

# INFLUENCE OF NANOCATALYST SIZE ON HYDROGEN FORMATION DURING WATER RADIOLYSIS UNDER IONIZING RADIATION AT ROOM TEMPERATURE

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Formation of molecular hydrogen during radiolysis of water with  $\text{Al}_2\text{O}_3$  nanoparticles of various sizes is investigated. It was found that the molecular hydrogen yield depends on size of the catalyst. The yield of molecular hydrogen formed on the surface of small nanoparticles is 1.4–1.6 times higher than that on the surface of large nanoparticles. Homogeneous distribution of nanocatalyst in the water and increase of the catalyst surface that is adsorbing water molecules make the radiolysis more efficient.

## INTRODUCTION

The choice of such size range is not accidental, but it is determined by the existence of a number of size effects and crystallite size coincidence with characteristic dimensions for various physical phenomena. The lower limit is considered to be associated with a lower limit of symmetry of nano crystalline materials [1]. The fact is that by decreasing size of the crystal is characterized by a strict set of symmetry elements, there comes a time when there will be loss some elements of symmetry.

In spite of the number of investigations deal with decomposition of water in the presence of different catalysts under effect of ionizing rays, but it has been devoted less studies on this process in the presence of nanoparticles [2]. Recently it has been increased the interest for science and research work in the field of radiolysis chemical conversion of water and carbon hydrogens on the nanocatalyst's surface [2–8].

One of the main directions in the study of radiation heterogeneous processes is increasing the coefficient of transformation of adsorbed beam energy in solid-phase to system and improvement of product yield. In physical stage of radiation heterogeneous processes is occurred absorption of beam energy transformation, transportation and transmission processes. The efficiency of heterogeneous processes mainly depends on parameters of this stage [4].

This research deals with formation of molecular hydrogen from the radiolysis of  $\text{Al}_2\text{O}_3$ -nanocatalyst with different sizes, which used in radiation-catalytic processes and water system and study of impact of nano-catalyst to the yield of hydrogen. The main purpose of the study was set. The main purpose of the investigation is discovering the correlation between used catalyst for transformation maximum energy to the system and amount of water and investigation of impact of nanocatalyst's size on product yield.

## EXPERIMENTAL PART

Radiolysis process carried out under the influence of gamma-rays at a room temperature in the presence of nanoparticles of different sizes. Nanoparticles and bi-distilled water in a ratio of 1:100 were taken. The experiments were conducted under stationary conditions, samples were irradiated by gamma-rays at an isotope  $^{60}\text{Co}$  with dose rate  $P = 1.04$  kGy/h. A system composed of  $d = 5 \dots 50$  nm-sized and bi-distilled water is prepared; 5 ml of the prepared solution is taken and filled in glass vials (15 ml). Ready samples are ejected for a few times and made gas-free at a vacuum facility in liquid nitrogen  $T = -196$  °C temperature and shut down. The hydrogen obtained as a result of radiolysis was analyzed on a gas analyzer.

The concentration of hydrogen gas generated due to the radiolysis process has been determined at "Gaschrom-3101" and "Svet-101" device by a chromatographic method. The hydrogen sensitivity of the device equals to  $K(\text{H}_2) = 6.0 \cdot 10^{13}$  mol./( $\text{cm}^3 \cdot \text{mm}$ ).

## RESULTS AND DISCUSSION

The dependence of  $\text{H}_2$  concentration on adsorbed doses is given Fig. 1. From the obtained kinetic curves it seems that though in the range of  $\Delta\tau = 0 \dots 20$  hours the formation of molecular hydrogen rises linearly, in next interval of irradiation time  $\Delta\tau = 20 \dots 60$  hours relatively it goes down to approaching stationary state.

As can be seen from Fig. 1 molecular  $\text{H}_2$  produced on the surface area of the catalyst within 7 hours of at a linear kinetic region had the rate  $W = (7.83 \dots 11.90) \cdot 10^{13}$  mol./( $\text{g} \cdot \text{s}$ ), and the radiation-chemical yield as  $G(\text{H}_2) = 1.16 \dots 5.97$  mol./100 eV.

The main essence of radiation catalytic processes is transferring the unbalanced charges formed by absorbed ionizing radiation energy on the surface of the catalyst to the adsorbent adsorbed on the surface of the catalyst or the system [4].

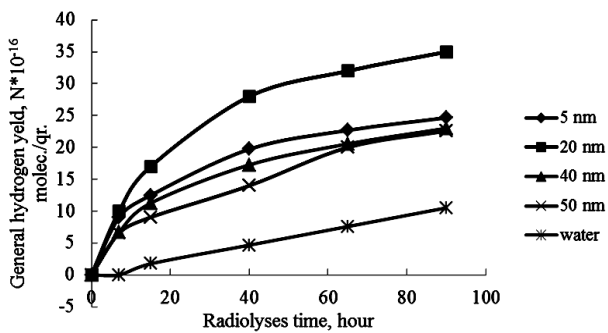


Fig. 1. The kinetic dependence ( $m_{cat}/m_{water}=1:100$ ,  $m_{cat} = 0.01$  g,  $T=300$  K,  $P=1.04$  kGy/h) of molecular hydrogen produced from the radiolysis of water and  $d = 5, 20, 40,$  and  $50$  nm-sized nanoparticles  $Al_2O_3$

Fig. 2 describes the dependence of molecular hydrogen yield depending on the size of the given nanoparticles. The dependence can be divided into two parts; the output from the 20 nm-sized nanoparticles is more than that from 40 nm-sized nanoparticles for 1.4–1.6.

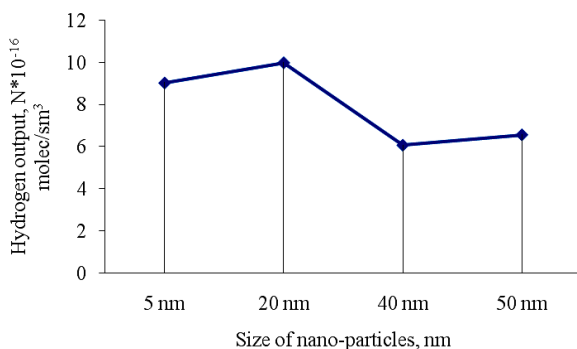


Fig. 2. Molecular hydrogen output formed as a result of nano- $Al_2O_3+H_2O$  system radiolysis ( $M_{part}/M_{water}=1:50$ ,  $m_{cat} = 0.05 \dots 0.1$  g,  $d = 5, 20, 40, 50$  nm,  $t = 24$  °C,  $P = 1.04$  kGy/h,  $\tau = 7$  hours)

As shown (see Fig. 2) the hydrogen output was higher on the surface of the small-sized nanocatalysts, it once again prove that the smaller size of catalyst is, the higher its specific area become which naturally results in better absorption of ionizing radiation on the surface of the catalyst and the efficient transfer of the energy carriers formed the surface to the system [8, 9].

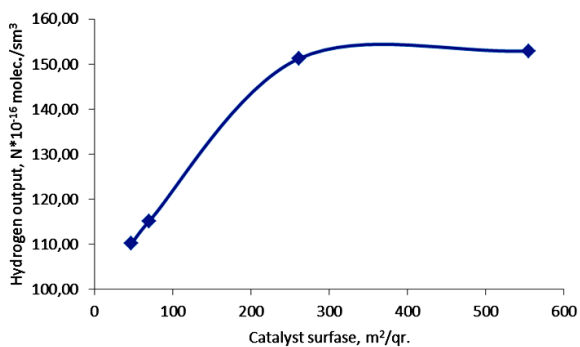


Fig. 3. Dependence of hydrogen yield formed from radio-catalytic decomposition of water and surface area of catalyst

Fig. 3 describes the formed molecular hydrogen output dependence of depending on the surface size of

the taken nanoparticles. As shown (see Fig. 3) by increasing specific area of catalyst the formed hydrogen output grows. Obtained graph can be divided into two parts, the specific surface  $< 80$   $m^2/g$  and  $\geq 200$  part relatively the yield is increased by 1.38–1.64 times.

The carried out studies allow the high efficient using of catalyst surface in radio-catalytic decomposition of water. Hence, it has been given dependence graph of amount of formed hydrogen on the unit surface and surface area of catalyst (Fig. 4). Fig. 4 describes high efficiency using of the taken nanoparticles' actual surface.

As can be seen from Fig. 4 by using small-sized nanoparticles in the system the hydrogen yield, formed per unit surface of catalyst is low by multitudes. It means that used catalyst's surface doesn't use completely. Though nanoparticles' size decreased, they couldn't use completely in the process of radio-catalytic decomposition of water. It could be explained by the obtained intermediate products around the catalyst surface, which weakens formation of hydrogen.

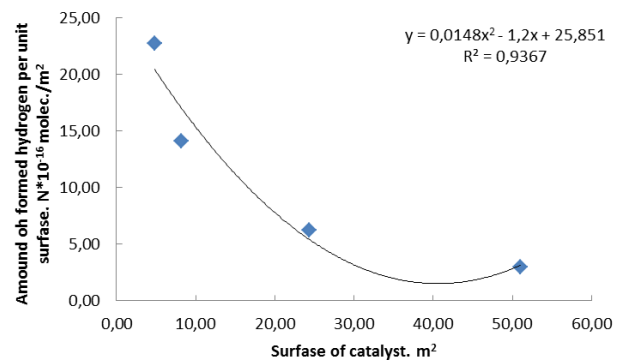


Fig. 4. Dependence of amount of hydrogen formed per unit catalyst surface and catalyst's actual surface

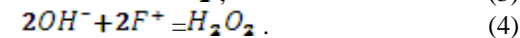
In order to support more efficient transmission of ionizing beam energy to adsorbed molecules in the system of water and nanoparticles, so that to get high efficiency decomposition of the system under the radiation effect is needed to solve the following matters: equal distribution of nanocatalyst as suspected state in the system, preventing coagulation of nanoparticles and getting homogeneous system. If per unit surface of catalyst is absorbed much more water molecules, consequently it accelerates the transmission of non-equal surface energy formed on the nanocatalyst surface and then water decomposition process increases [9, 10].

As a result of water radiolysis formed intermediate active particles and molecular products are studied [4–12].

It seems from the obtained curves that the formation of molecular hydrogen increases linearly for all taken nanoparticles with various size, approaches a saturation state in the ratio of water 1:100 and more.

Radiation is mainly absorbed by a catalyst when nanocatalyst is ejected into water system; consequently additional radiation energy is transmitted to the system which mainly generates due to the catalyst volume and formation of radiation defects. Under the effect of ionizing radiation one or two valence electrons ( $F^+$  and  $F$ ) and hole centers ( $V$ ,  $V^+$ ,  $V^{2+}$ ) form in aluminum oxide crystals [4, 7–9]. As for relatively bigger-sized

catalysts the electrons formed in bulk migrate to the surface, captured by the existing holes on the surface and are recombined (reactions 1 and 2):



By reducing the sizes of the catalysts the defects formed in bulk migrate to the surface and as the result, the numbers of the defects on the surface of the catalyst are increases. In addition, the electrons formed on the surface migrate to the medium and accelerate the reactions (3) and (4) in radiation-catalytic reactions the surface defects play a key role in the processes of surface defect formation, adsorption and decomposition resulting in increase in the output of the final product. Excess of electron density formed in radiation defects migrate from the surface to adsorbents and weakens the in chemical bonds of the adsorbent, water decomposition process accelerates. Under the radiation effect  $AlO_3$ ,  $AlO_5$  type vacancy oxygen clusters generate on the surface of the catalyst and the chemical bond energy of the water molecules ( $O_3Al-OH_2$ ) localized on the surface of this cluster is reduced from 1.9 up to 1.5 eV [12], consequently this accelerate water decomposition and raise the output of the (3) and (4) reaction products.

## RESULTS

- It was investigated that, the yield of molecular hydrogen formed from the radiolysis of homogeneous liquid solutions of catalysts varies related to the size of the catalyst. Thus, radiation-chemical yield at  $d = 5...20$  nm small-sized catalysts is higher 1.4–1.6 times than it is at  $d = 40...50$  nm high-sized particles. Depending on the amount of the water in the system the molecular-hydrogen output on the surface of a nanocatalyst of different sizes is growing.

- It was established that, within nano- $Al_2O_3+H_2O$  system radiolysis, formed hydrogen output increases depends on specific surface of catalyst.

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## ВЛИЯНИЕ РАЗМЕРА НАНОЧАСТИЦ КАТАЛИЗАТОРА НА ОБРАЗОВАНИЕ ВОДОРОДА ПРИ РАДИОЛИЗЕ ВОДЫ ПОД ДЕЙСТВИЕМ ИОНИЗИРУЮЩЕГО ОБЛУЧЕНИЯ ПРИ КОМНАТНОЙ ТЕМПЕРАТУРЕ

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Исследовано образование молекулярного водорода при радиоллизе воды в присутствии наночастиц  $Al_2O_3$  различного размера. Установлено, что выход молекулярного водорода зависит от размера частиц катализатора. Выход молекулярного водорода на поверхности наночастиц катализатора малых размеров в

1,4–1,6 раз больше, по сравнению с выходом на поверхности наночастиц большего размера. Повышению эффективности радиолитического процесса способствуют однородное распределение наночастиц катализатора в водной среде и увеличение суммарной поверхности катализатора, на которой адсорбируются молекулы воды.

### **ВПЛИВ РОЗМІРУ НАНОЧАСТИНОК КАТАЛІЗАТОРА НА УТВОРЕННЯ ВОДНЮ ПРИ РАДІОЛІЗІ ВОДИ ПІД ДІЄЮ ІОНІЗУЮЧОГО ОПРОМІНЕННЯ ПРИ КІМНАТНІЙ ТЕМПЕРАТУРІ**

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Досліджено утворення молекулярного водню при радіолізі води в присутності наночастинок  $Al_2O_3$  різного розміру. Встановлено, що вихід молекулярного водню залежить від розміру частинок катализатора. Вихід молекулярного водню на поверхні наночастинок катализатора малих розмірів у 1,4–1,6 разів більше, в порівнянні з виходом на поверхні наночастинок більшого розміру. Підвищенню ефективності радіолізу сприяють однорідний розподіл наночастинок катализатора у водному середовищі і збільшення сумарної поверхні катализатора, на якій адсорбуються молекули води.