

Kinetics of Maleic Acid Hydrogenation over Skeleton Nickel in Aqueous Solutions

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Abstract: The kinetics of liquid-phase hydrogenation of maleic acid to succinic acid was studied over skeleton nickel catalyst in aqueous solution at different values of pH. The dependence of the substrate concentration and the amount of hydrogen absorbed on time were used to determine the reaction orders and rate constants. The effect of external and internal diffusion was evaluated and taken into account. Different reasons for the effect of pH on kinetic parameters are discussed for the reaction occurring in aqueous solutions. The values of the reaction orders found in the pH interval under investigation differed from one and changed in the range of 0.7-0.85 and 0.50-0.85. Activation energies of maleic acid, the hydrogenation reaction in aqueous solution of sodium hydroxide with pH 7.8 and 13.9 equal to 39 ± 2 and 62 ± 5 kJ mol⁻¹, respectively. Thus maleic acid hydrogenation reaction on a skeleton nickel in aqueous solutions despite simple kinetic regularities of the reaction process represents a complex non-stationary process complicated by strong diffusion retarding while constructing a kinetic model of the process under study.

Key words: Reaction order, diffusion rate constant, hydrogen adsorption skeleton nickel

INTRODUCTION

The catalytic hydrogenation and half-hydrogenation of aromatic and aliphatic organic compounds in the liquid as well as in the gas phase over single metal powders, bimetallic glasses and supported and unsupported catalysts are of a scientific and industrial importance, where they have been the subject of many studies in the last decades^[1-7].

It is well known that supported group VIII metals especially Ni, Pd, Pt and Rh are very efficient catalysts in the hydrogenation reaction^[5,8].

For example, the kinetics of the hydrogenation of benzene, toluene, phenyl acetylene, some acetylenes and other compounds were studied and a reaction models were proposed^[4,6,7].

Several kinetic investigations of maleic acid derivatives hydrogenation have been done in various media to establish the specific effect of different experimental conditions on the rate, selectivity, mechanism and rate determining step. This was found to depend on temperature, solvent, substituent, concentration and type of catalyst employed^[9-11].

The present study was conducted on catalytic liquid phase hydrogenation of maleic acid to succinic acid over skeleton nickel at different values of solution pH. The

effect of pH, mass transfer, associative and disassociative adsorption of hydrogen and maleic acid, temperature and internal and external diffusion was evaluated.

MATERIALS AND METHODS

Solvents: Aqueous solutions of sodium hydroxide with pH : 7.8, 12.0, 12.9 and 13.9 were used as solvents.

Preparation of a skeleton nickel catalyst: Skeleton nickel catalysts are obtained by the treatment of dispersed nickel alloys with an inert component-aluminum, magnesium, silicon etc. with aqueous solutions of hydroxides and carbonates of alkaline metals^[1,2].

In the research industrial nickel-aluminum alloys of Ni: Al:Fe = 49.85:50:20.3 mass % was used. The alloys was grinded on a disk dispergator of impact-reflective action and it was separated to the fraction of different dispersity in an air separator of Gonnell. Skeleton nickel was obtained by the treatment of some fractions of nickel-aluminum alloys by 25% aqueous solution of sodium hydroxide during 1 h at 273-278 K and during 4 h at 368-373 K. After 2 h of treatment hydroxide solution saturated with sodium aluminates was changed by freshly prepared solution. After the treatment the catalyst was washed from the admixtures of hydroxide and

aluminates with distilled water till neutral reaction on phenolphthalein (ph.ph) and it was kept under the layer of water not more than two days^[13].

The active skeleton nickel obtained according to this method had specific gravity equal to $90 \pm 2 \text{ m}^2 \text{ g}^{-1}$, the porosity is $0.5 \pm 0.05 \text{ cm}^3 \text{ cm}^{-3}$ of a catalyst and maximum function of pores distribution along radii corresponding to the average radius of pores equal to $20^\circ \text{A}^{[14,15]}$.

Kinetic method: The kinetic experiments were carried out in a reactor of liquid-phase hydrogenation with intensive stirring the liquid phase and the possibility of controlling the process by a volumetric method measuring the volume of the absorbed hydrogen. The reactor design allowed to pour the solution of a hydrated compound and the selection of hydrogenisate samples for the determination of reagent concentrations by physico-chemical methods of analysis. The hermetization of the mill drive was done with magnet-liquid packing of a special design which excluded the flow of hydrogen from a reaction system.

To carry out the experiment 0.25-1.25 g of a skeleton nickel and 100 g of a solvent was loaded into the reactor, the system was hermetized, blown with hydrogen and thermostated at the temperature of the experiment. Further the catalyst during stirring was saturated with hydrogen from a gas phase during 15-30 min. Then a calibrated volume of maleic acid solution of the known concentration was introduced into the reactor and then the reaction of hydrogenation was carried out during which the absorption rate of hydrogen from a gas phase was measured by a volumetric method and 7-10 samples of hydrogenisate were taken at different time moments. The measurements were completed during full ceasing hydrogen absorption from a gas phase.

The concentrations of the samples of a liquid phase were determined with the help of polarography. The polarographic analysis was carried out on PU-1 polarograph in a citrate-phosphate buffer with pH equal 12.0-12.5 on a mercury drop electrode in the period of pouring 0.4 S^{-1} in the regime of alternative current polarography by the method of calibration graph. Oxygen from a polarographic cell was removed by flowing argon during 20 min. Half wave potential of maleic acid in the conditions of polarography was -1.16 V . The results of standard mixtures analysis showed that the error in determining the concentrations of maleic acid in the reaction did not exceed 3% as compared with the value being measured.

All kinetic experiments were carried out under hydrogen pressure equal atmospheric, at the temperature of 303 K and mixing up rates of a liquid phase equal $240\text{-}550 \text{ S}^{-1}$. The data of the authors showed that such

regime of kinetic experiments allows to exclude fully the effect of dissolution stages of hydrogen on the experimental results.

RESULTS AND DISCUSSION

According to the quantity of hydrogen absorbed in the reaction taken under ordinary conditions the concentrations of maleic acid hydrogenation product succinic acid were calculated and on the base of polarographic analysis the concentrations of a hydrated compound in the process of the reactions were calculated. Then the dependencies of maleic acid concentrations and the reaction product upon the time were treated with the help of leveling and interpolating spline-functions and the observed hydrogenation reactions rates were found according to the concentration of a hydrated compound C_R and according to the quantity of an absorbed hydrogen C_{RH_2} in different time moments of the reaction by the numerical differentiation of the mass of spline-interpolated data obtained.

In the preliminary experiments the effect of initial concentration of a hydrated compound, catalyst mass, the mixing up rate and the size of the particles of skeleton nickel of the rate of hydrogenation was studied. As an example of an original information obtained from the kinetic experiment, Fig. 1 shows the dependencies of the observed rate of hydrogen absorption from a gas phase upon quantity of the absorbed hydrogen and Fig. 2 shows the dependencies of the observed reaction of maleic acid C_R . From the data in Fig. 1 and 2 it follows that

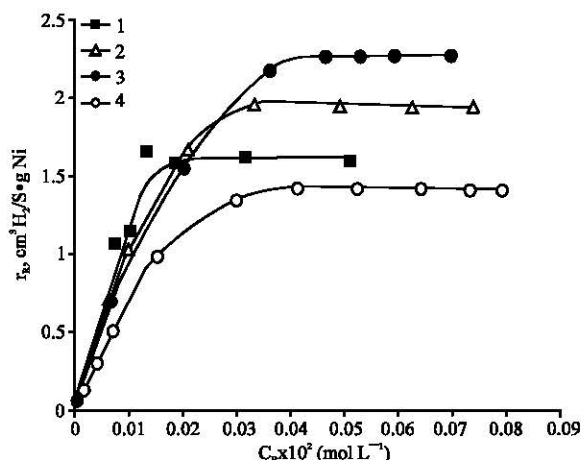


Fig. 1: The dependence of the observed hydrogenation reaction rate on skeleton nickel r_R calculated according to the concentration of maleic acid the concentration C_R in aqueous solutions of sodium hydroxide with pH: 1-7.8, 2-12.0, 3-12.9, 4-13.9, at temperature 303 K

Table 1: Constants of hydrogen outer diffusion in aqueous solutions with different pH at 303K

pH	The rate of stirring S^{-1}	R_k μm	D_{H_2} $cm^2 S^{-1}$	$P_s \times 10^{-5}$ $Erg S^{-1} g^{-1}$	K $cm S^{-1}$
7.8	250	4.8	4.0	9.5 ± 0.8	0.26 ± 0.01
	450	4.8	4.0	$(1.3 \pm 0.1) \times 10^6$	1.90 ± 0.09
12.0	250	4.8	4.8	0.8 ± 0.1	0.20 ± 0.01
	450	4.8	4.8	600.0 ± 50	0.61 ± 0.24
	250	7.5	4.8	5.5 ± 0.3	0.23 ± 0.02
12.9	250	4.8	3.6	200.0 ± 15	0.41 ± 0.03
	450	4.8	3.6	-	8.00
13.9	250	4.8	3.6	42.0 ± 4	0.31 ± 0.02
	450	4.8	3.6	-	8.00

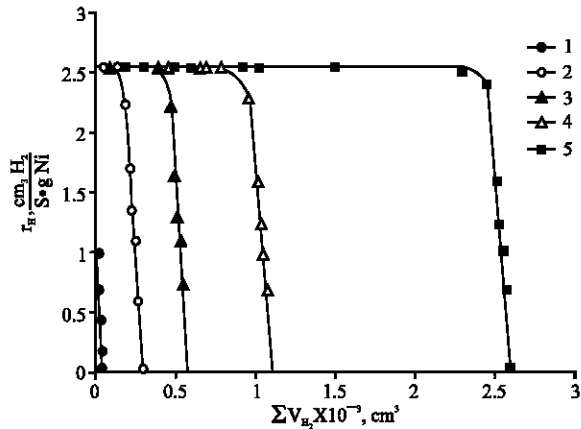


Fig. 2: Dependence of the observed maleic acid hydrogenation r_H on skeleton nickel with $R_k = 4.2 \mu m$ in aqueous solution of sodium hydroxide with pH = 12.0 upon the volume of the absorbed hydrogen ΣV_{H_2} at 303 K and the mixing up rate equal $480 S^{-1}$. Initial concentration of maleic acid in a solution, $mol L^{-1}$: 1-0.02, 2-0.12, 3-0.24, 4-0.5 and 5-1.16

in all kinetic curves at initial maleic acid concentrations higher than $3.5 \times 10^{-2} M$ irrespective of pH of medium there was realized the region of constant reaction rate corresponding to the kinetic equation of zero order reaction according to the hydrated compound. At initial concentrations lower than $1.5 \times 10^{-2} M$ hydrogen absorption rate increased with the growth of concentration and the character of its change corresponded to the kinetic equation of the first order reaction on hydrated compound.

From the data in the Fig. 2 and 3 showed the kinetics of maleic acid hydrogenation reaction on skeleton nickel in the solutions with some other pH values, it follows that on all kinetics curves three characteristic plots can be differentiated.

In the beginning of the reaction the concentration of maleic acid decreased sharply and the rates of hydrogen absorption decreased down the values which depended upon the conditions of the process.

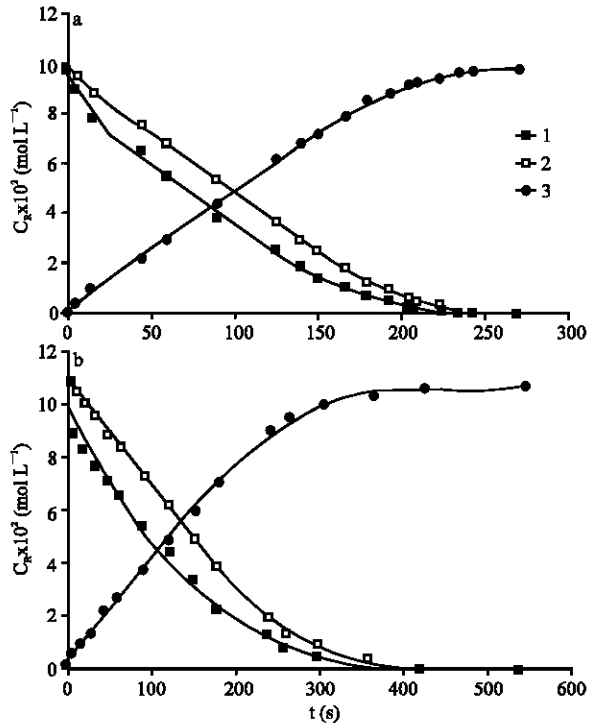


Fig. 3: The dependence of sodium maleate concentrations determined analytically-1 and calculated according to the quantity of hydrogen absorbed in the reaction-2, the reaction product C_{RH_2} upon the time t in sodium maleate reaction on skeleton nickel catalyst with $R_k = 4.2 \mu m$ aqueous solutions of sodium hydroxide with pH: a) -12.0, b) -13.9, $T = 303 K$, stirring rate = $250 S^{-1}$

The length of this plot irrespective of initial concentrations of a hydrated compound in all solvents did not exceed 10 s. Further maleic acid concentration and the reaction product in time changed linearly and the rate of hydrogen absorption remained nearly constant.

In Fig. 3 the dependencies of the concentrations of maleic acid C_R , the reaction product C_{RH_2} upon the time t in the process of hydrogenation reaction of maleic acid on a skeleton nickel catalyst in aqueous sodium hydroxide solutions with pH equal 12.0 and 13.9 are shown. Besides that Fig. 3 demonstrates the concentrations of maleic acid calculated on the base of absorbed hydrogen taking into account the stoichiometry of the reaction. Similar dependencies were obtained in the process of hydrogenation reaction in other solvents with different concentrations of hydrated compound^[10].

The rate constants: The values of the observed rate constants K_H in the region of zero order were calculated from the observed reaction rate R_H according to the equation.

Table 2: Kinetic parameters of maleic acid hydrogenation reaction over skeleton nickel in aqueous solutions with different pH $R_k = 4.2 \mu\text{m}$, $T = 303\text{K}$, the rate of stirring = 250 S^{-1}

pH	The region of zero point in maleic acid				The region of low concentration maleic acid			
	Reaction parameter*		Reaction parameter**		Reaction parameter*		Reaction parameter**	
	$K_H^0 \text{ S}^{-1}$	$K_S^0 \text{ S}^{-1}$	$K_H^0 \text{ S}^{-1}$	$K_S^0 \text{ S}^{-1}$	Order, n	$K_H, \text{mole}^{1-n} \cdot \text{l}^{n-1} \cdot \text{S}^{-1}$	Order n	$K_H, \text{mole}^{1-n} \cdot \text{l}^{n-1} \cdot \text{S}^{-1}$
7.8	420±25	1200±10	440±10	1300±240	0.960	1.46±0.036	0.572	0.14±0.024
12.0	560±25	2800±300	550±11	2900±230	0.812	0.85±0.062	0.576	0.25±0.020
12.9	670±50	3000±600	670±11	3000±350	0.763	0.61±0.060	0.497	0.34±0.075
13.9	54±7	2200±450	550±13	2200±520	0.976	0.92±0.160	0.848	0.57±0.051

*Calculated according to the dependence of concentrations of maleic acid upon the time

** Calculated according to the dependence of the quantity of absorbed hydrogen upon the time

$$K_H = \frac{4.5}{C_{H_2}^0 \cdot (\tilde{P}_{exp} - \tilde{B})^{r_H}} \quad (1)$$

Where, $C_{H_2}^0$ - is Bunsen coefficient, $\text{cm}^3 \text{ H}_2/\text{cm}^3 \text{ l.ph}$ (liquid phase) for hydrogen at the experimental temperature, p_{exp} -is the relative pressure in the experiment; B-is the relative equilibrium pressure of the water vapors at the temperature of the experiment.

The data on the hydrogen solubility used in solvents were obtained experimentally and were taken from the literature^[16].

The values of the observed rate constants K_H in the region of the first order on the hydrated compound were calculated by classical treatment of concentration dependencies of maleic acid upon the time in the coordinates of the first order equation.

The result of the preliminary experiments showed that the hydrogenation reaction rate in all solvents at concentrations of a skeleton nickel higher than $2 \times 10^{-3} \text{ g per } 1 \text{ cm}^3$ of a liquid phase was proportional to the catalyst mass.

The effect of mass transfer: The evaluation of retarding contributions on hydrogen and organic reagent, carried out according to the method allowed to state that even in the region of low concentrations of maleic acid in all solvents the reaction was limited by diffusion retarding on hydrogen, If the rate of stirring is higher than 500 S^{-1} the outer mass transfer of hydrogen did not affect significantly the hydrogenation. However even in the samples of a catalyst with the average radius less than $4 \mu\text{m}$ the contribution of inner mass transfer into total reaction rate was rather great (Table 1).

Thus for calculating the rates and the reaction rate constants on the equally available surface of r_s and K_S according to the values r_H and the observed reaction rate constants K_H the equations 2 and 3 were used^[17,18]:

$$\frac{1}{r_H} = \frac{(PR)^2}{3r_s \cdot (PR \text{cth}(PR) - 1)} + \frac{R_K}{3K C_{H_2}^0} \quad (2)$$

$$\frac{1}{K_H} = \frac{(PR)^2}{3K_s \cdot (PR \text{cth}(PR) - 1)} + \frac{R_K}{3K} \quad (3)$$

where, R_K -is the radius of catalyst particles, $C_{H_2}^0$ - is the solubility of hydrogen in a solvent, k -is the constant of outer diffusion, PR-is Til modulus determined by the equation:

$$PR = \left(\frac{R_s}{C_{H_2}^0 \cdot D_{H_2}^*} \right)^{\frac{1}{2}} \cdot R_k \quad (4)$$

Where, $D_{H_2}^*$ - is the effective coefficient of hydrogen diffusion^[19].

The constants of outer mass transfer k necessary for the calculations were determined according to the capacity of energy dissipation P_s which was evolved during the mixing up of a liquid phase in the presence of a catalyst with the use of equation^[20]:

$$k = 1.0 \cdot \left(\frac{P_s \cdot D_{H_2} \cdot \rho_s}{4\eta_s \cdot R_k^2} \right)^{\frac{1}{6}} \quad (5)$$

where, ρ_s , η_s are density and dynamic viscosity of a solvent D_{H_2} is the coefficient of hydrogen diffusion in a solvent under study.

The values of the capacity of dissipation energy of stirring up P_s were measured experimentally according to the intensity of heat evolution in the process of, mixing the catalyst suspension in a solvent by a calorimetric method^[18].

Table 2 gives the observed constants K_H and the constants of the reactions on the surface of catalyst K_S in the region of zero order on a hydrated compound calculated according to the dependencies of maleic acid concentrations and the quantity of absorbed hydrogen upon the time. These values in the limits of the experimental error coincide with the constants calculated according to the rate of hydrogen absorption.

The values of the reaction orders found in the pH interval under investigation differed from one and changed in the range of 0.7-0.85 and 0.50-0.85.

The effect of temperature: From the temperature dependence of the observed constants and reaction rate constants on the surface of a catalyst in the region of zero order on hydrated compound obtained experimentally activation energies of maleic acid hydrogenation reaction on a skeleton nickel with average radius of particles equal 4.2 were calculated. For the hydrogenation reaction in aqueous solution of sodium hydroxide with pH 7.8 and 13.9 equal to 39 ± 2 and 62 ± 5 kJ mol⁻¹, respectively. Similar experiments in the solutions with other pH showed that the activation energy had the values close in the limits of the error to the values of activation energy of hydrogenation reaction in 0.01 M solution of sodium hydroxide.

Thus maleic acid hydrogenation reaction on a skeleton nickel in aqueous solutions despite simple kinetic regularities of the reaction process represents a complex non-stationary process complicated by strong diffusion retarding while constructing a kinetic model of the process under study.

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