Powdery metal nanoparticle-based catalysts prepared by spark ablation for CO_2 methanation

P. Hongmanorom[1], D.P. Debecker[1]*
[1]*Institute of Condensed Matter and Nanoscience, UCLouvain, Louvain-La-Neuve, Belgium*
*damien.debecker@uclouvain.be

Introduction

Wet chemical methods are the most common processes implemented for both lab- and industrial-scale production of metal nanoparticles and supported metal nanoparticles. These processes usually generate large amounts of liquid waste, making use of solvents, ligands, surfactants, counter ions, etc. Also, they mostly rely on multi-step energy-intensive procedures, such as aging, drying, calcination, and reduction.[1] 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 primary 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. We propose for the first time to modify a spark nanoparticle generator to allow a direct deposition onto pulverulent materials.[4] 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 electrodes are used to generate Ni nanoparticles as the active phase, forming the Ni/TiO_2 catalyst for CO_2 methanation.

Materials and Methods

In Figure 1 (Left), TiO_2 P25 (Degussa) powder was aerosolized from a mechanically vibrating reservoir by a 4-jet vortex fed with N_2 (99.9%; 3 L/min). The aerosolized powder was transported through a venturi for de-agglomeration before injection into the spark generator. Sparks generated between the Ni electrodes (99.99%; 3mm diameter) with a gap voltage of 1.3 kV and a charging current of 10.4 mA produced Ni clusters, which were carried by N_2 (99.9%; 3 L/min) to form Ni nanoparticles deposited onto TiO_2 particles. The resulting Ni/TiO_2 catalyst was collected on filter paper. The catalyst (200 mg) was reduced at 500°C for 2 h under a flow of 20 mL/min (50% H_2/50% He) prior to the reaction testing in the 200-400°C range with a gas mixture of 20 mL/min (10% CO_2 and 40% H_2 diluted in He). Catalyst characterization was performed using N_2 physisorption, H_2-TPR, XRD, ICP-AES, and HR-TEM.

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. After Ni loading (2.3 wt% determined by ICP-AES) and CO_2 methanation reaction, the TiO_2 diffraction peaks are unchanged in intensity, positions and width, which suggests that TiO_2 crystallites are unaffected by the catalyst preparation and reaction conditions. 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/NiO crystallites larger than 5 nm. TEM images further confirm this observation, showing many small Ni nanoparticles (<5 nm) well-dispersed on TiO_2. HRTEM images also reveal 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. 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 1 (Right). After the reaction, HRTEM images show 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, 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. 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.

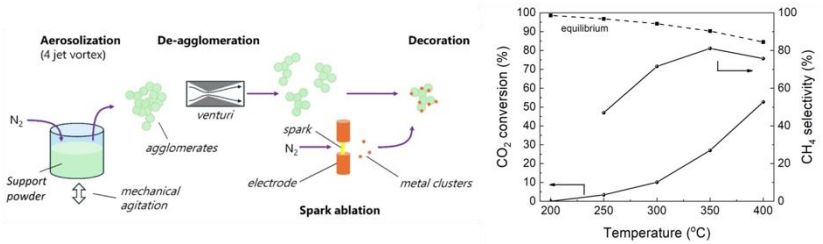

Figure 1. (Left) Schematic view on the set-up used to prepare powdery Ni/TiO_2 catalyst. (Right) CO_2 conversion and CH_4 selectivity of Ni/TiO_2 catalyst as a function of temperature.

Significance

We report the first synthesis of the powdery heterogeneous catalyst using spark ablation technology. The resulting Ni/TiO_2 catalyst is readily active in the hydrogenation of CO_2 to CH_4. This disclosed method opens new avenues for heterogeneous catalyst preparation.

References

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