From phase transition of boehmite, dealumination in zeolites to visualization of random walk in colloidal systems

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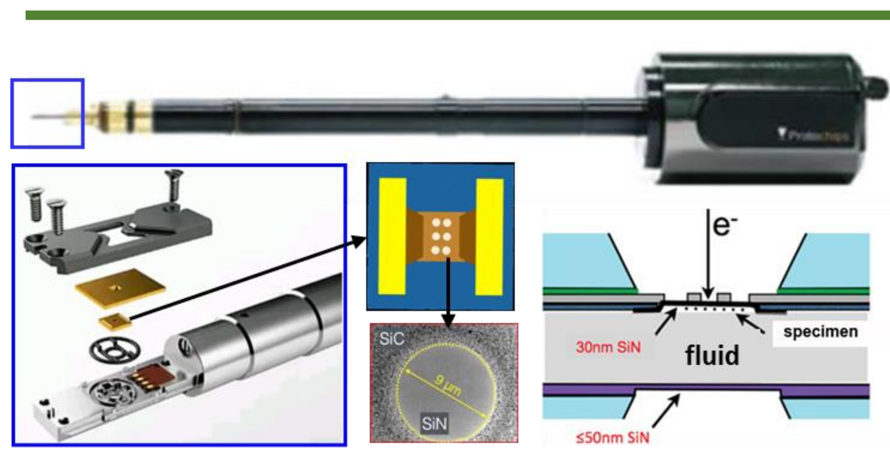
Introduction

The study at high spatial resolution of the properties and dynamic behavior of nanostructured materials in their equilibrium state or in environments representative of their formation or use in applications is a major challenge. Through the understanding of the physical and chemical mechanisms that govern the properties of these materials, it allows to solve questions with a strong societal impact such as research on the catalysis of the future and new forms of energy storage or conversion. In-situ studies using the environmental mode based on enclosed cells which allows to study nanomaterials in gaseous atmosphere (Boehmite), at atmospheric pressure and high temperature, or in liquid medium (SiO_2 colloid).

Objectives

- Phase transition of boehmite to alumina in air → *in situ* XRD, *in situ* TEM, *in situ* tomography
- Dealumination OF Y-Zeolites → STXM-XANES
- Brownian motion of SiO_2 nanoparticles

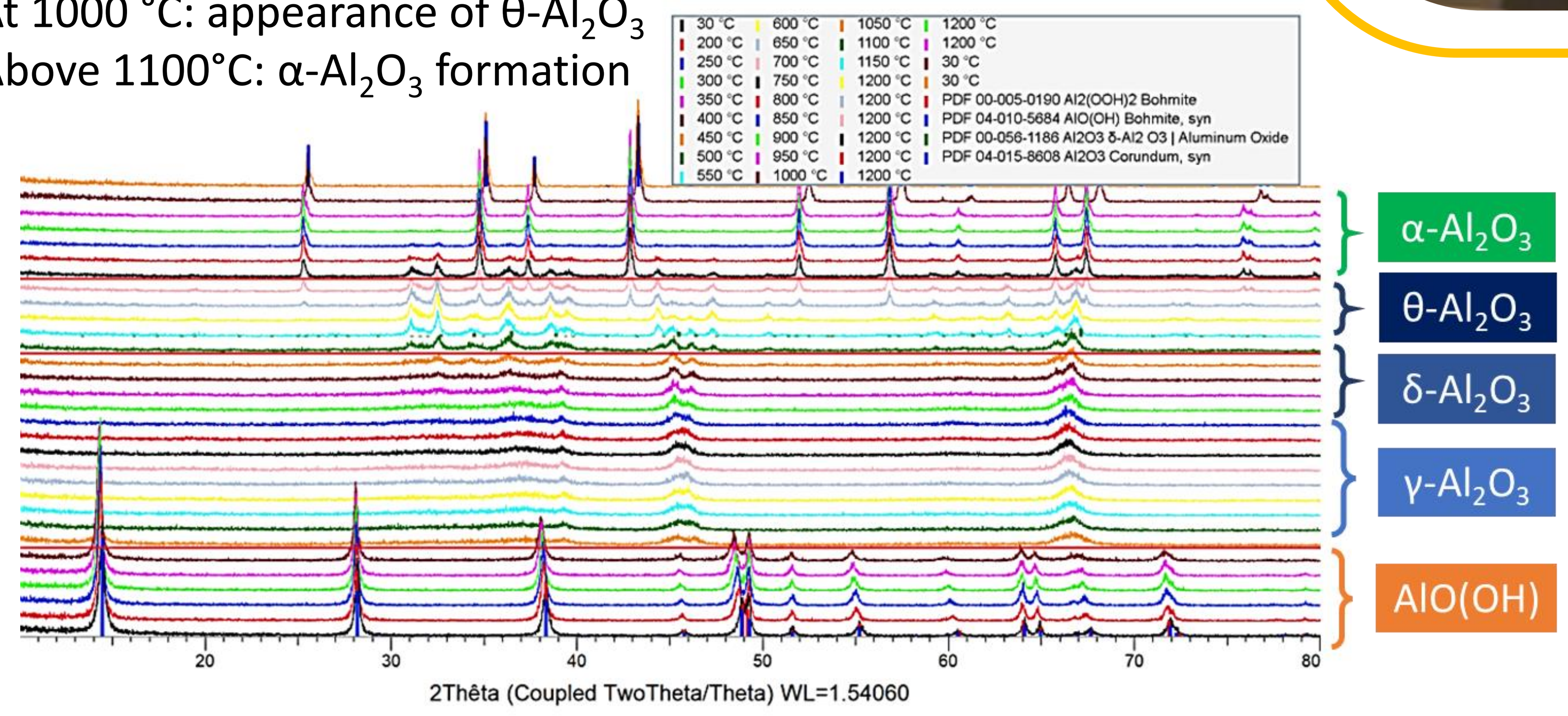
Methodology



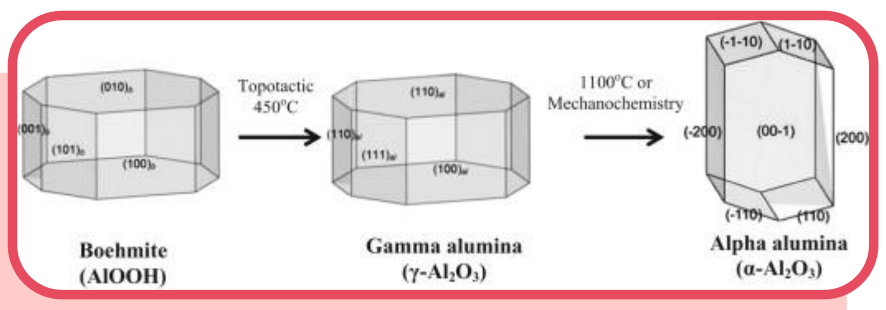
- *In situ* and *operando* conditions
- Gas and liquid phase
- Adequate spatial and temporal resolution

In situ XRD calcination

- At 500 °C: transformation to γ-Al_2O_3
- At 850 °C: appearance of δ-Al_2O_3
- At 1000 °C: appearance of θ-Al_2O_3
- Above 1100°C: α-Al_2O_3 formation



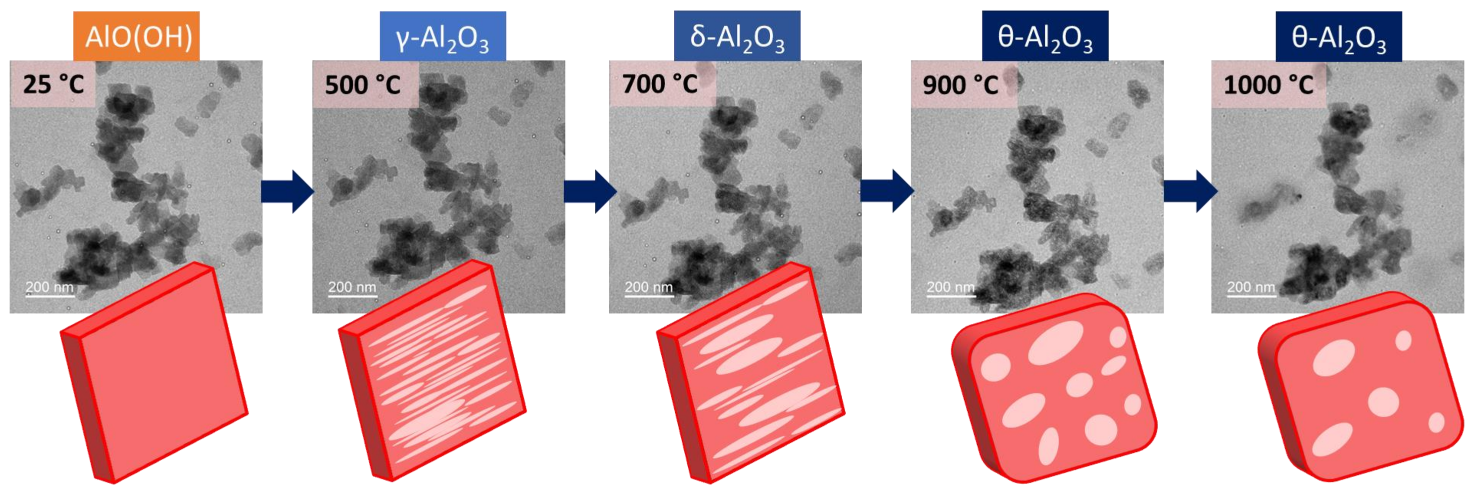
Phase transition of boehmite



Boehmite (AlOOH) is an important precursor material for the alumina synthesis, with industrial applications such as catalysts support ($\gamma/\delta/\theta$-Al_2O_3). or refractory materials (α-Al_2O_3). The thermal treatment during the catalytic reaction may lead to phase transition of the alumina resulting in morphological evolution. Several factors including crystallite size, presence of water and metallic phase (such as active phase) may alter the support due to phase transition, thus, affecting the catalytic activities [1]. Therefore, it is crucial to understand the impact of thermal treatment on the phase and morphology of the boehmite precursors.

In situ TEM calcination

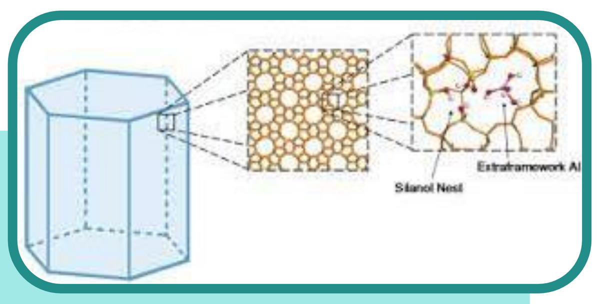
- Introduction of porosity in the particles due to loss of H_2O during AlO(OH) → Al_2O_3
- Pore size increases with T °C
- Rounding of the edges of the platelets



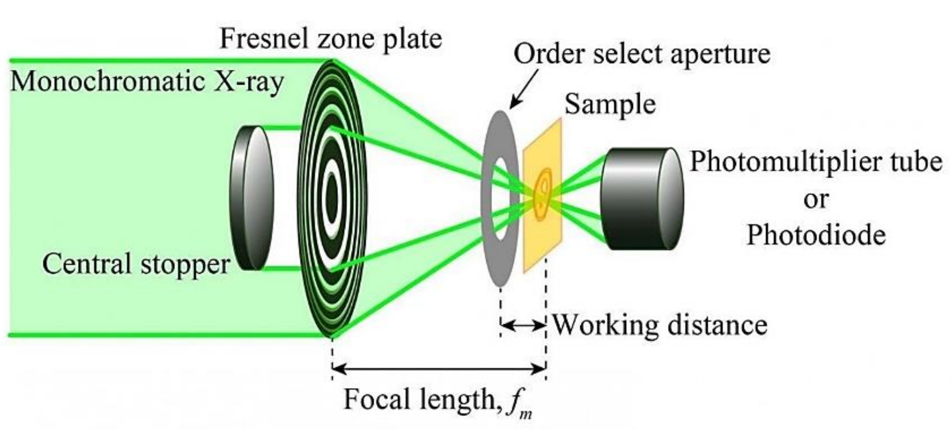
- ➢ Detailed structural analysis of the different alumina phases → Rietveld refinement
- ➢ Visualization of the porosity formation in 3D → *in situ* TEM tomography
- ➢ Connecting the local surface area and porosity measurement with bulk characterizations (N_2 physisorption)

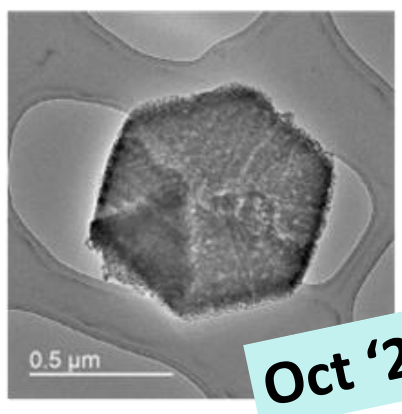
Aug '22

Dealumination of Y-Zeolites



The Faujasite (FAU) Y zeolites are crystalline aluminosilicates composed of tetrahedral units TO_4 (T=Si or Al) with a microporous structure, with interest in oil refining, biomass conversion and pollution abatement. To facilitate molecular diffusion, hierarchical porosity is induced by introducing mesopores via hydrothermal treatment (dealumination). During the dealumination some of the Al atoms (known as Extra-Framework Al or EFAl) are removed from their lattice framework. The EFAl are mobile with a possible octahedral coordination (AlO_6), compared to the FAl with AlO_4 species, within the zeolite matrix.





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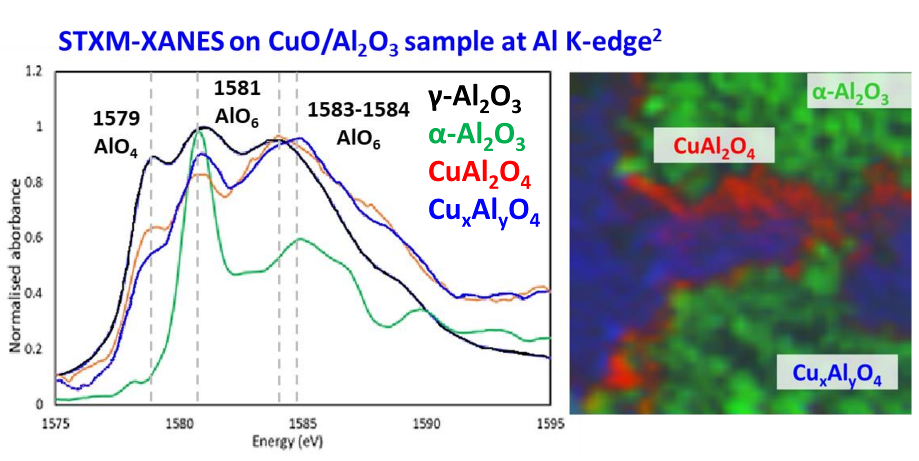
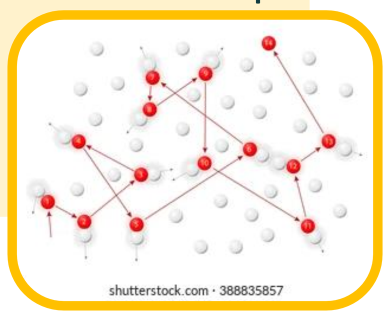


- ➢ STXM-XANES at Al K-edge
- ➢ Spatial distribution of Al-species as a function of the dealumination steps
- ➢ Mechanism of mesoporous network formation

Brownian motion of SiO_2 nanoparticles

Soil pollution is a crucial environmental problem. The treatment of contaminated soils involves molecular or colloidal transport processes, coupled with adsorption/desorption phenomena at solid/liquid interfaces. In that context, clays and silts (SiO_2) play a paramount role, comprising the major component of the soil. Studying the dynamics (such as **Brownian motion**) of the SiO_2 particles can help understand the flocculation/dispersion behavior of the particles in a liquid medium. Thus, providing insights into interparticle and particle-solvent interactions, as well as self-assembly and 3D structuration[3].



Estimation of diffusion coefficient:
Stokes-Einstein relation

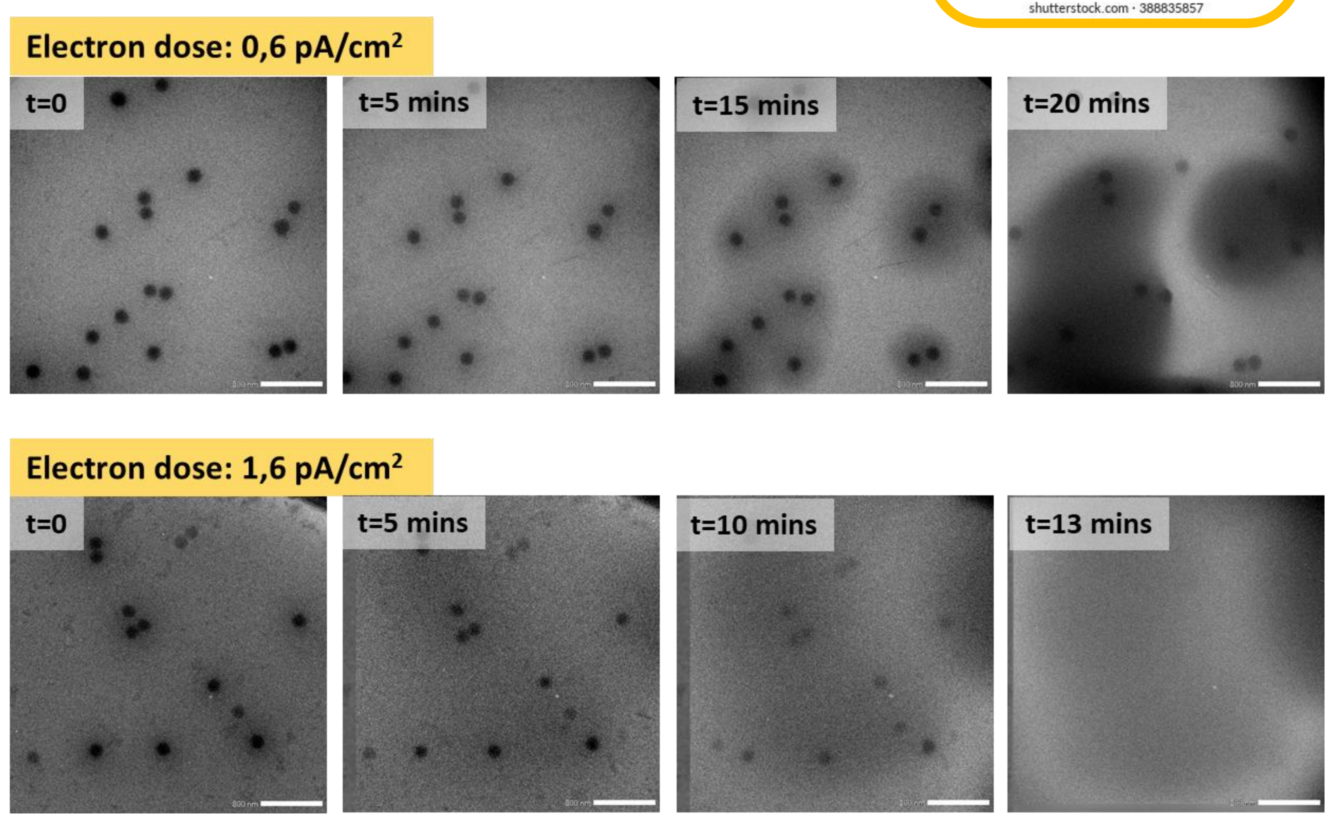
$$D = \frac{k_B T}{6\pi\eta R_h}$$

D – diffusion coefficient
µ – solvent viscosity
R_0 – solute radius
k_B – Boltzmann's constant
T – temperature (K)

- First trial: ~160 nm SiO_2 NPs in glycerol carbonate
- Theoretical diffusion coefficient ~10^{-14} m^2s^{-1}
- No Brownian motion yet!

→ sedimentation

→ NP-membrane interactions
- Effect of beam dose is important
- Degradation of the solvent and/or the SiO_2 NPs



- ➢ Trial with flow-mode
- ➢ Lower particle size and/or lower viscosity

Sep '22

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