Studies on nickel-containing Ziegler-type catalysts
V. Dimerization of propylene to 2,3-dimethylbutenes. Part III. 1,1,1,3,3,3-Hexafluoro-2-propanol as a new efficient activator[1]

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Abstract

1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) worked as an efficient activator for the catalyst system comprising nickel-naphthenate (Ni(II)naph.), triethylaluminum, tricyclohexylphosphine, and isoprene in place of the known activator, 2,4,6-trichlorophenol (TCP) and water, which we reported in the preceding papers [H. Sato, T. Noguti, S. Yasui, Bull. Chem. Soc. Jpn. 66 (1993) 3069; H. Sato, T. Noguti, H. Tojima, Bull. Chem. Soc. Jpn. 66 (1993) 3079] for regioselective dimerization of propylene to 2,3-dimethylbutenes. The new HFIP-containing catalyst has a high selectivity of 2,3-dimethylbutenes in contrast to a low selectivity of propylene dimers. These properties come from the Lewis acidity of ethylaluminum-1,1,1,3,3,3-hexafluoro-2-propoxide **5** formed in situ between triethylaluminum and HFIP. Introduction of an Al–Cl bond to **5** takes a balance of the selectivities between 2,3-dimethylbutenes and propylene dimers. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Dimerization; Propylene; Nickel; Catalyst; Hexafluoro-2-propanol; 2,3-Dimethylbutenes

1. Introduction

2,3-Dimethylbutene-1 (DMB-1) and 2,3-dimethylbutene-2 (DMB-2) are key starting compounds for musk fragrance (**1**; HAT™ from Sumitomo Chemical [1]) and insecticide (**2**; Danitol™ and Rody™ from Sumitomo Chemical [2]), respectively (Fig. 1). The pioneering work of the regioselective dimerization of propylene to DMB-1 and DMB-2 (DMBS) was done by Wilke et al. using a catalyst comprising a combination of π-allyl nickel complex and Lewis acid (such as aluminum trichloride) [3]. At the same time, Evers also reported a nickel-containing Ziegler type catalyst for regioselective

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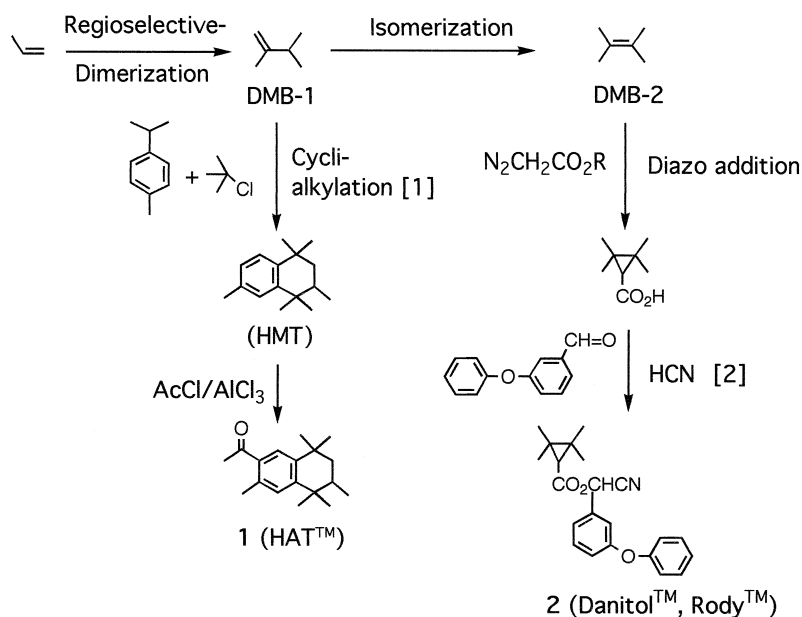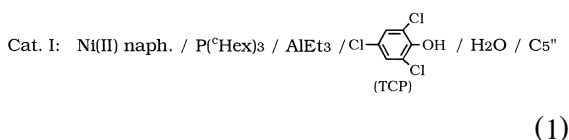[1] For IV and part II, see Refs. [5,6].

Fig. 1. Fragrance and insecticide derived from a propylene dimer, DMB-1 or DMB-2.

dimerization of propylene [4]. In the preceding papers [5,6], we already reported an efficient catalyst for regioselective dimerization of propylene to DMB-1 and DMB-2 (DMBS). The catalyst (Cat. I) consists of six components; nickel-naphthenate (Ni(II)naph.), tricyclohexylphosphine (P(^{c}Hex)$_3$), triethylaluminum (AlEt$_3$), 2,4,6-trichlorophenol (TCP), water, and isoprene (C$_5''$):

$$\text{Cat. I: } \text{Ni(II) naph. / P(}^c\text{Hex)3 / AlEt3 / Cl-}\underset{\underset{\text{(TCP)}}{Cl}}{\overset{Cl}{\bigcirc}}\text{-OH / H}_2\text{O / C}_5''$$

$$(1)$$

We proposed that, among these components, TCP and water promote the dimerization activity through in situ formation of a Lewis acidic complex with AlEt$_3$. The proposed structure of the complex **3** is illustrated in Eq. (2).

$$2 \text{ AlEt3} + 2 \text{ Cl-}\bigcirc\text{-OH} + \text{H2O} \longrightarrow \mathbf{3}$$

$$(2)$$
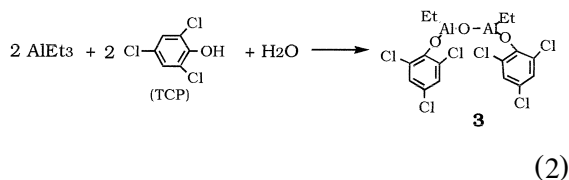
However, in a hydrocarbon solvent such as toluene, this complex tends to form precipitates which cause process troubles. Therefore, in order to explore a more efficient and soluble activator in place of TCP and water, we investigated many organic compounds having electronegative groups which might form a Lewis acidic complex through in situ reaction with triethylaluminum, and succeeded in finding an efficient activator 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) in place of TCP as was already reported in our patent literature [7]. Recently, Nomura et al. reported [8] an enhancing effect of trifluoromethane sulfonic acid (CF$_3$SO$_3$H) for the HFIP-containing catalyst developed by us. However, in their paper, they did not refer to our original finding of HFIP which is an essential activator to the Ni catalyst, but they only made a detailed examination of the enhancing effect of CF$_3$SO$_3$H which works as a subsidiary activator in the catalyst because it exhibits no promoting effect in the absence of HFIP. Therefore in the following sections, we wish to make clear the detailed feature of the activating effect of HFIP.

2. Experimental

2.1. Materials

Propylene (C_3') was evaporated from the container and cold-trapped over the molecular sieve (3A). Toluene (solvent) and isoprene (C_5'') were distilled and dried over the molecular sieve 3A. Triethylaluminum ($AlEt_3$) was used as obtained. Tricyclohexylphosphine (TCHP) was carefully stored and used under nitrogen atmosphere in order to avoid the contamination by the oxidized form, tricyclohexylphosphine oxide. Other catalyst components such as nickel-naphthenate (Ni(II)naph.) 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and pentafluorophenol (PFP) were of extra pure chemical grade, and were dried over the molecular sieve (3A).

2.2. Experimental procedure and analysis

Propylene dimerization was conducted using a stainless steel autoclave. 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 added as an internal standard).

3. Results and discussion

3.1. Investigation to develop a new and efficient activator

Only an extremely low activity can be recognized in Cat. II

$$\text{Cat. II: } Ni(II) \text{ naph. } / P(^cHex)_3 / AlEt_3 \quad (3)$$
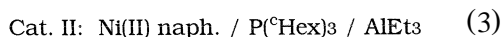
consisting of nickelnaphthenate/tricyclohexylphosphine/triethylaluminum/isoprene, where isoprene acts as a stabilizer through coordination to a low valent nickel complex. As we already reported in the preceding paper [5], an addition of chlorinated phenol (e.g., TCP) to Cat. II as an activator increased the activity drastically (Cat. III in Eq. (4)).

Cat. III: Ni(II) naph. / P(^{c}Hex)₃ / AlEt₃ / / C5''

$$(4)$$
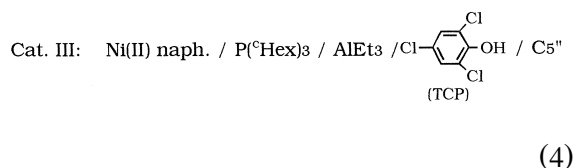
We reported further in the preceding paper [6] that the addition of a trace amount of water to Cat. III improves the activity, thus incidentally affording Cat. I (Eq. (1)). We explained the role of these activators (TCP and H_2O) as to induce the dimerization activity of the central Ni(0) species by withdrawing a part of the electron on it [5,6]. This electron withdrawing effect comes from the Lewis acidity of in situ reaction complex **3** between triethylaluminum, TCP, and water (Eq. (2)).

Therefore, in the investigation to find a new and efficient activator instead of TCP and H_2O, we examined multifunctional organic compounds having two kinds of functional groups; one is an electronegative group, and another is a reactive group with triethylaluminum. The results are summarized in Table 1 (halogenated phenols) and Table 2 (halogenated aliphatic compounds). In evaluating these data, the first priority should be given to the catalytic activity and the second priority should be to the DMBS selectivity, because a high DMBS selectivity is crucial in separating DMBS by distillation from other propylene dimers which have very close boiling points for each other.

The results with halogenated phenols are listed in Table 1. Compared with the superior properties of the present activator TCP + H_2O (catalytic activity is as high as 29.2×10^3 mol-propylene/mol per Ni/h, and the DMBS selec-

Table 1
Activating effects of multifunctional organic compounds for Cat. I: (1) Halogenated phenols

Run no.	Compound added	Amount[a]	Catalytic activity[b]	Dimer sel./%[c]	DMBS sel./%[d]	Isomzn./%[e]
Ref. [1]	TCP	70	15.0×10^3	54.2	85.1	94.5
Ref. [2]	TCP/H_2O	70/10	29.2×10^3	57.5	85.5	83.8
1	2,4,6-Tribromophenol	30	0.5×10^3	71.2	60.2	0
2	Pentabromophenol	70	2.1×10^3	29.1	68.2	93.7
3	Pentabromophenol/H_2O	30/10	5.5×10^3	40.3	77.9	94.1
4	Pentafluorophenol (PFP)	30	2.2×10^3	34.7	84.0	2.5
5	Pentafluorophenol (PFP)	60	8.2×10^3	30.0	81.6	94.0
6	2,3,5,6-Tetrafluorophenol	60	4.1×10^3	30.8	87.1	94.6
7	2,3,5,6-Tetrafluorophenol/H_2O	60/10	3.1×10^3	33.2	88.2	93.4
8	*p*-Trifluoromethylphenol	30	0.2×10^3	13.4	66.2	0

Cat. I: Ni(II)naph./P(^{c}Hex)$_3$/C$_5''$/AlEt$_3$ = 1/1/80/20 (molar ratios). Reaction conditions: solvent (toluene) = 30 ml, Ni(II)naph. = 0.045 mmol. propylene pressure was kept at 4 atm for 1 h at the reaction temperature of 20°C.
[a] Molar ratio(s) to Ni(II)naph.
[b] Converted propylene (mol)/mol per Ni/h.
[c] Dimer selectivity: (propylene dimers/converted propylene) × 100 (%).
[d] DMBS selectivity: [(DMB-1 + DMB-2)/propylene dimers] × 100 (%).
[e] Isomerization degree: [DMB-2/(DMB-1 + DMB-2)] × 100%.

tivity is also as high as 85.5% [6]), other halogenated phenols (in some cases, used with H_2O) are inferior in the catalytic activity. Their values are almost one-third as large as that of TCP + H_2O. However, the DMBS selectivities of penta- or tetra-fluorinated phenols are comparable with that of TCP + H_2O. Among halogenated phenols other than TCP, pentafluorophenol (PFP) shows a comparatively high catalytic activity

(8.2×10^3) with high enough DMBS selectivity (81.6%) (Cat. IV in Eq. (5)).

Cat. IV: Ni(II) naph. / P(^{c}Hex)$_3$ / AlEt$_3$ /

(PFP)

/ C5''
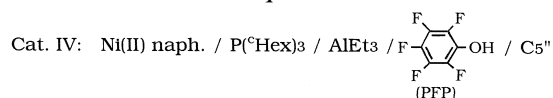
$$(5)$$

As for the degree of isomerization in DMBS, one can obtain freely either DMB-1 (run no. 4)

Table 2
Activating effects of multifunctional organic compounds for Cat. I: (2) Halogenated aliphatic compounds

Run no.	Compound added	Amount[a]	Catalytic activity[b]	Dimer sel./%[c]	DMBS sel./%[d]	Isomzn./%[e]
Ref. [1]	TCP/H_2O	70/10	29.8×10^3	54.1	84.2	84.7
Ref. [2]	Evers' catalyst[f]		94.5×10^3	89.8	50.7	16.7
1	1,1,1-Trichloroacetone	15	6.9×10^3	79.4	61.4	3.4
2	1,1,1-Trifluoroacetone	70	0.5×10^2	12.1	78.4	0
3	Trichloroacetic acid	10	13.8×10^3	100	43.4	67.2
4	Trichloroacetic anhydride	5	10.4×10^3	96.5	46.4	30.1
5	Trifluoroacetic acid	10	~ 0	–	–	–
6	Trifluoroacetic anhydride	10	0.7×10^2	5.5	40.8	0
7	Methyl-trichloro acetate	10	8.9×10^3	95.3	46.6	31.9
8	1,1,1,3,3,3-Hexafluoropropan-2-ol (HFIP)	30	23.4×10^3	41.1	89.4	93.5
9	1,1,1,3,3,3-Hexafluoropropan-2-ol (HFIP)	25	17.9×10^3	43.1	88.3	7.2
10	1,1,1-Trifluoropropan-2-ol	30	0.9×10^3	30.7	86.5	1.7
11	1,1,1,3,3,3-Hexachloroacetone	15	96.3×10^3	88.6	48.7	15.3

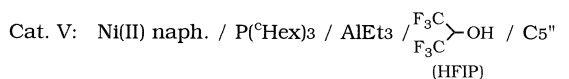Cat. I: Ni(II)naph./P(^{c}Hex)$_3$/C$_5''$/AlEt$_3$ = 1/1/80/20 (molar ratios).
Propylene dimerization conditions, see footnotes in Table 1.
[a] to [e], see footnotes in Table 1.
[f] Evers' catalyst: Ni(II)naph./P(^{c}Hex)$_3$/AlEt$_{1.5}$Cl$_{1.5}$ = 1/1/20 (molar ratios).

or DMB-2 (run no. 5) by controlling the amount of PFP. However, its dimer selectivity is too low (30.0%) even compared with the relatively low value (57.5%) of TCP + H_2O. In Section 3.2, the improvement of this point will be discussed. Another feature of the fluorine containing activator is the inhibiting effect of water (run no. 7) in contrast to the enhancing effect in the TCP containing catalyst [6].

The results with halogenated aliphatic compounds are summarized in Table 2. Among halogenated compounds examined (ketones, carboxylic acids, carboxylic anhydrides, alcohols), 1,1,1,3,3,3-hexachloroacetone showed the highest activity as 96.3×10^3 mol-propylene/ mol-Ni/h. However, its DMBS selectivity is too low as 48.7%, which means that it is almost impossible to separate DMBS by distillation from other propylene dimers. On the contrary, 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) exhibited a fairly high activity as 23.4×10^3 mol-propylene/mol-Ni/h with a high enough DMBS selectivity as 89.4% (Cat. V in Eq. (6)).

Cat. V: Ni(II) naph. / P(^{c}Hex)$_3$ / AlEt$_3$ / F$_3$C–⟨⟩–OH / C5″
                                                                    F$_3$C
                                                                  (HFIP)

$$(6)$$

As for the degree of DMBS-isomerization, one can obtain either DMB-1 (run no. 9) or DMB-2 (run no. 8) freely by controlling the amount of HFIP. However, the dimer selectivity (41.1%) is

not high enough. Therefore, although HFIP and pentafluorophenol (PFP) are the best candidates for a new activator, both activators have to be improved in the dimer selectivity.

3.2. Consideration on the dimer-selectivity and the DMBS selectivity

Table 2 shows the general tendency that the chloride derivatives afford a low DMBS selectivity in spite of a high dimer selectivity. This tendency corresponds to a similar tendency (run no. Ref. [2] in Table 2) of the Evers' catalyst comprising Ni(II)naph./P(^{c}Hex)$_3$/AlEt$_{1.5}$Cl$_{1.5}$ [4]. Therefore, in the case of chloride derivatives, the Al–Cl bonds formation **4** is proposed through an in situ exchange reaction between Et-groups in AlEt$_3$ and Cl atoms (Eq. (7)).

AlEt3 + Cl$_3$C–Y–CCl$_3$ ⟶ Cl$_x$AlEt3-x + Cl$_3$C–Y–CCl$_3$-xEtx
                   O   **4**   O

$$(7)$$
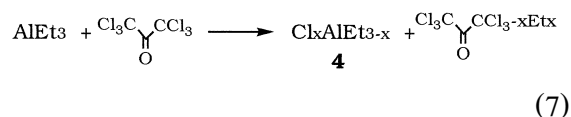
This exchange reaction is reasonable because of the high reactivity of the Cl atoms on the trichloromethylcarbonyl group toward organoaluminum compounds.

On the contrary, fluoride derivatives afford the reverse tendency to that of chloride derivatives. They afford a high DMBS selectivity with a low dimer selectivity. This tendency is very similar to that of the present catalyst I where the

Table 3
Influences of Cl/Al atomic ratios on the catalytic performances (1): PFP-containing catalyst

Run no. Ref. [1]	TBC/AlEt$_3$/PFP[a] Cat. III	Cl/Al[a]	Catalytic activity[b]	Dimer sel./%[c]	DMBS sel./%[d]	Isomzn./%[e]
		–	29.2×10^3	57.5	85.5	83.8
1	0/20/60	0	8.3×10^3	30.0	81.6	94.0
2	2/20/60	0.1	9.2×10^3	42.7	80.0	93.8
3	10/20/60	0.5	10.6×10^3	49.0	85.4	94.1
4	0/10/30	0	9.7×10^3	34.7	84.0	92.1
5	1/10/30	0.1	12.5×10^3	46.0	85.8	93.8
6	5/10/30	0.5	21.1×10^3	65.6	81.5	87.9

Catalyst: Ni(II)naph./P(^{c}Hex)$_3$/C$_5''$/AlEt$_3$/PFP = 1/1/80/10–20/30–60; molar ratios.
Propylene dimerization conditions, see footnotes in Table 1.
[a]Molar ratios of TBC to AlEt$_3$.
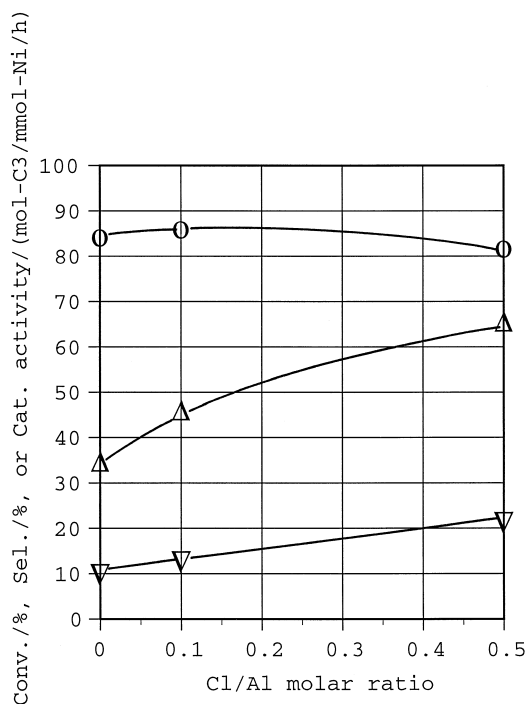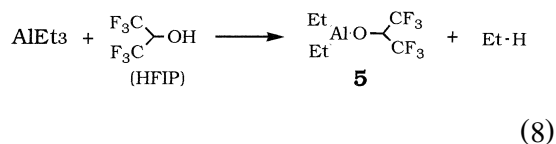[b] to [e], see footnotes in Table 1.

Fig. 2. Influences of Cl/AlEt$_3$ molar ratios on the catalytic performances (1): PFP-containing catalyst; PFP/AlEt$_3$ = 3/1 (molar ratio). $\triangledown$: Catalytic activity, $\triangle$: Dimer selectivity, $\bigcirc$: DMBS selectivity.

formation of a bulky organoaluminum-phenoxy complex **3** is proposed through the reaction between triethylaluminum, TCP, and H$_2$O as shown in Eq. (2) [5,6]. Therefore, in the case of HFIP, the formation of the following organoalu-

minum alkoxide **5** is proposed similarly (Eq. (8)).

$$\text{AlEt3} + \underset{(\text{HFIP})}{\overset{F_3C}{\underset{F_3C}{>}}\text{-OH}} \longrightarrow \underset{\mathbf{5}}{\overset{Et}{\underset{Et}{>}}\text{Al·O}\overset{CF_3}{\underset{CF_3}{<}}} + \text{Et·H}$$

$$(8)$$

The differences in selectivities described above originate from the differences in both steric and electronic circumstances around the square planer Ni (0) complex **6** (Eq. (9))

$$R_3P\text{—Ni}\underset{H}{\overset{\overset{\text{Al Complex}}{\diagup}}{\overset{C\text{-}C}{\underset{C}{<}}}} \qquad (9)$$

$$\mathbf{6}$$
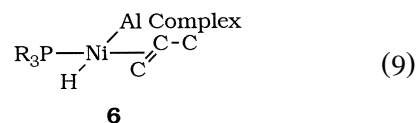
as we explained in the preceding paper [5]. Considering the above discussion, the incorporation of Al–Cl bond in the organoaluminum complex seems to improve the dimer selectivity. Therefore, in Section 3.3, the incorporation of Al–Cl bond will be examined in detail in order to improve the dimer selectivity in both catalysts activated by PFP (in Cat. IV) and HFIP (in Cat. V).

3.3. Improvement of the dimer selectivity by incorporation of Al–Cl bonds

3.3.1. PFP-containing catalyst; CAT. IV

We chose *tert*-butylchloride (TBC) as an active chloride compound, and examined the in-

Table 4

Influences of Cl/Al molar ratios on the catalytic performances (2): HFIP-containing catalyst

Run no. Ref. [1]	TBC/AlEt$_3$/HFIP[a] Cat. III	Cl/Al[a]	Catalytic activity[b]	Dimer sel./%[c]	DMBS sel./%[d]	Isomzn./%[e]
		–	29.2×10^3	57.5	85.5	83.8
1	0/10/30	0	23.4×10^3	41.1	89.4	93.5
2	1/10/30	0.1	30.3×10^3	66.6	82.8	94.2
3	2/10/30	0.2	27.9×10^3	72.5	78.8	94.4
4	3/10/30	0.3	31.0×10^3	78.9	74.7	91.9
5	5/10/30	0.5	37.5×10^3	87.8	71.4	93.9

Catalyst: Ni(II)naph./P(^{c}Hex)$_3$/C''$_5$/AlEt$_3$/HFIP = 1/1/80/10/30; molar ratios.
Propylene dimerization conditions, see footnotes in Table 1.
[a]Molar ratios of TBC to AlEt$_3$.
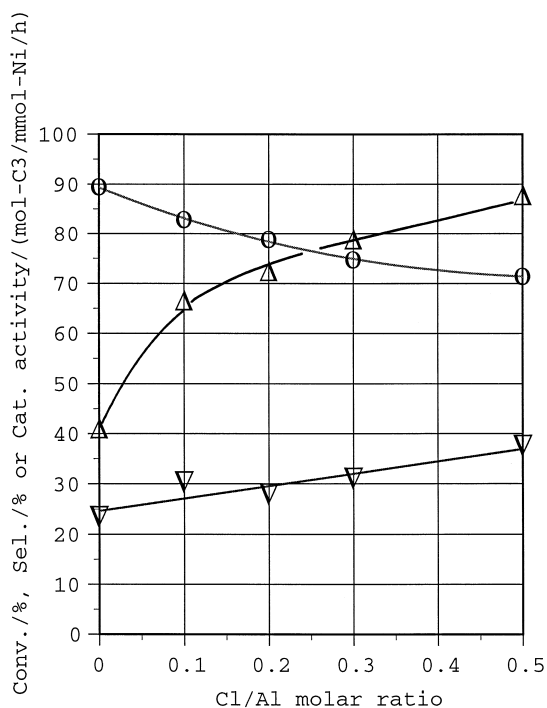[b] to [e], see footnotes in Table 1.

Fig. 3. Influences of $Cl/AlEt_3$ molar ratios on the catalytic performances (2): HFIP-containing catalyst; $HFIP/AlEt_3 = 3/1$ (molar ratio). $\triangledown$: Catalytic activity, $\triangle$: Dimer selectivity, $\bigcirc$: DMBS selectivity.

Fig. 4. Influences of $HFIP/AlEt_3$ molar ratios on the catalytic performances: $Cl/AlEt_3 = 0.2/1$ (molar ratio). $\triangledown$: Catalytic activity, $\triangle$: Dimer selectivity, $\bigcirc$: DMBS selectivity.

fluence of the Cl/Al molar ratio on the catalytic properties. The chlorine atom on TBC can reasonably react with $AlEt_3$ to form ethylaluminumchloride, liberating an inert compound 2,2-dimethylbutane. The results are summarized in Table 3 and Fig. 2. With an increase of the Cl/Al ratios, both the catalytic activity and the dimer selectivity increased with a little decrease of the DMBS selectivity. Thus, we could obtain
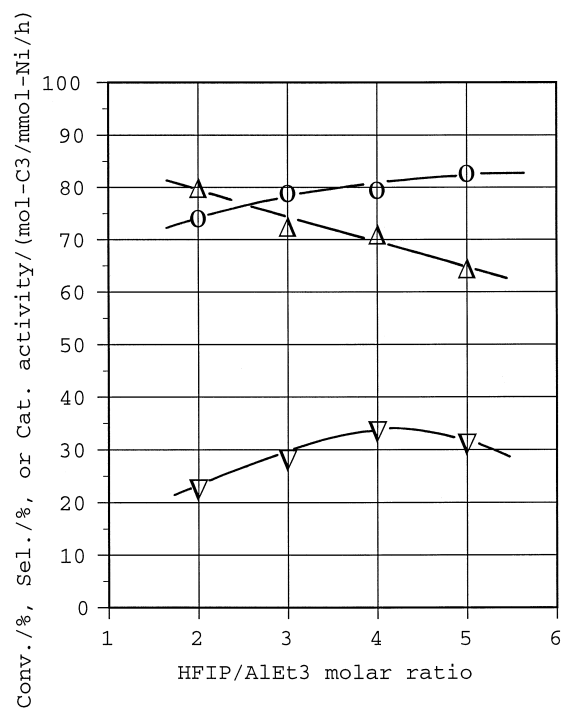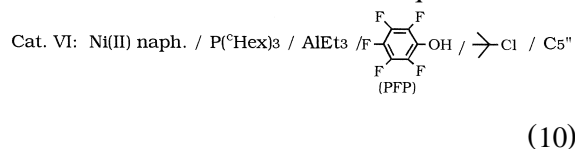
a fairly improved catalyst having a better balance of selectivities (Cat. VI in Eq. (10)).

Cat. VI: Ni(II) naph. / P(^{c}Hex)3 / AlEt3 /F—[PFP ring]—OH / $>$Cl / C5″

$$(10)$$

However, the catalytic activity is not high enough compared with that of Cat. I.

Table 5
Influences of $HFIP/AlEt_3$ molar ratios on the catalytic performances: TBC-containing catalyst

Run no. Ref. [1]	$HFIP/AlEt_3/TBC$[a] Cat. III	$HFIP/Al$[a]	Catalytic activity[b]	Dimer sel./%[c]	DMBS sel./%[d]	Isomzn./%[e]
		–	29.2×10^3	57.5	85.5	83.8
1	20/10/2	2.0	22.3×10^3	79.9	74.0	13.7
2	30/10/2	3.0	27.9×10^3	72.5	78.8	94.4
3	40/10/2	4.0	33.3×10^3	71.0	79.4	93.0
4	50/10/2	5.0	30.9×10^3	64.5	82.6	93.6

Catalyst: $Ni(II)naph./P(^cHex)_3/C_5''/AlEt_3/TBC = 1/1/80/10/2$; molar ratios.
Propylene dimerization conditions, see footnotes in Table 1.
[a] Molar ratios.
[b] to [e], see footnotes in Table 1.

Table 6
Influences of H_2O on the catalytic performances: (HFIP + TBC)-containing catalyst

| Run no. Ref. [1]	$H_2O/AlEt_3$[a] Cat. III	H_2O/Al[a] 0.5	Catalytic activity[b] 29.2×10^3	Dimer sel./%[c] 57.5	DMBS sel./%[d] 85.5	Isomzn./%[e] 83.8
1	0/10	0	30.3×10^3	66.6	82.8	94.0
2	2.5/10/2	0.25	16.5×10^3	48.1	85.4	94.6
3	5.0/10/2	0.5	11.0×10^3	39.4	83.5	94.2

Catalyst: Ni(II)naph./P(^{c}Hex)$_3$/C$_5''$/AlEt$_3$/HFIP/TBC = 1/1/80/10/30/2; molar ratios.
Propylene dimerization conditions, see footnotes in Table 1.
[a] Molar ratios.
[b] to [e], see footnotes in Table 1.

3.3.2. HFIP-containing catalyst; Cat. V

In the case of Cat. V also, with an increase of the Cl/Al molar ratio by addition of TBC, both the catalytic activity and the dimer selectivity increased with a fairly large decrease of the DMBS selectivity as summarized in Table 4 and Fig. 3. Compared at the same level of DMBS selectivity, both the catalytic activity and the dimer selectivity are almost comparable between Cat. I and Cat. V which is modified by TBC. Thus, we have succeeded in developing an alternative catalyst (Cat. VII in Eq. (11))

Cat. VII: Ni(II) naph. / P(^{c}Hex)$_3$ / AlEt$_3$ / $\overset{F_3C}{\underset{F_3C}{>}}$OH / $>$Cl / C$_5''$
(HFIP)
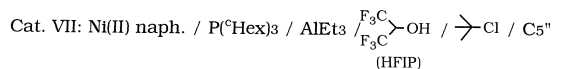
$$(11)$$

which has almost the same catalytic performance (Run no. 2 in Table 4: catalytic activity; 30.3×10^3, dimer selectivity; 66.6%, DMBS selectivity; 82.8%) with that of Cat. I.

Influences of the HFIP/AlEt$_3$ molar ratio were examined in Cat. VII at a fixed molra ratio of TBC/Al = 0.2. The results are summarized in Table 5 and Fig. 4. With an increase of the

HFIP/Al molar ratio, both the catalytic activity and the DMBS selectivity increase proportionally, while the dimer selectivity decreases. These tendencies are similar to those in the PFP containing catalyst. Considering that the increase in the molar ratios of HFIP/AlEt$_3$ and Cl/AlEt$_3$ means the increase of Lewis acidity, it is very interesting that these molar ratios influence the dimer selectivity and the DMBS selectivity in the reverse way. These differences seem to come from the steric difference between ethylalumimum-hexafluoro-isopropoxide **5** (Eq. (8)) and Al–Cl bond.

3.4. Influences of water on the HFIP containing catalyst; Cat. VII

The influences of water on the HFIP-containing catalyst are summarized in Table 6. Both the catalytic activity and dimer selectivity decrease drastically by addition of a trace amount of water ($H_2O/AlEt_3$ molar ratios; 0.25 to 0.5). This negative effect of water on Cat. VII shows a sharp contrast to the positive effect of water

Table 7
Comparison of the catalytic performances between the TCP-containing catalyst Cat. I and HFIP-containing catalyst Cat. VII; Catalyst compositions[a]

Cat. no.	Ni compd.	Ligand	Reducing agent	Stabilizer	Activator	Subsidiary activator
I	Ni.naph. (1)	P(^{c}Hex)$_3$ (1)	AlEt$_3$ (20)	C$_5''$ (80)	TCP (70)	H_2O
VII	Ni.naph. (1)	P(^{c}Hex)$_3$ (1)	AlEt$_3$ (10)	C$_5''$ (80)	HFIP (30)	TBC (2)

Reaction conditions: solvent (toluene) = 300 ml, Ni(II)naph. = 0.45 mmol. Propylene pressure was kept at 4 atm for 3 h at the reaction temperature of 20°C.
[a] Figures in parentheses are molar ratios.

Table 8

Comparison of the catalytic performances between the TCP-containing catalyst Cat. I and HFIP-containing catalyst Cat. VII; reaction results[a]

Cat. no.	Conv./% of propylene	Yd./% of DMB-2	Yd./% of DMB-1	Isomzn./%[a]	DMBS sel./%[b]
I	98.3	47.3	2.6	94.8	88.1
VII	99.1	51.7	3.0	94.6	80.7

[a](DMB-2/DMBS) × 100.
[b](DMBS/Dimers) × 100.

on Cat. I. The reason for this difference is not clear, but it seems to come from the difference between ethylaluminum-hexafluoro-isopropoxide **5** (Eq. (8)) and ethylalumuminum-trichlorophenoxide **3** (Eq. (2)).

3.5. Comparison of the catalytic performances between Cat. I and Cat. VII

In Tables 7 and 8 is summarized the comparison of catalytic performances in a 1.5 l autoclave scale between the TCP-containing catalyst Cat. I and the HFIP-containing catalyst Cat. VII. Almost the same results are obtained for both catalysts. Thus, we have confirmed the effectiveness of the HFIP-containing catalyst which is completely homogeneous throughout the dimerization procedure.

4. Conclusion

We found a new efficient activator, 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), for the catalyst system comprising nickel-naphthenate (Ni(II)-naph.), triethylaluminum, tricyclohexylphosphine, and isoprene in place of the former activator, TCP and water, which we reported in the preceding papers [5,6] for the regioselective dimerization of propylene to 2,3-dimethylbutenes. The new HFIP-containing catalyst has a high selectivity of 2,3-dimethylbutenes in contrast to a low selectivity of propylene dimers. These properties come from the Lewis acidity of ethylaluminum-1,1,1,3,3,3-hexafluoro-2-propoxide **5** formed in situ between triethylaluminum and HFIP. Introduction of an Al–Cl bond to **5** by addition of an active chlorine compound such as *tert*-butylchloride (TBC) takes a balance of the selectivities between 2,3-dimethylbutenes and propylene dimers. Thus, we have succeeded in obtaining a new catalyst, Cat. VII, having an excellent dimerization performance with no process trouble by a catalyst deposition which was often observed in the TCP-containing catalyst Cat. I.

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