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# PROBLEMS OF THE PRODUCTION OF MODIFIED FATS

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## Abstract

The article provides an overview of the catalysts used to obtain modified fats. The main types of contacts are analyzed: the efficiency of dispersed copper-nickel catalysts promoted by palladium, platinum, and chromium is studied; supported copper-nickel catalysts and alloy catalysts are studied. The influence of such factors as composition, preparation methods, methods of modification on their activity, selectivity, and isomerizing ability is considered. The types of promoters and their classification are presented. It is shown that for the hydrogenation of vegetable. in particular. of cottonseed oils, alloyed nickel-aluminum catalysts with various additives are the most promising. The use of palladium, molybdenum, and rhodium as promoters in the hydrogenation of cottonseed oil and miscella improves the catalytic properties of these contacts.

**Keywords:** transacids, active sites, hydrogenation, catalyst activity and selectivity, promoters.

## Introduction

One of the sources of solid fats is the process of hydrogenation of vegetable oils. This method allows you to convert liquid vegetable oils into solid ones by changing their molecular structure. In this case, the saturation of unsaturated fatty acids with hydrogen occurs. Hydrogenated fats have a greater hardness and melting point, the shelf life increases, and the taste changes.

However, in the process of hydrogenation, the spatial configuration of unsaturated fatty acids changes with the formation of their trans-isomers [1, p.147]. The nutritional value of such oils is significantly reduced [2, p. 6].

The change in the spatial configuration of fatty acids that make up triglycerides occurs under the influence of various factors: the composition of raw materials, high temperature, type of catalyst, its properties, etc. In this regard, the amount of trans-isomerized fatty acids in modified vegetable oils is different. The amount of trans acids can be reduced by increasing the hardness of the final product, i.e. increase in the proportion of saturated fatty acids. Such oils can be used to make spreads, interesterified fats, etc. Solid fats are also used for other purposes [3, p.63, 4, p.44]. Therefore, it is not advisable to completely abandon the production of hydrogenated fats.

**Main Part**

The main raw material in the production of solid hydrogenated fats in the republic is cottonseed oil, which has a complex composition. Compared to other vegetable oils, raw cottonseed oil has a high acid number (up to 7 mg KOH or more), the toxic substance gossypol, which gives the oil a dark color. The technology of its processing is also complex [1, p.21, p.82].

The purpose of this work is to analyze the factors influencing the process of hydrogenation of cottonseed oil in order to obtain high-solid tallow. To do this, it is necessary to carry out the following: to conduct a comparative analysis of existing hydrogenation catalysts; to analyze the effect of accompanying substances of vegetable oils and hydrogen on the process of hydrogenation of triacylglycerols; explore ways to prevent poisoning of oil hydrogenation catalysts.

Catalysts are one of the main components of the technological system for the hydrogenation of vegetable oils. Based on differences in preparation and external structure formation, catalysts are classified into the following groups:

-Metals-catalysts for the hydrogenation of oils and fats;

-Supported catalysts;

-Alloy nickel-aluminum catalysts.

The study of the effectiveness of the action of copper-nickel catalysts on gumbrine with the addition of palladium, platinum and chromium showed that the catalyst with the addition of palladium exhibits the highest activity during the hydrogenation of cottonseed oil using various solvents [5, p.16].

In the study of catalysts 0.6% Pd/NaUK, 0.6% Pd/NaAH, 5% Pd/CaAH (NaU, NaA, CaA - zeolite grades), it was found that the rate and selectivity of hydrogenation of cottonseed oil depend both on the application method, and on the concentration of the active metal (Pd) on the surface of the catalyst [6, p.14]. When hydrogenating a 10% cottonseed oil emulsion in water on a 0.6% Pd/NaA catalyst prepared in the form of granules, the contact time to obtain lard with an iodine value of 82.3% J2 is 0.7 hours, but the selectivity of the process is low (52.4%), which does not allow obtaining food lard. In this regard, the present method was recommended for the production of tallow for technical purposes.

The use of diatomaceous earth in copper-nickel catalysts improves the lard filtration process. In this regard, the most effective is the use of nickel-kieselguhr catalysts of the “ВНИИЖ” type, copper-nickel catalysts in the form of "copper-nickel oxide". the composition of the hydrogenation product, which complicates its regeneration, etc.

Metal-ceramic (Ni) catalyst of A.A. Schmidt [7, p.23] is devoid of the listed disadvantages and makes it possible to obtain lard for both technical and food purposes. It is prepared by pressing and sintering agglomerated nickel powders with a size of 100-500 microns, followed by activation of catalyst granules, i.e. pre-treatment of the granules with formic acid in combination with impregnation of the framework with nickel formate. The catalyst is dried and reduced at a temperature of 270-2800C.

Alloy nickel-aluminum catalysts for the hydrogenation of oils and fats with various additives can also be attributed to the most promising catalysts. The introduction of promoters is dictated by the need to improve the properties of the alloy catalyst.

In [8, p.2], the hydrogenation of cottonseed oil on stationary catalysts prepared by partial leaching of NiAl3, Ni2Al3 intermetallic compounds and Ni 50%, Al, NiAl3 1 at % Cu, Ni2Al3, 1 at % Cu alloys was studied. The structure, physicochemical properties of the catalyst, and the composition of the hydrogenation products have been studied. It was found that the activity of a stationary catalyst depends on the shape of the pores and the distribution of their volume over effective radii, and the stability depends on the metal-hydrogen bond energy.

One of the advantages of alloyed catalysts is that their catalytic properties can be controlled by introducing special substances: sodium polyphosphate to increase the isomerizing ability, organosulfur compounds [9, 10, 11] and water [12] to increase the selectivity of the hydrogenation of oils and fats, etc.

By changing the preparation technology or introducing various promoters (minor additions of other metals) into the composition of the nickel alloy, it was found that some promoters (titanium, molybdenum, chromium, magnesium, copper, cobalt, platinum, palladium, rhodium, etc.) significantly increase the activity, stability and selectivity of the catalysts.

Based on the results of a systematic study of the hydrogenation of cottonseed oil on nickel-aluminum catalysts (50% Ni) with various additives, it was found that their activity, selectivity, and trans-isomerizability depend on the nature of the promoter, and the studied catalysts are arranged in the following descending series [13, c .21]:

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- by activity: Ni-Al-V> Ni-Al-Mo> Ni-Al-Nb> Ni-Al-Pd> Ni-Al> Cu> Ni-Al-Rh> Ni-Al-Fe> Ni-Al- Ga> Ni-Al-Co> Ni-Al. The highest activity of promoted catalysts was achieved at 20% V and Pd; 12% Mo and Nb; 5% Rh and Cu; 10% Co and Fe; 2% Cu;
-by selectivity: Ni-Al-Pd> Ni-Al-Nb> Ni-Al-Mo> Ni-Al-Gr> Ni-Al> Ni-Al-V> Ni-Al-Rh> Ni-Al-Fe> Ni-Al-Co > Ni-Al;
-by trans-isomerizability: Ni-Al-Mo> Ni-Al-Nb> Ni-Al-Ru> Ni-Al-Fe> >Ni-Al> Ni-Al-Pd> Ni-Al-V> Ni-Al -gr.

Based on the analysis of these series, it can be assumed that nickel-molybdenum-aluminum and nickel-palladium-aluminum catalysts are the most efficient.

The work [14, p.91] presents the results of the development of new active Pt-Pd catalysts for the hydrogenation of palm oil, which have high selectivity to obtain a high yield of lard without double bonds and trans isomers. Platinum contacts deposited on aluminosilicate were used as catalysts. On the developed Pt-Pd/SiO2 catalyst, the optimal temperature and pressure are 2000C and 1.5 MPa; under these conditions, the final product is completely free of double bonds and trans fatty acids.

Currently, much attention is paid to the interesterifying activity of catalysts, while their properties to form trans acids in the composition of lards are being studied, methods are being developed to reduce them by changing the work of active centers both on the surface and in the internal pores of deposited nickel catalysts or by adding promoters [15, p. .31, 16, p.428]. For example, in the Moscow branch of "ВНИИЖ" under the leadership of Arkhipov P.A. Nickel-copper catalysts ("ВНИИЖ"-1, "ВНИИЖ"-2, etc.) with enhanced transesterifying properties were developed. On the surface and internal pores of these contacts, along with active centers of hydrogenation, oxides of nickel, copper, iron and other metals are formed, which, under certain conditions, participate in the processes of intramolecular and intermolecular transesterification [17, p.227]. Alkaline earth metal oxides are considered promising catalysts for the transesterification of vegetable oils [18, p.1107, 19, p.1387, 20, p.633].

The efficiency of the used catalyst for the hydrogenation of vegetable oils is determined not only by their activity, but also by their selectivity. As experimental data show, this indicator depends on such factors as the composition and structure of catalysts, their composition, synthesis method, carrier type, particle size, and activation conditions [21, p.3].

The activity and selectivity of a stationary Ni-Cu-Ti-Al catalyst without additives and with the addition of 0.1% palladium in the hydrogenation of cottonseed oil were studied. Promotion of the catalyst with palladium led to an increase in its activity and selectivity [22, p.6].

The proposed nickel catalysts with the addition of silver, although they have high selectivity and activity [23, p. 423], are not used in industry due to their high cost.

Good results were obtained in the hydrogenation of cotton miscella on a nickel–copper–aluminum catalyst with the addition of molybdenum [24]. The addition of the latter contributed to an increase in the stability of the nickel-copper-aluminum catalyst.

Similar results [25, p.2] were obtained with the introduction of rhodium into the nickel-copper-aluminum catalyst. In addition, the addition of rhodium increased the selectivity and performance of the nickel-copper-aluminum catalyst. The resulting fats have a melting point of 33.6-34.80C and a hardness of 160-280 g/cm according to Kaminsky.

In the 2000s researchers proposed to use group VIII metals supported on various substrates (aluminum, silicon, titanium oxides) as hydrogenation catalysts. For example, tin-promoted ruthenium catalysts, $Pt/TiO_2$ and $Pt\text{-}Re/TiO_2$ have found application [26, pp. 174, 27, s.1110, 28, s.410, 29, s.253]. The main problem of the studied catalysts is the low yield of the target product.

As can be seen, possible ways of modifying alloyed catalysts should not be considered in isolation from each other. As a rule, several factors of different nature act simultaneously. According to the classification of promoters [30, p.98], given in Table. 1, the reasons for the change in the activity of the skeletal nickel catalyst can be explained.

Table 1 - Classification of the influence of modifying additives of the skeletal nickel catalyst

| **Elements of additives** | **Causes of Changes in Skeletal Catalyst Activity** | |
|---|---|---|
| | **main** | **additional** |
| Pb,Nb,Ta,W | Equilibrium shift in the Ni:Al system | Not |
| Rh | Same | The contribution of the skeletal catalyst formed from aluminum alloying components |
| Pd,Rh,Sn,Gr | -//- | Formation of a solid solution of an alloying element in nickel |
| Cu | -//- | Formation of ternary aluminides |
| V,Re,Ti,Ru,Mn | -//- | The effect of oxidized forms of the alloying element formed during the leaching of the original alloys. |
| Pt | Formation of a solid solution of an alloying element in nickel | Not |
| Fe, Ce | Same | Displacement equilibrium in the system Ni:Al |
| | -//- | Formation of ternary aluminides. |
| | -//- | The effect of oxidized forms of alloying elements |
| Zr, Mo | Formation of ternary aluminides | Shift in equilibrium in the system Ni:Al |
| | Same | The effect of oxidized forms of alloying elements |

Optimum properties are possessed by those catalysts with metal additives, which, as a result of leaching, are converted into oxidized forms with a high specific surface area. These contacts contain an amorphous carrier that forms nickel phases. In addition, oxides (TiO, MgO, etc.) inhibit the growth of nickel phase crystals and sharply increase the stability of the catalysts.

## Conclusion

Thus, from the analysis of literary sources it is established. that the developed alloy catalysts for the hydrogenation of oils and fats are either not stable enough and subject to poisoning by oil or solvent concomitant substances, or not selective enough, etc. High performance catalysts can be obtained by promoting a nickel-molybdenum-aluminum alloy. The greatest effect is observed when small doses of the promoter are introduced into the initial alloy. The introduction of metals such as palladium, platinum, and rhodium increases the cost of the nickel catalyst by no more than 10% with an increase in its activity by 50–100% [6].

In general, alloy catalysts can be attributed to promising contacts for the hydrogenation of vegetable oils and fats, in particular cottonseed oils and fats, and new technological solutions for improving the production of fats, in our opinion, should be associated with their use.

At the next stage of research, it is necessary to analyze the effect of accompanying substances of vegetable (cotton) oils and hydrogen on the process of hydrogenation of triacylglycerols; study ways to prevent poisoning of cottonseed oil hydrogenation catalysts.

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