

ON THE HYDROGEN PRODUCTION BY CATALYZED RADIOLYSIS OF WATER

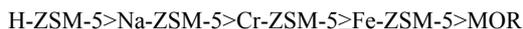
Alexandru CECAL,^{* a} Ada MACOVEI,^a Gabriela TAMBA,^a Oana HAUTA,^a Karin POPA,^a
Dumitru GANJU^a and Ioana RUSU^b

^a “Al.I.Cuza” University, Faculty of Chemistry, 11 Carol I Bvd., 700506 Iasi, Roumania

^b “Al.I.Cuza” University, Faculty of Physics, 11 Carol I Bvd., 700506 Iasi, Roumania

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The present paper deals with the study of water splitting in the presence of certain zeolites as catalysts, in order to get hydrogen as non-polluting energy carrier. Irradiation has been performed using a γ -rays ^{60}Co source, with $3 \cdot 10^4$ Ci activity and 8.3 kGy/h dose rate. The developed molecular hydrogen as a stable product of radiolysis was determined by mass spectrometry. The radiolytic yield G_{H_2} in the water radiolysis versus irradiation time or catalyst quantity has been established. For the studied systems, the values of G_{H_2} decreased as follows:



The most active catalyst toward the decomposition of water upon γ -ray irradiation corresponds to H-ZSM-5, depending on zeolites pore dimensions. At the same time, to study the effect of the pH solution on hydrogen evolution, zeolites in the water were irradiated by different pH. The interdependence between the pH values and the developed hydrogen quantity was studied, remarking that the radiolytic yield G_{H_2} remains rather constant.

INTRODUCTION

The research topic concerns the radiolytic splitting of water molecules which had been systematically studied by several authors and the results obtained were published in a number of papers and books.¹⁻⁵ These studies basically address to the kinetic and thermodynamic parameters which describe the water decomposition under the nuclear radiations and to radiolytic yields of the radiolysis products. In this respect, Maeda *et al.*⁶ investigated the evolution of hydrogen from water molecules radiolysis under γ rays, which were inserted in SiO_2 or TiO_2 cavities. Rotureau *et al.*⁷ studied the formation of molecular hydrogen in the radiolysis of water confined in nanoscale pores of SiO_2 and mesoporous molecular sieves, receiving a value of $G_{\text{H}_2} = 3$.

Lately water radiolysis was studied as a cheap method to get hydrogen, an environmental-friendly energy carrier. Therefore there are a number of

studies concerning the hydrogen output by water decomposition using heat / nuclear rays into nuclear reactors. Related to this matter, the water splitting was tested in I-S, Ca-Br, Cu-Cl thermochemical cycles, or by electrolysis and radiolysis processes.⁸⁻¹⁰ Recently, Yildiz and Kazimi¹¹ described the hydrogen output from alternative nuclear energy facilities, including the high level radioactive wastes which resulted from nuclear power plants. Meanwhile, Brewer *et al.*¹² used some supramolecular complexes of ruthenium and rhodium for water splitting under radiant energy.

The present study is a continuation of some former research^{13,14} regarding hydrogen output from water radiolysis, using as an irradiation source the ^{60}Co radionuclide, with $3 \cdot 10^4$ Ci activity, which stimulated the radioactive wastes resulted from reprocessing of spent nuclear fuel elements much more active: 10^8 - 10^9 Ci. The water's decomposition process under nuclear radiations could be catalyzed by means of certain natural or synthetic zeolites.

EXPERIMENTAL

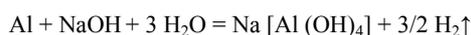
In some vials of 30 ml, different catalyst quantities of H-ZSM-5, Na-ZSM-5, Cr-ZSM-5, Fe-ZSM-5 and MOR (got as described in literature¹⁵) were introduced. Then volumes of 10 ml distilled water were added and each vial was tightly closed with rubber cork and outside paraffined to hinder the release of gaseous radiolysis products. The pH value for each prepared sample was 6.5.

To follow the dependence of water radiolysis versus pH values, in the vials for irradiation 8 mL water and 2 mL buffer solution: CH₃-COOH/CH₃COONa for pH=4.6 and NH₄OH/NH₃ for pH=9.1 were poured. A blank sample was prepared in the same conditions but without catalyst, to follow the simple water radiolysis.

Irradiated sample → Mass spectrometer → PC → Printer

The molecular hydrogen (as a stable radiolysis product) and other chemical species were measured using an original connection device placed between the irradiated sample and the spectrometer, based on a metallic capillary needle of chromatographic syringe. The needle bottom was fitted to the entrance of this apparatus, while with the top, the rubber cork of each irradiated vial was pushed, to establish the connection with mass spectrometer.

A vacuum of approximately 10⁻⁷ Torr was reached inside of ionization chamber before each measurement, in order to



between a given amount of aluminum and concentrated NaOH solution, in a hermetically closed vial but without any irradiation.

XRD studies clearly indicate that the zeolites used as catalysts, after irradiation, did not change their crystalline structures and didn't react with water molecules.

RESULTS AND DISCUSSION

From the obtained results, only hydrogen output from catalyzed radiolytical splitting of water molecules was considered in this paper, but not the other radiolysis products. Practical results reached in different experimental conditions are drawn out in Figures 1 and 2, and also in Table 1.

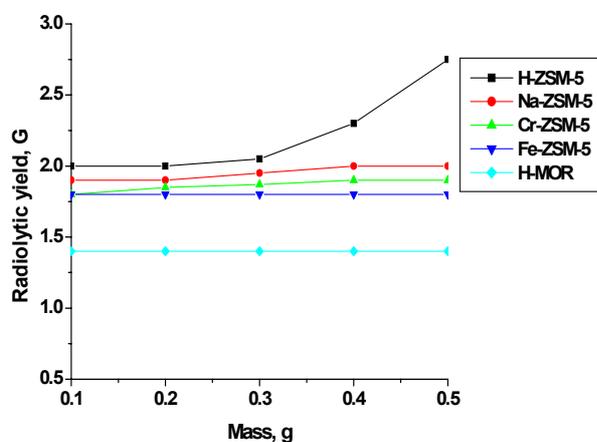


Fig. 1 – Plots of radiolytic yield vs catalyst's amount.

Furthermore it was proved that the zeolites did not react with the solvent used, resist to the action of nuclear rays and did not catalyze the water decomposition at room temperature developing hydrogen measured in outside.

The samples prepared were left in a hole-made metallic cylinder with 30 cm diameter, having in the middle a β-γ rays irradiation source of ⁶⁰Co. This β-γ source had a 3·10⁴ Ci activity and supplied 8.3 kGy/h dose rate. The samples were placed around the source, near of the cylinder wall. The cylinder was further immersed in a water pool. From time to time, the samples irradiation was interrupted to determine qualitatively and quantitatively all appeared stable radiolysis products or other chemical species, using a VESTEC mass spectrometer, adapted for these experiments, as is pointed out below:

avoid the contamination risk for the following vial with the chemical species of the previous sample. Computer plots the obtained experimental results as spectrograms, in the coordinates: Mass number= f (Peak intensity). The peak intensity is proportional to a given amount of the radiolytic products or any other chemical species, inside of each irradiated vial.

In order to calibrate the mass spectrometer for hydrogen measurements as a main radiolysis product, it was necessary to achieve a chemical reaction:

The amount of zeolites taken into considerations in the Figure 1 and Table 1, was 0.1 g, while in the figure 2, data correspond to the irradiation time of 24 h, in each studied case. In these 2 figures and the table, G represents the radiolytic yield of molecular hydrogen.

The experimental data presented above pointed out that radiolytic yields of molecular hydrogen increased with irradiation time (for a given quantity of catalyst), or zeolite mass (for the same absorption dose rate). Further G_{H_2} didn't depend on pH.

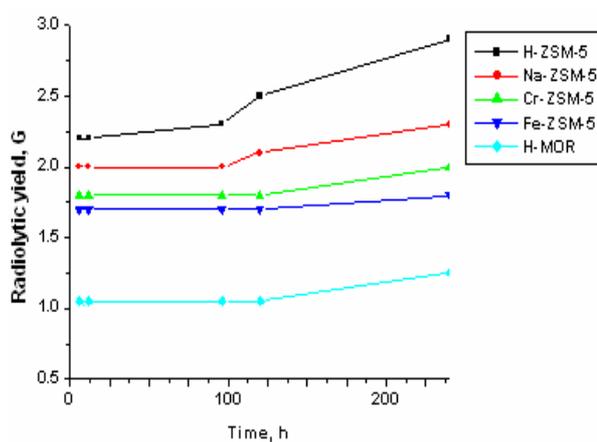


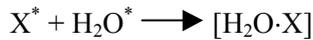
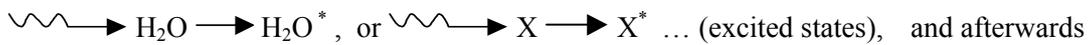
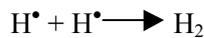
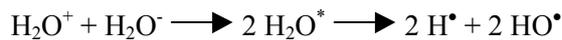
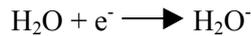
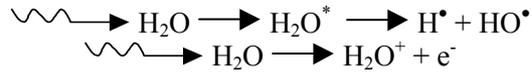
Fig. 2 – Plots of radiolytic yield vs. time.

Table 1

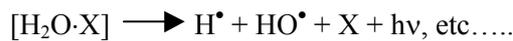
Radiolytic yield for different values of pH

Catalyst	H-ZSM-5			Na-ZSM-5			H-MOR		
pH	4,6	6,5	9,1	4,6	6,5	9,1	4,6	6,5	9,1
Radiolytic yield	2,0	2,0	2,0	1,9	1,9	1,9	1,2	1,2	1,2

The process of radiolytic decomposition of water molecules may be shown as follows⁴:



appearing perhaps excited species between solvent molecules and active centers inside the zeolite' surface, which could accelerate the water radiolytic splitting:



$$G = \frac{c \cdot N_A \cdot 100}{D_a \cdot \rho \cdot 1000 \cdot 6,24 \cdot 10^{15}} = \frac{c}{D_a \cdot \rho} \times 9,66 \cdot 10^6 \quad (1)$$

where:

D_a represents the absorption dose in Gy (1J/kg or $6.24 \cdot 10^{15}$ eV/g), as a product between rate dose (D) and irradiation time (t), while ρ is the density of irradiated material (g/cm^3) and N_A the Avogadro number.

If it considers the determined hydrogen amount from the calibration of mass spectrometer (b, mol/L) having I_{et} the peak intensity value, the hydrogen concentration after irradiation, with the measured peak (I_x) for the mass number 2, in a given vial, will be:

$$c = b I_x / I_{et} \quad (2)$$

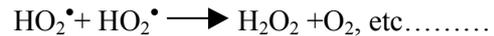
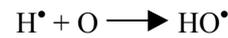
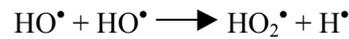
so the radiolytic yield of molecular hydrogen can be:

$$G_{H_2} = \frac{b \cdot I_x}{D \cdot t \cdot \rho \cdot I_{et}} \times 9,66 \cdot 10^6 \quad (3)$$

The radiolytic yields calculated for $b=1.67$ mol H_2 / 1kg H_2O , $D=8.3$ kGy/h, conduct to the value.
 $I_{et} = 7.8 \cdot 10^6$ arbitrary units.

Explaining catalytic effect

Water molecules will be catalytically transformed, following the mechanism presented



In the presence of a X catalyst (including zeolite types), the following reaction sequences could be proposed:

Radiolytic yield of hydrogen, G_{H_2} , the radiolytic yield (number of transformed, or appeared molecules for 100eV absorbed energy, by γ -ray irradiation) was calculated using Henglein-Kiefer^{3,5} formula:

above, if they have similar dimensions like zeolites cavities and can penetrate the crystalline structure of these catalysts¹⁶. The cavities (as channels with elliptic surface sections) correspond to rings of 5, 8, 10 oxygen atoms from the structural units of SiO_4 but also AlO_4 , disposed across in parallel layers which have certain cavities. For example, for ZSM-5, which has 10 oxygen atoms in the ring, the bidimensional pore sizes: are 5.1×5.5 Å, while for MOR, which has 12 oxygen atoms in the ring, those are 6.7×7.0 Å.

As a matter a fact higher the catalytic effect (or the higher values of G_{H_2}) smaller zeolites cavities are. Taking into account the experimental data presented in the figures 1-2, the radiolytic yield G_{H_2} for all the studied systems varies as following:



probably due to the increasing of those cavities. The cavity sizes (depending on metallic cations radii) of zeolites can be changed using ion exchange methods, placing Na^+ , Cr^{3+} , Fe^{3+} cations instead H^+ ions. Moreover, it is possible the water

radiolysis process is explained by the increasing of interactions between the water dipoles (which penetrate the zeolites cavities) and the some ions or charged species as AlO_4^- , into the crystalline structure of catalysts.

The experimental G_{H_2} -value for pure water is 0.47, close to the reported one 0.45.

pH influence on the radiolytic water split in presence of catalysts

This study does not point out a major influence of pH on the radiolysis process, at least for the pH interval 4.6-9.1. This is in good agreement with the Buxton's ones,¹⁷ which shows that even for the interval 1-13, the pH has no a major influence on the radiolytic yield G_{H_2} . Contrary, Dainton and Paterson¹⁸ emphasized a conclusion that radiolytic yields of oxidized or reduced products increase with decreasing of pH solution.

CONCLUSIONS

This work pointed out the possibility of hydrogen output by radiolytical split of water molecules in the presence of some aluminosilicates. The radiolysis products were determined by mass spectrometry. In addition, a formula to determine the radiolytic yield of molecular hydrogen using mass spectrometry, was proposed.

The resulted hydrogen quantity and radiolytic yield depend on the catalyst's type. Smaller the catalyst pore size, higher the amount of obtained hydrogen from water splitting. At room temperature, the aluminosilicates themselves are not able to decompose the water molecules.

Instead of a ^{60}Co irradiation γ source, can be proposed high-level radioactive wastes (without

economic value) from spent nuclear fuel, to get cheaper hydrogen, in a higher quantity, in a continuously radiolytical decomposition process of water molecules.

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