

HYDROGEN PRODUCTION IN THE COMBINED PHOTO (RADIATION)-THERMOCHEMICAL CYCLE

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1.INTRODUCTION

The stages of a photo (radiation)-thermochemical production of hydrogen in the combined cycle are investigated. In the first stage of process the reaction between $\text{Fe}^{3+}/\text{Fe}^{2+}$ and I_3^-/I^- is investigated by a photo and radiation and the efficiency of process is shown ($\eta=28\%$)

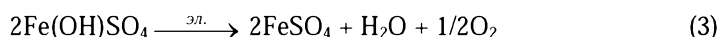
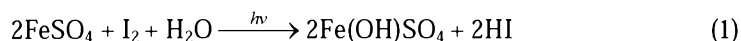
The second stage of process which is carried out conversion HI acid, is braked by return reaction. At effective division of components of reaction (the porous tube "Vigor glass") is possible substantial growth of hydrogen yield. Is investigated radiolysis the diluted water solutions HI acid.

The concept "of hydrogen power" in a most "pure" kind assumes reception of hydrogen by decomposition of water with an expense nuclear and solar energy and is called to define its real opportunities and prospects in power system of the world.

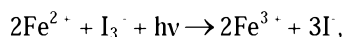
At a choice suitable thermochemical cycle it is necessary to satisfy with many criteria: efficiency of process, availability and relative cheapness reagents, and also ease of division and complete regeneration of intermediate products.

From this point of view use of a solar energy for splitting water on the basis of a combination of photochemical processes with electrolysis and thermochemical processes is a subject of wide researches in Japan, USA and Germany [1].

Photo-thermochemical production of hydrogen can be carried out in cycle of 3-steps with use of radiation in seen area of a spectrum under the following circuit:



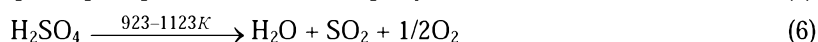
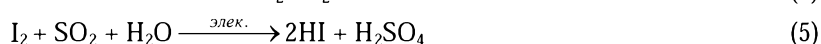
Reaction (1) known as reaction Karl-Fisher [2] proceeds at length of a wave 430-740 nm, on which it is necessary 30 % of a solar energies. The major characteristic of the first step is the oxidation-reducing reaction between $\text{Fe}^{3+}/\text{Fe}^{2+}$ and I_3^-/I^- , which can be expressed as follows [3]:



where I_3^- works in quality of photosensibilizator.

It is necessary to note, that now with development high-temperature nuclear reactors (АТЭ) interest to development of the similar combined cycles of reception of hydrogen known as Mark-11,13,16 sharply has increased.

The essence of a method consists in realization cycle of 3-steps Mark-16 under the circuit:



High-temperature stage (6) of these cycles, which is opposite to process of manufacture of a sulfuric acid, fast catalytic process, well enough mastered by a chemical industry [4].

2. PURPOSE AND TECHNIQUE OF EXPERIMENTAL WORKS

The purpose of the present work was the research photo-thermochemical reactions (1,2) for hydrogen production in the combined cycle. Reaction (1) carried out under action of ultra-violet radiation with the help of a lamp ДКсТБ2000 [5], simulating 30 % of solar radiation. The analysis on formation of HI acid carried out titrymeter [6]. Method allows to define 0,1mg [I] more in 20ml of a solution with satisfactory accuracy. For realization of reaction (1) used $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 5 % solution iodine in alcohol, containing also 2 % KI. Reaction carried out in a quartz vessel blown by an air flow. For reaction (1) removed kinetic of process. Similarly, the same reaction carried out under action of radiation. Reaction (2) carried out thermocatalytic decomposition of HI acid, formed on reaction (1). As the catalyst used the catalysts platforming and "Цеокар-2". Temperature of decomposition was investigated in an interval 500-900 K. The products of decomposition determined on chromatograph Gasochrom-3101 on the contents of gases (CO , H_2 , CH_4).

3. RESULTS AND DISCUSSION

1. Photochemical stage.

In a fig. 1 is submitted kinetic curve of accumulation of HI acid from time of a ultra-violet irradiation.

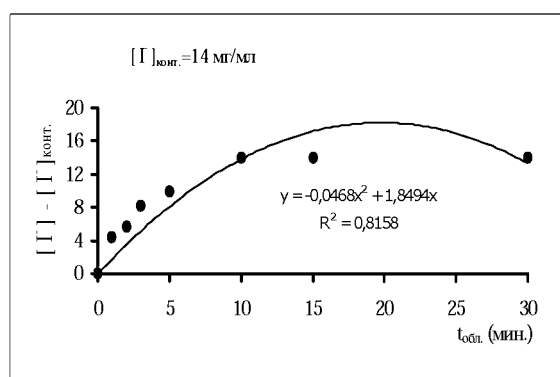


Fig. 1.

Kinetic curve can be described as a curve of the second order

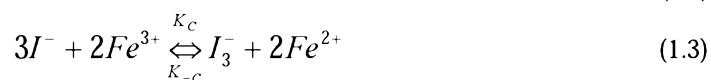
$$[I] = f(t)^2 \text{ or } [I] = -0,0468 t^2 + 1,8494 (t) \quad (7)$$

The concentration curve is described from 10 % by accuracy.

In this case speed of reactions of formation [I] as first derivative of reaction (7) will make

$$\omega = d[I]/dt_{t=0} = 1,849/60 \approx 0,03 \text{ mg/ml.s.}$$

Achievement of stationary concentration [I] occurs for 10 mines., and itself chimism of photochemical process is described by 4 elementary processes



The reactions (1.1) - (1.4) reproduce the subsequent photochemical and return reactions, and also reaction desactivation.

In a fig. 2 curves of accumulation HI acid from a doze of an irradiation with %5 -s' accuracy, are described by a parabola of the second order

$[\text{I}^-] = (-0,027\text{D}^2 + 1,2525\text{D}) \cdot 10^{19} \text{ ions/g.}$ The initial radiation-chemical output (G) of ions I has made $G(\text{I}) = 5 \cdot 10^4 \text{ ions/100eV.}$

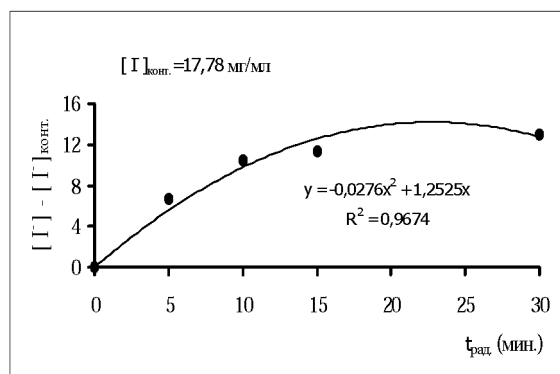


Fig. 2.

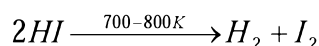
Such output of ions I^- speaks about chain oxidation of ions Fe^{2+} . If solution contains 10^{-3} mol/l it radicals mainly react with ions (I^-). There of the radicals I and I^2 on reactions participate in oxidation Fe^{2+} :



Thus, each atom iodine reproduces 2 ions (I^-) and each other.

2. Thermolys and radiolysis of water solutions HI acid

a) The second step of the combined photo (radiation) thermochemical cycle includes thermolys of HI acid



HI-thermic unstable connection and at the raised temperatures dissociated on iodine and hydrogen. To the positive parties of this reaction it is necessary to attribute: ease of division of components of a mix and rather not high temperatures of thermolys. It is one of the main conditions of realization thermochemical cycles. On the other hand negative party of process is the convertibility of reaction which is not allowing to reach of high degrees conversion (on hydrogen).

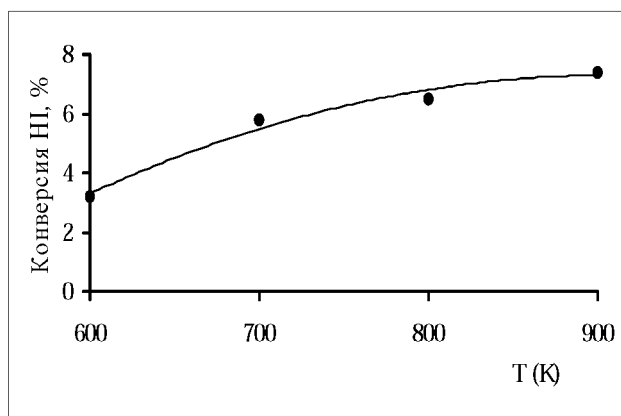


Fig. 3. Temperature dependence of conversion HJ

In a fig. 3 the temperature dependence of conversion HI acid is submitted. The equilibrium concentration of hydrogen at catalytic decomposition HJ makes only 7,4 % at 900K and 1atm.

b) Radiolys of the diluted water solution of HI acid.

In such solutions received at an irradiation of system $[Fe^{2+} - I_2^-]$ after filtering, the water solutions HJ. It are formed at an irradiation it is possible to neglect, direct interaction ion radiation with dissolved HJ, owing to their low concentration. Therefore specified processes grow out interactions of the dissolved substances with products radiolysis of water, that is on the mechanism of indirect action of radiation. In this case oxidizing

particles formed at radiolysis of water (OH) mainly react with ions (J-), forming J and then J-2 [7]. Then, the maximal output of hydrogen will make:

$$G(H_2) = G(H_2) + 1/2 G(H)$$

The output of molecular hydrogen in reaction ($H+H=H_2$) is rather small and is equal 0,005. It is connected that in addition an initial output(exit) of radicals OH is much more, than radicals H ($G(OH)=6,82$, $G(H)=0,84$) and consequently the probability recombination of hydrogen atoms is small in comparison with reaction ($H+OH=H_2O$). The total output of hydrogen will make: $G(H_2) = 0,45 + (1/2) 0,85 = 0,87$, that will well be coordinated to experimental data.

In a fig. 4 the curve accumulation of hydrogen for pure water and diluted water solution of HI are submitted. The radiation-chemical outputs of hydrogen have made

$G_1(H_2) = 0,45 \pm 0,05 \text{ molec./100eV}$ and $G_2(H_2) = 0,80 \pm 0,05 \text{ molec./100eV}$ accordingly.

Thus, the situation proves to be true, that the ions iodine are effective in quality accepters of oxidizing particles radiolysis of water (OH) of radicals.

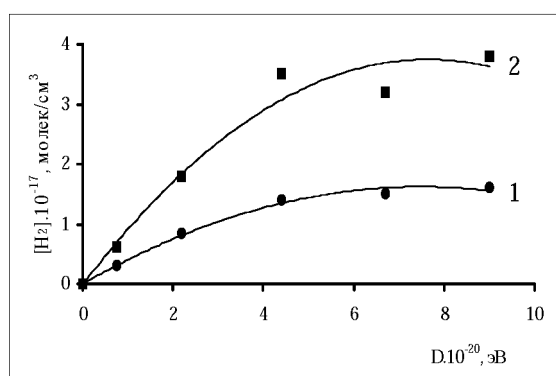


Fig. 4. Curve accumulation of hydrogen from the absorbed dose of radiation in pure water (1) and in the diluted water solution of HI acid (2) $[HI] = 5 \cdot 10^{-3} \text{ mol/l}$.

4. CONCLUSION

Are investigated the first and second step of the combined photo (radiation)-thermochemical cycle of reception of hydrogen. Is shown, what the first stage easily proceeds under action solar and γ -radiation.

The second stage thermo-catalytic of conversion HI acid is connected to the certain difficulties. For the maximal conversion HI it is necessary to use porous glass capable to divide components of a mix (I_2 , I_2) at the moment of their formation. The radiation-chemical formation of hydrogen in the diluted solutions HI is investigated.

5. REFERENCES

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