



HAL
open science

Stabilization mechanisms of pure tetragonal zirconia nanocrystallites using an original supercritical-based synthesis route

Gilles Philippot, Aimery Auxemery, Cyril Aymonier, Denis Testemale,
Jean-Louis F Hazemann, Bo Iversen

► To cite this version:

Gilles Philippot, Aimery Auxemery, Cyril Aymonier, Denis Testemale, Jean-Louis F Hazemann, et al.. Stabilization mechanisms of pure tetragonal zirconia nanocrystallites using an original supercritical-based synthesis route. 29th Annual Meeting of German Crystallographic Society - Deutschen Gesellschaft für Kristallographie - DGK, Deutschen Gesellschaft für Kristallographie - DGK, Mar 2021, On Line, Germany. pp.46. hal-04571349

HAL Id: hal-04571349

<https://hal.science/hal-04571349v1>

Submitted on 7 May 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial - NoDerivatives 4.0
International License

transformation of molecular precursors into multiferroic $\text{Bi}_2\text{Fe}_4\text{O}_9$ with a second-scale time resolution. The precursors were synthesized by the sol-gel process using the respective metal nitrates and meso-erythritol as the complexing agent. We show how the crystallization pathways and kinetics of the target compound can dramatically be changed by variation of the synthesis medium and ratio of metal nitrate to the complexing agent and relate this to the precursor structure. As an example, using small amounts of complexing agent leads to a crystalline precursor which first gets amorphous at 613 K, crystallizes into BiFeO_3 at 706 K, and subsequently transforms into $\text{Bi}_2\text{Fe}_4\text{O}_9$ at 815 K. On the other hand, bigger amounts of complexing agent produce an amorphous precursor which directly crystallizes into $\text{Bi}_2\text{Fe}_4\text{O}_9$ at 762 K. Using PDF we reveal the importance of the initial gel structure in the overall crystallization behaviour of the system.

References

- [1] Samarth, N. *Nat. Mater.*, 2017, 16, 1068.
- [2] Niederberger, M. *Acc. Chem. Res.*, 2007, 40, 793.

Stabilization mechanisms of pure tetragonal zirconia nanocrystallites using an original supercritical-based synthesis route

G. Philippot¹, A. Auxemery², D. Testemale³, B. Iversen⁴, C. Aymonier²

¹ University of Bordeaux, Bordeaux, France

² CNRS, ICMCB, Pessac, France

³ Institut Neel, Grenoble, France

⁴ Aarhus University, Aarhus, Denmark

Zirconium dioxide (ZrO_2) 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, undoped bulk ZrO_2 is stabilized in the monoclinic structure (m- ZrO_2) at ambient temperature and atmospheric pressure. However, these last years, studies showed that it was also possible to stabilize pure t- ZrO_2 without cationic substitution. To do so, three main effects are identified in the literature: (i) the presence of oxygen vacancies, (ii) the existence of structural similarities, and (iii) the size effect, with the existence of a critical size below which pure t- ZrO_2 is formed.

In this presentation we will introduce the synthesis of quasi pure t- ZrO_2 nanocrystals in supercritical fluids using borderline nonhydrolytic sol-gel (B.N.H.S.G.) conditions. The term borderline is used to express the nuance from nonhydrolytic sol-gel (N.H.S.G.) reactions when small amounts of water molecules are generated

in situ from solvent (alcohols) decomposition to trigger hydrolysis/condensation. This amount of water being controlled, the reaction kinetics can be tuned and slow down. This enabled us to performed in situ total scattering measurements in order to catch the various stages of the nanocrystal formation upon various conditions (temperature, nature of the alcohols and presence of surfactants). These observations were combined to various ex situ characterizations (Raman, PDF, EXAFS, HR-TEM, XRD, etc.) to discuss the existence of a critical size below which pure t- ZrO_2 is formed, as reported in literature and propose a formation mechanism in this specific synthesis route.

Selective in-situ exsolution of catalytically active metals from doped perovskites during methane dry reforming

F. Schrenk¹, L. Lindenthal¹, D. Hedda¹, R. Rameshan¹, C. Rameshan¹

¹ TU Wien, Institute of Materials Chemistry, Vienna, Austria

Perovskite type oxides, doped with catalytically active metals, have shown great potential to catalyse MDR (Methane Dry Reforming) [1]. These materials can undergo exsolution, the formation of metallic nanoparticles on the surface, of B-site elements if reducing conditions are applied [2]. These exsolved nanoparticles are leading to an increase in catalytic activity. A Ni-doped perovskite ($\text{Nd}_{0.6}\text{Ca}_{0.4}\text{Fe}_{0.97}\text{Ni}_{0.03}\text{O}_3$) and a Co-doped perovskite ($\text{Nd}_{0.6}\text{Ca}_{0.4}\text{Fe}_{0.9}\text{Co}_{0.1}\text{O}_3$) were investigated in MDR conditions with a CH_4 excess of 2:1 over CO_2 . To investigate the changes the catalyst undergoes during the reaction *in situ* NAP XPS (Near Ambient Pressure X-ray Photoelectron Spectroscopy) as well as *in situ* XRD (X-Ray Diffraction) experiments were performed. The XRD data showed the formation of a bcc phase at higher temperatures which cannot be assigned to Fe or the dopant (Ni/Co) due to the bad signal to noise ratio (Figure 1). The XPS data reveals that Ni is exsolving before Fe, as the Ni2p signal is shifting from the oxidized state into a metallic state between 600 °C and 650 °C and the Fe2p signal does not show a metallic component even at 700 °C, as seen in Figure 2. For the Co-doped catalyst, the formation of a metallic Co component was observed while no metallic Fe was detected.

References

- [1] D. Pakhare and J. Spivey, "A review of dry (CO_2) reforming of methane over noble metal catalysts," *Chem. Soc. Rev.*, vol. 43, no. 22, pp. 7813-7837, Nov. 2014, doi: 10.1039/c3cs60395d.