Hydrogenation of Carboxylic Acids by Rhenium-Osmium Bimetallic Catalyst

Koji Yoshino*, Yasushi Kajiwara, Naotake Takaishi, Yoshiaki Inamoto and Jiro Tsuji[a]
Kao Institute for Fundamental Research Laboratories, Kao Corp., 2606, Akabane, Ichikai-machi, Tochigi 321-34, Japan and [a]Tokyo Institute of Technology, Megro, Tokyo 152, Japan

Hydrogenation of carboxylic acids to alcohols at low temperature and under low pressure was achieved by using a new catalyst system, a rhenium-osmium bimetallic catalyst. The most active catalyst was prepared by the reduction of the corresponding metal oxides with hydrogen in the presence of succinic acid. Decanoic acid was hydrogenated to decanol in high conversions at 25∼100 atm and 100∼120°C. Decane was formed as a by-product by overreduction of the alcohol. The selectivity of alcohol was improved by the addition of thiophene as a modifier of the catalyst.

Hydrogenation of fatty acids or their esters to alcohols is an important industrial process. A number of catalysts are known for the hydrogenation of carboxylic acids and their esters (1). Copper chromite or its modified catalysts (2,3) are commonly employed, but the reaction requires high pressure (300 atm) and high temperature (250°C). Ruthenium dioxide (4) is an active catalyst for the reduction of acetic acid only at high pressure (700∼900 atm). Rhodium oxide (5) reduces carboxylic acids at 2000 psig and 150∼175°C, but a large amount of esters is formed as a by-product. Ruthenium carbonyl compounds (6,7) reduce acetic acid and lower carboxylic acids under homogeneous conditions. However, they require also severe conditions (130 atm, 200°C) and are less active for higher fatty acids.

Broadbent *et al.* (8,9) showed that rhenium was an excellent catalyst for the hydrogenation of fatty acids. Trivedi *et al.* (10) studied the synergistic effect of Ru/C or Pd/C on the rhenium catalyst, and observed an enhanced catalytic activity for reduction of fatty acids by the combination of rhenium with Ru/C, Rh/C, or Pd/C. Using these bimetallic catalysts, they attempted hydrogenation of fatty acids under low pressure and at low temperature. However, besides alcohols, hydrocarbons and esters were obtained as unfavorable byproducts at 200∼230°C and 500∼800 psig.

Thus, there is no satisfactory catalyst which can catalyze the hydrogenation of fatty acids in high alcohol selectivity under mild conditions, and the discovery of very active catalysts is highly desirable. Under these circumstances, we have initiated studies to discover active catalysts for the hydrogenation of fatty acids to alcohols. We have developed a highly active bimetallic rhenium-osmium catalyst, which is a new composition as far as we are aware. The results are presented in this paper.

EXPERIMENTAL PROCEDURE

Preparation of rhenium catalyst. All materials are commercially available. Rhenium heptoxide (Re_2O_7) and additives were dissolved in dioxane (26 g) and reduced in a 100 ml SUS-316 magnet-drive autoclave (Nitto Koatsu Ltd.) at 100 atm of hydrogen pressure and 140°C for 1 hr. Precipitated catalysts were isolated by centrifugation, washed several times with dioxane and then used for the hydrogenation.

Preparation of rhenium—other metal catalysts. Re_2O_7 and osmium tetroxide (OsO_4) or carbon-supported catalysts were dissolved or suspended in ethyl acetate (26 g). They were reduced by the same procedure described above.

Hydrogenation of hexanoic acid. Hexanoic acid (11.62 g, 100 mmol), dioxane (26 g), and the catalyst were charged in a 100 ml autoclave. After being flushed with hydrogen to remove air, the reactor was heated to 110°C and pressured to 100 atm with hydrogen. Consumed hydrogen was resupplied periodically to keep the pressure at 100 atm. After 4 hr, the reactor was cooled and the reaction mixture was analyzed by gas chromatography (GC) by using toluene and pentadecane as internal standards (2 m column packed with Silicone SE-30 20% on Shimalite W and 1 m column packed with polyester FF 15% on Neosorb NS and He as a carrier gas).

Hydrogenation of decanoic acid. Decanoic acid (17.23 g, 100 mmol), dioxane (26 g), tridecane (1 g) as an internal standard for GC analysis, and the catalyst (and thiophene in the case of hydrogenation under mild conditions) were charged in a 100 ml autoclave. After being flushed with hydrogen to remove air, the reactor was heated to the desired temperature and pressured with hydrogen. Consumed hydrogen was resupplied periodically. Samples were taken out periodically and analyzed by GC (1 m column packed with polyester FF 15% on Neosorb NS and He as a carrier gas). The hydrogenation procedure was performed in a large scale (1 mol of decanoic acid) under the same conditions as those of Table 4. The product decanol was distilled under reduced pressure and identified by ^{1}H-NMR, mass spectroscopies and elemental analysis.

RESULTS AND DISCUSSION

Broadbent *et al.* prepared rhenium catalysts which showed different activities depending on methods of preparation (8,9,11-14). The most active catalyst was prepared by the reduction of Re_2O_7 by hydrogen. They observed that the activities of "rhenium" black catalysts depended on the solvents in which catalysts were prepared. This finding suggests to us that the catalytic activities are enhanced by the addition of appropriate compounds when catalysts are prepared. Table 1 shows the effect of various additives on the activities of rhenium catalysts. As a whole, addition of carboxylic acids showed excellent effect, especially, benzoic acid which enhanced the activity about three times in comparison with the case of no addition. The activities

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*To whom correspondence should be addressed.

TABLE 1

The Effect of Additives on the Catalytic Activity of Rhenium Catalyst[a]

Additive	Conv. (%)	Products (%) Hydrocarbon	Alcohol	Ester
—	14.5	0.2	14.3	1.3
Acetone	9.1	0.1	6.5	0.7
Diethylamine	5.3	0.1	2.6	0.3
Triethylamine	4.3	0.1	0.7	0.2
Ethanol	10.5	0.1	7.8	0.7
1-Hexanol	12.9	0.1	11.3	0.8
1-Tetradecanol	15.3	0.1	10.6	0.8
1-Hexadecanol	15.3	0.2	13.3	1.0
Acetic acid	30.8	0.2	27.8	2.0
Pyvalic acid	25.8	0.2	24.7	1.8
Acrylic acid	38.4	0.3	33.9	1.8
Benzoic acid	48.0	0.3	43.9	2.3
Malonic acid*	36.3	0.2	33.4	1.8
Succinic acid*	17.4	0.2	12.2	1.2

[a] Raction conditions; hexanoic acid 11.62 g, dioxane 26 g, H_2 100 atm, 110°C, 4 hr. Precursors of catalysts; Re_2O_7 4.0 mg atom and additive 30 mmol (*15 mmol).

of rhenium catalysts, however, are considered not to be satisfactory for hydrogenation of carboxylic acids under mild conditions.

In the course of searching for more active catalysts, we gave our attention to bimetallic catalysts. We found that the bimetallic catalyst prepared by the new combination of rhenium and osmium reduced carboxylic acids at an enhanced rate. Table 2 shows the effect of co-catalysts on the hydrogenation of decanoic acid. The hydrogenation was carried out at the hydrogen pressure of 100 atm and a temperature of 130°C. The synergistic effect of Ru/C reported by Trivedi *et al.* was confirmed. On the other hand, addition of Pd/C showed a negative effect. That is, Pd/C not only lowered the catalytic activity, but also produced nonane as a decarboxylation product of acid. When the rhenium catalyst was prepared in the presence of OsO_4, the catalytic activity was enhanced markedly. It should be noted that the osmium catalyst itself showed almost no catalytic activity.

In Table 3 the effect of atomic ratios of rhenium to osmium is shown. The highest activity for hydrogenation was observed at Re:Os=1:2~3. Furthermore, the catalytic activity was enhanced when the catalyst was prepared in the presence of succinic acid.

Most known catalysts for hydrogenation of carboxylic acids require high pressure and high temperature. The high pressure is unfavorable in industrial processes, and at high temperature esters are produced as a by-product, which lowers the selectivity of alcohols. Therefore, carboxylic acids must be hydrogenated under conditions as mild as possible. From these standpoints, use of the rhenium-osmium catalyst realized marked improvement. The catalysts were prepared from Re_2O_7 (0.5 g, 2.0 mg atom) and OsO_4 (1.0 g, 4.0

TABLE 2

Effect of the Addition of Other Metals on Activity of Rhenium Catalyst[a]

Precursors of catalysts[b]	Conv. (%)	Products (%) Hydrocarbon	Alcohol	Ester	Selectivity of Alcohol (%)
Re_2O_7	31.0	1.4	22.9	13.2	73.9
$Re_2O_7 + OsO_4$	94.4	11.7	79.8	5.8	84.5
OsO_4	3.4	1.1	1.6	1.3	47.1
Re_2O_7 + 5% Ru/C[c]	62.3	3.3	54.1	10.0	86.8
Re_2O_7 + 5% Pd/C[c]	8.7	2.0[d]	4.7	3.2	54.0

[a] Reaction conditions; decanoic acid 17.23 g, dioxane 26 g, H_2 100 atm, 130°C, 8 hr.

[b] Re_2O_7; 1.0 mg atom, other metals; 0.5 mg atom.

[c] ca 50% wet.

[d] Hydrocarbon is nonane in the case of Pd/C.

TABLE 3

The Effect of Atomic Ratios of Rhenium to Osmium on the Catalytic Activity[a]

Atomic ratio of Os/Re Re[b]	Os	Conv. (%)	TOF[c] (h^{-1})	Products (%) Hydrocarbon	Alcohol	Ester	Selectivity of Alcohol (%)
1	0	4.7	2.4	Trace	4.5	0.2	95.7
1	1	19.8	9.9	1.2	18.2	0.4	91.9
1	2	38.6	19.3	3.3	34.1	0.6	88.3
1	3	41.1	29.6	3.5	36.4	0.9	88.6
1	2[d]	59.6	29.8	3.4	52.9	0.7	88.8

[a] Reaction conditions: decanoic acid 17.23 g, dioxane 26 g, H_2 100 atm, 110°C, 1 hr.

[b] Re_2O_7; 2.0 mg atom.

[c] TOF (turnover frequency) is expressed in units of molecules reacted per Re atom per hour.

[d] Succinic acid (0.89 g, 7.5 mmol) was added when the catalyst was prepared.

TABLE 4

Hydrogenation of Decanoic Acid under Mild Conditions[a]

Pressure (atm)	Temp. (°C)	Time (hr)	Conv. (%)	TOF[b] (h^{-1})	Products (%) Hydrocarbon	Alcohol	Ester	Selectivity of Alcohol (%)
100	100	4.6	96.2	10.5	13.9	79.2	0.9	82.3
50	110	5.8	93.8	8.1	23.1	68.1	1.6	72.6
25	120	6.2	93.7	7.6	28.1	63.4	2.5	67.7

[a] Reaction conditions; decanoic acid 17.23 g, dioxane 26 g. Precursors of the catalyst; Re_2O_7 2.0 mg atom, OsO_4 4.0 mg atom and succinic acid 7.5 mmol.

[b] TOF (turnover frequency) is expressed in units of molecules reacted per Re atom per hour.

mg atom) in the presence of succinic acid (0.89 g, 7.5 mmol). Decanoic acid was reduced at such a lower temperature range of 100∼120°C and the hydrogen pressure of 25∼100 atm.

The results of the hydrogenation with rhenium-osmium catalyst under various conditions are shown in Table 4. High conversion was obtained even at 25 atm and, especially, the formation of the ester was kept at a very low level. However, the formation of undesirable hydrocarbon was observed. Figure 1 shows the distribution of hydrogenation products as a function of time in the case of 100 atm and 100°C. The hydrocarbon increased gradually from the beginning of the reaction. When most of the carboxylic acid was consumed, the amount of the hydrocarbon increased sharply with a decrease of the reduced alcohol. As a separate experiment, reduction of decanol was carried out by using a rhenium-osmium catalyst. Figure 2 shows that the rate of reduction of alcohol is higher than that of carboxylic acid. This finding suggests that the hydrocarbon was produced mainly by the overreduction of the alcohol (15). In order to suppress the formation of the hydrocarbon, hydrogenation of the carboxylic acid was performed in the presence of a modifier of catalysts (15-17). Among many compounds tried, thiophene was found to be the best. The results are given in Table 5. Although thiophene slightly decreased the reaction rates, the formation of the hydrocarbon was markedly suppressed.

A highly active catalyst for the hydrogenation of carboxylic acids was prepared by the new combination of rhenium and osmium. The catalyst could reduce decanoic acid even at 25 atm and 120°C. Little is known for the reasons of synergistic effects of this catalyst system and the promotional effect of succinic acid, for example, whether rhenium and osmium are alloyed or

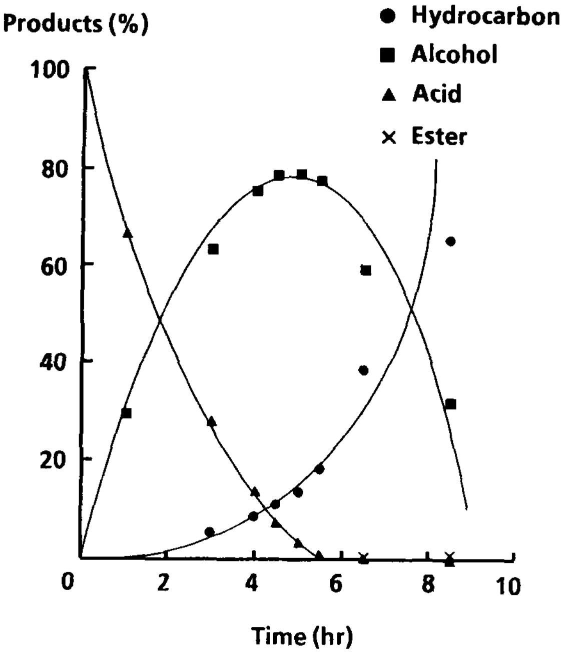

FIG. 1. Hydrogenation of decanoic acid. Reaction conditions; decanoic acid 17.23 g, dioxane 26 g, H_2 100 atm, 100°C. Precursors of the catalyst; Re_2O_7 0.5 g, OsO_4 1.0 g and succinic acid 0.89 g.

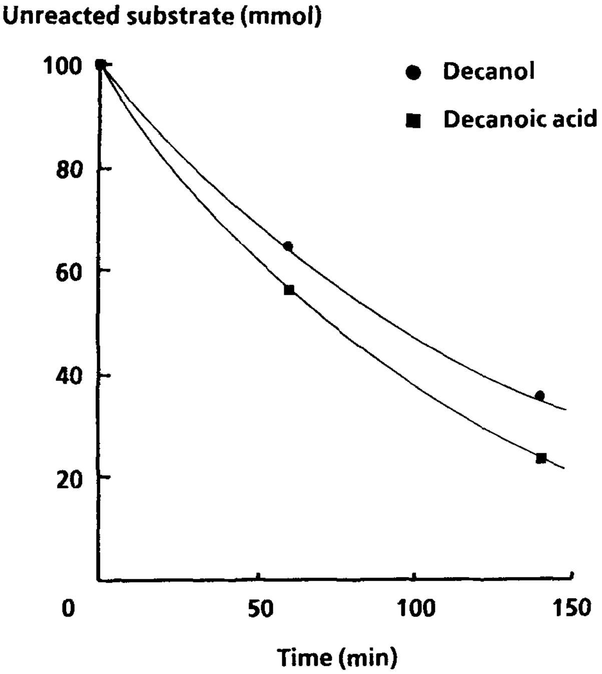

FIG. 2. Hydrogenation of decanoic acid and decanol. Reaction conditions; decanoic acid 17.23 g, decanol 15.83 g, dioxane 26 g, H_2 100 atm, 100°C. Precursors of the catalyst; Re_2O_7 0.5 g, OsO_4 1.0 g and succinic acid 0.89 g.

TABLE 5

Hydrogenation of Decanoic Acid Under Mild Conditions in the Presence of Thiophene[a]

Pressure (atm)	Temp. (°C)	Time (hr)	Thiophene (mmol)	Conv. (%)	TOF[b] (h^{-1})	Products (%)			Selectivity of alcohol (%)
						Hydrocarbon	Alcohol	Ester	
100	100	6.6	0.1	94.4	7.2	8.2	84.9	1.4	89.9
50	110	7.5	0.2	94.4	6.3	12.7	79.6	3.1	84.3
25	120	8.5	0.2	91.5	5.4	17.1	71.9	4.8	78.6

[a] Reaction conditions; decanoic acid 17.23 g, dioxane 26 g. Precursors of the catalyst; Re_2O_7 2.0 mg atom, OsO_4 4.0 mg atom and succinic acid 7.5 mmol.

[b] TOF (turnover frequency) is expressed in units of molecules reacted per Re atom per hour.

not. The detailed understanding of these phenomena requires further work and we intend to characterize the rhenium and osmium bimetallic catalyst.

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