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Abstract

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Rhenium as a Hydrogenation Catalyst

Relatively few works have been devoted to the study of the hydrogenating properties of rhenium. M. S. Platonov and co-workers (1) showed that rhenium obtained by reduction of ammonium perrhenate at room temperature does not hydrogenate a double bond (maleic acid, cyclohexene). The same follows from the recent work of P. F. Ni and N. D. Sokol’ skii (2). However, in the colloidal state rhenium hydrogenates maleic and cinnamic acids at room temperature (3, 4). Raising the temperature to 250° leads to the appearance of activity of rhenium (M. S. Platonov’ s catalyst) with respect to the hydrogenation of cyclohexene to cyclohexane. However, benzene could not be hydrogenated under these conditions.

A detailed examination of the hydrogenating properties of rhenium was the work of Broadbent, Campbell, Bartley, and Johnson (5), in which organic compounds of various classes were subjected to hydrogenation in the presence of rhenium “black,” obtained by reduction of rhenium anhydride in various solvents in an autoclave at 120-200° and an average hydrogen pressure of 150-200 atm.

Reduction of Re_2O_7 was carried out both before hydrogenation and simultaneously with the substance being hydrogenated. The authors showed that rhenium “black”is a good catalyst for the reduction of carboxylic acids and their amides to alcohols and, correspondingly, amines. Reduction conditions: temperature 150-250° and hydrogen pressure on the order of 200 atm. In the presence of rhenium “black,” at high temperature and pressure, double bonds, the carbonyl group, and the nitro group are hydrogenated; the aromatic nucleus is reduced with difficulty: at 330° and 230 atm benzene could be hydrogenated only halfway.

In the present work we studied the hydrogenating properties of a catalyst obtained by reduction of the dioxane complex of rhenium anhydride, described earlier by some of us (6, 7) and studied with respect to the dehydrogenation reaction, in particular, the dehydrogenation of cyclohexane, for which the activity of Re had been predicted by the multiplet theory.

In addition, we obtained a skeletal rhenium catalyst by leaching a rhenium-aluminum alloy (containing 50% Re), which was kindly provided to us by M. A. Tylkina and K. B. Povarova, staff members of the Institute of Metallurgy of the Academy of Sciences of the USSR, for which the authors express their gratitude. On both catalysts, the hydrogenation of compounds containing a double bond, carbonyl and carboxyl groups, and an aromatic nucleus was studied.

Experimental Part

Catalysts Re/C were obtained by reduction of the dioxane complex of rhenium anhydride deposited on activated carbon. The preparation procedure is described in (6, 7).

The skeletal rhenium catalyst Re was prepared as follows. To a solution of 105 g NaOH (chemically pure) in 140 ml of water, gradually, with stirring,

21 g of powdered rhenium–aluminum alloy was introduced. After the reaction had ceased, the reaction mixture was boiled for another 30 min. The resulting catalyst was washed with distilled water to remove alkali until a negative reaction to phenolphthalein was obtained, and was stored under water. The dried catalyst heats up somewhat on contact with air, but it is not pyrophoric. Colorimetric analysis of the catalyst, carried out according to (8, 9), showed that the catalyst obtained in this way contains 86.5% metallic Re. Before use, the catalyst was washed several times with alcohol and with the substance to be hydrogenated.

Experimental conditions. Most experiments were carried out in a rotating autoclave of 225 ml capacity. In addition, experiments were performed in a "duck" and in a flow apparatus at atmospheric pressure.

The reaction products were analyzed by chemical and chromatographic

Table 1

Hydrogenation in the Presence of Rhenium Catalysts

Substance hydrogenated	Amount, ml	Catalyst, g	°C	Initial H_2 pressure, atm	Duration, h	Hydrogenation product	Yield, %
Cyclohexene	20	Re/C 0.7	160	110	2	Cyclohexane	100
»	20	Re_{sk} 0.65	160	110	2	»	100
Octene	15	Re/C 0.7	180	100	2	*n*-Octane	100
»	15	Re_{sk}	180	100	2	»	100
Benzene *		Re/C	190	—	—	Cyclohexane	85
»	20	Re_{sk} 0.65	190	130	4	»	100
Acetone	20	Re/C 1	160	70	1	Isopropyl alcohol	100
»	20	Re_{sk} 0.65	160	100	1	»	100

Substance hydrogenated	Amount, ml	Catalyst, g	°C	Initial H_2 pressure, atm	Duration, h	Hydrogenation product	Yield, %
Dimethyl ester of maleic acid**		Re_{sk}	20	1	10	Dimethyl ester of succinic acid	100

* Hydrogenation in a flow system; catalyst volume 36 ml; benzene feed rate 0.1 ml/min. The catalyst obtained in one pass contained 85% cyclohexane.
** Hydrogenation in a "duck."Under these conditions Re/C does not hydrogenate dimethyl maleate.

methods. Carbonyl compounds were isolated and identified as 2,4-dinitrophenylhydrazones and semicarbazones, and alcohols as phenylurethanes.

Hydrogenation of the double bond and the carbonyl group. Cyclohexene, octene, dimethyl maleate, benzene, and acetone were chosen as substrates. The conditions and results of hydrogenation are given in Table 1. As is evident from the table, in the presence of rhenium catalysts, under fairly severe conditions (high temperature and pressure), hydrogenation of the double and aromatic bonds and of the carbonyl group proceeds practically quantitatively. Hydrogenation of benzene over the catalysts Re/C and Re_{sk} shows that these catalysts, in this respect, differ both from rhenium "black" and from the Platov catalyst. In order at least qualitatively to compare the rates of hydrogenation of the double bond and of the carbonyl group, we studied the hydrogenation of crotonic and cinnamic aldehydes in the presence of both catalysts. Hydrogenation was carried out as follows: 20 ml of aldehyde, 50 ml of ethyl alcohol, and 0.7 g of catalyst were charged into the autoclave. During the hydration, samples were taken for analysis. The hydrogenation temperature was 170–180°, and the initial hydrogen pressure was 110–130 atm.

The results of the experiments are presented in Tables 2 and 3, from which it is evident that, in the presence of both catalysts, hydrogenation of the carbonyl group proceeds faster than that of the double bond for both crotonic and cinnamic aldehydes; therefore, toward the end of hydrogenation, the unsaturated alcohol accumulates, while the saturated aldehyde is already absent. For rhenium "black" in work (5), this selectivity is expressed much more sharply: the authors succeeded in obtaining a hydrogenation product containing 94% crotyl alcohol.

Hydrogenation of carboxylic acids. Hydrogenation of acetic acid in the presence of the Re/C catalyst at 200° and an initial hydrogen pressure of 120 atm leads, in 4-5 hr, to the formation of a mixture of ethyl alcohol (20%), ethyl acetate (50%), and acetic acid (30%). An attempt to suppress the esterification reaction by adding water led to a sharp decrease in the rate of hydrogenation and to a decrease in the yield of its product.

Table 2

Hydrogenation of cinnamic aldehyde

H/aldehyde (mole/mole)	Cinnamic aldehyde	Hydrocinnamic aldehyde	Cinnamyl alcohol	Hydrocinnamyl alcohol
Catalyst Re/C	**Catalyst Re/C**	**Catalyst Re/C**	**Catalyst Re/C**	**Catalyst Re/C**
0.91	8.8	28.4	62.8	–
1.01	–	31.0	67.8	1.2
1.29	–	10.8	60.2	29.0
1.68	–	–	31.7	68.3
1.77	–	–	23.0	77.0
2.00	–	–	–	100
5.00*	Cyclohexylpropyl alcohol—100%	Cyclohexylpropyl alcohol—100%	Cyclohexylpropyl alcohol—100%	Cyclohexylpropyl alcohol—100%
Catalyst Re_sk	**Catalyst Re_sk**	**Catalyst Re_sk**	**Catalyst Re_sk**	**Catalyst Re_sk**
0.50	49.5	17.0	33.5	–
0.84	16.5	37.0	46.5	–
5.00*	Cyclohexylpropyl alcohol	Cyclohexylpropyl alcohol	Cyclohexylpropyl alcohol	Cyclohexylpropyl alcohol

* The hydrogenation temperature was raised to 250°. At a lower temperature, hydrogenation of the benzene ring is not observed.

Table 3

Hydrogenation of crotonic aldehyde

H/aldehyde (mole/mole)	Crotonic aldehyde	Butyraldehyde	Crotyl alcohol	Butyl alcohol
Catalyst Re_sk	**Catalyst Re_sk**	**Catalyst Re_sk**	**Catalyst Re_sk**	**Catalyst Re_sk**
0.59	40.8	28.0	31.2	–
0.94	6.0	37.6	56.4	–
1.47	–	11.7	41.0	47.3
2.00	–	–	–	100
Catalyst Re/C	**Catalyst Re/C**	**Catalyst Re/C**	**Catalyst Re/C**	**Catalyst Re/C**

H/aldehyde (mole/mole)	Crotonic aldehyde	Butyraldehyde	Crotyl alcohol	Butyl alcohol
1.02	–	34.6	63.0	2.4
1.79	–	–	21.0	79
1.82	–	–	18.0	72

The Re_sk catalyst proved to be more active in the hydrogenation of acetic acid, which made it possible to lower the reaction temperature. The hydrogenation product obtained at 170° and an initial hydrogen pressure of 120 atm was a mixture of 17.5% ethyl alcohol, 54.5% ethyl acetate, and 28% acetic acid; hydrogenation of this mixture at 250° led to the formation of ethyl alcohol (83.4%) and ethyl acetate (16.6%).

In the reduction of acetic anhydride in the presence of the Re_sk catalyst at 150° and an initial hydrogen pressure of 145 atm, ethyl acetate was obtained in 60% yield.

Propionic acid is hydrogenated much more slowly than acetic acid; at 150°, over 20 hr, only 0.5 mole of hydrogen was absorbed, calculated per mole of acid being hydrogenated; raising the temperature to 250° led to the absorption, in 5 hr, of another 0.5 mole of hydrogen. The hydrogenation product consisted of two layers; in the lower layer the catalyst had caked. This, in all probability, also caused the decrease in the rate of hydrogenation. The anhydrous hydrogenation product had the following composition (wt.%): propyl propionate 59, propyl alcohol 8.7, propionic acid 32.4. In order to prevent separation of the aqueous layer and caking of the cata-

of the catalyst, hydrogenation was carried out in the presence of ethyl alcohol, dioxane, and propionic anhydride. The results of the experiments are presented in Table 4. As was to be expected, the rate of hydrogenation in the presence of solvents that prevent caking of the catalyst increased sharply. The best results are obtained when hydrogenation is carried out in the presence of dioxane.

Table 4

Hydrogenation of propionic acid in the presence of the catalyst *Re*

Hydrogenation temperature, °C	Initial pressure, atm	H/acid, (mol/mol)	Hydrogenation duration, h	Solvent	Propyl alcohol, wt. %	Propyl propionate, wt. %	Propionic acid, wt. %
175	100	1.20	3	Dioxane	57.0	43.0	–

Hydrogenation temperature, °C	Initial pressure, atm	H/acid, (mol/mol)	Hydrogenation duration, h	Solvent	Propyl alcohol, wt. %	Propyl propionate, wt. %	Propionic acid, wt. %
275	110	1.55	8	C_2H_5OH	64.2	ethyl propionate 27.2; ethyl acetate 5.2	3.4
170	110	1.9	4	Propionic anhydride	3.5	57.1	39.4
285	105	3.4	4	Propionic anhydride	5.5	78.0	16.5

Thus, it has been shown that metallic rhenium supported on activated carbon, and rhenium obtained by leaching a rhenium-aluminum alloy, are effective catalysts for the hydrogenation of double and aromatic bonds, and of carbonyl and carboxyl groups, under pressure and at high temperatures.

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