JOURNAL of THE Turkish CHEMICAL Society
SECTION: A
CHEMISTRY

TURKISH CHEMICAL SOCIETY

Investigation of Radiation-Heterogeneous and Catalytic Processes In The Surface Of $(RaO)_x(SiO_2)_y$ $+H_2O$ System

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Abstract: In the study, heterogeneous radiolysis of water in adsorption and liquid form was studied in the $(RaO)_x(SiO_2)_y+H_2O$ system. The effect of radioactivity of radium cations and process temperature on the release of molecular hydrogen was determined (T=300–673K). The mechanism of heterogeneous radiolysis of water with the participation of the studied system $(RaO)_x(SiO_2)y+H_2O$ has been proposed.

Keywords: $(RaO)_x(SiO_2)_y+H_2O$ system, heterogeneous radiolysis, the yield of molecular hydrogen, gamma-radiation.

Submitted: May 19, 2022. **Accepted:** April 25, 2023.

Cite this: Imanova G. Investigation of Radiation-Heterogeneous and Catalytic Processes In The Surface Of $(RaO)_x(SiO_2)_y$ $+H_2O$ System. JOTCSA. 2023;10(2):487-492.

DOI: https://doi.org/10.18596/jotcsa.1118855

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1. INTRODUCTION

Due to their radiation and thermal stability and unique physicochemical properties, radium silicates are of great interest in various fields of nuclear and radiation technology. Interesting results on the effect of different types of radiation on the physicochemical properties of radium silicates were obtained (1–3). Radium silicates are also of great interest as nuclear materials for high-temperature nuclear and radiation technologies. Therefore, recently there has been growth of interest in radium silicates, and large-scale research of their properties under the action of ionizing radiation is being pursued (4–6).

The regularities of the effect of the composition on the radiation-heterogeneous processes of water decomposition in contact with silicate systems are unknown, and from this point of view, its study is of great interest in radiation catalysis. For this purpose, the kinetics of radiolytic decomposition of water in contact with radium silicate of different activity was studied. In the process of thermovacuum processing in silicate systems, the electron acceptor centers cause deformation in the electronic structure of water molecules adsorbed. Therefore, most of these centers on the surface affect the decomposition of water in contact with radium-silicate systems. Some of these centers may be catalytically active in the thermal decomposition of water.

In these studies (7-13) it is noted that the process of water decomposition in contact with zeolite systems occurs in the temperature range T=723–773K. In this case, the change in thermodynamic functions is due to the presence of strong chemisorption bonds of water molecules in the crystal lattice of zeolite.

Thermocatalytic decomposition of water occurs on the surface of radium silicate systems in the temperature range T=723–773K. These processes play a role in the radiation-thermocatalytic decomposition of water. In order to reveal the share of thermocatalytic processes in the process of radiation-thermocatalytic decomposition of water, the kinetics of hydrogen formation during thermocatalytic and radiation-thermocatalytic decomposition of water in contact with radium-silicate in the temperature range T=573–773K was studied. It was found that radium-silicate systems have thermocatalytic activity in the process of water decomposition at temperatures T≥573K. Therefore, the amount of water in the reaction environment of radiation-heterogeneous processes is usually expressed by the density of water vapor (ρH_2O) mQ/cm^3 (14-18).

The purpose of this article is to identify the impact of the activity of radium in the water radiolysis and obtaining molecular hydrogen at the radiolytic decomposition of water in the system $(RaO)_x(SiO_2)_y$ +H_2O at different temperatures (T=300–673K).

2. EXPERIMENTAL

Radium-silicate compounds with unique physical and chemical properties with resistance to radiation and temperature are of great interest in the field of nuclear and radiation technologies. Heterogeneous radiolysis of water was carried out in special quartz ampoules under static conditions. The mass $(RaO)_x(SiO_2)_y$ +H_2O system studied in the ampoules is approximately $m=4\cdot10^{-2}$g. Distilled water was taken for research. Water was injected into the ampoules at room temperature in two ways.

In the first case, at high temperatures of T≥373 K, in experiments, the required amount of water is adsorbed in the vapor phase in a pre-calibrated known volume. In the second case, water is added until it completely covers the surface of radium silicate with mass $m_{cat}=4\bullet10^{-2}$g (m_{liq}=0.2g).

Radiation and radiation-thermal processes carried out on an isotope source of γ-quanta ^{60}Co. Power of the absorbed dose of gamma radiation is determined by ferrosulfate, cyclohexane, and methane dosimeters.

The absorbed radiation dose in the studied systems is determined by the relation of their electronic density and dosimetric systems. Ampoules opened in special cell, from where products of a radiolysis came to a chromatographic column. The analysis of products of radiation and heterogeneous processes was carried out on the gas- chromatograph "Svet-102" and gas analyzer "Gazokhrom-3101".

3. RESULTS AND DISCUSSION

The kinetics of the formation of molecular hydrogen at T=300 K during the heterogeneous radiolysis of water in the $(RaO)_x(SiO_2)_y+H_2O_{ads}$ and $(RaO)_x(SiO_2)_y+H_2O_{liq}$ systems was studied.

Figure 1 shows the kinetic curves of molecular hydrogen formation during heterogeneous radiolysis of $(RaO)_x(SiO_2)_y$ +H_2O system in two methods at T=300K.

In the studied systems, based on the starting line part of the kinetic curves, $(RaO)_x(SiO_2)_y+H_2O_{ads}$ (a) (T = 300K, ρ_{H2O}=5 mg/cm^3, D = 0.28 Gy/s) and $(RaO)_x(SiO_2)_y+H_2O_{liq}$ systems (b) (T=300 K, m_{H2O}=0,02 g, D=0,28 Gy/s), the values of kinetics and velocity of molecular hydrogen formation during radiation heterogeneous decomposition of water were determined. It can be seen from the kinetic curves that the stationary region is observed in both systems after a certain time. Therefore, two sections can be distinguished on the curves:

I. relatively high hydrogen accumulation rate;
II. relatively slow stage of molecular hydrogen accumulation.

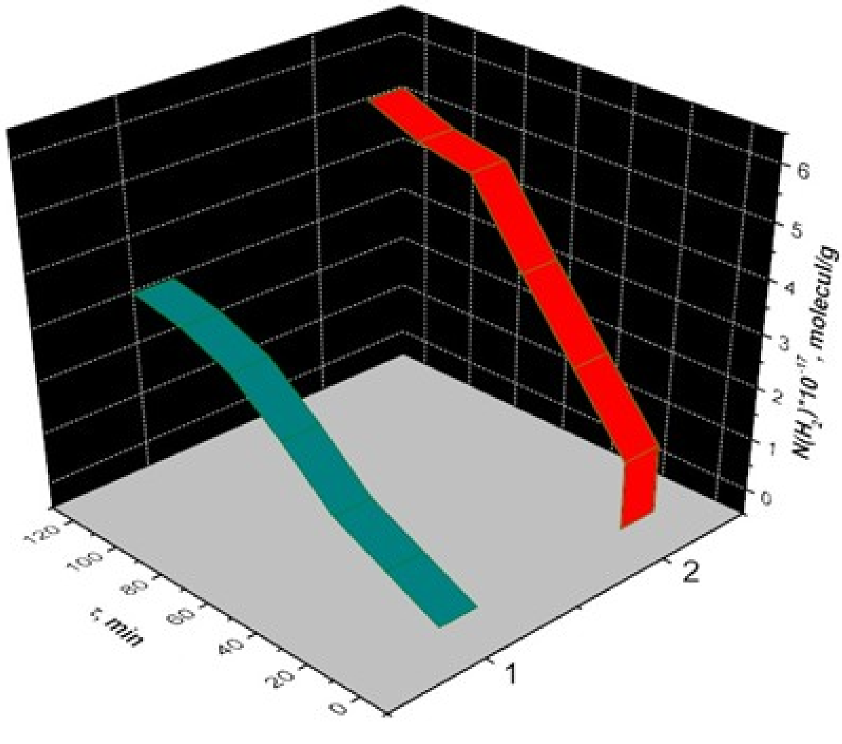

Figure 1: Kinetics of the formation of molecular hydrogen during the radiation-heterogeneous decomposition of water in the systems $(RaO)_x(SiO_2)_y+H_2O$ liquid (1) and adsorbed (2), T=300 K.

The value of the rate of accumulation of molecular hydrogen and the radiation-chemical yield of molecular hydrogen [G(H2)] is determined by the initial linear regions of the kinetic curves, which are given in Table 1.

Table 1: Estimation of molecular hydrogen formation rate and radiation-chemical yield at T =300K.

№	**Irradiated systems and process temperature, K**	**$W(H_2)$, molecule.g^{-1}.s^{-1}**	**$G(H_2)$, molecule/100 eV**
1	$(RaO)_x(SiO_2)_y + H_2O_{ads}$, T=300K	$2.22 \cdot 10^{12}$	0.13
2	$(RaO)_x(SiO_2)_y + H_2O_{liq}$, T=300K	$8.30 \cdot 10^{12}$	0.47

As can be seen, when the surface of radium silicate is completely covered by water, the solid-phase sensors carry more efficient energy transfer processes to the water molecules. As a result, we observe that the value of radiation-chemical emission observed in $(RaO)_x(SiO_2)_y+H_2O_{liq}$ is ca. 3.6 times higher than that of the liquid-adsorbed $(RaO)_x(SiO_2)_y+H_2O_{ads}$ system. This, in turn, clearly shows that energy carriers migrating to the surface have the opportunity to be more actively involved in the breakdown of water molecules.

It was revealed that zirconium dioxide has thermocatalytic activity in the water decomposition process at T > 373 K temperature.

$$H_2O_{abs.} \rightarrow H_2 + \frac{1}{2}O_2$$

Experimentally it is possible to obtain information about the radiation-thermal processes of hydrogen accumulation during radiation-heterogeneous processes of water decomposition. Kinetic curves of radiation-thermal and thermal processes of water decomposition at temperatures T=373-673 K are shown in Figures 2 and 3. The second slow stage of hydrogen accumulation is not observed in some curves with increasing temperature. The radiation component of radiation-thermal processes in the first approximation is defined as:

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

where $W_R(H_2)$ - the rate of formation of molecular hydrogen at the radiation component of processes, $W_{RT}(H_2)$ and $W_T(H_2)$ – the rate of formation of molecular hydrogen during radiation-thermal and thermal processes of water decomposition.

Comparison of the results of experiments carried out under the same conditions shows that when radium-silicate is surrounded by water, the energy carriers formed under the influence of gamma quanta on its surface undergo radiolytic decomposition of water molecules both at surface levels and in contact. The results of radiation-heterogeneous radiolysis of water at different temperatures with the participation of the system $(RaO)_x(SiO_2)_y$ can be explained within the electrophysical model of radiation-heterogeneous processes.

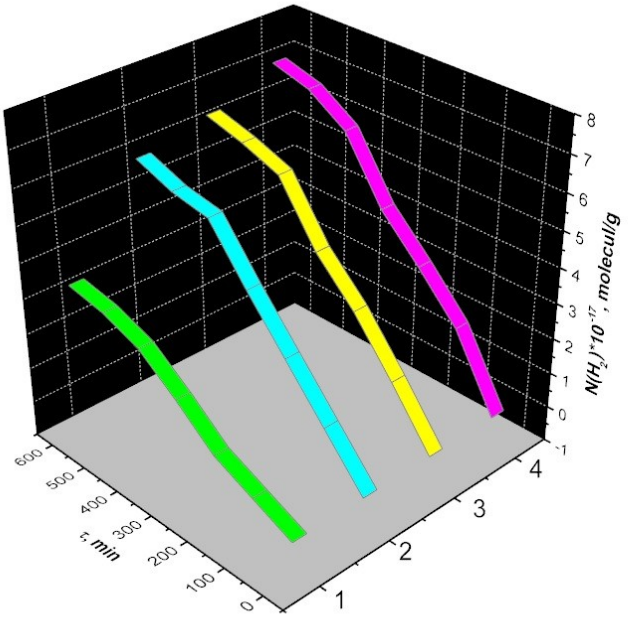

Figure 2: Kinetics of molecular hydrogen accumulation during thermal decomposition of water on the $(RaO)_x(SiO_2)_y+H_2O_{ads}$ system at different temperatures: 1-T=373,2-T=473, 3-T=573, 4-T=673 K, ρ_{H2O}=5mQ/cm^3, D=0,28 Gy/s.

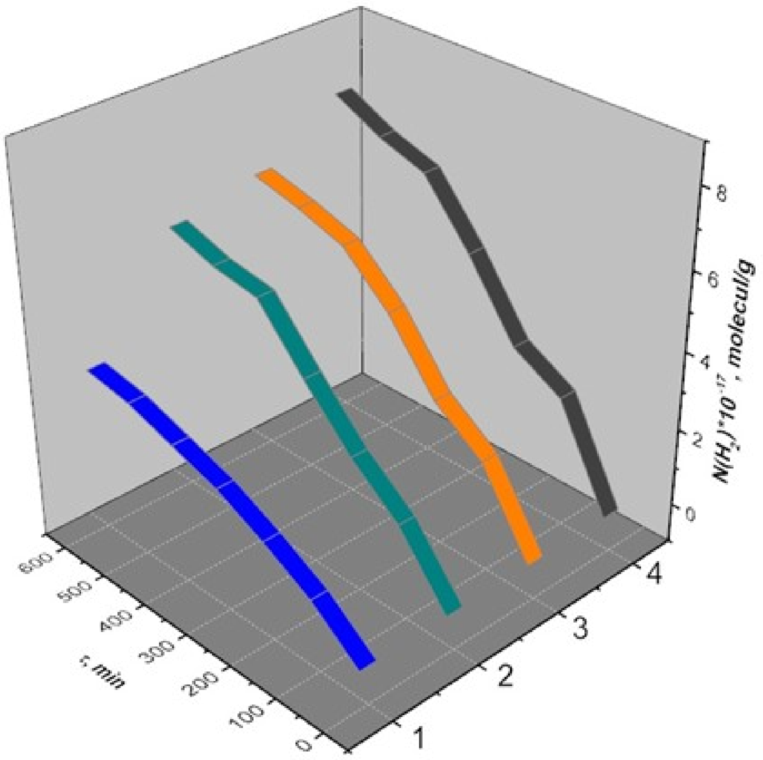

Figure 3: Kinetics of molecular hydrogen accumulation during radiation-thermal decomposition of water on the $(RaO)_x(SiO_2)_y+H_2O_{ads}$ system at different temperatures: 1-T=373,2-T=473, 3-T=573, 4-T=673 K, ρ_{H2O}=5 mQ/cm^3, D=0,28 Gy/s.

The values of radiation-chemical yields were determined from the rate of formation of molecular hydrogen with the radiation component of radiation-thermal processes of water decomposition (Table 2).

Table 2: Velocities of formation of molecular hydrogen and radiation-chemical yields as a result of radiation-thermal and thermal processes with the decomposition of water at different temperatures in the system $(RaO)_x(SiO_2)_y$

№	**T, K**	**$W_{RT}(H_2)$, molecule.g^{-1}.s^{-1}**	**$W_T(H_2)$, molecule.g^{-1}.s^{-1}**	**$W_R(H_2)$, molecule.q^{-1}.s^{-1}**	**$G(H_2)$, molecule/10 eV**
1	373	-	-	$0.42\cdot10^{13}$	0.18
2	473	$1.75\cdot10^{13}$	$0.06\cdot10^{13}$	$1.69\cdot10^{13}$	0.85
3	573	$3.05\cdot10^{13}$	$0.11\cdot10^{13}$	$2.94\cdot10^{13}$	1.12
4	673	$8.61\cdot10^{13}$	$4.44\cdot10^{13}$	$4.17\cdot10^{13}$	1.63

Figure 4 shows the molecular hydrogen yield values in the temperature range T=300–673K in radiation-heterogeneous processes in the system $(RaO)_x(SiO_2)_y+H_2O$.

The results from Figure 4 show that an increase in temperature from 300 to 673 K increases the radiation-chemical yield of hydrogen from 0.78 to 1.63 molecules/100 eV. The observed increase in the chemical yield of radiation is explained by the effect of temperature on the process of energy transfer in the system $(RaO)_x(SiO_2)_y+H_2O$. Based on the obtained results, it can be concluded that the surface of radium silicate has thermocatalytic active centers that are activated at different temperatures. Relatively low active centers are involved in the process of thermocatalytic decomposition with increasing temperature. Thus, thermocatalytic and radiation-thermocatalytic cleavage of water occurs during heterogeneous radiolysis of water in contact with radium silicate at T>573K.

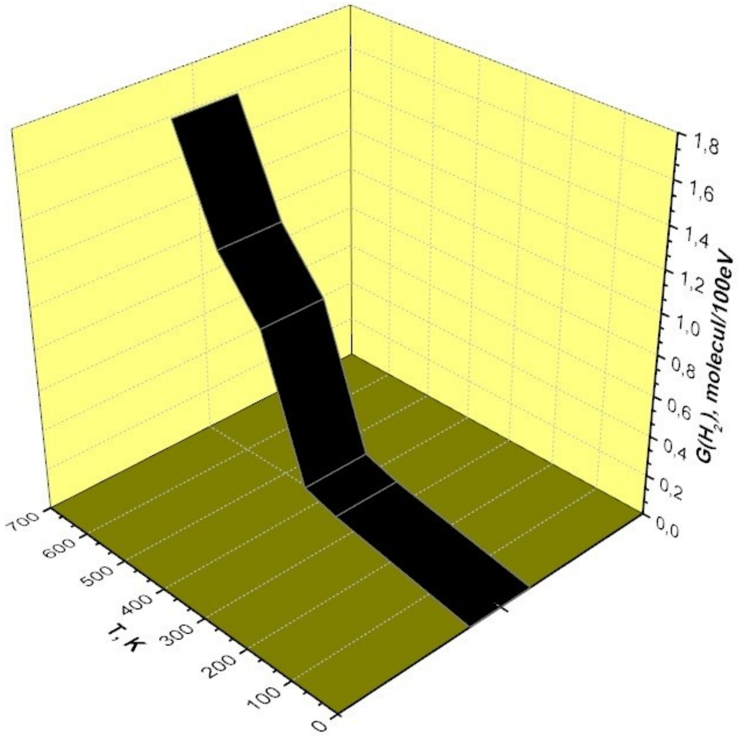

Figure 4: Temperature dependence of the radiation-chemical yields of molecular hydrogen in the $(RaO)_x(SiO_2)_y+H_2O$ system, D=0,3–0,26 Gy/s.

4. CONCLUSION

The kinetics of molecular hydrogen production as a result of radiation-catalytic decomposition of water in the system $(RaO)_x(SiO_2)_y+H_2O$ was studied in the temperature range T=300–673K. It was found that while the liquid water completely covers the surface of the catalyst layer, the radiation chemical yield of molecular hydrogen $G(H_2)$ is higher due to more efficient energy transfer to the water molecule by the particles formed in the solid phase.

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