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Efficient Dimerization of Propene by Nickel-Phosphine Catalysis in the Presence of Sulfonic Acids and/or Dialkyl Sulfates. Effects of Phosphine Ligands and Additives

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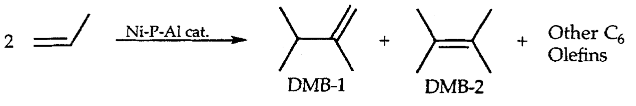
The effect of the phosphines for the dimerization of propene using a nickel catalyst system consisting of nickel naphthenate, tertiary phosphine (PCy_3, $P(i\text{-}Pr)_3$, PEt_3, PEt_2Ph, and PPh_3; Cy = cyclohexyl), triethylaluminum, and 2,4,6-trichlorophenol in the presence of sulfonic acids and/or dialkyl sulfates was investigated. A remarkable increase in both the catalytic activity (turnover number (TON) for the formation of C_6 olefins) and the selectivity of dimers (selectivity of dimers based on the propene reacted) was observed, especially upon the addition of sulfonic acids, such as $MeSO_3H$, CF_3SO_3H, and/or dialkyl sulfates (Me_2SO_4 or Et_2SO_4). The reaction products formed by the above catalyst system with PEt_3 and PEt_2Ph were exclusively C_6 olefins (selectivity of dimers: 97 and 93%, respectively). It was also revealed in this catalyst system that the electronic factor of phosphine is important for the catalytic activity, and that the dimer's proportion greatly depends upon the kind of phosphine used.

Selective organic synthesis catalyzed by transition metal complexes has been one of the most fascinating subjects in the field of catalysis.[1] In particular, the chemoselective oligomerization of olefins has been one of the most attractive subjects in the fields of homogeneous catalysis.[2,3] Since C_6 olefins are important key intermediates required for pharmaceuticals, agricultural chemicals, perfumes, and polymers,[4—7] considerable attention has been paid to the selective dimerization of propene by homogeneous catalysis.[2,3]

Many studies have been reported concerning the dimerization of propene using various nickel-phosphine catalysts to increase both the selectivity and the catalytic activity.[2,3] One of the interesting approaches is, we believe, the synthesis of 2,3-dimethylbutenes using a nickel-phosphine catalyst in the presence of a chlorophenol-modified trialkylaluminum species consisting of nickel naphthenate, PCy_3 (Cy: cyclohexyl), $AlEt_3$, and 2,4,6-trichlorophenol,[8] because the selectivity of 2,3-dimethylbutenes in C_6 olefins was especially higher in this case than that obtained by using other catalyst systems consisting of $Ni(acac)_2$, PCy_3, Et_2AlCl or $Et_2AlCl{\cdot}EtAlCl_2$.[9] The desired product, 2,3-dimethylbutenes, with high purity can thus be easily obtained from the reaction medium by a simple fractional distillation.[10] Under these circumstances, we started work to search for new types of catalyst systems which improve both the catalytic activity and the selectivity.

We have recently observed a remarkable increase in the turnover number for the formation of C_6 olefins for a catalyst system consisting of nickel naphthenate, PCy_3, $AlEt_3$, and 2,4,6-trichlorophenol (TCP) when we employed $MeSO_3H$ and/or dialkyl sulfates (Me_2SO_4 and Et_2SO_4) as an additive for the synthesis of 2,3-dimethylbutenes.[11] This new catalyst system has great value from industrial as well as synthetic viewpoints because the amount of nickel species can be reduced without decreasing in the selectivity of C_6 olefins.[11] We have also found that fluorinated alcohol can be used in place of TCP.[12] However, the reason why strong sulfonic acids and/or dialkyl sulfates are so effective, as mentioned above, has not yet been elucidated.

In this paper we present the results for the dimerization of propene catalyzed by the above-mentioned TCP-based catalyst system with various phosphine ligands either in the presence or absence of sulfonic acids and/or dialkyl sulfates (Eq. 1). On the basis of these results, we present our idea with respect to the role of the tertiary phosphines as well as the role of the above-mentioned additives in these catalyst systems.



Catalyst: nickel naphthenate/ tertiary phosphine(s)/ $AlEt_3$/ 2,4,6-trichlorophenol - RSO_3H and/or R_2SO_4.

(1)

Experimental

All experiments were carried out under a nitrogen atmosphere, or in vacuo, using standard Schlenck technique. All of reagents were of reagent grade, and were stored under dehydrated or deaerated conditions. Toluene was freshly distilled in the presence of dried molecular sieves (3A). The catalytic reactions were carried out using an autoclave (stainless steel, 100 or 500 ml scale).

The catalyst solution was prepared under an inert gas atmosphere below 20 °C. The standard procedure for preparing the catalyst (Run 6, Table 2) is as follows. In a 50 ml Schlenk tube filled with nitrogen were placed 0.375 ml of toluene containing 0.01 mmol of nickel naphthenate, 0.01 mmol of tricyclohexylphosphine (20% toluene solution), and 0.8 mmol of isoprene, followed by the addition of 0.2 ml of toluene containing 0.2 mmol of $AlEt_3$ at $<20°C$. Then, methanesulfonic acid (0.03 mmol) and 0.35 ml of toluene containing 0.35 mmol of 2,4,6-trichlorophenol were added to the stirred reaction mixture. The thus-obtained catalyst solution and the additional toluene (2 ml) were introduced into an autoclave (100 ml) under a stream of nitrogen (15 °C) by means of a hypodermic syringe.

Propene was then led to the autoclave in order to adjust the internal pressure to 6 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 ^1H 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 the internal-standard method (pentane) after any purging unreacted propene. Any propene which remained in the reaction mixture was also analyzed quantitatively in the same manner. The turnover number (turnovers, TON) and selectivity used were calculated as follows:

turnover number (Turnover, 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 product (g) and propene remained in the product solution (g); selectivity of 2,3-dimethylbutenes (DMBs) (%) = [the amount of DMBs (g)/the amount of C_6 olefins (g)] × 100.

Results and Discussion

As shown in Table 1, the catalyst system consisting of nickel naphthenate, tertiary phosphine, $AlEt_3$, and 2,4,6-trichlorophenol (TCP) showed moderate catalytic activity (the turnover number for the formation of C_6 olefins: 2150—4300) for dimerization of propene. On the other hand, the reaction did not take place or became extremely sluggish without 2,4,6-trichlorophenol (TCP), which turned out to be the best among the chlorinated phenols examined (2,4,5- or 2,4,6-trichlorophenol, 2,4,5,6-tetrachlorophenol, and pentachlorophenol).[8a)] It should be noted that a usable catalyst solution can be prepared below 20 °C, and that the coexistence of isoprene plays an important role to improve the stability of the catalyst solution at room temperature. The molar ratios of the catalyst ingredients were optimized in terms of the stability of the catalyst solution as well as the observed selectivity of the desired product.

It was revealed that the dimer's proportions were highly dependent upon the kind of the tertiary phosphine used (Table 1), and this tendency has been known in the case of the π-allyl nickel complex catalyst.[3)] Interestingly, the selectivity of 2,3-dimethylbutenes in C_6 olefins produced by the present catalyst with PCy_3 (83.1%, Run 1) was higher than that by other catalyst systems (<58—65%).[9)] The rate of these catalytic reactions were relatively fast at the initial stage of the reaction (less than 30 min), and gradually became slow due to dilution of the catalyst with the products, or due to deactivation of the catalyst in the reaction mixture. The selectivity of the reaction products did not change during the catalytic reaction, and the turnover number for the formation of 2,3-dimethylbutenes did not change with the molar ratio of TCP/Al = 1.5—3.5.[13)]

It is important to note that the turnover number for the formation of C_6 olefins significantly increased upon the addition of a small amount of Me_2SO_4 (Table 2). A notable increase in the selectivity of dimers based on the reacted propene has been achieved in this catalysis, especially in both the PEt_3- (77→90%) and the PEt_2Ph-based catalysts (75→87%). The turnover number for the formation of the C_6 olefins in the PEt_2Ph-based catalyst was lower than those in catalysts with PEt_3, P(*i*-Pr)$_3$, and PCy_3: the PPh_3-based catalyst showed the lowest turnover number. The reaction rate based on the reacted propene (molar amount of propene reacted/molar amount of nickel metal used) increased in the order: PCy_3 (2.99×10^4 turnovers/h) > PEt_3 (1.87×10^4 turnovers/h), P(*i*-Pr)$_3$ (1.79×10^4 turnovers/h) > PEt_2Ph (1.11×10^4 turnovers/h).[14)] These results suggest that

Table 1. Dimerization of Propene by Nickel–Phosphine–$AlEt_3$–Trichlorophenol Catalysts

Run No.	Phosphine	Turnovers[a)] total C_6'	Selectivity of dimers[b)]	Product distribution in C_6 olefins (%)[c)] DMB-1	DMB-2	4M1,2P	2M1P	2M2P	Hex
1	PCy_3[d)]	4300	59	83.1	0.5	3.2	11.5	1.3	2.4
2	P(*i*-Pr)$_3$	4060	59	79.7	0.3	8.3	4.0	1.1	0.7
3	PEt_3	3650	77	19.8	0.9	25.5	25.2	17.4	1.1
4	PEt_2Ph	3210	75	30.1	1.1	20.4	26.0	21.3	1.2
5	PPh_3	2150	76	14.6	0.4	32.1	28.9	20.7	3.4

Reaction Conditions: Nickel naphthenate/tertiary phosphine/$AlEt_3$/isoprene/2,4,6-trichlorophenol = 1/1/20/80/35 (molar ratio), nickel 0.02 mmol, toluene 4 ml, 100 ml autoclave, 18—20 °C, propene 6 atm, 1 h.

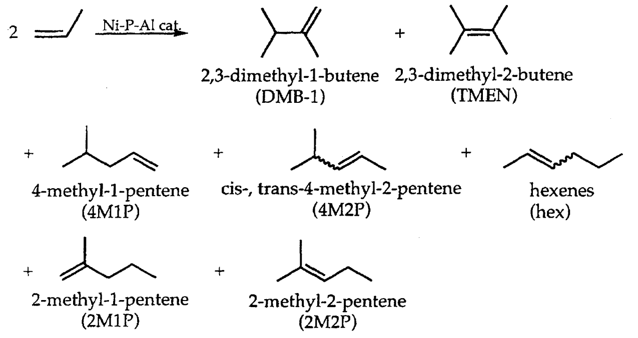
a) Turnovers = total C_6 olefins produced (mmol)/nickel (mmol). b) Selectivity of dimers (%) = [total C_6 olefins produced (g)/total propene consumed (g)] × 100. c) Total C_6': total C_6 olefins; DMB-1: 2,3-dimethyl-1-butene; DMB-2: 2,3-dimethyl-2-butene; 2M1P: 2-methyl-1-pentene; 2M2P: 2-methyl-2-penene; 4M1,2P: 4-methylpentenes; Hex: hexenes. d) Reaction time 1.5 h.

Table 2. Dimerization of Propene by Nickel–Phosphine–$AlEt_3$–Trichlorophenol Catalysts —Effect of Me_2SO_4—

Run	Phosphine	Turnovers[a)]	Selectivity	Product distribution in dimers (%)[a)]					
No.		total C_6'	of dimers[a)]	DMB-1	DMB-2	4M1,2P	2M1P	2M2P	Hex
1	PCy_3[a)]	4300	59	83.1	0.5	3.2	11.5	1.3	2.4
6	PCy_3	18240	61	74.6	6.2	6.3	9.7	2.5	0.7
7	$P(i\text{-}Pr)_3$	11480	64	67.6	9.5	9.3	9.3	3.4	0.9
3	PEt_3[a)]	3650	77	19.8	0.9	25.5	25.2	17.4	1.1
8	PEt_3	16820	90	26.7	1.0	29.6	14.7	24.7	3.3
9	PEt_2Ph	9620	87	25.2	2.7	26.3	19.8	26.0	—

Reaction Conditions: Nickel naphthenate/tertiary phosphine/$AlEt_3$/isoprene/2,4,6-trichlorophenol/Me_2SO_4 = 1/1/15/80/50/2.5 (molar ratio), nickel 0.01 mmol, toluene 2 ml, 100 ml scale autoclave, 18—20 °C, propene 6 atm, 1 h. a) See Table 1.

both an electronic and a steric factor of the phosphine ligand is important. The isomer distribution in the dimer depends upon the kind of the tertiary phosphine used (Eq. 2 and Table 2); this trend did not change upon the addition of Me_2SO_4.



(2)

It is also important to note that a further increase in the turnover number for the formation of C_6 olefins was observed along with the addition of Et_2SO_4–$MeSO_3H$ (Table 3). A catalyst system with PEt_3 or PEt_2Ph exclusively gave C_6 olefins (selectivity of dimers: 97% (PEt_3) and 93% (PEt_2Ph), respectively). It was also revealed that the isomer distribution depended upon the kind of the phosphine used, and did not change upon the addition of both $MeSO_3H$ and Et_2SO_4. The effect of the tertiary phosphine on the catalytic activity in this system (Table 3) seems to be the same as that observed in the above Me_2SO_4-added catalyst systems.

It is highly interesting to note that the turnover number for the formation of C_6 olefins in the CF_3SO_3H-added Ni-PPh_3 catalyst (Run 16) was very much higher than that in the $MeSO_3H$-added catalyst (Run 15). It is also interesting to note that the selectivity of C_6 olefins based on the reacted propene was lower for the bulky phosphine such as $P(i\text{-}Pr)_3$ or PCy_3 than that for PEt_3 or PEt_2Ph. We assume that this might be due to the difficulty for elimination processes of intermediary σ-nickel species bearing the bulky phosphine ligand during the catalytic reaction.

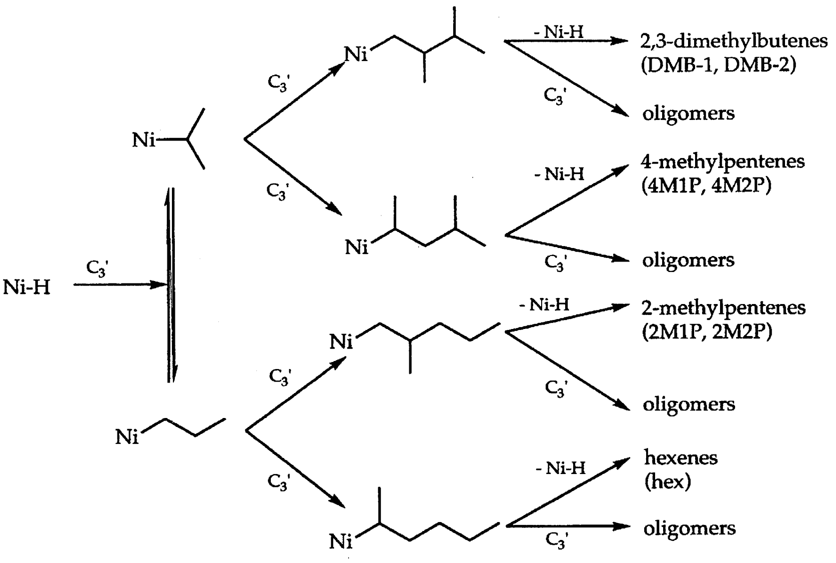
Taking into accounts the above-mentioned results, we can assume that the basic catalytically-active nickel species is the same in these catalysts because of the effect of phosphines on the catalytic activity; also, the dimer's proportion showed no significant change regardless of the kind of catalyst systems used (Tables 1, 2, and 3). We can also assume that the role of tertiary phosphines in the catalytic cycle would be to control the initial insertion reaction of propene to the catalytically active metal center (Scheme 1), as was previously postulated,[3)] which might be reflected in the isomer distributions.

It turned out that ^{31}P NMR spectrum of a solution consisting of nickel naphthenate, PCy_3 (1 mol amt. to nickel), $AlEt_3$, and isoprene showed only one peak at 2.2 ppm. This chemical shift value (2.2 ppm) was located between that

Table 3. Dimerization of Propene by Nickel–Phosphine–$AlEt_3$–Trichlorophenol–Et_2SO_4–RSO_3H Catalysts —Effects of Phosphines, Sulfonic Acids, and/or Dialkyl Sulfates—

Run	Phosphine	RSO_3H	Turnovers[a)]	Selectivity	Product distribution in dimers (%)[a)]					
No.			total C_6'	of dimers[a)]	DMB-1	DMB-2	4M1,2P	2M1P	2M2P	Hex
10	PCy_3	$MeSO_3H$	19000	65	70.8	10.6	7.2	7.7	2.6	1.1
11	$P(i\text{-}Pr)_3$	$MeSO_3H$	20130	66	66.5	10.8	10.3	7.9	3.2	1.2
12	$P(n\text{-}Bu)_3$[b)]	$MeSO_3H$	17330	90	23.1	8.7	27.4	10.3	26.1	4.4
13	PEt_3	$MeSO_3H$	17580	97	22.6	5.4	25.5	9.6	31.6	5.2
14	PEt_2Ph	$MeSO_3H$	8720	93	17.7	9.6	25.0	10.5	31.6	5.4
5	PPh_3	None	2150	76	14.6	0.4	32.0	28.9	20.7	3.4
15	PPh_3[b)]	$MeSO_3H$	6480	89	8.5	4.0	29.8	9.6	29.9	18.2
16	PPh_3[b)]	CF_3SO_3H	23810	93	1.7	7.8	29.0	4.5	36.2	20.8

Reaction Conditions: Nickel naphethenate/phosphine/isoprene/$AlEt_3$/2,4,6-trichlorophenol/Et_2SO_4/RSO_3H=1/1/80/20/50/1.4/3 (molar ratio), 500 ml scale autoclave, nickel 0.1 mmol, toluene, propene 4 kg cm^{-2}, 10 °C, 1.5 h.
a) See Table 1. b) Propene 5 kg cm^{-2}.



Scheme 1.

(-2.5 ppm) observed for a system consisting of Ni(1,5-cyclooctadiene)$_2$, PCy$_3$ (1 mol amt. to nickel), and AlEt$_3$ and that (10 ppm) observed for a system consisting of Ni(1,5-cyclooctadiene)$_2$ and PCy$_3$. This result strongly suggests the exclusive formation of the Cy$_3$PNi(isoprene) species.

Ethane was formed (ca. 1 mol amt. to MeSO$_3$H) after the addition of MeSO$_3$H into the above-mentioned toluene solution consisting of nickel naphthenate, PCy$_3$ (1 mol amt. to nickel), AlEt$_3$, and isoprene, suggesting the formation of a sulfonated aluminum species. However, the exact role of sulfonic acid and/or dialkyl sulfates has not yet been elucidated. One possible explanation for the remarkable increase in both the catalytic activity and the selectivity of dimers might be the promotion of an elimination process of the σ-nickel species in this catalytic reaction. Further studies are in progress, and the detailed resutls will be introduced in the near future.

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14) The optimized molar ratios in the catalyst systems with PCy$_3$, PEt$_3$, and P(i-Pr)$_3$ might be different. The accurate order based on the propene reacted might be thus difficult among these catalyst systems.