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Studies on Nickel-Containing Ziegler-Type Catalysts. III. Dimerization of Propylene to 2,3-Dimethylbutenes. Part-I

Hiroshi SATO,* Takanobu NOGUCHI,† and Seimei YASUI†
Organic Synthesis Research Laboratory, Sumitomo Chemical Co., Ltd., Tsukahara, Takatsuki, Osaka 569
†Tsukuba Research Laboratory, Sumitomo Chemical Co., Ltd., Kitahara, Tsukuba, Ibaraki 300-32

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A new selective catalyst was developed for the dimerization of propylene to 2,3-dimethylbutenes (DMBS). It comprises five components: nickel naphthenate (Ni(naph)$_2$)/AlEt$_3$/PR$_3$/diene/chlorinated phenol. Among them, chlorinated phenol is an essential component for activating the catalyst. Both the dimerization of propylene and the isomerization of the produced 2,3-dimethyl-1-butene (DMB-1) to 2,3-dimethyl-2-butene (DMB-2) are accelerated in proportion to the content of the chlorinated phenol as well as to the number of chlorine atoms on the chlorinated phenol. These effects are attributed to the Lewis acidity of the reaction product between AlEt$_3$ and the chlorinated phenol. Thus, either DMB-1 or DMB-2 can be produced selectively by controlling the composition of the catalyst.

The content of DMBS mainly depends upon the phosphine ligand; this ligand effect is discussed in terms of the ^{31}P NMR chemical shift. A high content of DMBS of up to 85% in propylene dimers was attained when phosphines with chemical shifts between 0 and −30 ppm were used.

In 1966, Wilke et al. developed an efficient η-allylnickel complex catalyst for the dimerization of propylene.[1] At the same time, Evers developed a Ziegler-type dimerization catalyst, comprising Ni(acac)$_2$/Al$_2$Et$_3$Cl$_3$/trialkylphosphine (PR$_3$).[2]

Among the isomers of the propylene dimers, 2,3-dimethylbutenes (DMBS) are especially important, since they can be used as key starting olefins for pesticides, perfumes and other fine chemicals (Fig. 1). Concerning the selectivity of DMBS (i. e. the content of DMBS in dimers) and the isomerization of 2,3-dimethyl-1-butene (DMB-1) to 2,3-dimethyl-2-butene (DMB-2), the abovementioned two catalysts are not sufficient. To improve these points, we conducted a detailed investigation, and succeeded to develop a new efficient Ziegler-type catalyst, which is described below.

Experimental

Materials. Propylene, solvents (toluene and chlorobenzene), and other catalyst component were used after being dried with 3A molecularsieve (MS). Triethylaluminum was used as obtained.

Experimental Procedure and Analysis. Propylene dimerization was conducted using a stainless-steel autoclave (0.3 or 1.0 L). After the catalyst components had been mixed in the autoclave, propylene was fed in either of two ways. One way involved continuous feeding in the liquid or gas phase; the other involved feeding all at once. The isomers of the propylene dimers and propylene, itself, were analyzed by gas chromatography (GC) (a glass column (4 m) with 5% sebaconitrile on shimalite; a column temperature of 40 °C; *n*-pentane was used as an internal standard).

Results

Activators for a Ni(naph)$_2$/AlEt$_3$/PR$_3$ Catalyst. The Ni(naph)$_2$/AlEt$_3$/PR$_3$ catalyst has almost no activity for the dimerization of propylene, in which Ni(naph)$_2$ denotes nickel naphthenate. Among the many substances examined, chlorinated phenols were found to be efficient activators for the catalyst. In preparing the catalyst, 1,3-conjugated diene (butadiene or isoprene) was found to have a stabilizing effect for the catalyst. Thus, the new efficient catalyst (A) had the following composition:

$$\mathrm{Ni(naph)_2/AlEt_3/PR_3/diene/chlorinated\ phenol.} \qquad \text{(A)}$$

The representative results for catalyst (A) are summarized in Table 1. These results are illustrated in relation to the Hammet σ-value of chlorinated phenols, as shown in Fig. 2. The catalytic activity increases with the sum of the Hammet σ-value of the chlorinated phenols. The content of DMBS in dimer olefins (DMBS selectivity) is as high as 85%, though the selectivity of the dimers in converted propylene (C6 olefins selectivity) is 58%. These selectivities are almost independent of the Hammet σ-value.

Comparison of the Catalytic Properties between Catalyst (A) and Evers' Catalyst (B). The catalytic properties of catalyst (A) and Ever's catalyst (B) were compared with each other;

$$\mathrm{Ni(naph)_2/AlEt_{3-\mathit{n}}Cl_{\mathit{n}}/PR_3/propylene.} \qquad \text{(B)}$$

In catalyst (B), propylene was used as a stabilizer instead of isoprene, because isoprene rather inhibited the activity of catalyst (B). The reaction results with catalyst (B) are summarized in Table 2. Comparisons between catalysts (A) and (B) are illustrated in Figs. 3, 4, and 5. In these figures, the *x*-axes represent either the number of chlorine atoms in chlorinated phenol for catalyst (A) or the number of chlorine atoms in ethylaluminum chloride for catalyst (B). The catalytic activities of these two catalysts change similarly with the number of chlorine atoms. This means that the catalytic activity is proportional to the electronegativity

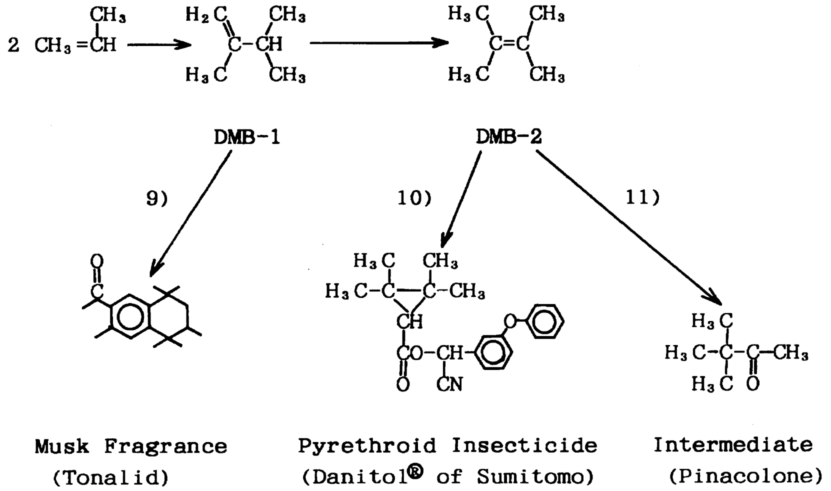

Fig. 1. Fine chemicals derived from DMB-1 and DMB-2.

Table 1. Influences of Chlorinated Phenols on $Ni(naph)_2/AlEt_3/P(c\text{-}C_6H_{11})_3$/Isoprene Catalyst[a)]

Run No.	Chlorinated phenol[b)] Position of Cl atoms	Hammet σ-value	Calatytic activity[c)]	Selectivity of dimers/%	Selectivity of DMBS/%
1	None	—	0.09×10^3	—	—
2	3-Chloro	0.373	0.72×10^3	68.6	83.0
3	3,4-Dichloro	0.599	2.70×10^3	55.0	85.4
4	3,5-Dichloro	0.746	4.90×10^3	53.2	86.0
5	2,4,6-Trichloro	0.826	7.17×10^3	58.4	81.5
6	2,3,4,6-Tetrachloro	1.20	9.83×10^3	57.8	81.5
7	Pentachloro	1.57	11.42×10^3	56.1	82.8

a) Molar ratios; $Ni(naph)_2/AlEt_3/P(c\text{-}C_6H_{11})_3$/isoprene=1/20/1/80, $[Ni]_0=4.5\times10^{-3}$ mol dm^{-3}, Dimerization; Solv.=chlorobenzene, $P(C_3H_6)=4$ atm, 20 °C, 3 h. b) Molar ratio to $AlEt_3=1.75$. c) Converted propylene(mole)/$Ni(naph)_2$(mole)/h.

Table 2. Dimerization of Propylene over the Evres Catalyst (B)[a)]

Run No.	Organoaluminum compound	Catalytic activity[b)]	Selectivity of dimers/%	Selectivity of DMBS/%
1	$AlEt_2Cl$	1.57×10^3	81.4	43.3
2	$Al_2Et_3Cl_3$	10.67×10^3	81.1	57.0
3[c)]	$Al_2Et_3Cl_3$	0.82×10^3	81.0	57.5
4	$AlEtCl_2$	7.39×10^3	79.6	58.0

a) Catalyst; $Ni(naph)_2/AlEt_{3-n}Cl_n/P(c-C_6H_{11})_3=1/20/1$ (molar ratios), trace amount of propylene being added as stabilizer, $[Ni]_0=4.5\times10^{-3}$ mol dm^{-3}, Dimerization; Solv.=chlorobenzene, $P(C_3H_6)=4$ atm, 20 °C, 3 h. b) Converted propylene(mole)/$Ni(naph)_2$(mole)/h. c) In the presence of trace amount of isoprene.

of either the chlorineted phenol in catalyst (A) or the organoaluminum in catalyst (B) (Fig. 3). The most distinct differences are the selectivities of the products. The DMBS selectivity is higher in catalyst (A), whereas the C6 olefins selectivity is higher in catalyst (B) (Fig. 5). These differences compensate for each other to give a slightly higher yield of DMBS in catalyst (A) (Fig. 4). From an industrial point of view, the separation of DMBS from C6 olefin isomers is very difficult, since the boiling points of these isomers are very close to each other. Therefore, the high selectivity of DMBS is advantageous in industrial processes; this is one of the characteristics of catalyst (A).

Influences of Phosphines. In both Wilke and Evers catalysts, the isomer distribution of C6 olefins is mainly controlled by the phosphine ligand, and the DMBS selectivity is interpreted to increase with the basicity of phosphine.[3)] In catalyst (A), the same tendency was also observed, as is illustrated in Fig. 6. The basic phosphines, such as $P(i\text{-}Pr)_3$, $P(c\text{-}C_6H_{11})_3$, and $P(s\text{-}Bu)_3$, are suitable for the selective formation of DMBS. However, more basic phosphine, $P(t\text{-}Bu)_3$, deviates from this tendency; this deviation seems to arise from its steric hindrance. On the other hand, the

Table 3. Influences of Dienes[a)]

Run No.	Diene	Conversion of propylene/%	Selectivity of dimers/%	Selectivity of DMBS /% DMB-1	DMB-2	(DMBS)
1	—[b)]	45.7	64.5	27.1	27.8	(54.9)
2	Isoprene	80.6	63.0	71.1	0	(71.1)
3	Isoprene[c)]	92.0	65.0	82.1	0	(82.1)
4	1,3-COD[d)]	61.6	69.5	61.1	0	(61.1)
5	1,5-COD[d)]	12.0	54.0	78.0	0	(78.0)

a) Catalyst; Ni(naph)$_2$/AlEt$_3$/P(i-Pr)$_3$/Diene/C$_6$Cl$_5$OH=1/10/1/80/15 (molar ratios), $[\mathrm{Ni}]_0=6.25\times10^{-4}$ mol dm^{-3} Dimerization; Solv.=chlorobenzene, [propylene]=1.0 mol dm^{-3} (being fed continuously for 3 h at 20 °C.) b) A small amount of propylene was used as catalyst stabilizer. c) Propylene containing 0.8% of isoprene was used as a monomer. d) COD; Cyclooctadiene.

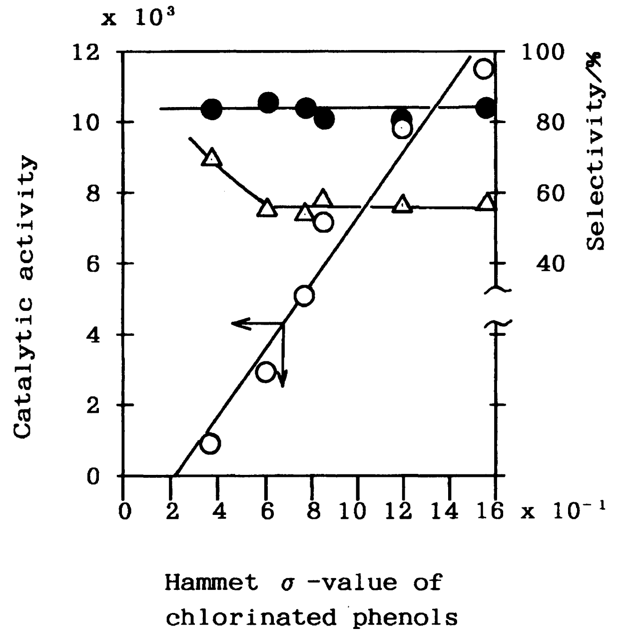

Fig. 2. Relations between the Hammet σ-value of chlorinated phenol and the dimerization activity of nickel catalyst (A). ○ ; Catalytic activity (converted propylene(mole)/Ni(mole)/h); ● ; DMBS Selectivity/%, △ ; C6 olefins Selectivity/%

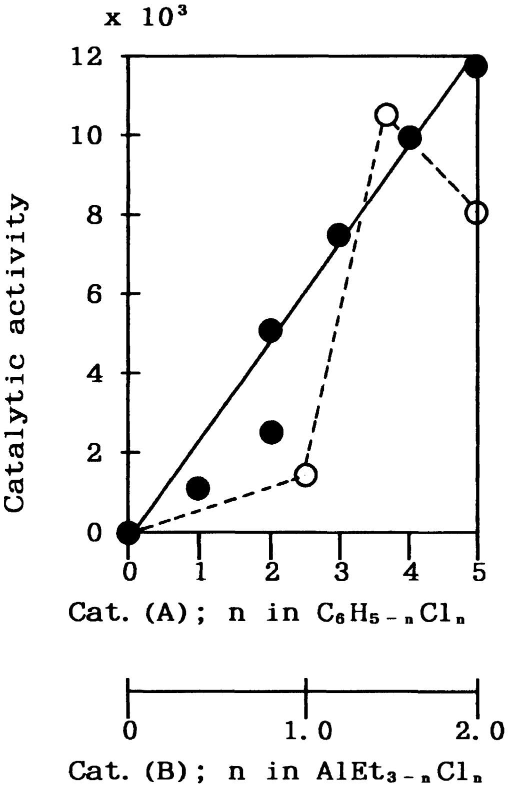

Fig. 3. Dependencies of the catalytic activities on the number of chlorine atoms either of chlorinated phenol (●) in catalyst (A) or of ethylaluminum chloride (○) in the Evers catalyst (B). Catalytic activity (converted propylene(mole)/Ni(mole)/h).

C6 olefins content simply decreases with the basicity of phosphine. This means that higher oligomers then n=3 increase with the basicity of the phosphines.

Influences of Diene. In contrast to catalyst (B), a catalytic amount of diene improved the perfoemance of catalyst (A) significantly. The first influence is a stabilizing effect on the catalyst; the second is an improvement in the DMBS selectivity. Table 3 summarizes the influence of some dienes. Among the dienes, isoprene is the most effective, and non-conjugated 1,5-cyclooctadiene rather retards the activity. Isoprene stabilizes the catalyst though coordination to the low-valent nickel species and, thus, prevents any coagulation of the active species. Isoprene thus accelerates the dimerization activity, as can be observed more distinctly when a trace amount of isoprene is fed continuously with propylene during dimerization (Run No. 3 in Table 3). Along with an increase in the isoprene/nickel molar ratio, the DMBS selectivity increase from 54.9% to 82.1%.

In the case of catalyst (B), a catalytic amount of isoprene inhibited the activity. (Run No. 3 in Table 2); this is one of the chracteristic points which distinguishes catalysts (A) and (B).

Isomerization of DMB-1 to DMB-2. Successive Isomerization (1). As shown in Fig. 1, both DMB-1 and DMB-2 are key olefins for many fine chem-

Table 4. Successive Isomerization by the Addition of an Active Organohalogen Compound[a)]

Run No.	Organohalogen compound Formula	Organohalogen compound Amount[b)]	Temp/°C	Content of DMBS in C6 olefins /% DMB-1	DMB-2	DMBS	Degree of isomerization[c)]/%
1[d)]	—	—	—	72.8	3.5	76.3	4.5
2	—	—	20	72.8	3.5	76.3	4.5
3	—	—	80	71.6	4.7	76.3	6.2
4	*t*-BuCl	1.0	20	22.4	54.2	76.7	70.8
5	*t*-BuCl	1.0	60	5.8	70.4	76.2	92.4
6	*t*-BuCl	0.5	20	12.3	62.4	74.7	83.5
7	*t*-BuCl	1.0	20	4.7	70.2	74.9	93.7
8	$CH_2=CH-CH_2Br$	1.5	80	4.2	75.6	79.8	94.8
9	$CH\equiv C-CH_2Br$	1.5	80	7.0	68.6	75.6	90.7
10	$C_6H_5CH_2Cl$	1.0	20	4.9	69.1	74.0	93.4

a) Active organohalogen was added soon after dimerization of propylene. Dimerization catalyst; Ni(naph)$_2$/AlEt$_3$/P(*i*-Pr)$_3$/isoprene/C_6Cl_5OH=1/10/1/80/15 (molar ratios), $[Ni]_0=4.5\times10^{-3}$ mol dm^{-3} Dimerization; Solv.=chlorobenzene, $P(C_3H_6)=5$ atm, 20 °C, 3 h. b) Molar ratio to AlEt$_3$. c) (DMB−2/DMBS)×100. d) Reaction mixture of dimerization just before isomerization.

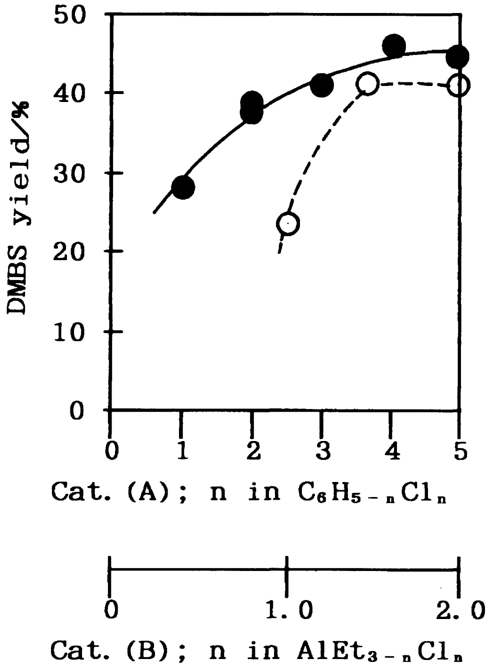

Fig. 4. Dependencies of the DMBS yield on the number of chlorine atoms of either chlorinated phenol (●) in the catalyst (A) or ethylaluminum chloride (○) in the Evers catalyst (B).

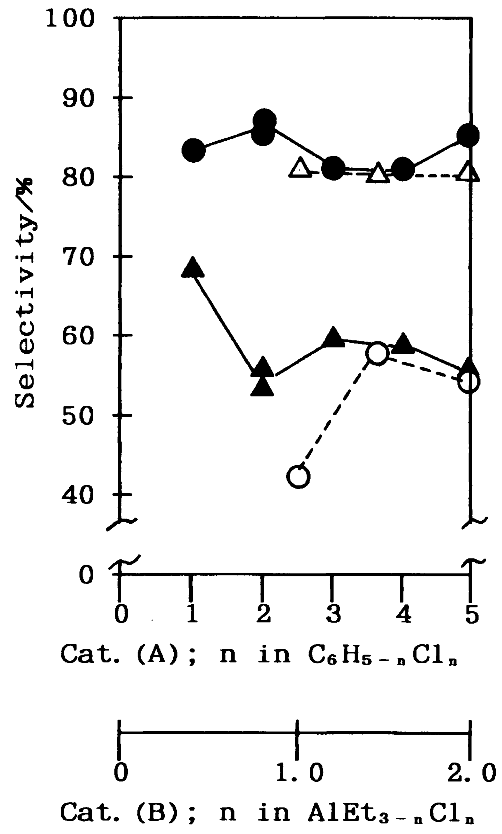

Fig. 5. Dependencies of the DMBS selectivity and C6 olefins selectivity on the number of chlorine atoms of either chlorinated phenol in catalyst (A) or ethylaluminum chloride in the Evers catalyst (B). Catalyst (A) : ● ; DMBS selectivity/%, ▲ ; C6 olefins selectivity/%. Catalyst (B) : ○ ; DMBS selectivity/%, △ ; C6 olefins selectivity/%.

icals. It is, therefore, desirable to produce each of them selectively. Since the initial product of dimerization is DMB-1, it must be isomerized into DMB-2. A very convenient and efficient method for isomerization, successive isomerization soon after dimerization, was found. This method involves adding an organohalogen compound into a reaction solution successively after dimerization. Organohalogen compounds containing active halogen atoms are effective, such as 1,1-dimethylalkyl, benzyl, allyl or propargyl halides (Table 4). Without these additives, no isomerization proceeded, even at 80 °C; however, in the presence of more than an equimolar amount of the organohalogen compound to AlEt$_3$, an almost thermodynamically equilibrium isomerization (≒94% at 20 °C) was obtained at room temper-

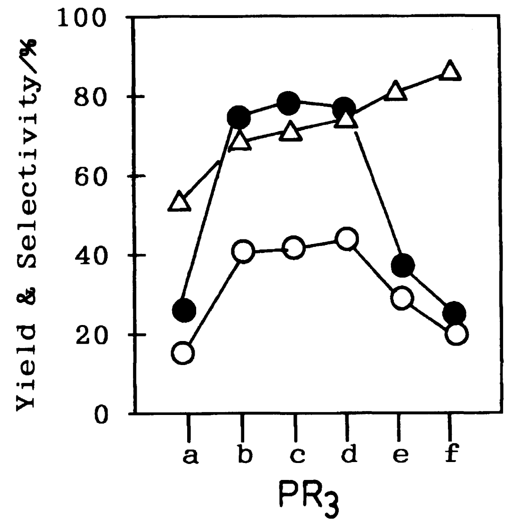

Fig. 6. Influences of trialkylphosphines on the dimerization activity of catalyst (A). ○ ; DMBS yield/%, ● ; DMBS selectivity/%, △ ; C6 olefins selectivity/%. R in PR_3: a; *t*-Bu, b; *s*-Bu, c; *i*-Pr, d; c-C_6H_{11}, e; *i*-Bu, f; *n*-Bu. Catalyst; $Ni(naph)_2/AlEt_3/PR_3$/isoprene/TCP = 1/15/1/10/22.5 (molar ratios), Ni=3 mmol, Toluene=67 g, propylene=200 g. Catalyst and propylene were fed continusouly at 20 °C for 3 h.

ature. These effects are attributed to an enhancement of the Lewis acidity of $AlEt_3$ according to the following equation:

$$AlEt_3 + nR\text{-}X \rightarrow AlEt_{3-n}X_n + nR-Et \quad (0 < n < 3). \quad (1)$$

Successive Isomerization (2). Taking the above results into consideration, the successive addition of chlorinated phenol was examined. Good results were obtained, as shown in Fig. 7. The degree of isomerization increased with the amount of chlorinated phenol being added after dimerization.

In order to estimate the active species for isomerization, various combinations of the catalyst components were examined for the conversion of DMB-1 to DMB-2, as shown in Table 5. The highest activity was obtained for the combination of $AlEt_3$ and pentachlorophenol (Run No. 4 in Table 5); nickel played no role in the isomerization. This means that the active species is a Lewis-acidic component resulting from the interaction between $AlEt_3$ and pentachlorophenol, and that nickel hydride played almost no role in this case.

Direct Synthesis of DMB-2. The above-mentioned results incidate that if a sufficient amount of chlorinated phenol exists in the dimerization process, DMB-2 would be obtained directly through the in-situ isomerization of DMB-1. Although we were anxious that an excess amount of chlorinated phenol would depress the dimerization activity, a proper choice of the mixing order of the catalyst components solved this problem. That is, when chlorinated phenol was added after reducing $Ni(naph)_2$ with $AlEt_3$, the excess amount of chlorinated phenol did not interfere with the dimerization activity, and DMB-2 was obtained directly in high selectivity (Fig. 8). However, if an excess amount of chlorinated phenol was added before reduction, the dimerization activity was completely inhibited, because no residual active Et–Al bond existed, which is necessary for reducing $Ni(naph)_2$.

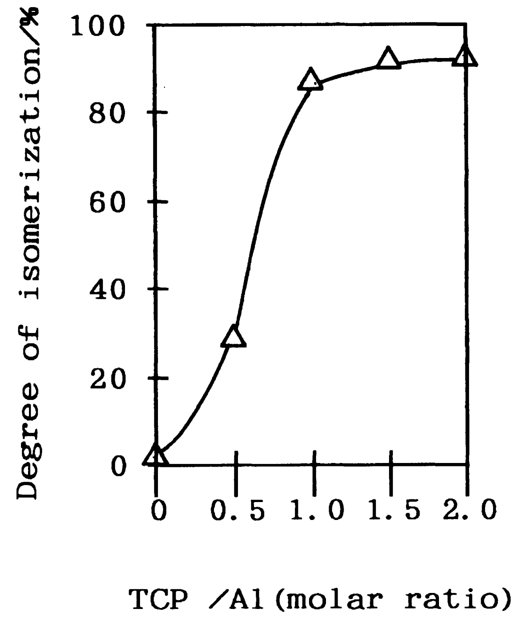

Fig. 7. Successive isomerization by an additional amount of 2,4,6-trichlorophenol (TCP). Dimerization: Catalyst; $Ni(naph)_2/AlEt_3/P(i\text{-}Pr)_3$/isoprene/TCP=1/10/1/20/15 (molar ratios), monochlorobenzene solvent, $[Ni]_0=4.5\times10^{-3}$ mol dm^{-3}, $P(C_3H_6)=4$ atm, 20 °C, 4 h. Isomerization: 20 °C, 1 h.

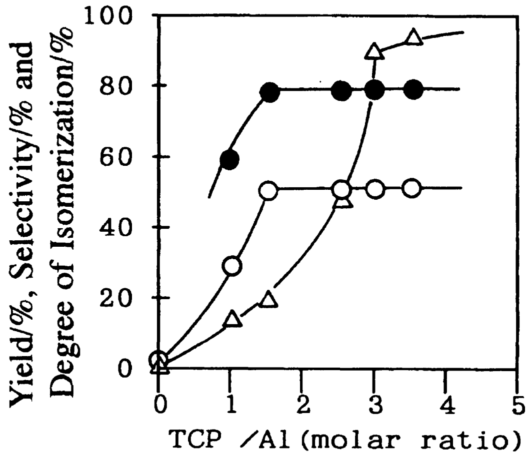

Fig. 8. Influences of the TCP/Al molar ratios on the dimerization activity of catalyst (A). ○ ; DMBS yield/%, ● ; DMBS selectivity/%, △ ; Degree of isomerization/%.

Influences of the Reaction Conditions. Solvent Effect. In the nickel-catalyzed dimerization

Table 5. Influences of the Catalyst Composition on the Isomerization of DMBS[a)]

Run	Composition of isomerization catalyst/mmol					Content of DMBS in C6 olefins/%			Degree of
No.	$Ni(naph)_2$	$P(i\text{-}Pr)_3$	isoprene	$AlEt_3$	C_6Cl_5OH	DMB-1	DMB-2	DMBS	isomerization%
1[b)]	—	—	—	—	—	74.9	3.6	78.5	4.6
2	0.047	0.047	3.76	0.47	0.7	74.3	4.0	78.3	5.1
3	0.047	—	3.76	0.47	—	73.2	4.7	77.9	6.0
4	—	—	—	0.47	0.7	5.0	73.0	78.0	93.5
5	—	—	—	0.47	—	63.2	14.3	77.5	18.4

a) All procedure was under nitrogen atmosphere. Solv. (chlorobenzene)=20 ml, DMBS=10 ml, Isomerization; 20 °C, 1 h.
b) Control experiment without isomerization catalyst.

Table 6. Solvent Effect on Dimerization[a)]

Run	Solvent	Catalytic	Selectivity	Selectivity of DMBS /%		
No.		activity[b)]	of dimers/%	DMB-1	DMB-2	DMBS
1	Toluene	2.65×10^4	62.5	3.0	76.2	79.2
2	Chlorobenzene	7.95×10^4	58.0	4.0	79.5	83.5

a) Dimerization catalyst; $Ni(naph)_2/AlEt_3/P(i\text{-}Pr)_3/isoprene/C_6Cl_5OH=1/20/1/80/60$ (molar ratios), $[Ni]_0=4.5\times10^{-3}$ mol dm^{-3} Dimerization;, $P(C_3H_6)=5$ atm, 20 °C, 1.5 h. b) Converted propylene(mole)/$Ni(naph)_2$(mole)/h.

of propylene, it is generally recognized that a halogenated solvent (e. g. chlorobenzene) is superior to a hydrocarbon solvent (e. g. toluene).[3—5)] The same tendency was observed for catalyst (A), as is shown in Table 6. The catalytic activity is about three-times higher in chlorobenzene than in toluene. This result means that the active nickel species bears some polar characteristic.

Influences of the Propylene Concentration. The influence of the propylene partial pressure ($P_{C_3H_6}$) on the dimerization rate was examined during the initial stage of dimerization; the results along with several $P_{C_3H_6}$ are illustrated in Figs. 9 and 10. From these results, it is concluded that the reaction rate is a second order of the propylene concentration.

Influences of the Catalyst Concentration. The initial reaction rates at various catalyst concentrations were calculated based on the initial slope of the converted propylene in the same way as mentioned above; the results are summarized in Fig. 11. The initial reaction rate (R_0) is proportional to the catalyst concentration ($(\mathrm{cat})_0-(\mathrm{cat})_s$) within a low concentration level, where $(\mathrm{cat})_0$ is the initial catalyst (nickel) concentration and $(\mathrm{cat})_s$ is interpreted as being the lowest catalyst concentration necessary to initiate a reaction. Based on these results, R_0 can be expressed as

$$R_0 = k\alpha((\mathrm{cat})_0 - (\mathrm{cat})_s)(\mathrm{propylene})^2, \qquad (2)$$

where k is a rate constant and α is the catalytic efficiency.

Discussion

Contributions of Chlorinated Phenol to the Dimerization. The necessity of Lewis acidity for the activation of η-allylnickel catalysts has been generally recognized since Wilke's work.[1,3)] The Evers-type catalyst (B) utilizes ethylaluminum chloride as both a reducing reagent of Ni(II) and a Lewis acidic component. On the other hand, our catalyst (A) utilizes $AlEt_3$ as a reducing reagent and chlorinated phenol as an acidic component. Chlorinated phenol ($HO\text{–}ArCl_m$) is estimated to exert Lewis acidity through a reaction with $AlEt_3$ according to

$$AlEt_3 + n\ HO\text{-}ArCl_m \rightarrow Et_{3-n}Al(OArCl_m)_n + n\ EtH. \qquad (3)$$

One of the distinct features of catalyst (A) is the high DMBS selectivity (≒ 85%), which is 30—35% higher than that of catalyst (B). On the other hand, the C6 olefins selectivity in catalyst (A) is lower. For a more detailed consideration, the isomer distributions are compared for the two catalysts (Table 7). Since the active species of nickel-catalyzed dimerization is generally recognized as being a nickel hydride complex,[3—5)] the isomer distibution can be considered according to the reaction scheme given in Fig. 12. Considering the isomer distribution given in Table 7, the relative orders of the rate constants can be depicted as follows:

Catalyst (A); $\underline{k_{11}\gg k_{12}}$, $k_{21}\gg k_{22}$, $\underline{k_{31}\fallingdotseq k_{32}}$
Catalyst (B); $\underline{k_{11}\fallingdotseq k_{12}}$, $k_{21}\gg k_{22}$, $k_{23}\gg k_{24}$, $\underline{k_{31}\gg k_{32}}$, $\underline{k_{35}\gg k_{36}}$

The main differences are in the first insertion steps to the Ni–H bond (k_{11}, k_{12}) and the final β-elimination steps (k_{31}, k_{32}, k_{35}, k_{36}). These differences are estimated to arise from differences in the electronic and steric circumstances around the Ni(0) complex. Presumably, the differences between $Et_{3-n}Al(OArCl_m)_n$ and $AlEt_{3-n}Cl_n$ in both the Lewis acidity and the degree of association are responsible for these differences

Table 7. Comparison of the Product Distributions

Catalyst[a)]	Oligomers distribution/%		Isomers distribution in dimers/%			
	Dimers	Trimers≤	DMBS	4MP[b)]	2MP[c)]	Hex[d)]
(A)	58.4	41.6	81.5	4.7	12.8	1.0
(B)	81.1	18.9	57.0	8.9	29.7	4.4

a) Catalyst (A); Ni(naph)$_2$/AlEt$_3$/P(c-C$_6$H$_{11}$)$_3$/isoprene/C$_6$H$_2$Cl$_3$OH=1/20/1/80/30 (molar ratios). Catalyst (B); Ni(naph)$_2$/Al$_2$Et$_3$Cl$_3$/P(c-C$_6$H$_{11}$)$_3$/isoprene=1/20/1/trace (molar ratios). b) 4-Methyl-1-pentene and 4-Methyl-2-pentene. c) 2-Methyl-1-pentene and 2-Methyl-2-pentene. d) n-Hexenes.

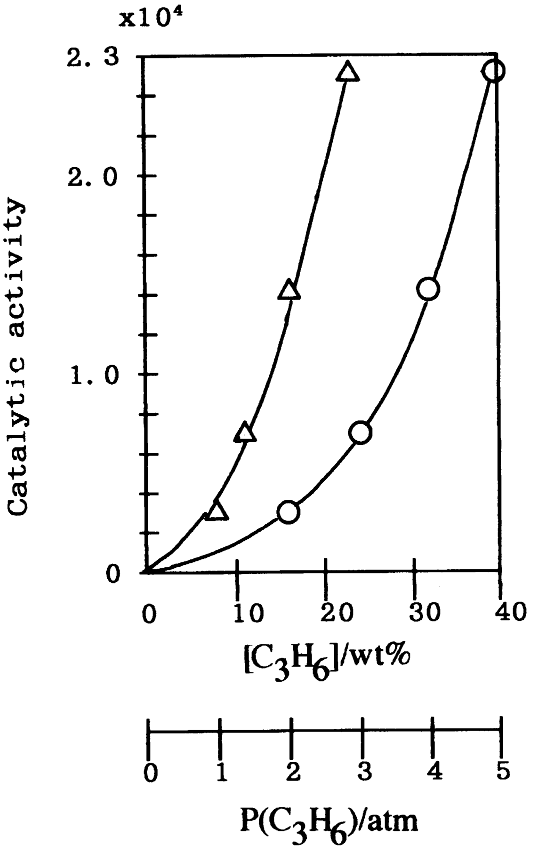

Fig. 9. Dependencies of the dimerization acrivity on either the partial pressure of propylene (P(C$_3$H$_6$)) (○) or the concentration of propylene ((propylene)) (△). Catalytic activity (converted propylene-(mole)/Ni(mole)/h).

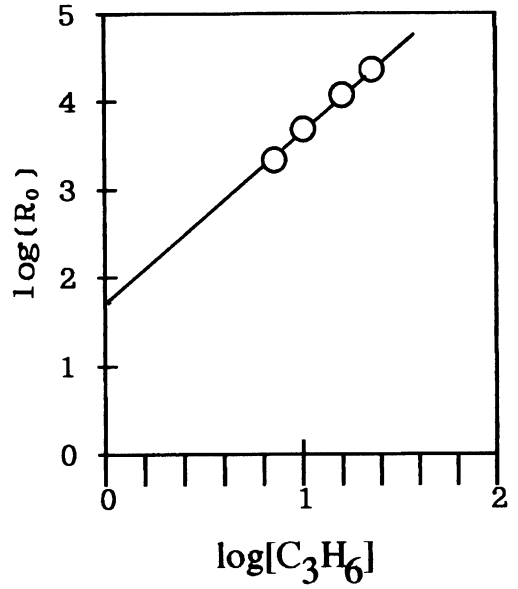

Fig. 10. Dependencies of the dimerization activity on the concentration of propylene ((propylene)); Logarithm plot.

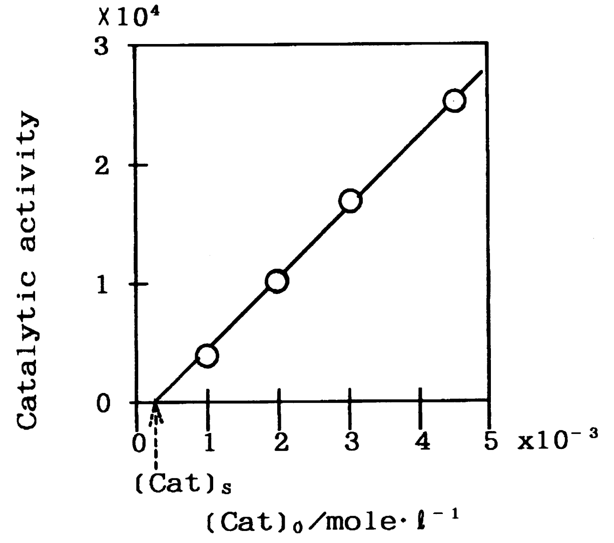

Fig. 11. Dependencies of the dimerization activity on the initial catalyst concentration (Cat)$_0$. (Cat)$_S$; Scavenger level. Catalytic activity (converted propylene(mole)/Ni(mole)/h).

in the rate constants. However, to confirm these estimations, additional analytical proof is necessary.

As for the isomerization of DMB-1 to DMB-2, the Lewis acidity of Et$_{3-n}$Al(OArCl$_m$)$_n$ also plays an important role, as was mentioned in the preceding section.

DMBS Selectivity. One of the characteristics of catalyst (A) is its high content of DMBS in dimer olefins (DMBS selectivity). In this catalyst, the DMBS selectivity is also mainly controlled by the kind of phosphines, as has been revealed by Wilke et al.[3)] They pointed out that the DMBS selectivity is higher with

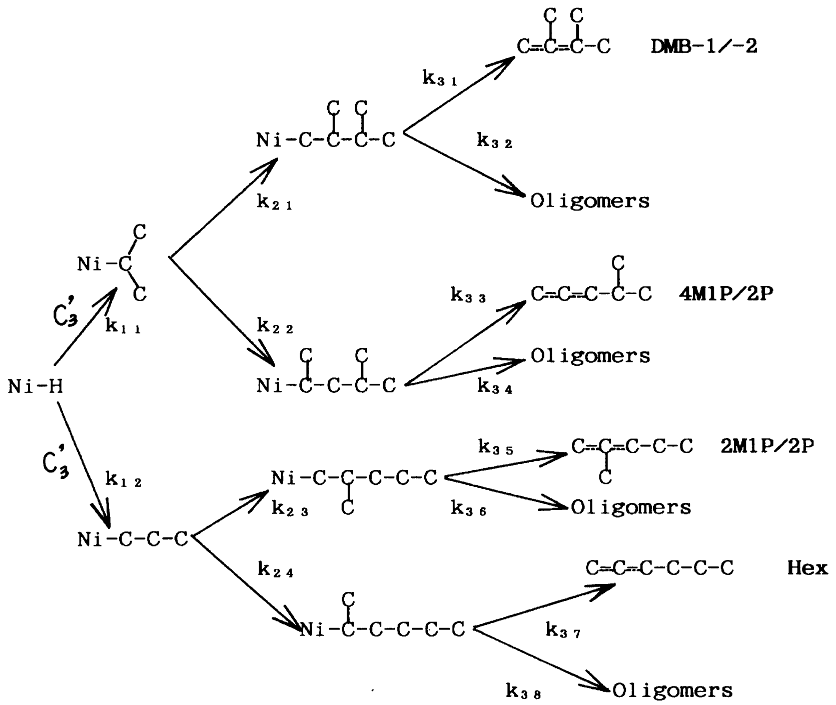

Fig. 12. Reaction pathways of propylene dimerization via hydridonickel.

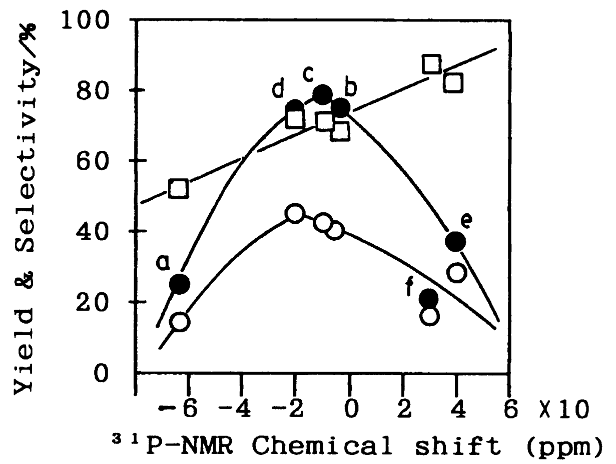

Fig. 13. Dependencies of the dimerization activity on the ^{31}P NMR chemical shift of trialkylphosphine. ○ ; DMBS yield/%, ● ; DMBS selectivity/%, □ ; C6 olefins selectivity/%. a—f: See Fig. 6.

basic phosphine, such as P(i-Pr)$_3$ or P(c-C$_6$H$_{11}$)$_3$; however, with a more basic phosphine, such as P(t-Bu)$_3$, the DMBS selectivity rather decreased due to a steric hindrance. In catalyst (A), the influence of phosphine is similar to that of Wilke et al., as shown in Fig. 6. The high DMBS selectivity is obtained with P(i-Pr)$_3$, P(c-C$_6$H$_{11}$)$_3$ or P(s-Bu)$_3$.

Since the electronic and steric factors of phosphine must be reflected in the ^{31}P NMR spectra, the results given in Fig. 6 are rearranged in relation to the ^{31}P NMR chemical shift,[6,7] as shown in Fig. 13. It is concluded that the selectivity of DMBS reaches a maximum when the values of the ^{31}P NMR chemical shift is within the 0 to −30 ppm range. Furthermore, it must be noticed that all of these preferable phosphines have a secondary alkyl group, such as i-Pr, c-C$_6$H$_{11}$ or s-Bu. From Fig. 13, it is also concluded that the dimer selectivity increases along with a shift to a higher magnetic field of the ^{31}P NMR chemical shift. From these results, the following important conclusion is derived: the reaction pathway of the dimerization (Fig. 12) is mainly controlled by the cone angle of the phosphine ligand coordinated to the hydridonickel complex.

In catalyst (A), a catalytic amount of diene enhances both the catalytic activity and the DMBS selectivity. This effect is specific to catalyst (A). For catalyst (B), diene works rather as an inhibitor (Run No. 3 in Table 2). This difference is attributable to the difference in the organoaluminum component, that is, the difference between AlEt$_{3-n}$(O–ArCl$_m$)$_n$ and AlEt$_{3-n}$Cl$_n$.

Isomerization of DMB-1 to DMB-2. DMB-1 or DMB-2 can be produced at will by controlling the amount of chlorinated phenol in catalyst (A) (Fig. 8). When chlorinated phenol is used at less than 1.5 moles per mole of AlEt$_3$, only DMB-1 can be obtained, and no isomerization is observed. On the contrary, when chlorinated phenol is used at more than 2.75 moles per AlEt$_3$, almost 90 to 95% isomerization to DMB-2 can be attained. This method is called the "direct synthesis of DMB-2".

In "successive isomerization", DMB-1 is first produced in dimerization; it is then successively isomerized to DMB-2 by adding an additional amount of chlori-

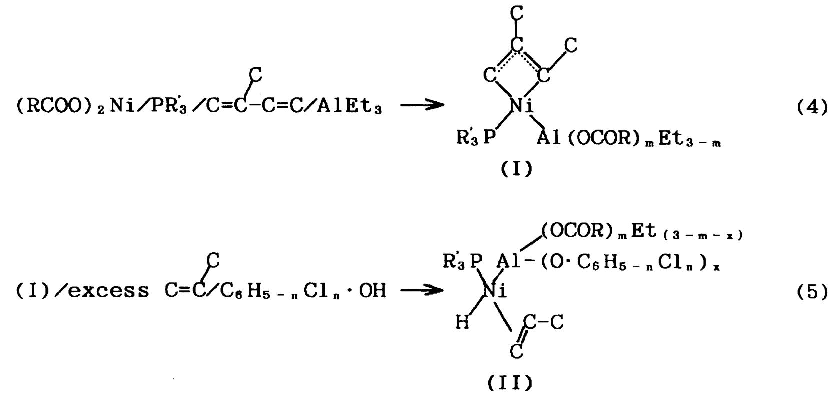

Fig. 14. Estimated structure of the active species of catalyst (A).

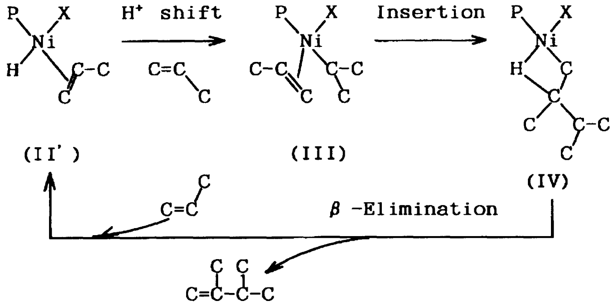

Fig. 15. Estimated mechanism of propylene dimerization.

nated phenol (Fig. 7) or an organohalogen compound, such as *t*-BuCl, *t*-BuBr or $ArCH_2Cl$ (Table 4). In both cases, $AlEt_3$ works as a precursor of the Lewis-acidic component, as well as a reducing agent of $Ni(naph)_2$. The results given in Table 5 show that the active species for isomerization is not a hydridonickel complex, as is generally recognized for a nickel catalyst,[3,8] but a Lewis-acidic reaction product of $AlEt_3$. Although the hydridonickel complex usually shows isomerization activity, when a basic phosphine, such as $P(i\text{-}Pr)_3$ or $P(c\text{-}C_6H_{11})_3$, coordinates to it, its isomerization activity decreases.[3] Therefore, in catalyst (A), when these basic phosphines are utilized, the contribution of the Lewis-acidic component prevails over that of the hydridonickel complex.

Estimation of Active Species of Dimerization. Based upon the above discussion, the active species of the dimerization can be estimated as in Fig. 14. The initially formed η-allylnickel complex (I) in Eq. 4 is then transformed into an active species, hydridonickel complex (II), through the addition of chlorinated phenol in the presence of excess propylene (Eq. 5 in Fig. 14). The estimated catalytic cycle of this complex is illustrated in Fig. 15, as was previously proposed by Eberhardt et al.[4] In complex (II'), the Al-containing group is represented as X and the phosphine ligand is represented as P, where X is an electron-attractive group and P is an electron-donative group. The catalytic cycle is explained as comprising a hydride shift (this hydride being positively polarized by the trans effect of X), insertion and β-hydride elimination.

Conclusions

1. An efficient catalyst (A) for propylene dimerization to 2,3-dimethylbutenes has been realized, in which chlorinated phenol works as an essential activator.

$$Ni(naph)_2/AlEt_3/PR_3/\text{diene}/\text{chlorinated phenol.} \qquad (A)$$

2. Chlorinated phenol ($ArCl_mOH$) is assumed to form a Lewis-acidic component (X) by an in-situ reaction with $AlEt_3$; the coordination of X to the nickel species is thought to be the main factor for activation.

$$X;\quad Et_{3-n}Al(OArCl_m)_n$$

3. The active species for the isomerization of DMB-1 to DMB-2 is not nickel, but Lewis-acidic X; DMB-1 or DMB-2 can be obtained separately by only controlling the molar ratio of chlorinated phenol to $AlEt_3$.

4. The DMBS selectivity is explained by the ^{31}P NMR chemical shift of PR_3. A high selectivity of 85% was obtained with phosphines having a chemical shift of from 0 to −30 ppm.

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