

Integrated DFT-Monte Carlo approach to modelling Co nanoparticles

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Despite its history spanning over almost a century, the Fischer-Tropsch (FT) process has recently gained renewed interest from the scientific community in light of its potential to speed-up the energy transition. In fact, by converting syngas into a wide variety of hydrocarbon products, this technology makes it possible to produce fundamental chemical commodities from renewable feedstocks.

Supported cobalt catalysts are particularly suitable for the FT synthesis as they showcase high activity under mild process conditions, with operating temperatures usually not exceeding 500 K.

While supported Co nanoparticles (NP) larger than 10 nm are generally reported to be structure insensitive, a positive correlation between turnover frequency (TOF) and particle size is often recorded for NPs smaller than 10 nm [1]. Hence, understanding how the NP structure evolves over this size range is important to unravel the reaction mechanism and might ultimately lead to the formulation of new strategies to produce better-performing catalysts.

In this work, we employed a paired DFT–Monte Carlo approach to generate low-energy structures of Co NPs in the 2-10 nm size range under operating conditions. In particular, both unsupported and Al₂O₃-, SiO₂- and TiO₂- supported FCC Co NPs were simulated and the site distribution over the considered size range was investigated. Additionally, the effect of the exposure of the Co NPs to typical FT CO partial pressure was considered and was shown to induce major surface reconstruction, as previously reported in experimental and theoretical works [2,3]. Finally, the obtained structures were used as inputs to model γ -Al₂O₃- and TiO₂-mediated Ostwald ripening. By doing so, we investigated how the particle size distribution evolves over an industrially meaningful time span.

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