

Electronic Supplementary Information

## Enhanced Porosity of Ni@HSZ for Dry Reforming of Methane

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### Catalyst synthesis

*Synthesis of Ni@SiO<sub>2</sub>@ZrO<sub>2</sub>.* 3 mL of aqueous 0.25M NiCl<sub>2</sub> and 11.5 mL of Brij L4 (Sigma-Aldrich) mixed with 40 mL of n-octane in a 250 mL 3-neck round bottom flask at 30 °C under N<sub>2</sub> atmosphere protection. The mixture was stirred for 10 minutes before 1 mL of 3.172 M ice-cold NaBH<sub>4</sub> solution quickly dropped into the flask. Immediately, the clear solution would turn pitch black, and bubbles generated. After 5 minutes of N<sub>2</sub> purge, the flask sealed. Next, the solution was stirred for 8 hours to form stable Ni colloids. The SiO<sub>2</sub> coating was achieved by subsequently adding 50 mL of n-octane, 2.4 mL Brij L4, 1.2 mL ammonia (26-28%), and 6 mL of TEOS into the solution. The solution was stirred continuously for 3 hours. After 3 hours, an additional 2 mL of TEOS was added and stirred for another 5 hours. The Ni@SiO<sub>2</sub> colloids were obtained after centrifugation and washed with acetone and ethanol twice, and then re-dispersed into 200mL ethanol. Subsequently, 0.6 mL of Brij L4 and 0.6 mL of H<sub>2</sub>O were added and stirred for 30 minutes. Then, 3 mL of Zr(OBu)<sub>4</sub> was added and vigorously stirred for 15 hours at 30 °C. The colloids were collected and re-dispersed into 40 mL deionized water with 0.001M NaBH<sub>4</sub> and aged for 8 hours. The sample was collected and dried for 105 °C for 3 hours and calcined at 750 °C for 3 hours.

*Synthesis of Ni@HSZ.* 0.5 g of a calcined powder dispersed into 10 mL of 0.4 M tetrabutylammonium hydroxide (TBAOH) solution and hydrothermal treat at 180 °C for 72 hours. The colloids were collected and dried at 105 °C for 3 hours. Then, the powder was calcined at 550 °C. Lastly, the obtained powder was reduced under 50H<sub>2</sub>/N<sub>2</sub> at 750 °C for 3 hours.

### **Catalyst characterization**

X-ray diffraction (XRD) spectra collected on a D8 Rigaku 9000 powder diffractometer, equipped with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) in the  $2\theta$  range of 10°-90° at operation voltage of 45 kV and current of 200 mA. The specific surface area was determined by the BET method with N<sub>2</sub> adsorption-desorption at 77 K using a Micromeritics Tristar II 3Flex. Prior to the measurements, the samples were degassed at 300 °C for 8 hours under vacuum. The structure and morphologies of the catalysts observed by an FEI Tecnai G2 F20 transmission electron microscope (TEM) operated at 200 kV. ICP-MS (Inductively Coupled Plasma Mass Spectrometry) was performed on an Agilent 720 system to obtain each sample's Ni wt% content. After each test, the acid-digested sample was diluted with deionized water to 100 mL before the analyzer. H<sub>2</sub> temperature-programmed reduction (H<sub>2</sub>-TPR) was carried out on a Micromeritics AutoChem II 2920 apparatus. 0.1 g of the sample was filled in the cell and heated in pure Ar gas at 300 °C for 30 min to remove surface adsorbed impurities. After cooling to 50 °C, a 10% H<sub>2</sub>/Ar mixture fed with a flow rate of 50 mL min<sup>-1</sup>. The catalyst was heated from 50 °C to 900 °C at a heating rate of 10 °C min<sup>-1</sup>. H<sub>2</sub> temperature-programmed desorption (H<sub>2</sub>-TPD) tests were carried out at the same chemisorption analyzer (AutoChem II 2920). 100 mg of catalyst was loaded into the quartz tube and reduced under a flow of 10% H<sub>2</sub>/Ar at 650 °C for 1 h. Then, the sample was cooled down to 50 °C and purged with pure Ar flow for 2 h to remove weakly adsorbed impurities. Finally, the temperature was increased from 50 °C to 650 °C at 10 °C min<sup>-1</sup>. The desorbs of H<sub>2</sub> were calculated by integrating the area of the H<sub>2</sub>-TPD profiles and using CuO TPR to calibrate the quantities. The surface relative mass of the

catalysts analyzed by X-ray photoelectron spectroscopy (K-Alpha<sup>+</sup>, Thermo Fisher Scientific) using 30 eV pass energy in CAE mode and Al K<sub>α</sub> radiation source (1486.6 eV) at room temperature and under a vacuum of 10<sup>-7</sup> Pa (10<sup>-9</sup> Torr). To quantify the amount of carbon deposition over a tested catalyst, thermogravimetric analysis (TGA) of tested catalyst subjected to temperature changes with 10 °C min<sup>-1</sup> heating rate to 1000 °C under air atmosphere and recorded using STA 449F3 (NETZSCH) equipment. Raman spectra of the tested catalysts were collected using a WITec Alpha 300R spectrometer (λ = 532 nm) equipped with a CCD detector. Each spectrum acquisition consisted of 3 accumulations for 45 seconds and recorded at ambient temperature.

### **Catalyst Evaluations**

Catalytic dry reforming of methane studied in a fixed bed quartz reactor (15 mm ID) under atmospheric pressure. Typically, 100 mg of catalyst diluted with filled zirconia ceramic sand of 2 cm length used. The quartz reactor loaded with catalyst was heated in an electric furnace, and the temperature of the bed controlled by a K-type thermocouple positioned at the center of the catalyst bed. Before the test, the catalyst was reduced in situ 750 °C with 50% H<sub>2</sub>/N<sub>2</sub> mixture (40 mL min<sup>-1</sup>) for 3 hours. A reaction mixture of N<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub> (ratio of 1:1:1) was fed using a gas hourly space velocity (GHSV) of 54 000 mL g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> and temperature raised to 800 °C. The composition of the effluent gases was analyzed by on-line gas chromatography (Fuli 9790) equipped with a packed column (TDX-01) and a TCD detector. A cold trap was placed before the GC to remove moisture in the gas products.

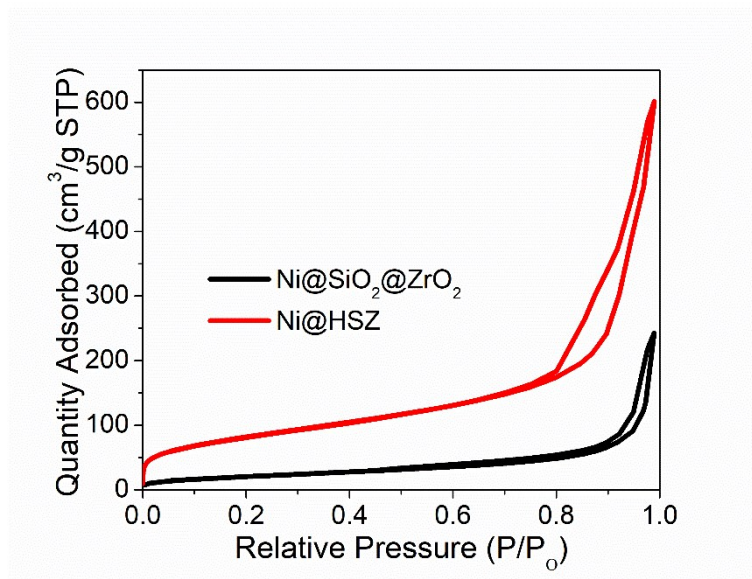


Figure S1. N<sub>2</sub>-isotherm of Ni@SiO<sub>2</sub>@ZrO<sub>2</sub> and Ni@HSZ catalysts.

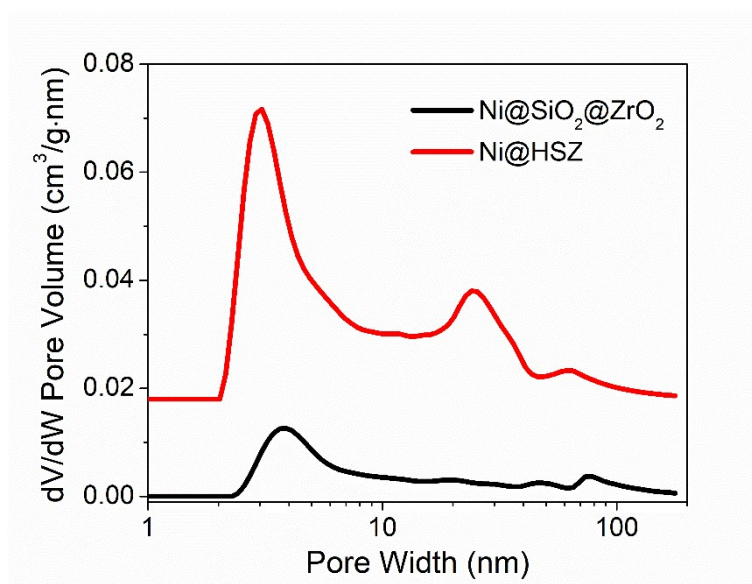


Figure S2. Pore size distribution of Ni@SiO<sub>2</sub>@ZrO<sub>2</sub> and Ni@HSZ catalysts.

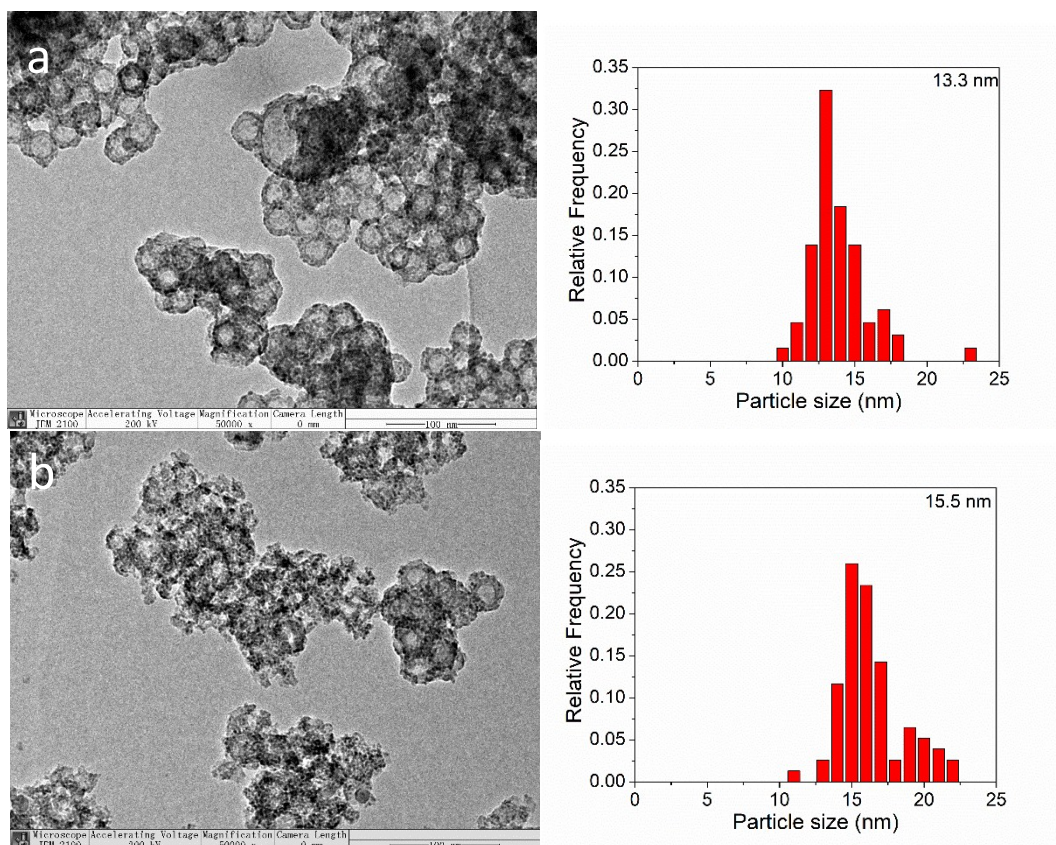


Figure S3. TEM images of tested Ni@SiO<sub>2</sub>@ZrO<sub>2</sub> (a), Ni@HSZ (b) catalysts and their respective Ni particle size distribution.

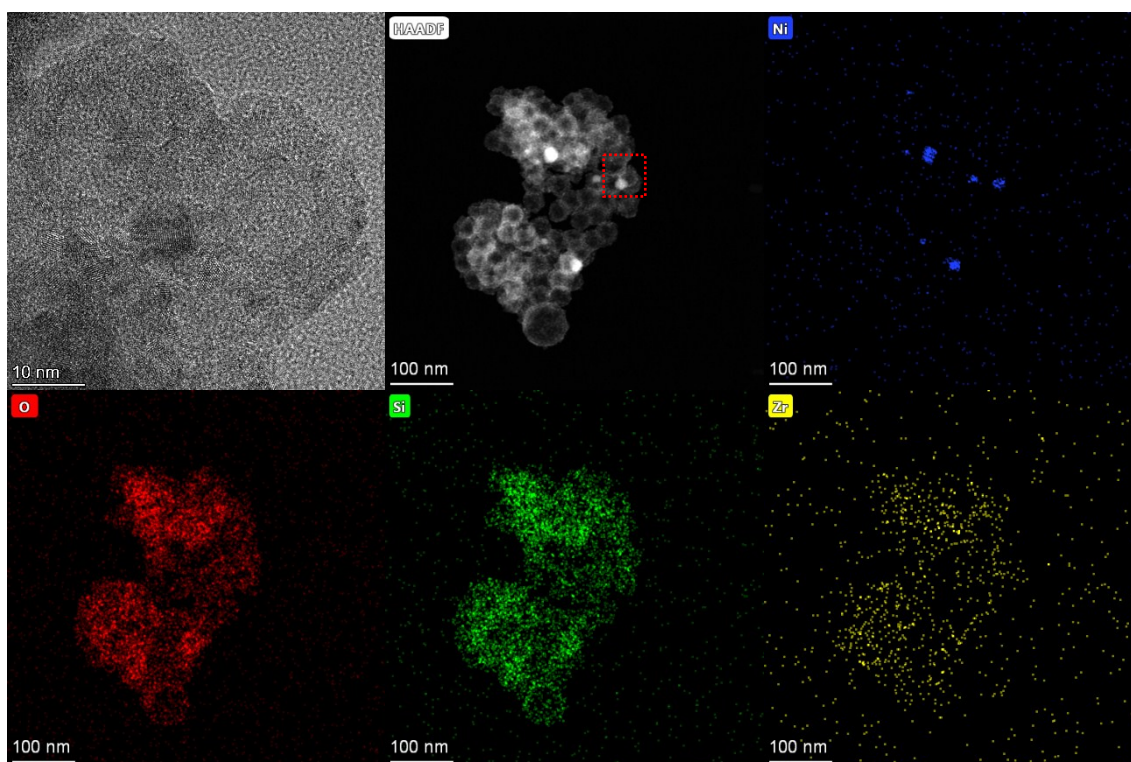


Figure S4. HRTEM and HAADF-STEM image of reduced Ni@SiO<sub>2</sub>@ZrO<sub>2</sub> catalyst.

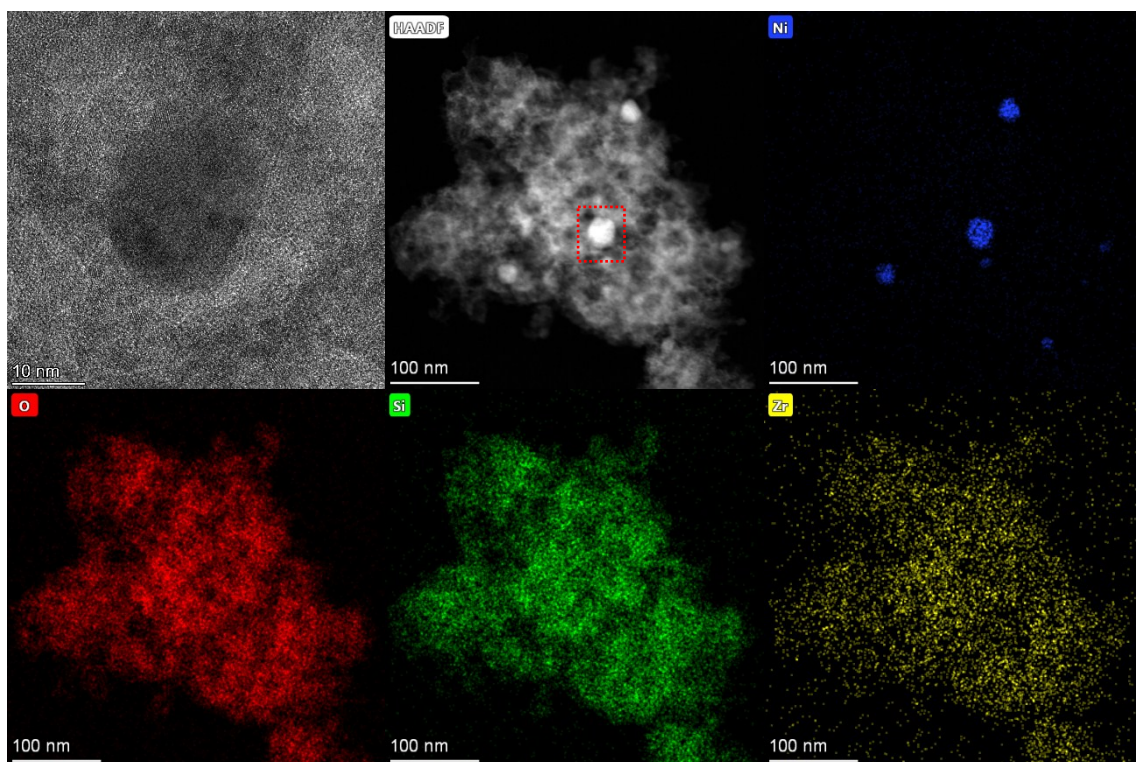


Figure S5. HRTEM and HAADF-STEM image of reduced Ni@HSZ catalyst.

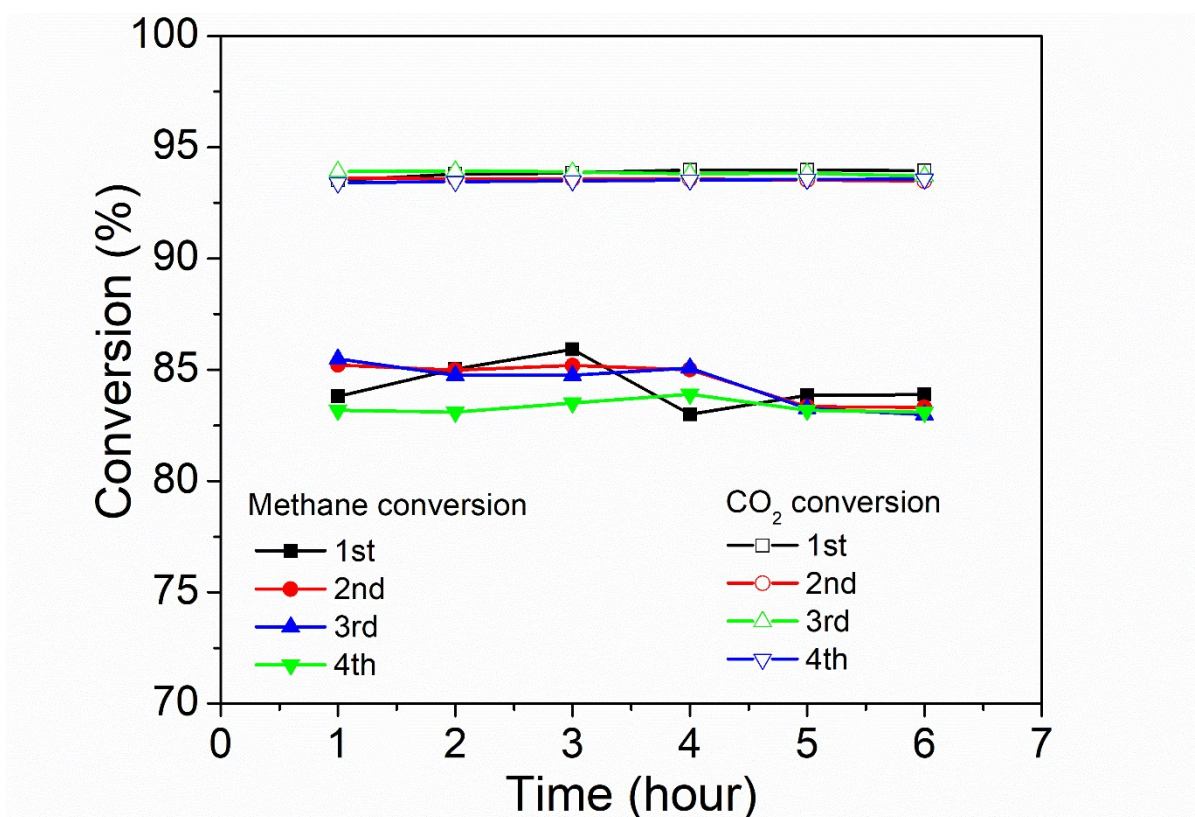


Figure S6. Recyclability test of Ni@HSZ catalyst on dry reforming of methane. The catalyst was tested for 6 hours, oxidizes in the air at 600 °C for 1 hour, reduced at the same temperature for 1 hour, and repeated these cycles for 4 times.

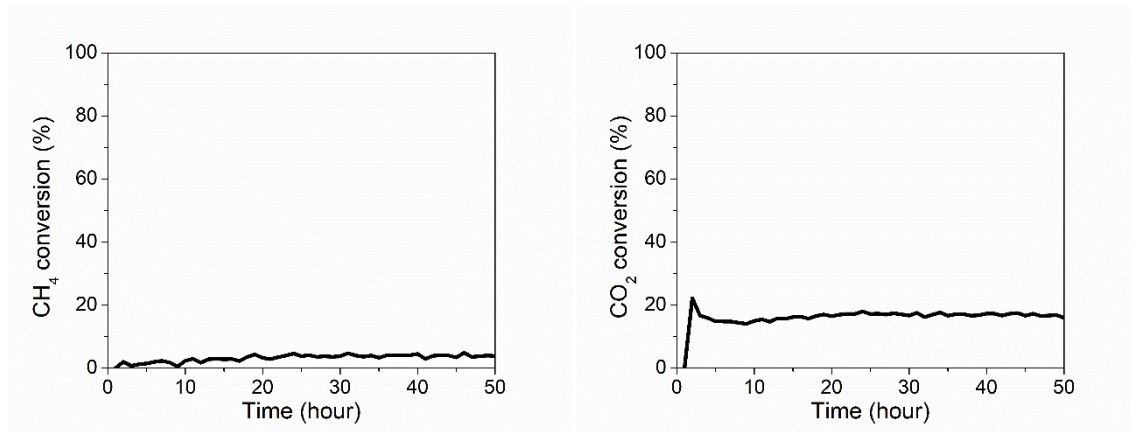


Figure S7. Catalytic performance of conventional impregnated 5% Ni/ZrO<sub>2</sub> catalyst for dry reforming of methane. Conditions: 800 °C, GHSV = 54 000 mL<sub>g<sub>cat</sub></sub><sup>-1</sup>h<sup>-1</sup>, and N<sub>2</sub>:CH<sub>4</sub>:CO<sub>2</sub> = 1:1:1.

Catalyst	Ni wt%	Reaction conditions	Methane conversion (%)	Carbon Deposition	Ref
Ni@SiO <sub>2</sub> @ZrO <sub>2</sub>	1.85	GHSV=54 L <sub>g<sub>cat</sub></sub> <sup>-1</sup> h <sup>-1</sup> N <sub>2</sub> :CH <sub>4</sub> :CO <sub>2</sub> =1:1:1	67	Negligible after 50 h TOS	This work
Ni@HSZ	2.31	GHSV=54 L <sub>g<sub>cat</sub></sub> <sup>-1</sup> h <sup>-1</sup> N <sub>2</sub> :CH <sub>4</sub> :CO <sub>2</sub> =1:1:1	83	≤ 1 % after 50 h TOS	This work
Ni@SiO <sub>2</sub>	4.93	GHSV=18 L <sub>g<sub>cat</sub></sub> <sup>-1</sup> h <sup>-1</sup> CH <sub>4</sub> :CO <sub>2</sub> =1:1	90	Negligible after 100 h TOS	[1]
Ni-yolk@Ni@SiO <sub>2</sub>	18.60	GHSV=36 L <sub>g<sub>cat</sub></sub> <sup>-1</sup> h <sup>-1</sup> N <sub>2</sub> :CH <sub>4</sub> :CO <sub>2</sub> =1:1:1	90	Negligible after 20 h TOS	[2]
LaNiO <sub>3</sub> -cube@meso-SiO <sub>2</sub>	8.10	GHSV=18 L <sub>g<sub>cat</sub></sub> <sup>-1</sup> h <sup>-1</sup> CH <sub>4</sub> :CO <sub>2</sub> =1:1	89	4% after 10h TOS	[3]

Catalyst	Ni-Zr-O (eV)	NiSiO <sub>3</sub> (eV)	Ni-Zr-O fraction (%)	NiSiO <sub>3</sub> fraction (%)
Ni@SiO <sub>2</sub> @ZrO <sub>2</sub>	855.6	856.9	51.7	48.3
Ni@HSZ	855.9	856.9	29.8	70.2

Catalyst	CH <sub>4</sub> conversion (%)	Amount of surface Ni <sup>a</sup> (10 <sup>-6</sup> mol g <sub>cat</sub> <sup>-1</sup> )	TOF <sub>CH<sub>4</sub></sub> (s <sup>-1</sup> )
Ni@SiO <sub>2</sub> @ZrO <sub>2</sub>	67	4.08	3.66
Ni@HSZ	83	3.03	6.13

<sup>a</sup> Determined from H<sub>2</sub>-TPD with adsorption stoichiometry of H/Ni = 1:1[4].

## References

- [1] H. Peng, X. Zhang, L. Zhang, C. Rao, J. Lian, W. Liu, J. Ying, G. Zhang, Z. Wang, N. Zhang, X. Wang, *ChemCatChem*, 9 (2017) 127-136.
- [2] Z. Li, L. Mo, Y. Kathiraser, S. Kawi, *ACS Catalysis*, 4 (2014) 1526-1536.
- [3] L. Zhang, J. Lian, L. Li, C. Peng, W. Liu, X. Xu, X. Fang, Z. Wang, X. Wang, H. Peng, *Microporous and Mesoporous Materials*, 266 (2018) 189-197.

[4] L. Li, S. He, Y. Song, J. Zhao, W. Ji, C.-T. Au, *Journal of catalysis*, 288 (2012) 54-64.