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The hydrogenation of ethyl acetate (EA) can be regarded as a model reaction for the preparation of higher alcohols from esters of synthetic fatty acids. Rhenium oxides display a high activity in this reaction. Thus, at 150°C and 170-190 atm (liquid phase, a static system), EA is reduced quantitatively on these catalysts to ethanol. Conventional catalysts of a liquid-phase hydrogenation (PtO₂, Raney Ni, RuO₂) and also the industrial copper-chromium catalyst are less active under these conditions [1]. It is natural to assume that Re oxides will act as effective components of deposited catalysts for the hydrogenation of esters. However, information on these catalysts is limited to a single patent [2].

We have already developed a method for the activation of low-concentration Re catalysts for the hydrogenation of benzene by treating a deposited Re(VII) by the reaction mixture at 180-250°C [3].

In the present work, we studied the catalytic properties of a 5% Re/ γ -Al₂O₃ contact in the hydrogenation reaction of EA. To clarify the paths of formation of the by products, experiments were also carried out with ethanol under the conditions of hydrogenation of EA.

EXPERIMENTAL

A catalyst containing 5% of Re was prepared by impregnating the support with an aqueous solution of NH₄ReO₄. It was then dried in a desiccator over a zeolite, in air at 120°C, and was calcined for 3 h at 300°C. An IK-02-200 brand γ -Al₂O₃ (biporous structure, a 0.4-0.8 mm sphere, Na₂O content - 0.04% and Fe₂O₃ 0.02%) was used as the support. After being dried over a CaA zeolite, the cp grade ethyl acetate contained <0.01% of H₂O. Hydrogen was purified from O₂ over the Cu/kieselguhr catalyst (50-100 gauge atmospheres, 280°C) and from H₂O vapor, by NaA zeolite at 20-25°C. The experiments were carried out on a flow-type apparatus (a stainless steel integral reactor with d_{ef} = 5.5 mm and coaxial housing for the thermocouple).

A 1.4-g portion of the catalyst was charged into the reactor. The samples were activated directly during the experiment. The liquid products were analyzed by the GLC method on an LKhM-8M chromatograph (Special Construction Bureau of the Institute of Organic Chemistry) (catharometer, carrier gas He, flow rate 30 ml/min, 155°C, a 1.8 m × 2 mm column, Porapak-Q) and on a Varian MAT-111 chromatograph/mass spectrometer (a 1.5 m × 3 mm column, 5% SE-30 on Chromatone, 50°C, flow rate of He 25 ml/min). The effluent gas was analyzed on an LKhM-8 MD chromatograph (catharometer, a 1.5 m × 3 mm column with CaA zeolite, 25°C, flow rate of He or N 30 ml/min).

According to the data of five parallel experiments on different catalyst samples (total conversion of EA 30-40%), the standard deviation of the conversion value of EA into ethanol was ± 9.7 rel. %. The selectivity of the catalyst was calculated as percent ratio of the conversion value into ethanol to the total conversion of EA (Table 1).

DISCUSSION OF RESULTS

Table 1 shows that the main product of the hydrogenation of EA is ethanol. In addition, Et₂O, water, and traces of acetaldehyde were found in the catalyzate. A qualitative proof for the presence of Et₂O in the reaction products is the presence of peaks with m/z₀ = 74 and 59 in the mass spectra. In the effluent gas, the main components were methane and ethane, as well as H₂; propane and butane were detected in trace amounts.

The values of overall conversion of EA into hydrocarbons listed in Table 1 were calculated from the formula

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TABLE 1. Influence of Temperature and Total Pressure on Properties of 5% Re/ γ -Al₂O₃ Catalyst (molar ratio H₂:EA = 5, V_{max} = 0.72 h⁻¹)

T, °C	P _{total} , atm	Comp. of catalyzate, %				Yield of liq. catalyzate	Conversion of EA, percent					S, %
		C ₂ H ₅ OH	Et ₂ O	H ₂ O	EA		C ₂ H ₅ OH	Et ₂ O	C ₁ -C ₄	coke plus losses	total	
190	30	16,7	0,7	0,6	82,0	100	15,9	0,8	1,0	0,3	18,0	88,3
210	30	28,1	1,6	1,5	68,8	100	26,8	1,9	2,7	0,2	31,2	85,9
230	30	33,0	2,5	2,8	61,7	99,5	31,4	3,0	5,3	1,1	36,6	81,3
250	30	46,0	4,8	6,5	42,7	93,0	40,9	5,3	12,1	2,0	60,3	67,8
270 [†]	30	30,0	4,4	13,4	51,3	72,3	20,7	3,8	21,8	15,7	62,9	32,9
230	5	5,3	0,9	0,6	93,2	99,7	5,1	1,0	0,8	0,2	7,1	71,8
230	15	12,9	1,7	1,0	84,5	100	12,3	2,0	1,4	0,2	15,5	79,4
230	60	51,8	2,3	4,4	41,8	98,9	49,0	2,7	9,3	2,3	58,7	83,5

*After 4.5-5 h of catalyst operation.

†Data at the end of 3 h of catalyst operation. Traces of acetic acid and 0.9% of acetaldehyde were detected in the catalyzate.

$$K = \left(a - \frac{M_{H_2O}}{M_{Et_2O}} e \right) \frac{M_{EA}}{2M_{H_2O}} B$$

where a is the weight fraction of H₂O in the catalyzate; e - the same in Et₂O, B is % yield of liquid catalyzate; M is the molecular weight.

Before the experiment, the catalyst was activated under standard conditions: 230°C, 30 atm, V_{max} = 0.7 h⁻¹, molar ratio H₂:EA = 5, at which a close to steady conversion of EA into ethanol and Et₂O was established after 1.5 h from the start of the experiment. The conversion into hydrocarbons was stabilized only after 3.5-4 h of the catalyst operation.

The high yield of ethanol after only 1.5 h of contact of the catalyst with the reaction mixture indicates completion of the process of its activation. Initially, Re(VII) is reduced to Re at a lower degrees of oxidation, as confirmed by the change in the initial white color of the samples to dark gray. A similar color of the catalyst is observed also after treatment with hydrogen under the same conditions.

The steady activity of the catalyst was retained under standard conditions, even after 40 h of the operation. The temperature of the process was then increased from 190 to 250°C, and the pressure from 5 to 60 atm. The content of coke in the sample was 0.19%.

Increase in the molar ratio of H₂:EA from 5 to 20 (230°C, 30 atm, V_{max} = 0.7 h⁻¹) leads to an inappreciable increase in the conversion into ethanol, and decrease in the selectivity of the reaction. Consequently further experiments were carried out at a ratio equal to five.

Table 1 shows that with increase in the temperature from 190 to 270°C, the overall conversion of EA increases only up to 250°C. At the same time, the conversion of EA into ethanol and Et₂O reaches maximal values of 40.9 and 5.2%, respectively. At 270°C, these values decrease sharply, while the yield of hydrocarbons increases over the whole range of temperatures.

The selectivity of the hydrogenation changes little in the range of 190-230°C, remaining at the level of above 80%, but rapidly decreases at higher temperatures. One of the main reasons for the decrease in the selectivity is probably the considerable acceleration of the conversion reaction of the alcohol into hydrocarbons. The occurrence of these reactions can be deduced from the character of the kinetic curves of formation of the main products of the conversion of EA at 270°C, 30 atm, H₂:EA = 5 (Fig. 1). With increase in the overall conversion of EA, the corresponding curves for ethanol and Et₂O pass through a maximum, while the rate of accumulation of hydrocarbons continues to increase. Hence it follows that ethanol and Et₂O are intermediate products in the successive conversion of EA into hydrocarbons. Under our experimental conditions, the catalyst retains its stability at low degrees of conversion of the ester, but its properties change irreversibly as the result of prolonged operation with a high conversion of EA (V_{max} = 0.7 h⁻¹). At the end of 3 h operation, traces of acetic acid appear in the catalyst, i.e., the hydrolysis of EA begins. This process increases

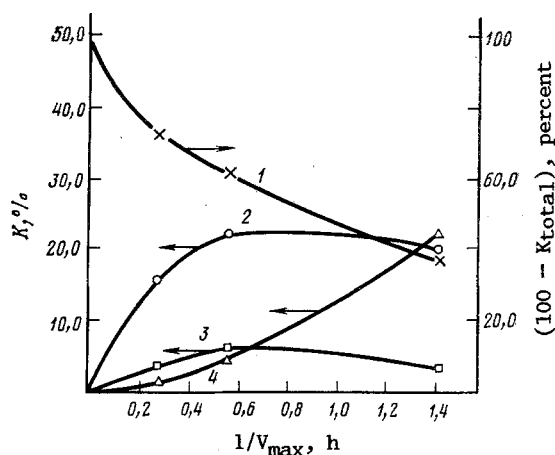


Fig. 1. Kinetic curves of conversion of EA at 270°C, $P_{\text{total}} 30$ atm, molar ratio of $\text{H}_2:\text{EA} = 5$: 1) K_{total} ; 2) $K_{\text{C}_2\text{H}_5\text{OH}}$; 3) $K_{\text{hydrocarb}}$; 4) $K_{\text{Et}_2\text{O}}$.

with time and does not cease even after the temperature has been decreased to 210°C. Since the hydrolysis of esters belongs to the class of reactions which are catalyzed by acids and bases, it can be assumed that under the influence of the reaction medium, the acid-base function of the catalyst surface intensifies.

Increase in the pressure from 5 to 60 atm (see Table 1) leads to a noticeable increase in the selectivity of hydrogenation. The conversion of EA into ethanol and hydrocarbons increases by one order of magnitude, while the conversion into Et_2O changes inappreciably and is practically independent of pressure in the 30-60 atm range.

At 60 atm, 230°C, and $\text{H}_2:\text{EA} = 5$, the kinetic curves of the accumulation of the reaction products (Fig. 2) have a different form from those in Fig. 1, despite the similar levels of the maximum overall conversion of EA in both cases. On the curves for ethanol and Et_2O , there are no maxima, while the rate of accumulation of hydrocarbons is independent of the degree of the overall conversion of EA. Thus, increase in pressure differently influences the rate of formation of ethanol and of byproducts.

On the strength of all the results obtained it can be concluded that under selected conditions, the 5% $\text{Re}/\gamma\text{-Al}_2\text{O}_3$ catalyst has multifunctional properties. Besides ethanol, Et_2O , CH_4 and C_2H_6 are also formed, and in general, the yield of hydrocarbons is higher than that of Et_2O . The byproducts can be obtained as the result of the dehydration of ethanol on $\gamma\text{-Al}_2\text{O}_3$, as well as by the hydrogenolysis of carbon-oxygen bonds in the alcohol and Et_2O on rhenium. It is known that on $\gamma\text{-Al}_2\text{O}_3$ at 230-270°C, mainly Et_2O is formed from ethanol [4]. The predominance of hydrocarbons in the byproducts of the hydrogenation of EA is probably a result of the occurrence of the above mentioned hydrogenolysis reactions under the experimental conditions.

These suppositions are qualitatively confirmed by specially devised experiments for studying the transformations of ethanol on the same catalyst. The samples were previously activated under standard conditions of hydrogenation of EA to a steady activity, and then H_2 was passed in for 2 h at atmospheric pressure at 230°C. The experiments with ethanol were carried at the same temperature, $V_{\text{max}} = 0.63 \text{ h}^{-1}$, $P_{\text{C}_2\text{H}_5\text{OH}} = 2.9$ atm, $P_{\text{H}_2} = 27.1$ atm. The partial pressure of ethanol corresponded to that obtained after the contact of the reaction mixture with the catalyst during the hydrogenation of EA under standard conditions. The main transformation products of ethanol are CH_4 , C_2H_6 as well as H_2O and Et_2O . The yield of diethyl ether from ethanol was half that obtained from EA, while that of hydrocarbons was 4-5 times higher. Similar experiments in He medium showed that in this case the conversion of the alcohol into hydrocarbons decreased ~ 4 times, i.e., the main part of their formation is hydrogenolysis, and not the dehydration of ethanol. The activity of the catalyst in the hydrogenation reaction of EA does not change after the experiments with ethanol in H_2 and decreases after treatment with ethanol in He medium.

The fact that Et_2O forms from ethanol at a lower rate than from EA is of interest. It is possible that there is a direct path of reduction of the ester into the ether by omission of the stage of formation of the alcohol, for example, via a semiacetal.

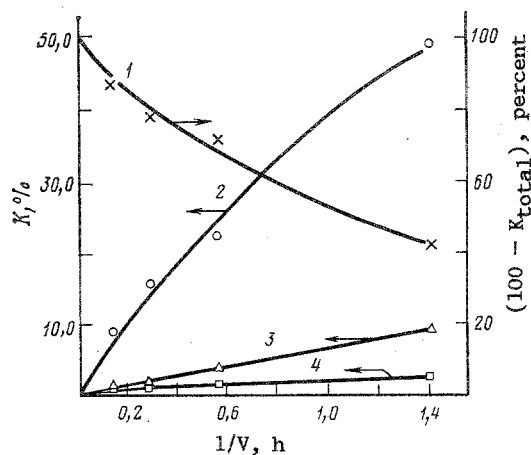
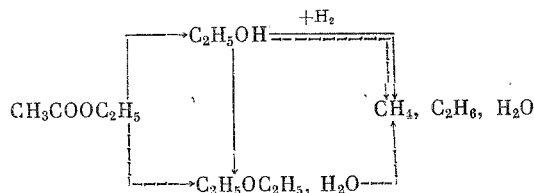


Fig. 2. Kinetic curves of conversion of EA at 230°C, P_{total} 60 atm, molar ratio $\text{H}_2 + \text{EA} = 5$: 1) K_{total} ; 2) $K_{\text{C}_2\text{H}_5\text{OH}}$; 3) $K_{\text{hydrocarb}}$; 4) $K_{\text{Et}_2\text{O}}$.

From the results obtained, the main paths of the conversion of EA into ethanol, diethyl ether, hydrocarbons, and water on a 5% $\text{Re}/\gamma\text{-Al}_2\text{O}_3$ catalyst can be represented in the following way:



CONCLUSIONS

1. The possibility was shown of the activation of the 5% $\text{Re}/\gamma\text{-Al}_2\text{O}_3$ catalyst for the hydrogenation of ethyl acetate directly into ethanol under the experimental conditions (230°C, 30 atm, molar ratio H_2 :ethyl acetate = 5). Thus, deposited rhenium(VII) is reduced to rhenium at lower degrees of oxidation.

2. In the range of conditions studied, the maximal conversion of ethyl acetate (EA) into ethanol is 49% (selectivity 83.5%), which is observed at 60 atm, 230°C, H_2 :EA = 5, $V_{\text{max}} = 0.7 \text{ h}^{-1}$. Increase in the temperature and molar ratio, and also decrease in pressure leads to a decrease in the selectivity of hydrogenation of ethyl acetate into ethanol.

3. Byproducts of the hydrogenation of ethyl acetate – diethyl ether and hydrocarbons – are formed not only as the result of dehydration of ethanol on $\gamma\text{-Al}_2\text{O}_3$, but also directly from ethyl acetate (diethyl ether) and also by the hydrogenolysis of the C-O bond in ethanol on rhenium (hydrocarbons).

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