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STABILITY OF STATIONARY CATALYSTS IN THE HYDROGENATION OF RAPESEED OILS

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The stability of a nickel–copper–molybdenum–aluminum catalyst without additives and with the addition of promoting metals (chromium and titanium) in the hydrogenation of rapeseed oils has been investigated. It has been established that the addition of a promotor to the composition of a known catalyst raises the activity and improves the stability of the alloy. The possibility has been revealed of using catalysts that have been poisoned by sulfur compounds, after their regeneration.

In the evaluation of a catalyst in the hydrogenation of vegetable oils and fats, not only is its activity important but so also is its stability, i.e., its resistance to the action of catalyst poisons. The stability of a catalyst is an important technical and economic index of the desirability of its use.

It must be mentioned that the main catalyst poisons in refined rapeseed oil are organic compounds of sulfur, which are difficult to eliminate from the oil and are capable of interacting with products of its oxidation and hydrolysis [1]. In the hydrogenation of an oil, because of adsorption on the active centers, these compounds form with the metal or an ion of the metal of the catalyst a strong – more accurately, coordination – bond and thereby exclude it from the catalytic act [2].

We have investigated the stability of a nickel–copper–molybdenum–aluminum catalyst having an Ni:Cu:Mo:Al ratio of 22:20.5:7.5:50 without an additive (catalyst 1) and that of the same catalyst with the addition of promoting metals – chromium, giving an Ni:Cu:Mo:Cr:Al ratio of 22:18.5:7.5:2.0:50 (catalyst 2), and titanium, giving an Ni:Cu:Mo:Ti:Al ratio of 22:18.5:6.5:3:50 (catalyst 3) in the hydrogenation of erucic-acid-free and erucic-acid-rich rapeseed oils.

At the present time in industry the hydrogenation of rapeseed oils is performed mainly on pulverulent copper–nickel catalysts. The hydrogenation of the rapeseed oil is then com-

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plicated as a consequence of the rapid poisoning of the catalyst by sulfur catalysts present in the oil. To eliminate these deficiencies, we have used stationary alloy catalysts for the hydrogenation of rapeseed oils. We have hydrogenated erucic-acid-free and erucic-acid-rich rapeseed oils with iodine numbers of, respectively, 110.8 and 107.9% mg I_2, acid numbers of 0.24 and 0.26 mg KOH, color values of 25 and 30 mg I_2, residual sulfur contents of $2.3 \cdot 10^{-4}$ and $9.4 \cdot 10^{-4}$%, and the following fatty-acid contents: myristic —0.3 and 0.6%; stearic — 1.6 and 2.6%; palmitoleic — 0.8 and 0.8%; palmitic — 4.2 and 3.8%; oleic — 57.5 and 24.5%; linoleic — 23.1 and 18.8%; linolenic — 8.6 and 7.9%; arachidic — 1.1 and 1.3%; eicosenoic — 1.2 and 7.8%; behenic — 0.4 and 0.4%; and erucic — 1.3 and 31.5%.

The experiments were performed in an autoclave of the column type by the "jet" method. The stability of the catalyst in the hydrogenation of the erucic-acid-free rapeseed oil was investigated at a constant temperature of 200°C, a pressure of hydrogen of 300 kPa, a space velocity of feed of the oil of 1.2 h^{-1}, and a space velocity of feed of excess hydrogen of 80 h^{-1}. The results obtained are given in Table 1 and Fig. 1. As Table 1 shows, with an increase in the time of operation the activity of the catalysts gradually decreased because of the deactivation of their active centers by catalyst poisons.

It must be mentioned that the promotion of a nickel—copper—molybdenum—aluminum alloy by chromium and titanium, in addition to increasing activity, also leads to a high stability of the catalysts in the hydrogenation of rapeseed oil. Thus, after 750 h of continuous operation of a catalyst without the addition of a promotor its activity fell by 94.4%, while with the addition of chromium the fall was only by 42.4% and with titanium by 39%. Consequently, catalysts 2 and 3 were more resistant to the action of catalyst poisons, particularly sulfur compounds.

At the present time, in oils and fats factories, in addition to erucic-acid-free rapeseed oil, erucic-acid-rich oil is produced which is used for obtaining hydrogenated fats. Table 2 shows the results of the hydrogenation of erucic-acid-rich rapeseed oil under the conditions of the preceding experiments.

The figures in Table 2 show that in the continuous hydrogenation of erucic-acid-rich oil the stabilities of the catalysts without an additive and with the addition of chromium and titanium were lower than for erucic-acid-free rapeseed oil. This is connected with the high residual sulfur content in the oil and also with the presence of erucic acid among the fatty acids of the rapeseed oil.

The working life of a stationary catalyst depends on its stability and the possibility of the regeneration of the spent catalyst. We have studied the degree of restoration of the initial activity after the regeneration of catalysts 2 and 3 that had been poisoned with sulfur compounds For regeneration, the surface of the spent catalyst was washed with a 10% solution of sodium tripolyphosphate at 70-80°C until the fat had been removed completely. Then the catalyst was reactivated with a 5% solution of NaOH and was washed to neutrality, after which it was dried at 110-130°C. Erucic-acid-free rapeseed oil was hydrogenated on the regenerated catalysts at 200°C, a pressure of hydrogen of 300 kPa, a space velocity of passage of excess hydrogen of 80 h^{-1}, and a space velocity of feed of oil of 1.2 h^{-1}. The results are given in Table 3.

A comparison of Tables 1 and 3 shows that after regeneration the catalysts had regained their initial activity almost completely. Thus, for example, the iodine numbers of the hydrogenated oils obtained on catalyst 2 before and after regeneration under otherwise identical conditions after working for 10 h were 67.4 and 67.8% I_2.

A similar picture was observed with catalyst 3. Thus, there are grounds for stating that catalysts poisoned with the sulfur compounds of rapeseed oil during its hydrogenation can regain their initial activity prctically completely after regeneration, thanks to which the working life of one portion of catalyst is increased.

EXPERIMENTAL

The experiments on the hydrogenation of rapeseed oils were performed in a laboratory apparatus with a column reactor by the "jet" method, i.e., the oil and the hydrogen were fed into the bottom of the reactor simultaneously [3].

TABLE 1. Change in the Activity of the Catalysts on the Hydrogenation of Erucic-Acid-Free Rapeseed Oil

Time of working of the catalyst, h	Catalyst 1			Catalyst 2			Catalyst 3		
	iodine No. of the hydrogenated oil, % I_2	activity of the catalyst $\frac{\Delta I.\ No.}{ml \cdot h}$	fall in activity, %	iodine No. of the hydrogenated oil, % I_2	activity of the catalyst $\frac{\Delta I\ No.}{ml \cdot h}$	fall in activity, %	iodine No. of the hydrogenated oil, % I_2	activity of the catalyst $\frac{\Delta I.\ No.}{ml \cdot h}$	fall in activity, %
10	75,4	0,354	0,0	67,4	0,434	0,0	65,3	0,455	0,0
50	78,2	0,326	8,0	69,0	0,418	3,7	66,6	0,442	2,9
150	82,5	0,283	20,1	71,8	0,390	10,1	69,1	0,417	8,4
250	86,7	0,241	32,0	74,3	0,365	15,9	72,4	0,384	15,6
350	89,8	0,210	40,7	76,5	0,343	21,0	73,8	0,370	18,7
450	94,5	0,163	54,0	78,8	0,320	26,3	76,7	0,341	24,1
550	100,2	0,106	70,1	80,3	0,305	29,7	78,5	0,323	29,1
650	104,8	0,060	83,1	82,5	0,273	37,1	80,4	0,304	33,2
750	108,7	0,021	94,4	85,8	0,250	42,4	83,5	0,278	39,0

TABLE 2. Change in the Activity of Catalysts in the Hydrogenation of Erucic-Acid-Rich Rapeseed Oil

Time of working of the catalyst, h	Catalyst 1			Catalyst 2			Catalyst 3		
	iodine No. of the hydrogenated oil, % I_2	activity of the catalyst $\frac{\Delta I.\ No.}{ml \cdot h}$	fall in activity, %	iodine No. of the hydrogenated oil, % I_2	activity of the catalyst $\frac{\Delta I.\ No.}{ml \cdot h}$	fall in activity, %	iodine No. of the hydrogenated oil, % I_2	activity of the catalyst $\frac{\Delta I.\ No.}{ml \cdot h}$	fall in activity, %
10	78,6	0,293	0,0	70,5	0,374	0,0	68,2	0,397	0,0
50	81,7	0,262	10,6	72,9	0,350	6,5	70,4	0,375	5,6
150	85,9	0,220	25,0	75,3	0,326	12,9	72,8	0,351	11,6
250	88,3	0,196	33,1	78,1	0,298	20,4	75,6	0,323	18,7
350	93,9	0,140	52,2	81,2	0,267	28,7	78,0	0,299	24,7
450	99,4	0,085	71,0	83,8	0,241	35,6	80,6	0,273	31,3
550	102,7	0,052	82,3	85,9	0,220	41,2	83,2	0,247	37,8
650	105,2	0,027	90,1	88,5	0,194	48,3	86,5	0,214	46,1
750	107,3	0,006	98,0	91,6	0,163	56,4	89,3	0,186	53,2

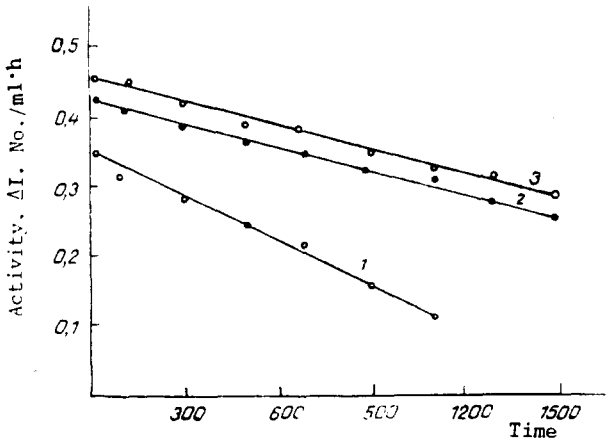

Fig. 1. Change in the activity of catalysts as a function of the time of their working: 1, 2, 3) the numbers of the catalysts.

The activation of a catalyst with a linear dimension of 3-5 mm was performed with a 5% aqueous solution of NaOH at 90-95°C until 15% of the aluminum had been extracted from it. The caustic soda solution was fed into the bottom of the reactor at a space velocity of 5.0 h^{-1}. The degree of extraction of aluminum from the alloy on its treatment with the alkali

TABLE 3. Activities of Catalysts 2 and 3 After Their Regeneration

Time of working of the catalyst, h	Catalyst 2		Catalyst 3	
	iodine No. of the hydrogenated oil, % I_2	activity of the catalyst $\frac{\Delta I.\ No.}{ml \cdot h}$	Iodine No. of the hydrogenated oil % I_2	activity of the catalyst $\frac{\Delta I.\ No.}{ml \cdot h}$
10	67,8	0,430	65,2	0,456
100	69,4	0,414	66,9	0,439
300	72,0	0,388	70,5	0,403
500	74,2	0,359	73,1	0,377

was calculated from the volume of hydrogen liberated during the dissolution process by means of the equation given in [4].

The iodine numbers of the hydrogenated oils were determined by the Wijs method [5].

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LIPIDS OF THE FRUIT OF Rumax paulsenianus

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The lipids of the fruit of Rumex paulsenianus have been investigated. The lipid content of the seeds was 7.8% and of the perianths 0.58%. Of the 18 classes of lipids detected, 16, including anthraquinone pigments, were identified by CC and TLC and by UV and IR spectroscopies and mass spectrometry. The low-molecular-mass triacylglycerols dimyristoylacetin, dimyristoylcaproin, myristoylcaproylacetin, and hydroxylipids have been detected in the fruit of plants of the Polygonaceae family for the first time.

Rumex paulsenianus Rech. fil. (Paulsen's dock) family Polygonaceae, grows in Central Asia, Iran, and the Hindu Kush [1]. Plants of this genus are known as sources of anthraquinones, flavonoids, and tanning substances, in view of which many species are used in the folk medicine of a number of countries as medicinal and homeopathic agents [2]. The medicinal raw material is mainly the roots, stems, and leaves of the plants, and the chemical composition of these organs has been studied to a greater degree than that of the fruit and seeds.

Information of the Remex genus is sparse. It has been reported that the amount of lipid in the seeds of individual representatives does not exceed 5%, the main fatty acids being the 18:1 and 18:2 types. The localization of the reserve lipids in the embryonal part of the seeds has been reported [3]. There is no information on the lipids of the fruit of Rumex paulsenianus.

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