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Thermal decomposition of calcite: Mechanisms of formation and textural evolution of CaO nanocrystals

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Abstract

Field emission scanning electron microscopy (FESEM), two-dimensional X-ray diffraction (2D-XRD), and transmission electron microscopy coupled with selected area electron diffraction (TEM-SAED) analyses of the reactant/product textural relationship show that the thermal decomposition of Iceland spar single crystals according to the reaction $CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$ is pseudomorphic and topotactic. This reaction begins with the formation of a mesoporous structure made up of up to four sets of oriented rod-shaped CaO nanocrystals on each rhombohedral cleavage face of the calcite pseudomorph. The four sets formed on $(10\bar{1}4)_{calcite}$ display the following topotactic relationships: (1) $(1\bar{2}10)_{calcite}//(110)_{CaO}$; (2) $(\bar{1}104)_{calcite}\perp(110)_{CaO}$; (3) $(\bar{1}018)_{calcite}//(110)_{CaO}$; and (4) $(0\bar{1}14)_{calcite}\perp(110)_{CaO}$; with $[841]_{calcite}//[1\bar{1}0]_{CaO}$ in all four cases. At this stage, the reaction mechanism is independent of P_{CO_2} (i.e., air or high vacuum). Strain accumulation leads to the collapse of the mesoporous structure, resulting in the oriented aggregation of metastable CaO nanocrystals (~5 nm in thickness) that form crystal bundles up to ~1 μm in cross-section. Finally, sintering progresses up to the maximum T reached (1150 °C). Oriented aggregation and sintering (plus associated shrinking) reduce surface area and porosity (from 79.2 to 0.6 m^2/g and from 53 to 47%, respectively) by loss of mesopores and growth of micrometer-sized pores. An isoconversional kinetic analysis of non-isothermal thermogravimetric data of the decomposition of calcite in air yields an overall effective activation energy $E_\alpha = 176 \pm 9$ kJ/mol (for $\alpha > 0.2$), a value which approaches the equilibrium enthalpy for calcite thermal decomposition (177.8 kJ/mol). The overall good kinetic fit with the F_1 model (chemical reaction, first order) is in agreement with a homogeneous transformation. These analytical and kinetic results enable us to propose a novel model for the thermal decomposition of calcite that explains how decarbonation occurs at the atomic scale via a topotactic mechanism, which is independent of the experimental conditions. This new mechanistic model may help reinterpret previous results on the calcite/CaO transformation, having important geological and technological implications.

Keywords: Calcite, lime, thermal decomposition, CaO nanocrystals, TEM-SAED, oriented aggregation, kinetics, topotactic