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Catalytic Dimerization of Propylene

II. Nickel Tetracarbonyl as Zerovalent Nickel Catalyst

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By mixing nickel tetracarbonyl, various phosphines and aluminum chloride in a suitable solvent, catalysts which are active towards the dimerization of propylene are formed. The total activity, dimer selectivity and isomerization activity are influenced by the nickel:phosphine: aluminum chloride ratio. Maximum activity is obtained with a phosphine:aluminum ratio of 2:1.

INTRODUCTION

The use of tetrakis(triphenyl phosphite) nickel as a source of zerovalent nickel for the dimerization of propylene (*1*) is subject to certain limitations. One of these is the fact that for each nickel atom four triphenyl phosphite ligands are present already. This precludes the possibility of either changing the nickel:base ratio or the use of other bases to study their effect on the dimerization reaction. This difficulty can be overcome through the use of nickel tetracarbonyl as nickel component in the catalytic system, because nickel tetracarbonyl can be made to undergo ligand exchange *in situ* with a range of Lewis bases (*2*).

METHODS

The apparatus used was the same as described previously (*1*), with the addition of an air lock for the introduction of aluminum chloride. This consists of a 4 × 2 cm diameter stoppered tube ending in a vacuum cock with a 10 mm straight bore. The tube is connected, through a three-way vacuum tap, to a vacuum pump and a source of purified argon.

It was found that the order of mixing of the catalyst components did not affect the activity or the selectivity of the dimerization system, when it was prepared according to methods A and B.

Method A. The phosphine was dissolved in 75 ml solvent in the reactor (in the case of chlorobenzene, Mereck's CP reagent, used without further purification). Nickel carbonyl ($13\ \mu l = 1.0 \times 10^{-4}$ mole in every case) was injected into the reactor through a gc septum. The solution was degassed by evacuation and purged several times with argon. The argon was purified by passing it over reduced copper at 320°C and then through a liquid oxygen trap. The reactor was again evacuated and filled with propylene (obtained from Sasol and used without further purification). As soon as the solution was saturated with propylene, the experiment was started by admitting the aluminum chloride under argon through the air lock.

Method B. The phosphine and aluminum chloride were mixed in the solvent in the

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TABLE 1

The Influence of the Aluminum Chloride Particle Size on the Dimerization of Propylene[a]

AlCl^3 (μm)	Total propylene conversion (moles/mole Ni)	Polymers (moles/mole Ni)	Dimers (moles/mole Ni)
Lumps, >1700	79×10^2	31×10^2	48×10^2
Powder, <840	108×10^2	78×10^2	30×10^2

[a] Ni:P:Al = 1:8:22.

reactor. The reactor was purged with argon and the solution was saturated with propylene as before. The experiment was then started by injecting nickel carbonyl into the reactor. As this was the more convenient of the two methods, it was adopted for most of the work reported here.

In both cases the catalyst solution was stirred magnetically at room temperature (22–24°C) until the dimerization reaction commenced, as was indicated by a sudden rise in temperature and gas uptake. The temperature was immediately lowered by circulating a cooling liquid through a coil in the reactor. After a suitable time the reaction was stopped by the addition of 1 ml distilled water to decompose the catalytic system. The products were analyzed by glc, using a 100 m × 0.5 mm capillary column at 0°C. Polypropylene glycol was used as a stationary phase. The various hexene isomers were identified through a gc–ms technique and comparison with standards. *n*-Heptane was used as an internal standard in quantitative calculations.

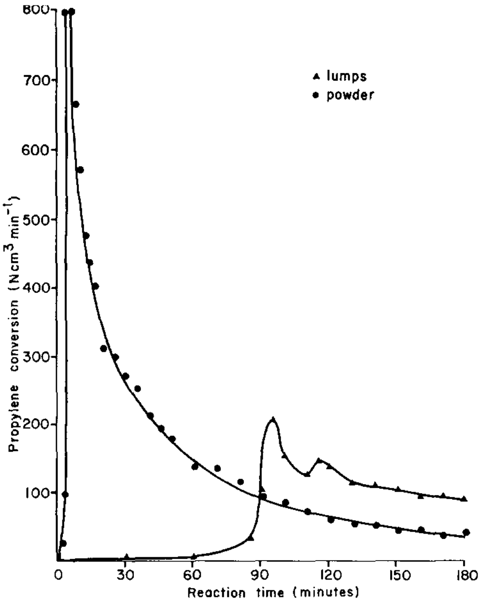


FIG. 1. The influence of aluminum chloride grain size on reaction rate (Ni:P:Al = 1:8:22).

RESULTS

The gradual solution of aluminum chloride in the solvent, containing the phosphine, nickel carbonyl and the monomer, is accompanied by a series of color changes, the colors ranging from bright yellow to red, indicating the formation of the active dimerization complex. At this stage the dimerization reaction starts, even though only part of the aluminum chloride has dissolved. As the catalytic system loses activity, the color turns to orange and finally to yellow. At high aluminum chloride to phosphine ratios the formation of the active complex is associated with a muddy brown color, followed by the formation of a black sludge on deactivation. This sludge turns green on exposure to air and is soluble in an excess of ethanol.

The particle size of the aluminum chloride appears to have a considerable influence on the dimerization activity as shown in Table 1. The effect is further stressed by Fig. 1, which illustrates the dependency of the rate of propylene conversion on the aluminum chloride particle size. This difference is attributable to the fact that the powdered aluminum chloride dissolves fast, causing excessive polymerization of the propylene at the cost of the dimerization reaction. This indicates that the formation of the active dimerization complex is relatively slow compared to the undesirable polymerization reaction, which,

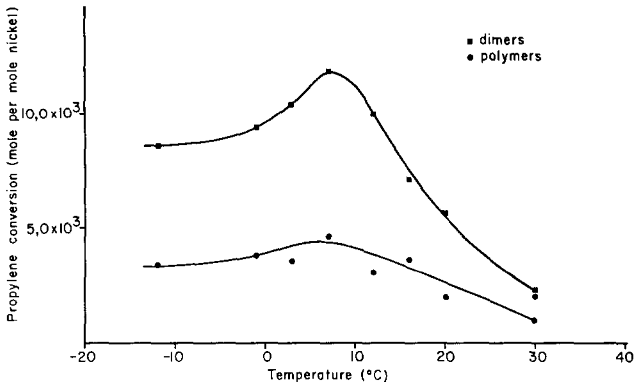


FIG. 2. The influence of temperature on propylene conversion (Ni:P:Al = 1:8:16).

in addition, is exothermic (*3*), thus deactivating the "thermally sensitive" (*1*) dimerization complex. Accordingly the relatively slow dissolution of the aluminum chloride lumps should render a more complete formation of the dimerization complex, thus favoring dimerization over polymerization, as is shown by the values in Table 1. Consequently, all further experiments were carried out using 840–1190 μm (16–20 mesh) aluminum chloride granules, obtained by screening under nitrogen.

The influence of temperatures on the dimerization reaction is shown in Fig. 2. In each case the catalytic system was developed at room temperature. Maximum total activity (i.e., dimerization as well as polymerization) was attained at about 7°C. The activity decline with increasing temperature is caused partly by the lower solubility of propylene at higher temperatures, but mainly by thermal deactivation of the catalytic system. At temperatures above 7°C, the initial activity increases with increasing temperature, but the rate of decline also increases sharply, leading to a lower overall activity.

With decreasing temperatures, the total activity also decreases in spite of the increasing solubility of propylene. This effect can be ascribed to a kinetic effect as well as the decreased solubility of the aluminum chloride. The temperature has little influence on the dimer to polymer ratio or on the degree of branching of the hexene products below 30°C. Above 30°C, however, the *n*-hexenes increase at the expense of the methylpentenes, while the dimethylbutenes are only slightly effected by temperature as shown in Table 2.

The influence of the nickel:aluminum ratio at nickel:phosphine ratios of 1:8 and 1:4 is shown in Figs. 3 and 4, respectively. In both cases the conversion to dimers reaches a sharp maximum at a aluminum:phosphine ratio of approximately 2:1, while the conversion to polymers rises constantly with increasing aluminum chloride concentration. At relatively high aluminum chloride concentration the grains become covered by the black sludge mentioned above. This prevents the aluminum

TABLE 2

The Influence of the Temperature on the Degree of Branching of the Dimers[a]

Temp (°C)	% *n*-Hexenes	% Methyl-pentenes	% Dimethyl-butenes
7	17.2	74.8	8.0
12	18.2	73.7	8.2
16	18.2	73.5	8.3
20	20.1	72.1	7.5
30	20.6	71.3	8.1
40	28.6	63.6	7.4

[a] Ni:P:Al = 1:8:16.

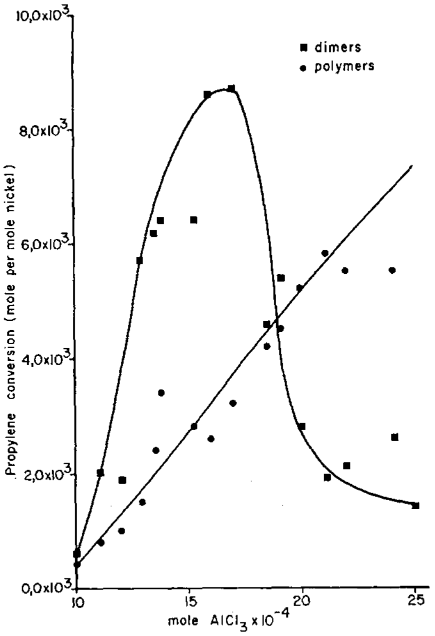


Fig. 3. The influence of aluminum chloride concentration at Ni:P = 1:8 on propylene conversion.

chloride from dissolving, accounting for the increasingly erratic results obtained at high aluminum chloride concentrations, illustrated in Fig. 3.

The rate of propylene conversion is also highly dependent on the aluminum chloride concentration, as is evident from Fig. 5. Both the maximum reaction rate and the induction period are clearly dependent on the aluminum chloride concentration, as was found before (*1*). The induction period is inversely proportional to the aluminum chloride concentration, which clearly indicates that the slow dissolution of aluminum chloride is a controlling factor in the start of the propylene conversion as well as in the rate of conversion. The fast initial conversion at high aluminum chloride concentration substantiates the conclusion come to by a comparison of the influence of aluminum chloride particle size on the propylene conversion. This is further verified by comparison of the dimer to polymer ratio at 10, 16 and 25 moles aluminum chloride/mole nickel shown in Fig. 3.

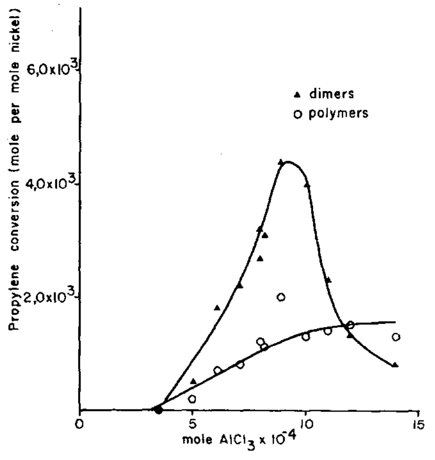


Fig. 4. The influence of aluminum chloride concentration at Ni:P = 1:4 on propylene conversion.

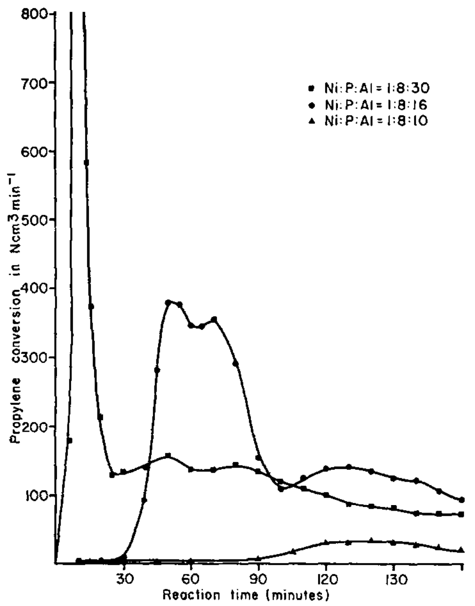


Fig. 5. The influence of aluminum chloride concentration at Ni:P = 1:8 on reaction rate.

At high reaction rates the catalytic system is deactivated faster than it can be reactivated by the slowly dissolving aluminum chloride, leading to a drop in reaction rate. As more aluminum chloride dissolves, the reaction rate increases again slightly. This phenomenon is always found at intermediate aluminum chloride levels

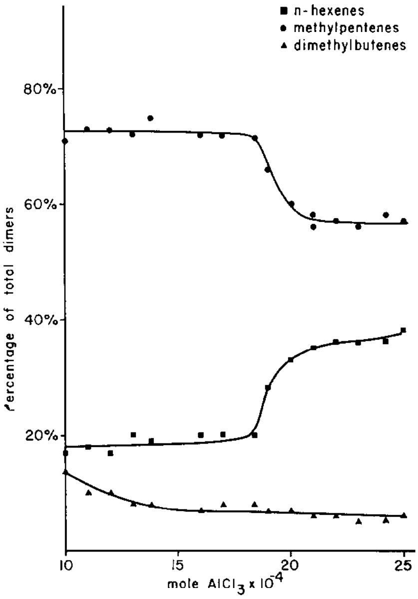


FIG. 6. The influence of aluminum chloride concentration at Ni:P = 1:8 on dimer selectivity.

and can be seen clearly in Fig. 5. Once the catalytic system has become completely deactivated, however, it cannot be revived by the addition of fresh aluminum chloride.

The nickel:aluminum ratio has a considerable influence on the degree of branching of the dimers. The product selectivity varies from 17% *n*-hexenes, 71% methylpentenes and 12% dimethylbutenes at low aluminum chloride concentrations to 38% *n*-hexenes, 56% methylpentenes and 5% dimethylbutenes at high aluminum chloride concentrations, as shown in Fig. 6. The sudden shift in *n*-hexene/methylpentene ratio above 18 × 10^{-4} mole $AlCl_3$ is caused by the sharp drop in methylpentene formation as shown in Fig. 7.

The yields of the different hexene isomers at nickel:phosphine ratios of 1:8 and 1:4 are shown in Figs. 7 and 8, respectively. According to Onsager *et al.* (*4*) and Wilke *et al.* (*5*) 2-methylpentene-1 ($2MC_5$-1) and 4-methylpentene-2 ($4MC_5$-2) are two of the possible primary products in the homogeneous dimerization of propylene. Both products are prone to ready isomerization to 2-methylpentene-2 by acid catalysts under mild conditions (*6*).

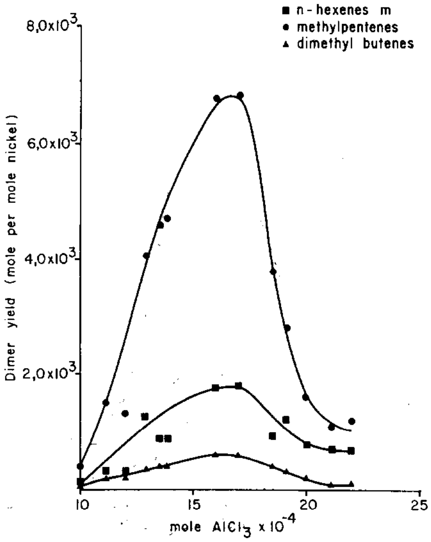
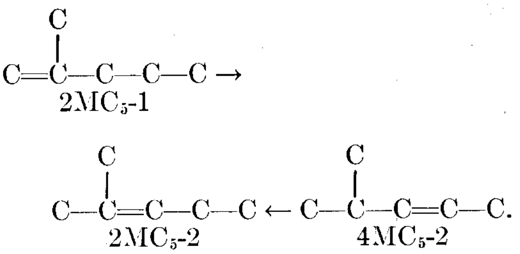


FIG. 7. The influence of aluminum chloride concentration at Ni:P = 1:8 on dimer yield.



$$\underset{\text{2MC}_5\text{-1}}{\mathrm{C{=}\overset{C}{\overset{|}{C}}{-}C{-}C{-}C}} \rightarrow$$

$$\underset{\text{2MC}_5\text{-2}}{\mathrm{C{-}\overset{C}{\overset{|}{C}}{=}C{-}C{-}C}} \leftarrow \underset{\text{4MC}_5\text{-2}}{\mathrm{C{-}\overset{C}{\overset{|}{C}}{-}C{=}C{-}C}}.$$

From Fig. 9 it is evident that both $2MC_5$-1 and $4MC_5$-2 suffer rearrangement

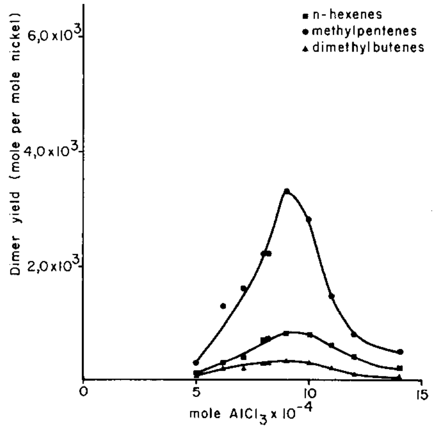


FIG. 8. The influence of aluminum chloride concentration at Ni:P = 1:4 on dimer yield.

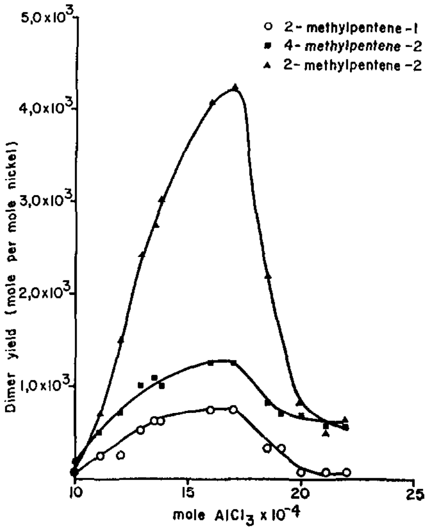


FIG. 9. The influence of aluminum chloride concentration at Ni:P = 1:8 on isomerization.

to 2MC$_5$-2 under the influence of aluminum chloride, which is a well-known isomerization catalyst. As 2MC$_5$-1 and 4MC$_5$-2 have comparable stabilities (7), they should exhibit the same tendency towards isomerization. One notes, however, that the yield of 4MC$_5$-2 exceeds that of 2MC$_5$-1 and that this difference is proportionally related to the Al:Ni ratio. This leads to the conclusion that more 4MC$_5$-2 than 2MC$_5$-1 is produced in the dimerization reaction and that the 2MC$_5$-1 formation is preferentially suppressed at high acid levels.

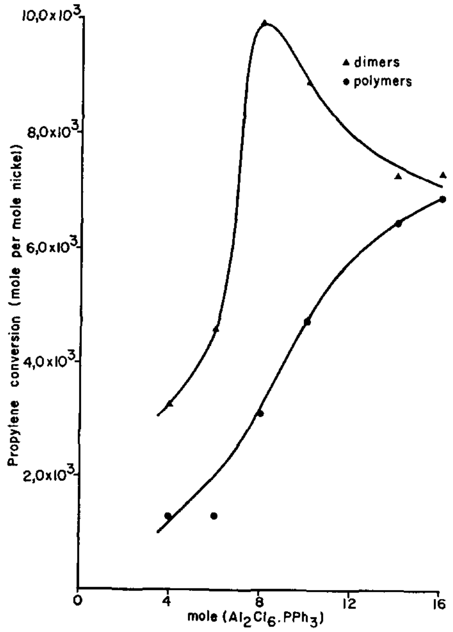


FIG. 10. The influence of aluminum chloride concentration at Al:P = 2:1 on propylene conversion.

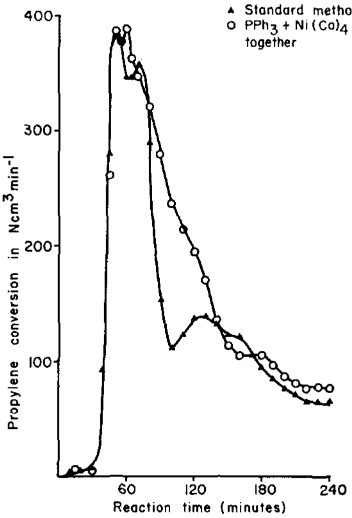


FIG. 11. The influence of catalyst preparation on propylene conversion.

The effect of varying the aluminum chloride plus phosphine to nickel ratio at a constant aluminum chloride:phosphine ratio of 2:1 is illustrated in Fig. 10. The maximum dimerization activity is again obtained at a nickel:phosphine:aluminum chloride ratio of 1:8:16 (cf. Fig. 3). This proves that the critical factor in the unwanted polymerization of propylene is the aluminum chloride in excess and not the aluminum chloride:phosphine ratio. It was further observed that the catalytic system retained its activity longer at higher phosphine concentrations and that in these cases an orange precipitate formed instead of the black precipitate mentioned above.

In an effort to obtain a more effective ligand exchange, nickel tetracarbonyl and triphenylphosphine were dissolved in chlorobenzene and warmed to 80°C in an argon atmosphere. After 2 hr the solution was cooled to room temperature and treated with propylene and aluminum chloride as in method A. The effect of this procedure versus the normal procedure is illustrated in Fig. 11. The reaction profiles are very similar for the first 75 min, after which the catalyst prepared according to the new method retains its activity somewhat better than the standard catalyst. Although the total propylene conversion is slightly higher in the former case, the dimer selectivity is somewhat lower (Table 3). The pretreated catalytic system retained its orange color throughout the experiment and an orange instead of black precipitate was formed.

Finely divided nickel, prepared by decomposing nickel tetracarbonyl in chlorobenzene, did not form an active dimerization catalyst on the addition of triphenylphosphine and aluminum chloride. This implies that direct ligand exchange is necessary for the formation of an active dimerization system.

TABLE 3

The Effect of Thermal Treatment Versus Normal Treatment of the Nickel Tetracarbonyl + Triphenylphosphine Mixture on the Propylene Conversion

Preparation	Moles/mole nickel		
	Total conversion	Dimers	Polymers
Standard	13.0×10^3	10.0×10^3	3.0×10^3
Preheated	14.0×10^3	9.5×10^3	4.5×10^3

In the hitherto mentioned work triphenylphosphine was used exclusively as Lewis base. In order to determine the influence of the base structure on the total activity and selectivity of the catalytic system, various phosphines and phosphites as well as two nonphosphorous bases were investigated. The results are given in Table 4. It is obvious that triphenylphosphine is the most suitable base tested with respect to both total activity and dimer selectivity. The dimethylbutene selectivity increases sharply in the order triphenylphosphine, tri-*n*-butyl phosphine, tricyclohexylphosphine, corresponding to an increase is basicity (*4*, *5*). However, the overall activity and dimer selectivity decrease in the same order. The phosphites and acrylonitrile seem to be rather unsuited as cocatalysts. With benzonitrile only a slight activity was observed.

The influence of base strength on the isomerization activity of the catalytic system is shown in Table 5. The values clearly illustrate that increasing base strength decreases the isomerization activity (i.e., the formation of $2MC_5$-2) of the catalytic system.

TABLE 4

The Influence of Base Structure on Propylene Conversion

Base	Moles × 10^3/ mole nickel		Percent		
	Dimers	Polymers	*n*-Hexenes	Methylpentenes	Dimethylbutenes
PPh_3	8.6	2.6	21	72	7
$P(nC_4H_9)_3$	2.0	2.8	10	69	21
$P(C_6H_{11})_3$	0.6	1.5	4	30	66
$P(OPh)_3$	0.8	1.2	25	70	5
$P(OCH_3)_3$	0.7	2.1	31	64	5
$CH_2{=}CH{-}CN$	0.1	1.7	26	66	8
C_6H_5CN	Slight reaction		—	—	—
None	0.0	4.6	—	—	—

TABLE 5

The Influence of Base Strength on Isomerization of the Primary Methylpentenes

Base	% $2MC_5$-1	% $4MC_5$-2	% $2MC_5$-2
PPh_3	8.3	14.6	49.1
$P(nC_4H_9)_3$	12.1	31.2	24.9
$P(C_6H_{11})_3$	14.2	—[a]	4.7

[a] Because of overlap of the $4MC_5$-2 peak by the 2,3 M_2C_4-1 peak in the gas chromatogram, this value could not be accurately evaluated.

DISCUSSION

The results discussed above lead to the following conclusions with regards to the dimerization of alkenes by complex transition metal compounds:

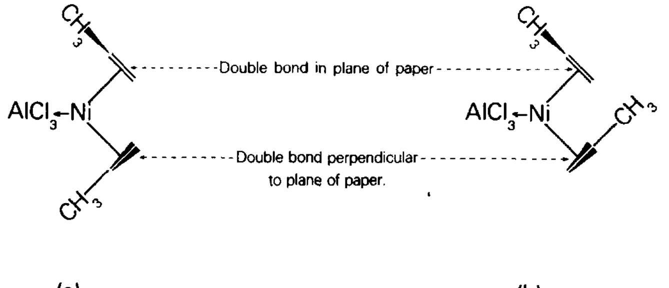
i. Zerovalent nickel is responsible for the dimerization activity of the catalytic system. This was further shown by the observation that a catalyst containing only aluminum chloride or aluminum chloride plus triphenylphosphine polymerized propylene at atmospheric pressure and at 10°C to heavy colorless oils containing no trace of dimers.

ii. One or more of the carbonyl groups attached to nickel tetracarbonyl have to be replaced by suitable Lewis bases before any catalytic activity is shown; a catalyst containing only nickel tetracarbonyl and aluminum chloride reacted the same as aluminum chloride alone, i.e., polymers were the only detectable product.

iii. The addition of a suitable Lewis acid is necessary to activate the nickel complex; a catalyst containing nickel tetracarbonyl alone or combined with triphenylphosphine is totally inactive and no traces of either dimer or polymer are formed.

iv. The nickel complex is a highly selective dimerization catalyst. The products formed in all experiments contained dimers and high molecular weight polymers only; no detectable amounts of either tri- or tetramers were found. The polymers are assumed to be formed by the excess aluminum chloride.

v. The decrease in total activity (dimerization, polymerization and isomerization) with increasing basicity of the Lewis base (Tables 4 and 5) can be explained by the SHAB theory; the more basic the Lewis base, the more it will preferentially combine with the stronger Lewis acid (aluminum chloride) rather than with nickel. This will lead on the one hand to a decreased formation of the active nickel complex, as less base is available to undergo the essential ligand exchange and on the other hand to a deactivation of the aluminum chloride, resulting in a lower dimerization, polymerization and isomerization activity. This hypothesis can also explain the low activity of the acrylonitrile



(a) (b)

FIG. 12. The "transoid" (a) and "cisoid" (b) orientations of the nickel–(propylene)$_2$–aluminum chloride complex.

system and the negative results obtained with benzonitrile.

The Mechanism of Propylene Dimerization

We believe that the phosphine ligands which stabilize the zerovalent nickel atom, are removed by the Lewis acid (aluminum chloride), whereby a trigonally hybridized nickel–(propylene)$_2$–aluminum chloride complex could be formed. The coordinated aluminum chloride serves to lower the electron density of nickel, thereby facilitating π-bonding of two propylene molecules to the central nickel atom. The complexed olefin moieties are allowed (*8, 9*) to rotate freely around the metal–olefin bond, enabling them to attain sterically suitable orientations, which will allow dimerization to proceed. From a study of molecular models it is clear that two different orientations (Fig. 12) will be favored, viz, a "transoid"(a) and a" cisoid"(b) orientation. In both cases the two olefinic bonds are perpendicular to each other.

Dimerization of the two coordinated propylene units can now take place through a concerted electronic rearrangement with a concommitant hydride shift. The electronic rearrangement can take place via metal *d*-orbitals of suitable symmetry in analogy to the mechanism suggested by Mango and Schachtschneider (*10*) for the cycloaddition of two olefins to form cyclobutanes (Figs. 13 and 14).

According to the postulated mechanism, the dimerization reaction proceeds in three distinct steps, i.e.,

i. Rotation of the coordinated olefins around the metal–olefin bond to assume orientations suitable for dimerization.

ii. Electronic rearrangement leading to the formation of a coordinated dimer and simultaneous coordination of a new monomer.

iii. Displacement of the dimer by a second monomer to reform the starting complex.

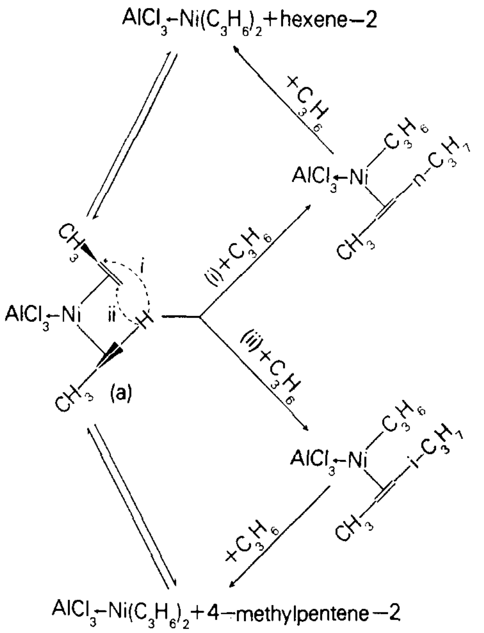


FIG. 13. Dimerization mechanism for the "transoid" orientation.

The proposed reaction scheme suggests that the primary products are hexene-2,

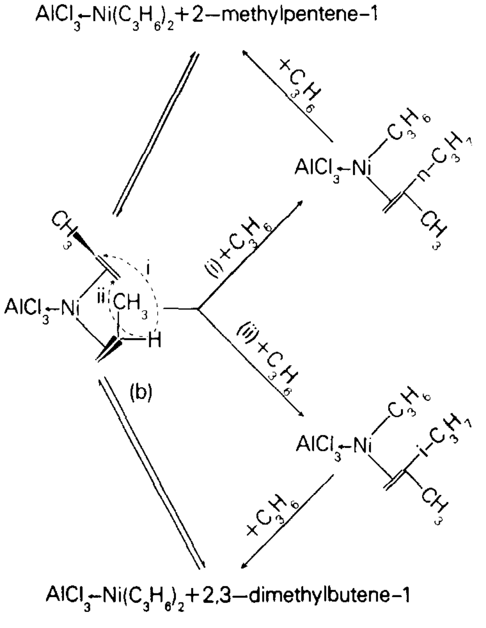


FIG. 14. Dimerization mechanism for the "cisoid" orientation.

4-methylpentene-2, 2-methylpentene-1 and 2,3-dimethylbutene-1. This is in agreement with the findings of other workers (*4*, *5*).

If the transoid and cisoid orientations were energetically equivalent, the ratio of hexenes : methylpentenes : dimethylbutenes should be 1:2:1. From Figs. 7 and 8 it is clear that the dimer product contains more hexenes than dimethylbutenes and that the ratio hexenes:dimethylbutenes increases with increasing aluminum chloride levels. This indicates that increasing acidity of the dimerization medium increasingly favors the transoid orientation, whereas increasing basicity favors the cisoid orientation (Figs. 7 and 8 and Table 4).

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