Mechanistic insight into Pt exsolution from a defective fluorite $Sm_2Pt_{0.1}Ce_{1.9}O_7$ solid solution

M. Janák [1], D. Piankova [1], A. Fedorov [1], P. M. Abdala [1], M. Plodinec [2,3], C. R. Müller [1]

1 Department of Mechanical and Process Engineering, ETH Zürich, CH 8092 Zürich, 2 Department of Chemistry and Applied Biosciences, ETH Zürich, CH 8093 Zürich, 3 Scientific Center for Optical and Electron Microscopy, ETH Zürich, CH 8093 Zürich

mjanak@ethz.ch

Late-transition-metal-doped fluorite oxides are an emerging class of precursors for the synthesis of supported metal catalysts via reductive exsolution. Compared to conventional deposition methods, exsolution provides a means to improve the utilization of the active metal and enhance catalyst stability under harsh reaction conditions such as the dry reforming of methane (DRM) [1]. While perovskites remain the most commonly exploited exsolution host structure [2], fluorite-type materials are increasingly explored due to their ability to accommodate defects [3], thereby enabling a homogeneous dopant incorporation into the host, which is essential for achieving a high metal nanoparticle dispersion upon exsolution. Optimizing doped fluorites for catalytic applications requires a detailed understanding of dopant migration from the bulk of the host structure to the surface. In this work, a DRM catalyst $Sm_2Pt_{0.1}Ce_{1.9}O_7$ was synthesized via a sol-gel method and subsequently activated by reductive exsolution at 800 °C. Structural evolution of the system was studied using X-ray absorption spectroscopy (XAS), X-ray total scattering (TS), X-ray diffraction (XRD), and scanning transmission electron microscopy (STEM). *In situ* XRD shows a phase transition of the support from a defective fluorite $Sm_2Pt_{0.1}Ce_{1.9}O_7$ (*Fm-3m*) to a C-type superstructure $Sm_2Ce_{1.9}O_7$ (*Ia-3*) (Figure 1a). Furthermore, the phase transition is accompanied by the formation of ~2 nm Pt nanoparticles at the surface (Figure 1b), which are thermally stabilized by epitaxial anchoring. *In situ* STEM further reveals a direct correlation between the onset of the phase transition and the emergence of Pt clusters, indicating that the phase transition proceeds gradually from the bulk to the surface, in parallel with the formation of nanocrystalline Pt nanoparticles with low mobility. These observations elucidate the key mechanisms underlying reductive exsolution in fluorite oxides.

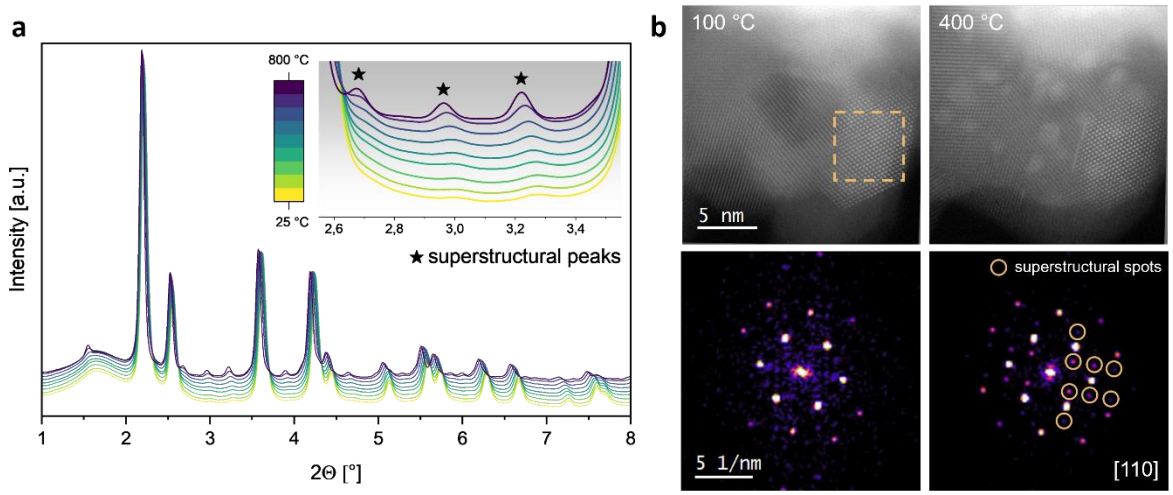


Figure 1. (a) *In situ XRD showing the phase transition from defective fluorite $Sm_2Pt_{0.1}Ce_{1.9}O_7$ (25 °C) to ordered C-type $Sm_2Ce_{1.9}O_7$ (800 °C) during reductive Pt exsolution (4 vol.% H_2 in N_2),* ***(b)*** *In situ HAADF STEM showing the transformation of $Sm_2Pt_{0.1}Ce_{1.9}O_7$ (100 °C) to exsolved Pt(0)/$Sm_2Ce_{1.9}O_7$ (400 °C) under reducing conditions at 1 bar (10 vol.% H_2 in He).*

[1] A. J. Carrillo, A. López-García, B. Delgado-Galicia, J. M. Serra, Chem. Commun. (2024). 60, 7987-8007.
[2] Y. H. Kim, H. Jeong, B. Won, H. Jeon, C. Park, D. Park, Y. Kim, S. Lee, J. Myung, Nano-Micro Lett. (2024). 16:33.
[3] M. A. Naeem, P. M. Abdala, A. Armutlulu, S. M. Kim, A. Fedorov, C. R. Müller, ACS Catal. (2020). 10, 1923-1937.

We thank ReMade@ARI funded by the European Union as part of the Horizon Europe call HORIZON-INFRA-2021-SERV-01 under grant agreement number 101058414 and co-funded by UK Research and Innovation (UKRI) under the UK government's Horizon Europe funding guarantee (grant number 10039728) and by the Swiss State Secretariat for Education, Research and Innovation (SERI) under contract number 22.00187.