

# The selective oxidation of 2-propanol is dominated by solid state chemistry

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Transition metal oxides are excellent catalysts for industrially relevant selective oxidation reactions, particularly of alcohols.<sup>1</sup> In the selectively catalyzed oxidation of 2-propanol to form acetone, the spinel cobalt(II, III) oxide (Co<sub>3</sub>O<sub>4</sub>) exhibits a peculiar behavior, which is expressed by changing the catalytic properties significantly, depending on the temperature: below 200 °C, the catalyst shows high acetone selectivity, but deactivates rapidly, while above 200 °C, stable conversions and steady-state conditions can be reached, at the expense of lowered selectivity due to total oxidation (to form H<sub>2</sub>O and CO<sub>2</sub>).<sup>2</sup> In addition, once the high-temperature regime has been reached, the low-temperature region gets deactivated completely, but can be recovered by re-oxidation. Thus, it would be beneficial to stabilize the low-temperature regime. However, a prerequisite for being able to accomplish this challenging task is gaining an understanding of the underlying processes.

Thus, we present a multimodal approach, that is based on *operando* transmission electron microscopy (OTEM), (*operando*) near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy experiments under reaction conditions. This way we are able to combine the spatial resolution of OTEM with the surface-sensitivity and energy-resolution of the X-ray techniques. With this methodological synergy, we elucidate a network of interconnected diffusional solid-state processes governing the catalytic activity of Co<sub>3</sub>O<sub>4</sub> in the selective oxidation of 2-propanol towards acetone, trapping the catalyst in a frustrated state at the transition between low- and high-temperature regimes, where it is dominated by exsolution, vacancy agglomeration and crystallization processes.

[1] S. Najafshirtari *et al.*, Chem. - Eur. J., 2021, **27**, 16809–16833, DOI:10.1002/chem.202102868

[2] S. Anke *et al.*, ACS Catal., 2019, **9**, 5974–5985, DOI:10.1021/acscatal.9b01048