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Efficient dimerization of propylene affording 2,3-dimethylbutenes by fluorinated alcohol modified nickel–phosphine catalyst system containing strong sulfonic acid and / or dialkyl sulfates

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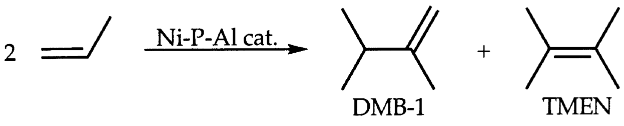
A remarkable increase of both catalytic activity and the selectivity of dimers has been found for propylene dimerization affording 2,3-dimethylbutenes by a nickel–phosphine catalyst system composed of nickel naphthenate/P(cyclo-C_6H_{11})$_3$/AlEt$_3$/(CF$_3$)$_2$CHOH in the presence of CF_3SO_3H and/or Me_2SO_4: a combination of these effective additives also enhanced the reaction rates.

Keywords: dimerization, propylene, 2,3-dimethylbutenes, nickel, tricyclohexylphosphine, trifluoromethanesulfonic acid, dimethyl sulfate, 1,1,1,3,3,3-hexafluoro-2-propanol

C_6 olefins are important key intermediates in the manufacturing of pharmaceuticals, agricultural chemicals, perfumes, and monomers [1–4]. 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 dimerization of propylene by nickel–phosphine catalysts [5–8], because the reaction proceeds with relatively high selectivity in dimers not only by varying the phosphine ligand but also by varying the additives. One of the interesting approaches is the selective synthesis of 2,3-dimethylbutenes by nickel–phosphine catalysts, especially composed of nickel naphthenate/tert-phosphine/trialkylaluminum in the presence of substituted alcohol [8].

Although a lot of studies have already been made for dimerization of propylene by nickel–phosphine catalysts, however, we explored a possibility to improve both the activity and the selectivity, because the chemical process affording 2,3-dimethylbutenes has already been accomplished by propylene dimerization and replacement by an efficient catalyst might be a better solution [8]. In this paper, we thus wish to present a new type of a remarkably efficient catalyst system containing fluorinated alcohol modified nickel–phosphine catalysts [1], especially in the presence of CF_3SO_3H and/or Me_2SO_4.



Catalyst: nickel naphthenate/ tert-phosphine/ AlEt$_3$/ hexafluoroisopropanol - RSO$_3$H and/or R'$_2$SO$_4$

All experiments were carried out under nitrogen atmosphere, or in vacuo, using the standard Schlenk technique. All reagents were of reagent grade, and stored under dehydrated and deaerated conditions. Preparation of the catalyst solution was performed under nitrogen [2]. The catalytic reactions were carried out in an

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[1] We have also recently discovered another catalyst system composed of nickel naphthenate/tricyclohexylphosphine/triethylaluminum/2,4,6-trichlorophenol in the presence of CF_3SO_3H and/or dialkyl sulfates (and/or water). However, a significant decrease of the selectivity to 2,3-dimethylbutenes was observed in some catalyst systems, although these catalyst systems showed high catalytic activities. These results would be published somewhere in the near future.

[2] An example for the preparation of catalyst (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 0.1 mmol of nickel naphthenate, 0.1 mmol of tricyclohexylphosphine (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 triethylaluminum. The reaction mixture was stirred at room temperature, then CF_3SO_3H and 1.5 ml of toluene containing 1.5 mmol of 1,1,1,3,3,3-hexafluoroispopropanol was added into the solution. The prepared catalyst solution was transferred by using a syringe into an autoclave filled with nitrogen.

Table 1
Efficient synthesis of 2,3-dimethylbutenes by dimerization of propylene using nickel–phosphine catalysts. Effect of $MeSO_3H$, CF_3SO_3H, or Me_2SO_4 [a]

Run No.	$Ni/PCy_3/AlEt_3/HFIP$ molar ratio [b]	Additives (molar ratio [b])	Selectivity of dimers [c] (%)	Turnovers (TON) [d]			Selectivity of DMBs [e] (%)
				total C_6'	DMB-1	TMEN	
1	1/1/10/30	none	37	4150	280	3340	87
2	1/1/20/30	Me_2SO_4 (2.5)	43	9320	7680	560	88
3	1/1/20/30	$MeSO_3H$ (7.0)	50	15410	7280	6160	87
4	1/1/10/15	none	34	2470	2180	tr.	89
5	1/1/10/15	$ClSO_3H$ (2.0)	97	8210	6040	10	74
6	1/1/10/15	CF_3SO_3H (1.0)	65	17320	13900	60	81

[a] Reaction conditions: nickel naphthenate/PCy_3/isoprene = 1/1/80 (molar ratio), propylene 6 atm, 18–20°C, 1 h, toluene 2 ml, 100 cm^3 autoclave, nickel 0.01 mmol (runs 1 and 4: nickel 0.02 mmol). PCy_3: tricyclohexylphosphine. HFIP: $(CF_3)_2CHOH$.

[b] Molar ratio of additives per nickel.

[c] Selectivity of dimers (%) = [amount of C_6 olefins produced (g)]/[amount of propylene consumed (g)] × 100.

[d] Turnovers (TON) = [amount of dimers or dimethylbutenes produced (mmol)]/[amount of nickel metal used (mmol)].

[e] Selectivity of DMBs (%): selectivity of 2,3-dimethylbutenes in C_6 olefins. DMBs: DMB-1 and TMEN. DMB-1: 2,3-dimethylbutene-1, TMEN: 2,3-dimethylbutene-2.

autoclave (100, 500 ml, or 1.5 ℓ). The reaction products were analyzed by GC (column: sebaconitrile 25% on Shimalite 3.1 m). The details of the procedure will be reported in our forthcoming full paper.

The reaction proceeded upon addition of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP: runs 1 and 4 in table 1). The reaction did not take place or extremely low activity was observed without HFIP (catalyst: nickel naphthenate/tricyclohexylphosphine/triethylaluminum = 1/1/20 (molar ratio)). The reaction rate was found to be increased by varying the HFIP/Ni molar ratio. The ratio of tetramethylethylene (TMEN)/2,3-dimethylbutene-1 (DMB-1) could be changed by varying the molar ratio of HFIP/Al, because HFIP-modified Al species also act as a catalyst for isomerization from 2,3-dimethylbutene-1 (DMB-1) to tetramethylethylene (TMEN) in the reaction mixture. Isoprene was used to stabilize the prepared catalyst solution: it could be easily replaced by other olefins such as norbornadiene or 2,3-dimethyl-1,3-butadiene.

It is important to note that both the dimerization rates and selectivity of dimers were found to be increased upon addition of strong sulfonic acids such as $MeSO_3H$, CF_3SO_3H or Me_2SO_4 (table 1). In particular, notable enhancement could be found in the presence of CF_3SO_3H (run 6) at lower HFIP/Ni molar ratio of 15, resulting in affording 2,3-dimethylbutene-1 in relatively high yield. The prepared catalyst solution was very stable for a long time at room temperature (< 25°C): this might be very important from the industrial point of view. The molar ratio of CF_3SO_3H/nickel was found to be also important for this reaction: a molar ratio of $CF_3SO_3H/Ni = 1.0$ might be preferred in this catalysis. $ClSO_3H$ was also found to be effective, although the selectivity of 2,3-dimethylbutenes decreased (74%). The CF_3SO_3H-based catalyst system with other tert-phosphine in place of $P(cyclo\text{-}C_6H_{11})_3$ also showed both remarkable activity and high selectivity of dimers [3].

It is also important to note that the reaction rate was further enhanced by the combination of effective additives such as Me_2SO_4 and CF_3SO_3H (table 2, runs 10–12). Interestingly, the catalytic activity was found to be increased on a larger reaction scale (the reaction using 1.5 ℓ autoclave: runs 12–14). TON (turnover numbers) of 43840 could be attained by adding the catalyst in several portions into the reaction solution. The selectivity of 2,3-dimethylbutenes in C_6 olefins was ca. 80%, which was almost the same as that using a previous catalyst system (see footnote 1), or higher than $Ni(acac)_2/P(cyclo\text{-}C_6H_{11})_3/Et_2AlCl$ (ca. < 65%) which was known as an effective catalyst [4] [5,8]. 2,3-dimethylbutenes could be thus obtained by using the present catalyst in high purity by fractional distillation from the reaction mixture.

In summary, we have presented an efficient catalyst system, especially in the presence of CF_3SO_3H and/or Me_2SO_4. Not only because the desired products, 2,3-dimethylbutenes, can be produced by using this catalyst, but also because the amount of nickel species required can be reduced; these results should be emphasized both from industrial and synthetic viewpoints. We are not sure about the role of strong sulfonic acids and/or dialkyl sulfates. Detailed studies including NMR experiments under various conditions and/or effect of

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[3] The result using PEt_2Ph in place of $P(cyclo\text{-}C_6H_{11})_3$ under the same conditions as run 6 was as follows: turnover numbers of total dimers 20870 (2,3-dimethylbutene-1: 26.6%; 2,3-dimethylbutene-2: 1.3%; 2-methyl-1-pentene: 22.5%; 2-methyl-2-pentene: 25.0%; 4-methylpentenes: 19.4%; others: 5.2%), selectivity of dimers 92%. Detailed results with the other tert-phosphines are in progress.

[4] The results of propylene dimerization using $Ni(acac)_2/Et_2AlCl$ catalyst, see, for example, ref. [9].

Table 2
Efficient dimerization of propylene affording 2,3-dimethylbutenes by nickel–phosphine catalysts containing trifluoromethanesulfonic acid and / or dialkyl sulfate [a]

Run No.	Additives	Molar ratio [b]	C_3' consumed ($g\text{-}C_3'$/mol-Ni)	Selectivity of dimers [c] (%)	Turnovers [c] (TON)		Selectivity of DMBs in C_6' [c] (%)
					total C_6'	DMBs	
7	H_2O [d]	3.0	9.3×10^5	62	6860	5860	85
8	CF_3SO_3H	0.5	1.40×10^6	79	13120	10990	84
9	CF_3SO_3H	1.0	1.92×10^6	84	19180	15080	79
10	Me_2SO_4/CF_3SO_3H	1.0/1.5	2.47×10^6	86	25290	19650	78
11	Me_2SO_4/CF_3SO_3H	1.0/2.5	2.63×10^6	84	26330	20240	77
12	Et_2SO_4/CF_3SO_3H	1.0/2.5	2.34×10^6	86	23980	18220	76
13 [e]	CF_3SO_3H	1.0	5.46×10^6	75	48740	38210	78
14 [f]	CF_3SO_3H	1.0	4.56×10^6	83	45010	35740	79
15 [f,g]	CF_3SO_3H	1.0	6.05×10^6	78	56210	43840	78

[a] Reaction conditions: nickel naphthenate / $P(c\text{-}C_6H_{11})_3$ / $AlEt_3$ / $(CF_3)_2CHOH$ / isoprene = 1 / 1 / 10 / 15 / 80 (molar ratio), toluene, propylene 4 atm, 18–20°C, 2 h, nickel 0.05 mmol (runs Nos. 7–9: 0.1 mmol), 500 ml autoclave.

[b] Molar ratios of additives per nickel.

[c] See table 1.

[d] Previous catalyst: nickel naphthenate / $P(c\text{-}C_6H_{11})_3$ / $AlEt_3$ / 2,4,6-trichlorophenol / isoprene = 1 / 1 / 20 / 25 / 80 (molar ratio), reaction time 3 h.

[e] The reaction using 1.5 ℓ autoclave, nickel 0.01 mmol, toluene 40 ml, propylene 3 atm, 10°C, 2 h.

[f] The catalyst solution was added to the autoclave by three portions (every 30 min), nickel 0.15 mmol, toluene 36 ml, propylene 3 atm, 10°C, total reaction time 3 h, 1.5 ℓ autoclave.

[g] Propylene 4 atm.

phosphine ligand are in progress: these results will be introduced in our forthcoming full paper.

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