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Regioselective Hydrogenation Using Platinum-Support Zeolite Modified by CVD-Method

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A platinum-support zeolite coupled with a silica layer was prepared by Chemical Vapor Deposition (CVD) of tetraethoxysilane, and was investigated in order to determine the catalytic characterization in an analysis of the surface. With this catalyst system, it was demonstrated that the terminal carbon–carbon double bond is preferentially hydrogenated in the case of several unsaturated hydrocarbons. Further, it was elucidated that a highly regioselective hydrogenation of compounds which possess plural double bonds was achieved over this catalyst system. As a result, a reaction model regarding this catalyst system has been put forward.

In order to achieve highly regioselective reactions with heterogeneous catalyst systems, it is desirable to have a high efficiency in substrate-recognizing ability. In previous papers,[1,2] we have reported that the regioselective hydrogenation of unsaturated alcohols and acids proceeded efficiently by the use of a platinum–silica or platinum–alumina catalyst modified by a long carbon-chain layer. However, these catalyst systems do not have a wide range of applications, since, for instance, the reactants are restricted to aliphatic alcohols or acids. Further, it is difficult to control the degree of modification of the surfaces on the catalysts in these systems.

It was reported that, using the CVD (Chemical Vapor Deposition)-method, a finely deposited silica layer can be formed on the surface of zeolite and, further, that the diameter of micro pores in zeolite can be controlled.[3–5] It is thought that the silica layer is combined to the silanol group on the zeolite surface by covalent bonds and not combined to any part of the metal. It is also expected that the degree of modification can be controlled by using the CVD-method. Accordingly, it is considered that the reaction field constructed by the CVD-method would be effective in the application of highly regioselective reactions.

A platinum–zeolite catalyst coupled with tetraethoxysilane was prepared by the CVD-method. Hydrogenation of the unsaturated hydrocarbons was carried out over this CVD-modified catalyst; it was elucidated that the differences in the hydrogenation rates were dependent on the positions of the carbon–carbon double bond in the unsaturated hydrocarbons. Compared with the modified catalyst previously reported by us, the following advantages exist: (1) highly regioselective hydrogenation, (2) no restrictions regarding the reactants, (3) high stability under various conditions.

In this paper we report that the regioselective hydrogenation of several compounds with plural double bonds was achieved over a CVD-modified catalyst, and that the terminal double bond is preferentially hydrogenated. The characterization of the CVD-modified catalyst was also investigated.

It was also investigated whether the reactivity and selectivity of the hydrogenation are influenced by the variety of active metals and solid-supports in a CVD-modified catalyst system.

Experimental

Materials. Commercial reagents were used for the reactions without further purification.

Preparation of CVD-Modified Catalyst. Using the ion-exchange method,[6] platinum on zeolite-4A was prepared. The CVD-treatments were performed in a glass-flow reactor in flowing nitrogen gas (60 $cm^3 min^{-1}$). The platinum–zeolite-4A catalyst (4.0 g) was treated at 400 °C for 2 h, at 100 °C for 1 h with diethyl ether (5 $cm^3 h^{-1}$), at 200 °C for 3 h with tetraethoxysilane (1 $mmol h^{-1}$)), at 200 °C for 1 h, and at 300 °C for 1 h with deionized water (hydrolysis treatment of ethoxyl group). This series of treatments was repeated several times and, finally, the catalyst was treated at 200 °C for 1 h without hydrolysis treatment.[7]

Analysis of CVD-Modified Catalyst. After the ion-exchange treatment, the filtrate was subjected to Inductively Coupled Plasma (ICP) analysis in order to determine the metal loading. The CVD-modified catalysts were analyzed by X-ray photoelectron spectroscopy (XPS) to determine the composition of the surface phase.

Hydrogenation of Mixture of Two Alkenes. In a 10 cm^3 round-bottom flask, 150 mg of a CVD-modified catalyst, or 30 mg of a 1.2% platinum–zeolite-4A (control catalyst), was suspended in 5 cm^3 of hexane containing 0.1 mmol of undecane as an internal standard; 5 cm^3 of hexane containing 1-octene (0.1 mmol) and *trans*-4-octene (0.1 mmol) was added 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). The compounds were assigned and their concentrations were determined using authentic 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 diene (0.1 mmol) were stirred with 300 mg of CVD-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 to that described above. The assignment of the products was performed using gas chromatography and GC-MS.

Results and Discusssion

Characterization of CVD-Modified Catalyst. The

CVD-treatment on the metal-supports was repeated 5 times. The surface of the platinum–zeolite-4A coupled with tetraethoxysilane by 5-cycle CVD-treatment (5cCVD-modified catalyst A) was analyzed by XPS; the results are listed in Table 1. The relative amounts of silicon and oxygen on the CVD-modified catalyst are larger than those in the non-modified catalyst. From these data, it was elucidated that the silica layer was deposited on the surface of the platinum–zeolite-4A.[8] The thickness of the silica layer on zeolite-4A is shown by the following Eq. 1, as reported by Niwa et al.:[9]

$$(\mathrm{Si/Al})_{\mathrm{xps}}=(d+t)/(d-t), \tag{1}$$

where $(\mathrm{Si/Al})_{\mathrm{xps}}$ is the ratio of Si atom to Al atom by XPS analysis, t: the thickness of silica, and d: the releasing depth of the photoelectron (ca. 50).

The value of $(\mathrm{Si/Al})_{\mathrm{xps}}$ was dependent on the Pt loading, which is shown in Fig. 1. As can be seen from the figure, a straight line is obtained. These results suggested that the silica layer was not combined with platinum particles by the CVD-treatment, and that the platinum was highly dispersed. It is reasonable to estimate the value of $(\mathrm{Si/Al})_{\mathrm{xps}}$ in the case of no Pt loading. As being ca. 1.8, and, using this in Eq. 1, the thickness of the silica in 5cCVD-modified catalyst A is estimated to be ca. 14.3 Å. On the basis of the XPS analysis, it was demonstrated that most of the catalyst surface is covered with the 5 layers of the silica except for platinum particles, and that the small holes in the silica layer were formed around these platinum particles.

Table 1. Ratio of Elemental of Surface Phase by XPS

Catalyst	Al	Si	O	Pt
Pt(1.2%)/zeolite (A)	1.00	0.98	3.02	0.08
5cCVD-A	1.00	1.44	3.79	0.07

5cCVD-A: 5cCVD-modified catalyst A.

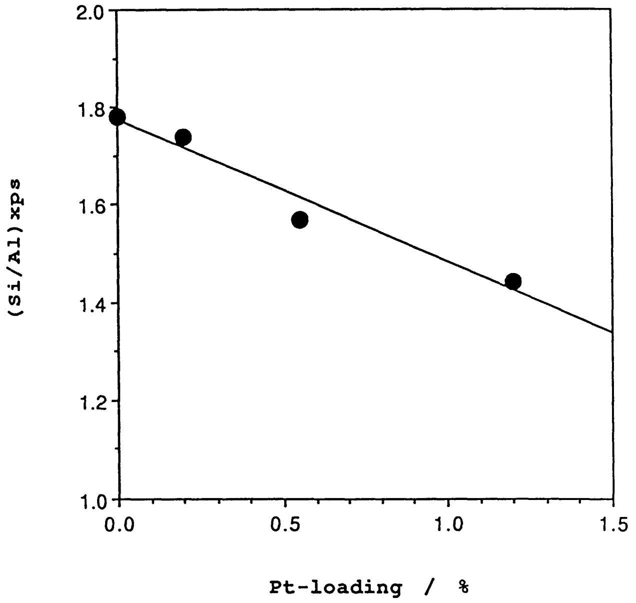

Fig. 1. Relation of Pt volume and $(\mathrm{Si/Al})_{\mathrm{xps}}$.

Competitive Hydrogenation of Two Alkenes. The hydrogenation of a mixture of 1-octene and *trans*-4-octene was carried out over the several CVD-modified catalysts. It was elucidated that R1/R2 (R1: initial rate of 1-octene, R2: initial rate of *trans*-4-octene) is dependent on the number of times of the CVD-treatment and the results are shown in Fig. 2. In the range of 0 to 5, R1/R2 increases with the number of the CVD-treatments. However, R1/R2 does not increase with more than 5 treatments. Consequently, it is considered that 5-cycle CVD treatment is the most effective to attain regioselective hydrogenation.

The hydrogenation of a mixture of 1-octene and other octenes was carried out over 5cCVD-modified catalyst A and platinum–zeolite-4A (control catalyst). As shown in Table 2, selective hydrogenation was observed by the use of 5cCVD-modified catalyst A in all cases. Compared with the hydrogenation over the control catalyst, R1/R2 was dependent on the variety of the other octene in the case of the hydrogenation over 5cCVD-modified catalyst A. In other words, the selectivity with regard to the double bond near the terminal site in the 5cCVD-modified catalyst A system is much higher in comparison with that in the control catalyst system. In the case of a mixture of 1-nonene and *trans*-4-nonene, the result was similar to those for the two-octene system.

In the case of these hydrogenations, it is considered that a catalytic active site mainly exists on the outside

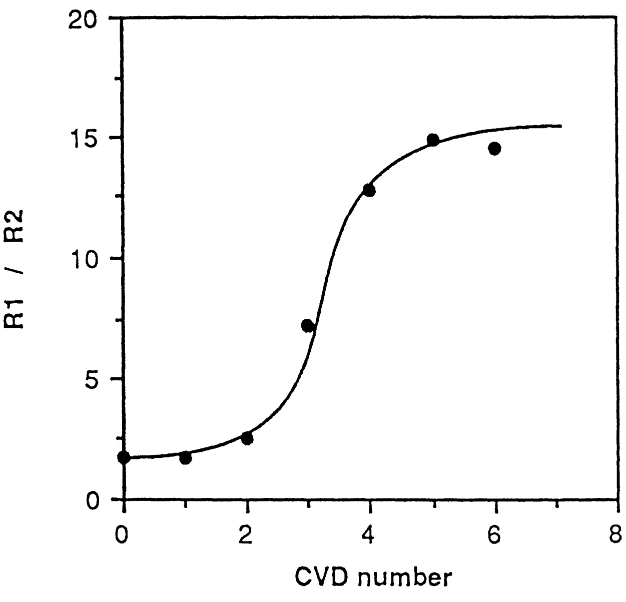

Fig. 2. Relation of R1/R2 and CVD number.
R1: Initial rate of 1-octene, R2: Initial rate of *trans*-4-octene.
Conditions: CVD-catalyst A, 150 mg; control catalyst, 30 mg; 1-octene, 0.1 mmol; *trans*-4-octene, 0.1 mmol; hexane, 10 cm^3; reaction temperature, 25 °C.

Table 2. Initial Rate of Hydrogenation for Mixture of Two Alkenes[a)]

Catalyst[b)]	Substrate		Initial rate/mol g^{-1} h^{-1}		R1/R2
	S1	S2	R1	R2	
Pt/zeolite-4A(A)	1-Octene	*trans*-4-Octene	6.56×10^{-3}	4.08×10^{-3}	1.61
5CVD-A	1-Octene	*trans*-4-Octene	4.89×10^{-4}	3.28×10^{-5}	14.90
Pt/zeolite-4A(A)	1-Nonene	*trans*-4-Nonene	7.28×10^{-3}	3.36×10^{-3}	2.17
5CVD-A	1-Nonene	*trans*-4-Nonene	4.77×10^{-4}	2.63×10^{-5}	18.14
Pt/zeolite-4A(A)	1-Octene	*trans*-3-Octene	6.38×10^{-3}	3.28×10^{-3}	1.95
5CVD-A	1-Octene	*trans*-3-Octene	5.96×10^{-4}	9.44×10^{-5}	6.31
Pt/zeolite-4A(A)	1-Octene	*trans*-2-Octene	7.10×10^{-3}	4.40×10^{-3}	1.61
5CVD-A	1-Octene	*trans*-2-Octene	5.64×10^{-4}	1.92×10^{-4}	2.94
Pt/zeolite-4A(A)	1-Octene	*cis*-2-Octene	8.24×10^{-3}	5.52×10^{-3}	1.49
5CVD-A	1-Octene	*cis*-2-Octene	7.20×10^{-4}	2.16×10^{-4}	3.33

a) Conditions: alkene, 0.1 mmol; hexane, 10 cm^3; reaction temperature, 25 °C. b) A, Pt(1.2%)/zeolite-4A (30 mg); 5CVD-A, 5cCVD-modified catalyst A (150 mg).

surface of zeolite. From the XPS data, it is suggested that the small holes are formed around the platinum particles, and the hydrogenation would be exclusively performed in these holes. Therefore regioselectivity would be caused by steric hindrance around the platinum in the holes. The carbon-carbon double bond in 1-octene can more easily approach the platinum than that in the other octenes, for instance *trans*-4-octene, because the conformation of the substrates is regulated by the silica layer on platinum-zeolite. Accordingly, the less hindered carbon–carbon double bond is easily hydrogenated in the 5cCVD-modified catalyst A system (Fig. 3).

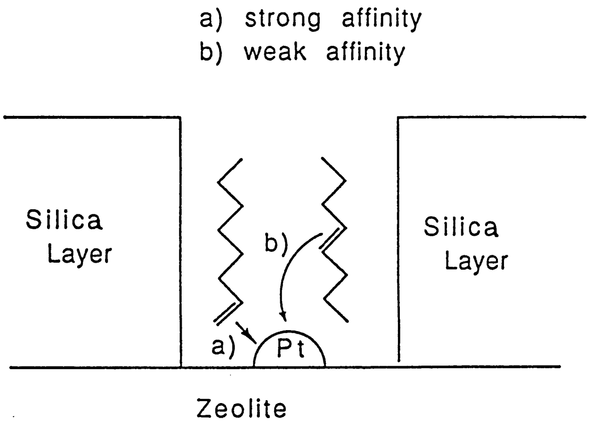

Fig. 3. Reaction Model for Hydrogenation of Octene in 5CVD-catalyst A system.

Dependence on Variety of Metals on Zeolite. In order to elucidate the dependence on the variety of metals in the CVD-modified catalyst, the hydrogenation of the mixture of 1-nonene and *trans*-4-nonene was carried out over several CVD-modified catalysts. These results are listed in Table 3. It was elucidated that the R1/R2 value in the 5cCVD-modified catalyst (5-cycle CVD-modified catalyst) system is much larger than that in the control catalyst in all cases. In the case of using platinum or rhodium-catalyst, isomerization did not occur during the reaction, but 10% of the isomers of nonene, for instance *cis*-*trans* isomer, were detected in the case of palladium. As the results show in Table 3, the CVD-modification (5-cycle) is effective in construction of a reaction field for the regioselective hydrogenation, regardless of the variety of metals.

Dependence on Variety of Supports. The hydrogenation of the mixture of 1-nonene and *trans*-4-nonene was carried out over a 5cCVD-modified catalyst with a variety of supports. The results are shown in Table 4. The R1/R2 values in the 5cCVD-modified catalyst system were much larger than those in the control catalyst in the cases of zeolite-4A, zeolite-13X, and silica. However, if titania or hydrous zirconium(IV) oxide is used as a support, the R1/R2 value in the 5cCVD-modified catalyst system is similar to that in the control

Table 3. Rate of Hydrogenation for 1-Nonene and *trans*-4-Nonene with a Variety of Metals[a)]

Catalyst	Initial rate of/mol g^{-1} h^{-1}		R1/R2
	1-Nonene(R1)	*trans*-4-Nonene(R2)	
Pt/zeolite-4A(A)[b)]	7.28×10^{-3}	3.36×10^{-3}	2.17
5cCVD-modified A[c)]	4.77×10^{-4}	2.63×10^{-5}	18.14
Rh/zeolite-4A(B)[b)]	1.50×10^{-3}	8.00×10^{-4}	1.88
5cCVD-modified B[c)]	9.33×10^{-4}	4.67×10^{-5}	19.98
Pd/zeolite-4A(C)[b)]	1.36×10^{-3}	4.65×10^{-3}	2.92[d)]
5cCVD-modified C[c)]	2.67×10^{-4}	5.83×10^{-6}	45.80[d)]

a) Conditions: 1-nonene, 0.1 mmol; *trans*-4-nonene, 0.1 mmol; hexane, 10 cm^3; reaction temperature, 25 °C. b) 30 mg. c) 150 mg. d) Isomerization occurred.

Table 4. Rate of Hydrogenation for 1-Nonene and *trans*-4-Nonene with a Variety of Supports[a]

Catalyst	Initial rate of/mol h^{-1} g^{-1}		R1/R2
	1-Nonene(R1)	*trans*-4-Nonene(R2)	
Pt/zeolite-4A(A)[b]	7.28×10^{-3}	3.36×10^{-3}	2.17
5cCVD-modified A[c]	4.77×10^{-4}	2.63×10^{-5}	18.14
Pt/zeolite-13X(D)[b]	6.47×10^{-3}	1.73×10^{-3}	3.73
5cCVD-modified D[c]	1.07×10^{-4}	4.00×10^{-6}	26.75
Pd/SiO_2(E)[b]	1.20×10^{-2}	5.49×10^{-3}	2.19
5cCVD-modified E[c]	2.67×10^{-3}	3.07×10^{-4}	8.70
Pt/hydrous zirconium oxide(F)[b]	1.57×10^{-4}	1.11×10^{-4}	1.41
5CVD-midified F[c]	2.40×10^{-5}	1.33×10^{-5}	1.80
Pt/TiO_2(G)[b]	1.11×10^{-2}	4.23×10^{-3}	2.62
5CVD-modified G[c]	1.06×10^{-2}	3.79×10^{-3}	2.80

a) Conditions: 1-nonene, 0.1 mmol; *trans*-4-nonene, 0.1 mmol; hexane, 10 cm^3; reaction temperature, 25 °C. b) 30 mg. c) 150 mg.

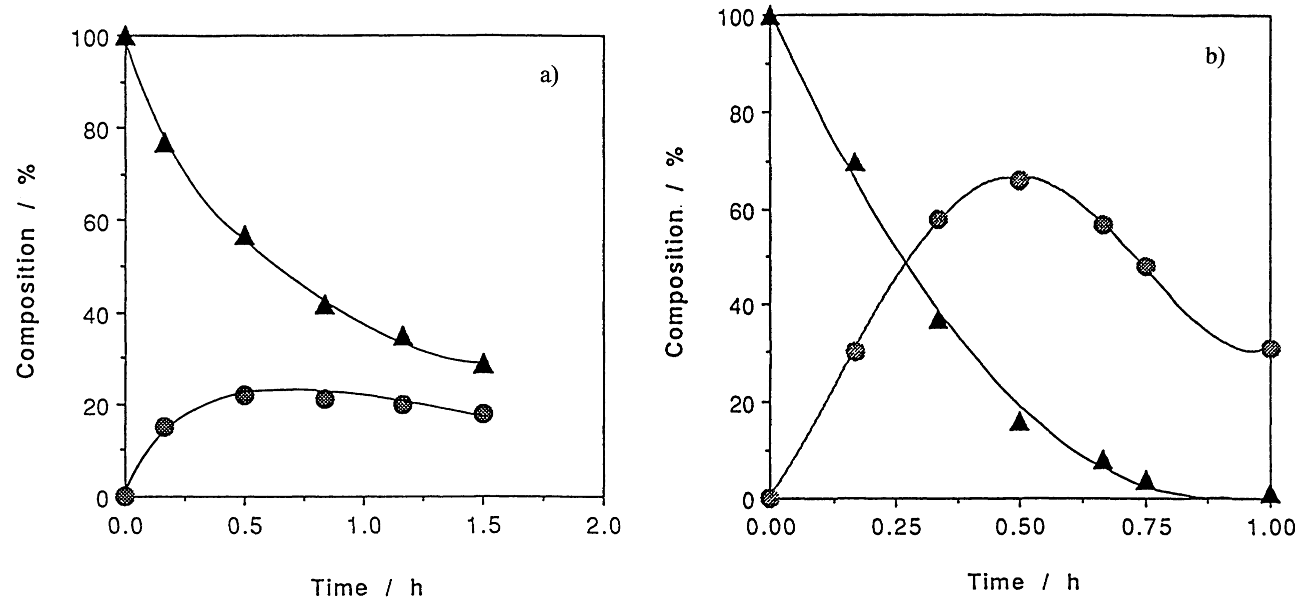

Fig. 4. Hydrogenation of 1,5-Tridecadiene. a) Control catalyst system. b) 5CVD-catalyst system.
Conditions: 5CVD-catalyst, 300 mg; control catalyst, 60 mg; 1,5-tridecadiene, 0.1 mmol; hexane, 5 cm^3; reaction temperature, 25 °C.
▲: $CH_2=CH(CH_2)_2CH=(CH_2)_6CH_3$. ●: $CH_3(CH_2)_3CH=CH(CH_2)_6CH_3$.

catalyst. It was also elucidated that the regioselectivity of the hydrogenation in the 5cCVD-modified catalyst is dependent on the variety of supports. The surface of zeolite was finely covered by a homogeneous silica layer because of the high reactivity between tetraethoxysilane and zeolite, and the reaction field was effectively constructed for the regioselective hydrogenation. On the other hand, the homogeneous silica layer was not finely constructed on titania and hydrous zirconium oxide because of the difference in ion radius between the support and silica layer. Accordingly, it is considered that zeolite is the best support as the binder of the silica layer.

Hydrogenation of Several Alkadienes. It was anticipated that the regioselective hydrogenation of a hydrocarbon possessing a number of carbon–carbon double bonds could be achieved since differences in the hydrogenation rates were found for different positions of the carbon–arbon double bond in octene and nonene. The hydrogenation of 1,5-tridecadiene was investigated over the 5cCVD-modified catalyst A and over the control catalyst. The regioselectivity for the hydrogenation of 1,5-tridecadiene was low over the control catalyst, as shown in Fig. 4a. However, when using 5cCVD-modified catalyst A, the highly regioselective hydrogenation of 1,5-tridecadiene was achieved (Fig. 4b). The hydrogenation of other alkadienes, for instance limonene, 8-cyclohexyl-1,5-octadiene, and 1,5-undecadiene, was carried out in the 5cCVD-modified catalyst A and control catalyst systems, these results are listed in Table 5. From these results, it can be seen that similar tendencies are observed in the hydrogenation of the other compounds as with 1,5-tridecadiene. Further, in the case of the hydrogenation conditions which are shown

Table 5. Regioselective Hydrogenation for Diene-Compounds Catalyzed by 5cCVD-Modified Pt/Zeolite-4A[a]

Catalyst	Substrate	Product	Max. Yield/%
Pt/zeolite-4A(A)[b]	1,5-Tridecadiene	5-Tridecene	20.8
5cCVD-A[c]	1,5-Tridecadiene	5-Tridecene	65.2
Pt/zeolite-4A(A)[b]	1,5-Undecadiene	5-Undecene	5.0
5cCVD-A[c]	1,5-Undecadiene	5-Undecene	34.8
Pt/zeolite-4A(A)[b]	Limonene	4-Isopropyl-1-methyl-1-cyclohexene	59.3
5cCVD-A[d]	Limonene	4-Isopropyl-1-methyl-1-cyclohexene	87.8
Pt/chacoal[e]	Limonene	4-Isopropyl-1-methyl-1-cyclohexene	78.9
Pt/zeolite-4A(A)[b]	8-Cyclohexyl-1,5-octadiene	1-Cyclohexyl-3-octene	2.4
5cCVD-A[c]	8-Cyclohexyl-1,5-octadiene	1-Cyclohexyl-3-octene	58.9
Pt/chacoal[e]	8-Cyclohexyl-1,5-octadiene	1-Cyclohexyl-3-octene	39.5

a) Conditions: Substrate, 0.1 mmol; hexane(solvent), 5 cm^3; reaction temperature, 25 °C. b) 60 mg. c) 300 mg. d) 600 mg. e) 10 mg.

in Table 5, it was also elucidated that the 5cCVD-modified catalyst is superior to platinum (5%)-charcoal which is known as an effective catalyst for the regioselective hydrogenation of limonene.[10]

In conclusion, a highly regioselective hydrogenation of the carbon–carbon double bond in unsaturated compounds was achieved with a CVD-modified catalyst.

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