Research Journal of Chemical and Environmental Sciences
Res J. Chem. Environ. Sci. Vol 8 [1] February 2020: 05-08
Online ISSN 2321-1040
CODEN: RJCEA2 [USA]

Website: www.aelsindia.com/rjces.htm

RJCES

ORIGINAL ARTICLE

Hydrogenation of Unsaturated Bonds Contained in The Molecule

N. Kh. Khaldarov*[1], S. Zh. Yegemberdiyeva[1], A. G. Rakhimkulov[2], A. A. Palmanova[1], Y. I. Kistaubayev[3], O. I. Kaladinov[3]

[1]M. Auezov, South Kazakhstan State University, Shymkent, Kazakhstan
[2]LLC Nauka, Salavat, Russia
[3]Regional Social and Innovation University, Shymkent, Kazakhstan
*Corresponding Author. Email: haldarov.nartai@mail.ru

ABSTRACT

A model of hydrogenation of fatty aldehyde containing butyl alcohol with activated intermediate complexes AK-I and AK-II is proposed. Structural thermal activation of reacting reagents and catalysts leads to deformation of chemical bonds in them, convergence of the high-voltage zones in the activated complexes, thereby resulting in a pressure of millions of atmospheres and increase in the reaction rate.

Keywords: *Catalyst, activation energy, activated complex, binding energy, adsorption, hydrogen, crystal structure.*

Received 02.01.2020 Revised 09.01.2020 Accepted 22.02.2020

INTRODUCTION

Due to the great practical importance of heterogeneous catalysis, the development of scientific basis for the selection of catalysts is one of the key issues in modern chemistry.

Due to the lack of a unified theory of catalysis, and the inability to fully explain all catalytic phenomena, it is difficult to develop the scientific basis of its working. Any theory explaining the catalytic action should take into account the structure of atoms, molecules, the composition and nature of the catalyst, its physical and phase state [1], and the geometry of the crystal lattice [2].

In addition, the theory must take into account the effect of temperature, pressure, vapor elasticity of metal atoms and other parameters of process [3]. The lack of such a theory hinders the selection of the most efficient catalysts and the improvement of technological schemes of chemical production.

A heterogeneous catalyst is a physical and chemical sorption of primary reagents and reaction products on its surface, which results in the release of sorption heat. The catalyst is involved in the formation of activated intermediate complexes (AC) in one of these stages of the reaction and is recovered after each cycle of the intermediate interaction. In this case, the effect of the catalyst may interfere with the passage of a certain chemical reaction (increase in taste) or interfere with it.

MATERIAL AND METHODS

Al-Ni and Al-Cu catalysts of different composition according to known technology (melt cooling in molds, mechanical crushing and dispersion into fractions) are prepared. Bulk density ranges from 1800 to 2000 kg/m^3.

The microscopic examination of the particle size distribution of the catalysts was carried out according to a known method. The aqueous suspension of the catalyst was thoroughly mixed and allowed to stand for 15-20 minutes (to establish adsorption equilibrium).

Next, the suspension was mixed and, taking a small portion (1-2 drops) with a pipette, was placed between two glass plates, after which under the microscope MNM-7 with an eyepiece and an objective, particle counting was started in 7-8 new fields vertically and horizontally, and the integral was built and differential distribution curves, which determined r_{max} - the radius of the particles prevailing in this system. The change in temperature ΔT depends on the law of heat capacity.

Phase composition and structure of alloys and catalysts were studied by X-ray and X-ray spectral analysis methods; sorption capacity by H_2 was determined by thermal desorption.

Specific surface of the catalyst was calculated using the Brunauer–Emmett–Teller (BET) method; activation energy, adsorption heat of hydrogen and raw molecules were determined using the Polanyi-Wigner equation.

The hydrogenation kinetics of oil aldehydes into butyl alcohol was studied in a flow reactor in the temperature region of 300-550 K, hydrogen pressure, P_{H2} of 0.1 - 5.0 MPa and leaching degree of the alloy up to 60%. Hydrogenation of oil aldehyde was analyzed by gas-liquid chromatography on chromatograph 'Chrom-4' with a flame ionization detector.

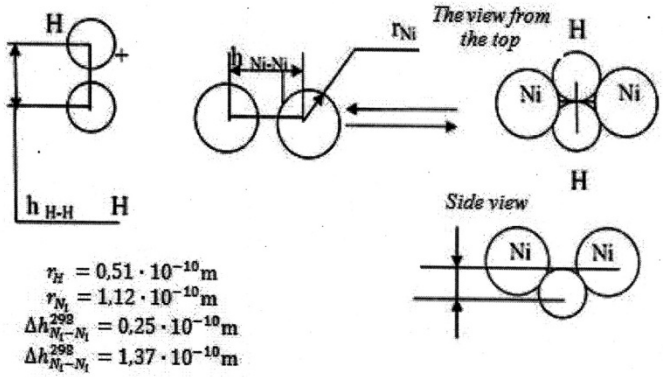
RESULTS AND DISCUSSION

Hydrogenation catalytic processes are effective methods for producing different classes of chemicals, and therefore is a growing interest in the study of the mechanism of action of hydrogen, functional groups of molecules of raw materials, the atomic structure of catalysts, and the kinetics of these processes [4].

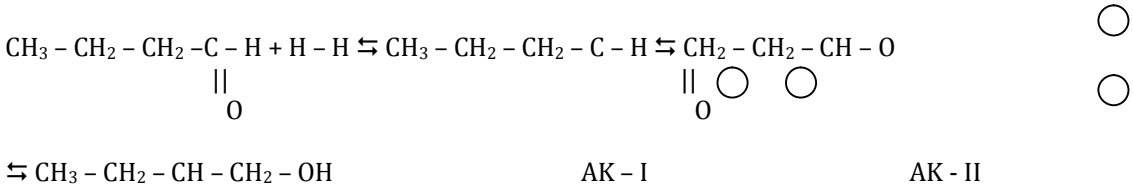
In many cases, hydrogenation catalysts are selected through long and time-consuming experimental search because there is currently no single catalytic theory that can predict the catalytic activity of solids in relation to hydrogenation and dehydrogenation reactions.

It is important to take into account the chemical interaction between different approaches to the mechanism of catalytic action (physical and chemical adsorption of reagents with high thermal effect), the structural thermal deformation of the parent molecules and the catalyst [5]. Under the influence of hydrogen pressure, the activated form of hydrogen is accumulated on the catalyst surface and in its bulk [4], and upon thermal activation the metal density $\rho(P_{H2},T)$ decreases [6]. In general, an increase in temperature T and hydrogen pressure P_{H2} leads to a cumulative decrease in the density of the solid catalyst, resulting in an increase in the internuclear distance $\Delta h(T,P_{H2})$.

Figure 1. Schematic of the catalytic complex formation, first step of activating the hydrogen molecule by two nickel atoms.



The complete hydrogenation reaction of fatty aldehyde to butyl alcohol occurs at a nickel catalyst temperature of 300-600K and a hydrogen pressure of P_{H2} = 0.1 - 5.0 MPa (Scheme 1) [2]:



Scheme 1 - Hydrogenation of fatty aldehyde to butyl alcohol , where AK-I and AK-II are activated complexes.

The function of the catalyst is to activate the chemical bond H-H, because the limiting stage of hydrogenation of the carbonyl group is to reduce the strength of the hydrogen bond in the kinetic zone of the reaction (E_{H-H}= 435 kJmol^{-1}), where the H-H and Ni-Ni molecules are in the high-voltage region. convergence (Figure 1). The initial data for calculation are shown in Table 1.

Table 1 - Initial data for calculating the intermediate catalytic complex of nickel hydride

Process parameters, properties of	Types of chemical bonds		
	Ni – Ni	H – H	Fat aldehyde
Temperature (K)			
Initial	416		
Final	453		
Temperature step	5		
Hydrogen pressure P_{H2} (MPa)	5		
Initial	0.1		
Final	5.0		
Pressure step	0.5		
Atomic mass, A	59	1	12
Validity, z (condition unit)	8	1	4
Nuclear distance h298, (10^{-10}m)	2.49	0.741	1.23
The orbital radius of the atom, r	1.12	0.53	
Standard heat capacity (J	25.97 (Тв)	28.8 (г)	103.835
Coefficients of the heat capacity equation:			
a (J $mol^{-1}\cdot K^{-1}$)	0.304	3.30	-18.4
в (J $mol^{-1}\cdot K^{-2}$)	$4.57\cdot10^{-4}$	$0.34\cdot10^{-3}$	447.3 - 296.2
c (J $mol^{-1}\cdot K^{-3}$)			

The temperature dependence of $E^{\#}$ and its relation to the height of the potential energy barrier is shown to be linear within the experimental error even in the extended temperature range in most of the Arrhenius plots. To date, it has been suggested that the activation energy ($E^{\#}$) does not change with temperature. If this is the case then $E^{\#}$ can be equated with its value at 0 K and it is a measure of the height of the potential energy barrier without taking into account the thermal energy.

Like the theory of collisions, the theory of transient states, and the formation of activated complexes, $E^{\#}$ assumes that it varies in proportion to the number of activated complexes depending on the temperature. [2]

According to the theory of the formation of activated complexes, the value $E^{\#} = H^{\#}$, which, as an isochoric process, changes with temperature according to the law of heat capacity:

$$\frac{dE^{\neq}}{dT} = \frac{d(\Delta H^{\neq})}{dT} = \Delta C_p^{\neq} + R \qquad (1)$$

where $\Delta C_p{}^{\#}$ is the difference between the heat capacity and the transition state of the reactants; $\Delta H^{\#}$ is the enthalpy of AK formation.

CONCLUSION

1. The change in $E^{\#}$ with temperature depends on the law of heat capacity.
2. According to Dulong's and Mi's law, the deformation of chemical bonds in molecules and crystals occurs as a result of an increase or decrease in temperature T and thermal energy RT according to the law of heat capacity. Therefore, not only the process parameters change, but also the crystal structure of atoms, molecules and catalyst .
3. The higher the temperature of the process, the greater the number of activated complexes in the product molecules and the structure of the catalysts. [1]
4. The heat capacity increases with increasing pressure to the critical parameters, so the increase in temperature and pressure leads to increase in the number of activated complexes, a decrease in activation energy and, as a result, an increase in the reaction rate constants (K^T and K^R), equilibrium distribution of molecules in space is maintained limited by the reaction kinetics.

ETHICS

This article is original and contains unpublished material. The corresponding author confirms that all of the other authors have read and approved the manuscript and no ethical issues are involved.

REFERENCES

1. Rakhimkulov AG, (1978).The process of producing acetopropyl alcohol. Discussion on the degree of Candidate of Technical Science, Ufa, Russia.
2. Rakhimkulov AG, (2004). Activated complexes and catalysis. Salavat.
3. Rakhimkulov AG, Akhmetov IZ, Journal of Applied Chemistry, 1993. Vol 66 No. 6 s 1303.
4. Rakhimkulov AG, Rysayev US, Rakhmatullina FT, Journal of Applied Chemistry, 1990, Vol 63 No. 6 p. 13-48
5. Kolesnikov IM, Rakhimkulov AG, Pototamin VA, Journal of Applied Chemistry, 1983 No. 11. p. 20-22
6. Rakhimkulov AG, Kolesnikov IM, Journal of Physical Chemistry, 1989, Vol 63, s 1989.
7. Mashnina A.V. Heterogeneous Catalysis In The Chemistry Of Organic Compounds. Science, 1977, p. 220-248

CITE THIS ARTICLE

N. Kh. Khaldarov, S. Zh. Yegemberdiyeva, A. G. Rakhimkulov, A. A. Palmanova[1], Y. I. Kistaubayev, O. I. Kaladinov Hydrogenation of Unsaturated Bonds Contained in The Molecule. Res. J. Chem. Env. Sci. Vol 8 [1] February 2020. 05-08