



ADSORPTION OF HYDROGEN BY NI-FE-AL₂O₃ BASED CATALYST FOR DECOMPOSITION OF WATER

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Abstract

The opportunity of compounds in catalyst to adsorb the hydrogen was studied. The adsorption capability of catalysts was studied within temperature interval 200-350-500⁰C. The probable mechanism of water catalytic decomposition has been worked out on the base of catalysts testing carried out by roentgen-phase analysis.

The spinels as NiAl₂O₄, FeAl₂O₄ and Fe⁰, Ni⁰ are formed during the preparation of catalyst in low pressure condition (P_{diff.}=10-15mmHg). The process of water decomposition to hydrogen and oxygen goes on in the presence of Fe⁰. Approximately 35% of produced hydrogen spent on formation of intrusion hydrides and 65% of hydrogen is in produced gas. The opportunity of compounds in catalyst to adsorb the hydrogen was studied. The adsorption capability of catalysts was studied within temperature interval 200-350-500⁰C. Due to oxidation of Fe⁰ to Fe₂O₃ activity of catalyst in water decomposition reaction gets down. Formation of FeAl₂O₄ also restricts catalysts activity because of active component of catalyst became be blocked. Decrease of specific density of Ni-Al₂O₃; Fe-Al₂O₃ goes on due to increasing the volume after intrusion of hydrogen into the crystal lattice of catalyst. Increasing of specific density of γ-Al₂O₃ goes on due to adsorption of hydrogen. Increasing of Ni-Fe-Al₂O₃ catalysts specific density after water decomposition (0.968 g/sm³) in comparison with catalysts treated with hydrogen (0.860 g/sm³) is explained with Fe₂O₃ formation. Parameters of crystal lattice and volume of elementary cell were calculated. The probable mechanism of water catalytic decomposition has been prepared on the base of catalysts testing carried out by rentgen-phase analyses.

Keywords: water decomposition, hydrogen, catalyst, metal hydrides, adsorption

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1. Introduction

The up-to-day status of global energetics based major on the traditional hydrocarbon sources is pre-critical even by optimistic forecasts. It isn't caused only with obvious reducing of its sources but also with increasing of the threat of global catastrophe as result of pollution of environmental area.

Wide using of hydrogen as a fuel will let considerably improve the ecological situation and reduce usage of hydrocarbon fuel.

Hydrogen is suitable for all types of heat engines. By the way hydrogen as a fuel has high energy potential on the mass -120.7MJ/kg it is more than any other type of organic fuel [1].

In table 1 the comparative energetic characteristics of various types of fuels are submitted [2]. The lower heat creature capability of hydrogen is more than of methane of gasoline heat creature capability in 2.4-2.7 times.

The world hydrogen market for today approximately is 50 mln. tones including 10 mln. tones in USA. According the forecast the hydrogen market will increase till 100 mln. tones in 2010 and 50 mln. tones form it will be for USA.

Fuels properties

Parameter	Hydrogen	Methane	Gasoline
Lower heat creature capability, kV·h·kg ⁻¹	33,33	13,9	12,4
Auto ignition temperature, K	858	813	601-774
Flame temperature, K	2318	2148	2473
The limits of ignition in air, vol.%	4-75	5,3-15	1,0-7,6
Lower auto ignition energy, mV·s ⁻¹	0,02	0,29	0,24
The rate of flame spread in air, m·s ⁻¹	2,65	0,4	0,4
Diffusion coefficient in the air, sm ² ·s ⁻¹	0,61	0,16	0,05
Toxicology	No	no	high

2. Experimental Part

During last years at the Institute of Petrochemical Processes of NAS of Azerbaijan have carrying out the wide researches in water's catalytic decomposition on the catalyst containing Ni-Fe-Al₂O₃ (15-60-25%) [10]. On this catalyst the 100% water conversion was observed. As initial components for catalyst preparation were used the following compounds Ni(NO₃)₂·6H₂O, Fe₂O₃ and Al₂O₃. For equal distribution of initial components it were mixed in water presence, dried (t=120⁰C) and calcined (t=620-640⁰C) in low pressure condition (P=10-15mm Hg). The analysis of catalyst was carried out by X-ray diffraction spectroscopy (XRD) method and the presence of Ni⁰, NiO, NiAl₂O₄, Fe⁰, FeO, Fe₂O₃, Fe₃O₄ and FeAl₂O₄ in catalyst was identified.

The investigation of water decomposition degree on Ni-Fe-Al₂O₃ catalyst in dependence of

For this day the major problems of hydrogen energy is development of effective as from economic as from technology points methods for hydrogen production, and problems with storage and transportation of hydrogen fuel. The special attention is paid for the storage of hydrogen as metals hydrides [3, 4-7].

It is offered [8] to produce the hydrogen in two-step process. The first step goes on at 2200⁰C:



The second step at 400⁰C:



One can try to solve the problem of hydrogen storage with Pd [9]. But this method is one of the limiting moments of development of hydrogen energy. Hydrogen adsorbed by palladium is easy liberated in to the vacuum under the weak heating, but this technology is very expensive so specialists in this area think more perspective to develop other methods of hydrogen storage and transportation.

Table1

temperature and volume velocity of water feed was carried out in reactor with fixed lay of catalyst (Fig.1) D_{reactor}= 22mm; S_{reactor}=2,3sm².

Pump (3) sucks the distilled water form the dropping glass (2) and sends it into the reactor (1). The flow direction is from down to up. The temperature in catalyst lay is controlled by thermocouple (5) and registries by potentiometer (4).

The gases form reaction zone flow in to the flow meter (8) to indicate its amount. Before flow meter the gases passes through cooler (6) and no converted water vapors are dropped in to the drum (7).

At the same reactor was carried out the saturation of catalysts by hydrogen to obtain the amount of hydrogen spent on hydrides formation and adsorbed by Al₂O₃.

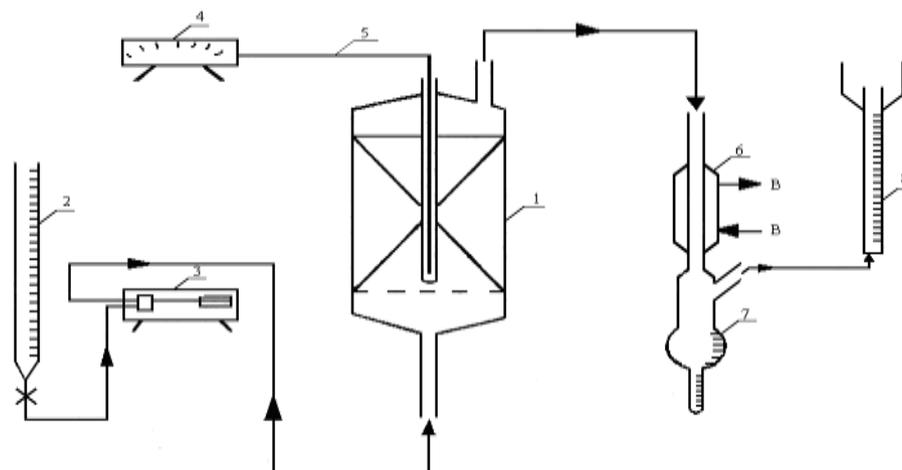


Fig 1. The principal technologic scheme of unit for hydrogen production by water catalytic decomposition.

1- reactor; 2 - dropping glass; 3 - pump; 4 - potentiometer; 5 – thermocouple; 6 – cooler; 7 - drum; 8 - flow meter.

For full reduction of metal oxides till it's the zero valence status catalysts was treated by hydrogen before experiments. The compound of gases was analyzed by Gas Chromatograph. The compound of catalysts was identified by rentgen phase analyzer (RPhA). X-Ray analyses of samples were carried out on DRON-3 device.

3. Results And Discussion

Due to carry out researches it was determinate that at temperature 200-300⁰C on catalyst containing Ni-Fe-Al₂O₃ full water decomposition was observed. Catalyst was prepared in low pressure condition (P=10-15mmHg). For comparison of influence of catalyst preparation conditions on its activity and mechanical stability catalyst was also prepared catalyst in atmospheric pressure condition.

During the preparation of catalysts in low pressure condition and in the hydrogen presence the processes of metal oxides reduction to the zero valence status (Ni⁰, Fe⁰) goes on. Besides, such compounds as NiAl₂O₄ and FeAl₂O₄ are formate in significant amount.

Due to NiAl₂O₄ has a well binder features the prepared catalyst is very fast. The presence of FeAl₂O₄ is impaired the process. Because, during its formation the process of active component (Fe⁰) binding is going on.

It should be noted that if the amount of Al₂O₃ is not significant - 25%, the quantity of formatted FeAl₂O₄ is low, due to the main part of Al₂O₃ is spent on NiAl₂O₄ formation. Due to water decomposition reaction the hydrogen and oxidizing forms of iron (Fe⁰) are formed (FeO, Fe₂O₃ and

spinal Fe₃O₄). The oxidation of Fe⁰ till the iron oxides decreases the activity of catalyst.

The estimated mechanism and routes (9 routes) of the water decomposition process over the mentioned catalyst is described on drawing 2. The observed quantity of produced hydrogen ($G_{H_2}^{obs}$) is the difference between the real quantity of produced hydrogen ($G_{H_2}^{real}$) and the amount of hydrogen spent on hydrides formation and adsorbed by Al₂O₃.

$$G_{H_2}^{obs} = G_{H_2}^{real} - G_{H_2}^{coms}$$

The researches for obtaining of amount of converted hydrogen into hydrides of indention into the metal in temperature interval 200-500⁰C were carried out. (table.2, Fig.3). The amount of adsorbed hydrogen was identified in dependence of temperature 200-500⁰C on the weight (volume) of catalyst.

The adsorption of hydrogen is associated by increasing of solid substance volume. The apparent density is decreased. Why? The atoms haven't exactly defined sizes. When we say that atoms are penetrated in empty spaces between the metal atoms we cannot believe these empty spaces clear limited in. Indeed these "empty" spaces are filled with electronic clouds of atoms and close to end of the spaces the density of electronic clouds is increased. Therefore the penetration even the little size atoms cause the repulsion between the electronic clouds of metals and hydrogen's atoms. As result the penetrated hydrogen atoms "push away" metals atoms. So, as result of this "push away" the increasing of volume is observed during adsorption. Therefore the density of metal saturated with hydrogen is low than the density of initial one (Fig.3).

On the surface of Al₂O₃ the processes of hydrogen adsorption is observed. Quantity of adsorbed hydrogen is 0.06-0.16 g on 1g Al₂O₃.

The defined amount of metals hydrogen saturation meets the various temperature and pressure. To find out the saturation degree at various temperatures we processed Ni-Al₂O₃, Fe-Al₂O₃, γ -Al₂O₃ and Ni-Fe-Al₂O₃ by hydrogen at 200°C, 350°C and 500°C at the same pressures. Results are presented in table 2.

As it seen from the Fig.3, increasing the temperature (200-500°C) leads the saturation of catalyst and at the same time amount of hydrogen adsorbed by γ -Al₂O₃ is getting down.

As optimal temperature was set 280-300°C. At this temperature the maximum hydrogen amount from the reaction zone was observed. It is explained by increasing of formation of metals hydrides of intrusion at temperature increasing.

Our target was to get the maximum amount of hydrogen to be sent to fuel element for burning in oxygen presence. Therefore we set the temperature 280-300°C the maximum quantity of hydrogen produced at.

For the main metals of the second part of d-series (Fe, Ni, Cu) energetic effects of intrusion hydrides formation is not large. For example for FeH₂ it is about +0.2 kcal/mole (0.836 kJ/mole). So, the degree of Ni-Al₂O₃, Fe-Al₂O₃ and Ni-Fe-Al₂O₃ catalysts saturation by hydrogen should decrease at temperature increase, but in our case degree of saturation is increased (Fig.4).

In initial fraction (2) the quantity of Fe₂O₃ is 57.6% (by weight) and Al₂O₃ is 42.4% (table 2). The specific density of initial fraction is about 0.791 g/sm³, but after adsorption the specific density gets down to 0.773 g/sm³ explained by formation of hydrides of intrusion. Charring out the water decomposition reaction on this catalyst leads decrease of specific density till 0.6913 g/sm³. This decrease is also explained by hydrides formation because of hydrogen formation took place from water decomposition. Increasing of specific density of γ -Al₂O₃ (3) from 0.666 to 0.675 and then till the 0.846 g/sm³ is due to adsorption of hydrogen on the surface γ -Al₂O₃.

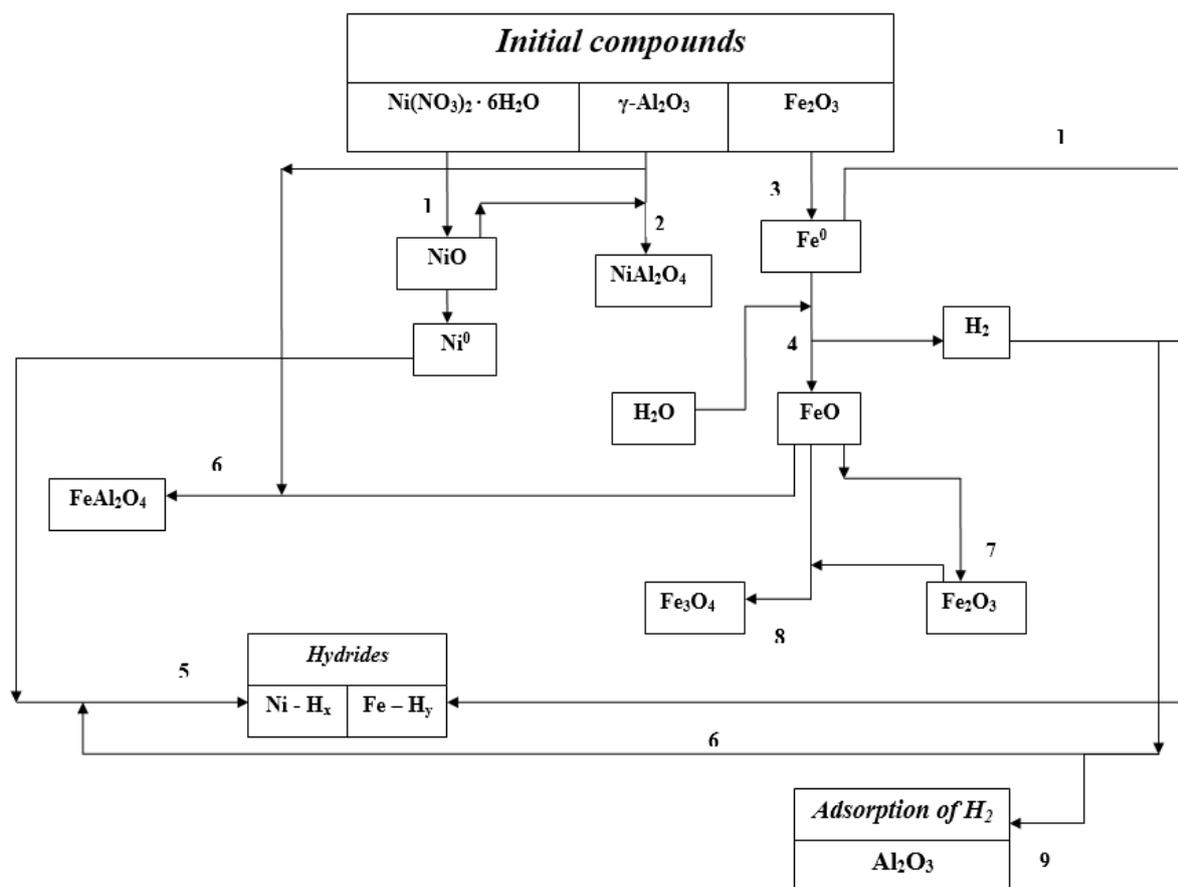


Fig.2 Estimated mechanism of catalytic decomposition of water

After treatment of Ni-Fe-Al₂O₃ in proportion (in initial fraction NiO-15%, Fe₂O₃-80%, Al₂O₃-5%) 13.6, 80.6, 5.8% catalyst by hydrogen the decrease of specific density from 0.989 to 0.86 g/sm³ is observed. It goes on because of hydrides formation. But during the water decomposition reaction we observed the increasing of specific density from 0.860 till 0.968 g/sm³. Probably, it goes on in the result of oxidation of Fe⁰ to Fe₃O₄. Before the treatment with hydrogen there are only NiO, α-Fe₂O₃ only Ni⁰. And after treat the catalyst with hydrogen its specific density decreases from 86 to 0.968 g/sm³. It goes on due to formation of intrusion hydrides leads increasing of volume [13]. But then if we carry out the water decomposition the Fe⁰ oxidizing to Fe₃O₄ goes on associated with

increasing of specific density from 0.860 to 0.968 g/sm³.

At Fig.3 the dependence of changes of catalysts specific density (ρ) on the water decomposition temperature changes is presented. Reducing of specific density of catalysts 1, 2, 4 goes on due to spending of some hydrogen forming from water decomposition on hydrides formation.

We can suppose that on the boarder with metal hydrogen probably dissociated on atoms and passed through inside and passed atoms fully or particularly dissociate on protons (H⁺ ions) and electrons. It is known that dissociation of hydrogen on ions is endothermic reaction.

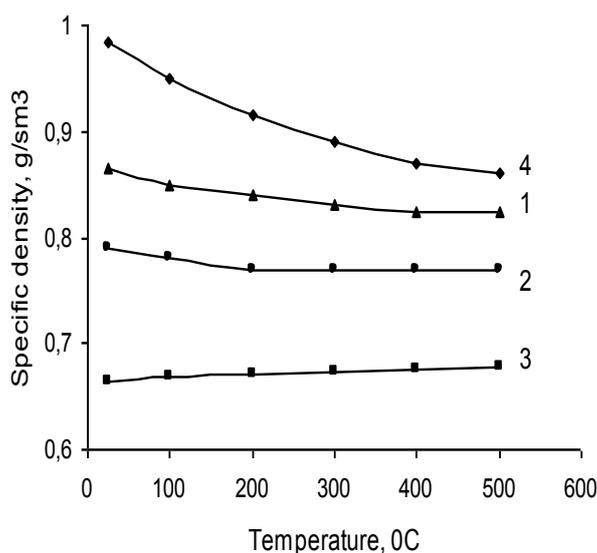
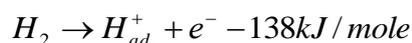


Fig. 3. Changes of catalysts specific density at saturation it with hydrogen in dependence of temperature.

1 - Ni-Al₂O₃; 2 - Fe-Al₂O₃; 3 - Al₂O₃; 4 - Ni-Fe-Al₂O₃

Table 2

Adsorption of hydrogen by catalysts in dependence of temperature

№	Catalyst		Specific weight of catalysts, g/sm ³			Amount of adsorbed hydrogen on the weight (volume) of catalyst					
	Compound	% mass.	Initial	After treatment with H ₂	After reaction with H ₂ O	t = 200°C		t = 350°C		t = 500°C	
						G_{H_2} / G_{cat} , g/g	V_{H_2} / V_{cat} , l/m ³	G_{H_2} / G_{cat} , g/g	V_{H_2} / V_{cat} , l/m ³	G_{H_2} / G_{cat} , g/g	V_{H_2} / V_{cat} , l/m ³
1	Ni-Al ₂ O ₃	12,2-87,8	0,837	0,828	0,8242	-	-	0,25	2,314	0,97	8,264
2	Fe-Al ₂ O ₃	45,1-54,9	0,791	0,773	0,6913	0,012	0,112	0,184	1,697	0,29	2,519
3	Al ₂ O ₃	100	0,666	0,675	0,846	0,16	1,208	0,1	0,743	0,06	0,448
4	Ni-Fe-Al ₂ O ₃	13,6-80,6-5,8	0,989	0,86	0,968	-	-	0,384	3,183	1,13	10,416

G_{H_2} - amount of H₂, g

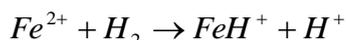
G_{cat} - quantity of catalyst, g

V_{H_2} - volume of H₂, l

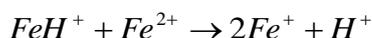
V_{cat} - quantity of catalyst, m³

The reaction rate should be increased in dependence of temperature. Probably it is because the saturation degree in dependence of increasing temperature gets down.

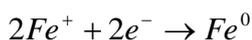
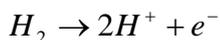
Reducing of iron goes on via the following steps:



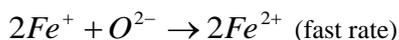
It is thermodynamically non efficient for FeH⁺ to lose the H⁺ with atom formation. Therefore FeH⁺ reacts with another Fe²⁺ ion:



The step of zero valence iron formation goes on by attraction of ion from hydrogen decomposition on ions:



In oxygen presence from water decomposition goes on oxidation of iron:



To define the parameters of crystal lattice catalyst from Ni and γ -Al₂O₃ [11, 12] was taken. After calcining of catalyst in low pressure condition the formation of NiAl₂O₄ and low temperature phase γ -Al₂O₃ was observed. After treatment with hydrogen transformation of low

temperature phase γ -Al₂O₃ into the high temperature phase, and also some displacement of curves is identified. Due to mentioned above and according the experimental data the parameters of crystal lattice of NiAl₂O₄ before and after treatment with hydrogen were calculated. Calculation was carried out base on curves (4,0,0) and (4,4,0) via formula:

$$a = d\sqrt{H^2 + K^2 + L^2}$$

Here: a - parameters of crystal lattice, \AA

d - interplanar spacing, \AA

(H, K, L) - Miller indexes of reflecting plane [11, 12]

Reflections from planes (4, 0, 0) and (4, 4, 0) were used for calculation. The following results were got:

$$a_{av.}(\text{before treatment with } H_2) = 8,037 \text{ \AA}$$

$$a_{av.}(\text{after treatment with } H_2) = 8,049 \text{ \AA}$$

Some increasing of $a_{av.}$ after treatment probably related due to adsorption of hydrogen.

In catalyst Ni-Fe-Al₂O₃ (table.2, sample 4) after calcine in low pressure condition phases Fe₂O₃ and NiO and spane Fe₃O₄ (FeO + Fe₂O₃), α -Fe⁰ и Ni⁰ after treatment were found out.

Parameters of crystal lattice are presented in table 3.

Table 3 Parameters of Ni-Fe-Al₂O₃ catalysts crystal lattice

№	Compound		Parameters of crystal lattice		Elementary volume, A^3
			a_0, A	c_0, A	
1	before treatment with H ₂	α -Fe ₂ O ₃	5,03	13,77	301,709
2		NiO	4,177		72,878
3	after treatment with H ₂	Fe ₃ O ₄	8,391		8590,8
4		α -Fe ⁰	2,866		23,591
5		Ni ⁰	3,524		43,756

1- hexagonal elementary cell;

2-5- cubic elementary cell;

a_0, A – parameter of crystal lattice by axis X;

c_0, A – parameter of crystal lattice by axis Z.

The change of parameter of crystal lattice and volume of elementary cell means that hydrides of intrusion into the catalyst lattice is formed in hydrogen presence and as result the volume of catalyst is increased [13].

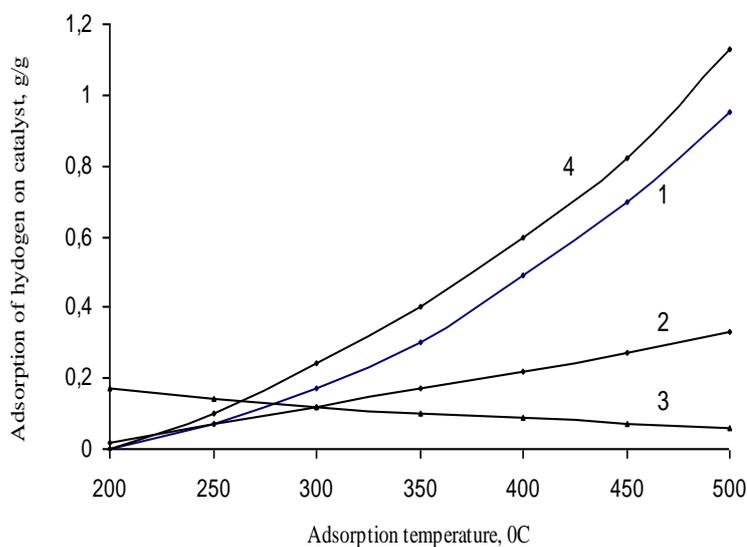


Fig.4. Dependence of amount of adsorbed hydrogen in dependence of temperature

1 - Ni-Al₂O₃ (12.2, 87.8%); 2 - Fe-Al₂O₃ (45.1, 54.9%)
3 - Al₂O₃ (100%); 4 - Ni-Fe-Al₂O₃ (13.6, 80.6, 5.8%)

In table 4 full material balance of hydrogen production by water decomposition on the Ni-Fe-Al₂O₃ catalyst is presented. As it seen from table 4

at full water conversion 35% of produced hydrogen is adsorbed by catalyst. Produced oxygen (3.64g) is spent on oxidizing of Fe⁰:



Due to oxidation of Fe⁰ catalyst's activity is get down. It goes on also due to formation FeAl₂O₄ decrease catalyst cativity. But the quantity

of found out in low amounts because the main quantity of Al₂O₃ spent on NiAl₂O₄ formation.

4. Conclusion

The full water conversion over Ni-Fe-Al₂O₃ catalyst is observed. Maximum quantity of hydrogen is observed at temperature 280-300°C. In these conditions only ~35% of produced hydrogen

is spent on hydride formation and 65% of it is observed it produced gas.

Decrease of catalysts activity goes on due to oxidation of Fe⁰ to Fe₂O₃ and formation of FeAl₂O₄ which decrease the quantity of catalysts active component.

Formation of intrusion hydrides is confirmed with changes of crystal lattice parameters and with increasing of elementary cell's volume.

Table 4. Material balance of water decomposition over Ni, Fe and Al₂O₃ (14.97; 59.62; 25.41% weight) catalyst. Volume of catalyst - 23 sm³, ρ = 0,989 g/sm³, t = 280°C

Initials	K _{H₂O}	Products			Balance for H ₂				O ₂ for oxidation Fe ⁰ to Fe ₂ O ₃	
					Free		Reacted		4 Fe ⁰ + 3 O ₂ →2 Fe ₂ O ₃	
H ₂ O		H ₂	O ₂	H ₂ O	H ₂	From total	H ₂	From total	Fe ⁰	O ₂
g	%	g	g	g	g	%	g	%	g	g
4,1	100	0,46	3,64	-	0,3	65	0,16	35	8,47	3,64

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