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Heterogeneous and retarded phase transformation of ferrihydrite on montmorillonite surface: The important role of surface interactions

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Abstract

The formation of heteroaggregates is critical to controlling the stabilization and transformation of nanominerals and mineral nanoparticles (NMMNs) in nature, but the underlying mechanisms remain to be deciphered. In this work, we study the effect of surface interactions between ferrihydrite (Fh) and montmorillonite (Mnt) within their heteroaggregates on the transformation behaviors of Fh. A series of heteroaggregates composed of Fh and Mnt were synthesized by modulating their mass ratios and synthesis methods, i.e., directly complexing Fh with Mnt (Fh-Mnt) or in situ growing Fh on Mnt (Fh/Mnt). Structural characterization using XRD, TG-DSC, TEM, and FTIR indicated that Fh particles coated more evenly on the Mnt surface within the heteroaggregates synthesized by in situ growing Fh on Mnt and with lower Fh to Mnt ratio, and accordingly these heteroaggregates showed stronger surface interactions between Fh and Mnt. The phase transformation of Fh to hematite (Hem) on the heteroaggregates can be significantly affected during the heating treatment. Compared with that of pure Fh, the transformation of Fh on all of the heteroaggregates was retarded (e.g., slower transformation rate and smaller produced Hem particles), particularly for the samples with stronger surface interactions (e.g., Fh/Mnt with lower Fh to Mnt ratio). Noticeably, the heated heteroaggregates may simultaneously contain pristine Fh, intermediate maghemite, and transformed Hem, showing a heterogeneous transformation behavior of Fh. The strong interactions between Fh and Mnt will enhance the dispersion of Fh and restrict the structural rearrangement of Fh (particularly those at the interface) during the phase transformation process, resulting in retarded and heterogenous transformation of Fh on these heteroaggregates. These findings not only enrich our knowledge of the phase transformation characteristics of Fh but also advance our understanding of the important role of mineral surface interactions in stabilizing NMMNs in nature.

Keywords: Nanominerals and mineral nanoparticles, ferrihydrite, clay minerals, surface interactions, phase transformation