

Interfacial structures and acidity constants of goethite from first-principles Molecular Dynamics simulations

YINGCHUN ZHANG¹, XIANDONG LIU^{1,*}, JUN CHENG², AND XIANCAI LU¹

¹State Key Laboratory for Mineral Deposits Research, School of Earth Sciences and Engineering, Nanjing University, Nanjing, Jiangsu 210023, P.R. China

²College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, Fujian 361005, P.R. China

ABSTRACT

In this paper, we report a first-principles Molecular Dynamics (FPMD) study of interfacial structures and acidity constants of goethite. The pK_a values of the groups on (010), (110), and (021) surfaces (space group *Pbnm*) are derived with the FPMD based vertical energy gap technique. The results indicate that major reactive groups include ≡Fe₂OH₂ and ≡FeOH₂ on (010), ≡FeOH₂, ≡Fe₃O_LH, and ≡Fe₃O_UH on (110), and ≡FeO_hH₂ and ≡Fe₂OH on (021). The interfacial structures were characterized in detail with a focus on the hydrogen bonding environment. With the calculated pK_a values, the point of zero charges (PZCs) of the three surfaces are derived and the overall PZC range of goethite is found to be consistent with the experiment. We further discuss the potential applications of these results in future studies toward understanding the environmental processes of goethite.

Keywords: Goethite, acidity constant, interfacial structure, first-principles Molecular Dynamics