# Formal Kinetic Description of Photocatalytic Hydrogen Evolution from Ethanol Aqueous Solutions in the Presence of Sodium Hydroxide

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Abstract—The dependences of the rate of the photocatalytic hydrogen production in ethanol aqueous solutions on the concentration of ethanol and sodium hydroxide on the 1% Pt/10% Ni(OH)<sub>2</sub>/Cd<sub>0.3</sub>Zn<sub>0.7</sub>S photocatalyst under visible light irradiation ( $\lambda = 450$  nm) are studied. To describe kinetic data, the Langmuir—Hinshelwood equation was modified. An equation was proposed that reflects the dependence of the reaction rate on the concentration of NaOH, and an equation was derived for the first time that shows the dependence of the rate of photocatalytic hydrogen production from the concentrations of both reactants, ethanol and sodium hydroxide. The validity of the proposed equations was confirmed by their use for the description of the experimental data obtained in this work and reported earlier.

*Keywords:* photocatalysis, hydrogen production,  $Cd_{1-x}Zn_xS$ , simulations, Langmuir–Hinshelwood equation **DOI:** 10.1134/S0023158418060101

# INTRODUCTION

A rapid decrease in the stocks of readily accessible hydrocarbons requires extensive development of alternative energy sources and raw materials for the chemical industry. One such alternative energy source is hydrogen, the heat of combustion of which is very high, and the product of combustion is water [1]. The photocatalytic water decomposition under sunlight illumination is a very promising method for obtaining hydrogen since in this case hydrogen is formed directly from renewable resources such as water and air. However, as indicated it the first works on the photocatalytic water splitting, in the case of the formation of hydrogen and oxygen in a single volume, the reaction between them can substantially reduce the quantum efficiency of the process. Therefore, considerable attention is given to the photocatalytic production of hydrogen by the decomposition of available organic and inorganic electron donors in aqueous solutions rather than by water splitting [2-9]. The tendency of using organic substances is attractive from the practical standpoint due to possible use of mono- and polyatomic alcohols formed by biomass processing [1].

The prediction of reaction rates obtained by varying different conditions (e.g., reactant concentrations) is one of the main problems of modern photocatalysis. For conventional industrial heterogeneous catalytic processes (such as the synthesis of sulfuric acid [10] or ammonia [11]), this problem has been solved by accumulating sets of reaction rate values obtained experi-

mentally under various initial conditions and their approximation by the equations. In this way, the mathematical description of the photocatalytic oxidation processes of organic substances in the gas phase was obtained [12]. In the case of photocatalytic reactions in solutions, several attempts have been made to obtain mathematical models that show the relationship between the rate of the photocatalytic process and the reactant concentrations, but all of them described the kinetic features of the photocatalytic hydrogen production in the aqueous solutions of sodium sulfides and sodium sulfites [13–15]. For the photocatalytic decomposition of organic substances in aqueous solutions an equation based on Langmuir-Hinshelwood model that describes the dependence of the reaction rate only on the concentration of organic substrate was proposed in [16, 17]:

$$W = \frac{kKC}{1+KC},\tag{1}$$

where W is the rate of the photocatalytic hydrogen production, k is the apparent rate constant, and K is the adsorption constant of the reactant molecule. With Eq. (1), the kinetics of photocatalytic hydrogen production in the aqueous solutions of alcohols (methanol [18], ethanol [19], glycerol [20]), glucose [21], acetic acid [22], triethanolamine [23], and organophosphorus compounds [24]) has been described.

However, there has been no equation published that describes the dependence of the reaction rate on



**Fig. 1.** Setup for photocatalytic hydrogen production: (1) LED, (2) reaction mixture, (3) magnetic stirrer, (4) anchor, (5) quartz window, (6) sampling tube.

the concentration of protons or hydroxide ions. Lyubina et al. [25] showed that the photocatalytic hydrogen production from aqueous solutions of organic alcohols can be approximated not in the full range of substrate concentrations: for example, Eq. (1) describes the dependence of the reaction rate on the glycerol concentrations in the range 0-0.3 mol/L. A similar pattern was reported for ethanol [26]. To construct kinetic models, it is necessary to analyze the reasons for the observed deviations.

The goal of this work was to derive and theoretically justify an equation that allows one to accurately describe the experimental dependences of the photocatalytic hydrogen production rate from aqueous ethanol solutions on the concentrations of ethanol and sodium hydroxide. Ethanol was chosen as an organic substrate, since it is the most convenient model compound for studying the kinetics of hydrogen production using aqueous solutions of alcohols. It has been shown earlier that the rate of hydrogen evolution normalized to the stoichiometric coefficient is a constant value for major organic alcohols [27]. The kinetics of photocatalytic hydrogen production was studied using composite photocatalyst 1% Pt/10% the  $Ni(OH)_2/Cd_0_3Zn_0_7S$ , which showed high activity in the target process.

#### EXPERIMENTAL

#### Photocatalyst Preparation

To prepare catalysts and carry out kinetic experiments, the following reagents were used:  $CdCl_2$  (Reakhim, reagent grade),  $Zn(NO_3)_2$  (Reakhim, high purity), NiCl<sub>2</sub> (Reakhim, reagent grade), NaOH (Reakhim, purity for analysis), Na<sub>2</sub>S ·  $xH_2O$  (Fluka,

32-38% H<sub>2</sub>O), H<sub>2</sub>PtCl<sub>6</sub> (Reakhim, reagent grade), NaBH<sub>4</sub> (Pulver, 98%), C<sub>2</sub>H<sub>5</sub>OH (96%).

The Cd<sub>0.3</sub>Zn<sub>0.7</sub>S photocatalyst was synthesized by the procedure described in [28]. The 10%  $Ni(OH)_2/Cd_{0.3}Zn_{0.7}S$  catalyst was prepared as follows: a solution of NiCl<sub>2</sub> (0.1 mol/L, 3.66 mL) was added dropwise to the 10-mL suspension containing 300 mg of  $Cd_{0.3}Zn_{0.7}S$ , stirred for 5 min, and then the stoichiometric amount of NaOH (0.1 mol/L) solution was added dropwise. The resulting suspension was stirred for 30 min, washed by distilled water ten times, centrifuged for 15 min and dried for 4 h at 80°C. The prepared photocatalyst was the solid solution of cadmium sulfide and zinc sulfide Cd<sub>0.3</sub>Zn<sub>0.7</sub>S modified with 10 wt % of nickel hydroxide on the surface. Before measurements of the hydrogen photoproduction rate 1 wt % of platinum was supported on the obtained photocatalyst (the method of platinization was described earlier in [25]).

### Measurement of the Rate of Photocatalytic Hydrogen Evolution

The process of photocatalytic hydrogen production was carried out in a glass reactor with a volume of 320 mL (Fig. 1), inside which the reaction suspension (2) was stirred using a magnetic stirrer (3), and the photocatalyst was illuminated with LED (1) through a quartz window (5).

The reaction rate of the photocatalytic hydrogen production from ethanol aqueous solutions was measured as follows: the calculated amount of NaOH and 50 mg of the photocatalyst were added to the mixture of ethanol and water (100 mL). The volume concentration of ethanol was varied in the range from 0 to 70%, while the concentration of NaOH was changed from 0 to 1 mol/L (a further increase in the NaOH concentration was limited by its solubility in the ethanol aqueous solutions). In all experiments the reactor was preliminarily purged with argon for 30 min until the complete removal of oxygen. Then the reactor was irradiated by visible light ( $\lambda =$ 450 nm) for 90 min; LED (240 mW/cm<sup>2</sup>) was a light source. The concentration of evolved hydrogen was determined using a gas chromatograph (Khromos, Russia). The carrier gas was argon. Origin Pro 2016 software was used to calculate the dependence of the amount of evolved hydrogen on time. The linear part of this dependence was approximated by the linear equation using the least-squares method. The rate of hydrogen production was taken equal to the slope.

# **RESULTS AND DISCUSSION**

# The Dependence of the Rate of Photocatalytic Hydrogen Evolution on the Ethanol Concentration

The rate of photocatalytic hydrogen production was measured for different initial concentrations of ethanol and sodium hydroxide. The resulting values are shown in Table 1. The reaction rate dependence on the ethanol concentration was considered at a constant initial concentration of NaOH (0.1 mol/L). In the absence of ethanol, low activity is observed in the photocatalytic hydrogen production directly from the aqueous NaOH solution. It has been shown earlier that aqueous solutions of NaOH may play a role of the hydrogen source in the photocatalytic reactions [29]. When a small amount of ethanol (5 vol %) was added. the reaction rate becomes almost five times higher and grows reaching 8.1 µmol/min at a volume concentration of ethanol of 50%. Table 1 shows that further increase in the ethanol concentration leads to the decrease in the reaction rate. Similar dependence of the reaction rate on the ethanol concentration has been described in the literature [26].

The analysis of the reaction mixture after 9 h of the photocatalytic reaction from ethanol aqueous solutions showed the presence of ethanol and acetaldehyde in the liquid phase. Therefore, at this stage of the process, hydrogen is evolved according to the following overall reaction:

$$CH_3CH_2OH \rightarrow CH_3CHO + H_2.$$
 (I)

According to Eq. (I), the rate of hydrogen formation is equal to the rate of ethanol consumption in the photocatalytic oxidation process, and the rate-limiting step of the photocatalytic alcohol decomposition is the cleavage of C–H bond in the  $\alpha$  position relative to the hydroxyl group [27]. The resulting experimental dependences of the rate of photocatalytic ethanol oxidation in aqueous solutions on the substrate concentration are approximated by the Langmuir-Hinshelwood equation for a monomolecular reaction (Eq. (1)) [16, 17]. This approximation means that monomolecular chemical reaction occurs on the surface, the adsorption of the reagent on the photocatalyst surface is described by the Langmuir isotherm. A specific feature of Langmuir-Hinshelwood approximation for a monomolecular reaction (Eq. (1)) is the tendency of the reaction rate to the maximum value with increasing substrate concentration. It should be noted that, for experimental data, this behavior is observed only for a certain concentration range, after which the rate of hydrogen production begins to decrease with increasing ethanol content. In the literature, the decrease in the rate of the hydrogen production at high ethanol concentrations is attributed to the saturation of the photocatalyst surface with ethanol and a relatively low surface concentration of water that is necessary for the formation of hydroxyl radicals and efficient ethanol oxidation [30]. Note that, when the alcohol concentration in the suspension grows, both the fraction of surface sites on which water and NaOH are adsorbed that are potential sources of hydroxyl radicals, and the fraction of free surface sites decrease. The free sites can also be used during the process, because they will adsorb the product of ethanol decomposition. Then from the formal point of view, the reactions

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**Table 1.** Rate of the hydrogen photoproduction at differentinitial conditions of ethanol and sodium hydroxide on the1% Pt/10% Ni(OH)<sub>2</sub>/Cd<sub>0.3</sub>Zn<sub>0.7</sub>S photocatalyst

Фсн.сн.он, %	$C_{\mathrm{CH}_{3}\mathrm{CH}_{2}\mathrm{OH}}^{0}$ ,	$C_{ m NaOH}^0$ ,	$W_0,$
FCH3CH20H7 +	mo	µmol/min	
0	0	0.1	$0.62\pm0.06$
5	0.86	0.1	$3.03\pm0.01$
10	1.72	0.1	$4.3\pm0.2$
20	3.43	0.1	$5.4 \pm 0.3$
30	5.15	0.1	$6.8\pm0.6$
40	6.86	0.1	$7.9\pm0.5$
50	8.58	0.1	$8.1\pm0.5$
60	10.29	0.1	$7.4 \pm 0.3$
70	12.01	0.1	$6.9\pm0.2$
50	8.58	0	$2.6\pm0.3$
50	8.58	0.05	$7.1\pm0.7$
50	8.58	0.2	$10 \pm 1$
50	8.58	0.4	$14 \pm 1$
50	8.58	1.0	$25\pm2$

The experimental conditions: weight of the photocatalyst was 50 mg, volume of suspension was 100 mL; temperature was 20°C; the light source was LED ( $\lambda = 450$  nm).

occurring on the surface are recorded as follows in the case of ethanol oxidation by directly photogenerated holes (reaction (II)) or hydroxyl radicals (reaction (III)):

$$Z-CH_{3}CH_{2}OH + Z + h^{+}$$
(II)

$$\rightarrow Z - CH_3 CH_2 O + Z - H ,$$

$$Z - CH CH OH + Z - OH'$$

$$\rightarrow Z - CH_3 CH_2 O' + Z - H_2 O, \qquad (III)$$

where Z is the free surface site,  $Z-CH_3CH_2OH$ ,  $Z-CH_3CH_2O^{\bullet}$ ,  $Z-H^+$ ,  $Z-OH^{\bullet}$  are the following species adsorbed on the photocatalyst surface  $CH_3CH_2OH$ ,  $CH_3CH_2O^{\bullet}$ ,  $H^+$ ,  $OH^{\bullet}$ , respectively.

According to reactions (II) and (III), the oxidation of ethanol is a bimolecular reaction, and its rate can be written as Eqs. (2) and (3), respectively, and the final expression is represented by Eq. (4):

$$W = k_{\rm II}\theta_{\rm EtOH}\theta_0 = \frac{k_{\rm II}K_{\rm EtOH}C_{\rm EtOH}}{\left(1 + K_{\rm EtOH}C_{\rm EtOH} + K_{\rm OH}C_{\rm OH}\right)^2}, \quad (2)$$

$$W = k_{\rm III} \theta_{\rm EtOH} \theta_{\rm OH}^{} = \frac{k_{\rm III} K_{\rm EtOH} C_{\rm EtOH} K_{\rm OH} C_{\rm OH}^{}}{\left(1 + K_{\rm EtOH} C_{\rm EtOH} + K_{\rm OH} C_{\rm OH}\right)^{2}}, (3)$$
$$W = k_{\rm II} \theta_{\rm EtOH} \theta_{0} + k_{\rm III} \theta_{\rm EtOH} \theta_{\rm OH}^{}$$
$$= \frac{K_{\rm EtOH} C_{\rm EtOH} (k_{\rm II} + k_{\rm III} K_{\rm OH} C_{\rm OH})}{\left(1 + K_{\rm EtOH} C_{\rm EtOH} + K_{\rm OH} C_{\rm OH}\right)^{2}},$$
(4)



**Fig. 2.** Approximation of the experimental data (curve 1,  $R^2 = 0.955$ ) and data described in the literature (curve 2 [31],  $R^2 = 0.861$ ) by Eq. (5). Experimental conditions: (1) 0.1 M NaOH, photocatalyst 1% Pt/10% Ni(OH)<sub>2</sub>/Cd<sub>0.3</sub>Zn<sub>0.7</sub>S, the catalyst concentration was 0.5 g/L, the volume of suspension was 100 mL, the temperature was 20°C, LED was the light source ( $\lambda = 450$  nm); (2) 0.1 M NaOH, photocatalyst CdS, the catalyst concentration was 40 mL, the temperature was 20°C, xenon–mercury arc lamp with light filter ( $\lambda > 400$  nm) was used as the light source.

where  $k_{\rm II}$  and  $k_{\rm III}$  are the apparent rate constants,  $K_{\rm EtOH}$  and  $K_{\rm OH}$  are the adsorption constants of ethanol and sodium hydroxide,  $C_{\rm EtOH}$  and  $C_{\rm OH}$  are the initial concentrations of ethanol and NaOH.

At a constant concentration of NaOH and in the absence of additional data on the value of the sodium hydroxide adsorption constant, it is advisable to use the general expression (Eq. (5)) as initial approximation, in which all the constant values, except for the ethanol adsorption constant, belongs to the effective rate constant, and the denominator is limited by the first two terms. This assumption is reasonable, since the surface of the photocatalyst is negatively charged in the alkaline medium in all the discussed experiments. Therefore, the negatively charged hydroxide ions will predominantly repulse from the sample surface, so the surface coverage by OH<sup>-</sup> will be low compared to coverages by other substrates.

$$W = \frac{K_{\text{EtOH}}C_{\text{EtOH}}(k_{\text{II}} + k_{\text{III}}K_{\text{OH}}C_{\text{OH}})}{(1 + K_{\text{EtOH}}C_{\text{EtOH}})^2}$$

$$= \frac{k_{\text{app}}K_{\text{EtOH}}C_{\text{EtOH}}}{(1 + K_{\text{EtOH}}C_{\text{EtOH}})^2},$$
(5)

where  $k_{\text{app}} = k_{\text{II}} + k_{\text{III}}K_{\text{OH}}C_{\text{OH}}$ .

Experimental data obtained in this work and described earlier [31] were approximated using

Eq. (5). Figure 2 shows the resulting data, where the solid line denotes the curve approximations by Eq. (5). It is seen from Fig. 2 that chosen approximation correctly reflects the characteristic feature of the dependence of the hydrogen production rate on the volume concentration of ethanol (its passage through a maximum) and describes well the kinetics of the studied process.

The Langmuir–Hinshelwood equation for the monomolecular reaction (Eq. (1)) and Eq. (5) were used to approximate data previously described in the literature for photocatalytic hydrogen evolution from aqueous solutions of methanol [30–32], ethanol [30, 31, 33], and *n*-propanol [33]; the parameters of approximation are shown in Table 2. It is seen from Table 2 that parameters  $k_{app}$  and K obtained in different approximations differ several times for the same systems. This fact is associated with different formulas for the calculating of approximation parameters from Eqs. (1) and (5), and also by the experimental difficulties in determining the adsorption constants under irradiation of the photocatalyst whose experimental values could verify the reliability of the K determination on the basis of the proposed simulations. Note that kinetic data can be described by both approximations almost in all cases, but the highest values of the correlation coefficient  $R^2$  are achieved in the case of Eq. (5). Moreover, when Eq. (5) is used, reasonable values of errors in the approximation parameters are achieved, which is not always possible when Eq. (1) is used. These facts confirm the validity of the use of Eq. (5) for describing the dependence of the rate of photocatalytic hydrogen production on the ethanol concentration.

# Dependence of the Rate of Photocatalytic Hydrogen Evolution on the Sodium Hydroxide Concentration

According to the experiments on the determination of the optimal composition of the ethanol-water mixture, the highest rates of photocatalytic hydrogen production is achieved at a volume concentration of ethanol of 50%. Different amounts of sodium hydroxide were added to ethanol solutions of this composition so that its concentration in the resulting solution was between 0 and 1 mol/L. The values of the reaction rates obtained in this set of experiments are shown in Table 1. In the presence of NaOH, a nonzero rate of the photocatalytic hydrogen production is observed. The oxidation of ethanol is likely to occur due to its interaction with the photoinduced holes or hydroxyl radicals formed from water. When a small amount of NaOH was added, the rate of hydrogen photoproduction drastically increases due to the formation of hydroxyl radicals.

Figure 3 demonstrates that a further increase in the reaction rate is linear with an increase in the NaOH concentration. Therefore, according to the experi-

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	Approximation by Eq. (1)			Approximation by Eq. (5)					
Photocatalyst	k <sub>app</sub> , μmol/min	<i>K</i> , L/mol	<i>R</i> <sup>2</sup>	k <sub>app</sub> , μmol/min	K, L/mol	<i>R</i> <sup>2</sup>	Reference		
Methanol									
0.6% Pt/TiO <sub>2</sub>	$0.07\pm0.03$	$0.2\pm0.1$	0.70	$1.0 \pm 0.3$	$0.07\pm0.02$	0.83	[23]		
Pt/TiO <sub>2</sub>	$4.2\pm0.8$	$0.6\pm0.2$	0.94	$15 \pm 3$	$0.09\pm0.01$	0.99	[30]		
Ethanol									
CdS	Not ap	proximated		$3.9 \pm 1.1$	$0.31\pm0.09$	0.86	[32]		
Pt/TiO <sub>2</sub>	$5\pm 2$	$1.9\pm0.6$	0.86	$20\pm 2$	$0.18\pm0.01$	0.87	[30]		
1% Pt/10% Ni(OH) <sub>2</sub> /	$12 \pm 4$	$0.3\pm0.1$	0.88	$34 \pm 5$	$0.08\pm0.01$	0.96	This work		
$Cd_{0.3}Zn_{0.7}S$									
9% C/TiO <sub>2</sub>	$0.2\pm0.1$	$0.5\pm0.3$	0.84	$2.1\pm0.4$	$0.07\pm0.02$	0.96	[33]		
Pt/CdS/TiO <sub>2</sub> /FTO	$0.21\pm0.05$	$1.8\pm0.5$	0.96	$0.9\pm0.1$	$0.20\pm0.02$	0.97	[30]		
Propanol									
9% C/TiO <sub>2</sub>	$0.2\pm0.1$	$0.7\pm0.6$	0.71	$0.9\pm0.1$	$0.09\pm0.01$	0.98	[33]		

**Table 2.** Approximation of the experimental data by Langmuir–Hinshelwood equations based on the monomolecular and bimolecular approximations

mental data, the dependence of the reaction rate on the NaOH concentration is described by the equation:

$$W = a + bC_{OH^{-}},\tag{6}$$

where the coefficient a is equal to the rate of hydrogen production in the absence of sodium hydroxide and bis the apparent constant of the reaction rate.

Data on the dependence of the photocatalytic hydrogen production rate on the sodium hydroxide concentration described earlier in the literature [34–38] were approximated by Eq. (6), and the approximation parameters are listed in Table 3. One can see that the proposed equation describes the experimental data with a high accuracy. Note that, earlier in the literature, no equations that describe the dependence of the rate of hydrogen photoproduction rate on the NaOH concentration were proposed.

Special attention should be given to the relationships between Eqs. (4)–(6). As noted earlier, the process of ethanol oxidation can occur both directly with the participation of the photogenerated holes (reaction (II)) and with hydroxyl radicals (reaction (III)), and Eq. (4) for the reaction rate takes into account both oxidation routes. If the term containing the dependence of the hydrogen production rate on the NaOH concentration is separated at the fixed ethanol concentration, then, taking into account that in the alkaline media the contribution of  $K_{OH}C_{OH}$  can be neglected in the denominator, the expression for the reaction rate takes the following form:

$$W = \frac{K_{\text{EtOH}}C_{\text{EtOH}}k_{\text{II}}}{\left(1 + K_{\text{EtOH}}C_{\text{EtOH}}\right)^2} + \frac{k_{\text{III}}K_{\text{EtOH}}C_{\text{EtOH}}K_{\text{OH}}}{\left(1 + K_{\text{EtOH}}C_{\text{EtOH}}\right)^2}C_{\text{OH}}.$$
 (7)

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Let us compare Eqs. (6) and (7). Since the equilibrium concentration of ethanol and the adsorption constant do not depend on the concentration of NaOH, then

$$a = \frac{K_{\text{EtOH}}C_{\text{EtOH}}k_{\text{II}}}{\left(1 + K_{\text{EtOH}}C_{\text{EtOH}}\right)^2},\tag{8}$$



**Fig. 3.** Dependence of the rate of photocatalytic hydrogen production on the NaOH concentration. The experimental conditions: 50 vol % ethanol, 50 mg of the 1% Pt/10% Ni(OH)<sub>2</sub>/Cd<sub>0.3</sub>Zn<sub>0.7</sub>S photocatalyst, the volume of suspension was 100 mL, the temperature was 20°C, the light source was LED ( $\lambda = 450$  nm). The dashed line shows the approximation by Eq. (6).

Dhotocotolyst	App	roximation by Eq	Concentration	Reference					
Thotocatalyst	a, µmol/min	mol/min $b, \mu L/min$			of NaOH, mol/L				
Methanol									
1.2% Au/TiO <sub>2</sub>	$0.08\pm0.01$	$0.09\pm0.01$	0.875	0.1-5	[34]				
Bi <sub>0.5</sub> Na <sub>0.5</sub> TiO <sub>3</sub>	$0.16\pm0.04$	$0.05\pm0.01$	0.888	3–9	[35]				
Ethanol									
1% Pt/10% Ni(OH) <sub>2</sub> /Cd <sub>0.3</sub> Zn <sub>0.7</sub> S	$3.3 \pm 0.7$	$25 \pm 4$	0.995	0-1	This work				
Ni(OH) <sub>2</sub> /CdS	$0.06\pm0.01$	$0.112\pm0.007$	0.996	0.01-5	[36]				
Glucose									
InVO <sub>4</sub> : Ni*	$0.024\pm0.003$	$0.44\pm0.09$	0.961	0-0.1	[37]				
0.5% Pt/17% ZnS/ZnIn <sub>2</sub> S <sub>4</sub>	0	$1.8\pm0.1$	0.989	0-0.125	[38]				

Table 3. Approximation of the dependences of the hydrogen production rate on the NaOH concentration by Eq. (6)

\*Indium vanadate doped with nickel.

$$b = \frac{k_{\rm HII} K_{\rm EtOH} C_{\rm EtOH} K_{\rm OH}}{\left(1 + K_{\rm EtOH} C_{\rm EtOH}\right)^2}.$$
(9)

Let us introduce new notation:

$$\alpha = k_{\rm II} K_{\rm EtOH},\tag{10}$$

$$\beta = k_{\rm III} K_{\rm EtOH} K_{\rm OH}.$$
 (11)

Then the dependence of the rate of photocatalytic hydrogen production on the initial concentrations of ethanol and sodium hydroxide is described by Eq. (12).

$$W = \frac{(\alpha + \beta C_{\text{OH}})C_{\text{EtOH}}}{(1 + K_{\text{EtOH}}C_{\text{EtOH}})^2}.$$
 (12)

Equation (12) was used to approximate experimental data presented in Table 1. The approximation parameters were  $\alpha = 2.1 \pm 0.2 \,\mu$ L/min,  $\beta = 6.9 \pm 0.7 \,\mu$ L mol<sup>-1</sup> min<sup>-1</sup>,  $K_{\text{EtOH}} = 0.08 \pm 0.01$  L/mol, and the correlation coefficient was 0.986. Thus, the proposed equation makes it possible to describe the experimental data with a high accuracy. Unfortunately, in the literature the dependences of hydrogen production rate on the concentrations of both reagents are rarely measured, and the set of available data is insufficient for accurate mathematical description. Therefore, it is impossible to consider the applicability of this equation to the literature data.

A surface plot defined by Eq. (12) reflects the main kinetic features of photocatalytic hydrogen production depending on the concentrations of ethanol and sodium hydroxide (Fig. 4). If one fixes the value of the initial NaOH concentration in Fig. 4 (this is most clearly seen for a NaOH concentration of 1 mol/L) and considers how the reaction rate changes with increasing ethanol concentration, it is seen that this dependence passes through a maximum, that agrees with the experimental results. If the ethanol concentration is fixed, the reaction rate linearly depends on the NaOH concentration, which also coincides with the experimental results. In addition, using Wolfram Mathematica 11.3 software, a counter plot was drawn from the surface plot defined by Eq. (12) (Fig. 5). This plot reflected a change in the rate of hydrogen production when the initial concentrations of both reactants are varied. Figure 5 shows that the highest values of the rate of the target process (>25  $\mu$ mol/min) are reached in the ranges of rather high initial concentrations of the reactants: the ethanol concentration should be



**Fig. 4.** Surface plot defined by Eq. (12) that shows the dependence of the rate of the photocatalytic hydrogen evolution on the concentration of ethanol (0-17 mol/L) and sodium hydroxide (0-1 mol/L).

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Fig. 5. Counter plot defined by Eq. (12).

higher than 6 mol/L, which corresponds to 35 vol %, and the concentration of NaOH should be higher than 0.86 mol/L. Note that, during kinetic experiments, a rate of hydrogen production of 25  $\mu$ mol/min was reached, and the initial concentrations of reactants shown in Table 1 were corresponded to the concentrations at which the highest values of the reaction rates were achieved in Fig. 5. Thus, Eq. (12) makes it possible to predict the rate of the photocatalytic hydrogen production for the range of ethanol concentrations from 0 to 17 mol/L and for the range of sodium hydroxide concentrations from 0 to 1 mol/L.

#### CONCLUSIONS

The dependences of the rate of the photocatalytic hydrogen production from ethanol aqueous solutions on the concentrations of ethanol and sodium hydroxide are studied on the 1% Pt/10% Ni(OH)<sub>2</sub>/Cd<sub>0.3</sub>Zn<sub>0.7</sub>S photocatalyst. The rate of the hydrogen production passed through a maximum with increasing ethanol concentration and grew linearly with an increase in the NaOH concentration. The obtained dependences were approximated by the equations based on Langmuir-Hinshelwood mechanism for the bimolecular reaction. These equations made it possible to describe the experimental data published earlier for the photocatalytic decomposition of aqueous solutions of primary alcohols with a high accuracy. The equation allowing one to determine the relationships between the rate of the photocatalytic hydrogen production and the concentrations of both reagents, ethanol and sodium hydroxide, was derived for the first time.

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