POTENTIOMETRIC INVESTIGATION OF THE HYDROGENATION OF COTTONSEED OIL IN SOLUTION

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On studying the chemistry of the hydrogenation of cottonseed oil in solutions, we have investigated this process potentiometrically, since it is possible from the potential of the catalyst to judge the concentration of hydrogen and of radicals of unsaturated fatty acids of the glycerides on its surface [1, 2]. The shape of the kinetic and, particularly, the potentiometric curves reflects a definite tendency in the change in the fatty-acid composition of oils during their saturation [3, 4].

As hydrogenation catalysts, we used an alloy based on aluminum, nickel, and copper (catalyst 1) and the same alloy with additions of a fourth metal (catalysts 2 and 3). In absolute ethanol, the reversible hydrogen potential for catalyst 1 was 660-670 mV, for catalyst 2, 705-710 mV, and for catalyst 3, 710-720 mV.

Figure 1 shows the kinetic and potentiometric curves of the hydrogenation of cottonseed oil on all the catalysts mentioned. It can be seen from the figure that when the sample of oil is added to the hydrogenaation vessel the potential of the catalyst shifts in the anodic direction from the reversible hydrogen potential. This is due to a disturbance of the equilibrium between the hydrogen of the gas phase and the hydrogen adsorbed on the surface of the catalyst.

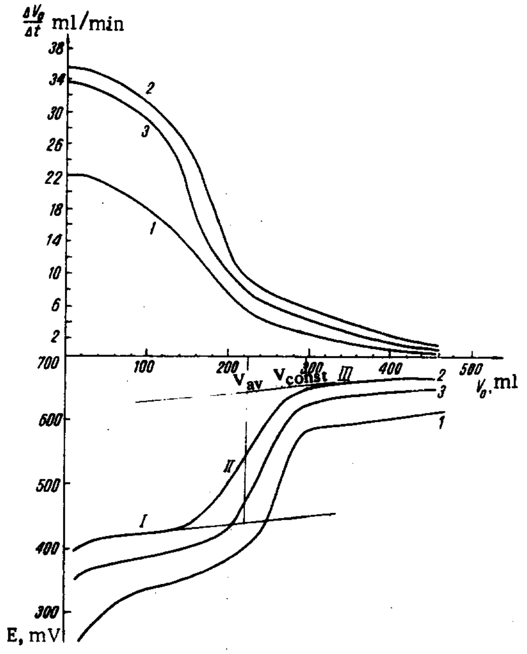

Fig. 1. Kinetic and potentiometric curves of the hydrogenation of cottonseed oil (sections I-III of the curves): 1) catalyst 1; 2) catalyst 3; 3) catalyst 2.

On analyzing the potentiometric curves, we noted that section I is characterized by intensive absorption of hydrogen from the gas phase. This indicates the predominant saturation of the glycerides of linoleic acid. Section II reflects the combined hydrogenation of glycerides of linoleic and oleic acid. After the absorption of 260-280 ml of hydrogen, the potential of the catalyst is close to the reversible potential and hydrogen takes place at low and gradually decreasing rates. This section (III) is characteristic of the hydrogenation of oleic acid glycerides.

On comparing the three potentiometric curves of the hydrogenation of cottonseed oil obtained, we come to the conclusion that the introduction of additives into the aluminum–nickel–copper catalyst leads to an increase in the rate of hydrogenation from 22 to 34-35 ml/min. Simultaneously with this there is a decrease in the shift of the potential of the catalyst from 410 to 340-315 mV. The maximum rate of hydrogenation corresponds to the lowest value of the potential shift (315 mV). Such a lowering of the potential (by 300-400 mV) on the addition of a sample of oil shows a considerable reduction in the concentration of hydrogen on the surface of the catalyst. In this case, the hydrogenation of the oil is limited by the activation of

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TABLE 1. Content of Trans Acids in the Hydrogenates

Iodine No., % I_2, of the hydrogenates	Amt. of trans acids, %		
	catalyst		
	1	2	3
80,9	15,45	6,06	6,84
62,3	40,69	26,15	25,08
52,0	50,67	35,08	31,92

the hydrogen, since a decrease in the anodic shift, i.e., a rise in the concentration of hydrogen, is accompanied by an increase in the rate of the reaction.

The same curves show that additions of a fourth metal to an aluminum–nickel–copper catalyst lead to an increase in the energy of the bond of the hydrogen with the surface of the catalyst, to a decrease in the mobile hydrogen and, consequently, to a rise in the sorption of hydrogen on the active centers of the catalysts. The rate of absorption of hydrogen falls more rapidly than the cathodic shift of the potential of the catalyst. Thus, on working with catalyst 2, the rate of absorption of hydrogen decreases from 35 to 20 ml/min while the value of the potential of the catalyst shifts only slightly in the cathodic direction, from 425 to 440 mV. A further decrease in the rate of absorbtion to 5 ml/min is accompanied by a marked displacement of the potential from 440 to 650 mV. This phenomenon is apparently due to the formation of trans acids, the rate of saturation of which is considerably lower than that of cis acids [5]. Trans acids were found in the hydrogenates that we obtained (Table 1).

The figures in Table 1 agree well with the results of the potentiometric investigation of the catalysts. A deficiency of hydrogen on the surface of the catalyst leads to an acceleration of the isomerization reaction [6], which we can also see by comparing the potentiometric curves of the catalysts studied.

From the same curves, it is possible also to find the selectivity index [7] characterizing the ratio of the amount of hydrogen necessary to saturate one double bond in linoleic acid radicals (V_{av}) to the amount of hydrogen absorbed up to the moment when the potential of the hydrogenation of the oleic acid radicals is established (V_{const}): $S = V_{av}/V_{const}$.

Calculations performed in this way have shown that the hydrogenation of cottonseed oil on the section with the greatest displacement of the potential of the catalyst takes place with selectivities of 0.85, 0.82, and 0.81 for catalysts 1, 3, and 2, respectively, i.e., with an increase in the activity of the catalyst, the selectivity falls, which agrees with literature data [8, 9].

EXPERIMENTAL

The cottonseed oil was hydrogenated at 60°C in a thermostated hydrogenation vessel (of special design) permitting the simultaneous measurement of the amount of hydrogen absorbed and the potential of the catalyst [1, 2]. Each experiment was performed with 6 g of cottonseed oil in 25 ml of absolute ethanol and the catalyst obtained from 1 g of alloy. The catalysts were prepared by leaching 1 g of the corresponding alloy in 60 ml of a 5% solution of NaOH in the boiling water bath for 1 h ([3], p. 44). The freshly prepared catalysts were washed with water (4 × 100 ml) and with ethanol (2 × 10 ml), transferred to the hydrogenation vessel, and saturated with hydrogen for 15-20 min. Then the oil was added to the vessel, and the amount of hydrogen absorbed and the potential of the catalyst were measured after predetermined intervals.

CONCLUSIONS

It has been shown by the potentiometric method that hydrogenation on catalysts with additions of a fourth metal to an aluminum–nickel–copper alloy takes place at a greater concentration of hydrogen on the surface, which leads to a greater rate of hydrogenation and reduces the isomerization process.

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