

Kinetics of CO₂ hydrate formation from water frost at low temperatures: Experimental results and theoretical model

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Abstract

The gas hydrate growth from frostlike powders composed of micrometer-sized ice particles does not start with hydrate shell formation, because the initial hydrate film thickness established in earlier work exceeds the ice particle dimensions. In this limiting case, the ice grains are directly consumed by a growing nucleus created on the particle surface. The conventional Johnson-Mehl-Avrami-Kolmogorov (JMAK) model,⁽¹⁾ which considers (re-) crystallization reactions phenomenologically in terms of the constituent nucleation and subsequent growth processes, cannot be directly applied to the hydrate formation from frost due to the assumption of an infinitely large domain of crystallization. We present here a modified approach to account for the small particle sizes of the starting material and extend the existing theory of gas hydrate formation from monodisperse ice powders⁽³⁻⁵⁾ to the low-temperature and low-ice-particle-size limit. This approach may also prove to be very useful for applying chemical reactions starting on the surface of nanomaterials. In situ neutron scattering was used to obtain the experimental degree of transformation as a function of temperature between 185 and 195 K. The data were analyzed with the modified JMAK model constrained by information from cryo-SEM and BET measurements. Based on the obtained activation energies for hydrate nucleation and growth, an estimate is given for the probability of formation of CO₂ hydrates at conditions relevant for Mars; a direct reaction of CO₂ gas with water frost is considered to be very unlikely on the Martian surface under current conditions. © 2011 American Chemical Society.

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