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KINETICS OF RADIATION-THERMOCATALYTIC DECOMPOSITION OF WATER ON THE SURFACE OF RADIUM-SILICATE DEPENDING ON THE DENSITY OF WATER VAPORS

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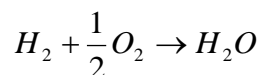
Abstract: The kinetics of molecular hydrogen accumulation during radiation-thermocatalytic decomposition of water in the presence of radium silicate from the density of water vapor has been studied. In the range of values up to $\rho_{\text{H}_2\text{O}} \leq 10 \text{ mG/cm}^3$, the radiation-chemical yield of hydrogen from the density of water vapor increases linearly, and after $\rho \geq 10 \text{ mG/cm}^3$ a stationary region is observed. It was established that a change in the density of water vapor in the range $\rho_{\text{H}_2\text{O}} \sim 10\text{--}30 \text{ mG/cm}^3$ does not affect the thermocatalytic decomposition of water in the presence of radium silicate.

Keywords: γ -radiolysis, radium silicate, kinetics.

1. Introduction

Regularities of influence of structure on radiation and heterogeneous processes of decomposition of substances in contact to silicate systems are not known and represent great value as from 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 thermovacuum processing in silicate systems the electron-acceptor centers are formed on which occurs a dissociative adsorption of water [1-10].

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 $T \geq 1750\text{C}$ [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 [12, 15] 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. Experimental

The radium content in the synthesized samples was varied from 260 to 6100 Bk/g. The radiation

catalytic action of radium silicate was studied on the samples with relatively high radium contents; their activity was $A = 6100$ Bq/g. The heterogeneous radiolysis of water was performed under the static conditions in special ampoules. The amount of radium silicate in the ampoules was approximately $m=4 \cdot 10^{-2}$ g. Twice distilled water was used. Water was introduced in ampoules by two techniques. The first method was adsorption from the vapor state (H_2O_s) on the surface of radium silicate at $T=77$ K. The amount of water introduced in ampoules corresponded to the density of water vapors in the ampoules $\rho = 5$ mg/cm³. In the temperature ranges under study, the amount of water in the vapor state is in equilibrium with that in the adsorbed state

The radiation and thermal radiation processes were performed on a ⁶⁰Co isotope source. The absorbed gamma radiation intensity was determined with chemical (ferrosulfate, cyclohexane, and methane) dosimeters [8, 9]. The products of heterogeneous radiation processes were analyzed on a “Svet-102” gas chromatograph and “Agilent-7890” gas analyzer [11].

3. Results and discussion

Because of that on surface radium - silicate systems also occurs strong adsorption binding of molecules of water, it is possible to expect course of thermo- catalytic decomposition of water in the range of temperatures $T=573 \div 673$ K. These processes can make a certain contribution in radiation and thermocatalytic water decomposition. For identification of a contribution of thermocatalytic processes in radiation and thermocatalytic decomposition of water the kinetics of accumulation of hydrogen is investigated at thermocatalytic and radiation and thermocatalytic decomposition of water at presence radium - silicate in the range of temperatures $T=573 \div 673$ K. It is established that radium - silicate systems at temperatures $T \geq 573$ K possess thermocatalytic 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 radiation and heterogeneous processes is usually expressed in terms of density of water vapors- ρ_{H_2O} (mg/sm³) [14-15]. On Fig.1 kinetic curve of accumulation of molecular hydrogen at catalytic decomposition of water are given in presence radium - silicate at temperature $T=673$ K.

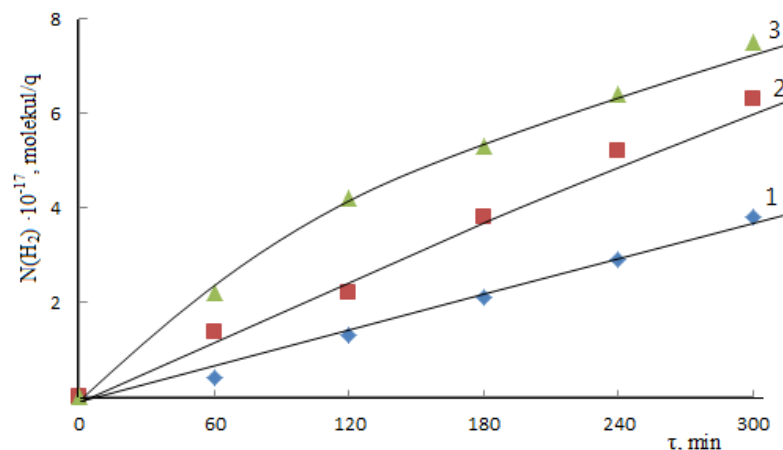


Fig 1. Kinetic curve of molecular hydrogen production at thermocatalytic (1) and radiation - thermocatalytic (2,3) decomposition of water in the presence of Ra-SiO₃ with activity of 6100 Bk/g at $T=673$ K, $D=0,30$ Gr/s, (1) $\rho_{H_2O}=5$ mg/sm³; (2) $\rho_{H_2O}=1,0$ mg/sm³; (3) - $\rho_{H_2O} = 5$ mg/sm³

Changes in density of water vapors in an interval $\rho_{H_2O}=10\div30 \text{ mg/sm}^3$ 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. In 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 thermocatalytic decomposition with temperature increase.

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

$$W_R(H_2) = W_{RT}(H_2) - W_T(H_2) \quad (1)$$

In the basis of values of speeds of a radiation component of radiation and thermo catalytic processes the chemical yield of molecular hydrogen are defined. In Fig.2. dependences of a radiation 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, $G(H_2)$ that is observed in initial areas of dependence of $G(H_2) = f(\rho_{H_2O})$ at $\rho_{H_2O} \leq 7-8 \text{ mg/sm}^3$.

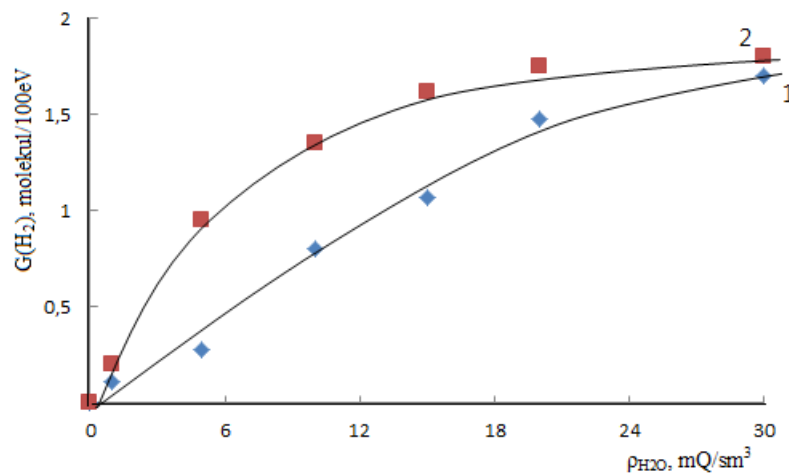


Fig.2. Dependence of a radiation of chemical yield of molecular hydrogen on waters vapor density in Ra-Si + H₂O system; (1) - at 573K, (2) – 673K

At values of water vapor density, $b\rho_{H_2O} \geq 1$ and $G(H_2) = K$, i.e. radiation of chemical yield of H₂ does not depend on water vapor density. As shown from fig. 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 $G(H_2)=f(\rho_{H_2O} \geq 1)$ 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 $T \geq 373K$ at heterogeneous radiolysis of water in the presence of radium-silicate occurs a thermocatalytic and radiation and thermocatalytic 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 identification of a role of such chemical reactions with a surface in the course of thermocatalytic 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 H_2 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 H_2 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 $T=573 \div 873K$ of samples of radium-silicate after thermocatalytic process of decomposition of water shows that at a dehydroxylation of a surface of Ra-Si at high temperatures $T=573 \div 873K$, generally H_2O forms. Therefore processes of chemical interaction with a surface, and also dehydroxylation of surfaces of radium-silicate can be eliminate as possible channels of formation of molecular hydrogen at thermo-catalytic decomposition of water.

4. Conclusions

Comparison of values of a radiation and chemical yield of hydrogen in stationary area of dependence of $G(H_2)=f(\theta)$ at radiation and catalytic and dependences of $G(H_2)=f(\rho_{H_2O})$ at radiation and thermocatalytic 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 $G(H_2)=2,23 \pm 0,10$ molecules/100 eV.

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КИНЕТИКА РАДИАЦИОННО-ТЕРМОКАТАЛИТИЧЕСКОГО РАЗЛОЖЕНИЯ ВОДЫ НА ПОВЕРХНОСТИ РАДИЙ-СИЛИКАТА В ЗАВИСИМОСТИ ОТ ПЛОТНОСТИ ПАРОВ ВОДЫ

З.А. Мансимов

Резюме: Исследована кинетика накопления молекулярного водорода при радиационно-термокаталитическом разложении воды в присутствии радий-силиката от плотности паров воды. В области значений до $\rho_{\text{H}_2\text{O}} \leq 10 \text{ мГ/см}^3$ радиационно-химический выход водорода от плотности паров воды линейно растет, а после $\rho \geq 10 \text{ мГ/см}^3$ наблюдается стационарная область. Установлено, что изменение плотности паров воды в интервале $\rho_{\text{H}_2\text{O}} \sim 10 \div 30 \text{ мГ/см}^3$ на термокаталитическое разложение воды в присутствии радий-силиката не влияет.

Ключевые слова: γ -радиолиз, радий-силикат, кинетика.

SU BUCHARININ SIKLIĞINDAN ASILI OLARAQ RADIUM-SİLİKATIN SƏTHİNDƏ SUYUN RADİASİYA-TERMOKATALİTİK PARÇALANMASININ KİNETİKASI

Z.Ə. Mənsimov

Xülasə: Radium silikatın iştirakı ilə suyun radiasiya-termokatalitik parçalanması zamanı su buxarının sıxlığından asılı olaraq molekulyar hidrogenin əmələgəlməsi kinetikası tədqiq olunmuşdur. Hidrogenin radiasiya-kimyəvi çıxımı, $\rho_{\text{H}_2\text{O}} \leq 10 \text{ mQ/sm}^3$ qiymətlərində suyun buxarının sıxlığından asılı olaraq xətti artır, $\rho \geq 10 \text{ mQ/sm}^3$ qiymətindən isə stasionar oblast müşahidə olunur. Su buxarının sıxlığının $\rho_{\text{H}_2\text{O}} \sim 10 \div 30 \text{ mg/sm}^3$ intervalında dəyişməsi nəticəsində suyun radium-silikatın səthində termokatalitik parçalanmasına təsir etmir.

Açar sözlər: γ -radioliz, radium-silikat, kinetika.