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INVESTIGATIONS ON CATALYTIC SYSTEMS CONTAINING NICKEL SUPPORTED ON SILICA GEL AND BONDED WITH ORGANIC LIGANDS AND COMPLEXED BY LEWIS ACIDS. II *

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Summary

The catalytic activity in the oligomerization of propylene, of compounds formed by reaction of $(C_3H_5)_2Ni$ with the hydroxide groups of silica gel and complexation with different Lewis acids, Lewis bases, or both, have been studied. $TiCl_4$, $AlCl_3$, $AlBr_3$ and R_nAlCl_{3-n} (R = Me, Et; n = 1, 1.5, 2, 3) were used as Lewis acids and PPh_3 as a Lewis base.

Systems complexed by Lewis acids showed differing activity. The greatest degree of conversion was obtained with catalysts containing alkylaluminium dichloride compounds. Systems complexed only by a Lewis base were inactive, and those complexed by a Lewis base and Lewis acid showed a decreasing activity with increasing content of Lewis base in the catalyst.

The order of acidity of Lewis acids as regards their activating influence on the catalysts studied was determined. The temperature at which the reaction proceeded was found to have an essential influence on the degree of conversion of the substrate.

Introduction

In the previous paper [1] the catalytic activity in the oligomerization of olefins, of the system resulting from the reaction of $(C_3H_5)_2Ni$ with hydroxide groups of silica gel and complexation with a Lewis acid $MeAlCl_2$, was described. This system showed high activity, dependent on the catalyst composition (Ni/OH and Al/OH) and on the rate of olefin flow through the catalyst bed. These features did not, however, influence the selectivity of the hexene isomers obtained.

The oligomerization of olefins with the catalyst described, proceeds via elim-

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* For part I see ref. 1.

ination of the allyl group from the initial form of the catalyst, probably via formation of new forms containing catalytically active Ni—H and Ni—alkyl bonds.

In this paper we present the results obtained from the oligomerization of propylene with analogous systems but complexed by different Lewis acids and bases.

Results and discussion

The homogeneous nickel catalysts which are active in the oligomerization of olefins, described previously [2,3], show different activity depending on the Lewis acid complexed with them. Therefore we studied the influence of different Lewis acids on the model catalytic system described in the previous paper. This model system was one in which silica gel (Aerosil) was roasted at 650° C (0.25 mmol [OH]/g; 1.1 [OH]/100 Å^2) and used as the carrier. Stoichiometric amounts of $(C_3H_5)_2Ni$ (Ni/OH 1 : 1) were deposited on the carrier in order for reaction with the OH groups to occur and then stoichiometric amounts of Lewis acids (Al/Ni 1 : 1; 3 : 1) were added in order to complex the surface nickel compound. The Lewis acids used were: $TiCl_4$, $AlCl_3$, $AlBr_3$, R_nAlCl_{3-n} (R = Me, Et; $n = 1, 1.5, 2, 3$). The propylene flow was 360 cm^3 min^{-1} g^{-1}. The results obtained are presented in Table 1.

The most effective and highly active catalysts were those containing alkylaluminium dichloride compounds, less active were those containing sesquialuminium chlorides and still less active were those containing $AlBr_3$ and dialkylaluminium chloride compounds. Trialkylaluminium compounds reduce nickel atoms in the surface compound and thereby destroy their catalytic properties. Generally, it can be stated that the surface active nickel compounds are activated to a greater extent by methylaluminium compounds than by ethylaluminium compounds.

In the case of catalysts containing $TiCl_4$ and $AlCl_3$, the oligomerization of propylene ceased only after the formation of a high molecular oligomer. This confirms the very high activity of these catalysts [3].

The oil obtained, a high molecular oligomer, which forms a thick layer (removed with difficulty), in the pores and on the surface of the catalysts, hindered the further course of the reaction. As a consequence, even the most active catalysts were not very efficient. The order of the activating influence of the Lewis acids on the surface nickel compounds is as follows: $AlCl_3 \simeq TiCl_4 \gg MeAlCl_2 > EtAlCl_2 > Me_3Al_2Cl_3 \approx Et_3Al_2Cl_3 > AlBr_3 > Me_2AlCl > Et_2AlCl \gg Me_3Al = Et_3Al$. This order is also in agreement with the increasing complexing properties and decreasing reducting properties of this type of Lewis acid. The only disagreement in the presented order is the position of $AlBr_3$ [3]. According to the complexing and activating properties, $AlBr_3$ should be placed between $EtAlCl_2$ and $Me_3Al_2Cl_3$. The low activity of the studied catalysts containing $AlBr_3$ can be explained by the large dimension of the $AlBr_3$ molecule complexed at the active centre. This molecule masks the approach of propylene molecules to the catalytic centre and hinders withdrawal of the product molecules.

The activating centres of olefin complexation, described by Karmann [3] for homophase nickel catalysts, have a great influence on the activity of the studied catalysts. In homophase systems, organoaluminium compounds weakly bonded

TABLE 1

INFLUENCE OF LEWIS ACIDS [LA] AND BASES [LB] ON THE YIELD AND COMPOSITION OF THE PRODUCTS OF PROPYLENE OLIGOMERIZATION WITH $-\overset{|}{\underset{|}{\text{Si}}}-\text{O}-\text{Ni}-\text{C}_3\text{H}_5-\text{LA}$ AND $-\overset{|}{\underset{|}{\text{Si}}}-\text{O}-\text{Ni}-\text{C}_3\text{H}_5-\text{LB}-\text{LA}$ SYSTEMS. CATALYST: 1 g SiO_2 (650°C 0.25 mmol [OH]/g). Ni/OH 1 : 1, Al/Ni 1 : 1. REACTION TIME 2.5 h. PROPYLENE FLOW; 360 cm^3 min^{-1} g^{-1}, COOLING OF CATALYST BED, −25°C [a]

No.	Lewis acid	Product (g)	Product (g/mmol Ni · h)	C_6 (% Wt)	C_9 (% Wt)	C_{12} (% Wt)	2.3DM1B (% Wt)	c-4M2P (% Wt)	t-4M2P (% Wt)	2M1P (% Wt)	t,c-3H (% Wt)	t-2H + 2M2P (% Wt)	c-2H (% Wt)	2.3DM2B (% Wt)
1	Me_2AlCl	8.5	14.5	87.3	12.5	0.2	1.4	6.5	50.1	2.4	4.0	31.9	3.4	1.2
2	Et_2AlCl	3.3	6.2	83.6	15.4	1.0	2.0	6.8	53.2	3.0	4.1	27.3	3.4	1.0
3	$AlBr_3$	9.6	15.5	85.6	12.2	2.2	1.9	6.8	54.4	1.3	3.8	26.1	3.2	2.6
4	Me_2AlCl [b]	31.3	50.7	81.4	17.0	1.6	1.6	5.6	41.5	3.5	3.8	39.5	2.5	2.2
5	Et_2AlCl [b]	38.0	62.3	81.3	16.7	2.0	1.5	6.0	42.1	3.7	4.1	37.4	3.0	2.1
6	$Me_3Al_2Cl_3$	39.3	61.0	80.4	17.4	2.2	1.6	6.6	45.2	3.3	4.0	35.1	3.0	2.3
7	Et_3AlCl_3	29.8	59.6	89.0	11.0	–	2.4	7.1	50.0	2.7	3.7	29.8	3.0	1.4
8	$MeAlCl_2$	57.6	93.5	78.0	19.0	3.0	1.4	5.2	35.3	4.5	4.1	42.8	2.9	3.8
9	$MeAlCl_2$ [c]	7.1	38.8	82.3	15.2	2.5	1.5	6.1	39.6	4.3	4.0	38.4	2.8	3.7
10	$EtAlCl_2$	44.6	74.0	77.0	20.0	3.0	1.8	6.0	41.0	3.6	4.2	37.1	3.4	2.9
11	$MeAlCl_2$ [d]	43.8	70.0	74.5	28.8	2.7	1.2	4.4	30.9	5.0	4.1	46.0	3.3	5.0
12	$MeAlCl_2$ [e]	40.9	65.5	84.2	13.7	2.1	1.4	4.8	36.1	5.1	3.5	42.6	3.1	3.4
13	$MeAlCl_2$ [f]	36.6	58.5	82.3	15.2	2.5	1.7	7.5	34.5	8.0	4.3	38.8	3.6	1.7

[a] 2.3DM1B 2,3-dimethyl-1-butene; c-4M2P *cis*-4-methyl-2-pentene; t-4M2P *trans*-4-methyl-2-pentene; 2M1P 2-methyl-1-pentene; c,t-3H *cis,trans*-3-hexene; t-2H *trans*-2-hexene; 2M2P 2-methyl-2-pentene; c-2H *cis*-2-hexene; 2.3DM2B 2,3-dimethyl-2-butene. [b] Al/Ni 3 : 1. [c] reaction temp. 32°C (without cooling); reaction time 0.75 h. [d] PPh_3/Ni 1 : 50. [e] PPh_3/Ni 1 : 10. [f] PPh_3/Ni 1 : 3.

to nickel complexes represent these activating centres and in the systems studied by us, the activating centres are the organoaluminium compounds complexed with the carrier's surface or the surface nickel compounds. Therefore, an increase in the Al/Ni molar ratio should cause an increase in the activity of the catalysts. However in the case of $MeAlCl_2$ the effectiveness of the catalyst decreases due to the reasons given for $AlCl_3$ and $TiCl_4$, but with weakly activating Me_2AlCl and Et_2AlCl a considerable increase in the activity of the catalyst is observed (Table 1, Nos 4, 5).

The degree of conversion of propylene for a particular catalyst is dependent on temperature. The catalyst working at 10—12° C (by cooling the catalyst bed to —25° C) gives a 2.5 fold product yield compared with the same catalyst working at 32° C (without cooling the bed), Table 1.

It seems that a higher temperature should increase the yield of product, due to the acceleration of the reaction and a quicker evaporation of the product from the catalyst's grains. The results obtained, however, show that at, low temperatures, due to a greater adsorption of propylene in the pores and onto the surface of the catalyst and a greater solubility of propylene in the product, the propylene molecules reach the active centres of the catalyst more easily, which explains the greater degree of conversion of propylene at low temperatures.

It can be assumed that an increase of propylene pressure and a rise of temperature or the application of a rapid flow of an inert solvent through the catalyst bed would allow full use of the activity of the surface nickel compounds.

If the reductive-complexing properties of Lewis acids influence the activity of the catalysts studied but have no influence on the selectivity; this would indicate similar steric surroundings of Ni—H and Ni—alkyl bonds; the proper catalytic forms in the catalysts studied.

To system I, formed in the reaction of $(C_3H_5)_2Ni$ with OH groups of silica gel (Ni/OH molar ratio 1 : 1), PPh_3 was added (PPh_3/Ni molar ratio 2 : 1 or 1 : 1 or 0.5 : 1). As a result, mixtures of nickelphosphine complexes passing from the surface to the solution, were obtained. The systems formed were inactive. Addi-

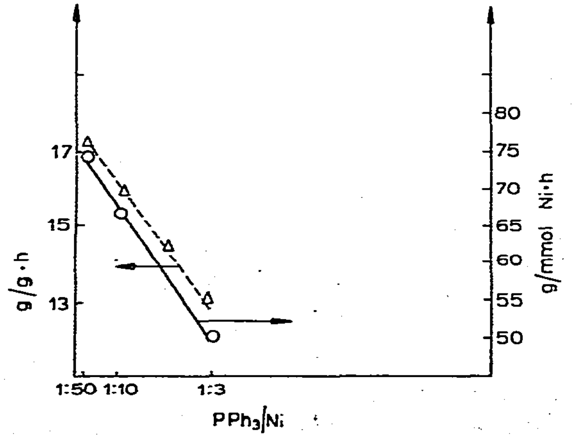

Fig. 1. The dependence of the degree of conversion of propylene to oligomers on the amount of triphenylphosphine added. Yields are given in grams of product per gram carrier per hour (left axis) and grams of product per mmol of supported nickel per hour (right axis).

tion of triphenylphosphine (P/Ni molar ratio 1 : 1 or 0.5 : 1) to the catalytically active systems (molar ratios Ni/OH 1 : 1 and $MeAlCl_2$/Ni 1 : 1) destroys their catalytic activity. By adding to system I first phosphine with molar ratios P/Ni 1 : 50; 1 : 10; 1 : 3 and then $MeAlCl_2$ (Al/Ni molar ratio 1 : 1) active catalysts were obtained, in which the activity decreased in proportion to the amount of phosphine added (Fig. 1).

On the basis of the results obtained the steric influence of triphenylphosphine on the selectivity of the studied catalysts can not be unequivocally determined.

Experimental

The preparation of silica gel, organoaluminium compounds, bis(allyl)nickel and the purification of solvents and propylene (Mazovian Petrochemical-Refinery Works, Płock, Poland) have been described previously [1].

Aluminium trichloride (Fluka AG) was purified by sublimation, titanium tetrachloride (Th. Schuchardt) was used without further purification. Aluminium tribromide (Reachim) and triphenylphosphine (Chemapol) were purified by recrystallization and drying under vacuum.

The determination of the OH groups in silica gel, the preparation of surface nickel compounds and the oligomerization of propylene have also been described previously [1].

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