DIMERIZATION OF ETHYLENE IN THE PRESENCE
OF HETEROGENIZED NICKEL
CARBONYLTRIPHENYLPHOSPHINE OBTAINED
BY COMPLEXATION ON THE SUPPORT SURFACE

D. B. Furman, N. V. Volchkov,
L. A. Makhlis, P. E. Matkovskii,
G. P. Belov, V. É. Vasserberg,
and O. V. Bragin

Simple Ziegler — Natta catalyst systems for the dimerization of lower olefins are often modified by donors such as phosphines and additives [1, 2]. Catalyst modification by the introduction of an additive to the reaction medium, in contrast to prior coordination of the phosphine as a ligand, does not always have a positive effect on selectivity. Thus, the dimerization of propylene on the $Ni(CO)_4 + PPh_3 + AlCl_3$ catalytic system proceeds with the formation of up to 20-25% polymer [3].

Another method involving fixation of nickel compounds by impregnation or grafting to an anchoring group of mineral or polymer supports leads to catalysts which retain their activity over long periods [4-6]. The preparation of catalysts by ligand exchange of $Ni(CO)_4 + PPh_3$ in the adsorbed layer of a support permits us to combine these two methods.

In the present work, a sample of nickel carbonyltriphenylphosphine/Al_2O_3 (Ct-1) was prepared according to our previous procedure [7] and the most important features and some kinetic relationships of the liquid-phase oligomerization of ethylene in the presence of the Ct-1 — organoaluminum Lewis acid catalytic system were studied.

EXPERIMENTAL

The Ct-1 catalyst was obtained by the reaction of PPh_3 with $Ni(CO)_4$ previously adsorbed on Al_2O_3 according to our previous procedure [7, 8]. The IR spectra of Ct-1 contained characteristic bands at 1945 and 2005 cm^{-1} given by Tolman [9] for $Ni(CO)_2(PPh_3)_2$. The dimerization of ethylene was carried out as in our previous study in a metallic reactor using dry heptane, benzene, ether, and THF as the solvent. The reaction products were analyzed by gas-liquid chromatography [8].

RESULTS AND DISCUSSION

The dimerization of ethylene under optimal conditions proceeds in the Ct-1 — $Et_3Al_2Cl_3$ system with high output (70-80 kg/g Ni per h) and high selectivity ΣC_4 90-94% (the remainder in hexenes) upon running the reaction in aromatic and aliphatic hydrocarbons at 40°C. This output and selectivity are significantly better than those found for active homogeneous systems [2, 3, 10].

Table 1 shows that running the reaction in heptane and in aromatic solvents gives reaction output, fraction composition, and reaction selectivity relative to dimer formation which are similar. This apparently indicates the similar nature of the active sites. In ether and THF, the ethylene dimerization rate (W_d, g C_2H_4/g Ni·min) is low. A sample of π-C_3H_5NiCl/Al_2O_3 prepared analogously in ether also did not reveal activity in this process [8]. This sharp decrease in W_d in ether and THF is apparently related to the low concentration of sites which are active in ethylene dimerization. It is not excluded that hindrance to the formation of active sites in ether and THF arises even in the step involving the reaction of the supported metal complex with the organoaluminum compound.

In the hydrocarbon solvents studied such as heptane, W_d in the steady-state segment increases linearly with increasing ethylene concentration from 0.3 to 1.7 mole/liter (Fig. 1) as previously found for π-C_3H_5NiX/Al_2O_3 (X = Cl and Br [8]).

TABLE 1. Effect of the Nature of the Solvent on the Yield and Composition of the Products of the Oligomerization of Ethylene in the Presence of Ct-1 – $Et_3Al_2Cl_3$ at 40°C after 30 min ($[C_2H_4]_0 = 1.2$ mole/liter, $0.42 \cdot 10^{-2}$ g starting nickel, Al : Ni =36)

Experiment	Solvent	Product weight, g	Output, g kg C_2H_4/g Ni·h	C_4, %	C_6, %	Fraction compositions, % *									
						C_4			C_8						
						1-B	trans-2-B	cis-2-B	3-M-1-P	1-H	3-H	trans-2-H	cis-2-H, trans-3-M-2P	cis-3-M-2-P
1	n-Heptane†	144,5	68	92	8	22	50	28	5,3	5,3	3,3	46,5	19,6	20,0
2	Benzene	150,9	71	91	9	26	51	23	4,8	6,5	3,5	50,4	17,4	17,4
3	Toluene	172,1	81	94	6	24	52	24	8,7	4,3	15,2	41,3	15,2	15,2
4	Ether‡	3,8	0,9	99	4	93	5	2	–	–	–	–	–	–
5	THF	0,64	0,3	99	1	44	37	19	–	–	–	–	–	–

* B) butene, H) hexene, Mp) methylpentene.

† C_8–C_{12} fraction found in trace amounts in experiments 1–3.

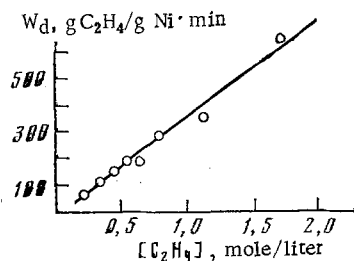‡ [Ni] =$1.44 \cdot 10^{-3}$ mole/liter, Al : Ni =50.

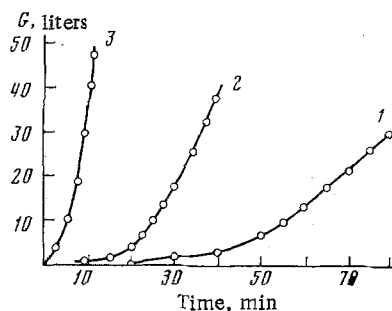Fig. 1   Fig. 2

Fig. 1. Dependence of the rate of ethylene dimerization on the monomer concentration in the presence of $Ni(CO)_2(PPh_3)_2/Al_2O_3 - Et_3Al_2Cl_3$ ($[Ni] = 2 \cdot 10^{-3}$ g-atom/liter, Al : Ni = 6, 20°C, heptane solvent).

Fig. 2. Effect of the C_2H_4 concentration on the duration of the induction period for ethylene dimerization in the presence of $Ni(CO)_2(PPh_3)_2/Al_2O_3 - Et_3Al_2Cl_3$ (G is the amount of absorbed ethylene): 1) 0.35, 2) 0.55, 3) 1.7 mole/liter.
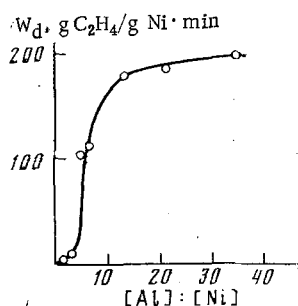

Fig. 3   Fig. 4
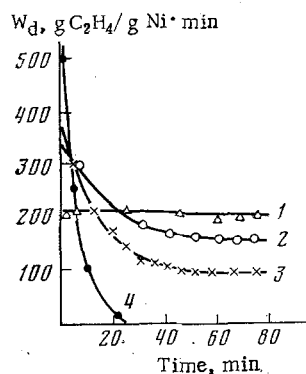
Fig. 3. Dependence of the rate of C_2H_4 dimerization on the Al : Ni molar rate ($[Ni] = 2 \cdot 10^{-3}$ g-atom/liter, 20°C, heptane solvent, $[C_2H_4] = 0.45$ mole/liter).

Fig. 4. Temperature effect on the activity and stability of $Ni(CO)_2(PPh_3)_2/Al_2O_3 - Et_3Al_2Cl_3$ in heptane solvent ($[Ni] = 1 \cdot 10^{-3}$ g-atom/liter, Al : Ni = 9.5, $[C_2H_4] = 0.45$ mole/liter): 1) 20°, 2) 40°, 3) 60°, 4) 80°C.

The kinetics for ethylene dimerization on $Ct-1 - Et_3Al_2Cl_3$ illustrated in Fig. 2 is characterized by an initial non-steady-state segment apparently related to the formation of active sites. The dependence of the duration of the induction period on the ethylene concentration shown in Fig. 2 was unexpected. This effect is apparently related to the participation of ethylene molecules in the formation of the catalytic sites responsible for this process.

The effect of the $Et_3Al_2Cl_3$ concentration and thus, of the Al : Ni ratio on W_d for constant [Ni] is illustrated in Fig. 3. For Al : Ni from 2 : 1 to 12 : 1, there is a sharp increase in W_d. A further increase in the Al : Ni ratio from ~ 12 to 35 has only a slight effect on W_d while a significant increase in the rate of oligomerization of lower olefins is characteristic for homogeneous Ziegler — Natta systems with an increase in the Al : Ni up to 100 [2,4]. Since a large excess of the organoaluminum component is required primarily to provide for active site regeneration cycles during the catalytic reaction [2, 11], the low sensitivity of the $Ct-1 - Et_3Al_2Cl_3$ system toward the $Et_3Al_2Cl_3$ concentration in the Al : Ni ratio from 12 to 35 is most likely a result of its rather high stability at 20°C.

Indeed, ethylene dimerization at 20°C in the presence of $Ct-1 - Et_3Al_2Cl_3$ over 1 h proceeds in a steady-state mode (Fig. 4). An increase in temperature leads to an increase in the rate of ethylene absorption but a drop in activity is noted over the course of the experiment due to the formation of inactive forms of the metal

TABLE 2. The Effect of Temperature on the Composition of the Products of the Oligomerization of Ethylene in the Presence of Ct-1 — $Et_3Al_2Cl_3$ in Heptane Solvent $(0.6 \cdot 10^{-2}$ g Ni, Al : Ni = 9.5, $[C_2H_4]$ = 0.45 mole/liter, τ = 30 min)

Experiment	T., °C	Yield, g	Selectivity, %	
			C_4	C_6
1	20	36	95	5
2	40	40	92	8
3	60	41	87	13
4	70	24	93	7
5	70 *	5	94	6

*Al : Ni = 6.
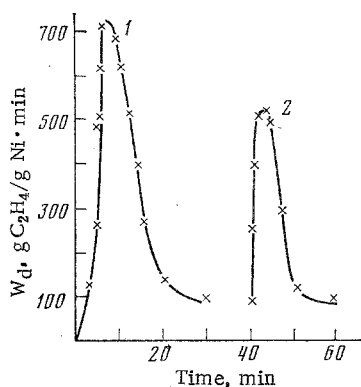
Fig. 5. Feasibility of reactivating the $Ni(CO)_2(PPh_3)_2/$ $Al_2O_3 - Et_3Al_2Cl_3$ catalytic system by the addition of a new activator portion in heptane solvent ([Ni] = 0.001 g-atom/liter, $[C_2H_4]$ = 1.0 mole/liter, 70°C): 1) [Al] = $2.2 \cdot 10^{-3}$ mole/liter, 2) additional introduction of 2.2 · 10^{-3} mole/liter $Et_3Al_2Cl_3$.

(probably, colloidal nickel). We should note that even at 60°C, the catalyst output after 1 h operation does not drop below 100 g C_2H_4/g Ni·min. At higher temperatures, the regenerating function of the organoaluminum component is more evident than at 20°C. Figure 5 shows that a new activator portion at 70°C restores the system activity by ~70%.

Such an effect may be the result of the involvement of a significant portion of deactivated nickel forms in the catalytic process [2, 4, 11]. An increase in the number of catalytic cycles is also found when using a higher initial $Et_3Al_2Cl_3$ concentration. Thus, an increase in the initial activator concentration by a factor of only 1.5 leads to a fivefold increase in the product yield (Table 2, experiments 4 and 5).

Homogeneous nickel catalyst systems are active at 0-10°C and are completely and irreversibly deactivated upon increasing the reaction temperature [4]. Our data show that the Ct-1 — $Et_3Al_2Cl_3$ system is capable, as noted above (see Fig. 5), of reactivation even at 70°C and has relatively high stability and capacity for olefin oligomerization at elevated temperatures which is typical for heterogenized metal complexes [4, 5].

The multifunctional role of the organoaluminum component in reactions catalyzed by Ziegler — Natta systems is evident in the significant effect of the composition and, thus, of the type of activator on the yield of ethylene dimerization products in the presence of a system with Ct-1 and an aluminum-containing Lewis acid (Table 3). The system output upon variation of the activator changes as follows: $AlCl_3 \ll AlEtCl_2 < Et_3Al_2Cl_3 \gg$ $Et_2AlCl > AlEt_3$. A similar effect of the type of aluminum-containing activator was found by Shmidt et al. [4, 11] for catalytic systems consisting of nickel compounds or their heterogenized analogs. The most effective of the activators is $Et_3Al_2Cl_3$ (see Table 3) which optimally combines the properties of the rather strong reducing agent and alkylating agent, Et_2AlCl and the strong Lewis acidity of $EtAlCl_2$. The reaction product yield is mini-

TABLE 3. The Effect of Reaction Conditions on the Oligomerization of Ethylene in the Presence of Ct-1 at 20°C in Heptane (1.2·10⁻² g Ni, τ* = 30 min)

Activator	Al atomic	C_2H_4, mole/liter	Product yield, g	ΣC_4, %	ΣC_6, %	Composition of product, %								
						1-B	trans-2-B	cis-2-B	3-M-1-P	1-H	3-H	trans-2-H + 2-E-1-B†	cis-2-H + trans 3-M-1-P	cis-3-M-2-P
AlCl₃	34	0,45	2,5†	90	10	9,0	74,0	17,0	9,0	19,0	—	54,0	9,0	9,0
EtAlCl₂	34	0,45	6,2	86	14	3,0	68,0	29,0	3,0	0,2	6,3	26,0	23,8	40,7
Et₂AlCl	34	0,45	1,2	90	10	6,0	67,0	27,0	6,0	0,2	2,8	20,0	21,0	50,0
Et₃Al₂Cl₃	6	0,2	20	93	7	2,0	70,0	28,0	4,5	0,3	8,2	39,0	20,0	28,0
Same	6	0,35	40	95	5	2,0	67,0	31,0	4,2	0,2	7,6	43,5	20,6	23,9
»	6	0,45	47	94	6	3,0	69,0	29,0	4,0	0,3	7,2	43,2	21,6	23,7
»	6	0,65	65	96	4	14,0	72,0	14,0	6,5	0,4	8,5	44,6	20,0	20,0
»	6	1,10	112	95	5	10,0	75,0	15,0	6,4	0,5	9,8	48,2	18,1	17,1
»	6	1,70	180	96	4	13,0	62,0	25,0	10,0	1,0	14,1	40,0	17,9	17,0
»	12	0,45	58	92	8	2,0	71,0	27,0	2,7	0,3	7,1	36,5	23,7	29,7
»	22	0,45	65	91	9	2,0	73,0	25,0	1,3	0,2	3,6	32,2	27,5	35,2
»	34	0,45	69	91	9	2,0	70,0	28,0	0,4	0,3	7,2	30,0	25,3	36,8
Et₃Al	34	0,45	Traces‡	—	—	—	—	—	—	—	—	—	—	—

*Without considering the production period.
†E) ethyl.
‡ After 8 h.

imal for use of $AlCl_3$ and Et_3Al as the activators. $AlCl_3$ does not have reducing properties and is a strong Lewis acid, while Et_3Al is an effective reducing agent but a weak Lewis acid [11].

Table 3 indicates that there are no sharp variations in the composition of the ethylene dimers and trimers or in the ratio of the C_4 and C_6 fractions, which would imply a change in the nature of the active sites of the Ct-1 – organoaluminum activator system. The dimer yield decreases slightly with increasing reaction temperature (see Table 2), with increasing Al : Ni ratio, with decreasing C_2H_4 concentration, and in going from $Et_3Al_2Cl_3$ to $EtAlCl_2$ (see Table 3). The α-olefin fraction in all the experiments was small due to rapid displacement of the double bond. The decrease in the amounts of 2-butene and 3-methylpentenes (the products of the copolymerization of 2-butene and ethylene) with increasing C_2H_4 concentration is striking. This effect indicates inhibition of the isomerization of the dimers and trimers formed by ethylene. Thus, the drop in the α-olefin fraction and enhanced yield of 3-methylpentenes with increasing concentration of alkylaluminum halide are explained by an acceleration of the isomerization.

Hence, ethylene dimerization in the presence of $Ni(CO)_2(PPh_3)_2/Al_2O_3 - Et_3Al_2Cl_3$ proceeds with high output and selectivity in a rather broad range of temperatures, ethylene concentrations, and catalyst component concentrations without a significant change in the product composition.

CONCLUSIONS

1. A study was carried out on the dimerization of ethylene in the presence of $Ni(CO)_2(PPh_3)_2/Al_2O_3$ catalyst obtained by ligand exchange on the support surface in various solvents using aluminum-containing Lewis acids as the activator, in the temperature range from 20° to 80°C and in the range of monomer concentrations from 0.3 to 1.7 mole/liter. The greatest output (70-80 kg/g Ni · h) and selectivity (90-94% C_4 fraction) was achieved using $Et_3Al_2Cl_3$ as the cocatalyst at 40°C.

2. The ethylene concentration affects the product yield, duration of the induction period, and dimerization selectivity.

3. A linear dependence was found for the reaction rate on the ethylene concentration. The Al : Ni ratio has a significant effect on the reaction output only in the range from 5 : 1 to 12 : 1.

LITERATURE CITED

1. P. Heimbach, P. Jolly, and G. Wilke, Adv. Organomet. Chem., 8, 29 (1970).
2. V. Sh. Fel'dblyum, Olefin Dimerization and Disproportionation [in Russian], Khimiya, Moscow (1978).
3. R. De Haan and I. Dekker, J. Catal., 44, 15 (1976).
4. V. S. Tkach, F. K. Shmidt, T. N. Sergeeva, and N. D. Malakhova, Neftekhimiya, 15, 703 (1975).
5. V. A. Kabanov, M. A. Martynova, S. K. Pluzhnov, V. I. Smetanyuk, and R. V. Chediya, Kinet. Katal., No. 4, 1012 (1979).
6. G. V. Lisichkin and A. Ya. Yuffa, Heterogeneous Metal Complex Catalysts [in Russian], Khimiya, Moscow (1981).
7. V. É. Vasserberg and I. V. Kalechits, in: Proceedings of the All-Union Conference on Catalysts Containing Supported Complexes [in Russian], Siberian Branch, Academy of Sciences of the USSR (1977), p. 15; D. B. Furman, T. M. Kharitonova, S. S. Zhukovskii, T. I. Nechaeva, B. M. Fedorov, A. M. Taber, V. G. Lipovich, O. V. Bragin, I. V. Kalechits, and V. É. Vasserberg, Izv. Akad. Nauk SSSR, Ser. Khim., 2278 (1979).
8. D. E. Furman, N. V. Volchkov, L. A. Makhlis, P. E. Matkovskii, F. S. D'yachkovskii, V. É. Vasserberg, and O. V. Bragin, Izv. Akad. Nauk SSSR, Ser. Khim., 1962 (1981).
9. C. A. Tolman, J. Am. Chem. Soc., 92, 2956 (1970).
10. J. Ewers, Angew. Chem., 593 (1966); West German Patent No. 1,520,964.
11. F. K. Shmidt, L. V. Mironova, V. V. Saraev, V. A. Gruznykh, T. V. Dmitrieva, and G. V. Ratovskii, Kinet. Katal., 20, 662 (1979).