Fluorinated alcohol modified nickel–phosphine catalyst system for efficient dimerization of propylene

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Abstract

Remarkable increase of the catalytic activity (turnover number for the formation of C_6 olefins or 2,3-dimethylbutenes) as well as the selectivity of C_6 olefins based on the reacted propylene has been exhibited for propylene dimerization by using the catalyst system composed of nickel naphthenate, *tert*-phosphine, $AlEt_3$, and $(CF_3)_2CHOH$ in the presence of CF_3SO_3H and/or Me_2SO_4. It turned out that the product distributions in dimers depended upon the kind of *tert*-phosphine ligand used. ^{31}P-NMR spectrum of the catalyst solution showed a peak at 33 ppm ($J_{P-H} = 458$ Hz): the corresponding peak on ^1H-NMR was observed at 4.3 ppm which could be confirmed by 2D NMR ($^{31}P–^1H$, COSY) and ^1H-NMR with ^{31}P (33 ppm) selective decoupling. The ^{27}Al-NMR spectrum of the same solution showed a relatively sharp resonance at 60 ppm. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Propylene dimerization; Nickel–phosphine complexes; ^{31}P-NMR; ^{27}Al-NMR

1. Introduction

C_6 olefins are important key intermediates as pharmaceuticals, agricultural chemicals, perfumes, and monomers [1–23]. [2] Efficient synthesis of C_6 olefins by catalytic oligomerization has thus been one of the most attractive subjects in the field of catalysis. In particular, considerable attention has been paid to the dimerization of propylene using nickel–phosphine catalysts [24–35], because the reaction proceeds with relatively high selectivity of the desired product not only by varying the

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phosphine ligand but also by varying additives. One of the interesting approaches is the selective synthesis of DMBs by nickel–phosphine catalyst, especially composed of nickel naphthenate (NIN), *tert*-phosphine, trialkylaluminum in the presence of halogenated phenols such as 2,4,6-trichlorophenol (TCP) [35]. However, the more efficient catalyst system which shows both the remarkable catalytic activity and the higher selectivity of the desired product has still been required for constructing an advantageous catalytic process in chemical industry, because the process producing DMBs has already been commercialized by the propylene dimerization.

After extensive efforts in this context, we have discovered a new type of an efficient catalyst system containing fluorinated alcohol modified nickel–phosphine catalyst, especially in the presence of CF_3SO_3H and/or Me_2SO_4 [36]. We found that these additives were also effective for TCP-based catalyst systems [37,38]. [3] In this paper, we would like to present the detailed results for the dimerization of propylene by using a catalyst system composed of NIN, *tert*-phosphine, $AlEt_3$, isoprene, and 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) in the presence of CF_3SO_3H and/or Me_2SO_4 (Eq. (1)). In particular, we would like to present our results concerning various factors affecting the catalytic activities including the effects of various phosphine ligands and additives. We also wish to present the results for ^{31}P-, ^{27}Al-NMR measurements of the prepared catalyst solution.

Catalyst: nickel naphthenate/ tert-phosphine/ $AlEt_3$/
hexafluoroisopropanol - RSO_3H and/or R'_2SO_4

(1)
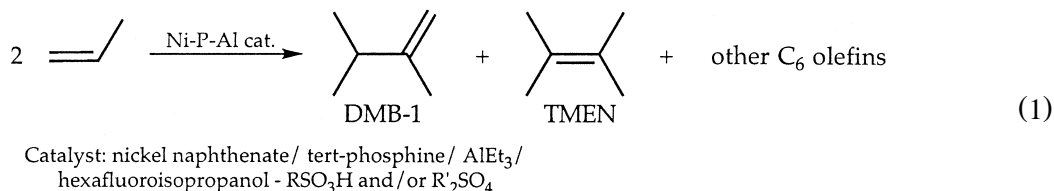
2. Experimental

All experiments were carried out under nitrogen atmosphere, or in vacuo, using a standard Schlenk technique. Toluene was used as 'freshly distilled' conditions in the presence of dried molecular sieves (3A), and was used directly from the distillation apparatus under nitrogen flow. Chemicals such as NIN, PCy_3 (Cy = cyclohexyl), $AlEt_3$, isoprene and CF_3SO_3H were purchased as reagent grades and stored under nitrogen. Preparation of the catalyst solution was performed under nitrogen atmosphere at lower than 20°C. The catalytic reactions were carried out by using an autoclave (stainless steel 100 or 500 ml, or 1.5 liter scale).

Standard procedure for the preparation of the catalyst solution (run 9 in Table 2): in a 50-ml Schlenk tube which had been cooled to 5°C and filled with nitrogen, 1.35 ml of toluene containing 0.10 mmol of NIN, 0.10 mmol of PCy_3 (20% toluene solution) and 8.0 mmol of isoprene were charged, followed by the addition of 1.0 ml of toluene containing 1.0 mmol of $AlEt_3$. The reaction mixture was stirred at room temperature, then CF_3SO_3H (0.10 mmol) and 1.5 ml of toluene containing 1.5 mmol of HFIP was added into the solution. The prepared catalyst solution and the

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[3] We have also recently discovered another catalyst system that consisted of NIN/PCy_3/$AlEt_3$/TCP in the presence of CF_3SO_3H and/or dialkyl sulfates (and/or water). However, a significant decrease of the selectivity of DMBs was observed in some catalyst systems, although these catalyst systems showed high catalytic activities [38].

additional toluene (18 ml) were added by using hypodermic syringe into an autoclave (500-ml scale) filled with nitrogen (15°C).

Propylene was then injected to a pressure of 4 kg/cm^2 to react at 18–20°C. After the reaction, the mixture was cooled to 5°C, followed by purging unreacted propylene slowly from the solution. The reaction products were then analyzed by gas chromatography (column: sebaconitrile 25% on Shimalite 3.1 m, and/or DB-1 0.25 μmϕ, 30 m). The reaction products were identified by comparisons of GC chromatograms with the corresponding authentic samples, GC-MS, and ^{1}H-NMR after an isolation.

The amounts of C$_6$ olefins such as 2,3-dimethyl-1-butene (DMB-1), 2,3-dimethyl-2-butene (tetra-methylethylene, TMEN), 4-methyl-1-pentene (4M1P), *cis-/trans*-4-methyl-2-pentene (4M2P), 2-methyl-1-pentene (2M1P), 2-methyl-2-pentene (2M2P), and hexenes (Hex) were analyzed quantitatively by GC using an internal standard (*n*-pentane) after purging unreacted propylene. Propylene remained in the resultant reaction mixture was also analyzed quantitatively in the same manner. Turnover number and selectivities used in this paper were calculated as follows:

$$\text{turnover number} = [\text{molar amount of dimers or DMBs produced}/\text{molar amount of Ni used}]$$

$$\text{selectivity of dimers}\,(\%) = [\text{amount of C}_6 \text{ olefins produced}\,(\text{g})/\text{amount of propylene reacted}\,(\text{g})]$$
$$\times 100$$

$$(\text{amount of propylene reacted}\,(\text{g}) = \text{total weight increased after the reaction}\,(\text{g})$$
$$- \text{propylene remained in the reaction mixture}\,(\text{g}))$$

$$\text{selectivity of DMBs}\,(\%) = [\text{amount of DMBs}\,(\text{g})/\text{amount of C}_6 \text{ olefins}\,(\text{g})] \times 100.$$

^{31}P-, ^{27}Al-NMR, and ^{31}P − ^{1}H 2D NMR (COSY) spectra were recorded on a JEOL JNM-EX270 spectrometer (270.2 MHz, ^{1}H). ^{1}H-NMR spectra with ^{31}P (33 ppm) selective decoupling was recorded on JEOL JNM-GX500 spectrometer (500 MHz, ^{1}H). NMR operating frequencies and reference standards for heteronuclei on the scale of ^{1}H (270.2 MHz, SiMe$_4$ at 0.00 ppm) are as follows: ^{31}P (109.4 MHz, H$_3$PO$_4$ 0.00 ppm), and ^{27}Al (70.4 MHz, Al(NO$_3$)$_3$ 0.00 ppm). Chemical shifts are in ppm, and coupling constants and line width are in Hertz. All spectra were acquired at < 25°C unless otherwise noted. Proton NMR were referenced using the partially deuterated solvents (toluene-d$_8$) as an internal reference. ^{31}P- and ^{27}Al-NMR spectra were referenced externally.

The ^{31}P- or ^{27}Al-NMR samples of the catalyst solution consisted of NIN, PCy$_3$, AlEt$_3$, HFIP, CF$_3$SO$_3$H, isoprene (molar ratios = 1/1/10/15/1/80, respectively, partly diluted with toluene-d$_8$) were prepared at lower than 0°C (see standard procedure for the preparation of the catalyst solution). Samples for ^{31}P–^{1}H 2D NMR (COSY) spectra and ^{1}H-NMR spectra with ^{31}P selective decoupling were prepared in the same manner except that NIN, PCy$_3$ and HFIP were not diluted with toluene, and that AlEt$_3$ was diluted with toluene-d$_8$.

3. Results and discussion

3.1. Efficient dimerization of propylene by fluorinated alcohol modified nickel–phosphine catalyst system in the presence of sulfonic acid and / or dialkyl sulfates

3.1.1. Effect of MeSO$_3$H, CF$_3$SO$_3$H, or ME$_2$SO$_4$

The catalytic dimerization of propylene proceeded upon the addition of HFIP (runs 1 and 6 in Table 1), and the turnover number for the formation of C$_6$ olefins increased by varying the HFIP/Ni

Table 1
Efficient synthesis of DMBs by dimerization of propylene using nickel–phosphine catalysts. Effect of $MeSO_3H$, CF_3SO_3H, or Me_2SO_4

Run no.	Ni/AlEt3/HFIP molar ratio[a]	Additives (molar ratio[a])	Selectivity of dimers[b] (%)	Turnover number[c]			Selectivity of DMBs[d] (%)
				Total C_6'	DMB-1	TMEN	
1	1/10/30	none	37	4150	280	3340	87
2	1/20/30	$MeSO_3H$ (7.0)	50	15410	7280	6160	87
3	1/20/30	Me_2SO_4 (2.5)	43	9320	7680	560	88
4	1/15/30	Me_2SO_4 (2.5)	44	11880	2340	7790	85
5	1/20/40	Me_2SO_4 (2.5)	53	17610	1270	13560	84
6	1/10/15	none	34	2470	2180	trace	89
7	1/10/15	$ClSO_3H$ (2.0)	97	8210	6040	10	74
8	1/10/15	CF_3SO_3eH (1.0)	65	17320	13900	60	81

Reaction conditions: NIN/PCy_3/isoprene = 1/1/80 (molar ratio), propylene 6 atm, 18–21°C, 1 h, toluene 2 ml, 100 ml autoclave, nickel 0.01 mmol (runs 1 and 6: nickel 0.02 mmol). HFIP: $(CF_3)_2CHOH$.
[a] Molar ratio based on nickel.
[b] Selectivity of dimers (%) = [amount of C_6 olefins produced (g)]/[amount of propylene reacted (g)] × 100.
[c] Turnover number = (molar amount of C_6 olefins or DMBs produced)/(molar amount of nickel used), DMB-1 = 2,3-dimethyl-1-butene, TMEN = 2,3-dimethyl-2-butene.
[d] Selectivity of DMBs (%) = selectivity of DMBs in C_6 olefins. DMBs = DMB-1 and TMEN.

molar ratio (15 → 30). On the other hand, the reaction did not take place or extremely low catalytic activity was observed without the addition of HFIP [catalyst: NIN/PCy_3/$AlEt_3$ = 1/1/20 (molar ratio)].

It is important to note that both the turnover numbers for the formation of C_6 olefins and the selectivity of dimers [(amount of C_6 olefins produced)/(amount of propylene reacted)] increased upon the addition of sulfonic acids ($MeSO_3H$ and CF_3SO_3H) or Me_2SO_4 (Table 1). Importantly, the notable enhancement in the turnover number could be achieved in the presence of CF_3SO_3H (run 8) at lower HFIP/Ni molar ratio of 15, resulting in affording DMB-1 in relatively high yield. $ClSO_3H$ was also effective to increase the turnover number, but the selectivity of DMBs decreased (74%) under the same reaction conditions (run 7). The product ratio of DMB-1/TMEN was dependent upon the HFIP/$AlEt_3$ molar ratio (e.g., ratio of DMB-1/TMEN = 7680/560 and 1270/13560 in the molar ratios of 30/20 (run 3) and 40/20 (run 5), respectively). This is probably due to that HFIP-modified Al species also act as an isomerization catalyst from DMB-1 to TMEN in the reaction mixture (Eq. (2)), as was previously demonstrated by the TCP-based catalyst. [4]

$$2 \quad \diagup\!\!\!= \xrightarrow{\text{Ni-P-Al cat.}} \quad \text{DMB-1} \quad \xrightarrow{\text{HFIP-Al cat.}} \quad \text{TMEN} \qquad (2)$$
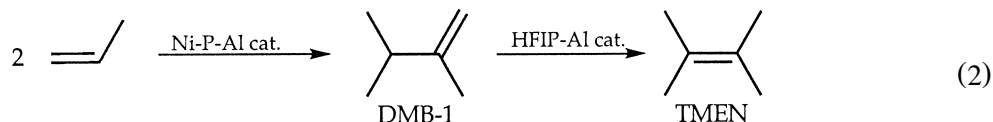
It turned out that the selectivity of C_6 olefins based on the reacted propylene increased on 500 ml scale experiments [65% (run 8, 100 ml scale) → 84% (run 9, 500 ml scale)], probably because the control of the reaction temperature would be easier on a larger reaction scale for this highly exothermic reaction. It is interesting to note that the catalyst system composed of NIN, PCy_3, $AlEt_3$, and CF_3SO_3H showed the low catalytic activity (run 11, Table 2), and the extremely low catalytic activity was observed when Ni(COD)$_2$–PCy_3 (COD = 1,5-cyclooctadiene) or Ni(COD)$_2$–PCy_3–

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[4] The similar results were introduced in Refs. [35,37,38].

Table 2
Various factors affecting the catalytic activity for dimerization of propylene

Run no.	$NIN/AlEt_3/CF_3SO_3H/HFIP/$ molar ratio[a]	Temperature (°C)	Selectivity of dimers[b] (%)	Turnover number[b]		
				Total C_6'	DMB-1	TMEN
8	1/10/1.0/15	18–21	65	17 320	13 900	60
9	1/10/1.0/15	18–20	84	19 200	14 900	140
10	1/10/1.0/15	10	80	15 000	11 540	30
11	1/10/−/15	10	31	930	420	380
12	1[d]/−/1.0/−	10	−	trace[c]	−	−
13	1[d]/−/−/−	10	−	trace[f]	−	−

Reaction conditions: NIN 0.10 mmol, PCy$_3$ 0.10 mmol, isoprene 8.0 mmol, propylene 4 atm, 1.5 h (run 9, 2 h), toluene 18 ml, 500 ml autoclave.
[a] Molar ratio based on nickel.
[b] See Table 1.
[c] Reaction conditions, see Table 1 (100-ml autoclave scale experiment).
[d] Ni(COD)$_2$ was used in place of NIN.
[e] Turnover number 36 based on GC analysis.
[f] Turnover number < 1 based on GC analysis.

Table 3
Efficient synthesis of DMBs by dimerization of propylene using nickel–phosphine catalysts. Effect of aluminum cocatalyst

Run no.	AlR_3	$Ni/AlR_3/$ $CF_3SO_3H/HFIP$ molar ratio[a]	Time (h)	C_3' (atm)	Temperature (°C)	Selectivity of dimers[b] (%)	Turnover number[b]		
							Total C_6'	DMB-1	TMEN
15	AlEt$_3$	1/8/1.0/10	1	6	18–20	67	10 600	8330	30
16	AlEt$_3$	1/10/1.0/10	1	6	18–20	66	9880	7890	20
8	AlEt$_3$	1/10/1.0/15	1	6	18–20	65	17 320	13 900	60
17	AlEt$_3$	1/10/1.2/10	1	6	18–20	72	15 700	12 600	50
18	AlEt$_3$	1/10/1.5/15	1	6	18–20	60	12 600	10 300	60
10	AlEt$_3$	1/10/1.0/15	1.5	4	10	80	15 000	11 540	30
19	Al(i-Bu)$_3$	1/10/1.0/12	1.5	4	10	70	19 100	15 800	110
20	Al(i-Bu)$_3$	1/10/1.0/10	1.5	4	10	74	21 800	17 300	60
21	Al(i-Bu)$_3$	1/10/0.8/12	1.5	4	10	73	19 000	15 370	70

Reaction conditions: NIN/PCy$_3$/isoprene = 1/1/80 (molar ratio), nickel 0.01 mmol (runs 10 and 19–21, 0.10 mmol), toluene 2 ml (runs 10 and 19–21, 18 ml), 100 ml autoclave (runs 10 and 19–21, 500 ml scale autoclave).
[a] Molar ratio based on nickel.
[b] See Table 1.

CF$_3$SO$_3$H system was used as a catalyst under the same conditions (runs 12 and 13). It is thus suggested that both AlEt$_3$ and HFIP play important roles for the high catalytic activity in this reaction. The addition of isoprene was important to stabilize the prepared catalyst solution, and that it could be easily replaced by other olefins such as 1,3-cyclooctadiene, norbornadiene or 2,3-dimethyl-1,3-butadiene. [5]

It also turned out that the molar ratio of CF$_3$SO$_3$H/Ni was important in order for this catalytic reaction to proceed at remarkable rates (Table 3), and the ratio of 1.0 was preferred. [6] The turnover number for the formation of C$_6$ olefins decreased by lowering the HFIP/AlEt$_3$ or HFIP/AlEt$_3$/Ni

[5] K. Nomura, unpublished results. The related results were introduced in Ref. [38].
[6] Turnover number for the formation of C$_6$ olefins and DMBs were 13 120 and 10 990 (selectivity of dimers 79%), respectively, when the catalytic reaction was performed under the same conditions as run 8 except that CF$_3$SO$_3$H/Ni molar ratio was 0.5 in place of 1.0.

Table 4
Dimerization of propylene yielding DMBs using nickel–phosphine catalysts in the presence of CF_3SO_3H and/or Me_2SO_4

Run no.	Additives (molar ratio[a])	Selectivity of dimers[a] (%)	Turnover number[a]			Selectivity of DMBs[a] (%)
			Total C_6'	DMB-1	TMEN	
22	H_2O[b] (8.0)	62	6860	4800	1060	85
9	CF_3SO_3H (1.0)	84	19 200	14 900	140	79
23	CF_3SO_3H (1.0)[c]	79	18 900	14 900	100	79
24	Me_2SO_4 /CF_3SO_3H (1.0/1.5)	86	25 300	19 000	650	78
25	Me_2SO_4 /CF_3SO_3H (1.0/2.5)	84	26 300	20 100	140	77
26	Et_2SO_4 /CF_3SO_3H (1.0/2.5)	86	24 000	18 000	220	76

Reaction conditions: NIN/PCy_3 /$AlEt_3$ /HFIP/isoprene = 1/1/10/15/80 (molar ratio), propylene 4 atm, 18–20°C, 2 h, nickel 0.05 mmol (runs 9–11, 0.10 mmol), 500 ml autoclave.
[a]See Table 1.
[b]Catalyst: NIN/PCy_3 /$AlEt_3$ /TCP/isoprene = 1/1/20/35/80 (molar ratio), 3 h [37].
[c]Catalyst solution was used after storing for 11 days under nitrogen atmosphere at 10 ± 5°C.

Table 5
Ni catalyzed dimerization of propylene affording 2,3-dimthelybutenes. Effect of various *tert*-phosphines (1)

Run no.	Nickel (mmol)	Temperature (°C)	*tert*-Phosphine	Selectivity of dimers[a] (%)	Turnover number[a]			Selectivity of DMBs (%)[a]
					Total C_6'	DMB-1	TMEN	
9	0.10	18–20	PCy_3	84	19 200	14 900	140	79
27	0.05	18–20	PCy_3	81	21 000	16 700	30	80
28	0.05	18–20	P(sec-Bu)$_3$[b]	81	22 700	17 500	50	77
29	0.05	10	PEt(i-Pr)$_2$	86	49 800	27 400	170	55
30	0.05	18–20	P(i-Pr)$_3$	95	34 900	26 600	130	77
31	0.05	10	P(i-Pr)$_3$[c]	86	28 000	14 600	140	53

Reaction conditions: NIN/*tert*-phosphine/$AlEt_3$ /HFIP/isoprene/CF_3SO_3H = 1/1/10/15/80/1.0 (molar ratio), nickel 0.05 mmol, 500 ml autoclave, propylene 4 atm, 18–20°C, 2 h, toluene 18 ml.
[a]See Table 1.
[b]Reaction time 1 h.
[c]CF_3SO_3H/Ni = 0.8 (molar ratio), 1 h.

molar ratios. It was also revealed that the use of Al(i-Bu)$_3$ in place of $AlEt_3$ was effective, although the optimized molar ratio was somewhat different compared with $AlEt_3$-based system (runs 19–21).

It might be interesting to note that the prepared catalyst solution was very stable for more than several days at room temperature without the decrease in the turnover number (run 23, Table 4). We believe that this fact is important from a practical viewpoint. It was also observed that the prepared catalyst solution separated in two liquid phases after standing for ca. 10 min, and became clear homogeneous red solution after ca. 1 day. Noteworthy is that the lower phase (deep purple–red), which showed higher phosphorus concentration (by ^{31}P-NMR) than upper portion (pale red), exhibited much higher catalytic activity by volume for the propylene dimerization than the upper phase. [7] This results suggest that phosphine-coordinated nickel species play important roles for the dimerization, as was previously reported [24–34].

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[7] The same spectra were observed by ^{31}P-NMR in both liquid phases. The ratio of the reaction product from upper/lower portion by the same volume (by volume of each solution) was ca. > 60/1. The prepared catalyst solution became clear homogeneous red–purple solution after ca. 1 day.

Table 6
Efficient catalytic dimerization of propylene by the nickel–phosphine catalysts. Effect of various *tert*-phosphines (2)

Run no.	*tert*-Phosphine	Reaction conditions	Selectivity of dimers[a] (%)	Turnover number (TON)[a]					
				Total C6′[a]	DMB-1	TMEN[a]	2M1P[b]	2M2P[b]	4M1,2P[b]
8	PCy$_3$	A	65	17 300	13 900	60	1870	170	1140
27	PCy$_3$	B	81	21 000	16 700	30	1700	170	220
32	P(*i*-Pr)$_3$	A	76	16 500	12 200	30	1750	170	2200
33	PEt$_3$	A	89	14 700	5670	150	3600	2720	2300
34	PEt$_2$Ph	A	92	20 900	5560	270	4700	5220	4050
35	P(*n*-Bu)$_3$	B	77	46 700	13 700	2100	5700	14 400	10 600

Reaction conditions: NIN/*tert*-phosphine/AlEt$_3$/HFIP/isoprene/CF$_3$SO$_3$H = 1/1/10/15/80/1.0 (molar ratio). Condition A: nickel 0.01 mmol, 100 ml autoclave, propylene 6 atm, 18–21°C, 1 h, toluene 2 ml. Condition B: nickel 0.05 mmol, 500 ml autoclave, propylene 4 atm, 18–20°C, 2 h, toluene 18 ml.
[a]See Table 1.
[b]See Eq. (3).

It is also important to note that turnover number for the formation of C$_6$ olefins further enhanced upon the combination of Me$_2$SO$_4$ and CF$_3$SO$_3$H (Table 4, runs 24–26). The optimized molar ratio of these effective additives was 1.0/2.5 (Me$_2$SO$_4$/CF$_3$SO$_3$H), and these results presume that the role of these additives are different.

### 3.1.2. Effect of various tert-phosphines.

As demonstrated previously [24–26,28–34], the reaction products from the propylene dimerization catalyzed by nickel–phosphine complexes containing bulky *tert*-phosphine gave DMBs as the major products. In order to increase the selectivity of DMBs in the formed C$_6$ olefins as well as to explore the role of *tert*-phosphine in the present catalyst system (NIN, *tert*-phosphine, AlEt$_3$, isoprene, HFIP, and CF$_3$SO$_3$H), we employed the catalytic reactions with the use of various bulky *tert*-phosphines.

It was revealed that DMBs were the major products in the P(*sec*-Bu)$_3$- and P(*i*-Pr)$_3$-based catalyst system (runs 28 and 30, respectively, Table 5), although the selectivity of DMBs in C$_6$ olefins decreased in the PEt(*i*-Pr)$_2$-based catalyst which showed highest turnover number for the formation of

Scheme 1.
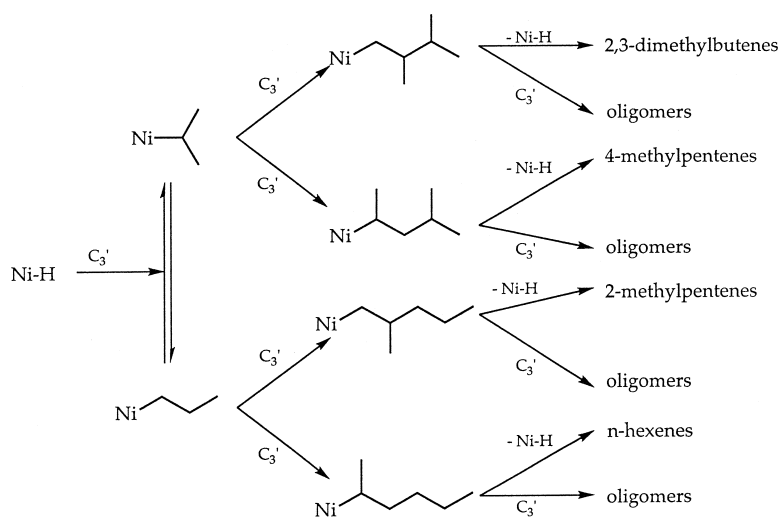
C_6 olefins among these catalyst systems (run 29). The selectivity of both C_6 olefins and DMBs in dimers decreased significantly by varying the molar ratio (CF_3SO_3H/Ni) or reaction temperature in the case of $P(i\text{-}Pr)_3$-based system (runs 30–31).

We further explored the effect of various *tert*-phosphine ligands on the propylene dimerization using the present catalyst system. It turned out that the product distributions in C_6 olefins depended upon the kind of the *tert*-phosphine used in these catalysts (Table 6), and that the tendency of the distributions was almost similar to that previously reported by π-allyl nickel–phosphine catalyst [24,34].

$$\text{(3)}$$
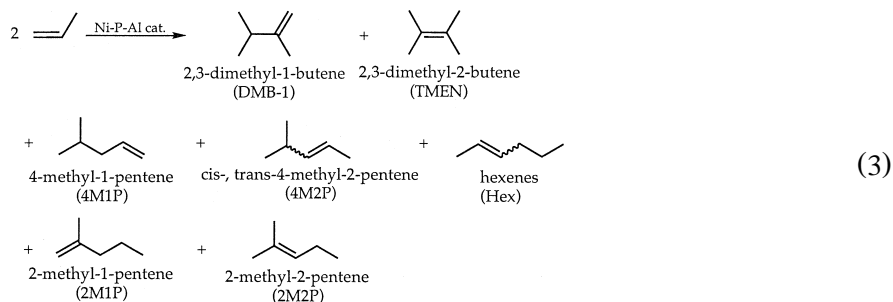
This result suggests that the role of tertiary phosphines in the catalytic cycle would be to control the selectivity for inserting olefins to the catalytically-active metal center (Scheme 1), as was previously postulated [24–26,34]. The turnover number for the formation of C_6 olefins increased in the order (100-ml scale reaction, conditions A in Table 6): PEt_2Ph (20 900 turnovers) > PCy_3 (17 300 turnovers), $P(i\text{-}Pr)_3$ (16 500 turnovers) > PEt_3 (14 700 turnovers). However, the turnover number changed by optimized both the molar ratio and the reaction conditions. [8]

Taking into account the above results (Tables 1–6), it is clear that CF_3SO_3H is an effective additive to increase both the turnover number and the selectivity of C_6 olefins for this catalytic reaction. However, the exact role of strong sulfonic acid and/or dialkyl sulfates is not clear at this moment. Since the product distributions in C_6 olefins depended upon the kind of the *tert*-phosphine ligand as was previously postulated, also since the selectivity of C_6 olefins increased upon the addition of sulfonic acid, therefore, these additives might assist the elimination of the product (C_6 olefins) from the metal center.

3.1.3. Efficient dimerization of propylene affording 2,3-dimethyl-1-butenes by HFIP-modified Ni–PCy_3–$AlEt_3$–CF_3SO_3H catalyst

It should be noted that the turnover number for the formation of C_6 olefins or DMBs increased on a larger reaction scale experiment (1.5 litter scale, Table 7). The selectivity of dimers and the turnover number decreased at higher reaction temperature (runs 36–38). The turnover number of 56 210 has been achieved by adding the catalyst in several portions into the reaction solution (run 41). The turnover number further increased at higher propylene pressure: the larger turnover number will be

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[8] The order in turnover number for the formation of C_6 olefins using 500-ml scale reaction (Tables 5 and 6) was as follows: $PEt(i\text{-}Pr)_2$ (49 800 turnovers) > $P(n\text{-}Bu)_3$ (46 700 turnovers) > $P(i\text{-}Pr)_3$ (34 900 turnovers) > $P(sec\text{-}Bu)_3$ (22 700 turnovers), PCy_3 (21 000 turnovers). We presume that an electronic nature of phosphine ligands is important in order for this reaction to exhibit the remarkable catalytic activity. However, significant decrease of the turnover number was observed by varying the molar ratios or the reaction temperature in $P(i\text{-}Pr)_3$-based catalyst.

Table 7
Efficient dimerization of propylene affording DMBs by CF_3SO_3H-added nickel–phosphine catalysts

Run no.	Ni (mmol)	C'_3 (atm)	Temper- ature (°C)	C'_3 reacted kg-C'_3/mol-Ni[a]	Selectivity of dimers[b] (%)	Turnover number[b]		Selectivity of DMBs in C'_6[b] (%)
						Total C'_6	DMBs	
9[c]	0.10	4	18–20	1920	84	19 200	15 040	79
36	0.15	2	5	3218	86	32 950	25 600	78
37	0.15	2	15	2248	82	21 940	17 050	78
38	0.15	2	25	2311	78	21 460	16 290	76
39	0.10	3	10	5459	75	48 740	38 210	78
40	0.15[d]	3	10	4555	83	45 010	35 740	79
41	0.15[d]	4	10	6053	78	56 210	43 840	78

Reaction conditions: NIN/PCy_3/AlEt$_3$/HFIP/isoprene/CF_3SO_3H = 1/1/10/15/80/1.0 (molar ratio), 1.5 liter autoclave, toluene 40 ml, 2 h.
[a] Amount of reacted propylene (kg)/mol-Ni.
[b] See Table 1.
[c] See Table 2 (500 ml scale experiment).
[d] The catalyst solution was added by three portions (every 30 min), nickel 0.15 mmol, toluene 36 ml, total reaction time 3 h.

expected at higher propylene pressures and/or the optimized reaction conditions. The selectivity of DMBs in C_6 olefins was ca. 80% which was almost the same as that using a previous TCP-modified catalyst system [35], or higher than that by a catalyst composed of Ni(acac)$_2$, PCy_3, and Et$_2$AlCl (ca. < 65%, acac = acetylacetonato) [28–33,35,39]. We believe that this fact is very important from the practical viewpoint, because TMEN, which can be easily isomerized from DMB-1 [40], can be thus obtained in high purity (> 99%) directly from the reaction mixture by a fractional distillation because of the major composition in C_6 olefins and its highest boiling point among other C_6 olefins in the reaction mixture. [9] It is also possible to obtain DMB-1 in high purity in the same manner.

4. NMR Studies of the prepared catalyst solution

As suggested from the above results, phosphine-coordinated nickel species play crucial roles for the dimerization of propylene. We thus measured various ^{1}H-, ^{31}P-, and ^{27}Al-NMR spectra of the prepared catalyst solution to obtain an information concerning the active species.

It was revealed that the solution consisted of NIN, PCy_3, and AlEt$_3$ in the presence of isoprene (molar ratios 1/1/10/80, respectively) showed a resonance at 2.2 ppm on ^{31}P-NMR in the large extent. This chemical shift is in the range between Ni(COD)$_2$–PCy_3 (10 ppm) and Ni(COD)$_2$–PCy_3–AlEt$_3$ (−2.5 ppm). In addition, we observed the evolution of ethane (ca. 2 equiv. to nickel by GC analysis) after the addition of AlEt$_3$. These results support the formation of nickel (O)–PCy_3–isoprene species.

It is interesting to note that the ^{31}P-NMR spectrum of the prepared catalyst solution composed of NIN, PCy_3, AlEt$_3$, isoprene, CF_3SO_3H, and HFIP showed almost one peak at 33 ppm which had 458 Hz of P–H coupling (Fig. 1c and d). This value (J_{P-H} = 458 Hz) was larger than $^2J_{P-H}$ coupling of

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[9] Boiling points of C_6 olefins in the reaction mixture are as follows: 2,3-dimethyl-1-butene 55.7°C, *cis*-4-methyl-2-pentene 56.4°C, 2-methyl-1-pentene 62.1°C, 2-methyl-2-pentene 67.3°C, and 2,3-dimethyl-2-butene 73.2°C, respectively.
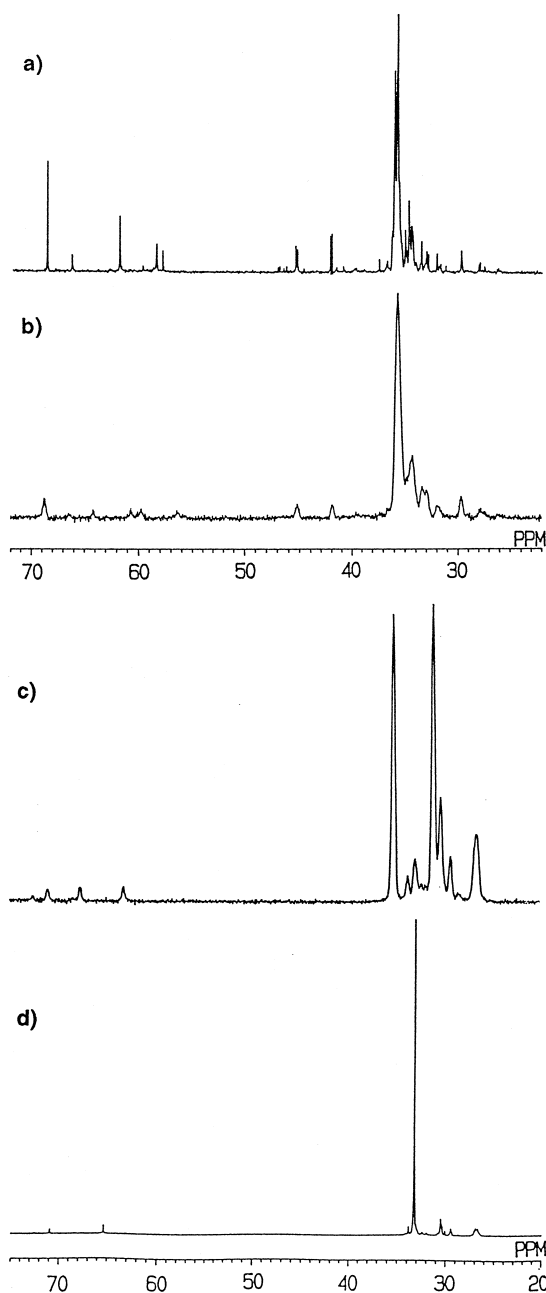
Fig. 1. ^{31}P-NMR spectra (toluene-d$_8$, non-decoupling) of (a) NIN/PCy$_3$/AlEt$_3$/isoprene/CF$_3$SO$_3$H (molar ratio = 1/1/10/80/1, respectively); (b) same solution of (a) (^{1}H complete decoupling); (c) NIN/PCy$_3$/AlEt$_3$/isoprene/CF$_3$SO$_3$H/HFIP (molar ratio = 1/1/10/80/1/15, respectively, non-decoupling); (d) same solution of (c) (^{1}H complete decoupling).

trans-(Cy$_3$P)$_2$NiHCl complex ($^2J_{P-H(cis)}$ = 73.5 Hz) [24,41–49] and was almost similar to that of P–H species such as dicyclohexylphosphine ($^1J_{P-H}$ = 429 Hz). It was revealed that the peak ascribed to the hydrogen was observed at 4.3 ppm on ^{1}H-NMR, which could be confirmed by ^{31}P–^{1}H 2D NMR (COSY) spectrum and ^{1}H-NMR spectra with ^{31}P (33 ppm) selective decoupling (Fig. 2). These
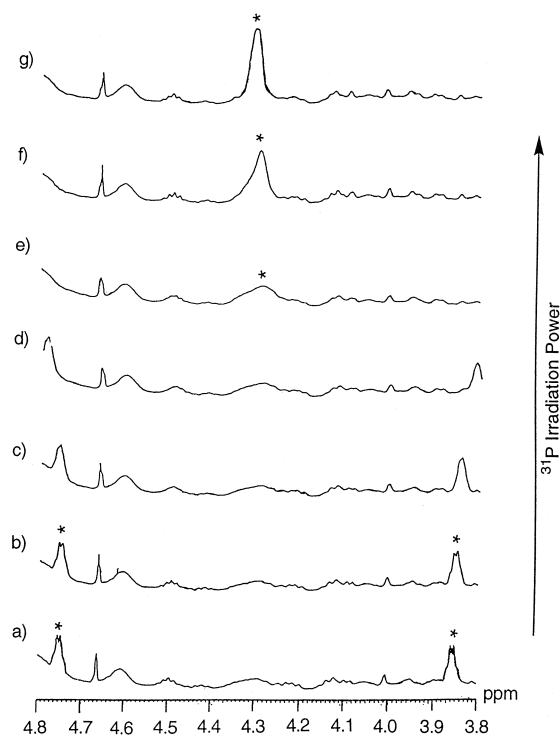
Fig. 2. ^{1}H-NMR spectra (with ^{31}P selective decoupling) of the prepared catalyst solution composed of NIN/PCy$_3$/AlEt$_3$/isoprene/ CF$_3$SO$_3$H/HFIP (molar ratio = 1/1/10/80/1/15, respectively). (a) normal (toluene-d$_8$); (b)–(g) spectra with ^{31}P (33 ppm) selective decoupling. (b) → (g): stronger irradiation power. ∗ corresponded ^{1}H peak(s) coupled with phosphorus.
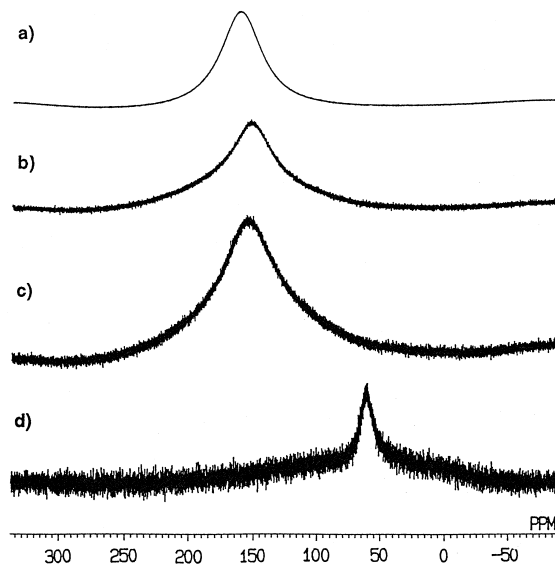

Fig. 3. ^{27}Al-NMR spectra (toluene-d$_8$) of (a) AlEt$_3$; (b) NIN/PCy$_3$/AlEt$_3$/ isoprene (molar ratio = 1/1/10/80, respectively); (c) NIN/PCy$_3$/AlEt$_3$/isoprene/CF$_3$SO$_3$H (molar ratio = 1/1/10/80/1, respectively); NIN/PCy$_3$/AlEt$_3$/isoprene/CF$_3$SO$_3$H/HFIP (molar ratio = 1/1/10/80/1/15, respectively).
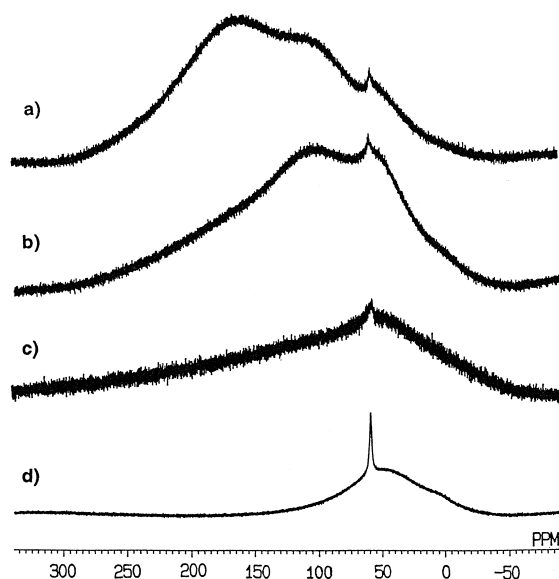
Fig. 4. ^{27}Al-NMR spectra (toluene-d_8) of mixed solutions composed of HFIP and AlEt$_3$ in the various molar ratios. Molar ratio of HFIP/AlEt$_3$ = (a) 1/1, (b) 3/2, (c) 3/1, and (d) 10/1, respectively.

results might be important to understand the catalytically active species, but this species would be assigned to a cationic nickel-hydride species (H–Ni$^+$–P) or other cationic species (ex. Ni–P$^+$–H) species is not clear at this moment. [10] It was also revealed that the ^{31}P-NMR spectrum of the prepared solution consisted of NIN, PCy$_3$, AlEt$_3$, isoprene, and CF$_3$SO$_3$H showed a peak that has a smaller P–H coupling constant ($J_{P–H}$ = 33 Hz, Fig. 1a and b). This coupling constant value might be attributed to a cis-$^2J_{P–H}$ coupling of P–Ni–H species, but we do not have enough evidence for the characterization yet.

It turned out that a relatively sharp resonance at 60 ppm was observed on ^{27}Al-NMR spectrum of the prepared catalyst solution (Fig. 3d), although a broad peak which was similar to AlEt$_3$ was observed in the solutions consisted of both NIN/PCy$_3$/AlEt$_3$/CF$_3$SO$_3$H and NIN/PCy$_3$/AlEt$_3$ in the presence of isoprene. This peak (60 ppm) could not be observed by measuring the mixed solutions of AlEt$_3$ and HFIP except that a large excess amount of HFIP was added to Al (Fig. 4d). These results suggest that aluminum species partly modified by HFIP would be interacted with nickel cationic species such as [Ni–P]$^+$[Al]$^-$. However, the exact species formed in this catalyst solution is not clear at this moment.

5. Concluding remarks

In conclusion, this paper can be summarized as follows.

(1) The present nickel–phosphine catalyst system consisted of NIN, *tert*-phosphine, AlEt$_3$, HFIP, CF$_3$SO$_3$H, and isoprene showed a remarkable turnover number for the formation of C$_6$ olefins for the

dimerization of propylene. The catalytic reaction also proceeds with high selectivity of the desired products such as DMBs (*tert*-phosphine = PCy_3). The turnover number further increased upon the addition of both Me_2SO_4 and CF_3SO_3H (Tables 1–4).

(2) The turnover number of 56 210 has been achieved on a large scale experiment (1.5 liter), and the turnover number increased at higher propylene pressure (Table 7). The prepared catalyst solution was very stable for more than 10 days without decreasing in the catalytic activity (Table 4).

(3) The product distributions in C_6 olefins depended upon the kind of the phosphine ligands used in this catalyst system (Tables 5 and 6).

(4) ^{31}P-NMR spectrum of the prepared catalyst solution showed a peak at 33 ppm which had P–H coupling of 458 Hz (Fig. 1). The peak ascribed to the hydrogen could be observed at 4.3 ppm on ^{1}H-NMR, which could be confirmed by ^{31}P–^{1}H 2D NMR (COSY) spectrum and ^{1}H-NMR spectra with ^{31}P (33 ppm) selective decoupling (Fig. 2). The ^{27}Al-NMR spectra of the same solution showed a relatively sharp resonance at 60 ppm (Fig. 3), although a broad resonance was observed from the mixed solutions composed of HFIP and $AlEt_3$ in various molar ratios.

Acknowledgements

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