DEPOSITION CO-CATALYSTS BASED ON TRANSITION METAL SPECIES ON THE SURFACE OF $Cd_{0,3}Zn_{0,7}S$ PHOTOCATALYST: EFFECT ON THE KINETIC FEATURES OF PHOTOCATALYTIC HYDROGEN PRODUCTION

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НАНЕСЕНИЕ СОКАТАЛИЗАТОРОВ НА ОСНОВЕ СОЕДИНЕНИЙ ПЕРЕХОДНЫХ МЕТАЛЛОВ НА ПОВЕРХНОСТЬ ФОТОКАТАЛИЗАТОРА $Cd_{0,3}Zn_{0,7}S$: ВОЗДЕЙСТВИЕ НА КИНЕТИЧЕСКИЕ ЗАКОНОМЕРНОСТИ ФОТОКАТАЛИТИЧЕСКОГО ВЫДЕЛЕНИЯ ВОДОРОДА

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Аннотация. *В ходе данной работы на поверхность фотокатализатора $Cd_{0,3}Zn_{0,7}S$ наносили гидроксиды никеля и цинка, сульфиды никеля и меди и измеряли скорость фотокаталитического выделения водорода. Для наиболее активных образцов были изучены зависимости каталитической активности от концентрации реагентов, содержания катализатора и интенсивности излучения и установлены корреляции между наблюдаемыми закономерностями и природой сокатализаторов.*

Introduction. The deposition of the transition metal compounds is known to be an effective way of the enhancing photocatalytic activity. From the practical point of view, it is important to predict the catalytic activity values under different experimental conditions; therefore, the aim of the work is to study the changes in kinetic features of the photocatalytic hydrogen production caused by the deposition of different co-catalysts.

Experimental. The photocatalysts modified by $Ni(OH)_2$ (NiOH-x, x is a weight content of the co-catalysts), NiS (NiS-x), $Zn(OH)_2$ (ZnOH-x), and Cu_xS (CuO-x) were prepared, and their catalytic activities were measured in aqueous Na_2S/Na_2SO_3 and ethanol solutions.. The catalytic activities of the most active samples were measured under various conditions such as the Na_2S concentration (0-0,4 M) and the Na_2SO_3 concentration (0-0,3 M) for $Cd_{0,3}Zn_{0,7}S$, NiOH-0,06, NiS-0.3, CuO-0,1, ZnOH-20 samples, the ethanol content (0-60 vol. %) and the NaOH concentration (0-1 M) for 1% $Pt/Cd_{0,3}Zn_{0,7}S$, 1% Pt/NiOH-10, 1%Pt/ZnOH-10. For all samples the catalyst concentration changed from 0,25 to 1,25 gL^{-1}, the light intensity varied from 21 to 454 $mW \cdot cm^{-2}$.

Results. The photocatalysts $Cd_{0,3}Zn_{0,7}S$, NiOH-0,06, CuO-0,1, NiS-0,3, and ZnOH-20 were tested in photocatalytic hydrogen evolution from Na_2S/Na_2SO_3 solutions. The reasons of its catalytic activities were discussed earlier [1-4]. In the present work we studied the kinetic features of hydrogen photoproduction at

different conditions. The dependence of reaction rate on concentrations of Na_2S and Na_2SO_3 is shown to be approximated by the following semiempirical equation [5]:

$$W = \frac{\left(\alpha + \beta \cdot C^0_{Na2SO3}\right) \cdot C^0_{Na2S}}{\left(1 + K_{Na2S} \cdot C^0_{Na2S} + K_{Na2SO3} \cdot C^0_{Na2SO3}\right)^2}, \quad (1)$$

where W is the reaction rate, α and β are the effective reaction rate constants, K_{Na2S} and K_{Na2SO3} are the adsorption constants of Na_2S and Na_2SO_3, respectively, C^0_{Na2S} and C^0_{Na2SO3} are the initial concentrations of Na_2S and Na_2SO_3, respectively. The obtained kinetic data were approximated by Equation (1), and the approximation parameters are given in Table 1. Table 1 demonstrates that the deposition of a co-catalyst in amount less 0,1 wt. % does not influence on the adsorption constants of the reagents while the further increase of the co-catalyst amount leads to the growth of the values of the adsorption constants due to the interactions between the co-catalyst and the adsorbed molecules. Besides, the deposition of the transition metal species such as $Ni(OH)_2$, NiS, Cu_xS, and $Zn(OH)_2$ improves the separation of the photoinduced charges, therefore, the effective reaction rate constants α and β grow.

Table 1

Approximation of the kinetic data by Equation (1)

Parameter \ Sample	$Cd_{0,3}Zn_{0,7}S$	NiOH-0,06	CuO-0,1	NiS-0,3	ZnOH-20
α, μL·min^{-1}	92 ± 19	188 ± 21	258 ± 43	240 ± 45	132 ± 21
β, μL·M^{-1}·min^{-1}	(1,9 ± 0,8)·10^3	(2,5 ± 0,3)·10^3	(5,6 ± 1,2)·10^3	(1,2 ± 0,4)·10^4	(5,7 ± 1,6)·10^3
K(Na_2S), M	14 ± 3	16 ± 2	24 ± 3	20 ± 3	17 ± 3
K(Na_2SO_3), M	10 ± 3	11 ± 2	18 ± 3	17 ± 3	25 ± 4
R^2	0,939	0,990	0,990	0,964	0,983

The photocatalysts 1%Pt/$Cd_{0,3}Zn_{0,7}S$, 1%Pt/NiOH-10, and 1%Pt/ZnOH-10 were tested in photocatalytic hydrogen evolution from aqueous ethanol solutions [4]. The dependence of reaction rate on concentrations of ethanol and sodium hydroxide is shown to be approximated by the following semiempirical equation:

$$W = \frac{\left(\alpha + \beta \cdot [OH^-]\right) \cdot C^0_{CH3CH2OH}}{\left(1 + K_{CH3CH2OH} \cdot C^0_{CH3CH2OH}\right)^2}, \quad (2)$$

where W is the reaction rate, α and β are the effective reaction rate constants, $K_{CH3CH2OH}$ is the adsorption constant of ethanol, $C^0_{CH3CH2OH}$ is the initial concentrations of ethanol, [OH^-] is the NaOH content. The obtained kinetic data were approximated by Equation (2), and the approximation parameters are given in Table 2. The deposition of $Ni(OH)_2$ and $Zn(OH)_2$ in amount equaled 10 wt. % changes the surface structure, therefore, the adsorption constants of pristine $Cd_{0,3}Zn_{0,7}S$ and the modified photocatalysts differ as shown in Table 2. The location of photocatalytically inactive 2D β-$Zn(OH)_2$ phase on the surface leads to the decrease in the α value for 1% Pt/ZnOH-10 while in other cases the deposition of metal hydroxides on the photocatalyst surface results in the increase of the values of effective reaction rate constants and the improvement of the photoinduced charge separation.

Table 2

Approximation of the kinetic data by Equation (2)

Photocatalyst / Parameter	1%Pt/$Cd_{0,3}Zn_{0,7}S$	1%Pt/NiOH-10	1%Pt/ZnOH-10
α, $\mu L \cdot min^{-1}$	0,38 ± 0,05	2,1 ± 0,2	0,16 ± 0,02
β, $\mu L \cdot M^{-1} \cdot min^{-1}$	4,0 ± 0,6	6,9 ± 0,7	4,9 ± 0,4
K(CH_3CH_2OH), M	0,20 ± 0,04	0,08 ± 0,01	0,24 ± 0,02
R^2	0,969	0,986	0,998

The dependence of reaction rate on the catalyst content has the volcano-type form for all samples and is typical of the photocatalysts. The correlation between the hydrogen photoproduction and the light intensity is linear for all studied photocatalysts, while the apparent quantum efficiency (AQE) depends on the type of the co-catalysts: in case of the NiOH-0,06, NiS-0,3, CuO-0,1, and $Cd_{0,3}Zn_{0,7}S$ the AQE is constant. For 1%Pt/NiOH-10, 1%Pt/ZnOH-10, and ZnOH-20 the AQE linearly grows with the increase in light intensity due to the transformations of the co-catalysts involving the photoinduced electrons.

Conclusions. The deposition of the co-catalysts based on transition metal compounds improves the photocatalytic activity. The form of the dependencies of the reaction rate on the reagent concentrations are the same for the modified and pristine photocatalysts. The influence of the catalyst concentration and the light intensity on the hydrogen photoproduction is connected with the optical effects. The correlation between the light intensity and the apparent quantum efficiency is determined by the co-catalyst transformations during irradiation.

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