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Evolution of silica walls of nanopores filled of water and ions

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Thermodynamic models and rate laws used to explain or predict materials dissolution kinetics and phases transformation generally take into account some thermodynamic and kinetics data arising from measurements in diluted media. However, the validity of these laws are not proved in nanoconfined media [1]. Indeed, in confined media, strong interactions between water molecules and pore surfaces are expected, structuring and slowing down water motions from nanoscale to macro-scale. These interactions depend on the composition, the pore morphology and the surface topology [2]. Furthermore, it is also expected that nanoconfined water molecules are strongly influenced by the presence of ions through sorption processes with the surface and ions solvation. The latter result is really important since the ion adsorption on the surface and the ion solvation strongly impact the hydrolysis rate of materials [3] and can modify the kinetics of dissolved elements recondensation into the pore.

Up to now, the characterization of the evolution of nanoporous materials in solution is based on bulk solution analysis. This makes the determination of the hydrolysis – recondensation rates of the confining materials difficult. Moreover, the characterization of such systems is really complex and even atomistic modeling is not able to reproduce the involved chemical processes. Recently, we have shown [4][5] that in-situ characterization using Small Angle X-ray Scattering (SAXS) of highly ordered mesoporous silica materials in water allows to determine a pore wall dissolution rate and a diffusion of water through the pore wall.

Based on this method, we have characterized the evolution of silica porous structure at 50°C in presence of water and in presence of aqueous solution (XCl_2 at 1 M) containing ions presenting a more or less kosmotrope character ($X = Mg^{2+}, Ca^{2+}, Fe^{2+}, Ba^{2+}$). We have used two types of hexagonal mesoporous silicas, MCM-41 and SBA-15, having pore sizes of 3 and 4 nm respectively. The results highlight first, that the kinetics of dissolution-recondensation of the silica pore wall depend on the aqueous solution and pore wall nature (dense or microporous) and second, that the impact of ions on the evolution of the porous structure depends on the morphology of the pore.

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