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INVESTIGATION ON CATALYTIC SYSTEMS CONTAINING NICKEL SUPPORTED ON SILICA AND BONDED WITH ORGANIC LIGANDS AND COMPLEXED BY LEWIS ACIDS

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Summary

The catalytic properties of the $\geqslant SiONiC_3H_5 \cdot nMeAlCl_2$ (n = 0-3) system, resulting from the reaction of $(C_3H_5)_2Ni$ with hydroxide groups of silica gel and complexation with a Lewis acid, $MeAlCl_2$, have been studied in the oligomerization of propylene. It has been ascertained that when $n > 3$ the excess of $MeAlCl_2$ is carried out from the catalyst bed by the products. The yield of the product is influenced by the rate of propylene flow and the composition of the catalyst. The yield of products increases with the rise in the propylene flow rate. The highest yield was obtained for n = 1 and the flow of propylene = 360 ml/min g. The elimination by the olefin of the allyl group from the complex in the initial stages of oligomerization was ascertained. This testifies to the formation of new forms of the surface nickel complex that should contain catalytically active Ni—H or Ni—R bonds. The EPR studies determined the valence of nickel in this system (n = 1) to be +2 and thus made it possible to propose its structure.

Introduction

Nickel complexes distinguished by a high catalytic activity are known and have been widely described [1-3]. Haloallylnickel compounds containing alkyl- (or aryl-) phosphines as ligands and complexed with different Lewis acids, for example, are characterized by high catalytic activity in the oligomerization of propylene [1,4].

Most of the studies have been concerned with the preparation and action of this type of catalytic system in solution. Recently, articles have appeared describing systems consisting of a carrier with a very extended surface on which allylnickel complexes are deposited. In this manner a system is obtained in which nickel is bonded from one side through oxygen with the carrier (silica or alumina gel) and from the other side with the π-allyl ligand. Such systems are catalytically active in the polymerization of butadiene [5,6].

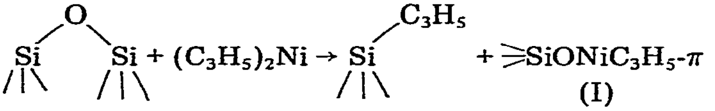
Results

Silica gel (Aerosil) roasted at 600, 650 and 700°C was used. The gels had specific surfaces and concentration of OH groups shown in Table 1·calculated per gram and per 100 Å^2).

Required amounts of silica gel and a solution of bis(allyl)nickel in cyclopentane were mixed at 20°C. Propylene evolved. The reaction of $(C_3H_5)_2Ni$ with the silica gel surface proceeds in the following way:

$$\geqslant SiOH + (C_3H_5)_2Ni \rightarrow \underset{(I)}{\geqslant SiONiC_3H_5\text{-}\pi} + C_3H_6 \qquad (1)$$

A reaction with stressed oxygen bridges in highly roasted gels (above 600°C) is also possible.



$$Si{-}O{-}Si + (C_3H_5)_2Ni \rightarrow Si{-}C_3H_5 + \underset{(I)}{\geqslant SiONiC_3H_5\text{-}\pi} \qquad (2)$$

Comparing the quantity of propylene evolved with the amount of nickel that bonded with the carrier, we came to the conclusion that the reaction in solution proceeds mainly according to eqn. 1.

The quantity of bis(allyl)nickel added in order to react with the gel was based on the amount of OH groups on the silica gel surface, which may be determined by the action of Et_3Al in a decaline solution on silica gel [7].

The amount of ethane evolved during the reaction of Et_3Al with OH groups is about equal to the amount of propylene evolved in the reaction of $(C_3H_5)_2Ni$ with silica gel OH groups, although Et_3Al reacts more quickly.

System I shows stereospecific activity in the polymerization reaction of butadiene; 97% of 1,4-*cis*-polybutadiene was obtained [6]. But this system is not active in the oligomerization of propylene under standard pressure and at temperatures from —70 to +70°C.

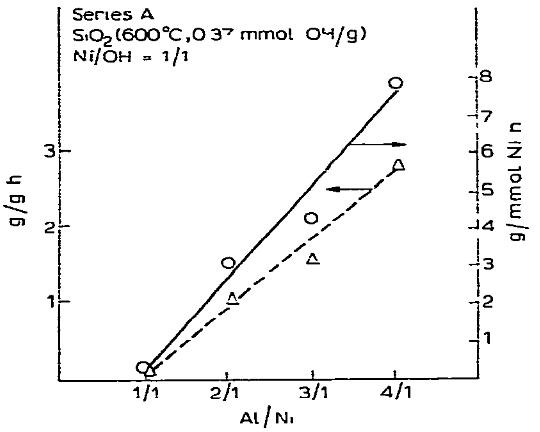
System II was obtained by treating system I with the $MeAlCl_2$ solution in CH_2Cl_2. Different molar ratios of Al/Ni were applied (Al/Ni = 1-4,6,8). We ascertained that in systems where Ni/OH = 1/1 and Al/Ni $\leqslant$ 3, the organometallic compounds are permanently bonded with the surface.

Systems II were highly active in the oligomerization of ethylene, propylene, n-butenes under standard pressure and at temperatures from —70 to +70°C. In

TABLE 1

SPECIFIC SURFACES, MMOL OF OH GROUPS PER GRAM AND QUANTITY OF OH GROUPS PER 100 Å^2 OF SILICA GELS ROASTED AT 600, 650 AND 700°C

Roasting temperature (°C)	Specific surface (m^2/g)	Concentration of OH groups	
		mmol/g	number/100 Å^2
600	150	0.37	1.5
650	140	0.25	1.1
700	138	0.20	0.9



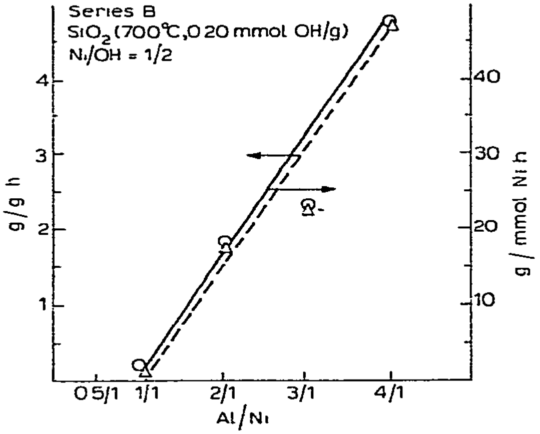
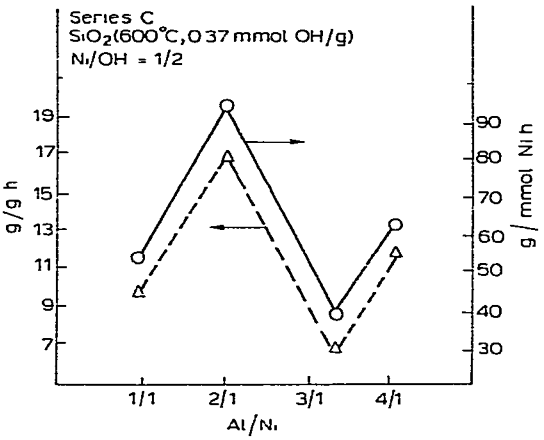


Fig. 1. Yields of propylene oligomers in relation to Al/Ni ratio. Series A. Flow rate of propylene = 120 ml/min (yield is given in grams of product per gram carrier per hour (left axis), and grams of product per mmol of supported nickel per hour (right axis)).

Fig. 2. Yields of propylene oligomers in relation to Al/Ni ratio Series B. Flow rate of propylene = 360 ml/min.



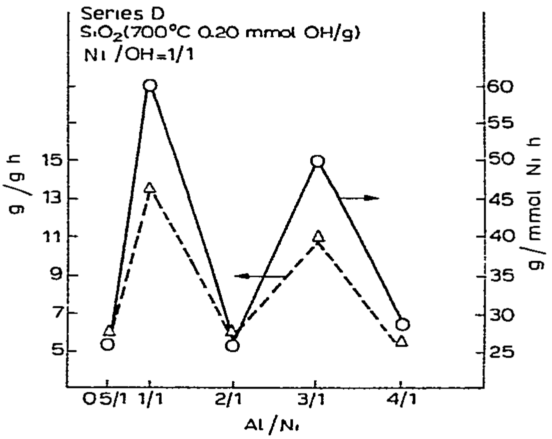


Fig. 3. Yields of propylene oligomers in relation to Al/Ni ratio. Series C. Flow rate of propylene = 360 ml/min.

Fig. 4. Yields of propylene oligomers in relation to Al/Ni ratio. Series D. Flow rate of propylene = 360 ml/min.

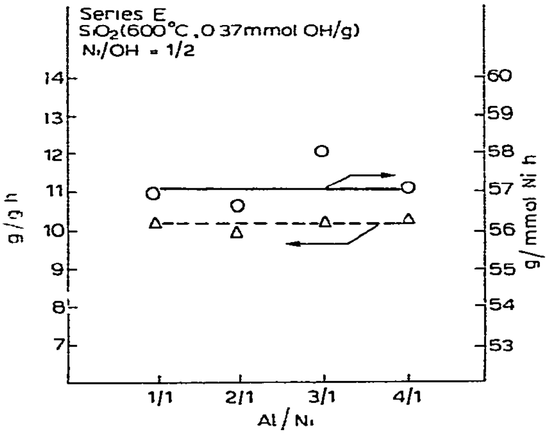


Fig. 5. Yields of propylene oligomers in relation to Al/Ni ratio. Series E. Flow rate of propylene = 240 ml/min.

our study we assumed the oligomerization of propylene as the model reaction.

The influence of the propylene flow rate (value proportional to the catalyst load) and catalyst composition (Ni/OH and Al/Ni) on the catalyst activity are shown in Figs. 1-5.

In the case of catalysts SiO_2 (600°C; 0.37 mmol OH/g; Ni/OH = 1/1, propylene flow = 120 ml/min) and SiO_2 (700°C; 0.2 mmol OH/g; Ni/OH = 1/2; propylene flow = 360 ml/min) the yield of product depends on and is proportional to the increase of Al/Ni ratio. The yields of products are small. The maximum yields are 2.9 and 4.65 g/g h respectively.

Catalysts SiO_2 (600°C; 0.37 mmol OH/g; Ni/OH = 1/2) and SiO_2 (700°C; 0.2 mmol OH/g; Ni/OH = 1/1) show different activities depending on the Al/Ni ratio. The catalysts of maximum activity are those in which the ratio is Al/Ni = 2/1 and Al/Ni = 1/1, which give yields of 17.2 and 13.8 g/g h. The minimum activity occurs with catalysts with Al/Ni ratios of 3/1 and 2/1 and the yields are 7.1 and 5.9 g/g h. Comparing the course of activity of these two series of catalysts it can be seen that catalysts Ni/OH = 1/2, Al/Ni = 2/1; 3/1; 4/1 correspond to catalysts Ni/OH = 1/1, Al/Ni = 1/1; 2/1; 3/1 respectively.

In the case of 240 ml/min flow catalysts SiO_2 (600°C; 0.37 mmol OH/g; Ni/OH = 1/2) show identical activity irrespective of the Al/Ni composition. The yield of product was ca. 10 g/g h.

Table 2 shows the composition of products ($C_6^=$; $C_9^=$; $C_{12}^=$) obtained in the oligomerization of propylene with the catalysts studied, and also the composition of hexene isomers obtained with catalysts with the composition SiO_2 (700°C; Ni/OH = 1/1; Al/Ni = 4/1; 3/1; 2/1; 1/1; 0.5/1) is shown.

The reaction products obtained in the presence of most of the catalysts contained mainly hexenes, nonenes and dodecenes. In the case of low active catalysts, no dodecenes were found in the reaction products. More long-chained

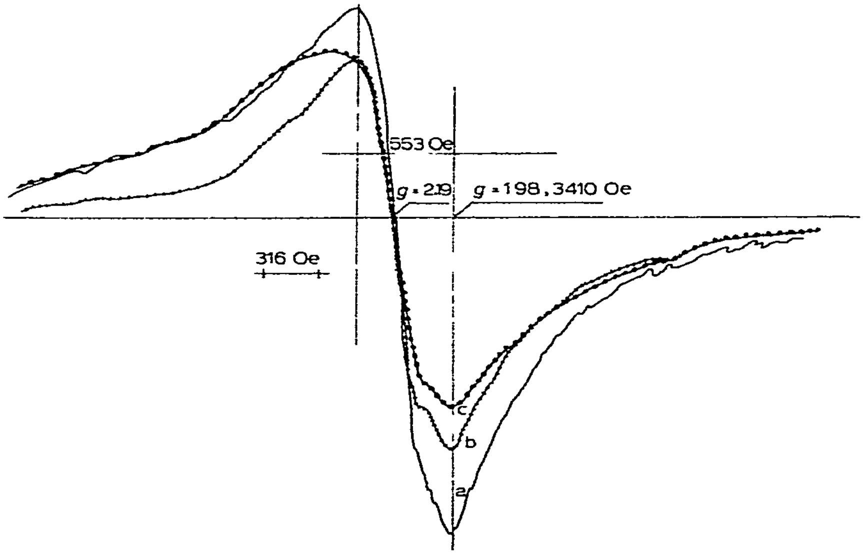


Fig. 6. ESR spectra of $\geqslant SiONiC_3H_5 \cdot nMeAlCl_2$ systems. (a) $n = 1$, (b) $n = 3$, (c) $n = 1$; sample was 4 min in propylene atmosphere.

TABLE 2

YIELD AND COMPOSITION OF PROPYLENE OLIGOMERS OBTAINED ON $\geqslant SiONiC_3H_5 \cdot nMeAlCl_2$ SYSTEMS[a,b]

Series Ni/OH	No.	Carrier SiO_2 (g)	Al/Ni	Temp.[c] (°C)	Flow rate of C_3H_6 (ml/min)	Product (g)	$C_6^=$ (% Wt)	$C_9^=$ (% Wt)	$C_{12}^=$ (% Wt)	23DM1B (% Wt)	c4M2P (% Wt)	t4M2P (% Wt)	1H+2M1P (% Wt)	ct3H (% Wt)	t2H+2M2P (% Wt)	c2H (% Wt)	23DM2B (% Wt)
A 1/1	1	1.52	1/1	−10	120	0.38	67.8	17.6	14.6								
	2	1.86	2/1	18, −40	120	4.8	54.3	22.5	22.2								
	3	1.89	3/1	20, −40	120	7.7	25.1	43.1	32.8								
	4	1.52	4/1	26, −40	120	13.3	44.3	26.4	29.3								
B 1/2	5	0.53	0.1/1	−14, −20	360												
	6	1.03	0.5/1	−14, −20	360												
	7	1.17	0.75/1	−14, −20	360	trace											
	8	1.23	1/1	−14, −25	360	0.35	100.0										
	9	1.20	2/1	11, −6	360	5.28	84.8	13.7	1.5								
	10	1.15	3/1	15, −9	360	6.63	88.2	11.8									
	11	1.21	4/1	22, 0	360	13.90	93.5	6.5									
C 1/2	12	0.99	1/1	26, 6	360	24.8	89.0	9.5	1.5								
	13	1.00	2/1	36, 20	360	43.1	89.0	9.5	1.5								
	14	0.95	3.4/1	35, 6	360	16.7	68.3	26.6	5.1								
	15	1.02	4/1	33, 11	360	30.4	76.0	22.5	1.5								
D 1/1	16	0.90	0.5/1	10, −10	360	12.9	86.7	13.3		2.0	6.5	50.0	2.9	4.1	29.3	3.3	2.3
	17	0.92	1/1	21, 12	360	31.5	80.2	16.2	3.6	2.3	6.5	44.6	3.1	1.3	33.1	3.1	2.3
	18	0.92	2/1	25, 2	360	13.5	82.2	15.4	2.6	1.6	6.6	48.2	2.2	4.4	31.0	3.4	1.6
	19	0.93	3/1	32, 4	360	26.3	74.6	21.8	3.6	1.9	6.0	43.0	3.2	3.9	36.0	3.2	1.9
	20	0.95	4/1	34, 3	360	14.1	81.6	15.8	2.6	1.8	7.2	45.2	2.7	3.6	34.0	4.0	1.5
E 1/1	21	1.67	1/1	17, 4	240	85.4	70.0	24.3	5.7								
	22	1.56	2/1	20, 8	240	77.8	81.0	16.9	2.1								
	23	1.52	3/1	26, 14	240	78.3	78.3	17.7	4.0								
	24	1.68	4/1	30, 14	240	86.5	70.0	24.3	5.7								

[a] Series A,C,E: SiO_2 (600°C, 0.37 mmol OH/g). Series B,D: SiO_2 (700°C, 0.20 mmol OH/g); Series A,B,C,D: reaction time 2.5 h; Series E: reaction time 5 h. [b] 23DM1B = 2,3-dimethylbutene-1; c4M2P = *cis* 4-methyl-2-pentene; t4M2P = *trans* 4-methyl-2-pentene; 1H = 1-hexene; 2M1P = 2-methyl-1-pentene; ct3H = *cis* and *trans*-3-hexene; t2H = *trans* 2-hexene; 2M2P = 2-methyl-2-pentene; c2H = *cis*-2-hexene; 23DM2B = 2,3-dimethyl-2-butene. [c] Temperature of catalystbed at the beginning and end of reactions.

olefins were obtained with higher concentrations of the nickel and aluminium surface compounds and/or with lower propylene flows. The composition of hexene isomers does not show a clear dependence on the Al/Ni ratio in the catalyst.

To explain the mechanism of dimerization and oligomerization of ethylene on the SiO_2 system (650°C; 0.25 mmol OH/g; Ni/OH = 1/1; Al/Ni = 1/1), the composition of the initial products was investigated. 2-Methyl-1-butene-1, -1-pentene and -2-pentene were present. The amount of these products decreased in time and vanished after about an hour. This confirms the gradual removal of the allyl group from the nickel atom and the formation of a new catalytic form. Fig. 6 shows the EPR spectra of active catalysts with the composition SiO_2 (650°C; 0.25 mmol OH/g; Ni/OH = 1/1; Al/Ni = 3/1; 1/1) and of a catalyst that was 4 min in a propylene atmosphere. In all cases there were very strong and wide signals (*g* values in the region 2.19 ± 0.1). This value indicates the nickel oxidation state in surface compounds is +2 [8]. The catalyst that was in propylene exhibits a considerably wider signal than the other catalysts; this confirms the more peturbed structure of the surface nickel complex.

Discussion

Taking into consideration the physico-chemical properties of the surface nickel compound formed in the reaction of $(C_3H_5)_2Ni$ and SiO_2 described above,

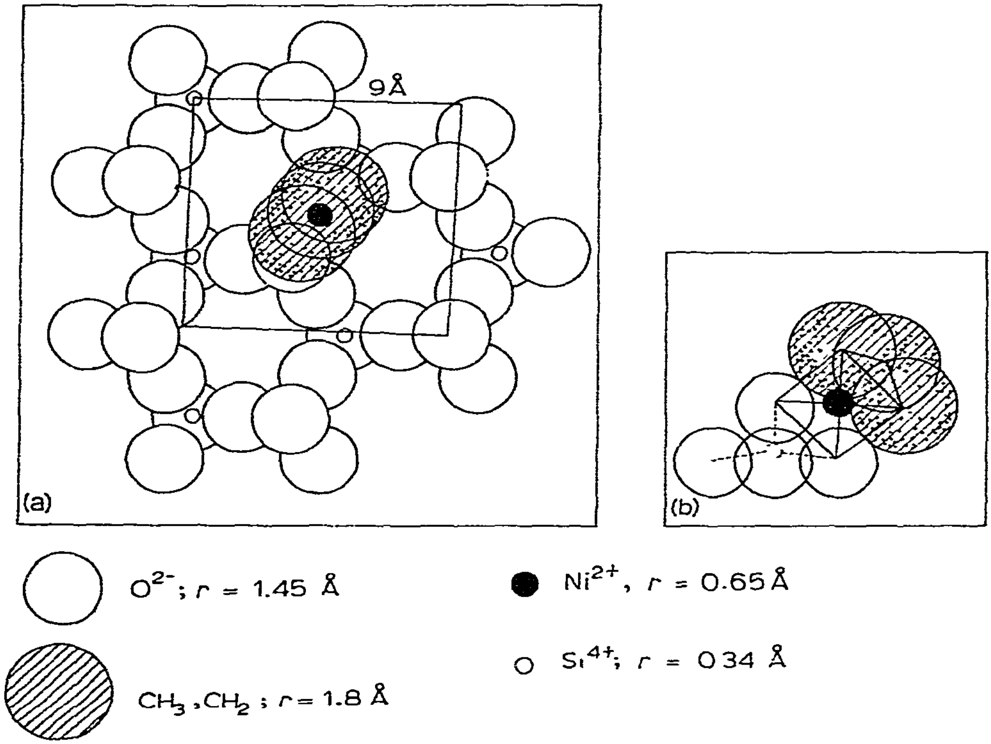


Fig. 7. $\equiv SiONiC_3H_5$ system I. (a) front view, (b) side view.

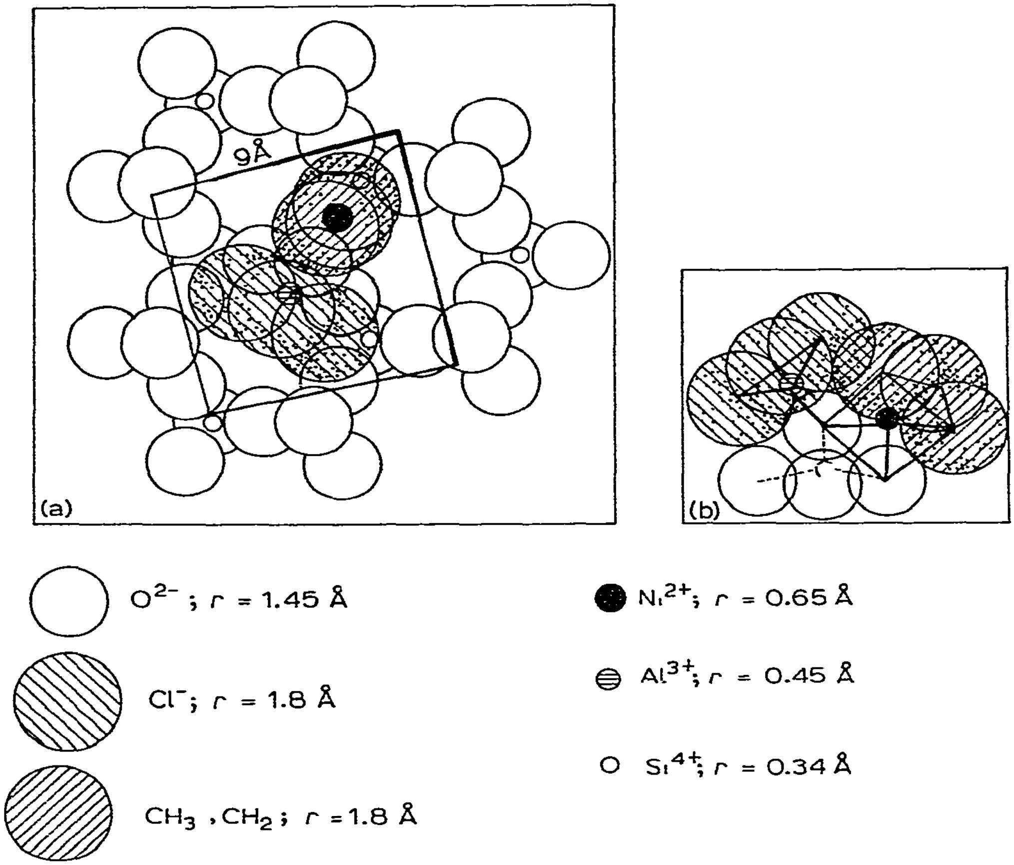


Fig. 8 $\geqslant SiONiC_3H_5MeAlCl_2$ system II. (a) front view, (b) side view.

the values of van der Waals' radii [9], and the silica gel structure [10], the structure shown in Fig. 7 is proposed for this compound. In this compound nickel exhibits a +2 oxidation state and forms a compound with a square-planar structure. The nickel atom is bonded by two σ-bonds with oxygen and an allyl group and by two π-bonds with the SiO_2 gel lattice oxygen and an allyl group.

The structure presented here is a more exact description of the surface compound proposed by Yermakow [11]. This structure explains the catalytic activity of this compound in the polymerization of butadiene. This compound exhibits analogous catalytic properties to the X—Ni—allyl system. In the surface system the role of halogen is represented by oxygen from the former hydroxyl group, and the role of a Lewis acid may be represented by the surface acid centre. The addition to System I of a strong Lewis acid, like $MeAlCl_2$, causes the formation of a new and catalytically active system in the oligomerization reaction of olefins. Taking into account its physico-chemical properties and its similarity to Wilke's system (comparable catalytic activity, similar reaction mechanism, similar or analogous composition), we propose the structure in Fig. 8.

In this compound, oxygen is bonded with the Lewis acid, and through a σ-bond with nickel. Due to steric effects (interference of the allyl group with chlorine atoms of $MeAlCl_2$), the bonding of a large $MeAlCl_2$ molecule with this oxygen atom causes the transition of the surface compound to a distorted tetragonal system (Fig. 8). Due to this the nickel compound is paramagnetic. Taking into account the variety of structures of the silica gel and also the variety of actions in this system, the wide band in the EPR spectrum indicating a high asymmetry of this system becomes intelligible. Calculations indicate that round the surface nickel compound shown in Fig. 8 almost two more $MeAlCl_2$ molecules can be included. It can be presumed that these molecules are strongly bonded by the surface due to complexation with lattice oxygens of the gel and with nickel through Ni—Cl interactions. The EPR spectrum of the system Ni/OH = 1/1, Al/Ni = 3/1 does not show any changes of symmetry in relation to the system Ni/OH = 1/1, Al/Ni = 1/1, but does not exclude the occurrence of the interactions mentioned above.

The EPR spectrum of the nickel compound II that was in the propylene atmosphere indicates changes of symmetry around nickel (widening of the band). This confirms the differences in ligands present in the surface compound.

The proposed structure of the catalytically active compound II and studies of the composition of initial products of olefin oligomerization permit us to suggest the following mechanism. Complexation of $MeAlCl_2$ on the oxygen atom, to which nickel is bonded by a σ-bond, causes the withdrawal of the electron cloud from the oxygen atom and such a displacement of the nickel electron that the bond with the allyl group is weakened. The allyl group becomes "dynamic" and liberates one of the nickel's coordination positions. At this place the olefin can be complexed and begin the dimerization process.

During the olefin oligomerization the surface system II forms systems in which nickel is bonded with hydrogen or an alkyl group. These bonds (Ni—H and Ni—alkyl) are sites where the catalytic oligomerization or isomerization proceeds. This property of the surface nickel compound II is in line with the generally accepted mechanism of action of nickel compounds with catalytic properties in homogeneous and heterogeneous catalysis [12,13].

Analysis of the initial reaction products shows that:

(a) the allyl group is displaced from the initial catalytic site,

(b) not all the initial active sites lose the allyl group immediately,

(c) the allyl form of catalyst is a stable one and passes into new (authentic) catalytic forms under the influence of the substrate,

(d) at a particular moment only some of the potentially active sites are responsible for the catalytic activity.

Propylene molecules may be hindered from reaching the active sites by the formation of a thick product layer on the grain (small propylene flow, catalyst series A, Fig. 1) or when there is a small concentration of active sites on the carrier surface (catalyst series B, Fig. 2). The catalysts working in these conditions are characterized by a low activity (proportional to the Al/Ni ratio). This dependence can be explained by the activating and complexing properties of $MeAlCl_2$.

The elimination of hindrances in propylene reaching the catalyst surface (high propylene flow — 360 ml/g min) and the concentration of active sites ca. 0.2 mmol/g increases the catalytic activity (catalysts series C and D, Fig. 3 and 4). In these catalyst series the most active were those in which the surface nickel compound I is complexed by one $MeAlCl_2$ molecule. This system should have the most accessible Ni—H and Ni—R bonds (active catalyst sites) for the reactants in comparison with systems with higher Al/Ni ratios. This accessibility is the reason for high activity. An activating influence of $MeAlCl_2$ is observed in the case of these catalysts.

In the action of series E catalysts (Fig. 5), where medium flows of propylene (ca. 130 ml/g min) are used and where propylene simultaneously has easier and more difficult conditions for reaching the active catalytic sites, the effects are summed. An identical yield of products is obtained irrespective of the Al/Ni ratio.

Equal selectivity of the catalyst, irrespective of the Al/Ni ratio, can be explained by an equal steric structure round the Ni—H or Ni—Al active groups of the surface compound; $MeAlCl_2$ molecules are far enough to influence the stereospecificity of propylene addition to the nickel complex. The predominance of 2-methylpentenes testifies to the predominance of propylene addition to the nickel atom (to Ni—H or Ni—C) in the isopropyl form.

Experimental

Materials

Silica gel was obtained by treating Aerosil (Deguss) with redistilled water and dried consecutively for 12 h at 40, 60 and 120°C and then for 24 h at 600°C. Before the organometallic compounds were deposited, the gel grains were roasted at 600, 650 and 700°C for 24 h in an air flow and then for 1 h in a nitrogen flow.

Triethylaluminium (Fluka) was used without further purification. Methylaluminium dichloride was prepared by a conventional method and purified by recrystallization before use. Bis(allyl)nickel was prepared by the method described by Wilke [14].

The solvents cyclopentane, decalin and methylene chloride were dried and deoxidized by conventional methods and stored over type 4A molecular sieves under nitrogen.

Propylene (Mazovian Petrochemical-Refinery Works, Płock, Poland), and ethylene (Heavy Organic Synthesis Works, Blachownia Śląska, Poland) were dried and deoxidized in washers containing Et_3Al on activated carbon (30%).

Method

The quantity of OH groups of silica gel and the relative reactivity towards them of triethylaluminium and bis(allyl)nickel was determined by Shima's method [7].

The surface complexes I and II were obtained by adding the required amount of $(C_3H_5)_2Ni$ in cyclopentane to silica gel. After the bis(allyl)nickel had reacted, the solvent was distilled from the grains under vacuum and the required amount of $MeAlCl_2$ in methylene chloride was added. After 12 h (the organoaluminium compound undergoes complexation, or if an excess is used, deposition on the silica gel surface) the solvent was distilled from the grains under vacuum.

The oligomerization and polymerization reactions were carried out in a typical tube flow reactor equipped with a cooling jacket. The catalyst carrier was cooled to —25°C. The reaction was started when the carrier temperature dropped to —15°C. From 1 to 1.8 g of catalyst was used and the propylene or butadiene flow was from 120 to 360 ml/g min.

Analysis and identification

Qualitative and quantitative analysis of the gaseous and liquid products was performed using Chrom-2 and Guide-4 chromatographs.

Specific surface measurements were carried out by the BET method. EPR measurements were recorded at room temperature using an apparatus constructed in the Institute of Organic Chemistry and Technology, Technical University (Politechnika), Warsaw, Poland.

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