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Formation mechanism of domain structure and defect of goethite surface

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Goethite (alfa-FeOOH) is one of the most common iron (oxyhydr)oxide minerals in surface environment of Earth and has huge specific surface area due to the small particle size. The surface of goethite plays an important role in many chemical reactions, e.g., adsorption, dissolution and precipitation, and thus their mechanism and kinetics are studied in detail using synthetic goethite. However goethite occurring in natural environment shows wide range of crystallinity (Kuhnel et al., 1975) and it is known that many properties, e.g. *a*-dimension of the unit cell and OH bending mode, are affected by the crystallinity (Schwertmann et al., 1985). Goethite with low crystallinity shows multidomain structure and weak hydrogen bonds owing to the -OH defects in the crystal structure and those characteristics accelerate the dissolution and adsorption rates (Strauss et al., 1997). In this study, we investigate the surface morphology and the ratio of surface hydroxyl group to oxygen, [-OH]/([-O] + [-OH]), of goethite with varying crystallinity and discuss the formation mechanism of multidomain structure and OH defects.

Goethite in this study was synthesized using ferric nitrate ($Fe(NO_3)_3$-$9H_2O$) and potassium hydroxide (KOH) as starting materials, according to Schwertmann et al. (1985). The dark brown precipitate, which is amorphous ferric oxide called ferryhydrite, was aged for 70 days at 4 oC (G-04), 30 days at 30 oC (G-30), 10 days at 50 oC (G-50) and 3 days at 70 oC (G-70). All products were washed with pure water, dried in nitrogen atmosphere and indentified as goethite by powder XRD analysis. The morphology of these goethite were observed using AFM and specific surface area were measured with 11-points BET method. X-ray photoelectron spectroscopy (XPS) was employed to analyze the ratio of surface hydroxyl groups to surface oxygen.

AFM observations revealed that all goethites have acicular morphology, however, goethite aged at high temperature has larger particle size ($>$ 1000 nm), higher aspect ratio and monodomain structure. On the other hand, goethite aged at low temperature has smaller particle size ($<$ 200 nm), lower aspect ratio and multidomain structure. This observation well agrees with TEM observation by Schwertmann et al. (1985). XPS analysis revealed that the ratio of surface hydroxyl group to oxygen, [-OH]/([-O] + [-OH]), was higher for the goethite aged at higher temperature.

Transformation of ferrihydrite into goethite proceeds in three stages (Cornell et al., 1989; Yuwono et al.): (1) crystallization of goethite nanoparticles from ferrihydrite nanoparticles, (2) oriented attachment of goethite nanocrystals and (3) development of crystal morphology by aging. In aging at high temperature, ferryhydrite nanoparticles crystallize rapidly and completely, and thus oriented attachment occurs without misalignments. As a result, goethite aged at high temperature has monodomain structure and high aspect ratio. On the other hand, in lower temperature, ferrihydrite crystallizes into goethite nanoparticles slowly and incompletely, hence aggregation of the goethite nanoparticles has many misalignments. The multidomain structure, OH defects and low aspect ratio of goethite aged at low temperature arise from the misalignments within the aggregate of nanoparticles as a precursor of aged goethite.

Keywords: crystallinity, crystal morphology, particle size, AFM, XPS