

Revealing the elementary processes controlling the conversion of CO₂ to MgCO₃

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Formed *via* aqueous carbonation of Mg²⁺ ions, the crystallization of magnesite (MgCO₃) is a promising route to carbon capture and reuse, albeit limited by the slow precipitation of MgCO₃. Although MgCO₃ is naturally abundant, forming at low temperature conditions, its industrial production is an energy-intensive process due to the temperatures required to prevent the formation of hydrated phases. The principal difficulty in aqueous conditions arises from the very strong Mg²⁺···H₂O interaction, with high barriers to Mg²⁺ dehydration. We present a theoretical investigation of the influence of thirty additive anions (Xⁿ⁻, n = 1–3), ranging from simple halides to more complex molecules, on the first two steps of MgCO₃ aggregation from solution: Mg²⁺ dehydration and subsequent pre-nucleative Mg²⁺···CO₃²⁻ pairing [1]. We computed the thermodynamic stability of solvent shared ion pairs (Mg²⁺···H₂O···Xⁿ⁻) and contact ion pairs (Mg²⁺···Xⁿ⁻) to reveal the propensity of additives to inhibit or promote Mg²⁺···CO₃²⁻ formation. We determined the stabilization of undercoordinated hydrated Mg²⁺ states with a vacant coordination site to which CO₃²⁻ can bind, subsequently initiating MgCO₃ nucleation or Mg²⁺ incorporation into the crystal lattice. While in pure liquid water Mg(H₂O)₆²⁺ is the only stable coordination state, anions may stabilise undercoordinated five-hydration configurations [2]. Extensive simulations of electrolyte solutions containing Na₂CO₃ with different sources of Mg²⁺ (i.e., MgCl₂, MgSO₄ and Mg(CH₃COO)₂), further show that the degree of dehydration of Mg²⁺ and the structure of prenucleation MgCO₃ clusters changes depending on counterion identity. The solution composition can lower the barrier to Mg²⁺ dehydration and subsequent incorporation into the lattice of Mg-carbonates, promoting low-temperature crystallisation. Through a fundamental understanding of the role of solution additives in the Mg²⁺ dehydration, our results help to rationalize previously reported experimental observation of the effect of solvation environments on the growth of magnesite [3]. This understanding may contribute to identifying solution composition promoting low-temperature CO₂ conversion into MgCO₃.

[1] Toroz, Song, Uddin, Chass & Di Tommaso (2021), *Cryst. Growth Des.* 22, 3080-3089

[2] Toroz, Chass & Di Tommaso (2021), *CrystEngComm* 23, 4896-4900.

[3] Power, Kenward, Dipple & Raudsepp (2017), *Cryst. Growth Des.* 17, 5652-5659.

