



Technical note

Use of some oxides in radiolytical decomposition of water

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Abstract

This paper deals with a study on the radiolysis of water in the presence of certain oxides: BeO, SiO₂, TiO₂, ZrO₂ acting as catalysts for the hydrogen production. A radionuclide of ⁶⁰Co with an activity of about 5×10^4 Ci was employed as an irradiation γ source. A considerable increase (up to ten times or more) of the amount of hydrogen resulting from the radiolysis of water in the presence of the above mentioned oxides was noticed in comparison with a reference sample, irradiated under the same experimental conditions, but without any catalyst. The radiolysis products have been identified by means of a method based on mass spectrometry. © 2001 Published by Elsevier Science Ltd.

1. Introduction

Due to the importance of hydrogen as a non-polluting energy source, several studies have been devoted to its production with respect to the profitable economic conditions in electrolysis, thermolysis, pyrolysis, etc., either in the presence or absence of certain substances, acting as catalyst in the decomposition of water or of other chemical compounds. Some series of well known thermodynamic cycles describing the decomposition of water under various experimental conditions have also been considered (Kliner et al., 1989; Nakashima and Masaki, 1996; Rooney and Lewis, 1996).

The appearance and development of nuclear energy initiated a lot of studies (Ibe and Uchida, 1985; Buxton, 1987; Bednar, 1989; Elliot, 1990; Henrie, 1990; Buxton and Elliot, 1991; Cobut et al., 1992; Elliot et al., 1992; Christensen et al., 1994; Ishigure et al., 1995; Wada et al., 1995; Katsumura et al., 1998) concerning the production of hydrogen through radiolysis of water under the action of both γ -rays and ionizing particles emitted by different radioactive nuclei or of neutrons.

The possibility of using radiation emitted by the unstable fission products which are contained in the spent nuclear fuel elements (10^7 – 10^9 Ci), for low-cost hydrogen production by catalyzed water radiolysis has also been mentioned.

2. Experimental

This paper describes a method for the production of hydrogen through catalyzed radiolysis of water on employing a γ radiation source of ⁶⁰Co with an activity of 5×10^4 Ci, at a dose rate of 8.6×10^4 Gy h⁻¹.

As catalysts, more oxides resistant to the action of nuclear radiations and with very low chemical reactivity on water splitting (under normal conditions), have been used: namely BeO, SiO₂, TiO₂ and ZrO₂. The catalysts specific surface area was determined using the BET method (Iordan et al., 1998). The obtained values were as follows: TiO₂ = 42.73 m² g⁻¹, ZrO₂ = 38.86 m² g⁻¹, BeO = 20.22 m² g⁻¹ and SiO₂ = 14.50 m² g⁻¹.

The amounts of the resulting radiolysis products, as well as of the air from the initially well closed vials subjected to irradiation, have been determined through mass spectrometry.

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The experiments have been performed in 30 ml glass vials that contained 10 ml distilled water and different amounts of solid catalysts: BeO, SiO₂, TiO₂ and ZrO₂. The vials were closed tightly, first with a rubber stopper, then with threaded lids.

For irradiation, the samples were placed around a ⁶⁰Co γ source ($\Phi \cong 0.3$ m) in a pool filled with water.

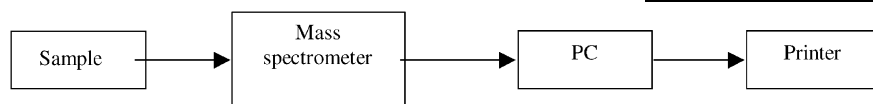
A suitable experimental device was built, for the transfer of gases from the irradiated vials into the mass spectrometer, with a tight connection between the two parts being assured by means of a chromatographic syringe needle.

The experiments were designed to determine the following:

- variation of the amount of hydrogen after irradiation (2×10^6 Gy) versus different amounts of oxides;
- variation of the amount of hydrogen as a function of irradiation time, having the same amount of catalysts.

The measurements of the gas volumes with the mass spectrometer (as peak intensity at a given mass number) have been performed 2 days after completion of irradiation.

The direct experimental results obtained in the mass spectrometer were recorded as mass unity versus peak intensity of the obtained radiolysis species (together with the air components inside of vials, which could not be avoided and removed). For this reason, the following devices schema was employed:

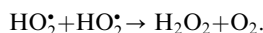
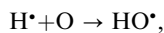
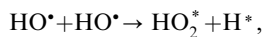
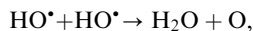
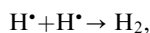
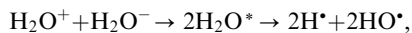
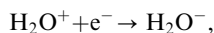
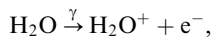
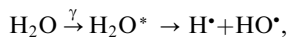


On the ordinates of the mass spectrograms, the peak intensities, which mean the amounts of given chemical species corresponding to different mass numbers, were represented in arbitrary units. But these units can be turned into the real amounts of hydrogen for example, using a non-irradiated, blank sample, prepared inside a closed vial with 10 ml NaOH solution (40%) and 0.1 g Al. The resulting hydrogen obtained after this chemical reaction is 1.12×10^{-2} g and corresponds to a peak intensity in the mass spectrogram of 2.85×10^6 arbitrary units.

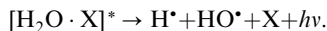
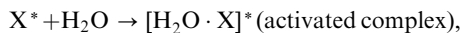
3. Results and discussion

It is generally known that after the radiolysis of water different chemical species appear, as follows: H₂, O₂, H₂O₂, HO•, O, HO₂• etc. (Draganic and

Draganic, 1971):



In presence of catalyst, the radiolysis can be represented as follows:



These species were found in the mass spectrograms.

These results were arranged as shown in Figs. 1 and 2.

The above given experimental data pointed out that:

1. The amounts of radiolytic hydrogen were higher in

the presence of BeO, SiO₂, TiO₂ or ZrO₂, compared with the uncatalyzed reference sample. No hydrogen was found after 5 days contact time between water and solid oxides in the mass spectrograms.

It may be possible that, under the action of γ rays the molecules of solid catalyst pass into an energetically activated state by forming with water unstable compounds of the [H₂OX*] type. This structure perhaps favors the radiolysis process and thus releases hydrogen through an indirect action of the radiation. The final results showed an amount of hydrogen (at least) 10 times higher in the presence of the above mentioned oxides than in the absence of these solid substances.

In the absence of catalysts, the hydrogen resulting from water radiolysis is less than 10⁴ a.u. in the mass spectra.

2. For each irradiated system under the two above-mentioned conditions (increasing of catalysts quantity

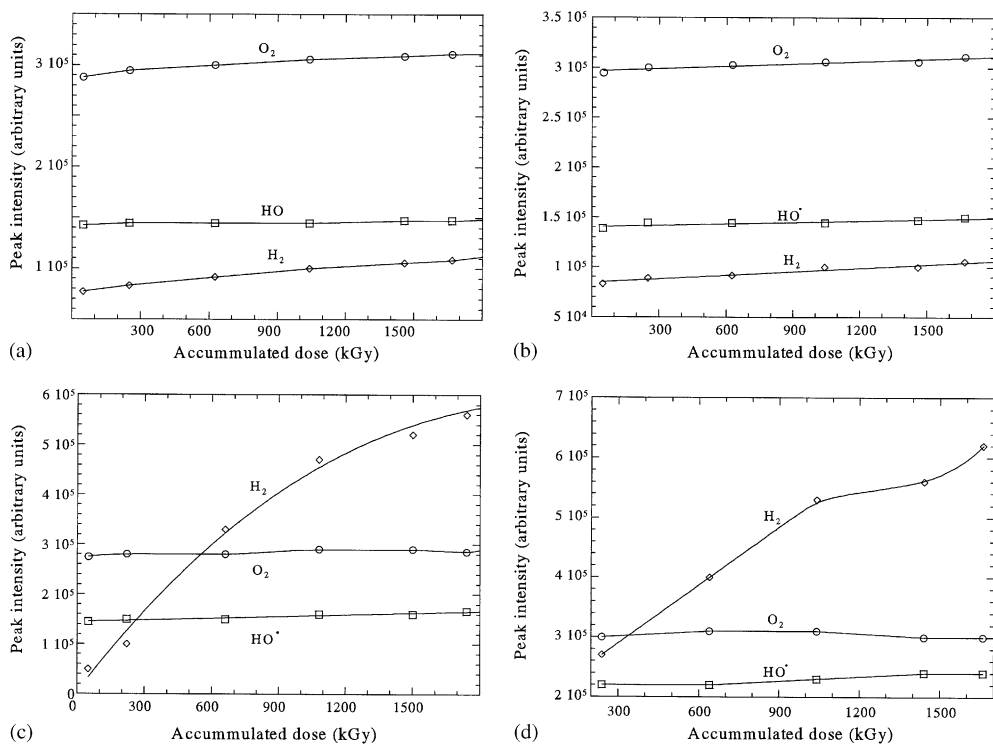


Fig. 1. Variation of the amount of radiolysis products versus the total absorbed dose for samples with 0.1 g catalyst: (a) BeO; (b) SiO₂; (c) TiO₂; (d) ZrO₂.

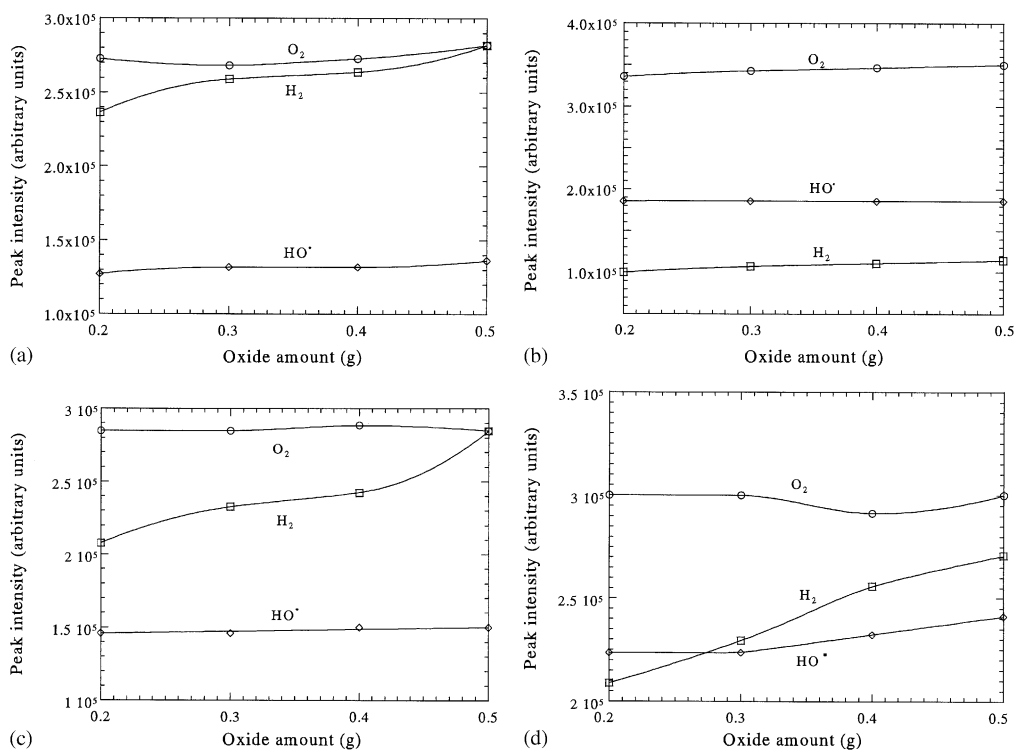


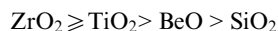
Fig. 2. Variation of the quantity of radiolysis products versus the amount of catalyst in the systems irradiated with 240 kGy: (a) BeO; (b) SiO₂; (c) TiO₂; (d) ZrO₂.

or irradiation time), the hydrogen production is much more pronounced. If the hydrogen released as a result of water radiolysis is found, on the whole, in the gases above the water in each tightly closed vial (besides oxygen and nitrogen from initial air), the quantity of oxygen resulting from the same process is not entirely found in this gaseous phase. It may be dissolved in water or may be adsorbed at the catalyst's surface, or it can form, to a very small extent, hydrogen peroxide or unstable HO_2^* radicals.

3. The amount of hydrogen produced increases as a function of dose and as a function of the amount of catalyst.

4. The presence of the species with mass number 17 may be explained either by the appearance of HO^* radicals formed by decomposition of activated water by catalysts, or by formation of NH_3 , in the irradiated systems which is less possible in the given experimental conditions.

5. The yield of water radiolysis products in the presence of the used catalysts (especially taking into account the hydrogen that appeared in this process) decreases in the series



in agreement with the specific surface area of these oxides and as shown in the Figs. 1(b) and 2(b).

Acknowledgements

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