

Letter

Efficient synthesis of 2,3-dimethylbutenes by dimerization of propylene using nickel–phosphine catalyst in the presence of strong sulfonic acids and/or dialkyl sulfates. Remarkable effect of strong sulfonic acids and/or dialkyl sulfates

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**Abstract**

Remarkable catalytic activities as well as high selectivities have been found for dimerization of propylene catalyzed by the nickel–phosphine system composed of nickel naphthenate/ $P(\text{cyclo-C}_6\text{H}_{11})_3/\text{AlEt}_3/2,4,6\text{-trichlorophenol (TCP)}$  especially in the presence of strong sulfonic acids ( $\text{CF}_3\text{SO}_3\text{H}$ ,  $\text{MeSO}_3\text{H}$ ) or dialkyl sulfates ( $\text{Me}_2\text{SO}_4$  and  $\text{Et}_2\text{SO}_4$ ). The catalytic activity was further increased upon the combination of these effective additives. The desired  $\text{C}_6$  olefins such as 2,3-dimethylbut-1-ene (DMB-1), 2,3-dimethylbut-2-ene (DMB-2, TMEN) could be obtained in relatively high yields by using these catalysts (selectivity of dimers = 70–80%; selectivity of dimethylbutenes in  $\text{C}_6$  olefins = ~80%). The ratio of DMB-1/TMEN could be controlled without changing the catalytic activities by varying the molar ratios of catalyst precursors.  $\text{CF}_3\text{SO}_3\text{H}$  was found to be the most effective additive for increasing the reaction rate, although the selectivity of dimethylbutenes decreased significantly. Addition of a small amount of water enhanced the reaction rate significantly (turnover numbers for 2,3-dimethylbutenes: 7046 → 30358). The importance of these catalyst systems should be emphasized, because the amount of nickel species required can be minimized compared with that required for the conventional process. © 1997 Elsevier Science B.V.

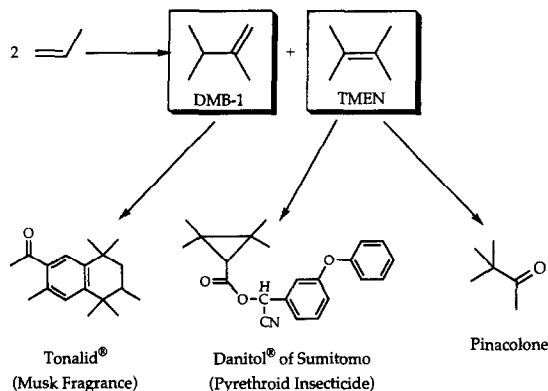
Oligomerization of olefins has been one of the most important subjects in the fields of homogeneous catalysis. Considerable attention has thus been paid to the selective catalytic dimerization of propylene especially after the discovery of Wilke-type nickel catalysis [1–4],

because  $\text{C}_6$  olefins are important intermediates as pharmaceuticals, agricultural chemicals, perfumes, and monomers [5–13]. A considerable number of studies using a variety of homogeneous catalyst systems have, therefore, been carried out in order to improve both catalytic activity and selectivity of the desired compound, and to meet the commercial use.

One of the interesting practical approach on this project is, the selective syntheses of 2,3-dimethylbutenes (2,3-dimethylbut-1-ene (DMB-1), 2,3-dimethylbut-2-ene (TMEN)) using the catalyst system composed of nickel naph-

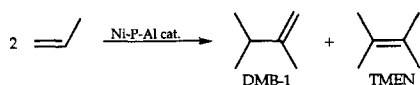
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Scheme 1.

thenate/ $P(\text{cyclo-C}_6\text{H}_{11})_3/\text{AlEt}_3/2,4,6\text{-trichlorophenol}$  (TCP) in the presence of a small amount of water, because not only the desired DMB-1 or TMEN can be obtained in relatively high yields but also the ratio of DMB-1/TMEN can be controlled by varying the molar ratios of catalyst precursors [14,15]. Since 2,3-dimethylbutenes are important intermediates for agricultural chemicals and perfumes in chemical industry as shown in Scheme 1<sup>2</sup>, we thus explored a possibility to improve both the catalytic activity and the selectivity. In this letter, we wish to present efficient catalyst systems which show remarkable catalytic activities as well as high selectivities under mild conditions.



Catalyst: nickel naphthenate/ $P(\text{cyclo-C}_6\text{H}_{11})_3/\text{AlEt}_3/2,4,6\text{-trichlorophenol}-\text{RSO}_3\text{H}$  etc.

All experiments were carried out under nitrogen atmosphere, or in vacuo, using standard Schlenk technique. All reagents were of reagent grade, and stored under dehydrated and deaer-

<sup>2</sup> As demonstrated previously, the desired product, especially 2,3-dimethylbut-2-ene could be obtained from the reaction solution by distillation in high purity (>99%). 2,3-Dimethylbut-1-ene could also be obtained in high purity by this procedure. See, for example, Ref. [16].

ated conditions. Preparation of the catalyst solution was performed under inert gas atmosphere<sup>3</sup>. The catalytic reactions were carried out by using an autoclave (100 or 500 ml), and the reaction products were analyzed by GC (column: sebaconitrile 25% on Shimalite 3.1m). Identification of the products was made by comparison of the GC chromatograms with those of standard chemicals, GC-MS, and <sup>1</sup>H NMR after an isolation. The details for the procedure will be reported in our forthcoming full paper.

The catalyst system composed of nickel naphthenate/tert-phosphine/triethylaluminum/2,4,6-trichlorophenol (TCP) has been reported to exhibit moderate catalytic activity for dimerization of propylene [14,15]. The reaction did not take place, or extremely low catalytic activity was observed in the absence of trichlorophenol<sup>4</sup>, although the reaction catalyzed by a known catalyst system,  $\text{Ni}(\text{acac})_2\text{-P}(\text{cyclo-C}_6\text{H}_{11})_3\text{-Et}_2\text{AlCl}$ , proceeded with moderate catalytic activity. The selectivity of 2,3-dimethylbutenes in dimers, however, could be improved by this TCP-based catalyst system (selectivity of dimethylbutenes in  $\text{C}_6$  olefins: <65% ( $\text{Ni}(\text{acac})_2/\text{P}(\text{cyclo-C}_6\text{H}_{11})_3/\text{Et}_2\text{AlCl}$  catalyst system), and ~80% (TCP-based catalyst system)): this fact is very important from an industrial viewpoint, because the desired product can be separated by a simple fractional distillation in high yields.

<sup>3</sup> Standard catalyst preparation procedure (run 3 in Table 1): in a 50 ml Schlenk tube which had been cooled to 5°C and filled with nitrogen, 1.35 ml of toluene containing 0.1 mmol of nickel naphthenate, 0.1 mmol of tricyclohexylphosphine (20% toluene solution) and 8 mmol of isoprene were charged, followed by the addition of 2 ml of toluene containing 2 mmol of triethylaluminum. To the reaction mixture was then added methanesulfonic acid (0.3 mmol), and 3.5 ml of toluene containing 3.5 mmol of 2,4,6-trichlorophenol. The prepared catalyst solution was added via a syringe into an autoclave filled with nitrogen.

<sup>4</sup> Alcohols other than 2,4,6-trichlorophenol were also employed. Chlorophenol derivatives such as tri-, tetra-, or penta-chlorophenol were found to be effective [14]. Fluorinated alcohols were also found to be effective. The molar ratios of these additives were optimized from the catalytic activity as well as the stability of catalytically active species.

Table 1  
Efficient dimerization of propylene using nickel–phosphine catalysts, effect of strong sulfonic acid and/or dialkyl sulfate

Run No.	Ni/TCP/MeSO <sub>3</sub> H/Me <sub>2</sub> SO <sub>4</sub> (molar ratio)	Selectivity of dimers <sup>a</sup>	Turnovers (TON) <sup>b</sup>		Selectivity of DMBs in C <sub>6</sub> <sup>c</sup>
			total C <sub>6</sub>	DMBs	
1	1/35/–/–	80	5320	4260	80
2 <sup>d</sup>	1/35/8.0/–	62	6860	5860	86
3	1/35/3.0/–	75	8790	7050	80
4	1/35/5.0/–	77	11000	8780	80
5 <sup>e</sup>	1/35/1.0/–	95	28800	17700	61
6	1/70/–/3.0	68	18100	14000 <sup>h</sup>	77
7 <sup>f</sup>	1/50/–/2.3	68	16400	12900 <sup>h</sup>	79
8 <sup>g</sup>	1/50/–/1.4	67	9400	7020	75
9 <sup>g</sup>	1/50/2.5/1.4	70	24100	18900	78
10 <sup>g</sup>	1/50/3.0/1.4	78	28800	22800	79
11 <sup>g</sup>	1/50/4.0/1.4	77	23800	18800	79

Reaction conditions: nickel naphthenate/P(cyclo-C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>/AlEt<sub>3</sub>/isoprene = 1/1/20/80 (molar ratio), nickel 0.05 mmol scale (run 1–5; Ni 0.1 mmol), propylene 4 atm, 18–20°C, 2 h (run 1–4; 3 h), toluene 18 ml, 500 ml autoclave.

<sup>a</sup>Selectivity of dimers (%) = [amount of dimers produced (g)/amount of propylene reacted (g)] × 100.

<sup>b</sup>TON = [amount of dimers produced (mmol)/amount of nickel metal used (mmol)].

<sup>c</sup>Selectivity of DMBs (%) = [amount of DMBs (g)/amount of C<sub>6</sub> (g)] × 100. DMBs: 2,3-dimethylbutenes (DMB-1 and TMEN).

<sup>d</sup>H<sub>2</sub>O was used in place of MeSO<sub>3</sub>H.

<sup>e</sup>CF<sub>3</sub>SO<sub>3</sub>H was used in place of MeSO<sub>3</sub>H, 10°C, 1 h.

<sup>f</sup>AlEt<sub>3</sub>/Ni = 15.

<sup>g</sup>Et<sub>2</sub>SO<sub>4</sub> was used in place of Me<sub>2</sub>SO<sub>4</sub>.

<sup>h</sup>DMB-1 2156 turnovers and TMEN 11852 turnovers (run 6); DMB-1 11011 turnovers and TMEN 1921 turnovers (run 7).

It should be noted that addition of MeSO<sub>3</sub>H resulted in the significant increase of the catalytic activity and, as a result, 2,3-dimethylbut-1-ene (DMB-1) was obtained in a relatively good yield (>60%; Table 1, run 3 and 4). CF<sub>3</sub>SO<sub>3</sub>H also enhanced the reaction rate, and increased the selectivity of dimers (run 5), although the selectivity of 2,3-dimethylbutenes in C<sub>6</sub> olefins decreased from 80% to 60%. Other sulfonic acids were also employed, and chlorosulfonic acid was also found to be effective. Strong carboxylic acids such as CF<sub>3</sub>CO<sub>2</sub>H or CCl<sub>3</sub>CO<sub>2</sub>H were also examined extensively, but these additives showed no positive effect. The reaction did not take place, or extremely low catalytic activity was observed in the absence of trichlorophenol (TCP), although both the catalytic activity and the selectivity of C<sub>6</sub> olefins did not drastically decrease by varying the molar ratio in the range between 30 and 70 (per nickel), as was previously reported [14]. These additives are also found to be effective for PPh<sub>3</sub>-based systems where PPh<sub>3</sub> is used in place

of P(cyclo-C<sub>6</sub>H<sub>11</sub>)<sub>3</sub><sup>5</sup>. The prepared catalyst solution was stable for more than 24 h at room temperature in the presence of isoprene. Isoprene was an effective additive to stabilize the catalytically active species [14]: it could be easily replaced by other dienes such as 2,3-dimethyl-1,3-butadiene, 1,3-cyclooctadiene, or norbornadiene.

It was also revealed that dimethyl sulfate or diethyl sulfate was effective for this reaction (Table 1, runs 6–8). Also importantly, the reaction rates were further enhanced by the combination of these effective additives (run 9–11). It is interesting that the product ratios of DMB-1/TMEN could be controlled by changing the

<sup>5</sup> We have found that these additives (strong sulfonic acid and/or Me<sub>2</sub>SO<sub>4</sub> or Et<sub>2</sub>SO<sub>4</sub>) were also very effective for the similar catalyst system with other phosphines. For example, turnover numbers of C<sub>6</sub> olefins with PPh<sub>3</sub> under the same conditions of run 10 (propylene 5 atm) were 6479 (89% selectivity of dimers), and 2145 (76% selectivity of dimers) in the absence of Et<sub>2</sub>SO<sub>4</sub> and MeSO<sub>3</sub>H, respectively. These results will be reported in the near future.

Table 2

Efficient dimerization of propylene affording 2,3-dimethylbutenes by nickel–phosphine catalysts, effect of water in the presence of sulfonic acid

Run No.	H <sub>2</sub> O/Ni <sup>a</sup>	MeSO <sub>3</sub> H/Ni <sup>a</sup>	C <sub>3</sub> ' consumed <sup>b</sup> (g-C <sub>3</sub> '/mol-Ni)	Selectivity of dimers <sup>c</sup>	Turnovers (TON) <sup>c</sup>		Selectivity of DMBs in C <sub>6</sub> ' <sup>c</sup>
					total C <sub>6</sub> '	DMBs	
12	3.0	3.0	5.44 × 10 <sup>6</sup>	72	46600	30400	65
13	3.0	5.0	5.53 × 10 <sup>6</sup>	65	42800	27300	64
14	3.0	7.0	5.81 × 10 <sup>6</sup>	66	45600	29100	64
2	8.0	–	9.3 × 10 <sup>5</sup>	62	6860	5860	86
1 <sup>c</sup>	–	–	5.6 × 10 <sup>5</sup>	80	5320	4260	80
3 <sup>c</sup>	–	3.0	1.20 × 10 <sup>6</sup>	77	11000	8780	80

Reaction conditions (run 11–14): nickel naphthenate/P(cyclo-C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>/AlEt<sub>3</sub>/isoprene/2,4,6-trichlorophenol = 1/1/20/80/70 (molar ratio), nickel 0.01 mmol scale, 100 ml autoclave, propylene 6 atm, 18–20°C, 1 h, toluene 2 ml.

<sup>a</sup>Molar ratios of H<sub>2</sub>O/Ni or MeSO<sub>3</sub>H/Ni.

<sup>b</sup>Amount of propylene (g) reacted per nickel.

<sup>c</sup>See Table 1.

molar ratios of the catalyst components (AlEt<sub>3</sub>–trichlorophenol–Me<sub>2</sub>SO<sub>4</sub>). The desired product can be thus obtained in high purity from the reaction mixture by fractional distillation due to its high selectivity of 2,3-dimethylbutenes in dimers [16].

It was also found that the catalytic activity was further increased upon addition of a prescribed, small amount of water (Table 2), although the selectivity of dimethylbutenes in C<sub>6</sub> olefins decreased. Both the order of addition of the catalyst components and the molar ratio of water per nickel were also found to be important in this catalyst system. The expected enhancement of the reaction rate could not be observed for CF<sub>3</sub>SO<sub>3</sub>H-based or Me<sub>2</sub>SO<sub>4</sub>-based catalyst systems yet.

We have shown that the significant increase of both catalytic activity and selectivities has been accomplished for dimerization of propylene in the presence of sulfonic acid such as MeSO<sub>3</sub>H, CF<sub>3</sub>SO<sub>3</sub>H, and/or dialkyl sulfate such as Me<sub>2</sub>SO<sub>4</sub>, Et<sub>2</sub>SO<sub>4</sub>. The reaction rates were enhanced by the combination of these effective additives, which leads to reduction of the amount of nickel species required for the desired products. The catalytic activity was also found to be further enhanced upon addition of a small amount of water. Since the reaction proceeds with both high activity and selectivity by these catalysts, their potential importance should

be emphasized not only from synthetic but also from industrial viewpoints. We are not sure about the role of strong sulfonic acid, dialkyl sulfates or other catalyst components. We believe that cationic nickel-hydride species play an important role for this catalytic reaction <sup>6</sup>.

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<sup>6</sup> Zero valent nickel species formed by addition of AlEt<sub>3</sub> into a toluene solution containing nickel naphthenate, P(cyclo-C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>, isoprene showed the <sup>31</sup>P NMR spectrum which was very similar to that of Ni(0)(1,5-cyclooctadiene)<sub>2</sub> with 1 equivalent of P(cyclo-C<sub>6</sub>H<sub>11</sub>)<sub>3</sub> in the presence of AlEt<sub>3</sub>. More detailed studies, including the mechanistic ones, are now in progress.

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