Synergic combination of miniemulsion and solvothermal routes: exploiting unconventional conditions for the synthesis of highly crystalline transition metal ferrites

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Water droplets dispersed in a continuous organic phase of an inverse miniemulsion, being stable against coalescence and diffusion, are able to act as nanoreactors and effectively confine crystallization of inorganic materials [1]. Physical and chemical properties of liquids in nanodroplets are substantially different from those of the bulk phase, and crystalline materials can be achieved in milder conditions than usually required [2]. So far, this exploitation of the miniemulsion route has been studied only under mild conditions (low/room temperature and ambient pressure).

Here, we combine the miniemulsion technique with the non-standard conditions provided by solvothermal procedures [3, 4], to investigate the effects on the crystallization and on the properties of the materials of increased pressure and the consequent not-standard solvent properties in terms of dielectric constant and viscosity. The synergic combination of the two routes allowed us to achieve crystalline and pure phase ferrites (MFe$_2$O$_4$ where M are Mn, Fe, Co, Ni, Cu, and Zn) at lower temperature (i.e. 80 °C) than usually required and without any post-synthesis thermal treatment. This is an unprecedented result, affording a greener route to low temperature crystallization and avoiding the coalescence with the confinement provided by the droplets.

The miniemulsion at ambient pressure and the batch condition either at ambient pressure or under solvothermal conditions, performed for sake of comparison, did not result in a comparatively highly crystalline ferrite, demonstrating the synergy. Furthermore, time-resolved experiments of crystallization of ferrites produced by the combination of the two routes showed that the crystallinity is achieved already after 3 hours of reaction, outlining the occurrence of a crystallization path requiring much less energy.

Ferrites produced in miniemulsion were assessed as heterogeneous catalysts for the oxidation of styrene in organic solvents: one of the main advantages is the improved dispersibility in organic media compared to the batch material due to the residual presence of surfactant from the synthesis. The conversion of styrene reached 100% after 24 hours with CoFe$_2$O$_4$, MnFe$_2$O$_4$ and CuFe$_2$O$_4$ and the catalyst, magnetically recovered with a magnet, showed no decrease in the conversion even after 4 cycles of reaction, showing good recyclability.