High-resolution imaging of Co₃O₄ nanoparticles via aberration-corrected exit wavefunction reconstruction

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The activation of cobalt (Co) in Fischer-Tropsch synthesis (FTS) has an effect on its catalytic activity and selectivity.¹ Since Co is rarely available as a pure reduced metal for industrial FTS, the production of active metallic Co typically occurs in the FTS reactor prior to the synthesis via reduction of cobalt oxide (Co₃O₄).¹ The surface structure of this precursor is therefore key to understanding preferential evolution pathways of Co surfaces in the activation of Co. Typical Co₃O₄ precursors have a normal-spinel crystal structure with an oxygen close-packed face centred cubic (fcc) lattice. The Co²⁺ and Co³⁺ cations occupy one-eighth of the tetrahedral interstitial sites (8a) and half of the octahedral sites (16d) per unit cell ([(Co²⁺)₈a][Co³⁺]₁₆d[O₄]₃₂e), respectively.² The complexity of this spinel structure offers several possible surface terminations depending on the shape of the crystal.

The local atomic structure of carbon supported Co₃O₄ nanoparticles has been studied by restoring the object exit wavefunction from a focal series of aberration-corrected TEM (AC-TEM) images. The phase of the exit wave can be directly related to the Co₃O₄ local structure, where both oxygen and cobalt atomic columns are resolved.³,⁴

In this study, we will show that by restoring the phase of the object wave function provides direct structural information on alternative active surface terminations of Co₃O₄ observed along several zone axes. Furthermore, combining this experimental data with simulations, we will show that is also possible to predict a model for the full three-dimensional shape of the catalyst particles.

References