FORMATION OF HYDRIDES ADOPTED IN THE CATALYST FOR WATER DECOMPOSITION

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Introduction

Current status of the world energetic based mainly on traditional hydrocarbons sources even in the most optimal forecast is estimated as precrisis. It caused not only with obvious depletion of resources, but also with growth of the danger of global ecological catastrophes as a result of environmental pollution.

Wide-spread usage of hydrogen as a form of fuel would have provided the humanity not only with alternative energy sources, but will improve ecological condition and decrease the using of hydrocarbon materials as well.

Nowadays the basic problem of hydrogen energy is to work out the efficient from the economical and technological point of view method of hydrogen production.

Today the researches related in the field of hydrogen production from the water through electrolysis [1], high-temperature pyrolysis [2], thermal catalytic decomposition [3] are carried out. However, the mentioned processes haven't taken wide spread due to its effectiveness and high energy expenditure.

Results and its discussion

During the recent years in the Institute of Petrochemical Processes of Azerbaijan National Academy of Sciences has been investigating the water decomposition over heterogeneous catalysis containing Ni, Fe/γ-Al_2O_3. For working out the optimal catalysis samples one (Ni-γ-Al_2O_3, Fe-γ-Al_2O_3), two (Ni-Fe/γ-Al_2O_3) component catalytic systems with different percentage content of components were prepared [4]. γ-Al_2O_3 in the content is used as a linking component. Catalysts were prepared in low pressure and in atmosphere pressure. It was defined in catalyst prepared in low pressure conditions the spines as $NiAl_2O_4$, $FeAl_2O_4$ are formed which are good linking component giving mechanical and thermal stability to catalytic samples.

The researches of influence of technological parameters on the water decomposition degree over the optimal catalyst were carried out. Water conversions degree at different volumetric speeds (V=0.1-0.4 h^{-1}) within temperature interval 250-500^{0}C was determined. At optimal temperature 280^{0}C and volumetric speed of water 0.14 h^{-1} at the reaction time 90 minutes 100% water conversion was observed.

It was determined that catalysis prepared at low pressure, contains higher amount of Fe^0 that leads the reactions of water decomposition.

It was determined that part of formed hydrogen is absorbed by catalysis. The level of its absorption depends on temperature. The quantity of absorbed hydrogen was determined in temperatures range 200-500^{0}C. Formation of hydrides adopted from metals is confirmed by decrease of catalysts specific weight at 13-15%.

Formation of hydrides is also confirmed by change of parameters of crystalline lattice of catalysis from 8.037Å to 8.049Å and change of size of elementary cell. The size of hecsagonal elementary cell is 301.7 Å^3 before processing by hydrogen and 590.8 Å^3 after the processing.

The probable mechanism of process was proposed in which part of formed hydrogen ~35% is spent on formation of hydride metals. Presence of hydrides is confirmed by decrease of catalysts specific weight and by the change of electrical conductivity of catalysts samples before and after reaction.

The regularity of changes in electrical conductivity in dependence of on temperature was studied. Hydrides of metals are formed due to hydrogen instilling into the catalysts lattice and in the giving of electricity ions of hydrogen located in the lattice are shifting. The change of electrical conductivity confirms the presence of hydride metals in the content of catalysis. It was clarified that conductivity of catalysts samples due to the temperature decreases within intervals of temperature till 200^{0}C. And starting from the temperature 230^{0}C to 300^{0}C conductivity is increased and stabilized at the level 300-350^{0}C which is related with wakening of connection Me-H that provides the mobility of ions of hydrogen causing higher electrical conductivity. Further sudden increasing of conductivity at temperature higher than 350^{0}C related with conversion of Fe_2O_3 into Fe_3O_4 is observed in reactions:

$$FeO + Fe_2O_3 \rightarrow Fe_3O_4.$$

Fe_3O_4 is ferromagnetic and has a high-level of electrical conductivity. It can be supposed that on the border with metal, hydrogen can be fallen into atoms and in this form can leak inside and instilling into the irons lattice, atoms of hydrogen are dissociated into protons and electrons.

It is known that the composition of H_2 into ions is endothermic reaction.

$$H_2 \rightarrow H^+ + e^- - 138 \text{ kJ/mole}.$$

The rate of this reaction increases with the temperature increasing. As obvious, it is explained with this, that level of saturation of catalysis increases according to increase of temperature. Reducing of iron goes with the following steps:

$$Fe^{2+} + H_2 \rightarrow FeH^+ + H^+.$$

In terms of energy it is not advantageous thermo-dynamically to the hydride FeH^+ to throw H^+ with formation of atom. That's why FeH^+ reacts with second ion Fe^{2+}.

$$FeH^+ + Fe^{2+} \rightarrow 2Fe^+ + H^+.$$

The stage of formation zerovalency iron occurs through the joining of electron formed by reaction of decomposition of hydrogen into ions:

$$H + Fe^{2+} \rightarrow 2Fe^+ + H^+$$

$$2Fe^+ + 2e^- \rightarrow 2Fe^0.$$

In the presence of oxygen formed during the water decomposition oxidation of iron with oxygen occurs.

$$2Fe^+ + O^{2-} \rightarrow 2Fe^{2+} \text{ (fast)}.$$

Conclusions

1. During the reaction of decomposition of water at the temperature $280\text{-}300^0$C over Ni, Fe/γ-Al_2O_3 catalyst 100% decomposition of water goes on.
2. 30-35% of formed hydrogen is spent on formation hydride metals, the presence that is confirmed by change of electrical conductivity in temperature till 300^0C.
3. The formed oxygen at decomposition of water oxidizes the iron till Fe_3O_4 that decreases activity of catalysis.

References

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