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INFLUENCE OF TEMPERATURE AND DENSITY OF WATER VAPOR ON THE YIELD OF MOLECULAR HYDROGEN IN THE PRESENCE OF RADIUM-SILICATE

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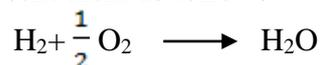
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Abstract: The kinetics of accumulation of molecular hydrogen is investigated at thermo catalytic decomposition of water at presence radium-silicate from density of vapors of water. It is established that change of density of vapors of water in the range of $\rho_{\text{H}_2\text{O}} \sim 1 \div 20$ of mG/sm^3 at radium-silicate presence doesn't influence on thermo catalytic decomposition of water.

Key words: γ -radiolysis, radium-silicate, absorbed dose rate.

1. Introduction

Regularities of influence of structure on radiating and heterogeneous processes of decomposition of substances in contact to silicate systems are not known and represent great value as from the point of view of a radiation catalysis, and radiation materials science. The kinetics of radiolytic decomposition of water in contact to radium-silicate is for this purpose studied at various activity. In the course of formation or thermo vacuum processing in silicate systems the electron-acceptor centers are formed on which occurs a dissociative adsorption of water. Adsorption of molecules of water on the strong electron-acceptor centers causes deformation in electronic structure of the adsorbed molecules of water. Therefore existence of such centers on surfaces can influence processes of decomposition of water in the presence of radium-silicate systems. A certain part of these centers can be catalytically active in processes of thermal decomposition of water. As it is known homogeneous thermal processes of pure water decomposition proceed with notable speed at high temperatures $T \geq 1750\text{K}$ [5, 12, 15] and systematically it is possible to present them as follows:

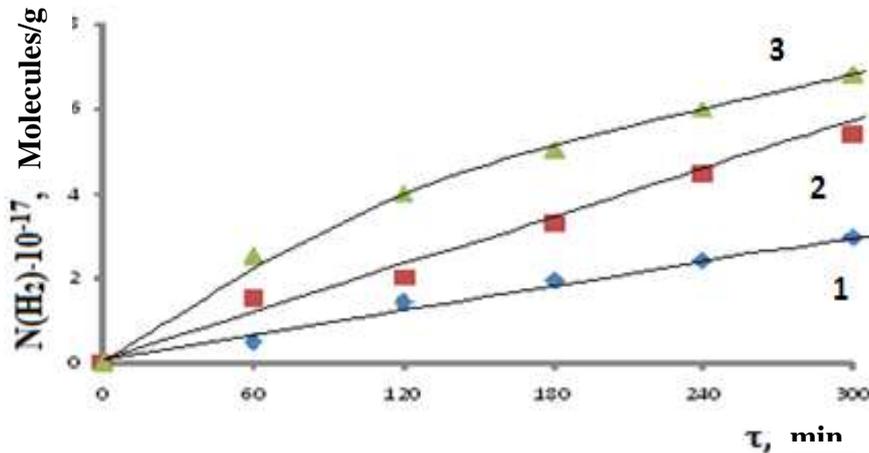


Change of standard values of energy of Gibbs, enthalpy and entropy for this process makes 285.76 kJ/mol, 241.84 kJ/mol and $44.55 \text{ Jmol}^{-1}\text{K}^{-1}$ respectively. In works [5, 12, 17] it is shown that in the presence of zeolite systems process of decomposition of water can be carried out in the range of temperatures 723-773K. Thus the change of thermodynamic functions providing course of process of decomposition of water at low temperatures, can be explained with existence of strong chemisorption communication of molecules of water in a crystal lattice of zeolite.

2. Results and discussion

In view of that on surface radium - silicate systems also occurs strong adsorption linkage of molecules of water, it is possible to expect course of thermo catalytic decomposition of water in the range of temperatures 723-773K. These processes can make a certain contribution in radiating and thermo catalytic water decomposition. For the purpose of identification of a contribution of thermo catalytic processes in radiating and thermo catalytic decomposition of water the kinetics of accumulation of hydrogen is investigated at thermo catalytic and radiating and thermo catalytic decomposition of water at presence radium - silicate in the range of temperatures 573-773K. It is established that radium - silicate systems at temperatures $T \geq 573\text{K}$

possess thermo catalytic activity in the course of water decomposition. Because in these series of experiments at big contents of water in ampoules and high temperatures the condition of water vapors strongly differs from ideal, pressure calculation of water vapors in the reactionary environment not always is correct. Therefore the content of water in the reactionary environment of radiating and heterogeneous processes is usually expressed in terms of density of water vapors - ρ_{H_2O} , mg/cm³ [13-14,16]. On Pic.1 kinetic curve of accumulation of molecular hydrogen at catalytic decomposition of water are given in presence radium - silicate at temperature T=673K.



Pic 1. Kinetic curve of molecular hydrogen production at thermo catalytic (1) and radiation - thermo catalytic (2,3) decomposition of water in the presence of Ra-SiO₃ with activity of 6100 Bk/g at T=673K, D=0,33 of Gr /s (1) - $\rho_{H_2O}=5$ mG/sm³; (2) - $\rho_{H_2O}=0,1$ mG/sm³; (3) - $\rho_{H_2O} = 5$ mG/sm³

Changes in density of water vapors in an interval $\rho_{H_2O}=0,1\div 20$ mG/sm³ in the presence of radium-silicate does not influence on thermo catalytic decomposition of water. The yield of molecular hydrogen thus depends generally only on temperature. On the basis of these results it is possible to make the assumptions that on a surface of radium-silicate are available various term catalytic active centers which become more active at various temperatures. Less active centers participate in the course of thermo catalytic decomposition with temperature increase.

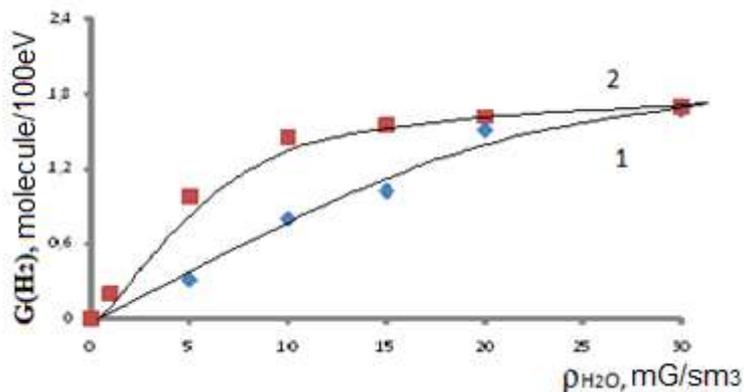
The kinetics of accumulation of molecular hydrogen is investigated at radiating and thermo catalytic decomposition of water in the presence of radium-silicate under identical conditions with thermo catalytic processes. Values of rates of radiating and thermo catalytic $W_{pr}(H_2)$ and thermo catalytic $W_T(H_2)$ processes of molecular hydrogen production are determined by an initial linear site of these curves. Rate of a radiating component of radiating and thermal heterogeneous processes was determined by a difference:

$$W_p(H_2) = W_{pr}(H_2) - W_T(H_2) \quad (1)$$

On the basis of values of speeds of a radiating component of radiating and thermo catalytic processes the chemical yield of molecular hydrogen are defined. On Pic.2. dependences of a radiating and chemical yield from water vapor density are given at heterogeneous radiolysis of water in the presence of radium-silicate at various temperatures. The given curves are described by the equation:

$$G(H_2) = \frac{Kb\rho_{H_2O}}{1+b\rho_{H_2O}} \quad (2)$$

Where K - a seeming constant of speed of process, b - a constant of adsorption balance, ρ_{H_2O} - density of water vapors in the $b\rho_{H_2O} \ll 1$ reactionary environment. From the equation it is visible that at small values of $Kb\rho_{H_2O}$ water vapors density, radiation-chemical yield of molecular hydrogen linearly depends on density of water vapors, $G(H_2) = f(\rho_{H_2O})$ that is observed in initial areas of dependence of $G(H_2) = f(\rho_{H_2O})$ at $\rho_{H_2O} = 7-8 \text{ mG/sm}^3$.



Pic.2. Dependence of a radiation of chemical yield of molecular hydrogen on waters vapor density in Ra-Si +H₂O system; (1) - at 573K, (2) – 673K

At great values of water vapor density, $b\rho_{H_2O} \gg 1$ and $G(H_2) = K$, i.e. radiation of chemical yield of H₂ doesn't depend on water vapor density. As shown from pic. 2 the radiation of chemical yield of molecular hydrogen does not depend on temperature and within accuracy of definition is equal to value $G(H_2)$ at heterogeneous radiolysis of water in the presence of Ra-Si at $T=300K$. Observable shift of stationary area in dependence of $G(H_2) = f(\rho_{H_2O})$ with temperature increase can explain that the temperature generally influences on speed of approach of adsorption balance in Ra-Si+water vapor system.

Thus at temperature increase $T \geq 573K$ at heterogeneous radiolysis of water in the presence of radium-silicate occurs a thermo catalytic and radiation and thermo catalytic decomposition of water. A certain contribution to thermal processes of accumulation of molecular hydrogen from water in contact to radium-silicate can bring chemical interaction of molecules of water with superficial defects of Ra-Si. For the purpose of identification of a role of such chemical reactions with a surface in the course of thermo catalytic production of hydrogen in the presence of Ra-Si at 723K dependence of speed of this process on number of its cycles is investigated. It is established that speed of process within accuracy of definition ($\pm 10\%$) remains stable during 3 multiple use of the catalyst and kinetic curve of H₂ production coincides with a curve 2 on fig. 1. It testifies to a small part of chemical interaction of water with a radium-silicate surface in the course of thermal accumulation of H₂ in contact of water with radium-silicate. However possibility of a hydroxylation of a surface of oxide catalysts as a result of interaction of intermediate products of decomposition of water with superficial defects is not excluded. Research of products $T=573-873K$ of samples of radium-silicate after thermo catalytic process of decomposition of water shows that at a dehydroxidising of a surface of Ra-Si at high temperatures 573-873K, generally H₂O forms [2-3]. Therefore processes of chemical interaction with a surface, and also dehydroxidising of surfaces of radium-silicate can be eliminated as possible channels of formation of molecular hydrogen at thermo catalytic decomposition of water.

3. Conslusions

Comparison of values of a radiating and chemical yield of hydrogen in stationary area of dependence of $G(H_2) = f(\theta)$ at radiating and catalytic and dependences of $G(H_2) = f(\rho_{H_2O})$ at radiating and thermo catalytic decomposition of water in the presence of Ra-Si shows that the temperature at heterogeneous radiolysis of water in the presence of amorphous radium-silicate does not influence an yield of products and in both cases $G(H_2) = 1,63 \pm 0,10$ molecules/100 eV.

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