EFFECT OF THE NATURE OF THE CARRIER AND REDUCTION
CONDITIONS ON THE PROPERTIES OF RHENIUM CATALYSTS
OF HYDROGENATION OF ETHYL ACETATE

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We previously [1] showed that 5% $Re/\gamma-Al_2O_3$ catalyst reduced with a mixture of H_2 and ethyl acetate (EA) hydrogenates EA into ethanol. Et_2O, H_2O, and hydrocarbons are formed as by-products. It was concluded that hydrogenation of EA, as well as hydrogenolysis of ethanol and possibly Et_2O, take place on the metal. Dehydration of the alcohol takes place on the carrier. Similar results were also obtained in hydrogenation of EA on Rh/Al_2O_3 catalysts [2].

The effect of the nature of the carrier ($\theta-$, $\delta-$, $\alpha-Al_2O_3$ and SiO_2) and the conditions of reduction (H_2 + EA reaction mixture at 230°C; H_2 at 500°C) on the properties of the prepared samples was investigated in the present study. To test the hypothesis advanced in [1] on the possibility of parallel formation of Et_2O and EtOH from EA on samples of $RE/\theta-Al_2O_3$, the dependence of the yield of these products on the feed rate of the reaction mixture was studied.

EXPERIMENTAL

The catalysts were prepared by impregnation of the carrier with rhenic acid by the method in [1]. The concentration of rhenium was 0.5 wt.%. The different modifications of Al_2O_3 which differed with respect to the crystal structure and S_{sp} were prepared by treatment of $\gamma-Al_2O_3$ in air at temperatures of 800-1200°C. The detailed characteristics of the starting $\gamma-Al_2O_3$ are reported in [1]. A sample based on SiO_2 (brand KSK contains 0.04% Fe_2O_3) was prepared for comparison.

The type of crystal structure of the carriers was determined by XPA on a DRON-2 diffractometer. S_{sp} was measured by low-temperature adsorption of nitrogen (BET). The properties of the prepared catalysts in the reaction of hydrogenation of EA were studied at 230°C, 3 MPa, with H_2:EA molar ratio = 5 and V_{wt} = 0.7 h^{-1}. The experimental method and method of analysis of the products are reported in [1]. The precision of determination of the material balance was ±7 rel.%. The samples were reduced by two methods: directly during the experiment with the reaction mixture (treatment 1) or with H_2, 3 h at 500°C (treatment 2). According to our data, significant changes in the hydrogenating properties of 0.5% $Re/\gamma-Al_2O_3$ are observed in the last case in comparison to treatment 1. The results of the experiments are reported in Table 1.

The dependence of the conversion of EA into Et_2O and EtOH on the reaction mixture feed rate (Fig. 1) was obtained on several samples of 0.5% $Re/\theta-Al_2O_3$ catalyst (treatment 2) at 270°C, 3 MPa, and H_2:EA = 5. In these conditions, the 30% selectivity of the reaction for ethanol changes insignificantly up to total conversion of EA, remaining within the limits of 37.4 ± 6.4%. The dispersion of the reproducibility of the values of conversion of EA into EtOH and Et_2O with a decrease in the total conversion of EA from 28.4 to 5.5% increased from 7.2 to 11.1 rel.% for ethanol and from 2.8 to 11.8 rel.% for Et_2O.

RESULTS AND DISCUSSION

As Table 1 shows, regardless of the conditions of reduction, $Re/\theta-Al_2O_3$ is most active in the reaction of hydrogenation of EA into ethanol. The other catalysts differ insignificantly in activity if they are reduced by the reaction mixture (K_{EtOH}^1). However, after treatment 2, conversion of EA into ethanol (K_{EtOH}^2) changes for all samples, and the differences between them become more pronounced. The catalysts studied in this case can be placed in the following order with respect to their activity in hydrogenation of EA into ethanol:

TABLE 1. Hydrogenation of EA on Rhenium Catalysts (230°C, 3 MPa, H_2:EA molar ratio = 5, V_{wt} = 0.7 h^{-1})

Carrier	S_{sp}, m^2/g	Treatment number	Conversion of EA (C), % into			K^1_{EtOH}/K^2_{EtOH}	Selectivity, %		
			EtOH	Et₂O	C₁—C₄*		EtOH	Et₂O	C₁—C₄
α-Al₂O₃	9,7	1	4,1	—	1,0	0,53	80,4	—	19,6
		2	7,7	—	1,5		83,7	—	16,3
δ-Al₂O₃	67,0	1	6,1	—	1,3	1,1	82,4	—	17,6
		2	5,6	—	1,2		82,4	—	17,6
θ-Al₂O₃	127	1	13,0	3,6	1,3	1,4	72,6	20,1	7,3
		2	9,1	4,5	0,4 **		65,0	32,1	2,9
γ-Al₂O₃	184	1	5,5	3,9	1,9	1,8	48,7	34,5	16,8
		2	3,1	4,6	0,3 **		38,8	57,5	3,7
SiO₂	286	1	4,5	tr.	1,4	1,2	76,3	—	23,7
		2	3,7	tr.	1,0		78,7	—	21,3

*C_3—C_4 no greater than 5% of C_1—C_4.
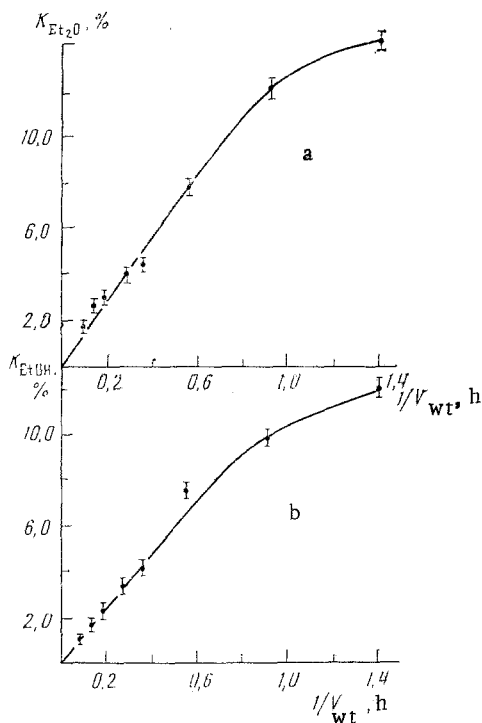**Conversion after 6–8 h of work.

Fig. 1. Kinetic curves of the formation of Et_2O (a) and ethanol (b) on Re/θ-Al₂O₃ catalyst reduced with H_2 at 500°C.

Re/θ-Al₂O₃ > Re/α-Al₂O₃ > Re/δ-Al₂O₃ > Re/SiO₂ ≈ Re/γ-Al₂O₃. Re/θ-Al₂O₃ is ∿3 times more active than Re/γ-Al₂O₃. The character of the effect of the method of reduction on the activity of the catalysts is graphically illustrated by the value of ratio K^1_{EtOH}/K^2_{EtOH} and is a function of the nature of the carrier. In the case of Re/γ-Al₂O₃, after treatment 2 conversion of EA into alcohol decreases by ∿2 times in comparison to treatment 1, while it increases for Re/α-Al₂O₃. As a result, in going from Re/α-Al₂O₃ to Re/γ-Al₂O₃, the value of K^1_{EtOH}/K^2_{EtOH} decreases by more than three times.

Regardless of the method of reduction, the selectivity of hydrogenation of EA into ethanol was maximum on the Re/α-Al₂O₃ sample. After treatment 2, its value decreased in the case of Re/γ-θ-Al₂O₃ and virtually did not change on the samples of Re/α, θ-Al₂O₃ and Re/SiO₂.

Et_2O is only formed in commensurate amounts in the presence of Re/γ-Al₂O₃ and Re/θ-Al₂O₃, and after treatment 2, its yield is ∿20% higher than on the unreduced catalysts. Treatment 2 is accompanied by a significant increase in the selectivity of formation of Et_2O. On Re/γ-Al₂O₃, this product becomes basic and its yield is 1.5 times higher than the yield of ethanol.

In contrast to Et_2O, C_1-C_4 hydrocarbons are formed on all of the catalysts after treatment 1. The maximum yield is observed on $Re/\gamma-Al_2O_3$, and the minimum is observed on $Re/\alpha-Al_2O_3$, although the differences are relatively small. The selectivity of formation of hydrocarbons is also weakly dependent on the nature of the carrier on the samples after treatment 1 and minimum for $Re/\theta-Al_2O_3$. Preliminary treatment 2 results in a sharp decrease in conversion of EA into hydrocarbons in the case of $Re/\gamma-$ and $\theta-Al_2O_3$. The yield of hydrocarbons, like the selectivity of their formation, changes insignificantly on the remaining catalysts.

Let us examine the effect of the nature of the carrier and the conditions of reduction on the activity of rhenium in the reaction of hydrogenation of EA to ethanol. These factors determine the degree of reduction and dispersion of the metal and the character of chemisorption of H_2 to a significant degree [3]. After treatment 2, Re(VII) applied to SiO_2 and $\theta-Al_2O_3$ is totally reduced. This does not take place in the case of $\gamma-Al_2O_3$. The dispersion of the metal decreases in the order $Re/\gamma-Al_2O_3 > Re/\theta-Al_2O_3 > Re/SiO_2$. The temperature of the desorption maximum (200-300°C) of hydrogen capable of participating in hydrogenation decreases in the same order [3]. Based on these data, the activity of the $Re/\theta-Al_2O_3$ catalyst, the maximum among the samples listed, can be attributed to the higher dispersion of rhenium in comparison to Re/SiO_2 and the higher degree of reduction of the metal in comparison to $Re/\gamma-Al_2O_3$.

In contrast to hydrogenation of benzene [3], no correlation between the reaction rate and bond strength of the chemisorbed hydrogen is observed in hydrogenation of EA into ethanol on catalysts reduced at 500°C.

For example, the samples of Re/SiO_2 and $Re/\gamma-Al_2O_3$ differ strongly in the character of chemisorption of H_2, but exhibit similar activity. The stage involving chemisorbed H_2 is apparently not limiting in hydrogenation of EA into ethanol on rhenium.

The activity of the catalysts after treatment 1 is usually higher than after treatment 2. The difference is particularly marked in the case of $Re/\gamma-Al_2O_3$, where the rhenium reacts strongly with the carrier and is correspondingly more difficult to reduce [4]. It is possible to hypothesize that like the $H_2 + C_6H_6$ mixture [4], H_2 + EA at 230°C is a more efficient reducing agent of applied Re(VII) than pure H_2 at 500°C [1]. It is also possible that a metal with a higher dispersion is formed in the soft conditions of treatment 1.

The different effect of the method of reduction on the activity of the catalyst as a function of the nature of the carrier (samples based on Al_2O_3) is apparently due to a change in the character of the reaction of the rhenium with the surface. In the case of $\gamma-Al_2O_3$, the perrhenate anion is apparently localized near acceptor centers of a defective spinel structure in the unreduced samples. The electron deficiency on the metal particles indicates that this localization is also preserved after reduction [4]. Annealing of $\gamma-Al_2O_3$ at high temperatures results in the formation of carriers with a less defective crystal structure. The number of acceptor (Lewis) centers, which are almost absent on the surface of $\alpha-Al_2O_3$, simultaneously decreases [5]. As a result, there is a significant change in the conditions of formation of particles of the active phase of rhenium and correspondingly, a different dependence of its hydrogenating activity on the reduction conditions is observed.

The presence of Lewis centers on the surface of $Re/\gamma-$ and $\theta-Al_2O_3$ catalysts also causes the side reaction of formation of Et_2O. On Rh/Al_2O_3, [2], the appearance of this product in the catalyzate is due to the successive dehydration of the ethanol obtained from EA on the carrier. As indicated in [6], this reaction takes place on the Lewis centers of Al_2O_3. This explanation does not correspond to the available experimental data in the case of rhenium catalysts, however.

According to [1], the yield of Et_2O from EA is higher than from ethanol on 5% $Re/\gamma-Al_2O_3$ with all other conditions being equal. For this reason, it was hypothesized that the reactions of formation of Et_2O and EtOH from EA can take place parallelly through the same transition state of the hemiacetal type. The kinetic features of formation of Et_2O and EtOH on a 0.5% $Re/\theta-Al_2O_3$ catalyst (sample 2) at 270°C and 3 MPa and with H_2:EA = 5 were studied to test this hypothesis. Similar values of the conversion of EA into alcohol and Et_2O were observed in these conditions, which ensures the equal precision of the measurements required for statistically substantiated conclusions.

The sample of catalyst selected has a higher stability than $Re/\gamma-Al_2O_3$, and the conditions of its activation permit suppressing the side reaction of formation of hydrocarbons. For parallel reactions, the ratio of their rates should approach a constant value with a decrease

in the contact time [7]. The kinetic dependences, in the shape of curves with saturation, obtained in the range of EA feed rates from 0.72 to 11.1 h^{-1} are shown in Fig. 1. Their initial segments can be approximated by linear functions of the following form:

$$1)\ K_{Et_2O} = (17,5 \pm 2,0)\ 1/V_{wt}\ ,\ 2)\ K_{EtOH} = (12,8 \pm 0,5)\ 1/V_{wt} \qquad (1)$$

In relative units, the dispersion of the adequacy for the first line is 11.2% and 3.6% for the second. In consideration of the dispersions of the reproducibility of the results with low conversions (11.1 and 11.8% for ethanol and Et_2O), it can be concluded that within the limits of the precision of the measurements, the rates of formation of these products are constant with brief contact times, i.e., their ratio is constant. The data obtained thus do not contradict the previous hypothesis in [1] concerning the parallel formation of ethanol and Et_2O during hydrogenation of EA.

Conversion of EA into EtOH (I) and Et_2O (II) on Re/γ- and θ-Al_2O_3 catalysts through the intermediate transition state of the hemiacetal type, formed on the surface of Re (S), can be represented by the following scheme
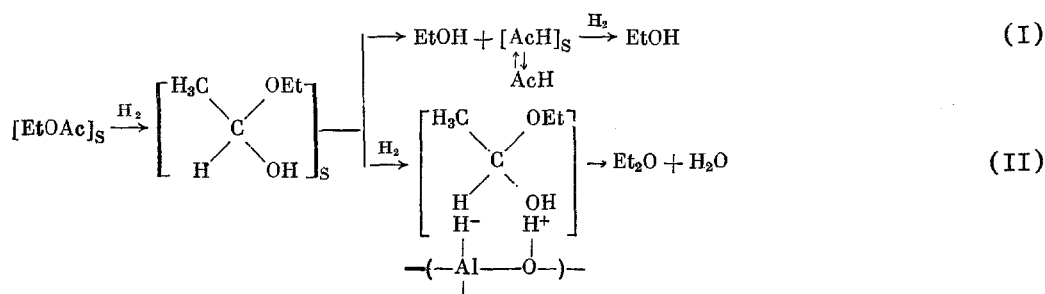
We will hypothesize that EtOH and Et_2O are formed on different active centers. In the first stage of reaction (I), the chemisorbed hemiacetal decomposes with liberation of alcohol in the gas phase and acetaldehyde (AcH) in the chemisorbed state. The latter is partially desorbed into the gas phase, and most is hydrogenated into EtOH, freeing an active center on the surface of the Re. It is also possible that the chemisorbed AcH can subsequently undergo hydrogenolysis into hydrocarbons.

Reaction (II) takes place on particles of Re located in the immediate vicinity of the Lewis centers on the surface of the Al_2O_3. Substitution of the hemiacetal OH group by the hydride ion of the H_2 molecule dissociated on the Lewis center with the participation of a neighboring oxygen atom, synchronously with splitting of H_2O, is one of the stages of reaction (II).

The above scheme is based on the following experimental data. Traces of acetaldehyde are always present in the products of the reaction. Et_2O is not formed on the Re/α-Al_2O_3 catalyst whose carrier has no Lewis centers. Heterolytic rupture of the H–H bond on the Lewis centers of Al_2O_3 takes place at ∿20°C [8]. We also found that the products of transformation of EA contain 1.3-1.7% Et_2O, water, and no ethanol on γ- and θ-Al_2O_3 at 270°C, 3 MPa, and with V_{wt} = 0.7·h^{-1}. Finally, according to [1], the selectivity of formation of Et_2O is significantly lower on 5% Re/γ-Al_2O_3 than on 0.5% Re/γ-Al_2O_3. The last findings indicate that some of the Lewis centers on the surface of Al_2O_3 become inaccessible for the reaction of formation of Et_2O with an increase in the concentration of Re and confirm the concepts concerning the site of localization of reduced Re.

We emphasize that we could not find the paths of direct reduction of an ester into an ether proposed above in the literature on organic synthesis.

The analysis of the data in Table 1 show that the activity of these catalysts in another side reaction, formation of hydrocarbons, cannot be directly correlated with the acid properties of the surface of the carrier. For example, α-Al_2O_3 and SiO_2 have extremely low activity in reactions of dehydration of alcohols [9], while regardless of the conditions of reduction, hydrocarbons are formed on the corresponding catalysts in an amount commensurate with the amount of Re/γ-Al_2O_3 (treatment 1). It thus follows that hydrocarbons are formed by hydrogenolysis of the C–OH bond of the alcohol on the metal, at least on these samples.

Assessing the contribution of reactions of hydrogenolysis and dehydration and the formation of hydrocarbons on Re/γ- and θ-Al_2O_3 is more complex. However, some hypotheses can be derived from a comparison of the data obtained after treatments 1 and 2.

The nature of the centers of the carrier responsible for the formation of hydrocarbons differs from the nature for Et_2O since high-temperature treatment with H_2 inhibits the first reaction but has little effect on the second. Part of the hydrocarbons is actively formed by dehydration of the alcohol on these carriers. This is indicated by the induction period (3 h) which arises after treatment 2, which is also characteristic of dehydration of ethanol on Al_2O_3 treated in similar conditions [10]. Nevertheless, the reaction of hydrogenolysis of the alcohol on Re is the basic source of hydrocarbons on Re/γ- and θ-Al_2O_3 catalysts, since the yield of hydrocarbons after the induction period is several times lower than on the samples with treatment 1. It also follows that the reaction of hydrogenolysis on these catalysts is almost toally suppressed after treatment 2. This finding can apparently be considered an indication of the high sensitivity of hydrogenolysis of ethanol in Re to the character of its reaction with the carrier. This treatment weakly affects the reaction in the presence of Re/α-Al_2O_3 and SiO_2, i.e., in those cases where the rhenium reacts with the carrier to an insignificant degree [3, 4].

CONCLUSIONS

1. It was shown that the activity of 0.5% Re/α-, δ-, θ-, and γ-Al_2O_3 catalysts in the reaction of hydrogenation of ethyl acetate into ethanol is a function of the nature of the carrier and reduction conditions to a smaller degree than in the side reactions of formation of diethyl ether and hydrocarbons. Re/θ-Al_2O_3 exhibits the maximum activity and Re/α-Al_2O_3 exhibits the maximum selectivity.

2. It was found that diethyl ether is only formed on Re/γ- and θ-Al_2O_3 catalysts. Preliminary treatment of these samples with H_2 at 500°C insignificantly decreases the yield of ethanol, increases the yield of diethyl ether, and almost totally suppresses the side reaction of hydrogenolysis of the alcohol into hydrocarbons.

3. Kinetic data were obtained which confirm the possibility of formation of diethyl ether directly from ethyl acetate, by-passing the stage of formation and desorption of ethanol.

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