Spark-ablated metal nanoparticle catalysts supported on TiO_2 for CO_2 methanation

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Significance and Relevance

We report the first synthesis of a powdery heterogeneous catalyst using spark ablation technology.[1] A spark nanoparticle generator is modified to allow a direct deposition onto pulverulent materials. The concept relies on the aerosolization of a powder, which is gas-transported and injected in the path of metal nanoparticle formation. Herein, TiO_2 powder is used as the catalyst support, while Ni or Ru electrodes are used to generate Ni or Ru nanoparticles as the active phase. The resulting Ni/TiO_2 and Ru/TiO_2 catalysts are readily active in the hydrogenation of CO_2 to CH_4.

Preferred topic and 2nd choice for the topic: "CO_2 utilization and recycling" and "Fundamental advances in understanding catalysis"
Preferred presentation: Oral only

Introduction and Motivations

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.[2, 3] Yet, for heterogeneous catalysis, powdery materials are needed.

Materials and Methods

In Figure 1, TiO_2 P25 powder was aerosolized from a mechanically vibrating reservoir by a 4-jet vortex fed with N_2. The aerosolized powder was transported through a venturi for de-agglomeration before injection into the spark generator. Sparks generated between the Ni or Ru electrodes produced Ni or Ru clusters, which were carried by N_2 to form Ni or Ru nanoparticles deposited onto TiO_2 particles. The resulting Ni/TiO_2 or Ru/TiO_2 catalysts were collected on filter paper.

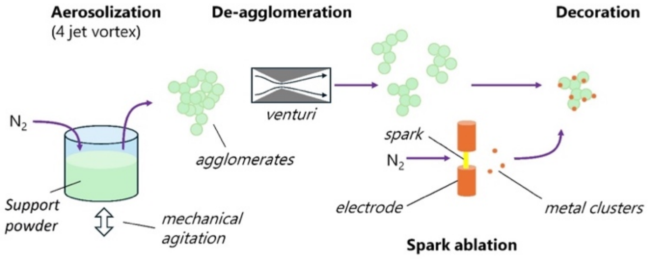

Figure 1. Schematic view on the set-up used to prepare powdery Ni/TiO_2 and Ru/TiO_2 catalysts.

Results and Discussion

The pristine TiO_2 support and the as-prepared Ni/TiO_2 catalyst exhibit a H3-type hysteresis loop, resulting from the interparticle voids in the loose aggregates of non-porous TiO_2 particles. The diffractograms of the TiO_2 support and the as-prepared Ni/TiO_2 catalyst are presented in Figure 2 (a). After Ni loading (2.3 wt% determined by ICP-AES), the TiO_2 diffraction peaks are unchanged in positions and width, which suggests that TiO_2 crystallites are unaffected by the catalyst preparation. Additionally, the main diffraction peaks of Ni ($2\theta = 44.6°$) or NiO ($2\theta = 43.1°$) crystalline phases are not detectable in the XRD pattern of the as-prepared Ni/TiO_2 catalyst, excluding the presence of Ni-based crystallites larger than 5 nm. HRTEM image (Figure 3(a)) further confirms this observation, showing small Ni nanoparticles (<5 nm) well-dispersed on TiO_2 and revealing the lattice fringes with inter-planar distances of 2.0-2.1 Å and 2.35-2.45 Å, corresponding to the (111) crystal plane of cubic Ni and NiO, respectively. It should be noted that the homogeneity of the deposit is still not optimal, as some "floating" Ni/NiO nanoparticles can also be observed, not being in contact with TiO_2 support, in Figure 3(b). Despite no interaction with TiO_2 support, these nanoparticles are very small (<5 nm). Although the Ni loading, Ni particle size and metal-support interaction have not been fully optimized, the Ni/TiO_2 catalyst achieves satisfactory CO_2 conversion of 53% and CH_4 selectivity of 76% at 400°C, as shown in Figure 2(b). After the reaction, HRTEM image (Figure 3(c)) shows that small Ni nanoparticles (a few nanometer), well-dispersed on TiO_2 support, remain stabilized after reductive pretreatment and subsequent reaction. Nevertheless, few large particles (50-80 nm) can also be found in Figure 3(d), likely stemming from the sintering of "floating" Ni nanoparticles without interaction with TiO_2. The presence of few large Ni nanoparticles is consistent with the small and relatively narrow XRD peak at 44.6° of the spent Ni/TiO_2 catalyst in Figure 2(a).

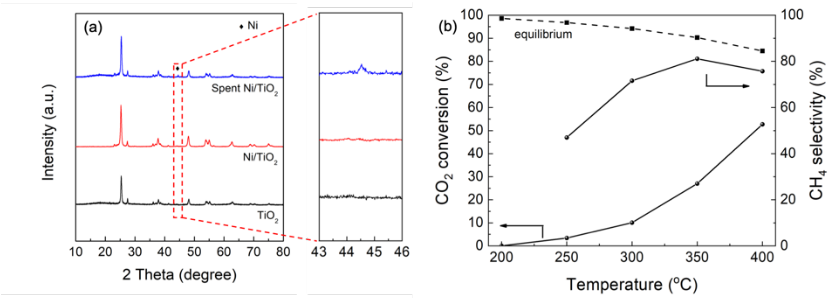

Figure 2. (a) XRD patterns of the TiO_2 support, as-prepared Ni/TiO_2 catalyst and spent Ni/TiO_2 catalyst. (b) CO_2 conversion and CH_4 selectivity of Ni/TiO_2 catalyst as a function of temperature.

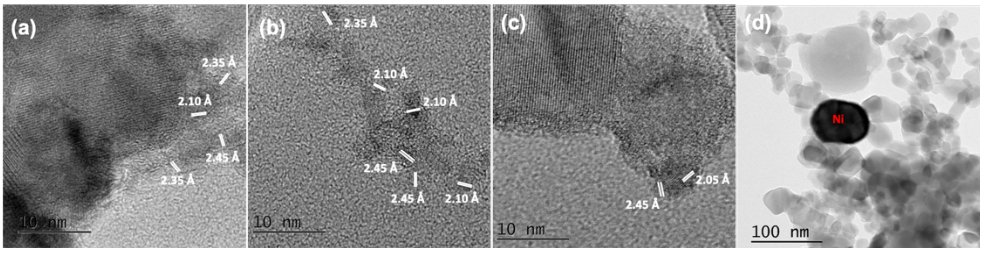

Figure 3. TEM images of (a) and (b) the as-prepared Ni/TiO_2 catalyst and (c) and (d) the spent Ni/TiO_2 catalyst.

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 CO_2 methanation. Currently, Ru electrodes are used to generate Ru nanoparticles deposited on TiO_2 powder. The resulting Ru/TiO_2 catalyst demonstrates promising catalytic performance, achieving 53% CO_2 conversion and 100% CH_4 selectivity at 300 °C.

References

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