

Spark ablation: a dry, physical, and continuous method to prepare powdery heterogeneous catalysts for CO₂ methanation

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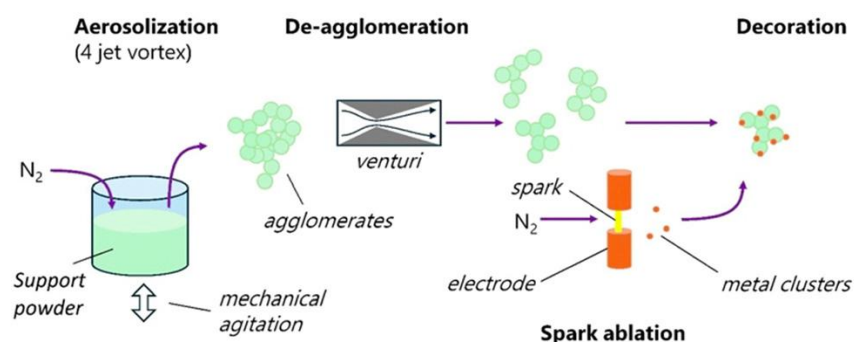
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Abstract

Spark ablation is a compelling alternative to traditional wet chemical methods, primed to reduced environmental impact (i.e., no use of solvents, precursors, salts, ligands, or high-temperature treatments). It was developed to generate nanoparticles, using electrical discharges between two electrodes of a target material in inert gas flow. This physical process yields metal particles in the 1-10 nm size range. The well-controlled deposition of generated metal nanoparticles onto flat surfaces has been well documented.^{1,2} Yet, for heterogeneous catalysis, powdery materials are needed. We report the first synthesis of a powdery heterogeneous catalyst using spark ablation technology.³ A spark nanoparticle generator is modified to allow a direct deposition onto pulverulent materials. The concept relies on the aerosolization of a powder from a mechanically vibrating reservoir by a 4-jet vortex fed with N₂. The aerosolized powder is then transported through a venturi for de-agglomeration before injection into the spark generator. Sparks generated between the metal electrodes produce metal clusters, which are carried by N₂ to form metal nanoparticles deposited onto powder particles. Herein, TiO₂ P25 powder is used as the catalyst support, while Ni electrodes are used to generate Ni nanoparticles as the active phase. The resulting 2.3wt%Ni/TiO₂ catalyst can be collected on filter paper. XRD and HRTEM analyses confirm the formation of small Ni/NiO nanoparticles (<5 nm) that are either well-dispersed on TiO₂ or “floating” without direct contact with TiO₂ support, as the homogeneity of the deposit is still not optimal. Although the Ni loading, Ni particle size and metal-support interaction have not been fully optimized, the Ni/TiO₂ catalyst achieves satisfactory CO₂ conversion of 53% and CH₄ selectivity of 76% at 400°C. Small Ni nanoparticles (<5 nm), well-dispersed on TiO₂ support, remain stabilized after the reaction. Nevertheless, few large particles (50-80 nm) can also be found, likely stemming from the sintering of “floating” Ni nanoparticles without interaction with TiO₂. The homogeneity of deposition could be further improved by improving the design of the mixing zone and better controlling the powder aerosolization. Additionally, the scope could be expanded to other

metals (e.g., Ru, Rh, Pd, Co, and Fe), which have been reported as active and selective metal catalysts for CO₂ methanation. Currently, Ru electrodes are used to generate Ru nanoparticles deposited on TiO₂ powder. The resulting 0.8wt%Ru/TiO₂ catalyst demonstrates promising catalytic performance, achieving 53% CO₂ conversion and 100% CH₄ selectivity at 300 °C.



Attached image: Schematic view on the set-up used to prepare powdery metal nanoparticle-based catalysts.

References

1. T.V. Pfeiffer, J. Feng, A. Schmidt-Ott, *Adv. Powder Technol.* **2014**, 25, 56.
2. S. Drdova, M. Gao, O. Sambalova, R. Pauer, Z. Zhou, S. Dimitriadou, A. Schmidt-Ott, J. Wang, *Environ. Sci.: Nano.* **2024**, 11, 1023.
3. D.P. Debecker, P. Hongmanorom, T.V. Pfeiffer, B. Zijlstra, Y. Zhao, S. Casale, C. Sassoie, *Chem. Commun.* **2024**, 60, 11076.