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Regioselective Hydrogenation of Unsaturated Compounds Using Platinum–Zeolite Coupled with Organosilicon Alkoxide by CVD Method

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The regioselective hydrogenation of unsaturated compounds was carried out by catalysis with platinum–zeolite coupled with an organosilicon alkoxide using a chemical vapor deposition method (CVD-modified catalyst). In hydrogenation of a mixture of 1-nonene and *trans*-4-nonene by this catalyst, the reaction rate of 1-nonene was much greater than that of *trans*-4-nonene. In particular, when diphenyldiethoxysilane was used as the coupling reagent on the platinum–zeolite, excellent selectivity was produced. Further, it was elucidated that the terminal carbon–carbon double bonds are preferentially hydrogenated in the case of some compounds possessing more than one carbon–carbon double bond.

It has been reported that the chemical vapor deposition (CVD) method is very effective for controlling the surface characterization of a solid catalyst. For instance, the diameter of a micro pore in zeolite could be controlled to the order of angstroms by the CVD method, and CVD-modified zeolite could distinguish clearly between butane and isobutane at the molecular level.[1–3] It is possible to control the degree of the coated layer on the surface of the solid by this method.

Recently, we reported that, in the presence of certain catalysts, the regioselective hydrogenation of unsaturated compounds proceeded efficiently.[4–6] In particular, it has been elucidated that a CVD-modified catalyst, such as platinum–zeolite-4A coupled with tetraethoxysilane by the CVD method, is the best agency for regioselective hydrogenation.

In this investigation, platinum–zeolite catalysts combined with an organosilicon compound were prepared by the CVD method. In this catalyst system, the hydrogenation of the carbon–carbon double bonds was performed regioselectively. Differences in the hydrogenation rates were found for the different positions of the carbon–carbon double bond in unsaturated compounds. In particular, when diphenyldiethoxysilane was used as the coupling reagent on the catalyst, excellent selectivity was observed.

Further, the regioselective hydrogenation of several dienes was achieved using this catalyst system. Similar results were also obtained when using rhodium as the active site in place of platinum.

Experimental

Preparation of Catalyst. Platinum on a zeolite catalyst (1.2 wt% platinum) was prepared by an ion-exchange method.[7] Calcination and the CVD treatment were performed in a glass reactor under flowing nitrogen gas (60 $cm^3\ min^{-1}$). The platinum-zeolite catalyst (4.0 g) was heated at 400 °C for 1 h and treated at 100 °C with diethyl ether (5 $cm^3\ h^{-1}$) for 1 h. The CVD treatment was carried out as follows: Diphenyldiethoxysilane (1 mmol h^{-1}) was deposited on a platinum–zeolite catalyst for 3 h at 300 °C; this modified catalyst was calcined at 300 °C for 1 h as the final treatment.

Analysis of CVD-Modified Catalyst. After an ion-exchanged treatment, the filtrate was subjected to an inductively coupled plasma (ICP) analysis in order to determine the metal loading. An elemental analysis was used to determine the composition of the CVD-modified catalyst.

Hydrogenation of Mixture of 1-Nonene and *trans*-4-Nonene. In a 10 cm^3 round-bottom flask, 150 mg of a CVD-modified catalyst, or 60 mg of platinum–zeolite (control catalyst), was suspended in 5 cm^3 of hexane containing 0.05 mmol of undecane as an internal standard. Further, 5 cm^3 of hexane containing 1-nonene (0.05 mmol) and *trans*-4-nonene (0.05 mmol) were added to the flask with stirring at 25 °C under a hydrogen atmosphere. The reactants and products were analyzed by gas chromatography (a capillary column DB-1 30 m and PEG 20M 25 m). The compounds were assigned and their concentrations were determined using anthentic samples and an internal standard.

Hydrogenation of Alkadienes. In a 10 cm^3 round-bottom flask, 5 cm^3 of hexane containing tetradecane (0.05 mmol) as an internal standard and alkadiene (0.1 mmol) was stirred with 250 mg of a CVD-modified catalyst or 60 mg of the control catalyst at 25 °C under a hydrogen atmosphere. Both the reactants and products were analyzed in a similar manner as described above. The assignment of the products was performed using gas chromatography and GC-MS.

Results and Discussion

Hydrogenation of a Mixture of 1-Nonene and *trans*-4-Nonene. The hydrogenation of a mixture of 1-nonene and *trans*-4-nonene was carried out over platinum–zeolite-4A coupled with diphenyldiethoxysilane by the CVD method (catalyst A) and non-modified platinum–zeolite-4A (the control catalyst). As can been seen from Table 1, the R_1/R_2 values (R_1: initial rate of 1-nonene, R_2: initial rate of *trans*-4-nonene) were much greater when hydrogenation was carried out using catalyst A. In other words, the selectivity in favor of a double bond near the terminal site in the catalyst A system is much higher compared with that in the control catalyst system. When using rhodium–zeolite-4A coupled with diphenyldiethoxysilane (catalyst X), similar results were obtained; these are shown in Table 1.

Characterization of CVD-Modified Catalyst. The composition of platinum–zeolite combined to an organosilicon compound by CVD-treatment was measured by elemental analysis; these results are listed in Table 2. The relative amounts of carbon atoms in the CVD-modified catalysts are larger than in the control catalyst. It is considered that the organosilicon alkoxide combines with the zeolite through a covalent bond, as also happens in the case of organosilicon compound and silica.[8–10] In addition, as can be seen in Table 2, it has been found that the ratio of the carbon atom is largest when using diphenyldiethoxysilane as an organosilicon alkoxide.

Dependence on a Variety of Organosilicon Alkoxide for Hydrogenation. The elemental analysis of the CVD-modified catalysts leads one to conclude that the selectivity and reactivity of hydrogenation are influenced by the variety of organosilicon alkoxide as a coupling reagent on platinum–zeolite. However, it is necessary to search for a good coupling reagent in order to achieve more selective catalysis. In this investigation, the hydrogenation of 1-nonene and *trans*-4-nonene was performed over catalysts coupled with several kinds of organosilicon alkoxides, such as diphenyldiethoxysilane (catalyst A), dimethyldimethoxysilane (catalyst B), diisopropyldimethoxysilane (catalyst C), methylphenyldimethoxysilane (catalysyt D), and diphenyldimethoxysilane (catalyst E). These results are listed in Table 3.

As can be seen in Table 1, when using the control catalyst (cont. cat. A), R_1/R_2 (R_1: initial rate of 1-nonene, R_2: initial rate of *trans*-4-nonene) is approximately 2. On the other hand, looking at Table 3, it can be seen that R_1/R_2 is much larger than 2 for every CVD-modified catalyst system. In particular, the value of R_1/R_2 was estimated to be 20.3 for catalyst A. Thus, selective hydrogenation could be performed for a mixture of 1-nonene and *trans*-4-nonene using the CVD-modified catalyst.

Table 1. Dependence on the Variety of Metal for the Hydrogenation of a Mixture of 1-Nonene and *trans*-4-Nonene[a)]

Catalyst	Initial rate/mol g^{-1} h^{-1}		R_1/R_2
	1-Nonene (R_1)	*trans*-4-Nonene (R_2)	
Catalyst A[b)]	1.49×10^{-3}	7.33×10^{-5}	20.3
Cont. cat. A[c)]	7.28×10^{-3}	3.36×10^{-3}	2.2
Catalyst X[b)]	6.80×10^{-4}	2.66×10^{-5}	25.6
Cont. cat. X[c)]	1.50×10^{-3}	8.00×10^{-4}	1.9

Catalyst A: Pt/zeolite-4A modified with diphenyldiethoxysilane, cont. cat. A: non-modified Pt/zeolite-4A, catalyst X: Rh/zeolite-4A modified with diphenyldiethoxysilane, cont. cat. X: non-modified Rh/zeolite-4A. a) Conditions: 1-nonene, 0.05 mmol; *trans*-4-nonene, 0.05 mmol; hexane, 5 cm^3; reaction temperature, 25 °C. b) 150 mg. c) 60 mg.

Table 2. Elemental Analysis

Catalyst	C/%	H/%
Pt/zeolite-4A	0.50	1.81
Catalyst A	0.92	1.88
Catalyst B	0.73	1.92
Catalyst C	0.86	1.90
Catalyst D	0.54	1.86

Catalyst A: Pt/zeolite-4A modified by diphenyldiethoxysilane, catalyst B: Pt/zeolite-4A modified by dimethyldimethoxysilane, catalyst C: Pt/zeolite-4A modified by diisopropyldimethoxysilane, catalyst D: Pt/zeolite-4A modified by methylphenyldimethoxysilane.

Table 3. Dependence on the Variety of Organosilicon Alkoxide for the Hydrogenation of a Mixture of 1-Nonene and *trans*-4-Nonene [a)]

Coupling reagent	Initial rate/mol g^{-1} h^{-1}		R_1/R_2
	1-Nonene (R_1)	*trans*-4-Nonene (R_2)	
Diphenyldiethoxysilane	1.49×10^{-3}	7.33×10^{-5}	20.3
Dimethyldimethoxysilane	1.92×10^{-3}	3.06×10^{-4}	6.3
Diisopropyldimethoxysilane	2.93×10^{-3}	3.73×10^{-4}	7.9
Methylphenyldimethoxysilane	3.08×10^{-3}	3.46×10^{-4}	8.9
Diphenyldimethoxysilane	1.59×10^{-3}	9.33×10^{-5}	17.0

a) Conditions: catalyst, 150 mg; 1-nonene, 0.05 mmol; *trans*-4-nonene, 0.05 mmol; hexane, 5 cm^3; reaction temperature, 25 °C.

Table 4. Dependence on the Variety of Organosilicon Alkoxide for Hydrogenation of 1,5-Undecadiene[a)]

Catalyst	Reactant	Product	Conv./%	Sel./%	Max yield/%
Catalyst A[b)]	1,5-Undecadiene	5-Undecene	96.5	77.5	74.8
Catalyst B[b)]	1,5-Undecadiene	5-Undecene	64.9	67.3	43.7
Catalyst C[b)]	1,5-Undecadiene	5-Undecene	57.4	77.9	44.7
Cont. cat.[c)]	1,5-Undecadiene	5-Undecene	56.9	8.8	5.0

Catalyst A: Pt/zeolite-4A modified by diphenyldiethoxysilane, catalyst B: Pt/zeolite-4A modified by dimethyldimethoxysilane, catalyst C: Pt/zeolite-4A modified by diisopropyldimethoxysilane, cont. cat.: Pt/zeolite-4A. Conditions: a) reactant, 0.1 mmol; hexane, 5 cm^3; reaction temperature, 25 °C. b) 250 mg. c) 60 mg.

In addition, it was also found that the selectivity of hydrogenation was highest when using diphenyldiethoxysilane as the coupling reagent on platinum–zeolite. Accordingly, it was concluded that diphenyldiethoxysilane is the best coupling reagent for a CVD-modification in order to achieve selective hydrogenation.

This concept can be applied to the hydrogenation of several dienes. In this investigation, the hydrogenation of 1,5-undecadiene was carried out using catalysts A, B, C, and the control catalyst; these results are listed in Table 4. It is obvious that the selectivity of 5-undecene over the CVD-modified catalyst is much higher than that over the control catalyst. In particular, the selectivity was highest when the CVD-modified catalyst coupled with diphenyldiethoxysilane was used.

Table 5. Dependence on a Variety of Supports for the Hydrogenation of a Mixture of 1-Nonene and *trans*-4-Nonene Using a Platinum-Support Catalyst Modified by Diphenyldiethoxysilane[a)]

Support	Initial rate/mol g^{-1} h^{-1}		R_1/R_2
	1-Nonene (R_1)	*trans*-4-Nonene (R_2)	
Zeolite-4A	1.49×10^{-3}	7.33×10^{-5}	20.3
Zeolite-13X	2.44×10^{-4}	1.11×10^{-5}	22.0
Silica	2.09×10^{-3}	1.60×10^{-4}	13.1

a) Conditions: catalyst, 150 mg; 1-nonene, 0.05 mmol; *trans*-4-nonene, 0.05 mmol; hexane, 5 cm^3; reaction temperature, 25 °C.

Dependence on a Variety of Supports. The dependence on the variety of supports has also been investigated for hydrogenation over platinum-loaded catalyst modified with tetraethoxysilane by the CVD method.[6)] Hydrogenation proceeded with high selectivity when using zeolite or silica as a support. However, selective hydrogenation did not proceeded efficiently in the case of titania or hydrous zirconium(IV) oxide. Thus, zeolite or silica was an effective support for achieving regioselective hydrogenation in this investigation. Accordingly, the hydrogenation of 1-nonene and *trans*-4-nonene was performed using a CVD-modified catalyst with either zeolite or silica as the support. The results are shown in Table 5. In all cases, the R_1/R_2 values for the CVD-modified catalyst system are much larger than those of the control catalyst system. In addition, the regioselectivity of the hydrogenation in the CVD-modified catalyst is dependent on the variety of supports. These results are attributable to both the affinity and stability of the organosilicon compound layer on the support. From these results, it is considered that zeolite is the best support as a binder of the organosilicon compound layer.

Hydrogenation of Alkadienes. The hydrogenation of 1,11-octadecadiene was investigated using catalyst A and the control catalyst. The usual heterogeneous catalyst does not discriminate between the two double bonds in

Table 6. Hydrogenation for Unsaturated Compounds Using Pt/Zeolite-4A Modified by Diphenyldiethoxysilane[a)]

Catalyst	Reactant	Product	Conv./%	Sel./%	Max yield/%
Catalyst A	1,11-Octadecadiene	7-Octadecene	98.4	92.9	91.5
Cont. cat.	1,11-Octadecadiene	7-Octadecene	54.8	36.5	20.0
Catalyst A	1,5-Tridecadiene	5-Tridecene	94.9	82.9	78.7
Cont. cat.	1,5-Tridecadiene	5-Tridecene	43.0	48.3	20.8
Catalyst A	1,5-Undecadiene	5-Undecene	96.5	77.5	74.8
Cont. cat.	1,5-Undecadiene	5-Undecene	56.9	8.8	5.0
Catalyst A	Myrcene	2,6-Dimethyl-2-octene	84.6	74.1	62.7
Cont. cat.	Myrcene	2,6-Dimethyl-2-octene	86.3	54.6	47.1
Catalyst A	8-Cyclohexyl-1,5-octadiene	8-Cyclohexyl-5-octene	69.0	68.2	47.1
Cont. cat.	8-Cyclohexyl-1,5-octadiene	8-Cyclohexyl-5-octene	81.6	2.9	2.4

a) Conditions: catalyst A (Pt/zeolite-4A modified by diphenyldiethoxysilane), 250 mg; cont. cat. (Pt/zeolite-4A), 60 mg; reactant, 0.1 mmol; hexane, 5 cm^3; reaction temperature, 25 °C.

Table 7. Hydrogenation for Unsaturated Compounds Using Rh/Zeolite-4A Modified by Diphenyldiethoxysilane[a)]

Catalyst	Reactant	Product	Conv./%	Sel./%	Max yield/%
Catalyst X	1,11-Octadecadiene	7-Octadecene	96.6	67.2	64.9
Cont. cat.	1,11-Octadecadiene	7-Octadecene	94.4	49.6	46.8
Catalyst X	Limonene	4-Isopropyl-1-methyl-1-cyclohexene	98.7	92.7	91.5
Cont. cat.	Limonene	4-Isopropyl-1-methyl-1-cyclohexene	83.0	28.0	23.2
Catalyst X	Myrcene	2,6-Dimethyl-2-octene	78.3	55.0	43.1
Cont. cat.	Myrcene	2,6-Dimethyl-2-octene	86.4	22.2	19.2
Catalyst X	Linalool	3,7-Dimethyl-6-octene-3-ol	90.0	80.6	72.5
Cont. cat.	Linalool	3,7-Dimethyl-6-octene-3-ol	85.2	63.1	53.8

a) Conditions: catalyst X (Rh/zeolite-4A modified by diphenyldiethoxysilane), 250 mg; cont. cat. (Pt/zeolite-4A), 60 mg; reactant, 0.1 mmol; hexane, 5 cm^3; reaction temperature, 25 °C.

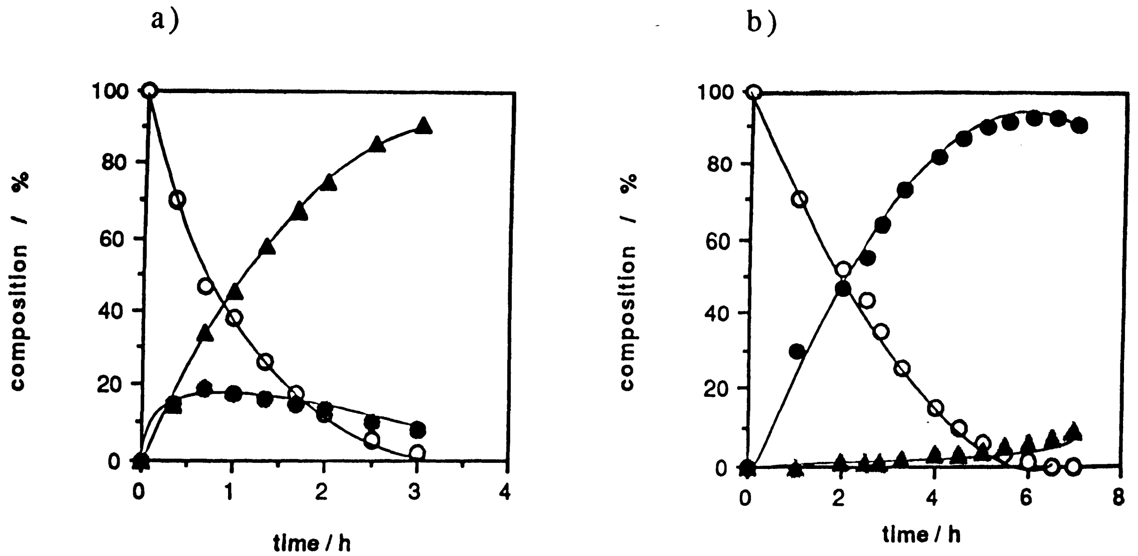

Fig. 1. Hydrogenation of 1,11-Octadecadiene: a) Control catalyst. b) Catalyst A. ○: $CH_2{=}CH(CH_2)_8CH{=}CH(CH_2)_5CH_3$, ●: $CH_3(CH_2)_9CH{=}CH(CH_2)_5CH_3$, ▲: $CH_3(CH_2)_{16}CH_3$. Conditions: Catalyst, 60 mg (control catalyst) or 250 mg (catalyst A); 1,11-octadecadiene, 0.1 mmol; hexane, 5 cm^3; reaction temperature, 25 °C.

the compound, and regioselective hydrogenation can not be achieved. As shown in Fig. 1a, regioselectivity in the hydrogenation of 1,11-octadecadiene was low over the control catalyst. On the other hand, a highly regioselective hydrogenation of 1,11-octadecadiene was achieved over catalyst A (Fig. 1b). Further, hydrogenations of other alkadienes were performed over catalyst A and the control catalyst. These results are shown in Table 6. From these results, the regioselectivity noted in the case of the hydrogenation of 1,11-octadecadiene can also be detected for other alkadienes. In addition, catalysis using catalyst A has been observed to be superior to that of platinum-zeolite-4A coupled with tetraethoxysilane or platinum (5%)-activate carbon which is known to be an effective catalyst for the regioselective hydrogenation of limonene.[11]

These results can be explained as follows: The double bond, which is more sterically hindered in the reactant, cannot easily approach the active site because of the steric regulation caused by the organosilicon compound layer in the catalyst A system. On the other hand, both of the two double bonds can easily approach the active site in the control catalyst system.

Further, the hydrogenation of alkadiene was carried out using rhodium as the active site in place of platinum in this catalyst system. These results are shown in Table 7. It was found that regioselective hydrogenation also proceeds efficiently over a rhodium-loading catalyst as well as a platinum-loading catalyst. In particular, highly regioselectivity is achieved when using limonene or linalool as a reactant. Accordingly, irrespective of loading metal, it is considered that the CVD-modified catalyst can be used to hydrogenate an alkadiene with high regioselectivity.

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