

Study of the stabilization mechanisms of pure tetragonal ZrO₂ nanocrystals prepared in supercritical fluids

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Zirconium dioxide (ZrO₂) has been of major industrial and scientific interest over the past decades for its wide range of applications, in particular thanks to its catalytic properties. Regardless the multiple synthesis routes employed such as: precipitation of metal salts; atomic layer deposition; ball-milling; chemical vapor deposition; radio frequency sputtering; *etc.*, undoped bulk ZrO₂ is stabilized in the monoclinic structure (m-ZrO₂) at ambient temperature and atmospheric pressure. There, the small cationic size of Zr⁴⁺ ionocovalently bonds to oxygen anions in a sevenfold coordination environment. However, improved catalytic properties are observed in tetragonal zirconia (t-ZrO₂) where Zr⁴⁺ is coordinated with eight oxygen anions.

To stabilize this allotrope under mild temperature and pressure conditions, it generally necessitates the use of iso- or aliovalent zirconium substitution with larger cationic radii such as Y⁴⁺, Ga³⁺, Gd³⁺, *etc.* Nevertheless, it is also possible to stabilize t-ZrO₂ without cationic substitution. To do so, three main mechanisms are identified in the literature: (i) the presence of oxygen vacancies, (ii) the existence of structural similarities and (iii) the size effect.

In this talk, we will connect these three parameters and present how the use of supercritical alcohols enables to synthesize pure t- ZrO₂ nanocrystals of 2 nm in borderline non-hydrolytic sol-gel (B.N.H.S.G.) conditions. First we will describe the ZrO₂ B.N.H.S.G. synthesis in supercritical fluids and present preliminary *ex situ* powders characterizations such as HR-TEM, XRD and EXAFS. Then we will move towards an *in situ* parametric study playing on the temperature, the presence of surfactant and the type of solvents. There where we were able to tracked in real time the ZrO₂ nanocrystals formation using total X ray scattering and treating the data with pair distribution function (PDF) analysis, to get information from the prenucleation cluster structures (Figure 1) to the nanocrystal growth. To conclude, we will propose a mechanism.

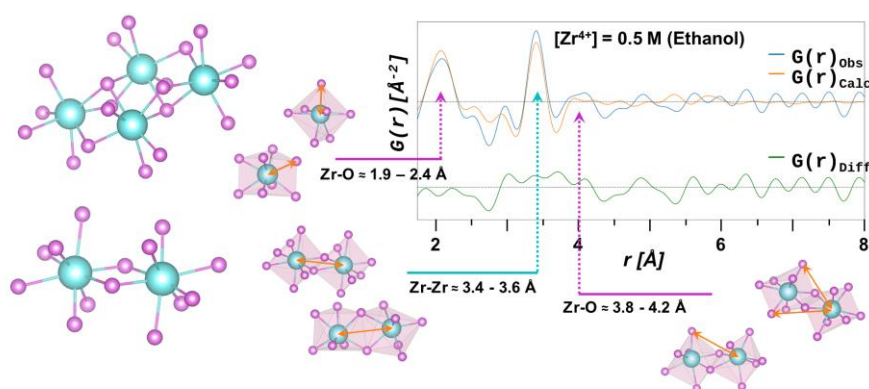


Figure 1. PDF modeling of the prenucleation clusters exhibiting the coexistence of bond distances belonging to t- and m- ZrO₂