

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 ([Co⁺²]_{8a}[Co⁺³]₂]_{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

1. Gnanamani, M.K. *et al.*, (2013), *Catal. Today*, 215, 13.
2. Yu, R. *et al.*, (2010) *Phys. Rev. Lett.*, 105(22), 226101.
3. Kirkland, A.I. and Meyer, R.R., (2004) *Microsc. Microanal.*, 10(4), 401.
4. Meyer, R.R. *et al.*, (2002) *Ultramicroscopy* 92(2), 89.