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ROLE OF SYNERGISM EFFECT IN MOLECULAR HYDROGEN FORMATION FROM PHOTOCATALITIC WATER SPLITTING

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Abstract: The paper deals with hydrogen production from using photocatalysis. In particular, we focus on the role of synergism on the reaction rate. Among the most studied examples for this phenomenon are catalysts based on TiO_2. For hydrogen production the photocatalyst is composed of nano-size metal oxides such as Al_2O_3. Yet, the presence of the two metal oxides together results in considerable enhancement of the reaction rate when compared to per oxide alone. 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. In this work, we review the few proposed models, so far, explaining the way by which this charge transfer occurs across both phases. It was investigated the mechanism of water splitting in presence of mixed nanocatalysed.

Keywords: TiO_2, nano Al_2O_3, synergistic effect, water splitting, photocatalys

1. Introduction

TiO_2 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_2 in relation to a large selection of redox potentials, TiO_2 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_2O, O_2 and CO over the single crystal rutile TiO_2 surface has been studied. Most of these results have been discussed in recent reviews [3–7]. Other recent reviews on photoreaction of powder systems are available and these include those of references [8, 9]. In 1972, Fujishima and Honda discovered the photocatalytic splitting of water on TiO_2 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_2 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 [10, 11]. Several authors have monitored H_2 production from various reactants over mixed phase TiO_2 photocatalyst.

The purpose of the 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.

2. Experimental part

In this study using m=0.02 g, d=20 nm sizes Al_2O_3, 0.1 g, d=20 mkm TiO_2 and distilled water. Equations radiation in optical quartz reactor (25 ml) intensity $I = 1.25*10^{15}$ kv/sec , $\Delta\tau=0\div1{,}0$ hour range in the low-pressure beam bulbs and various temprature. The analysis was done with a “Газохром-3101” instrument. Sensitivity of instrument for H_2 $K=8.6*10^{13}$ molec./(sm3*mm). Liquid phase absorption spectra of the resulting products analysis was done with UV-Visible Spectrophotometr Cary-50 (Varian) range of $\lambda=200\div800$nm. Quantity of H_2O_2 has been appointed titration with $KMnO_4$.

3. Results and discussion

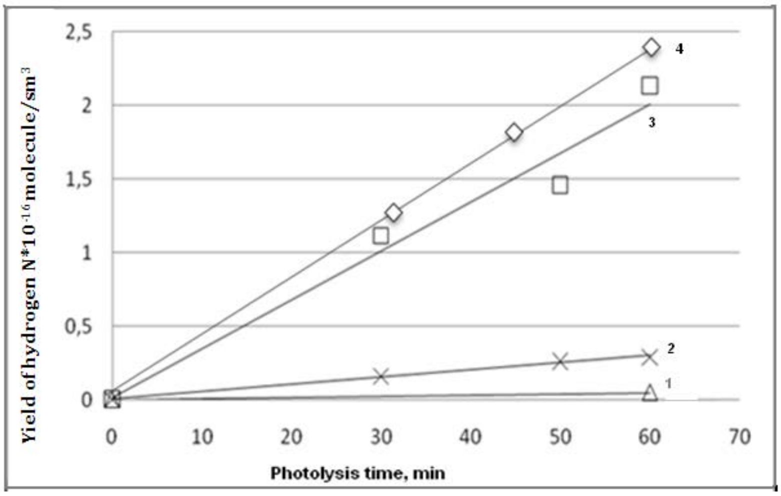

Fig. 1. Dependence of molecular hydrogen yield (1- pure water, 2-TiO_2+H_2O, 3-Al_2O_3+H_2O, 4-nano Al_2O_3 + dispers TiO_2 +H_2O T=24^{o}C, $\dot{I}=1.25*10^{15}$ kv./sec.) and photolysis time

As shown in Fig. 1. in all three cases the kinetic areas is linear, consequently the hydrogen generation rate being stable, for pure water + nano Al_2O_3 + dispers TiO_2 system $W(H_2)=0.98*10^{14}$, for nano Al_2O_3 + water system $W(H_2)=0.306*10^{14}$, TiO_2 + water system $W(H_2)=0.04*10^{14}$ and pure water $W(H_2)=0.00789*10^{14}$ molec./sec. The photocatalitic yield equal to $\varphi(H_2)=0.78$. $\varphi(H_2)=0.024$, $\varphi(H_2)=0.0032$ and $\varphi(H_2)=0.0005$ molec./kvant accordingly.

On base of these data we can say that with addition nanocatalyst to the systems the reaction rate increase several times, so with nano Al_2O_3 its accelerates 10, TiO_2 2.5 and nano Al_2O_3 + TiO_2 12 times, this case proves synergistic effect. The highest activity observed was for the photocatalyst with nano Al_2O_3 + TiO_2 ,which yielded a H_2 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_2 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.

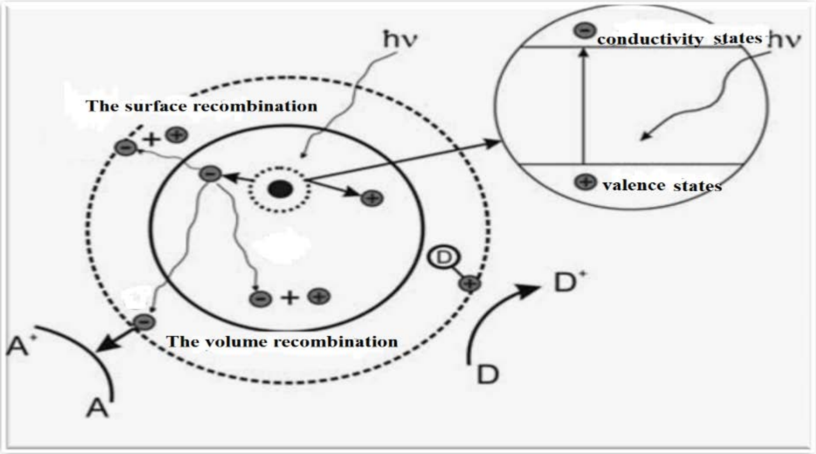

Fig. 2. Absorbing energy transmission to system on the catalyst surface

The enlarged section of Figure 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. Upon excitation, the fate of the separated electron and hole can follow several pathways. Figure 3 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) (pathway C); 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 (pathway B) 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 TixAlyOz. The corresponding surface trapped holes would interact with either water.

$$4H_2O + hv + TixAlyOz \rightarrow O_2 + 4H+ + 4e–$$
$$2H_2O \rightarrow O_2 + 4H+,\ 4H+ + 4e– \rightarrow 2H_2$$
$$H^+ + es \rightarrow H,$$
$$OH^- + hs \rightarrow O^{2-} + 2H^+,$$
$$O^{2-} + 2H^+ \rightarrow H_2O_2,$$
$$2H \leftrightarrow H_2.$$

$$O^{2-} + 2H^+ + K \rightarrow H_2O_2$$
$$H_2O_2 \rightarrow O + H_2O$$
$$H_2O \rightarrow H^+ + e$$
$$Ti^{4+}OH + e \rightarrow Ti^{3+}OH$$

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

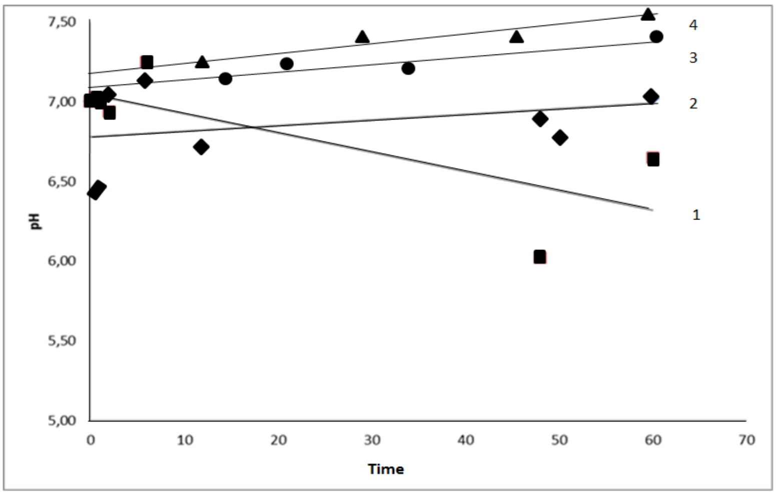

Fig. 3. The kinetic dependence (1- water; 2- nano Al_2O_3+H_2O; 3- dispers TiO_2 +H_2O; 4 - nano Al_2O_3 + dispers TiO_2 +H_2O) of media pH and photoreaction time

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

Table

% H_2O_2 Conc.	0	10	20	30	40	50	60	70	80	90	100
pH 25^0 C	7.0	5.3	4.9	4.7	4.6	4.5	4.5	4.5	4.6	4.9	6.2

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

4. Results

- Due to synergistic effect of mixed oxides the hydrogen quantum yield increases from φ=0.005 up φ=0.0244 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 occuring on mixed complex TixAlyOz oxide surfaces.

References

1. Ni, M., Leung, K.H., Leung, D., Sumathy, K.: A review and recent developments in photocatalytic water-splitting using TiO_2 for hydrogen production. Renew. Sustain. Energy Rev. 11, 401–425 (2007)
2. Linsebigler, A.L., Lu, G., Yates, J.T. Jr.: Photocatalysis on TiO_2 surfaces: principles, mechanisms, and selected results. Chem. Rev. 95, 735–758 (1995)
3. Idriss, H.: Photoreactions of organic compounds with TiO_2 single crystal surfaces. In: Anpo, M., Kamat, P. (eds) Environmentally Benign (Chapter 21), ISBN: 978-0-387-48441-9 (2010)
4. Waterhouse, G.W.N., Idriss, H.: Photoreaction of ethanol and acetic acid over model TiO_2single crystal surfaces. In: Vayssieres, L (ed) On Solar Hydrogen & Nanotechnology (Chapter 3). Wiley, New York (2009)
5. Henderson, M.A.: A surface science perspective on TiO_2 photocatalysis. Surf. Sci. Rep. 66, 185–297 (2011)
6. Yates J.T. Jr.: Photochemistry on TiO_2: mechanisms behind the surface chemistry. Surf. Sci. 603, 1605–1612 (2009)
7. Walter, M.G., Warren, E.L., McKone, J.R., Boettcher, S.W., Mi, Q., Santori, E.A., Lewis, N.S.: Solar water splitting cells. Chem. Rev. 110, 6446–6473 (2010)
8. Bowker, M.: Sustainable hydrogen production by the application of ambient temperature photocatalysis. Green Chem. 13, 2235–2246 (2011)

РОЛЬ СИНЕРГЕТИЧЕСКОГО ЭФФЕКТА В ПОЛУЧЕНИИ МОЛЕКУЛЯРНОГО ВОДОРОДА ПУТЕМ ФОТОКАТАЛИТИЧЕСКОГО РАЗЛОЖЕНИЯ ВОДЫ

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Резюме: Цель исследования получение молекулярного водорода методом фотокаталитического процесса. Для увеличение выхода молекулярного водорода фотокаталитическим методом использованы смесь оксидов нано Al_2O_3 и дисперсия TiO_2. В результате исследования процесса получения молекулярного водорода из совместных смесей оксидов двух металлов был выявлен синергетический эффект в гетерогенной системе. Методом фотолиза было исследовано образование молекулярного водорода действием фотохимических процессов на гетерогенную систему вода, нано Al_2O_3 и дисперсный TiO_2. Также было изучено влияние показания действия pH среды на скорость образования пероксида водорода. Определено эффективное распределение энергии, поглощенной поверхностью катализатора, по всей системе.

Ключевые слова: дисперсия TiO_2, нано Al_2O_3, синергетический эффект, разложение воды, фотокатализ.

SUYUN FOTOKATALİTİK PARÇALANMASINDAN MOLEKULYAR HİDROGENİN YARANMASINDA SİNERGETİK EFFEKTİN ROLU

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Xülasə: Tədqiqat işinin əsas məqsədi fotokataliz prosesi nəticəsində molekulyar hidrogenin alınmasıdır. Fotokataliz prosesində hidrogenin çıxımının artırılması üçün nano ölçülü metal oksid Al_2O_3 və dispers TiO_2 qarışığından istifadə olunmuşdur. Tədqiqatlar nəticəsində iki metal oksidinin birgə iştirakı ilə molekulyar hidrogenin alınması prosesində sinergetik effekt aşkar edilmişdir. Fotokimyəvi təsirlə su, nano Al_2O_3 və dispers TiO_2 heterogen sisteminin fotolizindən molekulyar hidrogenin yaranmasının kinetikası tədqiq edilmişdir. Həmçinin hidrogen peroksidin yaranma surətinə mühitin pH göstəricisinin təsiri öyrənilmişdir . Katalizator səthidə udulan enerjinin sistemə səmərəli ötürülməsi araşdırılmışdır. Məqalədə qarışıq metal oksid katalizatorlarının iştirakı ilə suyun parçalanma mexanizmi göstərilmişdir.

Açar sözlər :Dispers TiO_2, nano Al_2O_3, molekulyar hidrogen, sinergetik effekt, suyun parçalanması, fotokataliz