Modulation of exsolution dynamics through composition control of high-entropy spinel oxides

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Nanoparticle exsolution is a widely investigated route to build stable metal-oxide interfaces, in which reducible cations migrate from the host lattice and form embedded nanoparticles that are strongly anchored, resist agglomeration, and are stable under harsh conditions compared with conventionally impregnated catalysts [1,2]. High-entropy oxides (HEOs) push this concept further. Their chemically complex lattice tolerates higher densities of defects, stabilizes local disorder, accommodates metastable motifs, and facilitates ion mobility, making them compositionally programmable exsolution platforms for multimetallic exsolved nanoparticles with tunable metallic phase fraction and composition [3]. We have demonstrated that multimetallic nanoparticles can exsolve from HEO spinels when heated under a reducing atmosphere, and the structure is completely regenerated when exposed to an oxidizing environment. The structural evolution during the exsolution process was tracked by *in situ* PXRD, as shown in Fig. 1a-c for the spinel composed of $(Cu_{0.33}Ni_{0.33}Co_{0.33})(Cr_{0.5}Mn_{0.5})_2O_4$. HR-STEM coupled to EDS of the sample exsolved at 700 °C (Fig. 1d) confirmed the exsolution of multimetallic alloyed nanoparticles, composed of CoNiCu. By comparing different HEO spinel compositions, we demonstrated that exsolution proceeds through composition-dependent pathways dictated by the ability of the host oxide to undergo local structural rearrangements (Fig. 1e), observed using PXRD (long-range order) and PDF analysis (short-range order). The emergence of transient rocksalt-type motifs mediates cation transport within the spinel framework and drives greater exsolution extents and multimetallic nanoparticle formation. Overall, our findings show that exsolution in HEO spinels is a structure-governed process, in which local rearrangements and transient intermediates control the exsolved phase composition and the achievable exsolution extent.

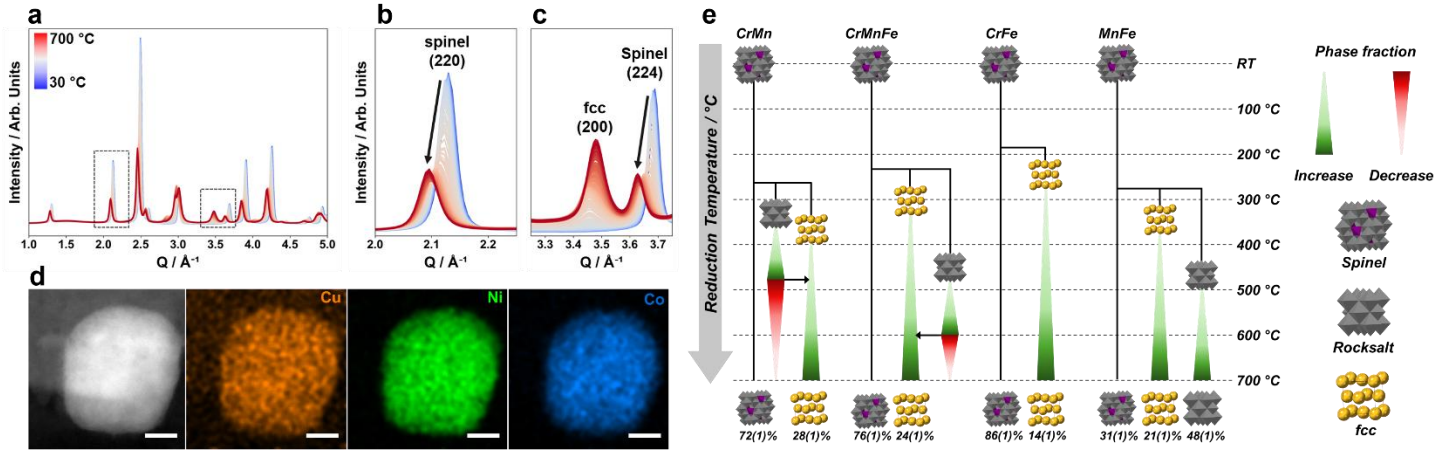


Figure 1. (a) In situ *PXRD patterns of* $(Co_{0.33}Ni_{0.33}Cu_{0.33})(Cr_{0.5}Mn_{0.5})_2O_4$ *upon heating under reducing atmosphere (4%* H_2*/Ar).* ***(b,c)*** *zoomed region highlighted in* ***(a)****.* ***(d)*** *HR-STEM HAADF and respective Cu, Ni, and Co EDS mapping after reduction at 700 °C, scale bar of 5nm.* ***(e)*** *Scheme of exsolution mechanisms and dynamics as a function of composition. The values below each phase correspond to the weighted phase fraction obtained from Rietveld refinements. The number in parentheses corresponds to the associated error. Nominal A-site =* $(Co_{0.33}Ni_{0.33}Cu_{0.33})$ *and B-site =* $(Cr_{0.5}Mn_{0.5})$*,* $(Cr_{0.5}Fe_{0.5})$*,* $(Mn_{0.5}Fe_{0.5})$*, or* $(Cr_{0.33}Mn_{0.33}Fe_{0.33})$*, labelled as CrMn, CrFe, MnFe, CrMnFe, respectively.*

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