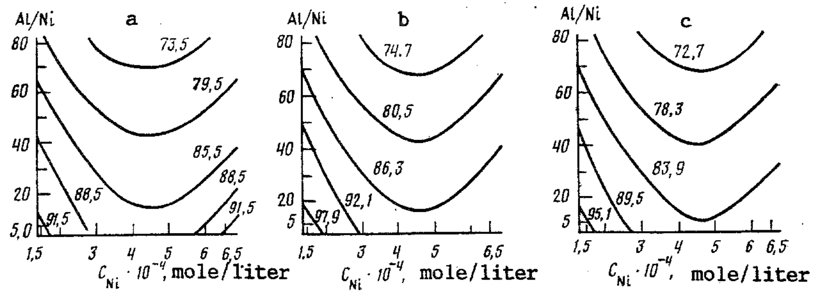

Fig. 2. Dependence of selectivity for propylene dimerization in Cat-1 systems on C_{Ni} and molar ratio Al/Ni at T, °C: a) 20, b) 40, c) 60.

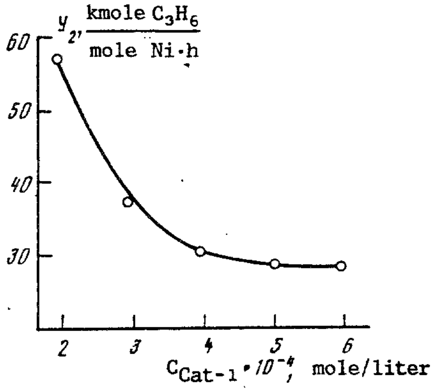

Fig. 3. Effect of C_{Ni} on the maximum yield.

ml) were put into the reactor, the ethylene pressure was adjusted to 1 MPa and the activator was added. The reaction time was measured from the moment of introduction of the activator.

Oligomerization was brought about by means of a liquid dosing apparatus. The catalyst, 90 g liquid propylene, and the calculated quantity of the solution of $Et_3Al_2Cl_3$ in heptane were successively introduced. The experiment was conducted with a single charge of propylene and discontinued after 1 h by introducing water into the reactor. The propylene conversion was determined from the difference between the initial charge and the unreacted propylene. Similarly from the decrease in pressure to 0.1-1.5 MPa the conversion achieved was judged to be 90%. The experimental results are presented in Tables 1 and 2.

Oligomerization products of ethylene and propylene were analyzed on a LKhM-8MD chromatographic apparatus fitted with an ionization detector and copper capillary column (50 m × 0.16 mm; stationary phase triethylene glycol dibutyrate; carrier gas H_2; 25-40°C).

All operations with Ni complexes and $Et_3Al_2Cl_3$ were conducted in an Ar atmosphere. The ethylene used for oligomerization was type TU-38 10282-75.

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