

# Acid–Base Properties of Cis-Vacant Montmorillonite Edge Surfaces: A Combined First-Principles Molecular Dynamics and Surface Complexation Modeling Approach

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Montmorillonite layer edge surfaces have pH-dependent properties, which arises from the acid-base reactivity of their surface functional groups. Edge surface acidity (with intrinsic reaction equilibrium constant,  $pK_a$ ) is a chemical property that is affected by crystal structure. While a cis-vacant structure predominates in natural montmorillonites, prior molecular level studies assume a centrosymmetric trans-vacant configuration, which potentially leads to an incorrect prediction of montmorillonite acid-base surface properties. We computed intrinsic acidity constants of surface sites of a montmorillonite layer with cis-vacant structure using the FPMD (First-Principles Molecular Dynamics) based vertical energy gap method. We evaluated  $pK_a$  values for both non-substituted and Mg-substituted layers on common edge surfaces (i.e. surfaces perpendicular to [010], [0(1)0], [110] and [(1)(1)0] crystallographic directions). The functional groups  $\equiv\text{Si}(\text{OH})$ ,  $\equiv\text{Al}(\text{OH})_2/\equiv\text{Al}(\text{OH})(\text{OH}_2)$  and  $\equiv\text{SiO}(\text{OH})\text{Al}$  sites on surfaces perpendicular to [010] and [0(1)0], and  $\equiv\text{Si}(\text{OH})^U$ ,  $\equiv\text{Si}(\text{OH})^L$ ,  $\equiv\text{Al}(\text{OH}_2)$  and  $\equiv\text{Al}(\text{OH})_2$  on surfaces perpendicular to [110] and [(1)(1)0] determine proton reactivity of non-substituted cis-vacant edge surfaces. The  $\equiv\text{SiO}(\text{OH})\text{Al}$  site was the unique site on edge surfaces on cis-vacant model. Moreover, the structural OH sites on edge surfaces had extremely high  $pK_a$  values, which do not show reactivity at a common pH. Meanwhile,  $\text{Mg}^{2+}$  substitution results in an increase in  $pK_a$  values at local or adjacent sites, in which the effect is limited by the distance between the sites. A surface complexation model was built with predicted  $pK_a$  values, which enabled to predict surface properties as a function of pH and ionic strength. The results indicate edge surface charge of both trans- and cis-vacant models had little dependence on  $\text{Mg}^{2+}$  substitutions, but the dependence on the crystal plane orientation