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Mechanistic understanding of the dehydroxylation reaction of smectites: Insights from reactive force field (ReaxFF) molecular dynamics simulation

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ABSTRACT

Smectite, a major barrier material for contaminants in Earth's critical zone, is a layered aluminosilicate mineral with *cis*-vacant (*cv*) and *trans*-vacant (*tv*) configurations. High-temperature transformations of smectite are directly related to smectite's thermal reactions. However, the precise thermal reaction mechanisms and thermally induced structural transitions of *cv* and *tv* smectite remain debated. In this study, we systematically investigated the mechanism of thermal reactions of *cv* and *tv* smectite models using reactive force field (ReaxFF) molecular dynamics. We explored the deprotonation and the intralayer dehydration steps of *cv* and *tv* smectites at 700 and 900 K. The results revealed that the dehydroxylation reaction of *cv* smectite exhibited more difficulty than *tv* smectite at 700 K, while demonstrating less difficulty at 900 K. Furthermore, it was found that the dehydroxylated *cv* and *tv* smectites evolved to a consistent structure spontaneously. Our findings further confirmed that *cv* smectite has a higher dehydroxylation temperature than *tv* smectite and thus provided a theoretical basis for distinguishing *cv* and *tv* smectites using thermogravimetric analysis (TGA). Moreover, we gathered TGA data of smectites from different regions, confirming that montmorillonites have a *cv* structure and almost all smectites from China (over 11 provinces) are *cv*. This study provides a molecular-level understanding of the thermal reaction mechanisms of smectites and a physical basis for further study and application of smectites.

Keywords: Reactive force field molecular dynamics, metadynamics, smectite, *cis*-vacant, *trans*-vacant, thermal reactions