

*Dedicated to the memory of
Professor Cristofor I. Simionescu (1920–2007)*

HYDROGEN YIELD FROM WATER RADIOLYSIS IN THE PRESENCE OF SOME PILLARED CLAYS

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The hydrogen production from catalyzed radiolysis of water was studied in the presence of several anionic and cationic pillared clays. Molecular hydrogen was detected by using a device based on mass spectrometry, after irradiation of some water samples, with a γ -rays ^{60}Co source under different experimental conditions. The radiolytic yield for molecular hydrogen was determined. A considerable increase of the amount of hydrogen resulted from the water radiolysis in the presence of the clays, comparing with the reference sample (without catalyst), under the same irradiated conditions, was noticed.

INTRODUCTION

Due of the importance of hydrogen as a non-polluting energy vector, several studies have been devoted to its production with respect to the profitable economic conditions by means of electrolysis, thermolysis, pyrolysis technics, etc., either in the presence or absence of certain substances, acting as catalyst in the decomposition of water.

Water radiolysis process in different experimental conditions was investigated by several authors. Some studies reported catalyst who favors the hydrogen production from the decomposition of some products rich in this element, with a minimum energy requirement. Several other studies on the hydrogen production from the water decomposition under γ -radiation (even with fission products contained in the spent nuclear fuel elements) were also reported.¹⁻⁹

Maeda *et al.*¹⁰ reported the evolution of molecular gases from γ -irradiation of silica gels and metal oxides dispersed in water. Water adsorbed on the surface of metal oxides shows more evolution of molecular hydrogen than pure water. It

was noticed that the molecular hydrogen evolution is maximized in the silica gels when the size of a silica gel cavity is about 2 nm, and the most active surface toward the decomposition of water upon γ -irradiation is that of SiO_2 dried at 100 °C.

Yamamoto *et al.*¹¹ used nanoparticles of TiO_2 as well as α - and γ - Al_2O_3 in their studies; they reported that the radiolytic yield of hydrogen molecular induced by γ -irradiation of α - and γ - Al_2O_3 in aqueous solution was 7-8 times higher than that of the pure water decomposition.

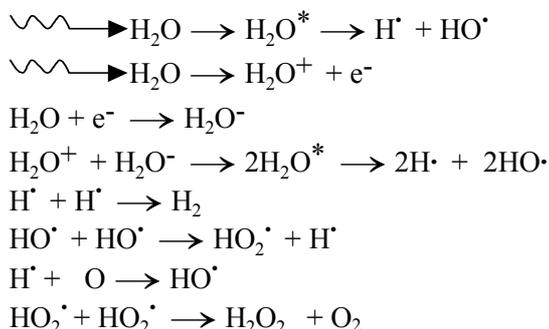
Jung *et al.*¹² studied the effect of addition of EDTA on the hydrogen gas evolution in the γ -irradiation of water containing TiO_2 and the conclusion was that the addition of EDTA increased the radiolytic yield of molecular hydrogen.

The present study is a continuation of some former research¹³⁻¹⁶ regarding hydrogen output from water radiolysis in different experimental conditions. In this case it is dealing with the radiolytic water decomposition in the presence of some anionic and cationic pillared clays.

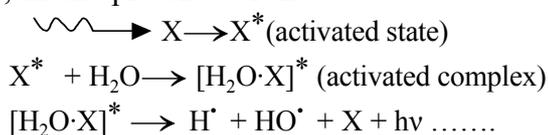
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RESULTS AND DISCUSSION

It's generally known that the radiolysis of water leads to the formation of different chemical



Considering that energy transfer from the clays to water plays an important role in the decomposition of water, in the presence of the



Radiolytic yield of hydrogen, G_{H_2} (number of transformed or appeared molecules for 100eV absorbed energy, by γ -ray irradiation) was

$$G_{\text{H}_2} = \frac{b \cdot I_x}{D \cdot t \cdot \rho \cdot I_{et}} \cdot 9.66 \cdot 10^6 \quad (1)$$

where:

$$D \cdot t = D_a - \text{represents the absorbed dose} \quad (2)$$

ρ - the density of irradiated material (g/cm^3)

b - hydrogen amount determined from the calibration of mass spectrometer (mole H_2 /1kg H_2O)

I_{et} - the peak intensity value of molecular hydrogen resulted from the mass spectrometer calibration reaction

I_x - the peak intensity value of molecular hydrogen resulted from the catalyzed water radiolysis

Several species (H^\cdot , HO^\cdot , HO_2^\cdot , and H_2O_2) were found in the mass spectra, but the radiolytic yield was determined only for molecular hydrogen.

Catalysts efficiency in water radiolysis process was shown by radiolytic yield values of the molecular hydrogen in different experimental conditions.

The subsequent action of the gamma rays produces a radiolytical split of water, releasing a radiolytic yield (G_{H_2}) higher than that produced from pure water splitting in the absence of the catalyst, irradiated in the same conditions (0.45) as the samples with catalyst.

species, such as: H_2 , O_2 , H_2O_2 , HO^\cdot , O , HO_2^\cdot , etc. via a number of reactions outlined below¹⁷:

catalysts, the radiolysis can be represented as follows:

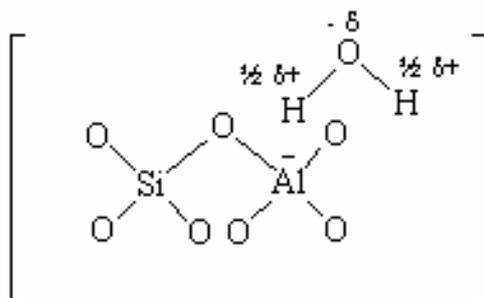
calculated using a formula deduced from Henglein-Kiefer¹⁸ expression:

In the case of pillared clays, cationic clays with Ti have a better efficiency. Of these two types of pillared clays, Răzoare clays (R_1) pointed out a higher radiolytic yield than Valea Chioarului clays (C_1).

Some decreasing values of radiolytic yield (G_{H_2}) when the rate dose increases, may be partially explained due to the loss of hydrogen through the walls of the experimental equipment, considering that this gas can even diffuse through a glass soldered seal.

Clays structure consists in bi-dimensional lattices formed by (SiO_4) and $(\text{AlO}_4)^-$ tetrahedrons, with Si and Al atoms in center and oxygen atoms in tops. Each $(\text{AlO}_4)^-$ group has a charge compensated by the Me^{nt} cationic charge.

In activated state, the catalyst creates a geometrical structural availability for dipolar water molecules to attach, in his pores. In this light disturbed configuration of catalyst, water dipoles undergo to the attraction-repulsion Coulomb forces by ionic species from clay structure, this being shown below:



Under γ -irradiation, H-OH bond of adsorbed water molecules on the catalysts surface is easier split than the bond of the un-sorbed water molecules.

EXPERIMENTAL

Anionic clays and cationic pillared clays from Valea Chioarului (C₁-Al, Fe, Cr and Ti) and Răzoare (R₁-Al, Fe, Cr and Ti) have been used as catalysts. The selection criteria were the resistance to the action of nuclear radiations and the very low chemical reactivity on water splitting (under normal conditions).

The purpose of this process is to introduce the microporosity in the system, micropore dimensions being similar with those of zeolites (20-70 nm). Pillars, homogeneous speeded on the clay surface, creates a bi-dimensional channels system. The new obtained clays have similar proprieties as zeolites (pores dimension and their shape, acidity and redox properties).¹⁹⁻²⁰

The raw clay has a complex mineralogical and chemical. 69.61% SiO₂, 19.7% Al₂O₃, 2.41% MgO, 0.90% CaO, 1.27% Fe₂O₃, 1.31 Na₂O, 0.18% K₂O, and 5.35 P.C. for the Răzoare clays. The CEC (cation exchange capacity) value was found to be 82 meq per 100 g clay and the specific surface area was 140 m²/g. Valea Chioarului clays have a similar chemical composition, but with a small variation of the SiO₂/Al₂O₃ ratio.²¹⁻²²

First, were prepared anionic clays and Al, Cr, Fe, Ti-pillared clays from natural aluminosilicates, using literature indications.²³⁻²⁵ For this purpose, by means of ionic exchange processes, cationic clays were turned into pillared forms.

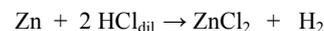
In the 30 ml glass vials different quantities of each catalyst were introduced and 5 ml of double distilled water were added. Each vial was tightly closed with rubber cork and outside paraphyned to hinder the release of gaseous radiolysis product. These vials were γ -irradiated in different experimental conditions, under different dose rates, at IFIN-Bucharest. A blank sample for comparison was also prepared under the same conditions but without the addition of the catalyst.

For this purpose, the vials were placed in four irradiation devices, in symmetrical position to the central source of ⁶⁰Co ($\Lambda=4.07$ PBq), places where the dose rate has the highest value. The average value for the dose rates in the four irradiation positions was (11.23 \pm 0.70) kGy/h. This value becomes (9.22 \pm 0.57) kGy/h, because of the decreasing sources activity. For a correct determination ECB dosimeters

were placed in a maximum and minimum position of the dose rate, corresponding to the irradiation geometry.

The radiolysis products but also other chemical species having 14 and 28 mass numbers (corresponding to N and N₂) were analyzed by mass spectrometry, using an original connection device between the irradiated sample and the spectrometer, based on a metallic capillary.

The mass spectrometer was first calibrated by means of the hydrogen resulted from a total chemical reaction:



This means that 1.08 g Zn corresponds to 0.0165 mole H₂ which further correspond to peak intensity (in arbitrary units) of $2.68 \cdot 10^7$ in the mass spectrum, for the species having the mass number 2.

A vacuum of about $4 \cdot 10^{-6}$ Torr was reached inside of ionization chamber before each measurement, in order to avoid the contamination risk for the following vial with the chemical species of the previous sample. Computer plots the obtained experimental results as spectra, in the coordinates: Peak intensity = f (Mass number).

CONCLUSIONS

This study pointed out the possibility of hydrogen output by radiolytical splitting of water molecules under γ -radiation, in different experimental conditions. The radiolysis products were determined by mass spectrometry. As catalysts were used anionic clays and cationic pillared clays.

A considerable increase of the hydrogen amount resulting from the radiolysis of water in the presence of the clays was noticed in comparison with the reference sample, irradiated under the same experimental conditions.

Răzoare pillared clays have a more important catalytic effect compared with those of Valea Chioarului, probably because of the different ratio SiO₂/Al₂O₃, but also of the presence of the 3d series microelements.

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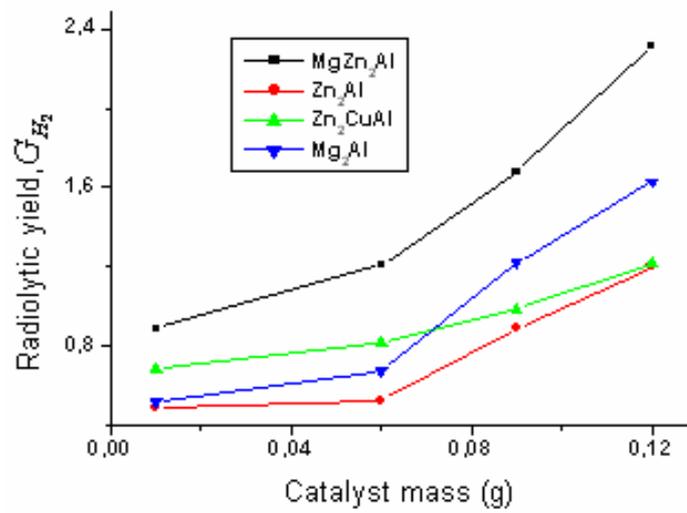


Fig.1.1

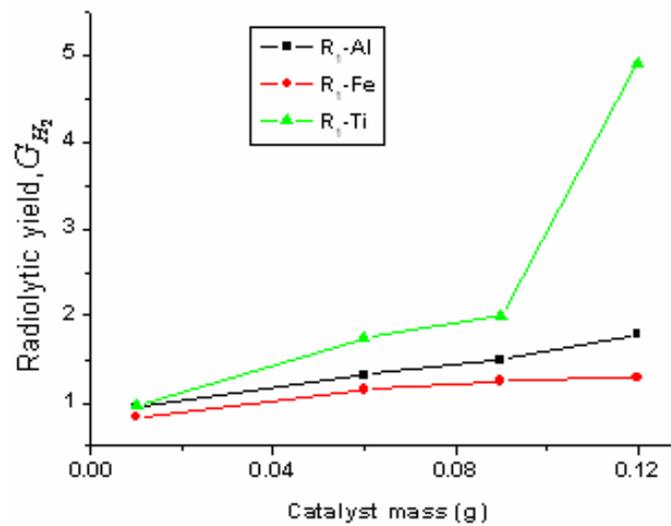


Fig.1.2

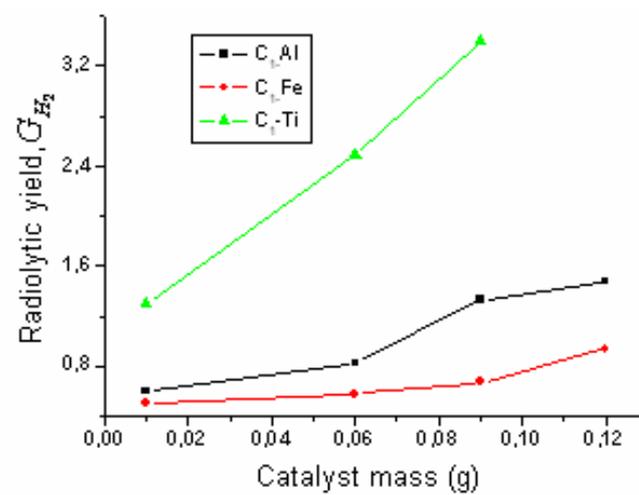


Fig. 2.3

Fig. 1 – Dependence of radiolytic yield of molecular hydrogen on the catalyst amounts for: (1.1) anionic clays, (1.2) R₁-clays and (1.3) C₁-clays.

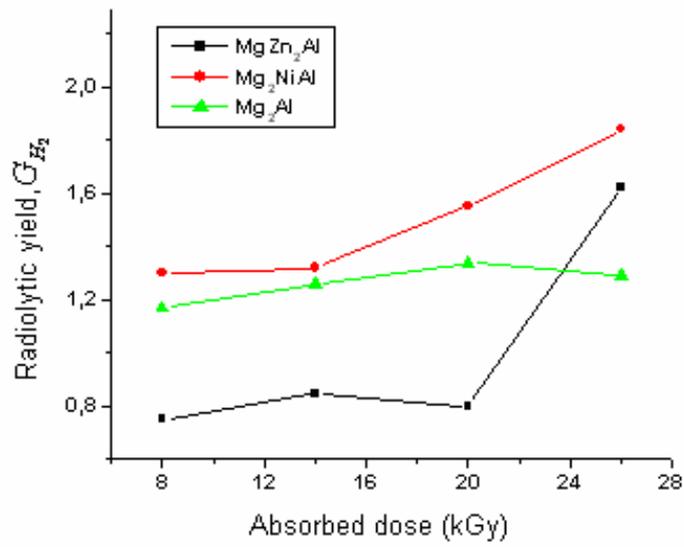


Fig.2.1.

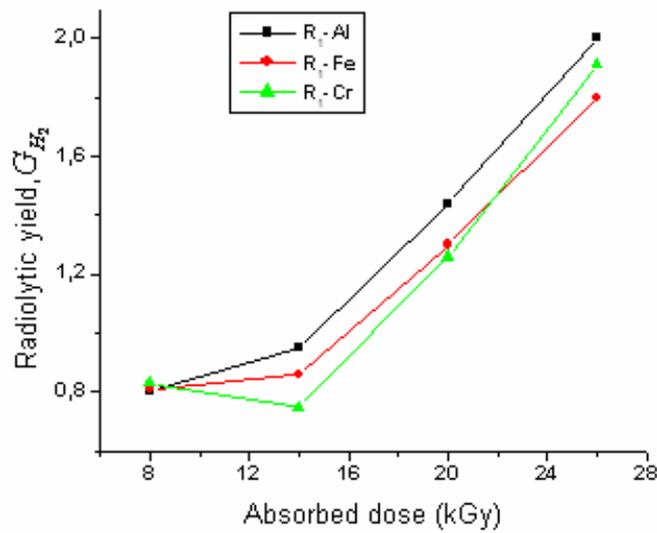


Fig. 2.2.

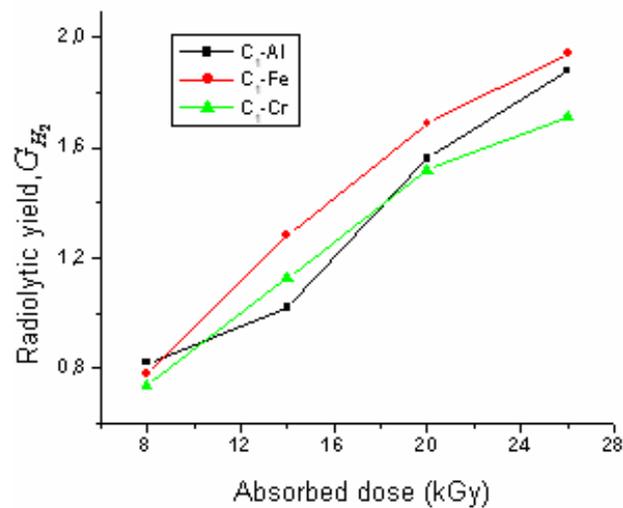


Fig. 2.3

Fig. 2 – Variation of radiolytic yield (G_{H_2}) vs. absorbed dose for: (2.1) anionic clays, (2.2) R₁-clays and (2.3) C₁-clays.

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