Watching nanoparticles form: a time resolved synchrotron radiation study of polyol-synthesized Co- and Fe-based nanoparticles

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The polyol synthesis process is a versatile route to magnetic nanoparticles (MNPs) because solvent, temperature, and water content can be adjusted to finely control phase composition, size, and morphology of MNPs. However, the process optimization remains difficult because nucleation and growth occur in solution through transient species that are easily missed by conventional ex situ characterization. Here, we present a systematic investigation of Co- and Fe-containing MNPs, carried out through the coordinated access to complementary synchrotron facilities provided within the CERIC-ERIC programme. Time-resolved X-ray powder diffraction (XRPD), small-angle X-ray scattering (SAXS), and X-ray absorption fine structure (XAFS) spectroscopy were combined with laboratory diffraction, electron microscopy, and magnetic measurements to connect synthesis conditions, formation mechanisms, and final MNP properties.

For CoO, varying the polyol chain length, temperature, and hydrolysis ratio broadened the synthesis window. Longer-chain polyols suppressed the reduction observed in diethylene glycol, enabling CoO to be produced up to 235 °C. Control over size and morphology allowed the Néel temperature to be tuned over approximately 80 K. Time-resolved XRPD and Co K-edge XAFS revealed a stepwise pathway in tetraethylene glycol (TEG): isolated CoO_6 octahedra evolve into one-dimensional chains and two-dimensional CoO_6/CoO_4 networks, including a layered hydroxyl-cobalt intermediate, before forming the three-dimensional nanocrystalline CoO [1,2]. More recently, cobalt ferrite ($CoFe_2O_4$) formation in diethylene glycol (DEG) has been investigated [3]. Preliminary results reveal a pre-crystallization regime: broad XRPD features at the principal spinel reflections precede long-range order, while SAXS follows the growth of nanoscale objects. Crucially, XAFS reveals that the Fe local environment evolves progressively with temperature and develops next-neighbour shell correlations well below the $CoFe_2O_4$ crystallization temperature T_c, while changes around Co appear only near T_c, thus revealing that the two cations participate differently in the early stages of the reaction.

These results evidence the importance of an integrated multi-technique approach to address complicated processes such as the polyol synthesis of MNPs. Through a single coordinated programme, CERIC-ERIC provided complementary facilities for XRPD, SAXS, and XAFS, enabling crystalline phase evolution, pre-crystalline nanoscale growth, and element-specific local structure to be investigated within a coherent experimental strategy. Such a combined approach revealed a complicated multiscale pathway inaccessible to any individual technique and provided mechanistic guidelines for tailoring MNP through synthesis.

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