

Theoretical investigation of heterogeneous oxidation of sulfuric dioxide on mineral dusts and its implication on atmospheric new particle formation

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Heterogeneous oxidation of sulfur dioxide on mineral dusts is an important source of atmospheric sulfate which affects solar radiation and air quality, but mechanistic understanding at molecular level is largely lacking. We employed in this work a novel computational approach to investigate this process on hematite, a chosen model mineral dust. This approach performs molecular dynamic simulations by incorporating the our own n-layered integrated molecular orbital and molecular mechanics (ONIOM) method and other advanced quantum and kinetic methods. Our results clearly showed that under low relative humidity sulfur dioxide can react with surface hydroxyl groups to produce interfacial sulfate, while in medium relative humidity it reacts with interfacial water to form HSO₃ radicals which then escape the surface and are further oxidized to gas-phase sulfuric acid. In addition, hydrophilic organic species can serve as water aggregator to alter heterogeneous reaction mechanisms. Our study demonstrated that reaction channels and subsequent impacts can be substantially different under various interfacial environments, which are closely correlated to relative humidity, and hence kinetic parameterization of each channel and corresponding impact should be respectively evaluated for further models of atmospheric chemistry. Atmospheric implication, in particular, contribution to new particle formation will be discussed.

Keywords: new particle formation, heterogeneous oxidation, sulfuric dioxide, mineral dusts, hematite, atmospheric radicals