

Nanoparticle-Derived Mesoporous Ceria-Zirconia Structures: Understanding the Low-Temperature Solid-State Intermixing

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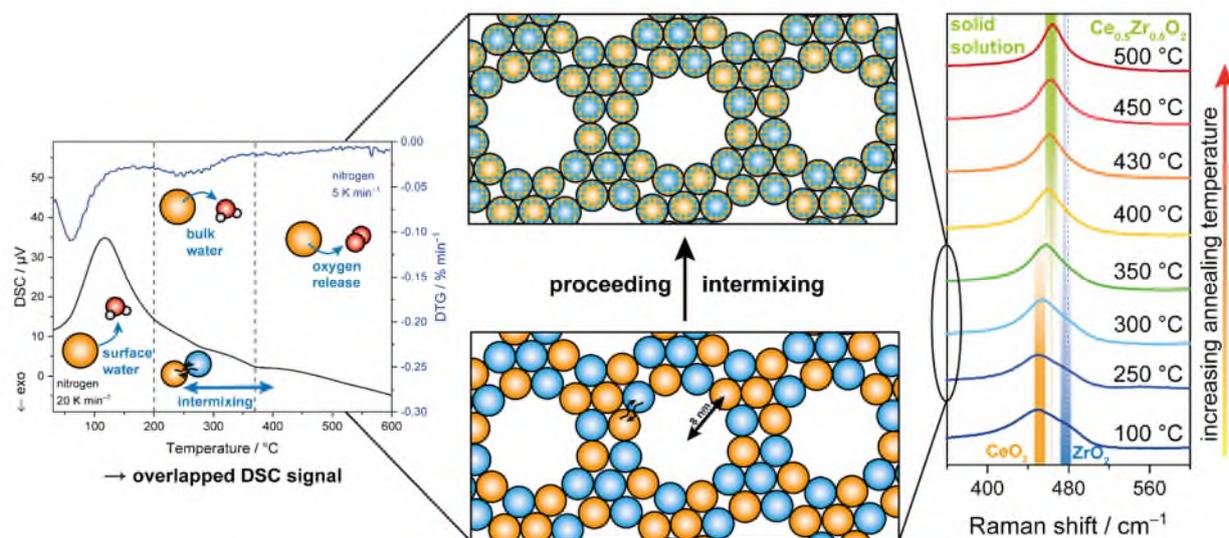
The Deacon process is an industrial method to recycle chlorine from the unpleasant and corrosive byproduct HCl accumulating in several industrial syntheses, such as the production of poly(vinylchloride) and poly(urethane). Ceria-zirconia materials are promising catalysts for the HCl oxidation – but also widely used as three-way catalysts in the soot combustion – due to their oxygen exchange properties as well as their stability against in-depth chlorination.^[1,2]

According to the benefits of the CeO₂-ZrO₂ interface, namely a catalytically stable and highly active ceria phase,^[2] we synthesized and mixed nanoparticles of each metal oxide to obtain a high amount of this ceria-zirconia interface along the particles' contact area. Nanoparticles of 3 nm in size were synthesized and transformed into porous particle-on-particle systems by soft-templating employing the diblock copolymer PIB₅₀-*b*-PEO₄₅ as structure-directing agent. Nitrogen physisorption measurements confirmed the existence of both mesopores around 15 nm introduced by the template and micropores derived from the interparticular gaps of the nanoparticles. Thus, a model catalyst with a high specific surface area of about 135 m² g⁻¹ was obtained.

However, powder X-ray diffraction and Raman spectroscopy indicate a solid solution formation already at relatively low temperatures starting from *circa* 250 °C. An intermixing at this relatively low temperature is remarkable as a solid solution formation between both metal oxides usually requires temperatures about 800 °C.^[3,4] Therefore, we carried out a temperature study including XRD, Raman spectroscopy, and thermal analysis in order to investigate the intermixing process more deeply. While *in situ* powder XRD confirmed an intermixing between 250 and 450 °C, the *ex situ* Raman spectra reveal that the mixing process of the former CeO₂ and ZrO₂ phases is already fully executed at 350 °C, which is very low in regard to the free mixing enthalpy.^[5] Additionally, the thermal evolution of both nanoparticles upon intermixing was tracked by differential scanning calorimetry. Both endothermic water release and metal oxide intermixing processes can be observed and the influence of the amount of water in the crystal lattice on the tendency for intermixing was investigated by thermogravimetric analysis. Coupling this method with mass spectrometry and infrared spectroscopy enables a differentiation of water release and oxygen release due to CeO₂ reduction. The amount of the latter would provide a further confirmation of the low initial defect concentration in the nanoparticles predicted by XRD.

The diffraction pattern of the pure CeO₂ nanoparticles evokes the low defect concentration as a possible explanation for the low-temperature intermixing since the

application of a Ce(IV) precursor leads to a lower Ce³⁺ concentration in the parent metal oxide compared to Ce(III) precursor, which have to be oxidized to form CeO₂. These findings show the impact of the precursor on the reactivity of the formed metal oxide and how syntheses of solid solutions can be optimized to reduce the energy demand of the reaction.



References:

- [1] A. P. Amrute, C. Mondelli, M. Moser, G. Novell-leruth, *J. Catal.* **2012**, *286*, 287–297.
- [2] Y. Sun, P. Cop, I. Djerdj, X. Guo, T. Weber, O. Khalid, Y. Guo, B. M. Smarsly, H. Over, *ACS Catal.* **2019**, 10680–10693.
- [3] C. H. Kanzler, S. Urban, K. Zalewska-Wierzbicka, F. Hess, S. F. Rohrlack, C. Wessel, R. Ostermann, J. P. Hofmann, B. M. Smarsly, H. Over, *ChemCatChem* **2013**, *5*, 2621–2626.
- [4] Y. Sun, C. Li, I. Djerdj, O. Khalid, P. Cop, J. Sann, T. Weber, S. Werner, K. Turke, Y. Guo, et al., *Catal. Sci. Technol.* **2019**, *9*, 2163–2172.
- [5] R. Grau-Crespo, N. H. De Leeuw, S. Hamad, U. V. Waghmare, *Proc. R. Soc. A Math. Phys. Eng. Sci.* **2011**, *467*, 1925–1938.