Hydrogenation of ethyl acetate over supported rhenium catalysts

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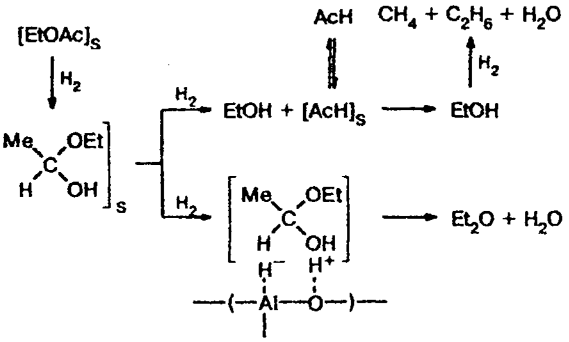
Re/Sibunite is a more active and selective catalyst for hydrogenation of ethyl acetate to ethanol under elevated temperatures and hydrogen pressures than Re/θ-Al_2O_3 and Re/γ-Al_2O_3. The activity of the catalyst is increased on replacing NH_4ReO_4 with $HReO_4$ and treatment of the support with a 13% solution of HNO_3.

Key words: supported Re catalysts, ethyl acetate, ethanol, diethyl ether, hydrogenation.

Ethanol and diethyl ether are the main products of hydrogenation of ethyl acetate (EA) over supported rhenium oxide catalysts.[1] The reaction proceeds *via* the formation of hemiacetal on the surface of Re_S particles according to the following scheme:



The nature of various modifications of alumina affects substantially the selectivity of the 0.5% Re/Al_2O_3 catalysts in EA hydrogenation to ethanol.[1] For instance, the use of γ-Al_2O_3 favors the interaction between rhenium and the support and reduces the yield of the hydrogenation products.[2] It was of interest to find out how replacing conventional oxide supports with a carbon support of the Sibunite type affects the activity and selectivity of the rhenium catalysts.

In this work, the effects of the nature of the starting Re^{VII} compounds deposited on the supported phase, the previous oxidative treatment, and the nature of the support on the hydrogenating activity and selectivity of the supported rhenium catalysts were studied.

Experimental

The catalysts were prepared by impregnation. NH_4ReO_4 or rhenic acid were used as the starting compounds. The support was pretreated with a 13% solution of HNO_3 or oxalic acid at the ratio ReO_4^- : $C_2O_4^{2-}$ = 1 : 5. The catalyst samples were dried at 120 °C and before the run were reduced with hydrogen at 500 °C. Sibunite (C), γ-Al_2O_3, and θ-Al_2O_3 were used as the granulated supports. Their characteristics are presented in Table 1.

The experiments were carried out in a flow system (an integral reactor of stainless steel (d_{eff} = 5.5 mm) with a coaxial pocket for a thermocouple). The reactor was loaded with the catalyst (1.4 g). Duration of the experimental runs was at least 5 h. The liquid reaction products were analyzed by GLC on an Avtokhrom chromatograph (SKB IOKh) (column 1.5 m × 3 mm, Porapak Q, heat-conductivity detector, hydrogen as the carrier gas, feeding rate 30 mL min^{-1}, 150 °C). The gaseous reaction products were analyzed on the same chromatograph at ~20 °C.

The results and conditions of the runs are shown in Table 2.

Results and Discussion

It has been shown previously that strong interaction between metal and support exists in supported rhenium oxide catalysts, which hinders reduction of the metal surface.[2] The reduction of the catalyst with hydrogen or the reaction mixture becomes more complete at a metal loading >1.5%. Therefore, we chose[3] a concentation of Re close to 2%. The findings are presented in Table 2.

Table 1. Characterization of the supports of rhenium catalysts[6]

Support	BW [a] /g cm^{-3}	S_{sp} [b] /m^2 g^{-1}	V_p [c] /cm^3 g^{-1}	l [d] /mm	F [e] (%)
Sibunite	0.60	680	0.32	2—3	300[f]
γ-Al_2O_3	0.63	235	0.65	0.8—1.2	4.1
θ-Al_2O_3 [g]	0.60	60	0.70	0.4—0.8	5.5

[a] Bulk weight. [b] Specific surface. [c] Pore volume.
[d] Size of granules. [e] Mechanical strength. [f] In kg cm^{-3}.
[g] Contains 5% γ-Al_2O_3.

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Table 2. Properties of the supported rhenium-containing catalysts in ethyl acetate hydrogenation (p = 3 MPa, H_2 : EA = 5 : 1; v_{wt} = 0.7 h^{-1})

Catalyst	T /°C	Conversion (%) overall	to EtOH	to Et_2O	to C_1—C_3	S[a] (%)
2% Re/C [b]	230	31.8	24.1	0.1	7.8	75.8
	250	46.1	30.9	0.2	15.0	67.0
	270	65.0	34.7	0.3	30.6	53.4
	230 [c]	30.6	22.3	0.1	8.2	72.9
2% Re/C [d]	230	49.5	38.5	0.1	10.9	77.8
	250	53.5	37.8	0.3	15.3	69.7
	270	69.2	36.2	0.3	32.6	52.3
	210 [c]	37.2	29.9	0.3	7.0	80.4
2% Re/C [e]	230	48.8	37.8	0.1	10.1	78.8
	250	58.8	39.5	0.2	19.1	67.2
	270	52.9	47.6	0.6	44.7	51.2
2% Re/C [f]	230	32.7	23.1	traces	9.2	71.8
	270	68.2	31.3	0.1	36.8	45.9
2% Re/C [g]	230	49.4	39.2	—	10.2	79.4
	250	55.9	36.9	—	19.0	66.0
	270	60.9	32.1	—	28.8	52.7
0.5% Re/γ-Al_2O_3	230	11.3	5.5	3.9	1.9	48.7
2% Re/γ-Al_2O_3	230	44.0	29.6	11.0	3.4	67.3
0.5% Re/θ-Al_2O_3	230	18.2	13.0	3.9	1.3	71.4
2% Re/θ-Al_2O_3	230	31.9	23.3	3.4	5.2	73.0
	250	47.0	29.6	6.1	11.3	63.0
	270	51.2	26.9	11.1	13.2	52.5
	230 [c]	28.4	19.5	2.7	6.2	68.7
2% Re/θ-Al_2O_3 [f]	230	37.2	29.0	3.3	4.9	78.0
	250	61.3	37.1	6.3	17.9	60.5
	270	77.1	36.7	7.2	33.2	47.6

[a] Selectivity of hydrogenation to ethanol.

[b] Prepared from NH_4ReO_4.

[c] After 20-h operation.

[d] The support was treated with a 13% solution of HNO_3 for 0.5 h.

[e] The support was treated with a 13% solution of HNO_3 for 1 h.

[f] The support was treated with oxalic acid.

[g] Prepared from $HReO_4$.

It follows from comparison of the activity and selectivity of the catalysts 0.5% and 2.0% Re/γ-Al_2O_3 and Re/θ-Al_2O_3 in EA hydrogenation to ethanol at 230 °C that when the rhenium loading is increased by 4 times, the overall conversion over the Re/γ-Al_2O_3 catalyst increases nearly by 4 times (from 11.3% to 44.0%) and the selectivity increases by the factor of 1.4. The overall conversion of EA over the 0.5% Re/θ-Al_2O_3 and 2.0% Re/θ-Al_2O_3 catalysts increases only by the factor of 1.8 (from 18.2% to 31.9%) and the selectivity of hydrogenation to alcohol changes only slightly. The selectivity of EA hydrogenation to ethanol over the 2% Re/C catalyst under similar conditions is 75.8% at an overall conversion of 31.8%. Diethyl ether is practically absent in the reaction products, whereas the conversions of EA to diethyl ether over the 2% Re/θ-Al_2O_3 and 2% Re/γ-Al_2O_3 catalysts are 3.4 and 11%, respectively. In the case of the 2% Re/C catalyst, an increase in the reaction temperature from 230 to 270 °C reduces the overall conversion and the yields of ethanol and C_1—C_3 hydrocarbons. After a 20-h run, the catalyst exhibits the initial activity. When ammonium perrhenate was replaced by rhenic acid during the preparation of the 2% Re/C catalyst, the catalyst activity was increased. Diethyl ether is absent in the reaction products, and this is likely caused by the fact that rhenium in rhenic acid is reduced more easily than that in ammonium perrhenate.

These findings show that the Re/C catalyst is more selective in EA hydrogenation than the rhenium oxide catalysts. The catalysts under study can be arranged in the series with respect to the selectivity to ethanol: Re/C > Re/θ-Al_2O_3 > Re/γ-Al_2O_3.

Previously,[4] the activity and selectivity of the 0.5% Re/Al_2O_3 catalysts prepared from α-, δ-, θ-, and γ-Al_2O_3 have been correlated with the valent state of rhenium estimated from the IR spectra of CO adsorbed on the catalysts prior to and after hydrogenation. As a result, a conclusion has been drawn that metallic rhenium exists on the surface of the catalysts in two states, Re_x^0 and Re_y^0, that differ by dispersion, the character of interaction with a support, and the capability of coking. EA is transformed into ethanol and hydrocarbons over Re_x^0 and into ethanol and diethyl ether over Re_y^0. The quanitative ratio between these different states of metallic rhenium determines their activity and selectivity in the EA conversion.

Similar results were obtained for the 2% Re/γ-Al_2O_3 and 2% Re/θ-Al_2O_3 catalysts. Ethanol and hydrocarbons are present in the reaction products over Re/C and diethyl ether is absent. Apparently, only one state of metallic rhenium, Re_x^0, occurs on the surface of Re/C. This can be due to the fact that in the Sibunite-supported Re, unlike Re/γ-Al_2O_3 and Re/θ-Al_2O_3, the strong interaction between rhenium and the support is absent and Re^{VII} is reduced completely to Re_x^0.

The treatment of the Re/C and Re/θ-Al_2O_3 catalysts with oxalic acid virtually does not affect their hydrogenating activity and selectivity. When the temperature is increased, overall conversion increases due to increasing fractions of by-products, C_1—C_3 hydrocarbons.

The pretreatment of the most active Re/C catalyst with a 13% solution of HNO_3 leads to a significant increase in the overall conversion in EA hydrogenation while maintaining the high selectivity to ethanol. Duration of the treatment (0.5 and 1 h) virtually does not change the activity and selectivity of the Re/C catalyst. Possibly, the size of the particles of reduced rhenium decreases and the dispersion increases because of the treatment of Sibunite with HNO_3. A similar effect has been observed[5] when the Pd/C catalyst was treated with nitric acid.

A considerable effect of the previous oxidative treatment of the 2% Re/C and 2% Re/θ-Al_2O_3 catalysts with nitric and oxalic acids on cyclohexane dehydrogenation to benzene at 350 °C, v_{wt} = 0.5 h^{-1}, and atmospheric pressure has been shown previously.[6]

Unlike hydrogenation, dehydrogenation is a structure-sensitive reaction, and the genesis of the catalyst, including acid pretreatments, has a more pronounced effect on its occurrence.

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A simple method for preparing racemic dolichols from the polyprenols of pine needles (*Pinus silvestris*)

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A simple method for preparing racemic mammalian dolichols by a three-stage transformation of a native mixture of plant polyprenols has been developed.

Key words: (±)-dolichols, polyprenols, oxidation, polyprenal, dolichal, 1,4-reduction of enals, sodium dithionite.

2,3-Dihydroprenols, which belong to a group of dolichols (**1**), are participants in biosynthesis of glycoproteins of mammalian cells.[1] Investigation of these vitally important processes has been intensively developing recently. Hence, the search for preparative methods of the synthesis of alcohols of type **1** for preparation of biosynthetic intermediates and modified analogs on their basis has become timely (see, for example, Ref. 2). At the same time the isolation of dolichols **1** from natural sources is a labor-consuming procedure since their contents in eukaryotic cells, where they exist as mixtures of isoprenologs, is extremely low (thus, for example, only 0.2 g of dolichols was isolated from 5 kg of pig liver[3]).

At the present time a number of methods of total synthesis of compounds of type **1** are known; however, they are not acceptable as preparative methods since they include too many stages (see reviews[4,5] and papers cited therein). Partial synthesis of dolichols **1** by transformation of significantly more available allyl alcohols of plant origin, polyprenols **2**, looks more attractive.[6] Two approaches to accomplish such transformation are described.[5] One of them is based on lengthening of the oligoisoprene chain of polyprenols **2** by a saturated unit using synthetic C_5-blocks specially prepared for this purpose. The alternative most effective method includes catalytic hydrogenation of allyl alcohols of type **2** or their derivatives. However, the disadvantage of this approach is the necessity of using very expensive catalysts to guarantee a high selectivity of hydrogenation of the terminal double bond in oligoolefins **2**.

In this paper we report a new method for the synthesis of a mixture of (±)-dolichols **1′** (Scheme 1) based on

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