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Synthesis of 2,3-Dimethylbutenes by Dimerization of Propene Using Highly Active Nickel-Phosphine Catalysts in the Presence of Sulfonic Acids and/or Dialkyl Sulfates

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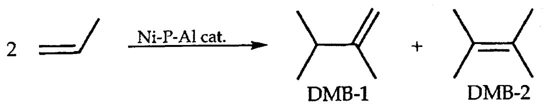
A nickel-phosphine catalyst system consisting of nickel naphthenate, P(cyclo-C_6H_{11})$_3$, $AlEt_3$, and 2,4,6-trichlorophenol (TCP) in the presence of sulfonic acids (CF_3SO_3H and $MeSO_3H$) or dialkyl sulfates (Me_2SO_4 and Et_2SO_4) exhibits remarkable catalytic activity for the dimerization of propene. The catalytic activity (turnover number (TON) for the formation of C_6 olefins or 2,3-dimethylbutenes) was enhanced when the catalyst was combined with effective additives, such as Et_2SO_4 and $MeSO_3H$. The reaction products consisted of 2,3-dimethyl-1-butene (DMB-1) and/or 2,3-dimethyl-2-butene (DMB-2) in high yields (selectivity of dimers based on the reacted propene = 70—80%: selectivity of 2,3-dimethylbutenes in C_6 olefins = 78—80%). The ratio of DMB-1/DMB-2 could be controlled by varying the molar ratios of the catalyst ingredients without decreasing in the turnover numbers. Although CF_3SO_3H was found to be the best additive as far as the catalytic activity and the selectivity of dimers (94—99%) are concerned, the selectivity of 2,3-dimethylbutenes in C_6 olefins decreased. The addition of a small amount of water was also effective to enhance the catalytic activity: The turnover number for the formation of 2,3-dimethylbutenes was raised from 7050 to 30360.

2,3-Dimethylbutenes [2,3-dimethyl-1-butene (DMB-1) and 2,3-dimethyl-2-butene (DMB-2)] are important intermediates required for pharmaceuticals, agricultural chemicals, perfumes, and other fine chemicals (Scheme 1).[1)] Extensive studies have thus been directed to their efficient syntheses and their derivatives, and some of them are now widely used in the chemical industry.[2—6)]

Many studies have been reported concerning the dimerization of propene yielding 2,3-dimethylbutenes, especially in the presence of various nickel-phosphine catalysts, not only to increase both the catalytic activity and selectivity of the desired compounds, but also to develop the commercial use of these products.[7—9)] One of the interesting practical approaches in this project is, we believe, the selective synthesis of 2,3-dimethylbutenes (DMB-1 or DMB-2) using a catalyst system consisting of nickel naphthenate, PCy_3 (Cy: cyclohexyl), $AlEt_3$, and 2,4,6-trichlorophenol (TCP) in the presence of a small amount of water.[9)] In this case, not only the desired DMB-1 or DMB-2 can be obtained in good yields, but also the ratio DMB-1/DMB-2 can be controlled by varying the molar ratios of the catalyst ingredients. It is thus possible to have 2,3-dimethyl-2-butene (DMB-2) with very high purity (> 99%) in hand by a fractional distillation of the reaction mixture due to the higher composition of 2,3-dimethylbutenes in C_6 olefins (> 80%) than that obtained by using a previous catalyst system consisting of Ni(acac)$_2$, PCy_3, and Et_2AlCl (< 58—65%).[7,9a)] 2,3-Dimethyl-1-butene was also available with high purity in the same manner.

In the light of this background, we started to investigate propene dimerization, because it still remains one of the desirable goals needed to improve both the catalytic activity and selectivity; a chemical process producing 2,3-dimethylbutenes by propene dimerization has already been accomplished, and the replacement of the present catalyst with a more efficient one might be a better solution.

After extensive efforts in this context, we discovered that a cationic nickel species exhibits very high catalytic activity in the presence of sulfonic acid and/or dialkyl sulfate.[10,11)] In this paper, we present detailed results concerning catalyst systems yielding 2,3-dimethylbutenes (Eq. 1).



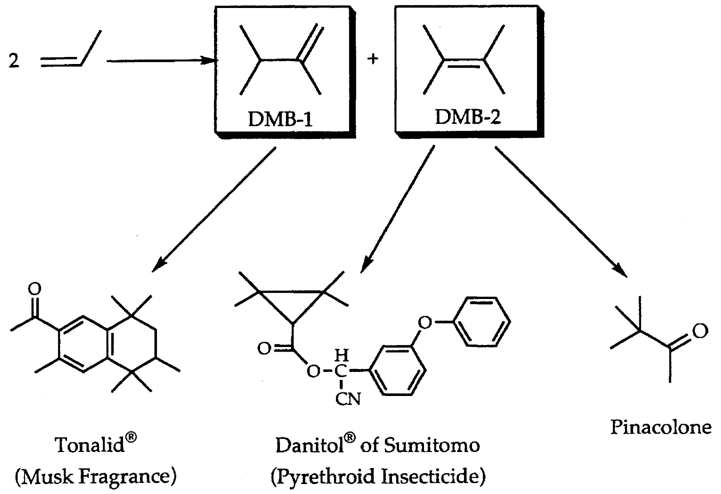
(1)

Catalyst: nickel naphthenate/ PCy_3/ $AlEt_3$/
2,4,6-trichlorophenol - RSO_3H etc.

Experimental

All experiments were carried out under a nitrogen atmosphere, or in vacuo, using a standard Schlenk technique. Toluene was freshly distilled in the presence of dried molecular sieves (3A). Chemicals such as nickel naphthenate, PCy_3, $AlEt_3$, isoprene, and CF_3SO_3H were purchased as reagent grades and stored under nitrogen. A catalyst solution was prepared under a nitrogen atmosphere at a temperature lower than 20 °C. The catalytic reactions were carried out using an autoclave (stainless steel, 100 or 500 ml scale).

The standard procedure for preparing the catalyst (Table 1, Run 3): In a 50 ml Schlenk tube filled with nitrogen were placed 1.35 ml



Scheme 1.

Table 1. Effect of Sulfonic Acid on Dimerization of Propene with Nickel-Phosphine Catalysts

Run No.	Additives (molar ratio)	Selectivity of Dimers[a)]	Turnovers (TON)[b)] Total C_6'	Turnovers (TON)[b)] DMBs	Selectivity of DMBs in C_6'[c)]
1	None (—)	66	5050	4160	83
2	H_2O (8.0)	62	6860	5860	86
3	$MeSO_3H$ (3.0)	75	8790	7050	80
4	$MeSO_3H$ (5.0)	77	11000	8780	80
5[d)]	CF_3SO_3H (1.0)	95	28800	17700	61

Reaction conditions: Nickel naphthenate/P(cyclo-C_6H_{11})$_3$/$AlEt_3$/isoprene/2,4,6-trichlorophenol (TCP)=1/1/20/80/35 (molar ratio), nickel 0.10 mmol, propene 4 atm, 18—20 °C, 3 h, toluene 18 ml, 500 ml autoclave. a) Selectivity of dimers (%)=[amount of dimers produced (g)/amount of propene reacted (g)]×100. b) TON=[amount of C_6 olefins or 2,3-dimethylbutenes (DMBs) produced (mmol)/amount of nickel metal used (mmol)]. c) Selectivity of DMBs (%)=[amount of DMBs (g)/amount of C_6' (g)]×100. d) 10 °C, 1 h.

of toluene containing 0.1 mmol of nickel naphthenate, 0.1 mmol of PCy_3 (20% toluene solution), and 8.0 mmol of isoprene, followed by the addition of 2.0 ml of toluene containing 2.0 mmol of $AlEt_3$ at <20°C. Then, $MeSO_3H$ (0.3 mmol) and 3.5 ml of toluene containing 3.5 mmol of 2,4,6-trichlorophenol were added to the stirred reaction mixture. The thus-obtained catalyst solution and additional toluene (18 ml) were introduced into an autoclave (500 ml scale) filled with nitrogen (15 °C) by means of a hypodermic syringe.

Propene was then led to the autoclave to indicate an internal pressure of 4 kg cm^{-2}, being reacted at 18—20 °C. After the reaction, the mixture was cooled to 5 °C, followed by slowly evaporating unreacted propene 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 isolation.

The amounts of C_6 olefins such as 2,3-dimethyl-1-butene, 2, 3-dimethyl-2-butene, 4-methyl-1-pentene, *cis*-/*trans*-4-methyl-2-pentene, 2-methyl-1-pentene, 2-methyl-2-pentene, and hexenes were analyzed quantitatively by GC based on an internal-standard method (pentane) after purging any unreacted propene. Propene remaining in the reaction mixture was also analyzed quantitatively in the same manner. The turnover number (TON) and selectivity used in this paper were calculated as follows: turnover number (Turnovers, TON)=[molar amount of dimers or 2,3-dimethylbutenes produced/molar amount of nickel metal used]; selectivity of dimers (%)=[amount of C_6 olefins produced (g)/amount of propene reacted (g)]×100 in which the amount of propene reacted (g) can be calculated as the difference between the weight of the reaction product (g) and propene remained in the product solution (g); the selectivity of 2,3-dimethylbutenes (DMBs) (%)=[the amount of DMBs (g)/the amount of C_6 olefins (g)]×100.

Results and Discussion

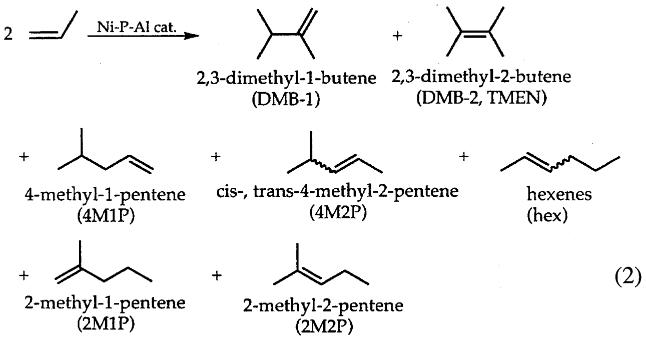
It has been reported that a catalyst system consisting of nickel naphthenate, tertiary phosphine, $AlEt_3$, and 2,4,6-trichlorophenol (TCP) shows moderate catalytic activity for the dimerization of propene.[9)] On the other hand, the reaction did not take place or become extremely sluggish without the addition of trichlorophenol, although the reaction indeed proceeded by using a catalyst system consisting of Ni(acac)$_2$, PCy_3, and Et_2AlCl.[7,9a)]

1. Efficient Synthesis of 2,3-Dimethylbutenes by Dimerization of Propene Using Nickel-Phosphine Catalyst System. **1-1. Effect of Sulfonic Acid Additives.** It should be noted that the turnover number for the formation of C_6 olefins increased upon the addition of a small amount of $MeSO_3H$ (Table 1, Run 3). The selectivity of dimers (C_6 olefins produced/propene reacted) increased to a small extent (from 66 to 75%) by using this acid, whereas the selectivity decreased by adding a small amount of water (Table 1, Run 2 and 3).[9a] It was thus possible to obtain 2,3-dimethylbutenes in relatively high yield (>60%). It turned out that the addition of CF_3SO_3H was so effective that both the turnover number and the selectivity of dimers very much increased, though the selectivity of 2,3-dimethylbutenes in C_6 olefins considerably decreased (ca. 80%→60%). Other sulfonic acids, such as $ClSO_3H$, was also found to be effective. Various carboxylic acids or acid anhydrides such as CF_3CO_2H, CCl_3CO_2H, $CHCl_2CO_2H$, CH_3CO_2H, $(CF_3CO)_2O$, and $(CCl_3CO)_2O$ were also examined, but showed almost no positive effect.

The rate of these catalytic reactions was notably fast, especially at the initial stage of the reaction (less than 1 h), but became gradually slow, probably due to dilution of the catalyst concentration by the reaction products, or due to deactivation of the catalytically-active species in the reaction mixture. The selectivity of the products did not change during this catalytic reaction. Both the turnover numbers and the selectivity for the formation of C_6 olefins almost remained constant when the molar ratio (2,4,6-trichlorophenol/Ni) was kept between 30 and 70, as was previously reported.[9a] The molar ratios for other components of the catalyst were optimized in terms of the catalytic activity as well as the stability of the catalyst solution. It turned out that isoprene played an important role in improving the stability of the catalyst solution at room temperature. Other phenols in place of 2,4,6-trichlorophenol were also examined, and we found that chlorophenol derivatives such as tri-, tetra-, or pentachlorophenol were likewise effective.[9a]

1-2. Effect of Me_2SO_4 or Et_2SO_4, and Product Distributions in Catalytic Reactions. A remarkable increase in the turnover number for the formation of C_6 olefins was observed upon the addition of dialkyl sulfates, such as Me_2SO_4 or Et_2SO_4 (Table 2, Runs 6—8). The selectivity of 2,3-dimethylbutenes in dimers almost remained constant for these catalyst systems (75—79%). It is strongly recommended that a small amount of these additives should be added, because it turned out that an excess amount of these additives would result in a decrease in the turnover numbers.

2,3-Dimethylbutenes were the major products among C_6 olefins in these catalytic reactions (Eq. 2, Table 2), and the DMB-1/DMB-2 ratio could be controlled by varying the molar ratios of the catalyst ingredients ($AlEt_3$/2,4,6-trichlorophenol (TCP)/Me_2SO_4). This is due to the fact that TCP-modified aluminum species can also act as an isomerization catalyst from DMB-1 to DMB-2 without decreasing the turnover numbers (Eq. 3), as previously reported.[9a] The molar ratios shown in Runs 6 and 7 (Table 2) were optimized for DMB-1 and DMB-2, respectively, which, however, are not the same as those in the previous catalysts.[9a]



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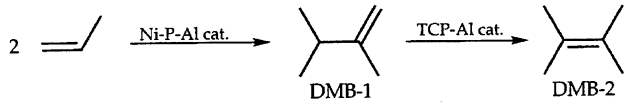

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Table 3 summarizes the results obtained at higher propene pressure (6 atm) than that employed in the standard procedure (see Experimental) by the nickel catalysts, especially with Me_2SO_4 or Et_2SO_4. A remarkable increase in the turnover number for the formation of 2,3-dimethylbutenes was observed upon the addition of a small amount of Me_2SO_4 or Et_2SO_4; also, the turnover number greatly increased in these cases, which were conducted at higher propene pressures. DMB-1 was the major product in these catalytic reactions, although a catalyst with the molar ratio of TCP/Ni=70 usually gave DMB-2 as a major product by isomerization (cf. Table 2). This was probably due to the fact that the dimerization rate by this nickel-phosphine catalyst was much faster than the isomerization rate by the TCP-modified aluminum species involved in this catalyst under these reaction conditions. We think that the effect of the solvent is not necessarily

Table 2. Effect of Me_2SO_4 or Et_2SO_4 on Dimerization of Propene with Nickel-Phosphine Catalysts, and Product Distribution of C_6 Olefins in the Catalytic Reactions

Run No.	$Ni/TCP/AlEt_3/MeSO_3H/Me_2SO_4$ (molar ratio)	Selectivity of dimers[a]	Turnovers (TON)[a]			Selectivity of DMBs in C_6'[a]
			Total C_6'	DMB-1	DMB-2	
1[a]	1/35/20/—/—	66	5050	4140	20	83
4[a]	1/35/20/5.0/—	77	11000	8680	100	80
6	1/50/15/—/2.3	68	16400	11000	1900	77
7	1/70/20/—/3.0	68	18100	2160	11900	79
8[b]	1/50/20/—/1.4	67	9400	5000	2030	75

Reaction conditions: Nickel naphthenate/$P(cyclo\text{-}C_6H_{11})_3$/isoprene=1/1/80 (molar ratio), nickel 0.05 mmol (Runs 1 and 4: 0.10 mmol), propene 4 atm, 18—20 °C, 2 h (Runs 1 and 4: 3 h), toluene 18 ml, 500 ml scale autoclave. TCP: 2,4,6-trichlorophenol.
a) See Table 1. b) Et_2SO_4 was used in place of Me_2SO_4.

Table 3. Effect of Me_2SO_4 or Et_2SO_4 (6 atm, 100 ml) on the Dimerization of Propene with Nickel-Phosphine Catalysts

Run No.	Additives (molar ratio)	Selectivity of dimers[a]	Turnovers (TON)[a] Total C_6'	DMB-1	DMB-2	Selectivity of DMBs in C_6'[a]
9[b]	None (—)	66	4300	3600	20	84
10[b,c]	None (—)	52	4100	3320	60	82
11	Me_2SO_4 (2.0)	64	28300	17500	4420	77
12[d]	Me_2SO_4 (2.0)	64	30500	18600	4340	75
13	Et_2SO_4 (3.0)	72	21300	14100	2180	76

Reaction Conditions: Nickel naphthenate/P(cyclo-C_6H_{11})$_3$/$AlEt_3$/isoprene/2,4,6-trichlorophenol (TCP)=1/1/20/80/70 (molar ratio), nickel 0.01 mmol, 100 ml autoclave, propene 6 atm, 18—20 °C, 1 h, toluene 2 ml. a) See Table 1. b) Nickel 0.02 mmol, TCP/Ni=35, 1.5 h. c) 2,3-Dimethyl-1,3-butadiene was used (20 mol amt. to nickel) in place of isoprene. d) *o*-Dichlorobenzene was used in place of toluene.

taken into account under these reaction conditions (solvent: toluene or *o*-dichlorobenzene, Runs 11 and 12 in Table 3), because the reaction mixture consisted of, for example, solvent 2 ml and C_6 olefins ca. 24 g (Run 11). Isoprene could be replaced by 2,3-dimethyl-1,3-butadiene (Run 10). Also, other olefins, such as 1,3-cyclooctadiene or norbornadiene, are usable in place of isoprene.

1-3. Effect of CF_3SO_3H. Table 4 summarizes the results of the dimerization of propene catalyzed by the nickel-phosphine system in the presence of CF_3SO_3H under various reaction conditions. The reaction products consisted exclusively of C_6 olefins (selectivity of C_6 olefins based on the reacted propene=94—99%). The turnover number became as high as 113000 by this catalyst at higher propene pressure under a lower catalyst concentration. However, the selectivity of 2,3-dimethylbutenes in C_6 olefins was not improved under these conditions.

2. Dimerization of Propene by Nickel-Phosphine Catalyst in the Presence of $MeSO_3H$. 2-1. Effect of Water. During the course of our catalyst screening studies, we observed the interesting fact that the turnover number for the formation of C_6 olefins increased upon the addition of a small amount of both water and $MeSO_3H$ (Table 5). In this case, the sequence of addition was important for preparing an active catalyst solution. The selectivity of 2,3-dimethylbutenes in dimers, however, decreased from 80 to 65% in this catalyst system. The expected enhancement of the reaction rate was not observed by the CF_3SO_3H- or Me_2SO_4-based catalyst systems in place $MeSO_3H$.

2-2. Efficient Catalytic Dimerization of Propene by a

Table 4. Effect of CF_3SO_3H on the Dimerization of Propene

Run No.	Additives (molar ratio)	Temp °C	Time h	Selectivity of dimers[a]	Turnovers (TON)[a] Total C_6'	DMBs	Selectivity of DMBs in C_6'[a]
4	$MeSO_3H$ (5.0)	18—20	3	77	11000	8780	80
5	CF_3SO_3H (1.0)	10	1	95	28800	17700	61
14	CF_3SO_3H (1.0)	10	1	99	70900	39200	55
15[b]	CF_3SO_3H (1.0)	10	0.67	94	113000	51500	46

Reaction conditions: Nickel naphthenate/P(cyclo- C_6H_{11})$_3$/$AlEt_3$/isoprene/2, 4, 6- trichlorophenol=1/1/20/80/35 (molar ratio), nickel 0.10 mmol (Runs 9 and 10: 0.02 mmol), propene 4 atm, toluene 18 ml, 500 ml autoclave. a) See Table 1. b) Propene 6 atm, 40 min.

Table 5. Effect of Water in the Presence of $MeSO_3H$ on Dimerization of Propene with Nickel-Phosphine Catalysts

Run No.	H_2O/Ni[a]	$MeSO_3H$/Ni[a]	Selectivity of dimers[a]	Turnovers (TON)[a] Total C_6'	DMBs	Selectivity of DMBs in C_6'[a]
9[b]	—	—	66	4300	3620	84
16	3.0	3.0	72	46600	30400	65
17	3.0	5.0	65	42800	27300	64
18	3.0	7.0	66	45600	29100	64
2[a]	8.0	—	62	6860	5860	86
3[a]	—	3.0	77	11000	8780	80

Reaction Conditions: Nickel naphthenate/P(cyclo-C_6H_{11})$_3$/$AlEt_3$/isoprene/2,4,6-trichlorophenol=1/1/20/80/70 (molar ratio), nickel 0.01 mmol, 100 ml autoclave, propene 6 atm, 18—20 °C, 1 h, toluene 2 ml. DMBs: 2,3-dimethylbutenes. a) See Table 1. b) Nickel 0.02 mmol, 1.5 h.

Table 6. Effect of Sulfonic Acid and Dialkyl Sulfate Additives on the Synthesis of 2,3-Dimethylbutenes by Dimerization of Propene with Nickel-Phosphine Catalysts

Run No.	$Ni/TCP/MeSO_3H/Et_2SO_4$[a] (molar ratio)	Selectivity of dimers[a]	Turnovers (TON)[a] Total C_6'	DMBs	Selectivity of DMBs in C_6'[a]
3[a]	1/35/3.0/—	75	8790	7050	80
7[a]	1/50/—/1.4	67	9400	7020	75
18	1/50/2.5/1.4	70	24100	18900	78
19	1/50/3.0/1.4	78	28800	22800	79
20	1/50/4.0/1.4	77	23800	18800	79

Reaction conditions: Nickel naphthenate/$P(cyclo-C_6H_{11})_3/AlEt_3$/isoprene=1/1/20/80 (molar ratio), nickel 0.05 mmol, propene 4 atm, 18—20 °C, 2 h, toluene 18 ml, 500 ml autoclave. a) See Table 1.

Nickel-Phosphine Catalyst Containing $MeSO_3H$–Et_2SO_4. It is important to note that the catalytic activity (the turnover number for the formation of C_6 olefins) could be further enhanced upon combination of $MeSO_3H$ with Et_2SO_4.[12] This system would be a better catalyst than those in the presence of only CF_3SO_3H or $MeSO_3H$–H_2O for producing 2,3-dimethyl-1-butene due to its higher selectivity. These results might suggest that the role of $MeSO_3H$ or Et_2SO_4 would be different in this catalytic reaction.

A turnover number (total C_6 olefins) of 28800 has been achieved (Run 20, Table 6). The amount of nickel species required for the desired product could thus be reduced by this catalyst system without decreasing the DMB selectivities. The major product, 2,3-dimethyl-1-butene, could be obtained in high purity from the reaction mixture by fractional distillation.

Summary

We have shown that sulfonic acids and/or dialkyl sulfates are highly effective additives for the dimerization of propene promoted by nickel catalyst consisting of nickel naphthenate, PCy_3, $AlEt_3$, and 2,4,6-trichlorophenol (TCP) in the presence of isoprene. The points are summarized as follows:

1) The turnover number for the formation of C_6 olefins could increase significantly upon the addition of sulfonic acid, such as $MeSO_3H$ or CF_3SO_3H. The selectivity of 2,3-dimethylbutenes in C_6 olefins was not improved by the CF_3SO_3H-based catalyst, although the products consisted of C_6 olefins exclusively (selectivity of dimers: 94—99%) with high catalytic activity (total C_6 turnovers: 28800—113000).

2) The addition of Me_2SO_4 or Et_2SO_4 was very effective to increase the turnover numbers. The turnover number of C_6 olefins increased at higher propene pressure without decreasing the selectivity of the desired products.

3) 2,3-Dimethyl-1-butene or 2,3-dimethyl-2-butene could be obtained as a major product by varying the molar ratio of the catalyst ingredients. This is due to the fact that TCP-modified aluminum species can isomerize DMB-1 to DMB-2 during the reaction without decreasing the turnover number.

4) The catalytic activity (turnover number/h) could be enhanced upon combining of water with $MeSO_3H$-based catalyst system. However, the selectivity of 2,3-dimethylbutenes decreased (65%).

5) A notable enhancement of the catalytic activity (the turnover number for the formation of C_6 olefins) could be attained upon the coexistence of both $MeSO_3H$ and Et_2SO_4 without decreasing the selectivity of the desired product. 2,3-Dimethyl-1-butene or 2,3-dimethyl-2-butene could thus be obtained in high purity from the reaction mixture by fractional distillation due to the high selectivity in C_6 olefins. This catalyst should be valuable, especially from a practical point of view.

6) The roles of sulfonic acids and dialkyl sulfates are not very clear at this moment. Detailed studies are still in progress.

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11) We have recently found that the addition of CF_3SO_3H and/or dialkyl sulfates (Me_2SO_4 or Et_2SO_4) was also effective to increase both the catalytic activity and the selectivity of C_6 olefins for dimerization of propene by using the catalyst system consisted of nickel naphthenate, PCy_3, $AlEt_3$, isoprene, and $(CF_3)_2CHOH$: K. Nomura, M. Itagaki, M. Ishino, M. Yamamoto, and G. Suzukamo, *Catal. Lett.*, in press.

12) We have found that these additives (sulfonic acid and/or Me_2SO_4 or Et_2SO_4) were also effective for this catalyst system with other tertiary phosphines. For example, turnover numbers for the formation of C_6 olefins with PPh_3 under the same conditions of Run 20 (propene 5 atm) were 6480 (89% selectivity of dimers), and 2150 turnovers (76% selectivity of dimers) without Et_2SO_4 and $MeSO_3H$, respectively: M. Itagaki, G. Suzukamo, and K. Nomura, to be published.