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Hydrogen Output from Catalyzed Radiolysis of Water

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Romania

1. Introduction

Energy is the source of the vitality of industrial civilization and a necessary condition to save the world from poverty.

Current methods of generating energy for the industrial civilization undermine local, regional, global environmental conditions, and are based mainly on the processing of fossil resources.

Nowadays, the dawn of a new renewable energy revolution is occurring. It is the use of hydrogen instead of using oil and its derivatives. The stakes are global. The fight against the greenhouse effect requires finding a solution for the production of green energy.

The relatively new method of producing electricity is based on conversion, in fuel cells, of heat and energy of certain chemical substances, in electricity.

Since fuel cells convert fuel directly in electricity two to three times more efficiently than the thermodynamic conversion, the fuel cell is, by definition, a very efficient technology and, being a potential source of high energy still, clean and, compatible with renewable energy policy, reliable and sustainable over time (does not contain moving parts).

Hydrogen is the key to the future of energy having the highest energy content per unit weight of all known fossil. When burned in an engine, hydrogen produces zero issues; when the power source in a fuel cell, clean waters it is the only residue at 250-300 $^{\circ}$C (International Atomic Energy Agency, [IAEA], 1999; Ohta&Veziroglu, 2006; Veziroglu, 2000). Combined with other technologies, such as carbon capture and storage, renewable energies, fusion energy, it is possible that the fuel cell will generate in future energies without harmful programs. Hydrogen is the only energy carrier making it possible to drive an aircraft using solar energy.

At the beginning of the XXIst century it is assumed that fuel cells will become a pervasive technology; hydrogen as fuel is becoming increasingly presented as the "solution", also by carmakers, ecologists, and governments who do not want to impose unpopular measures to limit car traffic.

The use of hydrogen will extend from cell phones to electric power plants.

Implementing the "hydrogen economy" will lead to changes not seen in the XIX century and early XX century when the world went through the experience of the last energy revolution.

Environmentalists argue that there is no alternative to a hydrogen based energy system because the reserves of exploitable oil and natural gas, indispensable resource materials not

only in energy industry, but also in petrochemicals (holds might miss today plastics), will be completely exhausted in less than a century.

T. N. Veziroglu summarizes some properties that recommend the use of hydrogen as energy carrier produced from unconventional technologies, because hydrogen is a concentrate (energy) sources of primary energy, presented to the consumer in a convenient form, having a relatively cheap production cost as a result of technological refinements. Moreover hydrogen has a high efficiency of converting in various forms of energy and represents an inexhaustible source, considering that it is obtained from water, and by use it becomes water.

Hydrogen production and consumption is a closed cycle, that maintains constant power production – water, and represent a classic cycle of raw material recycling – it is the easiest and cleanest fuel. Burning hydrogen is almost without polluting emissions, excepting NO_x, which can also be removed by proper adjustment of combustion conditions. It has a gravimetric "energy density" higher than any other fuel.

Hydrogen can be stored in several ways: gas at normal pressure or high pressure, as liquid or solid form of hydrides and can be transported long distances in any one of the above mentioned forms.

Assessing the effects of global economic shift to energetic system based on hydrogen it can be established that environmental pollution through energy production will not be a problem and hydrogen economy will lead to industrial transformations comparable to those produced in the microelectronics industry;

Moreover economic resources, financial, intellectual, intended for energy today and environmental and ecological problems, will be geared towards solving, for the good of mankind, other product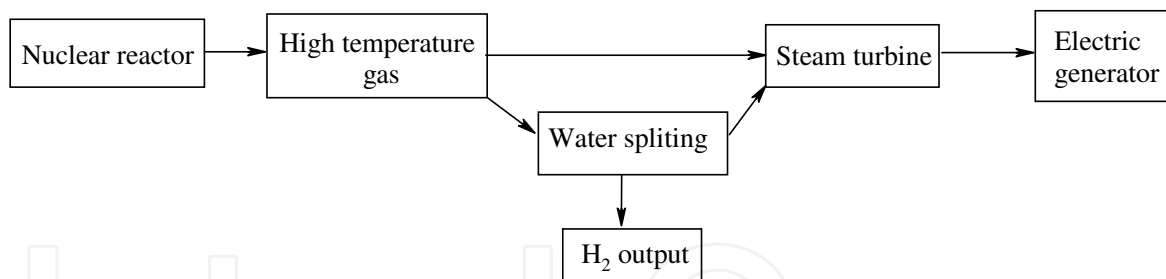ive tasks. Life will get better. The literature state that the idea of a "hydrogen economy" would have been born and developed under the impact of oil shock, using hydrogen as fuel being presented as the last cry of modernity. In fact, however, using hydrogen as a "universal fuel" devoid of pollutant emissions appeared long before the oil shock in 1973.

The literature state that the idea of a "hydrogen economy" would have been born and developed under the impact of oil shock, using hydrogen as fuel being presented as the last cry of modernity. In fact, however, using hydrogen as a "universal fuel" devoid of pollutant emissions appeared long before the oil shock in 1973.

2. Hydrogen production using the heat resulted in nuclear reactors after splitting the U-235 or Pu-239 nuclei
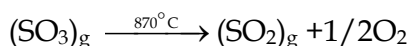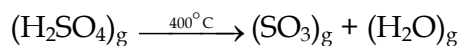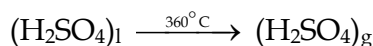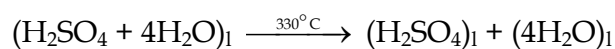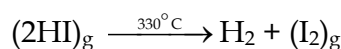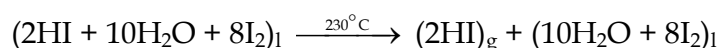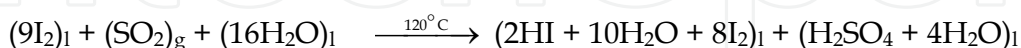
A series of tests are known to produce hydrogen by water splitting by making calls to the thermochemical cycles (hybrid) initiated by heat inside the reactor cores from fission of U-235, Pu-239, etc. (Besenbuch et al. 2000; Rahier et al., 2000; Tashimo et al., 2003, Verfondern, 2007)

An outline of such a plant for water decomposition through cycles of thermochemical reactions initiated by heat from inside a nuclear reactor is presented below:

To this end it used a series of thermochemical cycles or hybrid cycles that have been developed in different types of specialized research institutes or companies with business in areas of nuclear energy: General Atomics (USA) JAEA, Julich JRC, NRC -Ispra and other units from France, China, South Korea, Russia etc.
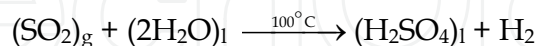
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┌─────────────────┐     ┌──────────────────┐              ┌──────────────┐     ┌──────────────┐
│ Nuclear reactor │ ──► │ High temperature │ ──────────►  │ Steam turbine│ ──► │   Electric   │
│                 │     │       gas        │              │              │     │  generator   │
└─────────────────┘     └──────────────────┘              └──────────────┘     └──────────────┘
                                    └────►  ┌──────────────┐  ──►
                                            │ Water spliting│
                                            └──────────────┘
                                                   │
                                                   ▼
                                            ┌──────────────┐
                                            │  H₂ output   │
                                            └──────────────┘
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a. *Sulfur-iodine cycle* is shown by the sequence of reactions that occur at different temperatures:

$$(9I_2)_l + (SO_2)_g + (16H_2O)_l \xrightarrow{120^\circ C} (2HI + 10H_2O + 8I_2)_l + (H_2SO_4 + 4H_2O)_l$$

$$(2HI + 10H_2O + 8I_2)_l \xrightarrow{230^\circ C} (2HI)_g + (10H_2O + 8I_2)_l$$

$$(2HI)_g \xrightarrow{330^\circ C} H_2 + (I_2)_g$$

$$(H_2SO_4 + 4H_2O)_l \xrightarrow{330^\circ C} (H_2SO_4)_l + (4H_2O)_l$$

$$(H_2SO_4)_l \xrightarrow{360^\circ C} (H_2SO_4)_g$$

$$(H_2SO_4)_g \xrightarrow{400^\circ C} (SO_3)_g + (H_2O)_g$$

$$(SO_3)_g \xrightarrow{870^\circ C} (SO_2)_g + 1/2 O_2$$

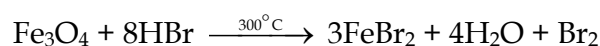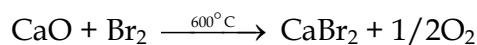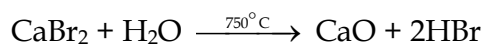At first, through the Bunsen reaction, there result two-phase nemiscible acids: HI and H_2SO_4.

These oxides, under the influence of high temperature, will decompose releasing hydrogen (and oxygen), and I_2 and SO_2, which will restore (as reactants) the Bunsen reaction.
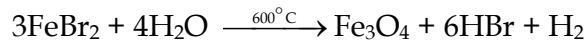
b. *Westinghouse cycle* takes place through two reactions, due to sulfuric acid:

$$(H_2SO_4)_g \xrightarrow{850^\circ C} (SO_2)_g + (H_2O)_l + 1/2 O_2$$

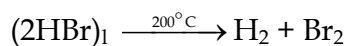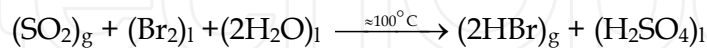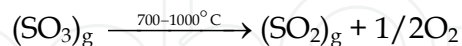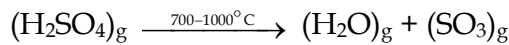$$(SO_2)_g + (2H_2O)_l \xrightarrow{100^\circ C} (H_2SO_4)_l + H_2$$

The second reaction takes place in an electrolytic cell at low temperature when there result hydrogen and sulfuric acid in the aqueous phase at a potential of 0.17 V and at a pressure of about 1 MPa. Then the cycle is repeated with gaseous H_2SO_4.

c. *UT-3 cycle*, developed in Japan, is represented by the following reactions:

$$CaBr_2 + H_2O \xrightarrow{750^\circ C} CaO + 2HBr$$

$$CaO + Br_2 \xrightarrow{600^\circ C} CaBr_2 + 1/2 O_2$$

$$Fe_3O_4 + 8HBr \xrightarrow{300^\circ C} 3FeBr_2 + 4H_2O + Br_2$$

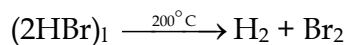$$3FeBr_2 + 4H_2O \xrightarrow{600^{\circ}C} Fe_3O_4 + 6HBr + H_2$$
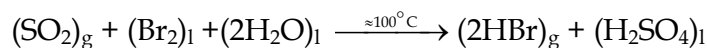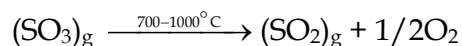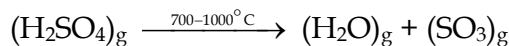
on the account of salts or metal oxides in solid form, as "spherical pellets". Due to the $CaBr_2$ high melting point, the efficiency of the hydrogen production process is of only 40%.

$$(H_2SO_4)_g \xrightarrow{700–1000^{\circ}C} (H_2O)_g + (SO_3)_g$$

$$(SO_3)_g \xrightarrow{700–1000^{\circ}C} (SO_2)_g + 1/2O_2$$

$$(SO_2)_g + (Br_2)_l + (2H_2O)_l \xrightarrow{\approx100^{\circ}C} (2HBr)_g + (H_2SO_4)_l$$

$$(2HBr)_l \xrightarrow{200^{\circ}C} H_2 + Br_2$$

d. *The Mark-13 or the cycle of H_2SO_4 - Br_2, is described by the following chemical transformations:*

$$(H_2SO_4)_g \xrightarrow{700–1000^{\circ}C} (H_2O)_g + (SO_3)_g$$

$$(SO_3)_g \xrightarrow{700–1000^{\circ}C} (SO_2)_g + 1/2O_2$$

$$(SO_2)_g + (Br_2)_l + (2H_2O)_l \xrightarrow{\approx100^{\circ}C} (2HBr)_g + (H_2SO_4)_l$$

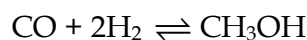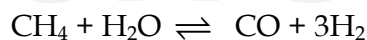$$(2HBr)_l \xrightarrow{200^{\circ}C} H_2 + Br_2$$

Here hydrogen is released by decomposing electrolytic HBr, with an efficiency of 37 %.

e. *Metal-metal oxide cycle* developed at PSI, Switzerland, schematically as follows:

$$M_mO_n \rightarrow M_mO_{n-x} + x/2O_2$$

$$M_mO_{n-x} + xH_2O \rightarrow M_mO_n + xH_2$$
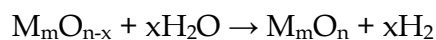
If water splitting occurs at 650 °C, the reduction of the metal oxide is at a temperature of 2000 ° C. The research was done on the system: Fe_3O_4/FeO; Mn_3O_4/MnO, ZnO / Zn; Co_2O_3/CoO or MFe_2O_4, where M = Cu, Ni, Co, Mg, Zn.

f. *Thermochemical cycle methane- methanol - iodomethane* was tested in South Korea and can be played as follows:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2$$

$$CO + 2H_2 \rightleftharpoons CH_3OH$$

$$2CH_3OH + I_2 \rightleftharpoons 2CH_3I + H_2O + 1/2O_2$$

$$2CH_3I + H_2O \rightleftharpoons CH_3OH + CH_4 + I_2$$

Transformations occur at 150 °C and a pressure of 1.2 MPa.
There are also known other hydrogen production processes based on thermochemical cycles, such as another one, HHLT and others.

g. *High-temperature electrolysis.* Hydrogen can be produced by electrolysis of water vapor at 750-950 ° C, by the reactions:

$$K(-): \quad 2H_2O + 4e^- \rightarrow 2H_2 + 2O^{2-}$$

$$A(+): \quad 2O^{2-} \rightarrow O_2 + 4e^-$$
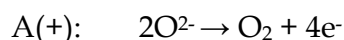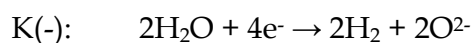
3. Radiolytic split of water molecules in several experimental conditions

In this sense, it know a number of studies respecting the hydrogen obtaining by catalyzed decomposition of water under the influence of nuclear radiation emitted by some sources, including fission products recovered from spent nuclear fuel.

Thus, Maeda and co-workers have studied obtaining of molecular hydrogen by irradiation with γ radiations of silicagels and metal oxides dispersed in water.

They found that a higher radiolytic yield was obtained in the silicagels case with pore diameter of about 2 nm, and the most active area against water decomposition under the action of γ radiation was the SiO_2 dried at 100 °C (Maeda et al., 2005).

Yamamoto and collab. have used in their investigations nanoparticles of TiO_2 and α- and β-Al_2O_3 noting that the radiolytic yield of molecular hydrogen production when irradiated with γ radiation of aqueous solutions with α- and β- Al_2O_3 is 7-8 times higher than water irradiation without catalyst (Yamamoto et al., 1999)

Jung and collab. studied the effect of adding EDTA on the reaction of water radiolysis containing TiO_2 and noted that the presence of this organic compound increased the radiolytic yield of molecular hydrogen (Jung et al.,2003).

Rotureau and collab. studied the obtaining molecular hydrogen from water radiolysis in presence of SiO_2 and of mesoporous molecular sieves obtaining a value of radiolytic yield of molecular hydrogen G_{H_2} = 3 (Rotureau et al. 2006).

Recently, Kazimi and Yildiz studied the obtaining of hydrogen through alternative nuclear energy, including radioactive wastes that result from nuclear plants (Yildiz & Kazimi, 2006).

Brewer and colleagues have used complex supramolecular of ruthenium and rhodium in the study of water decomposition under the action of radiant energy (Brewer & Elvington, 2006).

Masaki and Nakashima studied the gamma-irradiation of Y zeolites both in form Na (NaY) and form H (HY). Discussions on obtaining H and H_2 were based on comparing values G_{H_2} and G_H between systems NaY- and HY-water. They obtained higher values of radiolyitc yield of H_2 due to energy transfer from zeolite to absorbed water (Nakashima & Masaki, 1996).

The $G(H_2)$ values of HY system were 3 times higher than those of system NaY.

Seino and co-workers observed that the nanoparticles of TiO_2 and Al_2O_3 dispersed in water would lead to a significant increase of radiolytic yields of hydrogen to radiolytic yield of pure water. They also noted that radiolytic yield of hydrogen depends on gamma radiation dose absorbed and metal oxide particle size (Seino et al., 2001; Seino et al., 2001).

Yoshida and collab. proposed to get hydrogen by gamma irradiation of water in the presence of Al_2O_3 particles of different diameters. The maximum amount of hydrogen produced was 3.48 μmol/cm³ for water containing Al_2O_3 particles with diameter of 3 μm, value three times higher than the one obtained for the systems with pure water (Yoshida et

al., 2007). Hydrogen produced from catalyzed reactions of water radiolysis was determined by gas chromatography.

Cecal and others (intended to obtain hydrogen through water radiolysis in the presence of solid catalysts, in different experimental conditions, under the action of gamma rays emitted by a source of Co[60]. The produced hydrogen was determined by a device specially adapted for mass spectrometer (Cecal et al., 2001; Cecal et al., 2003; Cecal et al., 2004). This study may be accomplished using as irradiation γ source so called spent nuclear fuel elements extracted from nuclear plants as high level radioactive wastes, instead of the β-γ Co-60 or Cs-137 radionuclides.

4. Irradiation characteristics

Qualitative and quantitative effects of phenomena suffered by substances after interaction with ionizing radiation are determined by the characteristics of the irradiation process.

Irradiation process is characterized by the following quantities (Arnikor, 1987; Ferradini & Pucheault, 1983):

-    radiation intensity,
-    absorbed dose,
-    absorbed dose rate,
-    dose equivalent,
-    linear energy transfer radiation (LET).

Radiation intensity: This feature expresses the amount of energy emitted by source, and expressed in J/s.

Absorbed dose, denoted D_a, represents the amount of energy transferred by incident radiation to unit mass of matter, energy absorbed by matter, respectively. In I.S absorbed dose is expressed as *Gray (Gy):*

$1 \, Gy = 1 \, J/kg = 6, 24 \cdot 10^{13} \, eVg^{-1}$.

Absorbed dose rate represents the energy received by the unit of mass per unit time. It is usually expressed in Gy/s, but there are also used kGy/h, Mgy/h, as well as rad/s, rad/min, rad/day if necessary.

Equivalent dose represents the radiation effect on the organism. Even at the same absorbed dose biological effects on living organisms may be different. This differential action is quantified by introducing a quality factor of incident radiation. As unit of measurement in I.S. there is used *Sievert (Sv)*, which is defined as equivalent dose to the body (tissue) exposed to radiations with quality factor equal with unit when absorbed dose is 1 Gy.

$1 \, Sv = v \times 1 \, Gy$, where:

v – coefficient which depends on radiation quality, for X or γ, v = 1.

Linear energy transfer radiation (LET)

As a result of interaction with matter, electromagnetic radiations continuously lose energy, photon beam intensity gradually decreasing as they penetrate matter. The phenomenon is called linear energy transfer noted LET, and it is expressed quantitatively by the radiation energy loss per unit length, LET = -dE/dx, with the unit keV/μm.

Linear energy transfer should increase as the particle slows down towards the end of the journey so that much of the ionization and excitation produced by fast electrons is produced on the path of gamma radiation, where linear energy transfer value is much higher than average.

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With the linear energy transfer there can be characterized, by a number the „quality" of a radiation, not always describing the type of radiation and its energy.

5. Water radiolysis

5.1 General considerations

A permanent presence of water and ionizing radiation in nature, show the appearance of water radiolysis on Earth and outside it. Laboratory experiments and computer simulations of the processes induced by radiolysis relate to radioactive action of ^{40}K in the ocean 3800 Ma (1 Ma= 1 000 000 years ago) and natural radiation from the groundwater nuclear reactor of the Earth in its infancy.

Radiation-induced decomposition of water molecules, water radiolysis, is carefully studied for several authors, as Debiern, Marie Sklodowska Curie, O. Fricke, J. Franck, J. Weiss, Hart, Boag using different experimental conditions.

5.2 Mechanism of water radiolysis

As a result of water radiolysis with a beam of high-energy radiation as γ radiation or an accelerated electron beam, it occurs excitation and ionization of water molecules, phenomenon that leads to the formation of various ion species, radicals and new molecules – radical theory of water radiolysis (Belloni &Mostafavi, 2001; Kiefer, 1989; Majer, 1982).

According radicals' theory, radiolysis of water flows in three distinct phases:

a. *Physical stage*

A few pico-seconds after irradiation it is discovered the occurrence of excited molecules, H_2O^* and ionized H_2O^+ as of secondary electrons with high kinetic energy:

$$H_2O \xrightarrow{e^-,\gamma} H_2O^* \qquad (1.1)$$

$$H_2O^* \rightarrow H_2O+ \qquad (1.2)$$
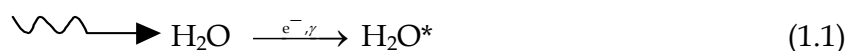
Secondary electrons, Compton or photoelectric are fast slowed down and thermalised, after which they are promptly captured by water molecules, hydrating themselves, (e_{aq}^-). Highlighting the hydrated electron is of great importance in the development of radiation chemistry. Electron hydration corresponds to the stabilization phase through dipole of solvent molecules:

$$e- + H_2O \rightarrow e_{aq}- \qquad (1.3)$$

$$e- + H_2O \rightarrow H. + OH- \qquad (1.4)$$

At physico-chemical stage, which takes about 10^{-13} s, absorbed energy is redistributed through interactions with other stable or excited molecules and ions by splitting olyatomic molecules or through ion-molecule reactions.

It is noticeable that ion-molecule reactions do not necessarily imply ionized molecule movement; interactions can take place in liquid and at a distance of order of several interatomic distances:
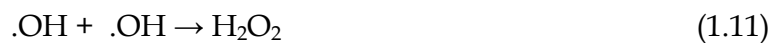
$$H_2O^* \rightarrow H. + .OH \qquad (1.5)$$

$$H_2O+ + H_2O \rightarrow H_3O+ + OH \tag{1.6}$$
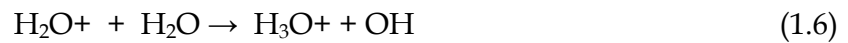
Ionized molecule can be neutralized by an electron:

$$H_3O+ + e- \rightarrow H_3O \tag{1.7}$$

which quickly dissociates:

$$H_3O \rightarrow H_2O + H. \tag{1.8}$$

$$H_3O \rightarrow e- + H_3O+ \tag{1.9}$$

Formed radicals can combine with each other, forming molecules:

$$H. + H. \rightarrow H_2 \tag{1.10}$$

$$.OH + .OH \rightarrow H_2O_2 \tag{1.11}$$

$$.OH + H. \rightarrow H_2O. \tag{1.12}$$

Chemical stage, which takes about 10^{-10} s is the phase in which there occur reactions between species formed in previous steps: recombination between radicals, ions, molecules and free electrons:

$$.OH + H_2 \rightarrow H_2O + H. \text{ reaction that inhibits radiolytic decomposition water} \tag{1.13}$$

$$H. + H_2O_2 \rightarrow H_2O + OH. \tag{1.14}$$

$$e- + H_2O_2 \rightarrow .OH + HO- \tag{1.15}$$

$$HO_2. + H. \rightarrow H_2O_2 \tag{1.16}$$
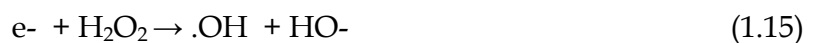
reaction which allows to explain the increase concentration of H_2O_2.
Molecular oxygen is produced through the following reactions:

$$OH + H_2O_2 \rightarrow HO_2. + H_2O \tag{1.17}$$

$$HO_2. + HO_2. \rightarrow H_2O_2 + O_2 \tag{1.18}$$

In the presence of dissolved molecular oxygen reaction takes place:

$$O_2 + H. \rightarrow HO_2. \tag{1.19}$$

Hydrated electron e_{aq}^- has both properties:

$$\text{- reducing: } e- + H_2O \rightarrow H + HO- \tag{1.20}$$

$$\text{- and basic: } e- + H+ \rightarrow H. \tag{1.21}$$
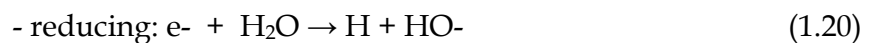
Therefore, a few nano-seconds after irradiation, in water there are present the following species ionics, radicalics and molecules:
H_3O^+, HO^-, $H·$, $·OH$, $HO_2·$, H_2, O_2, H_2O_2, of which the following are stable: **H_2, H_2O_2, H_3O^+**, and short-lived free radicals **e_{aq}^-, $H·$, $·OH$, $HO_2·$**.

5.3 Physical and chemical properties of primary species formed in water radiolysis

The properties of some primary species formed in water radiolysis are presented in Table 1.

Property	e^-_{aq}	H·	·OH
Absorption maximum(nm)	720	<200	225
ε, molar extinction coefficient, (L/mol·cm)	19.000 (720nm)	1620 (188nm)	240 (240nm)
Diffusion coefficient (cm²s⁻¹x10⁵)	4.9	8	2.3
Mobility (cm²V⁻¹s⁻¹x10³)	1.98	-	-
ΔH ionization, kJ/mol	-	9.6	11.9
Electrons affinity (eV)		0.776	1.83

Table 1. Properties of some primary products of water radiolysis.

1. *The hydrated electron e^-_{aq},* is present in system a few milliseconds in the most favorable case. The hydrated electron is considered as a chemical species with a very high reactivity being a very strong reductant; it attaches immediately to radicals molecules or to meet ions. The formed new product containing an extra electron is generally unstable and dissociates forming new radicals or ions in an unstable valence state. Except s block metals other metal, cations are reduced as following:

$$M^{n+}_{aq} + e^-_{aq} \rightarrow M^{n-1}_{aq} \qquad (1.22)$$

Anions F⁻, Cl⁻, Br⁻, I⁻, CN⁻, OH⁻, SCN⁻, with complete electronic layers and oxoanions $(SO_4)^{2-}$, $(PO_4)^{3-}$, $(ClO_4)^-$, $(CO_3)^{2-}$ do not react with the hydrated electron.

Organic molecules, aliphatic hydrides, alcohols, ethers and amines practically do not react with e^-_{aq}, while aliphatic carbonyl compounds such as aldehydes and ketones present a high reactivity.

Redox potential of water has high value $E^o (nH_2O/ e^-_{aq}) = -2.87$ V and it is not annihilated by any other species present in the system except the hydrated electron (e^-_{aq}) within dismutation processes.

$$e^-_{aq} + e^-_{aq} \rightarrow H_2 + 2HO^- \qquad (1.23)$$

2. *Hydrogen atom, H*

The hydrogen atom or atomic hydrogen is a strong reductant, almost as vigorously as the hydrated electron, with the standard potential $E^o (H_3O^+/H·)= -2.3V$, at pH=0.

It can uproot hydrogen from a C-H link from an organic compound to form H_2. It may also be a supplement to a double link.

Radical HO·

Radical HO· is a strong oxidant, extremely energetic with standard potential $E^0(HO/H_2O) = -2.76$ V; it is a species considered very dangerous for living cells in radiobiology. Oxidant properties of radical HO· depend on the pH of the medium. It is considered that at pH > 9, the radical is completely dissociated:

$$HO· \rightarrow H^+ + O^- \qquad (1.24)$$

Radicals ·OH may participate in reactions with various components of the system:

$$HO· + H^+ + e^-_{aq} \rightarrow H_2O \qquad (1.25)$$

$$HO. + H_2 \rightarrow H. + H_2O \qquad (1.26)$$

$$CO + HO. \rightarrow CO_2 + H \qquad (1.27)$$

Radical $HO\cdot$ reacts with organic compounds as it follows:
- extracting a hydrogen atom;
- can addition to a double bond;
- oxidizes primary alcohols to aldehydes in aqueous solutions;
- oxidizes aldehydes to acids, acids from peroxoacids etc.

In favorable conditions it can strip an electron from one molecule to form a cation.

4.   *Radical HO_2.*

HO_2 radicals are obtained by the reaction of $HO\cdot$ With H_2O_2 in general on the radiation trajectory or, possibly, in mass solution, if there are no $HO\cdot$ Radical traps and, of course, with a considerable concentration of H_2O_2. In accordance with this, the yield of these radicals would be higher in the case of low specific ionization radiation. Indeed, it was found that when water radiolysis with α radiation of ^{210}Po, radiochemical yield of $HO_2\cdot$ radicals is 0.23, while at the γ radiolysis G_{HO2}=0.02. Also, $HO_2\cdot$ radicals are obtained from radiolysis of aqueous solutions containing O_2, according to the reaction:

$$H. + O_2 \rightarrow HO_2 \qquad (1.28)$$

The presence of these radicals in aqueous solutions was highlighted both by indirect methods and direct methods. Indirectly, there was studied the variation of the conductivity of irradiated water containing O_2, in which case it has been detected the presence of some intermediate products with a lifetime in excess of 0.1 s and was attributed to O_2^- -ions radical, which could come from $HO_2\cdot$. $HO_2\cdot$ radicals were revealed by direct methods using pulse radiolysis of water containing O_2 .

Due to the complexity of the phenomenon taking place in a watery liquid system when it interacts with γ radiations this methodology was used for many purposes. This way, a new practical method for obtaining the most diverse products appeared, known as *radiolytic method*.

Within the research required in this paper, the radiolytic method is used to obtain hydrogen in the presence of different catalysts, using high-activity nuclear radiation about 5 x 10^4 Ci, emitted by spent nuclear fuel or ^{60}Co sources, process studied by other researchers, too.

5.4 Radiolytic yield

Radiolytic yield concept was introduced in order to quantify the effect of radiation, i.e. in order to calculate the amount of products formed depending on the dose of radiation absorbed.

There can be distinguished:
- *Ionic-yield*, g, also called ion pair yield, which is the ratio between the number of equivalents turned, the number of molecules that interact and the number of the formed ions.
- *Radiolytic yield*, G is the number of molecules (M) transformed by an energy equivalent to 100 eV absorbed

$$G = \frac{M}{100eV} \qquad (1)$$

This definition does not conform to International System units.

A new definition expresses G yield, as expressed in $mol \cdot J^{-1}$, equivalent to 9.65×10^6 molecules$/100$ eV, so that the defined value can be converted in I.S. units through multiplication with the 0.36×10^{-7} factor.

To determine the yield of radiolysis products there are considered the maximum yields of radiolytic decomposition of water in which:
-     W_a – the average ionization potential of water in the gas phase (30eV);
-     I_a – minimum ionization potential of water (12.56 eV)
-     E_a – the minimum excitation potential of water molecules (6.5 eV)
100 eV absorbed will form 100 / Wa water molecules ionized.

Formation of an ion consumes excitation energy equal to (W_a-I_a) eV, so, for $100/W_a$ ions, at absorption of 100eV there results an excitation energy of $100/W_a (W_a-I_a)$ eV.

In this way, due to excitation, there will be radiolysed $100(W_a-I_a) W_a E_a$ = water molecules.

$$G_a = \frac{100}{W_a} + \frac{100(W_a - I_a)}{W_a I_a} = \frac{100}{W_a}\left[1 + \frac{W_a - I_a}{E_a}\right] \text{molecules}/100eV \qquad (2)$$

$G_{a\ max}$ = 12 molecules$/100$eV.

In liquid phase $G_{a\ max}$ is approximately two times smaller.

In neutral aqueous solutions deaerated and irradiated with gamma radiation from a ^{60}Co source, the primary yield for radicals and molecules, in $\mu mol/J$ and atoms$/100$eV is shown in Table 2.

On the other hand, (Majer, 1982) radiolytic yield depends not only on the concentration (C_x) of the transformed reactant or on the reaction product occurred, but also on the irradiation time (t) with nuclear radiations having a rate dose (D):

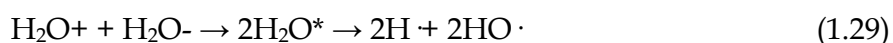$$G_x = \frac{C_x \cdot N}{D \cdot t} \cdot 100 \qquad (3)$$

N – Avogadro's number. Product $D \cdot t = D_a$ is dose of absorbed energy, expressed in $eV \cdot L^{-1} \cdot mol^{-1}$. Radiolytic yield for different species stable or unstable: $H\cdot$, $HO\cdot$, $HO_2\cdot$; H_2O_2, H_2, etc. is determined from the slope obtaining by plotting the previous relation (3) in coordinates $C_x = f (D_a)$.

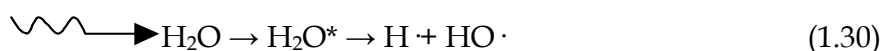The concentrations of chemical species encountered by primary irradiation ($H\cdot$ and $HO\cdot$) or subsequent reactions ($HO_2\cdot$; H_2O_2, H_2..) can be determined by physico-chemical methods such as: electron paramagnetic resonance (EPR), the pulse radiolysis, spectrophotometry etc. or from measurements of luminescence or radical capture.

Henglein proposed a similar formula to determine the radiolytic yield (Heinglein et al., 1969):

$$G_x = \frac{C_x \cdot N \cdot 100}{D_a \cdot g \cdot 1000 \cdot 6.24 \cdot 10^{13}} = \frac{C_x}{D_a \cdot g} \cdot 9.66 \cdot 10^8, \text{ mol} \cdot J^{-1} \qquad (4)$$

Given the sequence of chemical reactions initiated by nuclear radiation:

$$H_2O+ + H_2O- \rightarrow 2H_2O^* \rightarrow 2H + 2HO\cdot \qquad (1.29)$$

$$\text{WWW} \longrightarrow H_2O \rightarrow H_2O^* \rightarrow H + HO \cdot \tag{1.30}$$

$$H + H \cdot \rightarrow H_2 \tag{1.31}$$

$$HO \cdot + HO \cdot \rightarrow H_2O + O \tag{1.32}$$

$$HO \cdot + HO \cdot \rightarrow HO_2 \cdot + H \cdot \tag{1.33}$$

$$HO \cdot + HO \cdot \rightarrow H_2O_2 \tag{1.34}$$

$$H_2O_2 + HO \cdot \rightarrow H_2O + HO_2 \quad \cdot \tag{1.35}$$

$$H \cdot + O_2 \rightarrow HO_2 \cdot \tag{1.36}$$

It appears that the formation of a single pair of radicals $H\cdot$ and $HO\cdot$ (reaction 1.30) decomposes with a single molecule of water. For the appearance of molecular hydrogen (the stable product of radiolysis – reaction 1.31) two molecules of water will decompose, while producing a molecule of hydrogen peroxide (as a stable product) needed also two molecules of water (reaction 1.34).

The balance equation becomes:

$$G_{\left(-H_2O\right)} = G_{(H\times)} + 2G_{\left(H_2\right)} = G_{(HO\times)} + 2G_{\left(H_2O_2\right)} + 3G_{\left(HO_2\times\right)} \tag{5}$$

Type of γ radiation, 0.1-10MeV	Linear energy transfer, keV/μm	$G_{(H_2)}$ μmol/J	$G_{(H_2O_2)}$ μmol/J	$G_{(e_{aq})}$ μmol/J	$G_{(H)}$ μmol/J	$G_{(HO)}$ μmol/J	$G_{(HO_2)}$ μmol/J
pH=3-11	0.20	0.047	0.073	**0.28**	0.06	**0.28**	0.0027
pH=0.46	0.20	0.041	0.081	0	0.378	**0.301**	0.0008
		$G_{(H_2)}$ at/100eV	$G_{(H_2O_2)}$ at /100eV	$G_{(e_{aq})}$ at/100eV	$G_{(H)}$ at/100eV	$G_{(HO)}$ at/100eV	$G_{(HO_2)}$ at/100eV
pH=3-11	0.20	0.45	0.704	**2.7**	0.579	**2.79**	0.026005
pH=0.46	0.20	0.39	0.78	0	3.64	**2.9**	0.0077

Table 2. Primary radiolytic yield values for ions and radicals from irradiated water at 25 °C.

The values from Table 2 show that the prevalent species are the solvated electron and the OH radical.

In the range of pH = 3-12, forming efficiency of primary species does not vary, but the radicals may be located in various chemical forms depending on pH.

These existing acid-base equilibria are characterized by constant acidity / basicity.
For example, at pH = 7, $HO_2\cdot$, over 99 % of the radicals formed according to the reaction:

$$HO_2. \rightarrow H+ + O_2- \tag{1.35}$$

are represented as oxide, O^{2-}.
Table 3 shows acidic and basic forms of data and pK radicals.

Radicals	Acidic form	Basic form	pK
H·	H·	e^-_{aq}	9.6
e^-_{aq}	H·	e^-_{aq}	9.6
·OH	·OH	O·	11.9
$HO_2\cdot$	$HO_2\cdot$	O_2^-	4.8

Table 3. pK values for acidic and basic forms of the radicals formed from water radiolysis.

Among the primary species formed in the radiolysis reactions, important are the reactions of free radicals and radical solution.
Free radical reactions: the most species of free radicals are unstable in solution and hence highly reactive. They quickly recombine with each other to form stable molecular products.
As shown above, most of the molecular species formed during irradiation are formed by recombination of free radicals:

$$H. + H. \rightarrow H_2 \tag{1.36}$$

$$.OH + .OH \rightarrow H_2O_2 \tag{1.37}$$
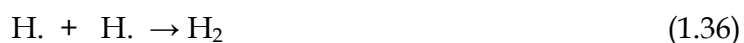
Radical reactions take place, generally, in solution and have fast kinetics.
Free radicals can react with molecules to form other molecules or free radicals, according to the general equation:

$$\text{Radical 1} + \text{Molecule1} \rightarrow \text{Radical 2} + \text{Molecule 2} \tag{1.38}$$
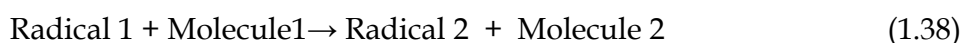
5.5 Considerations on the radiolytic yield (G_{H_2})

Mass spectrometer was calibrated before measurements of irradiated samples on the basis of resulted hydrogen in a total chemical reaction:
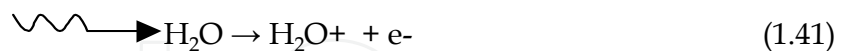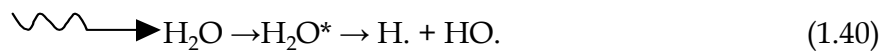
$$Zn + 2HCl_{dil} \rightarrow ZnCl_2 + H_2 \tag{1.39}$$

From 1.08 g Zn $\rightarrow$ 0.01 mol H_2 $\rightarrow$ the spectrogram corresponds in the table to a bit of $1.58 \cdot 10^6$ a.u. intensity (for anionic and cationic clays) and $2.68 \cdot 10^7$ a.u. for the species with mass number 2, respectively.
Schematic diagram of the measurements performed is given below:
Sample→ Mass spectrometer → PC→ Mass spectrogram
Before each measurement, to avoid any contamination of samples by chemical species remaining from the previous sample, the mass spectrometer was ensured a vacuum of 2.10^{-6} Torr. Mass spectrogram was recorded by a computer in coordinates peak intensity = f (Mass number), and recorded data were processed with chemistry program Origin 7.1.

It is well known that radiolysis of water through two stages, primary and secondary, leads to the formation of various chemical species such as: H_2, O_2, H_2O_2, $HO\cdot$, O, $HO_2\cdot$, etc. through a series of reactions with excited species, ionized and free radicals:

$$\rightsquigarrow H_2O \rightarrow H_2O^* \rightarrow H. + HO. \tag{1.40}$$

$$\rightsquigarrow H_2O \rightarrow H_2O+ + e- \tag{1.41}$$

$$H_2O + e- \rightarrow H_2O- \tag{1.42}$$

$$H_2O+ + H_2O- \rightarrow 2H_2O^* \tag{1.43}$$

$$H. + H. \rightarrow H_2 \tag{1.44}$$

$$HO. + HO. \rightarrow HO_2. + H. \tag{1.45}$$

$$H. + O \rightarrow HO. \tag{1.46}$$

$$HO. + HO_2. \rightarrow H_2O_2 + O. \tag{1.47}$$

Considering that energy transfer from the catalyst to water molecules plays an important role in the decomposition of water in the presence of catalyst, radiolysis can be expressed as:

$$XX^*(\text{activated state}) \tag{1.48}$$

$$X^* + H_2O \rightarrow [H_2O.X]^*(\text{activated complex }) \tag{1.49}$$

$$[H_2O.X]^* \rightarrow H. + HO. + X + h\nu \tag{1.50}$$

To calculate the *radiolytic yield* of hydrogen, Henglein's formula:

$$G = \frac{c \cdot N_A \cdot 100}{D_a \cdot \rho \cdot 1000 \cdot 6.25.10^{13}} = \frac{c}{D_a \cdot \rho} \times 9.66.10^8 \tag{6}$$

where:
D_a – absorbed dose Gy (1J/kg or 6.24. 10^{13} eV/g) representing the product of dose debit (D) and irradiation time (t)
ρ -   density of irradiated material (g/cm^3)
N_A –Avogadro number
Considering that:

$$c = b \cdot \frac{I_x}{I_{et}} \tag{7}$$

Radiolytic yield of hydrogen resulted from radiolysis are calculated with the expression derived:

$$G_{H_2} = \frac{b \cdot I_x}{D \cdot t \cdot \rho \cdot I_{et}} \cdot 9.66 \times 10^6 \tag{8}$$

where:

$$D \cdot t = D_a - \text{is absorbed dose in Gy} \qquad (9)$$

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

b – amount of hydrogen resulting from the spectrometer calibration (mol H$_2$/1kg H$_2$O)

I_{et} – intensity peak corresponding to molecular hydrogen from the reaction mass spectrometer calibration

I_x – intensity peak corresponding to molecular hydrogen from the reaction of catalyzed radiolysis

Radiolytic yield was calculated for:

$b = 1.53$ mol H$_2$/ 1kg H$_2$O, Iet $= 2.68 \cdot 10^7$ arbitrary unit (cationic and anionic clays)

$b = 1.556$ mol H$_2$/ 1kg H$_2$O, Iet $= 1.58 \cdot 10^7$ arbitrary unit (catalyst with and double perovskitic oxides)

In mass spectrograms there have identified a number of species (H$_2$, O$_2$, H$_2$O$_2$, HO·, O·, HO$_2$·), but radiolytic yield was established only for molecular hydrogen, which is a stable product of radiolysis. The other identified species (HO·, HO$_2$·…) may occur in the ionization source mass spectrometer from the decomposition of molecules of water (as vapor), whereas as free radicals, disappear immediately.

6. Experimental part

In order to study the catalyzed radiolysis of water under the action of nuclear radiation, with hydrogen release, there were used two types of catalysts:

a. *Clays.*

In this case natural anionic clays have been used, such as: (MgZn$_2$Al, Zn$_2$Al, Zn$_2$CuAl, Mg$_2$Al) and cationic R$_1$ and C$_1$ pillared with: Cr, Fe, Al and Ti.

Raw clay (R$_1$, C$_1$) have a complex mineralogical composition: SiO$_2$ – 69.61 %, Al$_2$O$_3$ – 19.7 %, MgO – 2.41 %, Fe$_2$O$_3$ – 1.27 %, Na$_2$O – 1.31 %, K$_2$O – 0.18 % etc. The cation exchange capacity (CEC) of 82 mEq/100 g clay was determined with ammonium acetate, and the specific surface area is between 140-142 m^2 / g.

At first there were prepared clays of the type C$_1$-Na and R$_1$-Na by cations exchanges naturally present, by dispersing those raw solid mass skins in a solution of 1M NaCl at a temperature of 22 °C and a contact time of 12 hours.

After that, the solid clay was separated by centrifugation as C$_1$-Na or R$_1$-Na of the remaining solid solution and dried at 110 °C. Clay particle size range was 0.2-0.8 mm (Van Olphen, 1963).

To obtain a microporous material with increasing interlamelare space and volume of pore, was performed Keggin inserting of the polications Al$_{13}^{7+}$ between the layers of clay, resulting in pillared samples (C$_1$-Al and R$_1$-Al) with a specific surface of 280 m^2/g and 320 m^2/g, respectively. Pillars of the cationic clays C$_1$-Na and R$_1$-Na with other cations were obtained by ion exchange Na-M^{n+} where M^{n+} is Cr^{3+}, Fe^{3+} and Ti^{2+} (Asaftei et al., 2002; Popovici et al., 2006).

b. *Site zeolites and mesoporous silica MCM-41.*

The Pt^{2+}-ZSM-5 samples with different SiO$_2$/Al$_2$O$_3$ ratios were prepared by ion exchange: H$^+$-ZSM-5-Pt^{2+} in a solution of H$_2$PtCl$_6$ (10^{-3}M) at a temperature of 22 °C and at a time 10 contact hours. Afterwards, the zeolitic precipitate was washed with distilled water and dried at 110 °C. Platinum content was 1-2%. The same process was applied to NH$_4$ – ZSM-5.

In order to prepare mesoporous silica MCM-41, there was made a mixture of: 27.3 % SiO_2 and 10.8 % NaOH, hexadecyl-trimethyl ammonium bromide, $C_{16}H_{33}N(CH_3)_3Br$ and H_2SO_4 (95 %), having the following molar ratio: 1m SiO_2: 0.297 m NaOH: 0.414m $C_{16}H_{33}N(CH_3)_3Br$: 0.277m H_2SO_4: 82.54m H_2O. After a contact time of 30 minutes, there has been obtain a gel which was then placed in an autoclave at 105 °C for 48 hours. After that, the resulting solid product was washed and dried at room temperature (Mastalir et al., 2008; Zholobenko et al., 1997).

The experiments proceeded as it follows (Cecal et al., 2008; Hauta et al., 2009): different amounts of each catalyst were weighed and introduced in 50 ml bottles, over which 30 ml distilled water were added. Then the glass vials were sealed with rubber cork, paraphyned outside and subjected to various doses of radiation energy. The stable radiolysis product, H_2, resulted in the above reactive systems, was determined quantitatively by a mass spectrometer, previously calibrated. The relationship between the irradiated sample and mass spectrometer was performed with a special device, which had at one end a chromatographic syringe needle that pierced the rubber stopper.

The obtained experimental results are represented in the following figures:

a.   b.
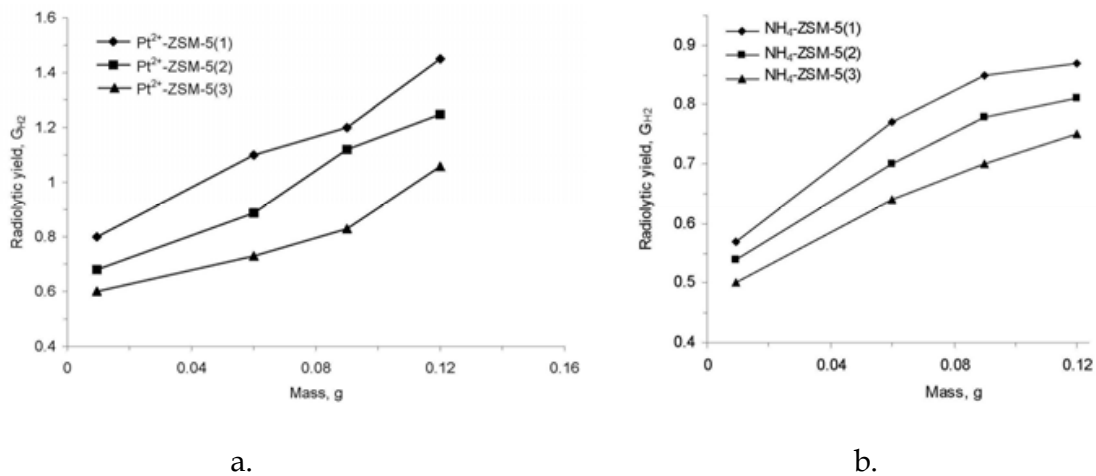
Fig. 1. Plots of radiolytic yield vs catalyst mass for a) Pt^{2+}-ZSM -5 and b) NH_4-ZSM-5 with different SiO_2/Al_2O_3 ratios SiO_2/Al_2O_3 = 140, (2) SiO_2/Al_2O_3 = 80, (3) SiO_2/Al_2O_3 = 15.
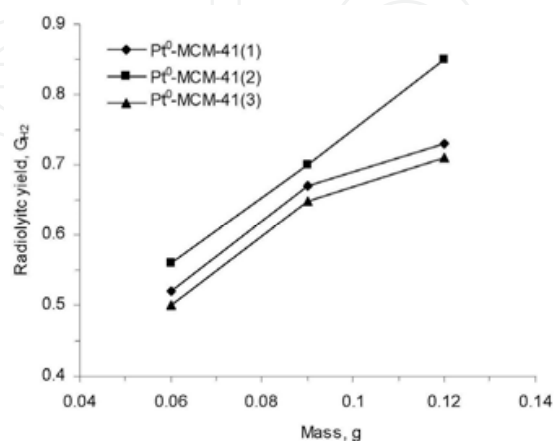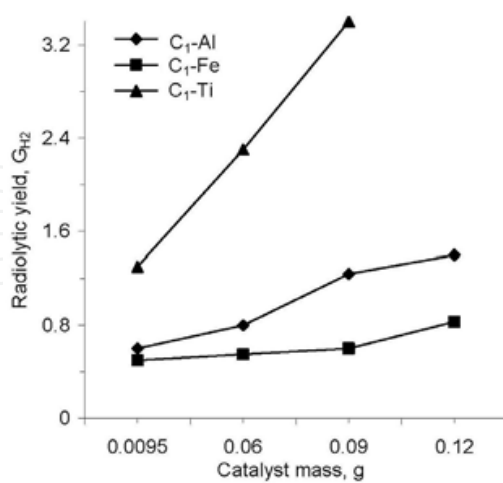

Fig. 2. Plots of radiolytic yield vs. catalyst mass for Pt^0-MCM-41 impregnated for 1) short temps 2) long temps, 3) before irradiation.
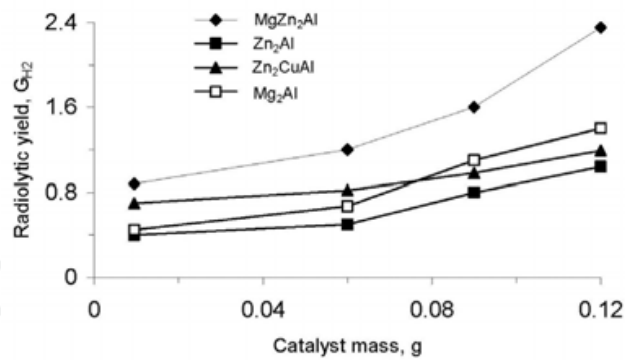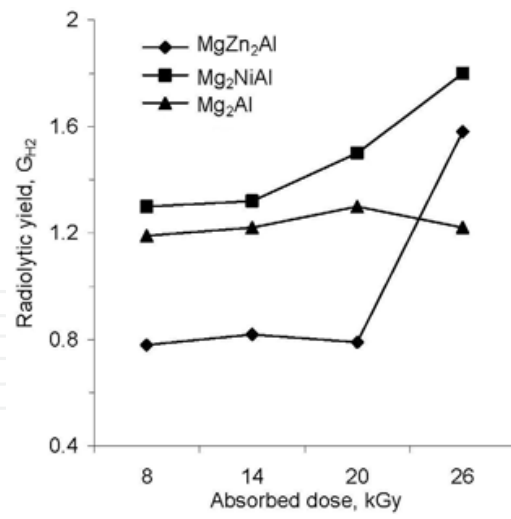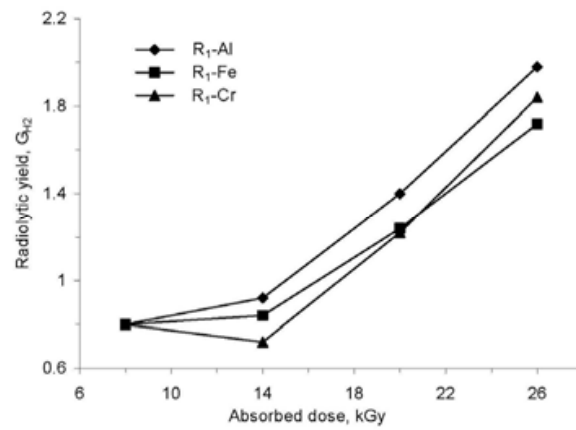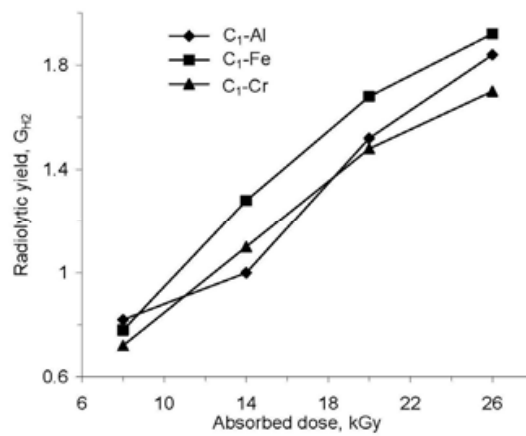
3.1
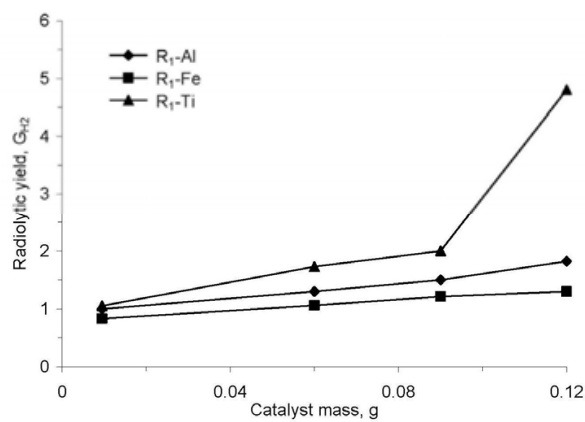
3.2

3.3

Fig. 3. Dependence of radiolytic yield of molecular hydrogen on the catalyst amounts for: (3.1) anionic clays; (3.2) R_1-clays and (3.3) C_1-clays.

4.1

4.2

4.3

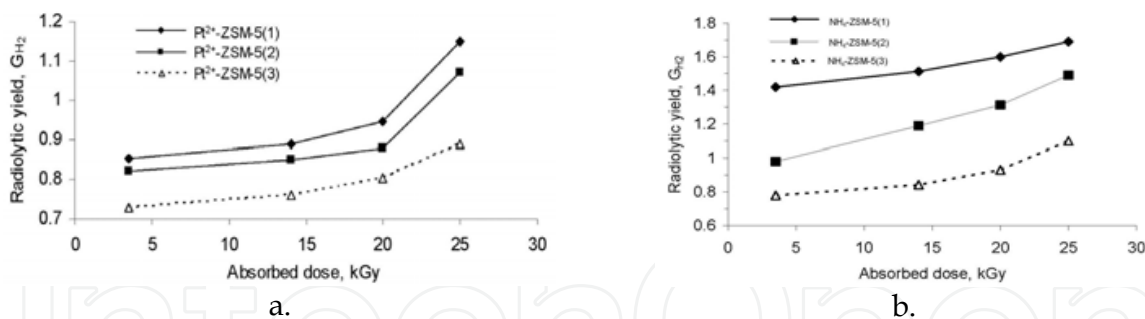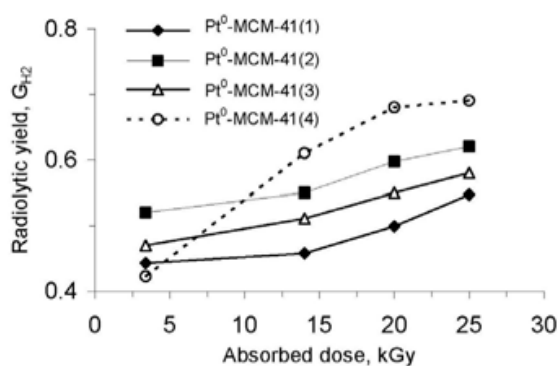Fig. 4. Variation of radiolytic yield (G_{H_2}) vs. absorbed dose for: (4.1) anionic clays, (4.2) R_1-clays and (4.3) C_1-clays.

a.

b.

Fig. 5. Plots of radiolytic yield vs. absorbed dose for: a) Pt^{2+}-ZSM-5 and b) NH_4-ZSM-5 with different SiO_2/Al_2O_3 ratios (1) $SiO_2/Al_2O_3 = 140$, (2) $SiO_2/Al_2O_3 = 80$, (3) $SiO_2/Al_2O_3 = 15$.

Fig. 6. Plots of radiolytic yield vs. absorbed dose for: a) Pt^0-MCM-41 impregnated samples for 1) short temps 2) long temps, 3) before irradiation, 4) after irradiation.

It is worth mentioning that the release of hydrogen was obtained only in the catalyst samples, previously subjected to irradiation with γ radiations.

Explanations of the catalytic effects could be: the catalytic role of clay could be explained by facilitating the appearance of intermediate structures.

In the case of clays studied as catalysts in water radiolysis, it can be considered that in active status, the catalyst creates a structural availability so that dipole water molecules can penetrate its pores.

In this excited configuration of the catalyst, water molecules are subjected to Coulomb forces of attraction-repulsion of the ionic species in the clay structure.
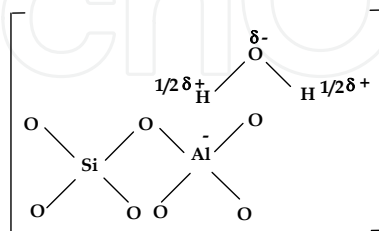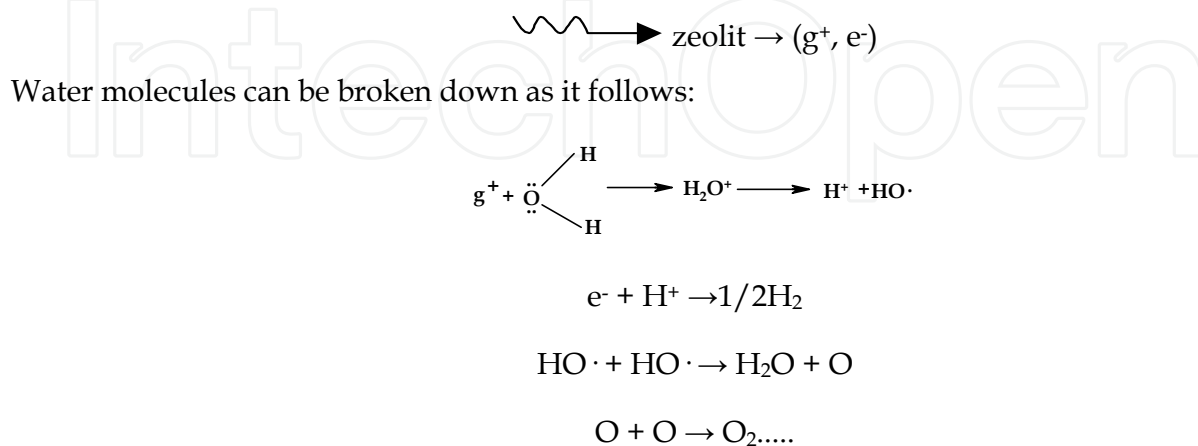

Under the action of gamma radiation, H-OH bonds in water molecules adsorbed on the catalyst surface will be easier to split towards non-adsorbed water molecules.

It has been noticed an increasing amount of hydrogen resulted from water radiolysis in the presence of clays in comparison with the reference sample, irradiated under the same experimental conditions. In the case of pillared clays, greater efficiency in the decomposition of water have the pillared with Ti.. Pillared clays R_1-metal had an important catalytic effect

towards C_1-metal, probably due to SiO_2/Al_2O_3 different ratio and the presence of 3d series microelements. Ionic species in the composition of clay acts as Coulomb attraction-repulsion forces on the dipole water molecules, facilitating H-OH bonds break under the action of nuclear radiation.

In the case of zeolites, through the interaction of nuclear radiation on the surface, there might appear "charge carriers" e- and goals+, namely:

$$\rightsquigarrow \longrightarrow zeolit \rightarrow (g^+, e^-)$$

Water molecules can be broken down as it follows:

$$g^+ + \ddot{\underset{..}{O}}\genfrac{}{}{0pt}{}{\diagup H}{\diagdown H} \longrightarrow H_2O^+ \longrightarrow H^+ + HO\cdot$$

$$e^- + H^+ \rightarrow 1/2 H_2$$

$$HO\cdot + HO\cdot \rightarrow H_2O + O$$

$$O + O \rightarrow O_2.....$$

The differences reported in the radiolytic yields are due to the respective catalyst involved in the radiolytic splitting of water (Chemerisov et al. 2001; Gondal et al. 2004).

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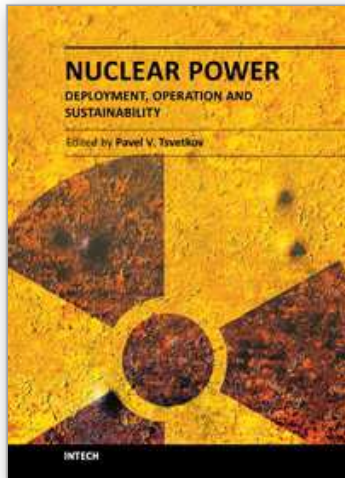
Nuclear Power - Deployment, Operation and Sustainability

Edited by Dr. Pavel Tsvetkov

We are fortunate to live in incredibly exciting and incredibly challenging time. Energy demands due to economic growth and increasing population must be satisfied in a sustainable manner assuring inherent safety, efficiency and no or minimized environmental impact. These considerations are among the reasons that lead to serious interest in deploying nuclear power as a sustainable energy source. At the same time, catastrophic earthquake and tsunami events in Japan resulted in the nuclear accident that forced us to rethink our approach to nuclear safety, design requirements and facilitated growing interests in advanced nuclear energy systems. This book is one in a series of books on nuclear power published by InTech. It consists of six major sections housing twenty chapters on topics from the key subject areas pertinent to successful development, deployment and operation of nuclear power systems worldwide. The book targets everyone as its potential readership groups - students, researchers and practitioners - who are interested to learn about nuclear power.

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