

IRRADIATION OF CONTROLLED PORE GLASSES WITH 10 MEV ELECTRONS

S. Le Caër¹, P. Rotureau¹, G. Vigneron¹, G. Blain², J. P. Renault¹ and J.- C. Mialocq¹

¹CEA/Saclay, DSM/DRECAM/SCM/URA 331 CNRS, F-91191 Gif-sur-Yvette Cedex, France

²Laboratoire de Chimie Inorganique, Institut de Chimie Moléculaire d'Orsay, UMR 8613 CNRS, Bâtiment 420, Université de Paris-Sud, F-91405 Orsay Cedex, France

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Abstract. Controlled Pore Glasses (8-300 nm pore diameter) have been irradiated with 10 MeV electrons. H₂ production in dried or hydrated glasses was measured as a function of the pore size: it increases when the pore size decreases. In the case of hydrated glasses, the hydrogen peroxide formation has been observed too. EPR measurements clearly show that the number of defects created under irradiation is significantly smaller in the presence of water, which indicates that water protects the glasses from paramagnetic centers formation. Last, FT-IR spectra have been recorded before and after irradiation: for hydrated glasses, irradiation leads to a strong dehydration of the system.

1. INTRODUCTION

Dihydrogen production by water radiolysis is a general problem encountered in the storage and disposal of nuclear wastes. However, although dihydrogen production has been extensively studied in the liquid phase [1-8], only few investigations exist for nuclear wastes, which are complex heterogeneous systems. Nevertheless, a few studies have been devoted to the description of the mechanisms leading to the H₂ production by radiolysis of water on model oxide surfaces [9-11]. The common understanding is that it is highly dependent on the substrate chemistry and in general more efficient than in pure water without any catalyst [12, 13].

We have focused our attention on mesoporous silica-water systems, especially controlled pore

glasses (CPG) [14] which can be obtained in various pore sizes. These porous materials together with various water fillings provide a well-characterised model system to mimic hydrated storage materials, with an emphasis on the effects of water confinement on dihydrogen production.

We have measured the H₂ production in the case of dried and hydrated glasses irradiated with 10 MeV electrons [15]. The results, summarised in Table 1, show that the dihydrogen radiolytic yield increases when the pore size decreases. Even though most of the hydrogen production comes from the nanoconfined water, there is also a contribution coming directly from the glass. Therefore it is important to know what is the hydrogen source in the glass and whether the oxidative species constituting the

Corresponding author: S. Le Caër, e-mail: lecaer@drecam.cea.fr

counterpart to hydrogen are produced in the pore or trapped in the glass.

To try to answer this question, the porous materials have been characterized in the present study before and after irradiation by means of EPR and FT-IR techniques.

2. EXPERIMENTAL SECTION

CPG glasses. The glasses used in the present study are borosilicate glasses mainly composed of 96.3% of SiO₂ and 2.95% of B₂O₃ [16]. They contain randomly interconnected pores with mean diameter ranging from 8 to 300 nm. The thickness of the walls increases with the pore size [17]. All characteristics for the CPG glasses under study (mean pore diameter, pore volume, specific area) are summarised in Table 2.

Preparation of the samples. Heat treatments were performed in air, using a muffle furnace. Dried (respectively hydrated) materials were obtained after baking at 140 °C for one hour and then at 500 °C during 6 hours (respectively at 400 °C during one hour). The glasses were then stored overnight at 60 °C before drying them under vacuum at 200 °C to further remove any moisture. We have checked by XPS spectroscopy that the thermal treatment of the hydrated glasses is sufficient to remove any trace of carbon. In this case, ultra-pure water with a conductivity of 18.2 MΩ and a very low total organic carbon content from a Millipore Alpha-Q apparatus was introduced in porous materials by capillary wetting. The volume of introduced water was fixed to 250 μL and the weight of the glass was calculated to saturate the pore volume.

The irradiation cell was designed so as to have a good overlapping of the sample with the electron beam. It was filled with 95 mg of glasses or glass-water samples and deaerated by several cycles of vacuum/argon exposure.

Irradiation with 10 MeV electrons. The irradiations were performed using the electron pulses of a

Table 1. Evolution of the dihydrogen radiolytic yield in dried and hydrated CPGs as a function of the pore size [15].

| Pore diameter of the glass (nm) | $G(\text{H}_2)$ (mol·J ⁻¹) | $G(\text{H}_2)$ (mol·J ⁻¹) |
|---------------------------------|--|--|
| | Dried glasses | Hydrated glasses |
| 8 | $(2.4 \pm 0.9) \cdot 10^{-9}$ | $(9.3 \pm 0.9) \cdot 10^{-8}$ |
| 25 | $(1.7 \pm 0.3) \cdot 10^{-9}$ | $(5.9 \pm 0.6) \cdot 10^{-8}$ |
| 50 | $(1.3 \pm 0.1) \cdot 10^{-9}$ | $(5.8 \pm 0.6) \cdot 10^{-8}$ |
| 300 | $(5.1 \pm 0.4) \cdot 10^{-10}$ | $(5.1 \pm 0.5) \cdot 10^{-8}$ |

Titan Beta, *Inc.* linear accelerator of 10 MeV electrons. The energy bandwidth of the electrons is ±15% [18]. In the present experiments, 10 ns pulses were used which enables us to work with a high repetition rate (30 Hz) and thus, to reach high doses (for example 1 MGy) in a reasonable exposure time (roughly 30 minutes). Under these conditions, the dose rate is 1.7 Gy/ns.

EPR measurements. The X band EPR studies were performed on a Bruker Eleksys 500 spectrometer at 100K using an Oxford cryogenic equipment. The microwave frequency was 9.39 GHz with a microwave power of 2.0 mW. Experiments were carried out with a four scans accumulation, a modulation amplitude of 0.25 mT and a 100 kHz modulation frequency. A Bruker NMR teslameter was used in order to increase the field measurement precision.

Diffuse reflectance spectroscopy. Diffuse reflectance UV spectra were recorded by means of a Varian (Cary 500) spectrophotometer equipped with a Praying Mantis (Harrick) accessory. The reference spectrum was always the non-irradiated sample.

FT-IR spectroscopy. FT-IR experiments were carried out on KBr pellets. All the spectra were obtained by accumulating 200 scans with a Bruker Vertex 70 equipment operating at 0.5 cm⁻¹ resolution. The background was always subtracted.

Table 2. Characteristics of the CPG glasses under study [17].

| Glass | Mean pore diameter (nm) | Pore distribution (±%) | Pore volume (cm ³ /g) | Specific area (m ² /g) |
|-----------|-------------------------|------------------------|----------------------------------|-----------------------------------|
| CPG00075C | 8 | 9 | 0.49 | 197 |
| CPG00240C | 25 | 6.8 | 0.96 | 82 |
| CPG00500C | 50 | 2.9 | 1.09 | 44 |
| CPG03000C | 300 | 5.9 | 1.1 | 8.4 |

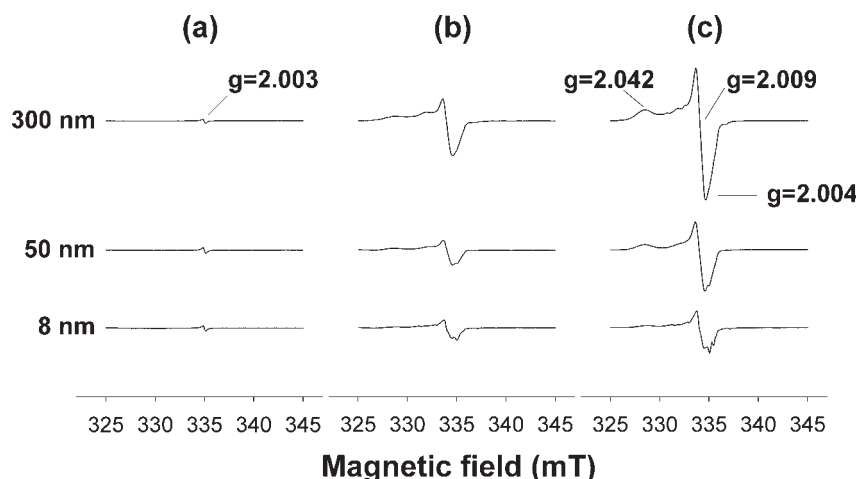


Fig. 1. EPR spectra of the 300, 50 and 8 nm pore diameter CPG – a) dried, b) hydrated and after 1 MGy irradiation, c) dried and after 1 MGy irradiation.

3. RESULTS AND DISCUSSION

3.1. EPR measurements

EPR spectra are given in Fig. 1 in the case of the 8, 50, and 300 nm pore diameter glasses before irradiation (Fig. 1a) and after irradiation for hydrated glasses (Fig. 1b) and dried glasses (Fig. 1c). The g values obtained may correspond to oxygen-associated hole centers (OHC's) as designated by Stapelbroek *et al.* [19,20] who distinguished the 'wet' OHC for $\equiv\text{SiO}\cdot$ and the dry OHC for the peroxy radical $\equiv\text{SiOO}\cdot$ (the ' \equiv ' notation denotes three bonds of the silicon atoms with oxygen atoms). The 'wet' OHC which consists of a hole trapped on a single nonbridging oxygen [20] is also called nonbridging oxygen hole center (NBOHC, $\equiv\text{SiO}\cdot$) [21-23]. The signal shape we have obtained is more in agreement with 'dry' OHC ($\equiv\text{SiOO}\cdot$) which has g values near 2.04. So, the EPR spectra can be attributed to peroxy radicals. The presence of these defects in the bulk of the material has been evidenced by the fact that the EPR spectrum does not change when exposed during a long time to a paramagnetic gas (dioxygen in our case). Last, we did not observe $\equiv\text{Si}\cdot$ type of defects.

Figs. 1b and 1c clearly evidence that the amount of defects formed in dried or hydrated glasses increases when the pore size increases, or when the specific area decreases. This is consistent with the presence of defects in the bulk of the glass, as the thickness of the silica walls increases when the pore size increases. When comparing Fig. 1b with Fig. 1c, one may notice that the number of created de-

fects is much smaller in the presence of water, which indicates that the hydration of the glass protects significantly the glass from paramagnetic centers formation.

3.2. Diffuse reflectance spectroscopy

Diffuse reflectance spectroscopy of dried glasses enables us to confirm the formation of peroxy radicals under irradiation. As a matter of fact, for the dried glass of 8 nm pore diameter irradiated at 1 MGy, we obtained by diffuse reflectance measurements a peak around 5.3 eV with a half width of 0.7 eV at room temperature (see Fig. 2). No photoluminescence bands were detected. The results are consistent with the presence of $\equiv\text{SiOO}\cdot$ radicals [24].

Moreover, we have recorded the diffuse reflectance spectrum for glasses filled with hydrogen peroxide in the 200-240 nm region: it is very similar to that of H_2O_2 [25]. Last, it is very similar to the spectrum obtained when irradiating hydrated glasses. This leads us to conclude that hydrogen peroxide is formed upon irradiation of hydrated glasses.

3.3. FT-IR spectra

The FT-IR spectra of hydrated 8 nm pore diameter glass in the 3000-4000 cm^{-1} region before and after irradiation are depicted in Fig. 3. This region is attributed to hydroxyls stretching [26], namely:

- O-H stretching of adsorbed water molecule for the 3400-3500 cm^{-1} energy range;
- SiO-H stretching of adjacent pairs of SiOH groups with hydrogens bonded to each other for the 3540-3550 cm^{-1} region;

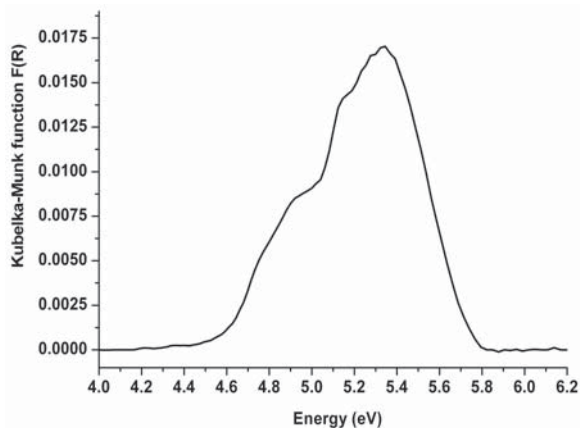


Fig. 2. Diffuse reflectance spectrum of the dried 8 nm pore diameter glass irradiated at 1 MGy. The reference spectrum is the non-irradiated glass.

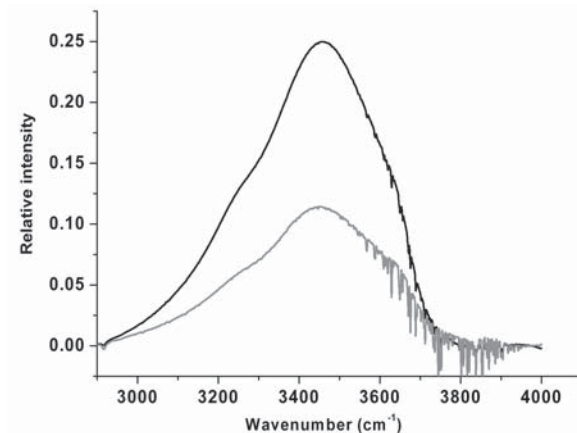


Fig. 3. FT-IR spectra in the 3000-4000 cm^{-1} region of the hydrated 8 nm pore diameter glass. The spectrum before irradiation is represented with a black line; the spectrum after 4 MGy with a grey line.

- SiO-H stretching of isolated pairs of adjacent SiOH groups (vicinal) mutual hydrogen bonded for the 3650-3660 cm^{-1} energy range.

The spectrum before irradiation is very similar to the one obtained in the case of water [27]. After irradiation, a strong dehydration of the system is observed. Moreover, the shape of the spectrum changes: the shoulder at 3600 cm^{-1} increases after irradiation and evidences the silanol groups, as water is consumed to form H_2 and H_2O_2 .

4. CONCLUSION

Under irradiation with 10 MeV electrons, dried or hydrated Controlled Pore Glasses (in the 8-300 nm pore diameter range) lead to the formation of H_2 . Moreover, hydrogen peroxide is formed under irradiation of hydrated glasses. Several techniques have been used to characterize the glasses after irradiation. EPR measurements and diffuse reflectance spectroscopy show that $\equiv\text{SiOO}\cdot$ radicals are created in the bulk of the material after irradiation. Moreover, the presence of water protects the materials from the creation of these radicals. Last, FT-IR spectra prove that irradiation is associated to a dehydration of the system.

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