

THE EVALUATION OF CATALYSTS FOR THE HYDROGENATION OF OILS AND FATS

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Abstract:

The paper gives a theoretical assessment of the hydrogenation of oils and fats using catalytic systems. Saturation equations for unsaturated bonds are given. The role of catalytic metals and promoting additives in the formation of the hydrogenating properties of catalysts is established.

Keywords: Theory catalysis, catalytic reactions, chemical conversion, catalyst systems, promoters hydrogenation properties.

INTRODUCTION

There are many theoretical developments in the technology of hydrogenation of oils and fats, which are formulated in a generalized form as theoretical foundations for the catalysis of unsaturated organic compounds [1-4]. The chemical composition of oils and fats also consists of fatty acids with unsaturated saturated compounds [5,6]. In this regard, the study and expansion of theoretical issues of hydrogenation of oils and fats, especially cotton and sunflower oils, on efficient catalytic systems is of both scientific and practical interest.

The purpose of the work is aimed at analyzing and evaluating the available theoretical ideas on the hydrogenation of oils and fats, and on this basis expanding the approach of assessments for this.

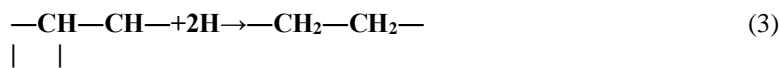
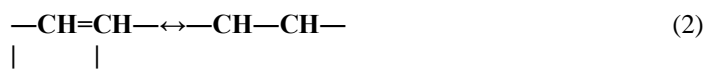
MATERIALS AND METHOD

To analyze and evaluate modern ideas on the hydrogenation of oils and fats, modern theories of the hydrogenation of organic compounds were used [7, 8]. The generalization was carried out by analyzing and evaluating own experimental results carried out in this direction [9-11].

Results and discussion

Many chemical reactions, which are fundamentally possible according to thermodynamic data, either do not take place under practically acceptable conditions, or proceed with negligible speed. The catalyst initiates and accelerates thermodynamically feasible processes [12].

The essence of the hydrogenation reaction of unsaturated substances, as well as the chemical reaction in general, consists in the rupture of the initial and the formation of new interatomic chemical bonds, which can be represented by the following scheme [13]:



Breaking interatomic bonds in molecules requires significant energy expenditure. The energy of breaking the interatomic bond in a hydrogen molecule is 436 kJ/mol. To break the ethylene bond in a monounsaturated carbon chain, energy in the amount of 271 kJ/mol is required [14]. Thus, in order to carry out hydrogenation according to the specified sequential scheme of breaking and creating interatomic bonds, the reacting system must have energy of at least 700 kJ/mol [15]. This level of energy corresponds to high temperatures at which organic compounds disintegrate.

However, studies of the kinetics and energy of chemical reactions have shown that the rupture of old and the formation of new chemical bonds do not occur at all in the form of successive acts [16, 17]. In fact, when performing a chemical transformation, each pair of approaching molecules first forms a configuration intermediate between the initial and final state of the system [18].

This configuration of reacting molecules is called a "transition state" or "activated complex" [19]:



∴ ∴

H---H

(4)

activated complex

In the activated complex, the initial interatomic bonds are still preserved, but at the same time new chemical bonds characteristic of the reaction product begin to form. Therefore, the energy required for the formation of the activated complex is significantly less than the sum of the bond-breaking energies in the initial molecules [20].

For exothermic reactions such as the addition of a hydrogen molecule to an ethylene bond, the activation energy of the reaction with the formation of an intermediate activated complex is approximately 30% of the sum of the energies of the breaking bonds and is 21 kJ/mol.

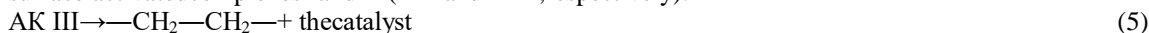
At this value of the activation energy, the fraction of reacting system molecules capable of carrying out a chemical reaction is 10-22 at 200 °C and 10-12 at 600 °C [21].

This means that a purely thermal hydrogenation reaction in the absence of a catalyst at 200 °C does not take place. Even at 600 °C, only one collision of molecules out of 1012 collisions can result in a chemical reaction [22].

A decrease in the activation energy of the reaction, and consequently, its significant acceleration occurs under the influence of a catalyst.

The initial molecules are chemisorbed on the catalytic surface, forming activated complexes. The force fields of the active centers of the catalyst weaken the interatomic bonds of the adsorbed molecules up to their rupture. As a result, the reactivity of activated molecules increases, and the interaction of molecules becomes possible at a lower energy level, i.e. the activation energy of the chemical reaction decreases.

The mechanism of heterogeneous catalytic hydrogenation is most likely, in which both reagents form intermediate surface activated complexes I and II (AKI and AKII, respectively):



It is known that metals of the platinum group [23] of the periodic table of elements exhibit high catalytic activity in reactions involving hydrogen, including in the hydrogenation reaction of triglycerides.

In connection with the development of ideas about the structure of the atom and the state of its electron shells, the catalytic activity of metals is compared with their electronic structure and, in particular, with the incompleteness of the d electron shell. At the same time, metals containing 2-4 unbound electrons exhibit high catalytic activity, and vice versa, metals that do not contain such electrons have very low catalytic activity or do not show it at all.

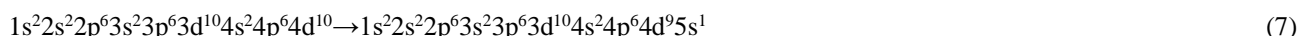
Table 1 provides information on filling in the electronic levels of the elements of the eighth group and some others.

The electronic configuration of group VIII elements is characterized by the completion of the internal d-orbitals of atoms in the presence of one or two external s-electrons. The total number of external electrons varies from 9 (Rh, Co, Ir) to 10 (Ni, Pd, Pt). It should also be noted that in palladium, with a small expenditure of energy (18.5 kcal / mol), which takes place during the implementation of a real catalytic process, an electron transitions to the outer s-orbital, and the atom transitions from the ground state to the d-state:

Table 1.

Structure of electron shells of some transition metals

Element	Number of electrons in orbitals														
	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5p	6s
Cobalt	2	2	6	2	6	7	2								
Nickel	2	2	6	2	6	8	2								
Copper	2	2	6	2	6	10	1								
Ruthenium	2	2	6	2	6	10	2	6	7	—	1				
Rhodium	2	2	6	2	6	10	2	6	8	—	1				
Palladium	2	2	6	2	6	10	2	6	8	—	1				
Rhenium	2	2	6	2	6	10	2	6	10	—					
Osmium	2	2	6	2	6	10	2	6	10	14	2	6	5	—	2
Iridium	2	2	6	2	6	10	2	6	10	14	2	6	6	—	2
Platinum	2	2	6	2	6	10	2	6	10	14	2	6	7	—	2
Element	2	2	6	2	6	10	2	6	10	14	2	6	9	—	1



ground state - d-state

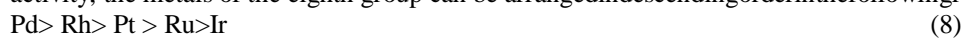
In the b-state, palladium (HD) has two free valences: due to an unpaired electron on 4d orbitals and electron transferred to

5sorbitals

The transition of electrons leads to the fact that unpaired electrons appear on the outer d- and s-orbitals, which provide both the formation of metal-metal covalent bonds and chemisorption necessary for the passage of a catalytic reaction.

Transition metals tend to adsorb electrons at their unfinished d-levels, and this tendency is manifested in nickel and palladium to a greater extent than in platinum.

In the course of studying the hydrogenation of cotton and sunflower oils, it was found that, according to the catalytic activity, the metals of the eighth group can be arranged in descending order in the following row:



The formation of chemisorption bonds between the catalyst and the reagent is a consequence of the structure of the outer electron shells of the catalyst, but the chemisorption mechanism does not exclude the role of geometric factors.

From the point of view of the most developed multiplet theory of catalysis, Balandin A.A. [24] the possibility of catalytic hydrogenation is determined by the existence of a certain structural and energy correspondence between the reagent and the catalyst. The principle of structural conformity is the minimum bond tension during the interaction of reagents with the surface of the catalyst. For activated adsorption of unsaturated triglycerides, the optimal distances between atoms in the catalyst lattice are 2.5-2.8 Å, for activated hydrogen adsorption – 3.5-3.8 Å.

Metals, in which the distances between atoms are optimal for the activation of both components, serve as the most active catalysts of hydrogenation.

In the table.2 shows the interatomic distances (Å) in two planes of the crystal of metals most commonly used as hydrogenation catalysts.

Table 2
Interatomic distances in two planes of the crystal lattice of metals

Crystallattice system	Element	Permanent	
		A	B
Face-centered, cubic	Pt	3,903	2,770
	Pd	3,873	2,740
	Ir	3,823	2,710
	Ni	3,502	2,480
	Cu	3,608	2,550
	Rh	3,800	2,650
	Co	3,550	2,510
Hexagonal	Re	4,450	2,750
	Ru	4,270	2,690
	Co	4,080	2,490
	Ni	4,080	2,490
	Os	4,310	2,730

Industrial heterogeneous catalysts usually consist of active components, promoters and neutral components of various chemical nature. As a rule, catalysts are not a mechanical mixture of these components, but a single system, the components of which are either introduced during the synthesis of the catalyst, or formed during its formation. For hydrogenation of fats, catalysts containing nickel and nickel oxides as active constituents are most widely used. Despite the higher catalytic activity of palladium compared to nickel, its use is limited due to the much higher cost.

In order to increase the activity, selectivity, stability and improve some other properties of catalysts, small amounts of promoters are introduced into them - substances that themselves may not have a noticeable catalytic effect, but enhance the effectiveness of the catalyst. 0.5 to 5% promoters are added to nickel catalysts for hydrogenation of fats, for example, zirconium oxides, manganese and some other metals, which increase the activity and selectivity of catalysts at moderate temperatures, stability during reuse.

Modern nickel-containing heterogeneous catalysts reduce the activation energy of hydrogenation of ethylene bonds by 5-10 times compared to a hypothetical non-catalytic process. This makes it possible, even in industrial conditions, to carry out fatty hydrogenation processes at a sufficiently high speed already at 120-130 °C with and a hydrogen pressure of 0.050.3 MPa.

CONCLUSION

The selection of catalysts for the hydrogenation of oils and fats is based on the structure of the electronic shells of transition metals in the alloys introduced into the composition as promoters;

Ensuring an increase in the activity, selectivity, selectivity and stability of catalysts is carried out by selecting the promoting metals and establishing their required content.

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