

# Influence of Nanoparticles (graphene, CuO) and Lithium Ions on Methane (CH<sub>4</sub>) and Carbon Dioxide (CO<sub>2</sub>) Hydrate Formation under Various Thermodynamic Conditions

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Clathrate hydrates of low-molecular-weight gases (e.g., methane and carbon dioxide) have gained significant attention for both energy applications and environmental management.<sup>1,2</sup> In this work, we investigate the formation of methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>) hydrates under various thermodynamic conditions, focusing on the impact of nanoparticle additives (graphene, CuO) and lithium ions (Li<sup>+</sup>). Using molecular dynamics simulations, we examined systems containing varying nanoparticle concentrations (0.5–5 wt.%) at temperatures near 270 K and pressures of 1.2 MPa (for CO<sub>2</sub>) and 2.4 MPa (for CH<sub>4</sub>), as well as a broader range of temperature and pressure values to assess changes in nucleation and growth kinetics. Our results show that an optimal nanoparticle content (~1 wt.%) significantly enhances hydrate nucleation, accelerates clathrate cage formation, and increases gas solubility compared to control samples without nanoparticles.

The promoting effect arises from localized rearrangements of water molecules at the nanoparticle–water–gas interface, leading to a shorter induction period for hydrate growth.<sup>3</sup> However, excessive nanoparticle loading (>1 wt.%) induces a disordered liquid phase that disrupts the hydrogen-bond network of water, constraining further improvements in formation kinetics.<sup>4</sup> Analyses of the structural order parameter (F<sub>4</sub>) indicated faster crystallization into hydrate-like configurations (F<sub>4</sub> ≈ 0.7) without the appearance of ice phases (F<sub>4</sub> ≈ −0.4).<sup>3</sup> Additionally, vibrational spectra confirm partial disorder at higher nanoparticle concentrations, in line with prior findings on the sensitivity of hydrate formation to interfacial phenomena.<sup>5</sup>

These observations highlight the dual role of nanoparticles: while moderate concentrations (including certain CuO loadings) significantly boost hydrate formation rates, higher doses increase system pressures and promote phase segregation. Likewise, lithium ion additions can alter local water structuring, influencing induction times and overall hydrate crystallization kinetics. Such tunable modifications may prove invaluable for optimizing hydrate-based technologies in greenhouse gas capture, thermal energy storage, and gas transportation under a range of thermobaric conditions. This work was supported by the Russian Science Foundation (project 22-19-00428).

## References

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