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Evolution of silica walls of nanopores filled with water and ions

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Abstract

The prediction of the evolution of nanoporous materials is of great interest in various fields particularly geology, environmental sciences, and nuclear waste management. Such prediction requires the use of modeling which is generally not adapted to confined media of few nanometers.

In the present study, we have characterized the evolution of hexagonal mesoporous silica having 5 nm pore size (SBA15 type) at 50°C in water and in 0.2 M XCl₂ aqueous solutions, where X are different ions (X = Mg²⁺, Ca²⁺, Fe²⁺, Ba²⁺), by in-situ Small Angle X-ray Scattering. The results allowed determination of the dissolution rates of the confining media, i.e. the silica, and water diffusion through the microporous silica wall as a function of the aqueous solution composition.

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Keywords: nanoporous silica; confined media; dissolution; water diffusion; SAXS; aqueous solution

1. Introduction

The prediction of the evolution of nanoporous materials such as clay materials, mineral phases, and alteration layers during alteration by aqueous solution is of great interest in various fields such as geology, environmental sciences, membranes, catalysis and nuclear waste management. Such prediction requires the use of modeling which is generally not adapted to confined media of few nanometers since the thermodynamic models and rate laws used are commonly rely on data obtained in diluted media⁰. Indeed, in confined media, water reactivity can be modified by the strong interactions between water molecules and pore surfaces, structuring water molecules and slowing down water motions from nanoscale to macro-scale. These interactions depend on the composition, the pore morphology and the surface topology⁰. Furthermore, it is also expected that nanoconfined water molecules are strongly influenced by the presence of ions through sorption processes with the surface and ion solvation. Such

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phenomenon is of primary importance since the ion adsorption on the surface and the ion solvation strongly impact the hydrolysis rate of materials^{0,0,0,0} and can modify the kinetics of dissolved elements recondensation into the pore.

Up to now, the characterization of the evolution of nanoporous materials in aqueous solution was based on bulk solution analysis. This makes the determination of the hydrolysis and condensation rates of the confining materials difficult. Moreover, the characterization of such systems is really complex and even atomistic modeling is not capable of reproducing the chemical processes. Recently, we have shown⁰ that in-situ characterization using Small Angle X-ray Scattering (SAXS) of model materials such as highly ordered mesoporous silica materials (SBA15 and MCM41 types) in water allowed the determination of a pore wall dissolution rate and a diffusion coefficient of water through the microporosity of the silica wall. The use of such model materials is a first step to understand basic processes involved in confined media, which are more difficult to characterize in natural confined materials.

In the present study, based on the same method, we have characterized the evolution of hexagonal mesoporous silica having 5 nm pore size (SBA15 type) at 50°C in water and in 0.2 M XCl₂ aqueous solutions (X = Mg²⁺, Ca²⁺, Fe²⁺, Ba²⁺) by in-situ Small Angle X-ray Scattering. The obtained results allowed the determination of several values as a function of the aqueous solution such as the dissolution rates of the confining media, i.e. the silica, and the water diffusion through the microporous silica wall.

2. Materials and Methods

SBA15 silica was prepared using the method described in⁰. A specific surface area of $S_{\text{BET}} (\text{m}^2 \cdot \text{g}^{-1}) = 863 \text{ m}^2 \cdot \text{g}^{-1}$, a porous volume $V_p(\text{BJH}) = 0.92 \text{ cm}^3 \cdot \text{g}^{-1}$ and a pore size of 4.3 nm were obtained from nitrogen adsorption-desorption (77 K) analysis. A pore wall thickness of 6.6 nm was determined by SAXS.

Alteration experiments of silica were performed at 50°C in various 0.2 M XCl₂ (X = Mg²⁺, Ca²⁺, Fe²⁺, Ba²⁺) aqueous solutions at a silica surface area to solution volume ratio (S/V) ranging between $0.25 \cdot 10^8$ and $0.6 \cdot 10^8 \text{ m}^{-1}$ i.e a S/V_{pore} around $9.4 \cdot 10^8 \text{ m}^{-1}$. The initial pH_{20°C} of the solutions were comprised between 5.2 and 5.7.

The evolution of the silica powder porosity was determined using in-situ SAXS characterization. Silica powder and the aqueous solution were inserted in a 2 mm diameter capillary. The capillary was sealed and then placed in an oven at $50 \pm 2^\circ\text{C}$ specifically dedicated to SAXS analysis. Scattering measurements were performed over 60 hours. The SAXS experiments were performed in the transmission geometry, using a molybdenum anode delivering a wavelength of 0.71 Å. The monochromation is achieved using a Xenocs Fox2D multishell mirror. Two sets of scatterless slits allow the beam to be collimated and to have a squared shape of side 0.8 mm. SAXS patterns are recorded on a MAR345 2D imaging plate, which enables the simultaneous detection over scattering vectors q ranging from 0.3 to 10 nm^{-1} .

From SAXS patterns, the ratio I₂/I₃ corresponding to the respective intensity of the Bragg peaks B₂ and B₃ indicated on the Fig. 1 was determined. The evolutions of this ratio as a function of time were related to a change of pore size. The values of I₂/I₃ were fitted using the model of Cambedouzou et al., already presented in details in^{0,0}. In this model, arrays of cylindrical pores of infinite length and of pore radius r_p having a Gaussian distribution are disposed on a hexagonal lattice with a paracrystalline disorder. Moreover, a layer of altered silica having a width denoted hlw , in the vicinity of the pores edge is included. Fig. 3 presents a schematic view of the mesoporous material and the fitted parameters.

3. Results and discussion

SAXS patterns obtained during silica alteration in the aqueous solutions are presented in Fig.1. The relative intensities I₂ and I₃ continuously evolve, showing a higher progressive decrease of I₂ than I₃ during alteration for all the experiments except for the SBA15 in FeCl₂ solution. In FeCl₂ solution, the possible precipitation of iron silicates can clog the porosity limiting the alteration of the silica pore wall. The position of B₂ and B₃ remains the same during the whole experiment, indicating that there is neither contraction nor dilatation of the pore lattice.

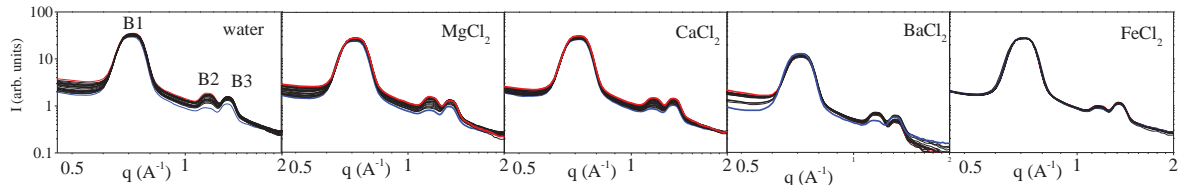


Fig. 1. Experimental SAXS patterns of the SBA silica during alteration in the various aqueous solutions at 50°C. blue line: t = 0 h and red line: t = 60 h.

The evolution of the I2/I3 ratio as a function of time presented in Fig. 2 (a) depends on the aqueous solution filling the porosity. The most important material alteration is obtained with the BaCl₂ solution. Based on the comparison between the I2/I3 ratio from the calculated patterns and the experimental ones, the evolutions of r_p and hlw were plotted as a function of alteration time and are presented on Fig. 2 (b).

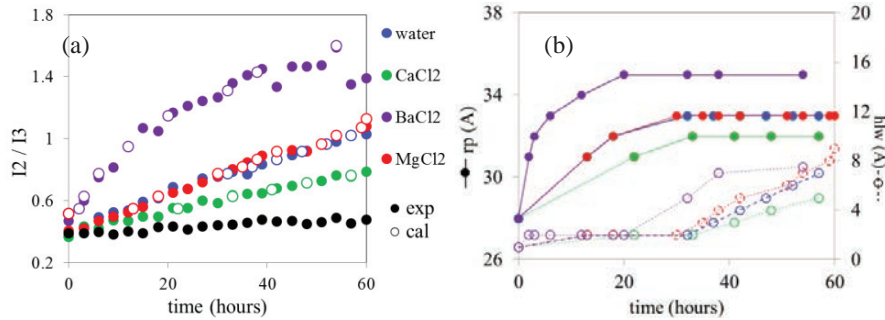


Fig. 2. (a) Evolutions versus time of the experimental and calculated ratio I2/I3 obtained from the SAXS patterns and (b) r_p and hlw obtained from the fit of the model as a function of time.

Whatever the solution, the results obtained from the calculations show an evolution in two stages as described in Fig. 3. During the first stage, the pore size r_p increases and the altered layer remains constant, highlighting a dissolution rate of the pore wall r_{SiO₂} equal to the penetration rate r_{sol} of the solution through the microporosity of the silica pore wall. During the second stage, the pore size does not evolve probably due to the attainment of the silica saturation C_{Si}* inside the pore and the altered layer grows.

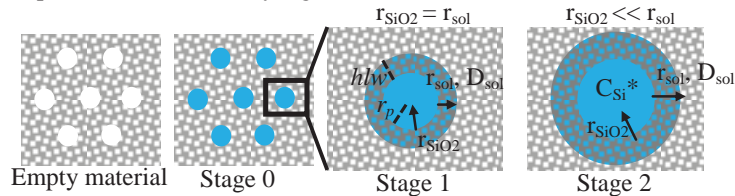


Fig. 3. Schematic representation of the proposed evolution of the SBA15 during alteration at 50°C in various aqueous solutions.

From these results, the dissolution rate of the SiO₂ pore wall r_{SiO₂} was calculated as the difference between the initial pore size r₀ and the pore size at silica saturation divided by the time required to reach the equilibrium. Moreover, the r_p and hlw parameters evolve with a power law of exponent 1/2, typical of a diffusion process. Assuming that diffusion is the limiting reaction, an apparent water diffusion coefficient D_{H₂O} was calculated from the equation (1) based on the first Fick⁰ law. The results are presented in the Table 1.

$$hlw + r_p = 2\sqrt{\frac{D}{\pi}}\sqrt{t} + r_0 \tag{1}$$

Table 1. Surface densities of ions assuming their adsorption in silica SBA15 in solution $XCl_2 = 0.2$ M, dissolution rates r_{SiO_2} of pore wall and apparent diffusion coefficient of water D_{H_2O} through pore wall of silica SBA15.

Aqueous solution	$X^{2+} \cdot nm^{-2}$	r_{SiO_2} (nm.year ⁻¹)	D_{H_2O} (m ² .s ⁻¹)
water	-	133	$6 \cdot 10^{-24}$
MgCl ₂	5.4	146	$9 \cdot 10^{-24}$
CaCl ₂	2.2	106	$4 \cdot 10^{-24}$
BaCl ₂	4.8	307	$6 \cdot 10^{-24}$
FeCl ₂	4.2	0	-

In the case of SBA15, as soon as the porous silica is in contact with water, an altered silica layer forms at the pore surface and dissolves at a rate from 106 to 307 nm.year⁻¹ depending on the aqueous solution. This mechanism leads to a pore size increase. When the silica saturation C_{Si}^* is reached, the silica dissolution rate strongly decreases and the altered layer growth follows a diffusive process with a diffusion coefficient D_{H_2O} around $4 \cdot 10^{-24}$ and $9 \cdot 10^{-24}$ m² s⁻¹. Therefore, the kinetics of SBA15 alteration could result from a competition between the solution diffusion/reaction through the microporous silica walls and the hydrolysis of the pore surface.

Generally, the dissolution rate of silica such as quartz can be related to the fraction of surface sites SiO^M^+ and to several physical properties of the cation such as its hydrated ionic radius, the number of water molecules in its coordination sphere or its diffusion coefficient in water^{0,0,0}. The rate-enhancing factors are also known to increase in the following order⁰: water << Mg²⁺ < Ca²⁺ < Ba²⁺. In the nanoporosity of the silica SBA15, the order is different Ca²⁺ < water < Mg²⁺ << Ba²⁺. Moreover, the rate-enhancing factors are not related to the surface densities of ions that we have determined on the same materials from the sorption isotherms, i.e., supposing that adsorption was the only process occurring (Table 1 - isotherms not supplied here). This could be explained by the impact of the confinement such as the pH (generally more acidic than in the bulk, and which could vary with the ions), the species speciation, or the water dynamics. These results suggest that water reactivity in confined media is not driven by the same basic processes occurring on the planar silica surface.

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