

UDC: 621.039.553

APPLICATION OF ZERO-VALENT IRON NANOPARTICLES FOR THE HYDROGEN PRODUCTION FROM USING PHOTOLYSIS

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Abstract: This study reports the hydrogen production from using photocatalyst. In particular we focus on the role of synergism on the reaction rate. The results reveal that the presence of nano Fe in bentonite–water systems exhibit higher photoactivity than pure one for the photolysis. As bentonite was used Dash-Salakhli bentonite clay. For hydrogen production the photocatalyst is composed of nano-size metal such as Fe. The presence of the montmorillonite and nanometal particles together results in considerable enhancement of the reaction rate when compared to per one alone. In this work the influence of Fe nanoparticles in the bentonite–water systems on the photocatalytic activities was investigated. Experimental results of FT-IR spectroscopy and SEM images show that the increase in activity is related to change in the lattice parameters and surface events.

Keywords: Iron nanoparticles, bentonite, water splitting, synergistic effect, molecular hydrogen

1. Introduction

Bentonite–water systems are of great importance for agricultural, industrial, environmental and civil engineering activities such as desiccant preparation, sea lant, ceramic, cat box adsorbent, iron ore pellet, molding sand for foundry, drilling mud and arrieres for water and protection from nuclear waste [1]. Bentonite (Dash-Salakhli bentonite) also was used for enhanced oil recovery – about 10 % increased oil production [2].

Dash-Salakhli bentonite deposit is located in Azerbaijan Republic, Dash-Salakhli village of Gazakh city. The deposit is represented by montmorillonite $((Na,Ca)_{0,33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O)$ and hydromica- montmorillonite clay [3]. Bentonite clays mined from Dash-Salakhli deposit contain more than 85% of montmorillonite, where Na and Mg cations prevail in CEC (Consumer Electronics Control) [3]. Exchange cations content makes 92-98 mg/100g. Chemical composition of bentonite clays mined from this deposit has the following characteristics.

Table

Chemical compound	%	Chemical compound	%
SiO ₂	58.60	MgO	2.30
Al ₂ O ₃	13.40	P ₂ O ₅	0.11
Fe ₂ O ₃	4.70	SO ₃	0.25
FeO	0.18	K ₂ O	0.39
TiO ₂	0.39	Na ₂ O	2.30
CaO	2.05	PPP	15.33
Total			100

1. Experimental part

The investigated was carried out in two stages:

a) Preparation of the bentonite/ Fe nanoparticles +water system.

Aqueous solution of bentonite (1-3 wt.%) prepared and added Fe nanoparticles (0.001-0.01 wt.%). As bentonite was taken Dash-Salakhli bentonite clay.

b) Nanosystems” photolysis.

Equations radiation in optical quartz reactor (25 ml) intensity $I = 1.25 \cdot 10^{15}$ kv/sec, $\Delta\tau=0\div 1,0$ hour range in the low-pressure beam bulbs at room temperature. After UV light influence was studied the rate of formation molecular hydrogen of the samples. The hydrogen generation rate for pure water $W(H_2)= 0.00789 \cdot 10^{14}$, bentonite+ water $W(H_2)=0.31 \cdot 10^{14}$, water+ nano Fe $W(H_2)=0.4 \cdot 10^{14}$, bentonite+nano Fe +water - $W(H_2)=0.51 \cdot 10^{14}$ molec./sec. Effect of Fe nanoparticles on aqueous solution of bentonite has been studied by SEM (Fig. 1) and FT-IR spectroscopy method (Fig.2-3) and studied its influence on hydrogen formation rate under UV light. Experiments confirm the synergistic effect in water splitting of photocatalytic reaction.

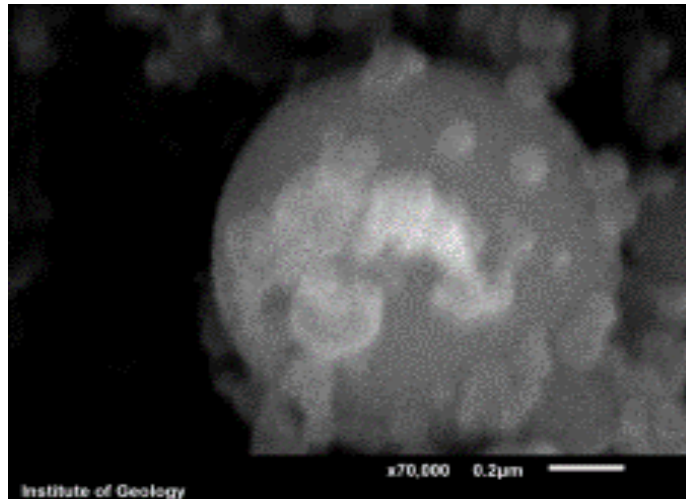


Fig. 1. SEM images of the bentonite/iron nanoparticles

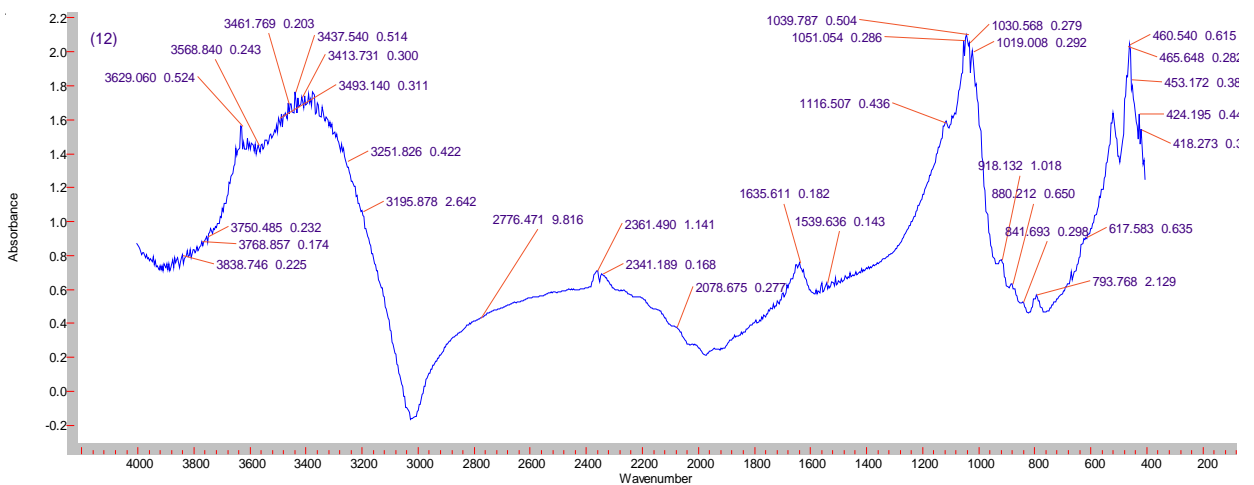


Fig 2. IR spectroscopy of the bentonite

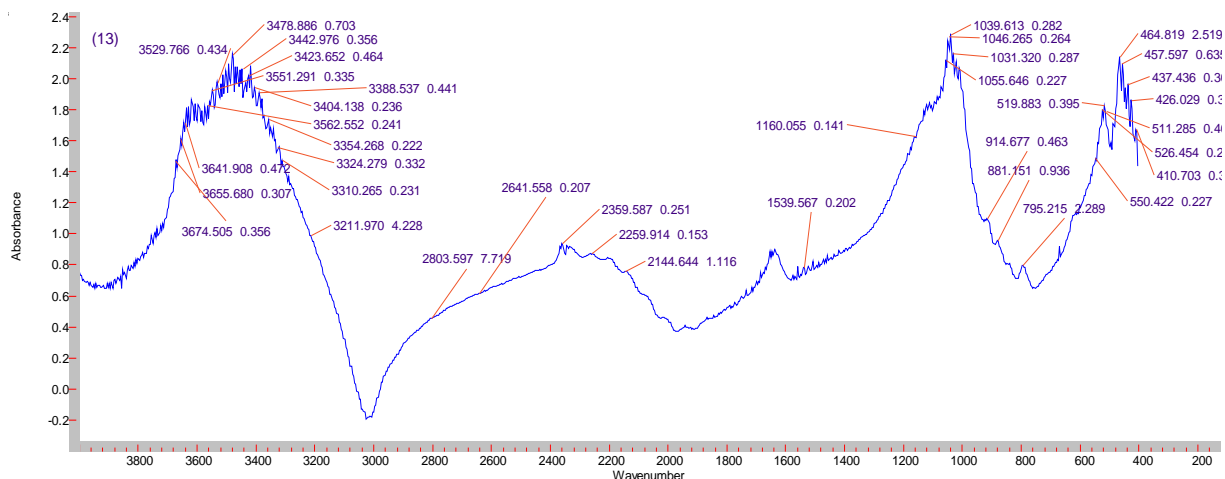


Fig 3. IR spectroscopy of the bentonite+ nano Fe

Several authors investigated synergistic effect in heterogeneous photocatalyst with nanoparticles [4]. Traditional water-splitting photocatalysts are based on transition metal oxides which form stable compounds due to the high electronegativity of oxygen atoms [5]. [6] have reported enhancement in photocatalytic water splitting activity of Fe-doped TiO₂, where Fe²⁺/Fe³⁺ acts as electron-trap centers and Fe³⁺/Fe⁴⁺ acts as hole-trap centers. It has been found that the existence of a mesoporous structure favors the rapid diffusion of products and suppresses the electron/hole recombination. Also, the morphology of the photocatalyst has a major effect on the photocatalytic activity. The close contact between (Na,Ca)_{0,33}(Al,Mg)₂(Si₄O₁₀)(OH)₂·nH₂O and Fe facilitated the generation of surface plasmon resonance induced electrons (Fig.4). By engineering the structure, the performance of hydrogen evolution under visible light irradiation could be improved.

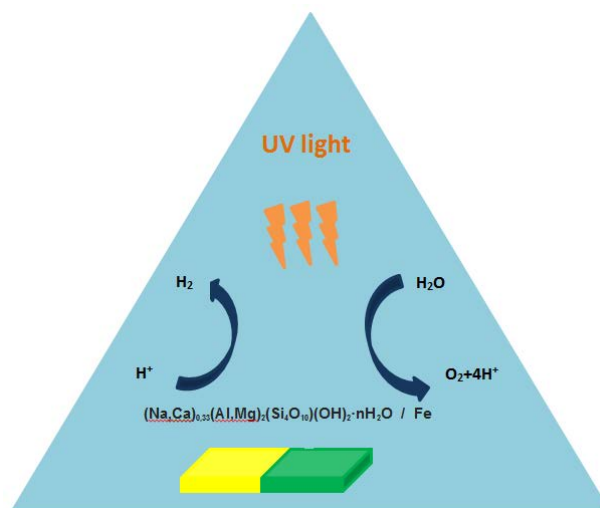


Figure 4. Schematic representation of photochemical water splitting.

Result:

Nanoparticles and montmorillonite coexist at the surface improves charge separation, reduces recombination and subsequently increases photocatalytic activity under UV light.

Acknowledgements

This work was financed by Azerbaijan National Academy of Science. The authors thank the Institute of Geology at Azerbaijan National Academy of Science for the assistance in the SEM measurements.

References

1. Zahra Darvishi, Ali Morsali.: Synthesis and characterization of Nano-bentonite by sonochemical method. Ultrasonics Sonochemistry 18 (2011) 238–242
2. Shahbazov E.Q., Hagiyeve H.Q. Ismayilova M.K. Azerbaijan Patent № I 2016 0001. 13.01.2016. Composition for the displacing the residual oil from the layer.
3. <http://www.azrpi.com/>
4. K. Connely, A.K. Wahab, Hicham Idriss.: Photoreaction of Au/TiO₂ for hydrogen production from renewables : a review on the synergistic effect between anatase and rutile phases of TiO₂. Mater Renew Sustain Energy (2012) 1- 3.
5. Sivula, K.; van de Krol, R. Semiconducting materials for photoelectrochemical energy conversion. Nat. Rev. Mater. 2016, 70, 15010:1–15010:7
6. Piskunov, S.; Lisovski, O.; Begens, J.; Bocharov, D.; Zhukovskii, Y.F.; Wessel, M.; Spohr, E. C-, N-, S-, and Fe-Doped TiO₂ and SrTiO₃ Nanotubes for Visible-Light-Driven Photocatalytic Water Splitting: Prediction from First Principles. J. Phys. Chem. C 2015, 119, 18686–18696

ПРИМЕНЕНИЕ НУЛЬ-ВАЛЕНТНЫХ НАНОЧАСТИЦ ЖЕЛЕЗА ДЛЯ ПРОИЗВОДСТВА ВОДОРОДА С ПОМОЩЬЮ ФОТОЛИЗА

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Резюме: Основная задача исследования получение водорода с помощью фотокатализатора. Особенно был изучен эффект синергизма в процессе фотокатализа. В исследовании были использованы бентонитовая глина с Даш-Салахлы и Fe наноразмера. Присутствие монтморилланита и наноструктурного металла вместе приводит к значительному повышению скорости реакции, чем при использовании каждого по-отдельности. В этой работе было исследовано влияние наночастиц Fe в бентонит-водных системах на фотокаталитические действия. Результаты эксперимента ПФ-ИК спектроскопии и РЭМ показывают, что увеличение активности связано с изменением параметров решетки и поверхностных событий.

Ключевые слова: наночастицы железа, бентонит, расщепление воды, синергетический эффект, молекулярный водород.

Fe NANOH SSƏC KLƏR N N TƏTB Q LƏ FOTOL Z ƏSASINDA H DROGEN N ALINMASI

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Xülasə: Tədqiqatın əsas məqsədi fotokataliz prosesindən istifadə etməklə hidrogenin alınmasıdır. Xüsusilə fotokataliz prosesində sinerqizm effektinin rolu öyrənilmişdir. Tədqiqat işində Daş-Salahlı bentonitindən və nano-ölçülü Fe-dan istifadə edilmişdir. Montmorillanit və nanostrukturulu metalın birgə iştirakı ilə reaksiyanın sürəti artdığına görə hidrogenin çıxımı hər birinin ayrı-ayrılıqda istifadəsinə nisbətən daha

yüksək olur. Məqalədə bentonit-su sisteminin fotokatalizində Fe nanohissəciklərin rolu araşdırılmışdır. FT-İR spektral analizinin nəticələri və SEM görüntüləri göstərir ki, aktivliyin artmasına səbəb kristal qəfəs parametrlərindəki dəyişiklik və səth hadisələridir.

Açar sözlər: dəmir nanohissəcikləri, bentonit, suyun parçalanması, sinergistik effekt, molekulyar hidrogen