

# ROLE OF SYNERGISM EFFECT OF MIXED METAL OXIDES ON MOLECULAR HYDROGEN FORMATION FROM PHOTOCATALYTIC WATER SPLITTING

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The paper deals with hydrogen production using photocatalysis. In particular, we focus on the role of synergism on the reaction rate. For hydrogen production presented photocatalyst is composed of nanoAl<sub>2</sub>O<sub>3</sub> and dispers TiO<sub>2</sub>. Yet, the presence of the two mixed metal oxides together results in considerable enhancement of the reaction rate. The main reason for this is the increase of the charge carriers' lifetime allowing for electron transfer to hydrogen ions and hole transfer to oxygen ions. It was investigated the mechanism of water splitting in presence of mixed nanocatalysed. It has been shown that the effect occurs during irradiation as a result of photooxidation of water with mixed metal oxides catalystr.

PACS: 621.039.553

## INTRODUCTION

TiO<sub>2</sub> has many properties that make it effective for use as a photocatalyst. It is cost effective, abundant, has good surface stability, is non-corrosive, environmentally friendly and has great versatility in its application [1]. Furthermore, due to the position of the conduction band (CB) and valance band (VB) of TiO<sub>2</sub> in relation to a large selection of redox potentials, TiO<sub>2</sub> also shows activity for a large number of surface reactions [2]. Photoreaction/oxidation of alcohols, carboxylic acids, acetaldehyde and acetone as well as for smaller molecules such as H<sub>2</sub>O, O<sub>2</sub>, and CO over the single crystal rutile TiO<sub>2</sub> surface has been studied. Most of these results have been discussed in recent reviews [3–6]. Other recent reviews on photoreaction of powder systems are available and these include those of references [7, 8]. In 1972, Fujishima and Honda discovered the photocatalytic splitting of water on TiO<sub>2</sub> electrodes. This event marked the beginning of a new era in heterogeneous photocatalysis. Since then, research efforts in understanding the fundamental processes and in enhancing the photocatalytic efficiency of TiO<sub>2</sub> have come from extensive research performed by chemists, physicists, and chemical engineers. Such studies are often related to energy renewal and energy storage. In a heterogeneous photocatalysis system, photoinduced molecular transformations or reactions take place at the surface of a catalyst. Depending on where the initial excitation occurs, photocatalysis can be generally divided into two classes of processes. When the initial photoexcitation occurs in an adsorbate molecule which then interacts with the ground state catalyst substrate, the process is referred to as a catalyzed photoreaction. When the initial photoexcitation takes place in the catalyst substrate and the photoexcited catalyst then transfers an electron or energy into a ground state molecule, the process is referred to as a sensitized photoreaction. The initial excitation of the system is followed by subsequent electron transfer and/or energy transfer. It is the subsequent deexcitation processes (via

electron transfer or energy transfer) that leads to chemical reactions in the heterogeneous photocatalysis process. There exists a vast body of literature dealing with the electron transfer and energy transfer processes in photocatalytic reactions. A detailed description of these processes is beyond the scope of this review. Several excellent review articles and books already exist. Here, we tend to focus on interfacial processes and to summarize some of the operating principles of heterogeneous photocatalysis.

Pure water splitting request high energy and for solve this problem using system physis-chemical effects of thermachemistry cycle and nano size. Several authors have monitored H<sub>2</sub> production from various reactants over mixed phase TiO<sub>2</sub> photocatalyst.

The purpose of the presented research is the obtaining malecular hydrogen from aqueous solutions based on various mixed oxide nanoparticles by means of photolysis way and increasing the yield of hydrogen resulted in catalytic influence of nanoparticles.

## 1. EXPERIMENTAL PART

In this study has been used  $m = 0.02$  g;  $d = 20$  nm nanosized Al<sub>2</sub>O<sub>3</sub>;  $m = 0.1$  g;  $d = 20$   $\mu$ m TiO<sub>2</sub>, and distilled water. Irradiation carried out in optical quartz reactor (25 ml) intensity  $I = 1.25 \cdot 10^{15}$  kV/s,  $\Delta\tau = 0 \dots 1.0$  hour range in the low-pressure beam bulbs at room temperature. The analysis was done with a "газохром-3101" instrument. Sensitivity of instrument for hydrogen  $K = 8.6 \cdot 10^{13}$  molec./cm<sup>3</sup>·mm). Liquid phase absorption spectra of the resulting products analysis was done with UV-Visible Spectrophotometr Cary-50 (Varian) range of  $\lambda = 200 \dots 800$  nm. Quantity of H<sub>2</sub>O<sub>2</sub> has been appointed titration with KMnO<sub>4</sub>.

## 2. RESULTS AND DISCUSSION

In this study, we compare the photoproduction of hydrogen by four cases: pure water; TiO<sub>2</sub>+H<sub>2</sub>O; Al<sub>2</sub>O<sub>3</sub>+H<sub>2</sub>O; nanoAl<sub>2</sub>O<sub>3</sub> + dispers TiO<sub>2</sub> +H<sub>2</sub>O (Fig. 1). This comparison is useful to pinpoint the best among the four we have chosen.

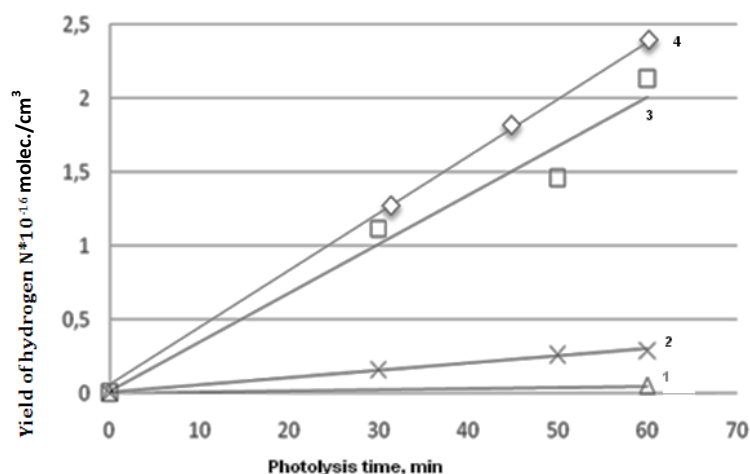


Fig. 1. Dependence of molecular hydrogen yield (1 – pure water; 2 – TiO<sub>2</sub>+H<sub>2</sub>O; 3 – Al<sub>2</sub>O<sub>3</sub>+H<sub>2</sub>O; 4 – nanoAl<sub>2</sub>O<sub>3</sub> + dispers TiO<sub>2</sub>+H<sub>2</sub>O. T = 24 °C; I = 1.25·10<sup>15</sup> kV/s) and photolysis time

As shown in Fig. 1 in all cases the kinetic areas is linear, consequently the hydrogen generation rate being stable, for pure water + nanoAl<sub>2</sub>O<sub>3</sub> + dispers TiO<sub>2</sub> system  $W(H_2) = 0.98 \cdot 10^{14}$ , for nanoAl<sub>2</sub>O<sub>3</sub> + water system  $W(H_2) = 0.306 \cdot 10^{14}$ , TiO<sub>2</sub> + water system  $W(H_2) = 0.04 \cdot 10^{14}$  and pure water  $W(H_2) = 0.00789 \cdot 10^{14}$  molec./s. The photocatalytic yield equal to  $\phi(H_2) = 0.78$ ;  $\phi(H_2) = 0.024$ ;  $\phi(H_2) = 0.0032$ , and  $\phi(H_2) = 0.0005$  molec./kV accordingly.

On base of these data we can say that with addition nanocatalyst to the systems the reaction rate increase several times, so with nanoAl<sub>2</sub>O<sub>3</sub> its accelerates 10, TiO<sub>2</sub> 2.5 and nanoAl<sub>2</sub>O<sub>3</sub> + TiO<sub>2</sub> 12 times, this case proves synergistic effect. The highest activity observed was for the photocatalyst with nanoAl<sub>2</sub>O<sub>3</sub> + TiO<sub>2</sub>, which yielded

a H<sub>2</sub> rate around twelve times greater than that observed for pure water alone. The photolyses of water in contact with oxides surfaces is of significant practical importance but is much more complex. Higher H<sub>2</sub> yields (as compared to bulk water) can be measured, demonstrating that a very efficient energy transfer can take place at the interface. Many parameters control this energy transfer, for instance the oxide band gap, the water adsorption form, and the energy migration distance. Nevertheless, the understanding of the phenomena happening during water photolysis in heterogeneous media is not complete, and theoretical framework has to be more firmly established.

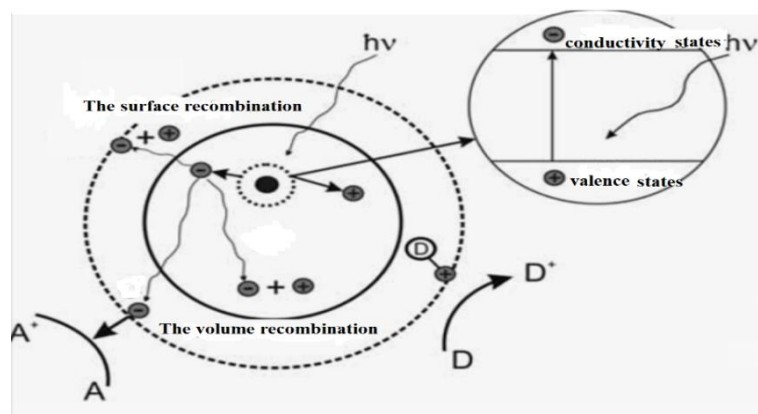


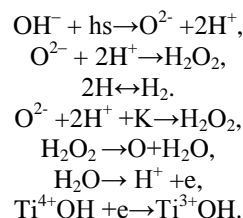
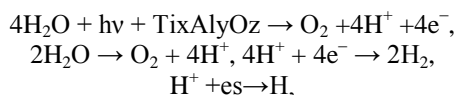
Fig. 2. Absorbing energy transmission to system on the catalyst surface [9]

The enlarged section of Fig. 2 shows the excitation of an electron from the valence band to the conduction band initiated by light absorption with energy equal to or greater than the band gap of the semiconductor [9]. Upon excitation, the fate of the separated electron and hole can follow several pathways. Fig. 2 illustrates some of the deexcitation pathways for the electrons and holes. The photoinduced electron transfer to adsorbed inorganic species or to the solvent results from migration of electrons and holes to the surface. The electron transfer process is more efficient if the species

are preadsorbed on the surface. While at the surface can donate electrons to reduce an electron acceptor (usually oxygen in an aerated solution); in turn, a hole can migrate to the surface where an electron from a donor species can combine with the surface hole oxidizing the donor species (pathway D). The probability and rate of the charge transfer processes for electrons and holes depends upon the respective positions of the band edges for the conduction and valence bands and the redox potential levels of the adsorbate species. In competition with charge transfer to adsorbed species is electron and

hole recombination. Recombination of the separated electron and hole can occur in the volume of the semiconductor particle or on the surface (pathway A) with the release of heat.

Below are the proposed chemical equations for hydrogen evolution. Following electron-hole formation under UV light, electrons are trapped at  $Ti_xAl_yO_z$ . The corresponding surface trapped holes would interact with another water.



Many parameters have been found to affect the hydrogen yield at the oxide/water interface, such as pH environment (Fig. 3).

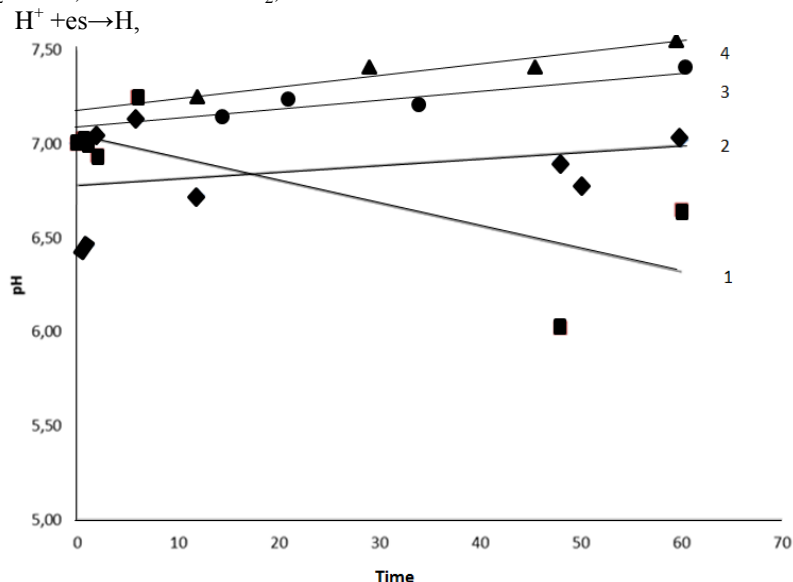


Fig. 3. The kinetic dependence (1 – water; 2 – nano $Al_2O_3 + H_2O$ ; 3 – dispers  $TiO_2 + H_2O$ ; 4 – nano $Al_2O_3 + dispers TiO_2 + H_2O$ ) of pH environment and photoreaction time

Mixed oxides participate increase molecular hydrogen yield of the systems. Correcting for apparent pH deviations, solutions of pure  $H_2O_2$  and water exhibit the pH which varies with concentration of  $H_2O_2$  as follows (Table).

$H_2O_2$  solutions are generally more stable at low pH. Consequently, the yield of molecular hydrogen increases at high pH.

Concentration of $H_2O_2$ , %	0	10	20	30	40	50	60	70	80	90	100
pH at 25 °C	7.0	5.3	4.9	4.7	4.6	4.5	4.5	4.5	4.6	4.9	6.2

### 3. CONCLUSIONS

- Due to synergistic effect of mixed oxides the hydrogen quantum yield increases from  $\phi = 0.0005$  up  $\phi = 0.78$  molec./kV.

- The amount of  $H_2O_2$  grows with addition mixed metal oxides during photoreaction.

- The molecular hydrogen yield increases at high pH.

In conclusion, the chemistry induced by photocatalyses at the oxide/adsorbate interface has many practical applications (transformation or transformation of pollutants for example). Therefore, there is need to fundamental understand the photocatalytic processes occurring on mixed complex  $Ti_xAl_yO_z$  oxide surfaces.

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*Статья поступила в редакцию 11.05.2017*

## **РОЛЬ СИНЕРГЕТИЧЕСКОГО ЭФФЕКТА СМЕСИ МЕТАЛЛООКСИДОВ В ПОЛУЧЕНИИ МОЛЕКУЛЯРНОГО ВОДОРОДА ПУТЕМ ФОТОКАТАЛИТИЧЕСКОГО РАЗЛОЖЕНИЯ ВОДЫ**

*Х.М. Махмудов, М.К. Исмаилова, Н.А. Джафарова, К.В. Азизова*

Исследовано получение молекулярного водорода методом фотокаталитического процесса. Для увеличения выхода молекулярного водорода фотокаталитическим методом использованы смесь оксидов наноAl<sub>2</sub>O<sub>3</sub> и дисперсного TiO<sub>2</sub>. В результате исследования процесса получения молекулярного водорода из совместных смесей оксидов двух металлов был выявлен синергетический эффект в гетерогенной системе. Методом фотолиза исследовано образование молекулярного водорода под действием фотохимических процессов на гетерогенную систему: вода, наноAl<sub>2</sub>O<sub>3</sub> и дисперсный TiO<sub>2</sub>. Также изучено влияние показателя действия pH среды на скорость образования пероксида водорода. Определено эффективное распределение энергии, поглощенной поверхностью катализатора, по всей системе.

## **РОЛЬ СИНЕРГЕТИЧНОГО ЕФЕКТУ СУМІШІ МЕТАЛООКСИДІВ В ОДЕРЖАННІ МОЛЕКУЛЯРНОГО ВОДНЮ ШЛЯХОМ ФОТОКАТАЛІТИЧНОГО РОЗКЛАДАННЯ ВОДИ**

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Досліджено отримання молекулярного водню методом фотокаталітичного процесу. Для збільшення виходу молекулярного водню фотокаталітичним методом використано суміш оксидів наноAl<sub>2</sub>O<sub>3</sub> і дисперсного TiO<sub>2</sub>. В результаті дослідження процесу отримання молекулярного водню зі спільних сумішей оксидів двох металів було виявлено синергетичний ефект у гетерогенній системі. Методом фотолізу досліджено утворення молекулярного водню дією фотохімічних процесів на гетерогенну систему: вода, наноAl<sub>2</sub>O<sub>3</sub> і дисперсний TiO<sub>2</sub>. Також вивчено вплив показників дії pH середовища на швидкість утворення пероксиду водню. Визначено ефективний розподіл енергії, поглиненої поверхнею катализатора, по всій системі.