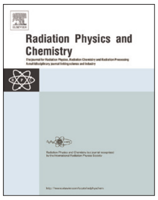
Radiation Physics and Chemistry 110 (2015) 6–11

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem



Hydrogen radiolytic release from zeolite 4A/water systems under γ irradiations

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HIGHLIGHTS

- We irradiated samples of zeolites 4A which contained different quantities of water.
- We measured the quantity of hydrogen released.
- Hydrogen radiolytic yields, present two maxima, for two water loading ratios.
- Hydrogen release is enhanced by the strength of the zeolite/water interaction.
- Hydrogen release is enhanced by the quantity of water interacting with the zeolite.

ARTICLE INFO

Article history:
Received 23 July 2014
Received in revised form
27 August 2014
Accepted 9 January 2015
Available online 10 January 2015

Keywords:
Zeolite
Adsorbed water
Radiolysis
Hydrogen
Molecular sieve
Microporous

ABSTRACT

Although the radiolysis of bulk water is well known, some questions remain in the case of adsorbed or confined water, especially in the case of zeolites 4A, which are used to store tritiated water. An enhancement of the production of hydrogen is described in the literature for higher porous structures, but the phenomenon stays unexplained. We have studied the radiolysis of zeolites 4A containing different quantities of water under ^{137}Cs gamma radiation. We focused on the influence of the water loading ratio. The enhancement of hydrogen production compared with bulk water radiolysis has been attributed to the energy transfer from the zeolite to the water, and to the influence of the water structure organization in the zeolite. Both were observed separately, with a maximum efficiency for energy transfer at a loading ratio of about 13%, and a maximum impact of structuration of water at a loading ratio of about 4%.

1. Introduction

Zeolites are widely used nanoporous materials. They are encountered in a broad field of applications, such as catalysis, filtration and isotopic separation (Kotoh et al., 2010, 2009; Montanari and Busca, 2008; Zhu et al., 2005). Zeolites A, which are hydrophilic, are also used to store tritiated water, generated and required by nuclear applications like ITER. This experimental reactor is supposed to produce, amongst other tritiated wastes, high quantities of pure tritiated water during its working period (Pamela et al., 2013). Its development requires safe storage solutions.

Synthetic zeolites A are built with corner sharing TO_4 tetrahedrons, where T corresponds to silicon or aluminum (Breck, 1974). At the nanometer scale, their crystalline structure is composed of two kinds of cages. Sodalite cages, also called β cages, are a truncated octahedral shape, with a diameter of 6.6 Å, disposed at each corner of a cubic arrangement. The second kind of cages, called supercages or α cages, are located in the center of this array, and are characterized by a diameter of 11.4 Å. Sodalites cages are linked together by prisms, called double-four-membered rings (D4R). The framework negative charge (induced by the aluminum valence) is compensated by cations, included in the structure. The nature and location of those cations affects the properties of the

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Abbreviations: WLR, water loading ratio; ZWS, zeolite 4A/water system

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http://dx.doi.org/10.1016/j.radphyschem.2015.01.008
0969-806X/

zeolite. In zeolites 4A, the positive charge is provided by monovalent sodium cations, leading to the following chemical composition for a unit cell: $[Na_{12}(SiO_4)_{12}(AlO_4)_{12}]$. The zeolite 4A is strongly hydrophilic. A unit cell can adsorb 27 molecules of water. Among those 27 molecules, some are commonly localized as molecules adsorbed in the crystalline structure: 4 or 5 in each sodalite cage and 20–23 in each supercage (Crupi et al., 2005; Demontis et al., 2008).

The quantity of water is expressed as water loading ratio (WLR) given in percentage, equal to the mass of water divided by the mass of zeolites. The maximum loading ratio for zeolites 4A depends on the synthesis method and the binder quantity, but is about 20%. It has been shown, considering the adsorption heat (Moïse et al., 2001) or FTIR results (Crupi et al., 2003), that the water adsorption is heterogeneous, and occurs in three-steps, leading to different kinds of confined water. The first adsorbed water molecules solvate the cations which then migrate, opening the access to the β cages. The α cages are then filled.

Even if bulk water radiolysis is well known, even in the case of self-radiolysis of tritiated water (Buxton et al., 1988; Ershov and Gordeev, 2008; Stolz et al., 2003), many questions remain about the radiolysis of adsorbed and confined water. An enhancement of hydrogen production, in some porous materials has been observed, for different irradiation conditions (Cecal et al., 2004; Le Caër, 2011; Le Caër et al., 2005; Rotureau et al., 2005). The same phenomenon is observed in the precise case of zeolites A (Nakashima and Aratono, 1993; Nakashima and Tachikawa, 1987), or structurally-closed zeolites: faujasites (Nakashima and Masaki, 1996), but the literature is quite limited in this area, even if the impact of confinement on radiolysis has been shown (Foley et al., 2005).

Since the interaction and behavior of water strongly depends on the loading ratio of zeolites, we followed gas production depending on the level of water filling of the zeolites. We chose gamma irradiations, which are close to β^- irradiations induced by tritiated water in terms of the dose rate. We took special care with respect to the dosimetry: the primary energy deposition in water is commonly estimated to be equal to the total energy deposited multiplied by its mass ratio (LaVerne and Tandon, 2002; LaVerne and Tonnies, 2003). We proposed an improvement of this consideration using Monte-Carlo simulation. We focused on the dihydrogen production since it may create, with dioxygen, an explosive atmosphere over a large range of concentration. We adopted two different approaches, regarding both primary energy deposition in the water and energy deposition in the whole system containing zeolites 4A and water.

2. Materials and methods

2.1. Sample conditioning

Synthetic hydrophilic zeolites 4A were supplied by Molsiv Adsorbents. Their maximum water capacity, expressed as the ratio of water mass under dried zeolite mass, given by the supplier is 19.6%. To improve the mechanical properties of zeolites 4A, a chemical inert non-porous binder, presenting the same atomic composition as the zeolites, is included during the synthesis. We estimated the proportion of binder by comparing the experimental water quantity adsorbed at saturation for our samples and that for a pure 4A sample, provided by CECA. The water saturation obtained by exposure to ambient water vapor, is investigated by thermogravimetry and is obtained as a mass percentage of 25% for pure zeolites, against 19% for our storage samples. The binder proportion is so estimated to be 24%. Nevertheless, as the atomic composition of binder is close to the one of pure zeolites, no significant influence on interaction sections, and thus on irradiation effects, is expected.

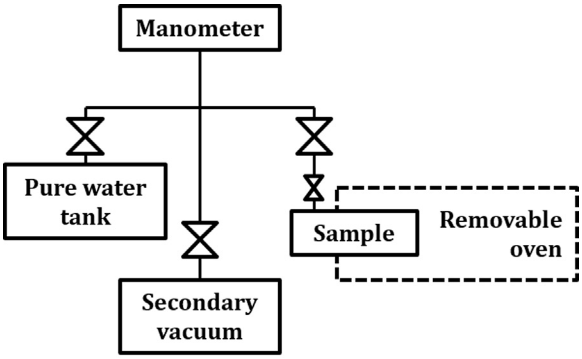

Fig. 1. Schematic representation of the bench used to adsorb controlled amounts of water.

4 g of zeolites 4A were introduced in 10 cm^3 air tight glass ampoules. Samples were then conditioned with a unique bench, comprising a pump, a pure water tank, a manometer and a junction to connect ampoules containing samples (Fig. 1). The use of a unique bench and of a unique ampoule for the different steps of samples conditioning prevents from the exposition of zeolites 4A to atmospheric water. As they are hydrophilic, such an exposition would have led to residual water adsorption by zeolites.

Each ampoule was degassed under vacuum at 623 K, during at least 12 h, to ensure the elimination of water from zeolites initially equilibrated with water vapor from the atmosphere. The complete dehydration has been checked by weighing, after isolation and removal of ampoules from the bench. Adsorption of controlled quantity of water, from about 3% to saturation, was realized by manometry. Zeolites were exposed to the chosen water vapor pressure, released in the line whose volume has been measured to 2.58 dm^3. The quantity of water adsorbed was thus pre-determined using the perfect gas equation, and checked by the mass increase. Details of the quantities of water adsorbed are given in Table 1.

Ampoules were then connected to the analysis bench, and filled with argon, used as gas carrier during irradiations and analysis, with a pressure of 1.46 bar. Each sample underwent several irradiations. The analysis line is also used to replace radiolysis gases after each irradiation and each measure, by pure argon. We then proceeded with the following irradiation.

2.2. Irradiations

γ Irradiations by a ^{137}Cs source were carried out with a dose rate of 5.4 Gy min^{-1}. The experimental dose was determined by irradiation using the Fricke dosimeter, irradiated under the same conditions as the zeolites samples (equivalent mass, equivalent ampoule and equivalent volume).

After the initial conditioning, consisting in water adsorption at controlled ratios, each ampoule underwent several cycles of irradiations. One cycle includes a filling with argon, used as the carrier

Table 1
Characteristics of irradiated zeolite 4A/water systems.

Water loading ratio (%)	3.1	4.1	5.6	7.1	13.0	19.1
F[a]	1.50	1.53	1.52	1.50	1.46	1.43
E_{water} (%)[b] (from mass ratio)	3.0	3.9	5.3	6.6	11.5	16.0
E_{water} (%)[b] (improved with MCNPX)	4.9	6.1	8.1	10.3	17.4	23.6

[a] Correction coefficient used to calculate total energy deposited in zeolite/water systems from energy deposited in the Fricke dosimeter.

[b] Percentage of total energy deposited in water.