Study of Catalysts for Water Photosonolysis to Increase the Hydrogen Production

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Abstract

This paper deals with an experimental investigation on water catalyzed photosonolysis for hydrogen production. This study was focused to identify the optima catalysts for photosonolysis at 1.0 pressure conditions. The identified catalysts are solid solutions of oxides based on Lanthanum, Indium and Gallium. They need a sacrificial agent to make the water sample able to absorb the sunlight visible components: it was requested that the sacrificial agent is a more oxidable substance with respect to the water oxygen. Thus, ethanol was chosen as sacrificial agent. Water splitting is obtained by the superposition of photolysis and sonolysis phenomena (photosonolysis) which are induced by the combined action of sunlight, catalysts and ultrasounds. An experimental device was built to investigate such phenomena; experimental tests were carried out for different concentrations and molar compositions of the identified oxides. Results show that hydrogen production obtained by the superposition of photolysis and sonolysis is higher than the algebraic sum of hydrogen produced singularly by sonolysis and photolysis. Thus, a synergy between sonolysis and photolysis is shown: the two phenomena help each other for hydrogen production. At last, results allowed to determinate the optimum catalyst and its solution concentration for hydrogen production.

Keywords: *hydrogen production, photolysis, sonolysis, catalysts*

1 Introduction

The utilization of solar energy for the production of hydrogen from water splitting has had a great attention because of the global problems in energy and environment [1-2].

Theoretically it is possible to produce hydrogen and oxygen from water by the direct reaction:

$$H_2O \rightarrow H_2 + \frac{1}{2} O_2 \qquad (1)$$

Light is composed of elementary particles called photons; each photon energy is related to the frequency by Planck's equation:

$$E = h\nu \qquad (2)$$

where E is the photon energy, $h = 6.626 \times 10^{-34}$ J·s is Planck's constant and ν is the frequency.

The O-H bond energy is 460 kJ/mol. Thus, the lowest wavelength suitable to split a water molecule into oxygen and hydrogen is 261 nanometers [3]; such wavelength is in the ultraviolet (UV) range. UV power is much lower than visible and infrared one in the solar spectrum; besides, ozone layer acts as a barrier for UV radiation. Thus, the available solar radiation for hydrogen production is very low on earth.

Similarly, it is possible to estimate the energy of visible region photons at the maximum emission of the sun that occurs for $\lambda = 550$ nm. $E = h\nu_{maxVIS} = 218$ kJ/mol. Besides, the theoretically available energy that occurs at the maxima solar emission is lower than O-H bond energy.

It's clear that hydrogen from water splitting cannot be obtained directly only with solar light but an auxiliary energy source is necessary.

This paper deals with the catalysed photosonolysis, a new method enhancing the efficiency of hydrogen production from water: liquid water is decomposed into hydrogen and oxygen stoichiometrically and continuously by a multiple effect of sonolysis and photocatalysis.

Recent studies show that ultrasound vibrations change the absorption properties of water [4]

The aim of the study is to investigate different photocatalyst oxides based on Lanthanum, Indium and Gallium to identify the optimum catalyst for photosonolysis.

The separated effect of sonolysis and photocatalysis was investigated to establish the optimal conditions of each process. Then, the checked conditions were applied to photosonolysis process.

2 Photosonolysis process

Photosonolysis process involves the simultaneous action of ultrasounds (sonolysis) and solar irradiation in presence of a photocatalyst (photocatalysis). In the following, the two processes are analyzed separately.

Sonolysis

Water sonochemical reactions steps are the followings:

$H_2O \rightarrow H\bullet + OH\bullet$ (3)

$H\bullet + H\bullet \rightarrow H_2$ (4)

$OH\bullet + OH\bullet \rightarrow H_2O_2$ (5)

$H_2O_2 \rightarrow H_2O + ½\, O_2$ (6)

$H\bullet + OH\bullet \rightarrow H_2O$ (7)

Sonolysis is produced by ultrasounds transmission in the water [5].

Ultrasounds are characterized by compression and expansion waves; they induce the acoustic cavitation phenomenon which gives the energy required for reaction (3).

Hydrogen and hydrogen peroxide are produced by the dimerization of their radicals (equations (4) and (5)). Hydrogen peroxide is unstable in standard conditions; thus, it splits into water and oxygen (equations (6) and (7)).

It's clear that the amplitude of pressure fluctuations of the sound wave decreases with the decreasing of the ultrasounds frequency. Thus, also the ability of the cavitation effect to break the water molecules decrease.

In aqueous solutions, sound absorption is strongly dependent by viscosity.

According to the Stokes formula with a correction on volume viscosity [6], the growing absorption of sound is the evidence of increasing structural viscosity:

$\alpha = \omega^2 (4\eta_s/3 + \eta_v)/2\rho c^3$ (8)

where η_s is shear viscosity, η_V is volume viscosity, $\omega = 2\pi f$, ρ is water density.

α represents the energy absorbed by water as heat. This energy is not useful to water splitting process.

Photocatalysis

The steps of water photocatalytic reactions are the followings:

$H_2O \rightarrow ½\, O_2 + 2H^+ + 2e^-$ (9)

$2H^+ + 2e^- \rightarrow H_2$ (10)

The energetic analysis of the process, taking into account the thermodynamic losses, defines the visible region of the spectrum as the inferior limit of the energy necessary for the water splitting reaction to proceed. [7].

Nevertheless water absorbs only in the IR region (for $\lambda < 200$ nm) where photonic energy is not sufficient for the photochemical process.

For enhancing the efficiency of solar water splitting the employment of photocatalysts is necessary; they can absorb the solar radiation and induce the oxidoreduction process.

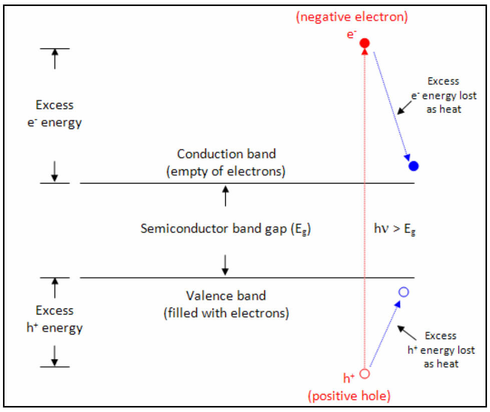

Fig. 1. Scheme of the photocatalytic process

The photocatalytic process involves three phases (Figure 1):

1) Absorption of the radiation and formation of the electron hole pair.
2) Migration of the charge carriers toward the surface of the semiconductor.
3) Transfer of the charge carriers to the species in solution and realization of the oxidoreduction process.

Semiconductors are ideal photocatalysts: they are photoactive and chemically and thermally stable.

The absorption of the photocatalysts depends on the energetic difference between the valence and the conduction band. They absorb photons having energy equal to greater than band gap (fig. 1).

Semiconductors, unlike metals, do not have a continuum of energetic states that promotes a recombination of the charges: this fact ensures a sufficient life time of the electron-hole pair and guarantees the electronic transfer at the solid-liquid interface.

For a solution with catalyst dispersed particles, the size of the particles influences considerably the photocatalytic process. The band gap increases with decreasing size, the charge separation is better but the absorption process is worse.

On the other hand, a little size guarantees a bigger surface area useful to the electrons transfer and reduces the charges path toward the surface of the catalyst speeding up their migration and reducing the possibility of recombination.

The oxidoreductive process can proceed only in thermodinamic favorable conditions.

The oxygen oxidation due to the electron transfer to the semiconductor is possible only if the valence band potential is higher than the oxidation potential of water: $E(VB) > E(O_2/H_2O)$

Simultaneously the reduction of the H^+ ions through the transfer of the electron on the catalyst surface is possible only if the conduction band potential is lower than the reduction potential of water: $E(CB)<E(H_2O/H_2)$.

In this paper, solid solutions of semiconductors have been selected as photocatalysts.

This choice is particularly advantageous: selecting opportunely the semiconductors and their stoichiometric ratios allows a wide band gap amplitude control.

A method to reduce the band gap amplitude and increase the absorption of a semiconductor is the doping.

Doping generates local energetic levels between the valence and the conduction band; thus, the band gap amplitude of the semiconductor decreases.

Employing semiconductors with a limited band gap, the introduction of a sacrificial agent is necessary. The sacrificial agent should be chosen among the chemical compounds more easily oxidizable than oxygen.

3 Experimental tests

Experimental apparatus

The experimental facility is made by a cylindrical reactor (where the water sample is inserted for the tests), the ultrasound generation system and a tool for the light irradiation (fig 2).

Ultrasound generation system, on the reactor bottom side, is constituted by a piezoelectrical transducer that produces the cavitation phenomenon in water; the transducer is characterized by a 38 kHz frequency and a 50 W power.

Light irradiation system, on the reactor upper side, is constituted by a xenon lamp whose spectrum is very close to the sunlight one; the lamp is able to produce a 500 W/m^2 radiation on the reactor upper side at a 0,05 m distance.

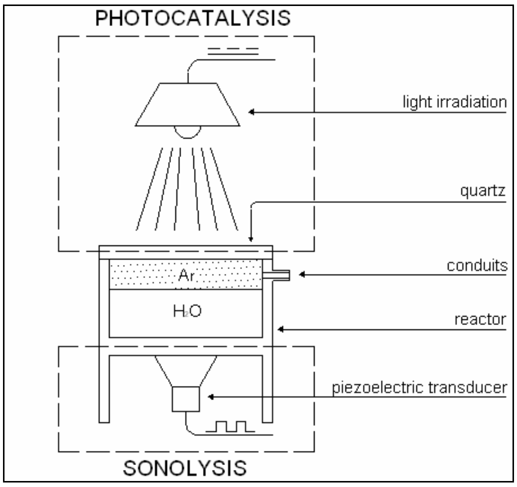

Fig. 2. Scheme of the experimental apparatus.

The reactor frame (fig. 3) is realized in AISI 304 stainless steel; the upper side is closed by a high pure quartz glass plate. This material has a high optical transmittance (over 60-70%) for a wavelength range much larger than the normal glass one.

Fig. 3. Reactor.

The quartz glass and the piezoelectric transducer plate are fixed to the reactor by means of flanged connections. Gas and water tights are guaranteed by means of two Viton O-Rings in each connection.

The reactor is surrounded by a cooling system that removes the heat generated by the lamp and the piezoelectric system.

The chamber cooling wall is needed to keep a constant thermodynamic state of the fluids inside the reactor and to evaluate the temperature influence on the reaction of photosonolysis.

The reactor is characterized by three cylindrical pipes: a first pipe is dedicated to the inlet of the water sample; a second pipe is connected to a porous septum and allows the extraction of the produced gas using a gas-tight syringe; the last tube connects the upper side of the reactor with a vacuum pump and a gas line of inert gas (argon) that allows the inertization of the reactor.

The temperature and the pressure in the reactor are respectively measured with thermocouples and a manometer.

Photocatalysts

The individuated photocatalysts are solid solutions of oxides based on Lanthanum, Indium and Gallium: $LaGa_{0,5}In_{0,5}O_3$ and $La_{0,8}Ga_{0,2}InO_3$, and successively sulphur doped $La_{0,8}Ga_{0,2}InO_3$.

These catalysts have been selected for the following reasons: Gallium oxide is characterized by a conduction band potential sufficiently negative to guarantee the evolution of hydrogen, indium oxide has a very limited band gap and allows the control of the band gap amplitude; lanthanum oxide, however, despite having a high value of band gap, was chosen for its oxidoreductive properties and for its ionic dimensions comparable with the other two metals.

The molecular weight of the selected catalysts are reported in tab. 1

Table 1. Molecular weight of the tested catalysts

Catalyst	Molecular weight (g/mol)
$LaGa_{0,5}In_{0,5}O_3$	279,18
$La_{0,8}Ga_{0,2}InO_3$	287,89
$S:La_{0,8}Ga_{0,2}InO_3$	416,154

The first photocatalysts to be tested were $LaGa_{0,5}In_{0,5}O_3$ and $La_{0,8}Ga_{0,2}InO_3$.

Figure 4 shows the absorbance spectra of the two catalysts. The spectrum of $La_{0,8}Ga_{0,2}InO_3$ is wider and has a greater intensity in the visible region than the spectrum of $LaGa_{0,5}In_{0,5}O_3$.

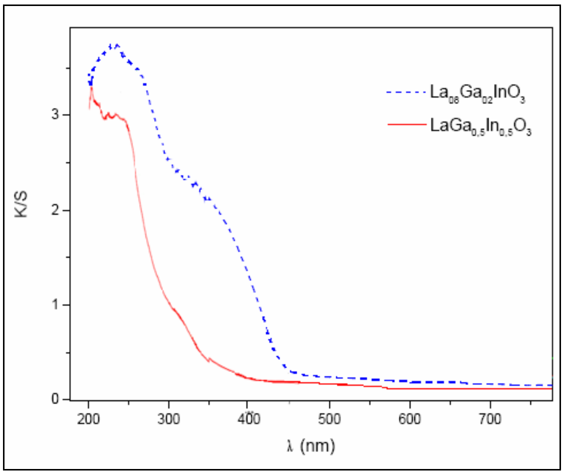

Fig. 4. Absorbance spectra of $LaGa_{0,5}In_{0,5}O_3$ and $La_{0,8}Ga_{0,2}InO_3$.

Test procedure

The same quantity of each photocatalyst (0,4 g) was suspended in two different volumes (200 and 1100 ml) of aqueous solution containing water and ethanol as sacrificial agent (ethanol/water volume ratio =1:10). Thus, also the influence of volume/irradiated surface ratio has been evaluated.

The internal pressure of the reactor is 1 bar for all tests; in fact, it was found as better value for sonophotolysis test in a previous work [8].

Hydrogen production by the separated and combined effect of sonolysis and catalyzed photolysis was investigated.

Gas sampling is made by a gastight syringe inserted into the reactor through the duct with porous septa in butilic rubber and teflon.

The sample gas composition has been determinated through a gascromatographic analysis to evaluate the hydrogen evolution from the tested aqueous solutions. The duration of the tests was 6 hours; gas sampling and analysis were made each hour.

Results of sonolysis, photolysis and photosonolysis tests with $LaGa_{0,5}In_{0,5}O_3$ and $La_{0,8}Ga_{0,2}InO_3$

Figures 5, 6 and 7 show the evolution of H_2 during the 6 hours sonolysis, photolysis and photosonolysis tests carried out with $LaGa_{0,5}In_{0,5}O_3$ and $La_{0,8}Ga_{0,2}InO_3$ in water-ethanol solutions.

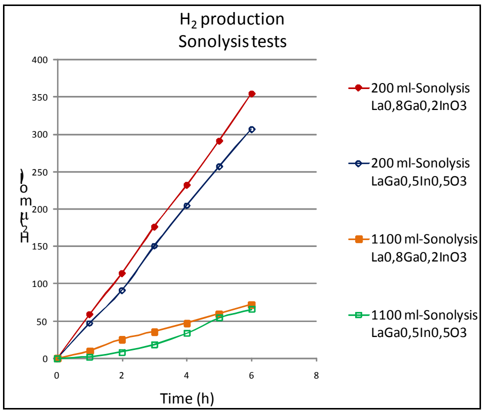

Fig. 5. Results of sonolysis tests with $LaGa_{0,5}In_{0,5}O_3$ and $La_{0,8}Ga_{0,2}InO_3$

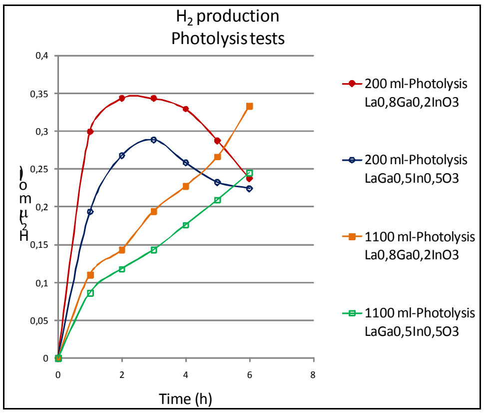

Fig. 6. Results of photolysis tests with $LaGa_{0,5}In_{0,5}O_3$ and $La_{0,8}Ga_{0,2}InO_3$

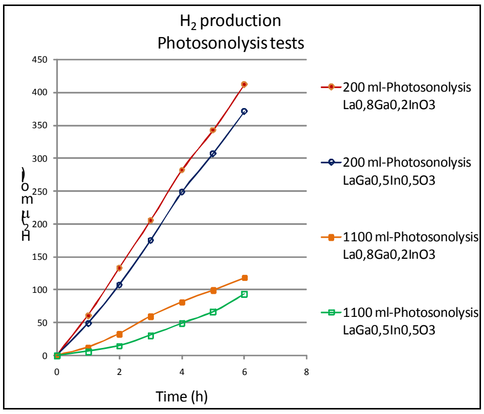

Fig. 7. Results of photosonolysis tests with $LaGa_{0,5}In_{0,5}O_3$ and $La_{0,8}Ga_{0,2}InO_3$

Sonolysis, photolysis and photosonolysis tests show that the best results are obtained with 200 ml than 1100 ml solutions. Thus, increasing the catalyst concentration improves the hydrogen production. $La_{0,8}Ga_{0,2}InO_3$ provides better results than $LaGa_{0,5}In_{0,5}O_3$ in all tests.

Photosonolysis tests show an effective synergy between the sonolytic and the photolytic effects: the combined action of the two processes shows an increase in hydrogen production, compared to the algebraic sum of the two individual effects considered separately (fig. 8, where photolysis+sonolysis is the algebraic sum of the two single contributions and photosonolysis is the result of the effective photosonolysis test)

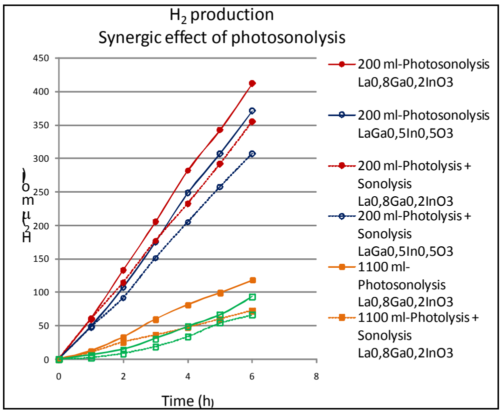

Fig. 8. Synergic effect of photosonolysis tests with $LaGa_{0,5}In_{0,5}O_3$ and $La_{0,8}Ga_{0,2}InO_3$

Since $La_{0,8}Ga_{0,2}InO_3$ provides better results than $LaGa_{0,5}In_{0,5}O_3$ in all tests, it was established to test the sulphur doped $La_{0,8}Ga_{0,2}InO_3$ ($S{:}La_{0,8}Ga_{0,2}InO_3$) to further increase the efficiency of the process in terms of hydrogen production .

Indeed the comparison between the absorbance spectra of $La_{0,8}Ga_{0,2}InO_3$ and $S{:}La_{0,8}Ga_{0,2}InO_3$, (fig.9), shows that $S{:}La_{0,8}Ga_{0,2}InO_3$ has an absorbance spectrum much wider in the visible region than $La_{0,8}Ga_{0,2}InO_3$.

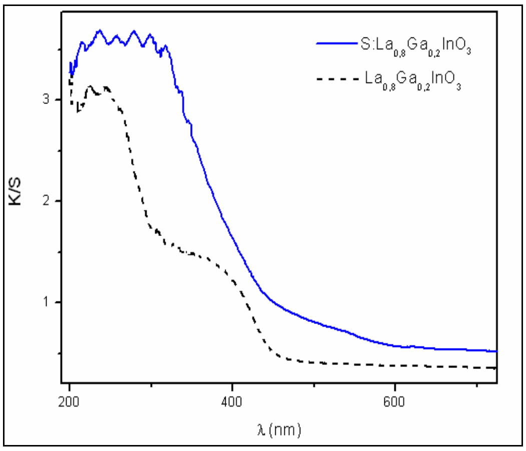

Fig. 9. Absorbance spectra of $La_{0,8}Ga_{0,2}InO_3$ and S: $La_{0,8}Ga_{0,2}InO_3$

Results of sonolysis, photolysis and photosonolysis tests with sulfur doped $La_{0,8}Ga_{0,2}InO_3$

Figures 10, 11 and 12 show the evolution of H_2 during the 6 hours sonolysis, photolysis and photosonolysis tests carried out with $S{:}La_{0,8}Ga_{0,2}InO_3$ in water-ethanol solution. The graphic trends of hydrogen evolution are compared with the result obtained with $La_{0,8}Ga_{0,2}InO_3$.

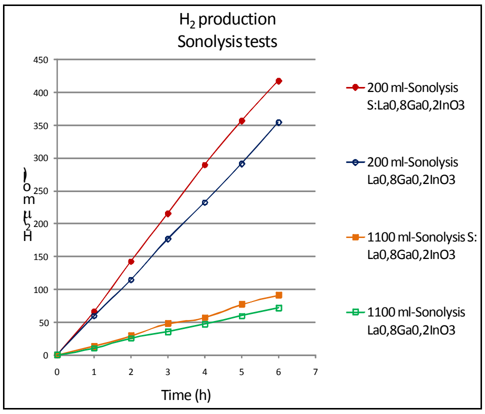

Fig. 10. Results of sonolysis tests with $S{:}La_{0,8}Ga_{0,2}InO_3$ compared with $La_{0,8}Ga_{0,2}InO_3$

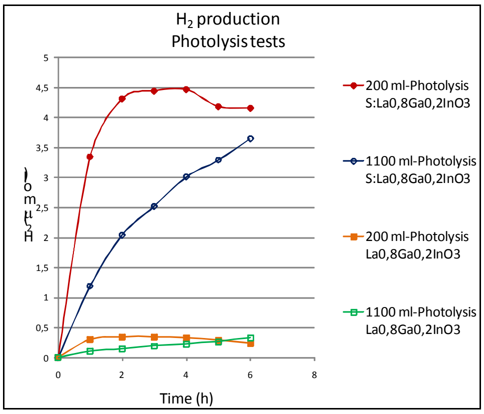

Fig. 11. Results of photolysis tests with $S{:}La_{0,8}Ga_{0,2}InO_3$ compared with $La_{0,8}Ga_{0,2}InO_3$

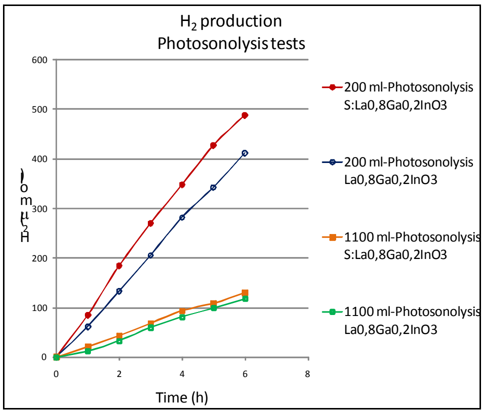

Fig. 12. Results of photosonolysis tests with $S{:}La_{0,8}Ga_{0,2}InO_3$ compared with $La_{0,8}Ga_{0,2}InO_3$

Sonolysis, photolysis and photosonolysis tests repeat that the best results are obtained with 200 ml than 1100 ml solutions. $S{:}La_{0,8}Ga_{0,2}InO_3$ provides better results than $La_{0,8}Ga_{0,2}InO_3$ in all tests.

Also the synergic effect in photosonolysis tests is confirmed (fig. 13, where photolysis+sonolysis is the algebraic sum of the two single contributions and photosonolysis is the result of the effective photosonolysis test).

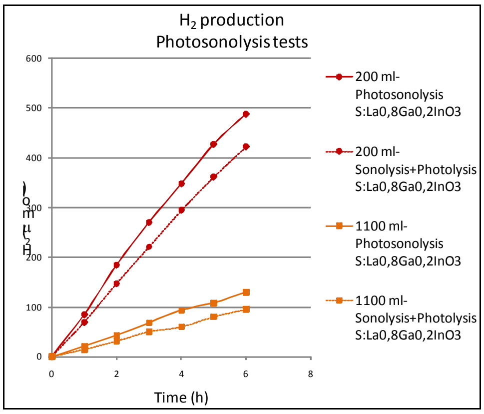

Fig. 13. Synergic effect of photosonolysis tests with S:$La_{0,8}Ga_{0,2}InO_3$

4 Conclusions

The study deals with the hydrogen production from water by the combined action of sonolysis and catalyzed photolysis.

The experimental activity was conducted to test the photosonolytic behavior of the following solid oxide solutions of Lanthanum, Indium and Gallium: $LaGa_{0,5}In_{0,5}O_3$ and $La_{0,8}Ga_{0,2}InO_3$, and successively sulphur doped $La_{0,8}Ga_{0,2}InO_3$.

Aqueous solutions containing water and ethanol as sacrificial agent (ethanol/water volume ratio =1:10) and 0,4 g of each catalyst were tested in an appropriately designed reactor.

Sonolysis, photolysis and sonophotolysis tests were carried out.

Sulphur doped $La_{0,8}Ga_{0,2}InO_3$ gave the best results in all experiments; $La_{0,8}Ga_{0,2}InO_3$ gave better results than $LaGa_{0,5}In_{0,5}O_3$.

The results in photolysis tests were predictable observing the absorption spectrum of the S:$La_{0,8}Ga_{0,2}InO_3$, that is wider in the visible region than the spectra of the other two catalysts.

In photolysis tests, the amount of the hydrogen produced in the 200 ml solutions with a higher content (mass percentage) of catalyst is greater than 1100 ml solutions containing the same catalyst.

In sonolysis tests the H_2 evolution is better in 200 ml solutions than in 1100 ml solution containing the same catalyst.

Sonolysis process depends on the part of the input energy which is spent for the activation of water; the other part is dissipated in the liquid as heat. The energy spent for the heating increases the mass of the involved solution. Also in sonolysis tests, the best results were provided by Sulphur doped $La_{0,8}Ga_{0,2}InO_3$ followed by $La_{0,8}Ga_{0,2}InO_3$ and $LaGa_{0,5}In_{0,5}O_3$. In the order they were written these catalysts give solutions with growing viscosity. In fact, viscosity, as noted in the literature, worse the production of hydrogen by sonolysis.

Photosonolysis tests gave the best results and the best catalyst is the same than the one shown by sonolysis and photolysis tests: Sulphur doped $La_{0,8}Ga_{0,2}InO_3$, followed by $La_{0,8}Ga_{0,2}InO_3$ and $LaGa_{0,5}In_{0,5}O_3$.

An important result should be stressed: photosonolysis tests showed an effective synergy between the sonolytic and the photolytic effect. In fact, the hydrogen production obtained by the superposition of photolysis and sonolysis is higher than the algebraic sum of hydrogen produced singularly by sonolysis and photolysis for all tests.

Future developments are going on: the introduction of different volume concentrations of sacrificial agents in the aqueous solutions, the use of new catalysts that can increase the efficiency of the process, the optimization of the volume/irradiated surface of water ratio, the application of piezoelectric transducers with different ultrasounds frequencies.

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