

Supplementary Information

Ceria-Zirconia Encapsulated Ni Nanoparticles for CO₂ Methanation

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Supplementary Information

1.1 Synthesis methods

Encapsulation of NiNPs in SiO₂ was carried out according to a literature procedure by Savithra et al.¹ and is discussed extensively in our previous work.² Colloidal NiNPs (ca. 100 mg) were dispersed in 5 mL CHCl₃ and was slowly added to 20 mL aqueous CTAB solution (0.1 M) at room temperature. The transfer and stabilization of NiNPs from the organic to the aqueous phase was facilitated by heating the mixture to 75 °C and slowly evaporating the CHCl₃ for ca. 20 min to obtain a homogeneous black solution in contrast to the original cloudy brown mixture. The Ni/CTAB/H₂O mixture was cooled to 50 °C and diluted with 130 mL deionized water, to which 2 mL NaOH solution (1 M) was added. In situ hydrolysis of SiO₂ was performed by injecting 2.7 mL TEOS to the Ni/CTAB/H₂O solution dropwise over 5 min under stirring at 50 °C. The resulting gel-like mixture was stirred for 18 h. The product was isolated and centrifuge-washed 3 times with deionized water and 3 times with methanol. The product (Ni@SiO₂) was dried in vacuo overnight.

In order to remove the organic ligands (OAm/OAc) and templating/stabilizing agent (CTAB), Ni@SiO₂ was calcined in 20 % O₂/N₂ mixture (50 mL/min) at 500 °C (1 °C/min, 10 h). The oxidized NiO@SiO₂ nanoparticles were reduced at 600 °C in 10 % H₂/He flow (5 °C/min, 6 h).

1.2 Additional results

1.2.1 Electron microscopy

Particle size distributions of unsupported NiNPs and mesoporous silica-encapsulated NiNPs were determined with TEM and HAADF-STEM respectively (Figure S1).

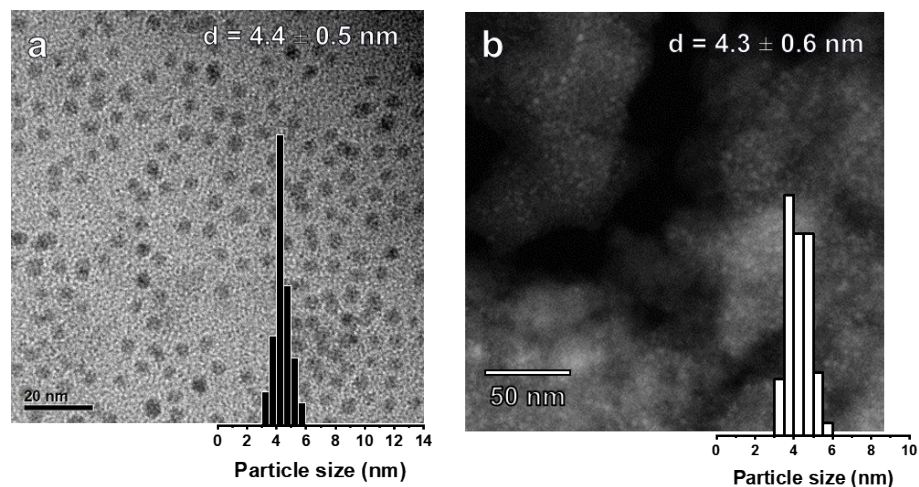


Figure S1: (a) TEM image and particle size distribution of colloidal NiNPs employed in this study. (b) HAADF-STEM image and particle size distribution of Ni(4.4)@SiO₂.

A bright-field TEM image of the ceria-zirconia (CZ) prepared *via* sol-gel after calcination at 500 °C is presented in Figure S2. This measurement demonstrates that the CZ crystallites (ca. 6 nm) form larger aggregates that are observed with HAADF-STEM.

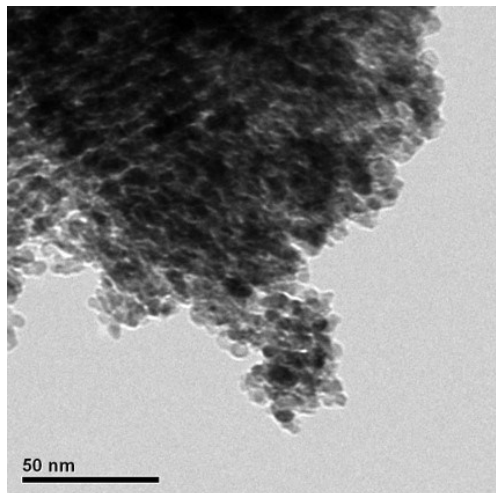


Figure S2: TEM image of ceria-zirconia prepared *via* sol-gel after calcination at 500 °C.

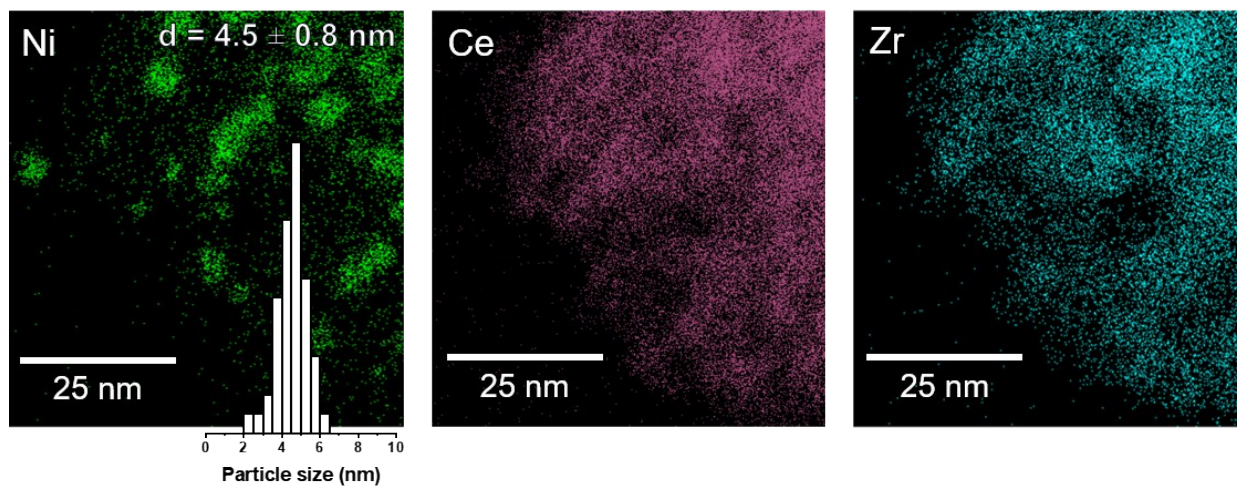


Figure S3: STEM-EDX mapping and particle size distributions of Ni(4.4)@CZ after reduction at 500 °C.

1.2.2 XPS

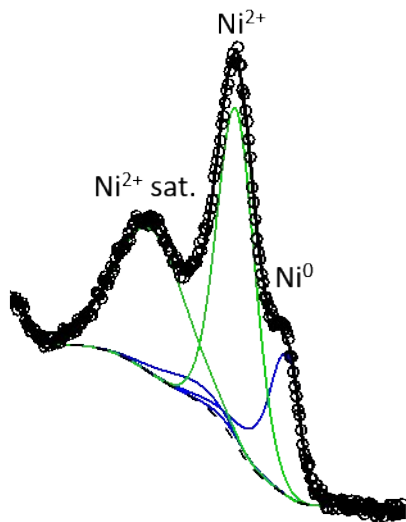


Figure S4: XP spectrum of colloidal NiNPs in Ni 2p region showing the presence of metallic Ni⁰ (blue) and oxidic Ni²⁺ (green).

1.2.3 XRD

XRD patterns of CZ after calcination at 500 °C and 800 °C were obtained to probe the stability of the CZ support. Figure S5 shows that the CZ remained phase-pure after calcination at elevated temperatures, although a slight narrowing of the XRD peaks indicated the slight aggregation of the CZ crystallites. For this reason, we calcined the Ni-CZ catalysts at 500 °C after synthesis.

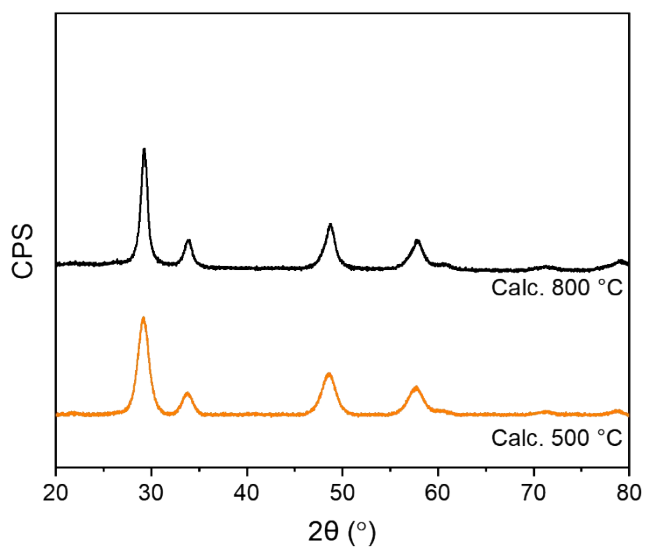


Figure S5: XRD patterns of CZ after calcination at 500 °C and 800 °C.

1.2.4 N₂ physisorption

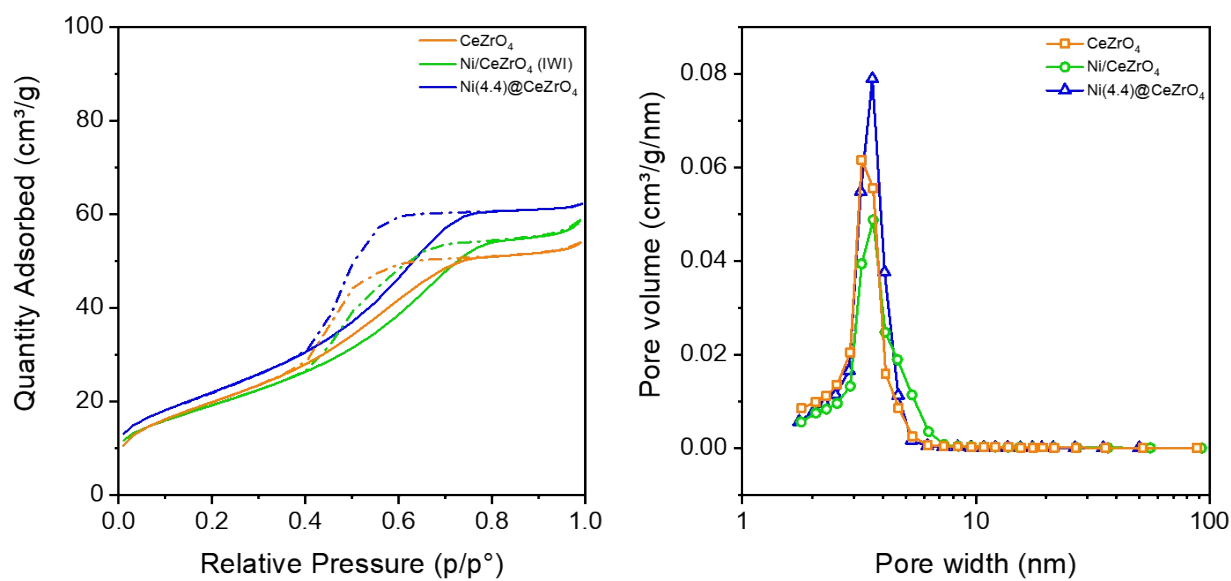


Figure S6: N₂ physisorption isotherms (left) and BJH pore-size distributions determined using the desorption branch of the isotherm (right).

1.2.5 Catalytic activity

Table S1: Kinetic results for supported catalysts for CO₂ methanation at 250 °C.

Catalyst	T (°C)	Conversion (%)	CH ₄ selectivity (%)	Rates (10 ⁻³ mol CH ₄ /mol Ni/s)	TOF (10 ⁻³ mol CH ₄ /mol active site/s) ^a	Ref.
Ni/CZ	250	3.7	95	2.35 (± 0.02)	9.61 (± 0.08)	This work
Ni(4.4)@CZ	250	9.5	100	6.15 (± 0.04)	29.3 (± 0.2)	This work
Ni(4.4)@SiO ₂	250	1.3	100	0.64 (± 0.03)	7.0 (± 0.4)	²

^a Determined by H₂ chemisorption.

References

- 1 G. H. Layan Savithra, E. Muthuswamy, R. H. Bowker, B. A. Carrillo, M. E. Bussell and S. L. Brock, *Chem. Mater.*, 2013, **25**, 825–833.
- 2 W. L. Vrijburg, J. W. A. van Helden, A. J. F. van Hoof, H. Friedrich, E. Groeneveld, E. A. Pidko and E. J. M. Hensen, *Catal. Sci. Technol.*, 2019, **9**, 2578–2591.