Deciphering Effects of Nanoparticles Shape and Size on the Structure Sensitivity of the CO_2 Methanation Reaction on Ni

Gabriele SPANO',[1‡] Matteo FERRI,[1‡] Raffaele CHEULA,[1] Matteo MONAI,[2]
Bert M. WECKHUYSEN,[2] Matteo MAESTRI[1*]

[1]*Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Politecnico di Milano, Via La Masa, 34, 20156, Milano, Italy.*
[2]*Inorganic Chemistry and Catalysis Group, Institute for Circular and Sustainable Chemistry and Debye Institute for Nanomaterials Science, Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, The Netherlands*.
‡These authors equally contributed to this work
**matteo.maestri@polimi.it*

Significance and Relevance

This work presents theoretical underpinnings that elucidate the nature of the high-debated structure sensitivity in CO_2 methanation over Ni, thus offering a framework that reconciles discrepancies in the experimental literature. By combining density functional theory with Boltzmann statistics, we capture the full diversity of Ni nanoparticle shapes under reaction conditions, revealing that shape, not just size, governs the overall catalytic performance. Our findings provide rational explanation to the different experimentally observed trends in the turnover frequency. Therefore, these insights can be applied to other structure-sensitive reactions, positioning this study as essential for advancing catalyst engineering and renewable energy solutions.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling; Multiscale modeling and advanced simulation aspects.
Preferred presentation: *Oral preferred or short oral*

Introduction and Motivations

Nickel nanoparticles are key catalysts for CO_2 methanation, a promising solution for renewable energy storage. For this reaction, the trend of turnover frequency (TOF) with Ni nanoparticle size remains debated. Some studies observe a maximum activity around 2.5 nm[1], while others report an increase of TOF with size, ultimately reaching a plateau[2]. This inconsistency highlights a lack of consensus regarding the origin of structure sensitivity for CO_2 methanation over Ni. Traditional particle models based on Wulff construction fail to explain these variations, as they rigidly provide only the equilibrium shape for each size. Thus, they overlook the diversity of nanoparticle shapes that can coexist for a given size under reaction conditions. To overcome these limitations, we employ the methodology proposed by Cheula et al.,[3] which allows to capture all the possible particle shapes for each size which exhibit a significant probability of occurrence. Our results reveal that TOF trends depend strongly on nanoparticle shape, not just size. The shape, in turn, can be affected by catalyst preparation method or choice of support material. Thus, we provide rational explanation to the different trends observed in the turnover frequency and offer critical insights for optimizing catalyst design.

Materials and Methods

DFT calculations are performed using the Quantum Espresso suite with the PBE functional. The nanoparticle ensemble, spanning sizes from 0.8 to 6.5 nm, is generated using the procedure from Cheula et al.,[3] based on cleaving bulk Ni into nanoparticles with various surface combinations. With a surrogate atomistic model, we compute the formation energy, and with a Boltzmann distribution we evaluate the probability of nanoparticle occurrence based on energy. Ni(111) and Ni(100) are found to be the most abundant facets of catalyst nanoparticles. Therefore, we adopt the microkinetic model proposed by Sterk et al.,[4] thus considering HCO^* dissociation into CH^* and O^* and $CH_3{}^*$ formation from

CH_2^* and H^* as rate determining steps over Ni(111) and Ni(100) respectively. In addition, we explicitly account for dissociation reactions that occur at the edge between these two facets.

Results and Discussion

As shown in Fig.1a, we obtain a TOF trend in excellent agreement with the experiments of Vogt et al.,[1] with a maximum activity around 2.5 nm. The overall activity is mainly attributable to the edge fraction of Ni(100) sites, since the active sites at the Ni(100)-Ni(111) interface are found to have the highest activity. However, particularly in proximity of the maximum between 1-3 nm, there is a broad distribution of particles whose activity significantly deviate from the average TOF trend. Indeed, multiple particle shapes coexist at the same size. Therefore, we divide Ni nanoparticles into families based on their shape, i.e., classifying them based on the fraction of Ni(100) sites, which spans in the range between 4-17%. Thus, we separately analyze the TOFs of the different Ni nanoparticles families. As shown in Fig1.b, particles with a high fraction of Ni(100) sites present a maximum in the activity around 2.2 nm. As the Ni(100) fraction decreases, the TOF flattens ultimately exhibiting a "hockey stick" behavior. These results show that the TOF trends are significantly different and depend strongly on the specific shapes of nanoparticle families. Therefore, this work highlights the critical need to consider both size and shape of catalyst nanoparticles to fully understand structure sensitivity of CO_2 methanation. The shape, in turn, can be affected by catalyst preparation method or the choice of support material. Operating conditions favoring particles with a high Ni(100) fraction lead to a maximum in the TOF with particle size. Differently, conditions promoting particles with a low Ni(100)-fraction results in a final plateau of the TOF, thus highlighting that shape, not just size, governs the overall catalytic performance. More broadly, these insights provide an explanation to the different trends experimentally observed in the turnover frequency and thus pave the way to study other structure-sensitive reactions, such as ammonia synthesis and decomposition.

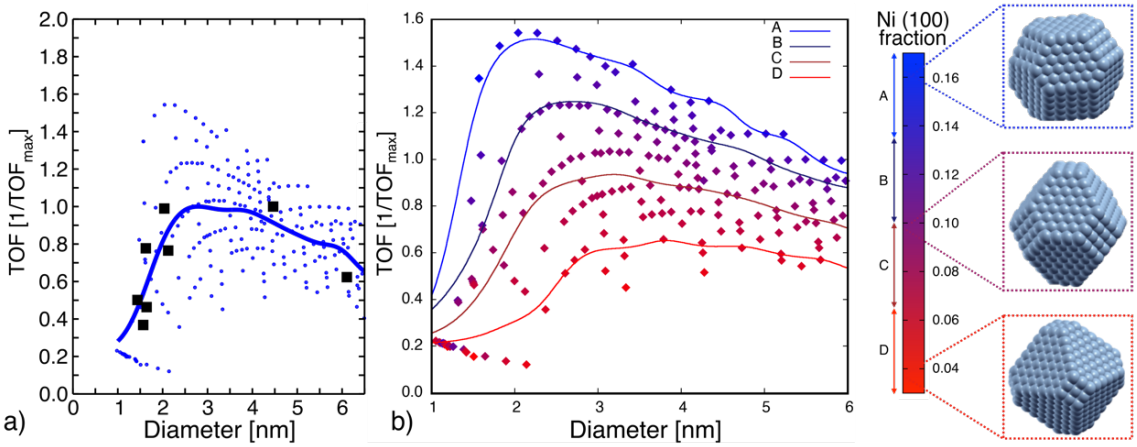

Figure 1. **(a)** TOF of the high-probability metal nanoparticles (dots) and filtered with a gaussian smearing (solid line) as a function of the diameter; experimental data of Vogt et al.[1] are reported as black squares. **(b)** TOF of the high-probability metal nanoparticles as a function of the diameter (dots), represented in terms of the Ni(100) sites fraction, according to the color bar. The lines represent a gaussian smoothing of four different families of metal nanoparticles, having similar Ni(100) fraction. Three selected metal nanoparticles with similar size (2 nm) and different shape (high, intermediate and low Ni(100) fraction) are reported in the insights of the color bar.

References

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