Gas-solid reaction modeling: CO_2 adsorption in potassium-doped lithium orthosilicate

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Carbon dioxide emissions from industrial processes and fossil-fuel power generation remain a major driver of climate change, and carbon capture and storage (CCS) technologies are essential for mitigating their impact. In particular, high-temperature carbon capture has emerged as an alternative to the common liquid-phase absorption with amine solutions, which require gas cooling to below 100 °C for effective capture, resulting in significant energy losses for high-temperature flue gas. Among solid sorbents for high-temperature CO_2 capture, lithium orthosilicate (Li_4SiO_4) stands out for its ability to chemisorb CO_2 at 450 - 700 °C, even at the low concentrations (2–5 vol%) typical of natural gas–fired plants. It also demonstrates good regeneration performance over multiple cycles. However, at low CO_2 partial pressures, adsorption is often limited by diffusion through the growing product layer. Doping Li_4SiO_4 with potassium carbonate (K_2CO_3) forms a molten eutectic phase that enhances CO_2 transport, thus increasing the reaction rate. Modeling the CO_2 adsorption process in lithium orthosilicate pellets is fundamental to improving the design of fixed or fluidized bed reactors to achieve better performance and effective CO_2 capture.

In this study, a detailed kinetic model is developed to describe the carbonation mechanism in K_2CO_3-doped Li_4SiO_4 pellets. The model is based on a modified shrinking-core framework that captures both the initial autocatalytic reaction phase and the subsequent diffusion-limited stage. The early chemical regime is modeled using an Avrami-type nucleation expression, which accounts for the rapid formation of product nuclei that accelerate the surface reaction rates. The later stage is governed by CO_2 diffusion through the carbonate product layer, represented by an exponential decay diffusion coefficient as pellet conversion increases, reflecting the thickening solid product layer due to the continuous reaction. Model parameters are obtained by fitting the time derivative of conversion data from thermogravimetric analyses under various temperatures and CO_2 concentrations. This approach enables the accurate determination of the kinetic parameters of the reaction under different conditions. The model successfully reproduces both the chemical and diffusion regimes, aligning well with the experimental data and providing mechanistic insight into the interplay of nucleation, molten-salt formation, and product-layer resistance.

Keywords: *CO_2 capture, Shrinking core model, gas-solid reaction, nucleation, diffusion*