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Studies on Nickel-Containing Ziegler-Type Catalysts. IV. Dimerization of Propylene to 2,3-Dimethylbutenes. Part-II

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A small amount of water was found to increase the activity of catalyst (A) for the selective dimerization of propylene to 2,3-dimethylbutenes (DMBS),

$$\mathrm{Ni(naph)_2/AlEt_3/PR_3/Diene/Chlorinated\ phenol}, \qquad (A)$$

where $Ni(naph)_2$ denotes nickel naphthenate. The activity increased by about three to five times upon the addition of H_2O in amounts of 0.2 to 0.8 mole per mole of $AlEt_3$; the maximum activity was obtained at around 0.5 molar ratio of H_2O to $AlEt_3$. On the other hand, the reaction product between H_2O and $AlEt_3$ in a molar ratio of 0.5 was isolated and was identified to be μ-oxo-bis(diethylaluminum), the accelerating effect of which was also proved to be high. It is, therefore, concluded that the Lewis acidity of μ-oxo-bis(diethylaluminum) activates the Ni–H bond of the active species through coordination to the square-planer complex of nickel.

In our preceding paper[1] we reported on a new efficient catalyst (A) for the dimerization of propylene to 2,3-dimethylbutenes (DMBS),

$$\mathrm{Ni(naph)_2/AlEt_3/PR_3/Diene/Chlorinated\ phenol}, \quad (A)$$

where $Ni(naph)_2$ denotes nickel naphthenate. This catalyst has some characteristics that are comparable to Wilke[2] and Evers[3] catalysts. The first is a high DMBS content in propylene dimers (DMBS selectivity), 86%, compared to 54% for the Wilke and Evers catalysts. The second is that free control in the ratio of 2,3-dimethyl-1-butene (DMB-1) and 2,3-dimethyl-2-butene (DMB-2) can be obtained at will by only controlling the molar ratio of chlorinated phenol to $AlEt_3$.

In this paper, a remarkable accelerating effect of H_2O on the dimerization activity of catalyst (A) is discussed in detail.

Experimental

Details concerning the experimental conditions (materials, experimental procedure, and analysis) were described in a preceding paper.[1] The materials were all of extra-pure chemical grade and were kept under anhydrous conditions. The abbreviations of the catalyst components are as follows:

$Ni(naph)_2$ for nickel naphthenate; $AlEt_3$ for triethylaluminum; PR_3 for trialkylphosphine (such as tricyclohexylphosphine $P(c\text{-}C_6H_{11})_3$ or triisopropylphosphine $P(i\text{-}Pr)_3$); Diene for conjugated diene such as isoprene; and $C_6H_{5-n}Cl_nOH$ for chlorinated phenol (such as 2,4,6-trichlorophenol (TCP) or pentachlorophenol (PCP)). The solvent was toluene (Tol) or monochlorobenzene (MCB); propylene was fed continuously at a constant pressure. The reaction results are summarized according to the following terms: DMBS means 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene; C6 olefins means propylene dimers; Catalytic activity means converted propylene(mole)/Ni(mole)/h; DMBS selectivity is the DMBS content in C6 olefins; and C6 olefins selectivity is the C6 olefin content in converted propylene.

Results and Discussion

Influences of the Water-Addition Sequence. In catalyst (A), the addition sequence of the catalyst components controls the catalytic activity.[1] Therefore, the influence of the water-addition sequence on the catalytic performance was examined in detail. The molar ratios of the catalyst components are expressed according to

$$\mathrm{Ni(naph)_2/AlEt_3/P}(c-\mathrm{C_6H_{11}})_3\mathrm{/Isoprene/C_6H_2Cl_3OH} = 1/20/1/80/35. \qquad (1)$$

The results are illustrated in Figs. 1 and 2. When water was added after preparing the catalyst as a final component, the change in the catalytic performance was small, as is shown in Fig. 1. This means that the added water did not have a sufficient chance to react with another catalyst component (e. g. $AlEt_3$), so as to modify the catalytic performance. Of course, the higher molar ratio of H_2O to $AlEt_3$ (greater than 1.0) deactivates the dimerization activity.

On the other hand, when water is added during the early stage of catalyst preparation (e. g. before the reduction of $Ni(naph)_2$ by $AlEt_3$), the dimerization activity rapidly increases with the molar ratio of H_2O to $AlEt_3$ (Fig. 2); the maximum activity is attained at around 0.5 of the water molar ratio to $AlEt_3$. In this case, it is estimated that water has a sufficient chance to react with $AlEt_3$, since during the early stage of preparation there are many active Al–Et moieties to be reacted as well as plenty of time for the reaction. The DMBS selectivity also increases from 76 to 86% with an increase in the $H_2O/AlEt_3$ molar ratio. Thus, an efficient catalyst (B) has been found,

$$\mathrm{Ni(naph)_2/AlEt_3/Trialkylphosphine\ (PR_3)/Diene/Chlorinated\ phenol/H_2O}. \qquad (B)$$

Influences of the Catalyst Concentration.

Along with a decrease in the initial catalyst concentration, the catalytic activity for dimerization apparently increases, as shown in Fig. 3. The increase is eminent for a catalyst prepared by the addition of water before reduction. This increase of the catalytic activity results from an increase in the catalyst efficiency; that is, at a rather higher concentration of the nickel component, the active species are prone to associate with each other. Thus, a high activity, such as 2.2×10^4 (converted propylen(mole)/Ni(mole)/h), was attained.

Successive Isomerization of DMB-1 to DMB-2. As was discussed in the preceding paper,[1] DMB-2 can be obtained through a successive isomerization of DMB-1 by the addition of an additional amount of chlorinated phenol soon after the dimerization of propylene to DMB-1 over catalyst (A). The successive isomerization was examined in the case of the catalyst being accelerated by water. The results are summarized in Table 1. In these cases, the added molar ratio of trichlorophenol (TCP) to $AlEt_3$ was 1.75, and the total molar ratio of TCP to $AlEt_3$ was 3.5. As can be seen from Table 1, along with a decrease in the initial catalyst concentration, although the dimerization activity increases (as explained above), the isomerization activity (the degree of isomerization) decreases. The isomerization activity seems to be proportional simply to the catalyst concentration at the end of dimerization. As was revealed in the preceding paper,[1] the active species for isomerization is the Lewis-acidic product between $AlEt_3$ and

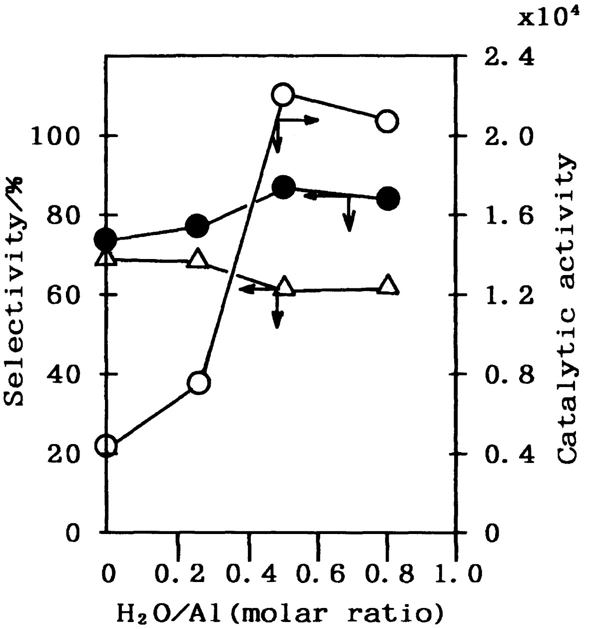

Fig. 2. Dependencies of the dimerization activities on H_2O/Al molar ratios (2); Water addition before reduction. ○ ; Catalytic activity (converted propylene(mole)/Ni(mole)/h), ● ; DMBS selectivity/%, △ ; C6 olefins selectivity/%. Catalyst and dimerization; See captions in Fig. 1.

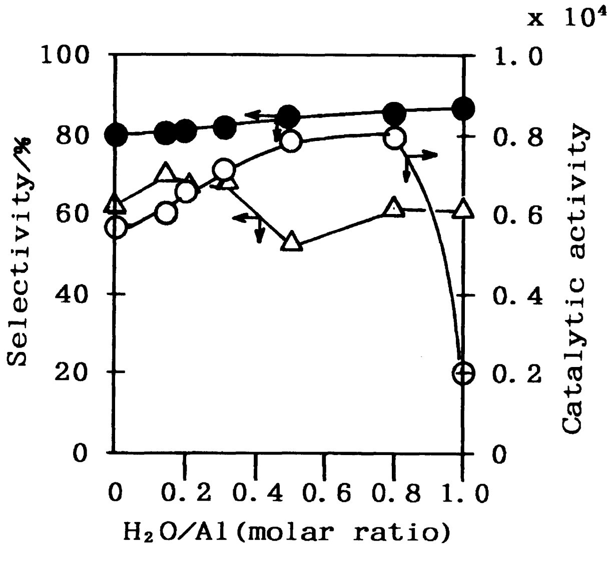

Fig. 1. Dependencies of the dimerization activities on H_2O/Al molar ratios (1); Water addition after reduction. ○ ; Catalytic activity (converted-propylene(mole)/Ni(mole)/h), ● ; DMBS selectivity/%, △ ; C6 olefins selectivity/%. Catalyst; Ni(naph)$_2$/$AlEt_3$/P(c-C_6H_{11})$_3$/isoprene/TCP = 1/20/1/80/35 (molar ratios). Dimerization; $(Ni)_0 = 3.9\times10^{-3}$ mol dm^{-3}, Toluene solvent, P(propylene)= 4 atom, 20 °C, 3 h.

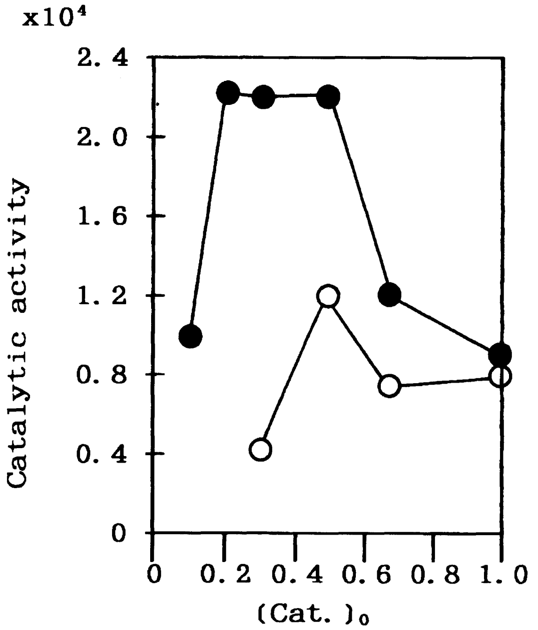

Fig. 3. Dependencies of the dimerization activities on the initial catalyst concentration $(Cat.)_0$. ○ ; Water addition after reduction, ● ; Water addition beofre reduction. Catalyst and dimerization; See captions in Fig. 1. $(Cat.)_0=1.0$ corresponds to $(Ni)_0=3.9\times10^{-3}$ mol dm^{-3}.

Table 1. Influences of the Catalyst Concentration on Propylene Dimerization a) and Successive Isomerization b)

Run No.	Initial catalyst concentration /mol dm^{-3}	Results of propylene dimerization				Succesive isomerization	
		Catalytic activity c)	Selectivity/%		Degree/% of d) isomerization	Concentration of [Al] e)	Degree/% of d) isomerization
			DMB-1	DMB-2			
1	1.30×10^{-3}	2.20×10^{4}	80.2	2.1	2.5	0.302×10^{-3}	7.8
2	1.95×10^{-3}	1.79×10^{4}	76.5	6.5	7.8	0.371×10^{-3}	18.4
3	3.90×10^{-3}	0.87×10^{4}	77.0	7.3	8.8	0.760×10^{-3}	93.0

a) Catalyst; $\mathrm{Ni(naph)_2/AlEt_3/P(\mathit{c}\text{-}C_6H_{11})_3}$/isoprene/TCP/$\mathrm{H_2O}$=1/20/1/80/35/10 (molar ratios) Dimerization; Solvent=toluene, P(propylene)=4 atm, 20 °C, 3 h. b) After dimerization, further amount of TCP (1.75 molar ratio to $\mathrm{AlEt_3}$) was added and stirred for 3 h at 30 °C. c) converted propylene(mole)/Ni(mole)/h, d) (DMB−2/DMBS)×100. e) Organoaluminum component(mole)/converted propylene(mole).

Table 2. Influences of the Catalyst Concentration on Propylene Dimerization; Direct Synthesis of DMB-2 a)

Run No.	Initial catalyst concentration /mol dm^{-3}	$\mathrm{H_2O}$/Al (molar ratio)	Catalytic activity b)	Selectivity/%				Degree/% of c) isomerization
				C6 olefins	DMB-1	DMB-2	DMBS	
1	3.90×10^{-3}	0	0.26×10^{4}	62.2	5.9	72.5	78.4	92.5
2	3.90×10^{-3}	0.5	0.98×10^{4}	64.8	15.9	67.3	83.2	80.9
3	1.95×10^{-3}	0.5	1.29×10^{4}	62.4	17.8	64.5	82.3	78.4
4	1.30×10^{-3}	0.5	2.17×10^{4}	65.0	64.7	20.0	84.7	23.6
5 d)	1.30×10^{-3}	0.5	2.17×10^{4}	65.0	5.8	78.7	84.5	93.2

a) Catalyst; $\mathrm{Ni(naph)_2/AlEt_3/P(\mathit{c}\text{-}C_6H_{11})_3}$/isoprene/TCP/$\mathrm{H_2O}$ = 1/20/1/80/70/10 (molar ratios). Solvent = toluene, P(propylene) = 4 atm, 20 °C, 3 h. b) , c) see Table 1. d) Further 2 h stirring was continued after purging residual propylene in Run No. 4.

Table 3. Influences of Water and Solvent on the Catalyst Containing TCP as Chlorinated Phenol a)

Run No.	Solvent	Molar ratio		Catalytic activity b)	Selectivity/%				Degree/% of c) isomerization
		TCP/Al	$\mathrm{H_2O}$/Al		C6 olefins	DMB-1	DMB-2	DMBS	
1	Toluene	1.75	0	0.43×10^{4}	67.9	75.5	0.2	75.7	0.3
2	Toluene	1.75	0.5	2.20×10^{4}	62.0	83.9	2.5	86.4	2.9
3	Toluene	3.50	0	0.36×10^{4}	62.2	9.0	69.4	78.4	88.5
4	Toluene	3.50	0.5	2.17×10^{4}	65.0	64.7	20.0	84.7	23.6
5	MCB	1.75	0	0.49×10^{4}	72.8	72.3	0.6	72.9	0.8
6	MCB	1.75	0.5	0.90×10^{4}	74.5	79.9	1.9	81.8	2.3
7	MCB	3.50	0	0.93×10^{4}	65.0	15.0	67.6	82.6	81.9
8	MCB	3.50	0.5	1.66×10^{4}	60.8	30.2	53.8	84.0	64.0

a) Catalyst; $\mathrm{Ni(naph)_2/AlEt_3/P(\mathit{c}\text{-}C_6H_{11})_3}$/isoprene/TCP/$\mathrm{H_2O}$=1/20/1/80/(35 or 70)/(0 or 10) (molar ratios). Dimerization; Solvent=toluene or monochlorobenzene (MCB), $[\mathrm{Ni}]_0=3.9\times10^{-3}$ mol dm^{-3}, P(propylene)=4 atm, 20 °C, 3 h. b) , c) see Table 1.

chlorinated phenol. The results given in Table 1 indicate that the addition of water does not accelerate the isomerization activity.

Direct Synthesis of DMB-2. DMB-2 can be obtained directly in the dimerization of propylene by increasing the molar ratio of chlorinated phenol to $\mathrm{AlEt_3}$ to more than 3 over catalyst (A).1) However, as is discussed above, water accelerates the dimerization activity, but does not accelerate the isomerization activity. Therefore, the influence of water on the isomerization activity was examined in detail in the case of a TCP/$\mathrm{AlEt_3}$ molar ratio of 3.5 and a $\mathrm{H_2O/AlEt_3}$ molar ratio of 0.5. The results are summarized in Table 2. With a decrease in the initial catalyst concentration, although the dimerization activity increases rapidly, the degree of isomerization decreases in a manner similar to the preceding results in Table 1. In this case, however, a high degree of isomerization can be attained by only continuing stirring for an additional 2 hours at 20 °C.

The Dependencies of the Water Effect on Chlorinated Phenol and Solvent. The promoting effect of water was found to depend upon the combination of chlorinated phenol and the solvent. In case of the TCP-containing catalyst, the increase in the dimerization activity is high (five to seven times) in a toluene solvent, and is moderate (twice) in a monochlorobenzene (MCB) solvent (Table 3). On the other hand, in the case of the PCP-containing catalyst, only a trace increase in the dimerization activity could be observed in both solvents (Table 4). As a result, in the case of the

Table 4. Influences of Water and Solvent on the Catalyst Containing PCP as Chlorinated Phenol[a)]

Run No.	Solvent	Molar ratio		Catalytic activity[b)]	Selectivity/%				Degree/% of[c)] isomerization
		PCP/Al	H_2O/Al		C6 olefins	DMB-1	DMB-2	DMBS	
1	Toluene	1.75	0	1.00×10^4	73.3	76.5	0.9	77.4	1.2
2	Toluene	1.75	0.5	1.30×10^4	52.4	3.1	71.1	84.2	84.5
3	MCB	3.50	0	2.56×10^4	58.8	7.8	74.7	82.5	90.6
4	MCB	3.50	0.5	2.63×10^4	55.7	16.1	68.4	84.5	81.0

a) Catalyst; $Ni(naph)_2/AlEt_3/P(c\text{-}C_6H_{11})_3$/isoprene/PCP/$H_2O$=1/20/1/80/(35 or 70)/(0 or 10) (molar ratios). Dimerization; Solvent=toluene or monochlorobenzene (MCB), $[Ni]_0=3.9\times10^{-3}$ mol dm^{-3}, P(propylene)=4 atm 20 °C, 3 h. b) , c) see Table 1.

Table 5. Comparison of the Solvent Effect in the Catalyst Activated by Water[a)]

Run No.[c)]	Solvent	Molar ratio		Catalytic activity[b)]
		TCP/Al	H_2O/Al	
3-2	Toluene	1.75	0.5	2.20×10^4
3-6	MCB	1.75	0.5	0.90×10^4
3-4	Toluene	3.50	0.5	2.17×10^4
3-8	MCB	3.50	0.5	1.66×10^4

a) , b) see Table 1 c) Same Run No. as in Table 3.

Table 6. Comparison of the Effect of Chlorinated Phenol in the Catalyst Activated by Water[a)]

Run No.[c)]	Solvent	Chlorinated pnenol		Catalytic activity[b)]
		Compound	Amount	
3-2	Toluene	TCP	1.75	2.20×10^4
4-2	Toluene	PCP	1.75	1.30×10^4
3-8	MCB	TCP	3.50	1.66×10^4
4-4	MCB	PCP	3.50	2.63×10^4

a) , b) see Table 1 c) Same Run No. as in Tables 3 and 4.

catalyst promoted by water, the TCP shows a rather higher activation effect than that of PCP does. These results are discussed in terms of the solvent effect as well as the influences of chlorinated phenols in the following paragraph.

Solvent Effect. In catalyst (A), the catalytic activity for dimerization is higher in a poler solvent (monochlorobenzene (MCB)) than in a nonpoler solvent (toluene).[1)] However, in case of the catalyst accelerated by water, the activity is higher in toluene than in MCB (Table 5). This indicates that the reaction of water with the catalyst component (e.g. $AlEt_3$) alters both the polarity and coordination state of the active-nickel species and, thus, the solvent effect has changed.

Influences of Chlorinated Phenols. In catalyst (A), both the dimerization activity and the isomerization activity increase with the number of chlorine atoms on chlorinated phenols.[1)] These tendencies can be explained in terms of the Lewis acidity of the reaction product (X) between $AlEt_3$ and chlorinated phenol according to

$$AlEt_3 + mC_6H_{5-n}Cl_nOH \rightarrow AlEt_{3-m}(OC_6H_{5-n}Cl_n)_m;\, X, \qquad (2)$$

where $0<m<3$. However, in case of the catalyst accelerated by water, the dimerization activity exhibited a somewhat complicated behavior (Table 6). That is, in the toluene solvent, the order of dimerization activity is inverted and TCP exhibits a rather higher activity than does PCP. This inversion can also be explained as changes in the polarity and the coordination state of the active nickel species (as mentioned above).

The Dependencies of the Water Effect on Phosphines. The promoting effect of water also depends upon the kind of phosphines, as shown in Table 7. Interestingly, and fortunately, water works most effectively with $P(c\text{-}C_6H_{11})_3$, which is the most favorable for the formation of DMBS. With $P(n\text{-}Bu)_3$ and $P(C_6H_5)_3$, the increase in the activity is small upon the addition of water.

Catalyst Containing μ-Oxo-bis(diethylaluminum) as an Organoaluminum Component. Considering that the effect of water has its maximum at around 0.5 of the $H_2O/AlEt_3$ molar ratio, the influence of μ-oxo-bis(diethylaluminum) on the dimerization activity was examined.

Synthesis of μ-Oxo-bis(diethylaluminum). Alan Storr et al. reported that μ-oxo-bis(diethylaluminum) was obtained by the reaction of 2 moles of $AlEt_3$ and one mole of water.[4)] To conduct a homogeneous reaction, they reacted highly diluted $AlEt_3$ with water vapor. Here, a slightly different, but more convenient, technique was devised. That is, water was added as saturated moisture in toluene as follows. To toluene containing 5 g of $AlEt_3$ was added moistured toluene (1 dm^3, H_2O=456 ppm) at room temperature for 3 h.; the stirring continued for 1 h. At this point, the liberated ethane in the solution was analyzed by GC to check the progress of the reaction. After the solvent had been distilled off at a temperature below 100 °C, a clear viscous liquid was obtained, and analyzed as follows; Molecular weight=561.7 (by cryoscopic method in benzene). ^{1}H NMR; $\delta_{Et}(CH_3\text{–}CH_2)=0.80$. These data coincide with those of μ-oxo-bis(diethylaluminum), $(Et_2Al)_2O$, reported by Alan Storr et al.[4)] The molecular weight indicates that this compound is trimeric in benzene. The recovered weight (3.73 g) was 91.6% of the theoretical

Table 7. Influences of Water and Phosphine on the Catalytic Performances[a]

Run No.	Phosphine	Molar ratio H_2O/Al	Catalytic activity[b]	Selectivity/% C6 olefins	Selectivity/% DMBS
1	$P(c\text{-}C_6H_{11})_3$	0	0.24×10^4	67.9	75.7
2	$P(c\text{-}C_6H_{11})_3$	0.5	2.20×10^4	62.0	86.4
3	$P(n\text{-}Bu)_3$	0	0.40×10^4	93.8	35.0
4	$P(n\text{-}Bu)_3$	0.5	0.44×10^4	93.1	36.5
5	$P(Ph)_3$	0	0.35×10^4	93.5	14.8
6	$P(Ph)_3$	0.5	0.49×10^4	92.7	18.5

a) Catalyst; $Ni(naph)_2/AlEt_3/PR_3$/isoprene/TCP/H_2O = 1/20/1/80/(35)/(0 or 10) (molar ratios). Dimerization; Solvent = toluene, $[Ni]_0 = 3.9\times10^{-3}$ mol dm^{-3}, P(propylene) = 4 atm, 20 °C, 3 h. b) see Table 1.

Table 8. Activities of the Catalyst Containing $(Et_2Al)_2O$ as an Organoaluminum Component[a]

Run No.	Solvent	Molar ratio TCP/2Al	Catalytic activity[b]	Selectivity/% C6 olefins	Selectivity/% DMB-1	Selectivity/% DMB-2	Selectivity/% DMBS	Degree/% of[c] isomerization
1	Toluene	1.75	2.04×10^4	58.8	81.2	3.9	85.1	4.6
2	MCB	1.75	1.47×10^4	59.7	72.9	11.2	84.1	13.3
3	Toluene	3.50	2.20×10^4	60.0	68.4	16.5	84.9	19.5
4	MCB	3.50	1.23×10^4	57.6	55.0	29.8	84.8	35.1

a) Catalyst; $Ni(naph)_2/(Et_2Al)_2O/P(c\text{-}C_6H_{11})_3$/isoprene/TCP = 1/10/1/80/(35 or 70) (molar ratios). Solvent = toluene, $[Ni]_0 = 3.9\times10^{-3}$ mol dm^{-3}, P(propylene) = 4 atm, 20 °C, 3 h. b) , c) see Table 1.

Table 9. Influences of Water on Three Types of Dimerization Catalysts[a]

Run No.	Organic aluminum component	Molar ratio TCP/Al	Molar ratio H_2O/Al	Catalytic activity[b]	Selectivity/% C6 olefins	Selectivity/% DMB-1	Selectivity/% DMB-2	Selectivity/% DMBS	Degree/% of[c] isomerization
1	$AlEt_3$	1.75	0	0.43×10^4	67.9	75.5	0.2	75.7	0.3
2	$AlEt_3$	1.75	0.5	2.20×10^4	62.0	83.9	2.5	86.4	2.9
3	$AlEt_3$	3.00	0	0.36×10^4	62.0	5.2	81.1	86.3	94.0
4	$AlEt_3$	3.00	0.5	2.17×10^4	65.0	5.8	78.9	84.7	93.2[d]
5	$(Et_2Al)_2O$	1.75	0	2.04×10^4	68.8	81.2	3.9	85.1	4.6
6	Wilke catalyst[e]		0	0.23×10^4	86.1	51.1	2.8	53.9	5.2
7	Wilke catalyst[e]		0.5	0	—	—	—	—	—
8	Evers catalyst[f]		0	0.41×10^4	87.4	50.2	1.8	52.0	3.5
9	Evers catalyst[f]		0.5	0	—	—	—	—	—

a) Catalyst; $Ni(naph)_2/Et_3Al/P(c\text{-}C_6H_{11})_3$/isoprene/TCP/$H_2O$ = 1/20/1/80/(35 or 70)/(0 or 10) (molar ratios). $Ni(naph)_2/(Et_2Al)_2O/P(c\text{-}C_6H_{11})_3$/isoprene/TCP = 1/10/1/80/(35) (molar ratios). Dimerization; Solvent = toluene, $[Ni]_0 = 3.9\times10^{-3}$ mol dm^{-3}, P(propylene) = 4 atm, 20 °C, 3 h. b) , c) see Table 1. d) Further 2 h stirring was continued after purging residual propylene. e) η-allylnickelchloride/ $P(c\text{-}C_6H_{11})_3/AlCl_3$ = 1/1/3 (molar ratios). f) $Ni(naph)_2/AlEt_{1,5}Cl_{1,5}/P(c-C_6H_{11})_3$ = 1/20/1 (molar ratios).

value.

Activity of a Catalyst Containing $(Et_2Al)_2O$. The dimerization activity of catalyst (C) was examined; its activity was found to be almost equivalent to that of a catalyst containing $AlEt_3$+0.5H_2O, instead of $(Et_2Al)_2O$ (Table 8),

$$Ni(naph)_2/(Et_2Al)_2O/P(c-C_6H_{11})_3/\text{isoprene}/\text{TCP}. \quad (C)$$

In this case, the activity is also higher in a toluene solvent than in a monochlorobenzene solvent; this trend is in accordance with the discussion given above. The promoting effect of water is thus attributed to the in situ formation of μ-oxo-bis(diethylaluminum). On the other hand, the combination of $AlEt_3/H_2O$ is known to have a strong Lewis-acidic character.[5] Therefore, the formation of μ-oxo-bis(diethylaluminum) means an increase in the Lewis acidity of the organoaluminum component. This increase of the Lewis acidity is presumably one of the main factors for promoting the dimerization activity.[1] Other factors, such as a change in the association of the organoaluminum component around the active nickel species, is also assumed to be important for activation through a stabilization of the nickel species.

Conclusions

Table 9 summarizes the typical catalytic performances of catalysts (B)$^{6)}$ and (C)$^{7)}$ as well as the Wilke catalyst$^{2)}$ and the Evers catalyst.$^{3)}$ From a comparison of these data, some characteristics of catalyst (A) and (B) are summarized as follows: a. A catalytic amount of water increases the dimerization activity remarkably, whereas, in the Wilke and Evers catalysts, water works as an inhibitor. b. The dimerization activity is about 5- to 10-times higher than those of the Wilke and Evers catalysts. c. The DMBS selectivity is as high as 86%, compared to low value of Wilke and Evers catalysts as 54%. d. DMB-1 or DMB-2 can be produced at will by only controlling the molar ratio of the catalyst components. e. The effect of water was elucidated as the insitu formation of μ-oxo-bis(diethylaluminum). The increase in the Lewis acidity, and presumably the change in the association of the organoaluminum component, are the main factors for the increase in the dimerization activity of the nickel species.

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