

Supporting information for

Synthesis of Porous Al₂O₃ Rod Supported Ni Nanoparticles for Catalytic Dry Reforming of Methane

Kefa Sheng*, Kai Cui

AnHui Province Key Laboratory of Optoelectronic and Magnetism Functional Materials,

School of Chemistry and Chemical Engineering, Anqing Normal University,

Anqing 246011, China

E-mail: kfshengchem@aqnu.edu.cn

Content

1. Characterizations	2
2. SEM and TEM image of AACH rods.....	3
3. TEM images of porous Al ₂ O ₃ rods calcined at 500 °C. NiO-Al ₂ O ₃ calcined at 500,700 and 900 °C, respectively.....	3
4. Optical images of NiO-Al ₂ O ₃ calcined at 500, 700 and 900 °C, respectively.....	4
5. XRD pattern and TGA and DSC curve of AACH.....	4
6. TGA analysis of Ni-Al ₂ O ₃ -500, Ni-Al ₂ O ₃ -700 and Ni-Al ₂ O ₃ -900 catalysts.....	5
7. TEM images of Ni-Al ₂ O ₃ -500, Ni-Al ₂ O ₃ -700 and Ni-Al ₂ O ₃ -900 catalysts after reaction for 6 hours.....	5
8. Atom concentration of Ni-Al ₂ O ₃ -700 catalyst from EDS analysis.....	6
9. The size and interplanar distance of Ni nanoparticles in three kinds of Ni-Al ₂ O ₃ -500, Ni-Al ₂ O ₃ - 700 and Ni-Al ₂ O ₃ -900 catalysts.....	6
10. The conversions of CH ₄ and CO ₂ catalyzed by Ni-Al ₂ O ₃ -500 and Ni-Al ₂ O ₃ -900 catalysts.....	7
11. The Raman spectra of Ni-Al ₂ O ₃ -700 catalyst after long-term DRM reaction.....	7
12. The FT-IR spectra of Ni-Al ₂ O ₃ -700 catalyst after long-term DRM reaction.....	8
13. Key words: Ni, Al ₂ O ₃ rod, Dry reforming of CH ₄	8
14. Comparison of TOF values [‡] of CH ₄ and CO ₂ catalyzed by Ni-based catalysts in literature.....	9

1. Characterizations

The morphologies of Ni-Al₂O₃ catalysts were characterized by Hitachi S4800 scanning electron microscope (SEM) and FEI Tecnai G2 F30 transmission electron microscope (TEM). The energy-dispersive spectroscopy (EDS) mapping of Ni-Al₂O₃-700 catalysts were also measured by F30 TEM under the mode of high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM). Nitrogen adsorption-desorption isotherms, BET (Brunauer-Emmett-Teller) surface areas, BJH (Barret-Joyner-Halenda) pore diameters and total pore volume of Ni-Al₂O₃ catalysts were measured at 77 K by a Belsorp-Max analyzer. Power X-ray diffraction (XRD) patterns were scanned from 10° to 90° with a speed of 30°/min by Rigaku Ultima IV X-ray diffractometer, which was operated at 35 kV and 40 mA with Ni-filtered Cu-K α radiation as X-ray beam source. The mass percentages of Ni contents supported on porous Al₂O₃ were measured by a Thermo IRIS Intrepid II XSP inductively coupled plasma-atomic emission spectrometry (ICP-AES). All Temperature programmed reduction (TPR) and Temperature programmed deposition (TPD) experiments of Ni-Al₂O₃ catalysts were performed on a tp5080 chemical adsorption analyzer equipped with a thermal conductor detector (TCD). X-ray photoelectron spectroscopy (XPS) for surface analysis of Ni-Al₂O₃ catalysts was performed on AXIS Ultra DLD. Thermogravimetric analysis (TGA) was measured to determine the amount of carbon deposition. Fourier transform infrared spectroscopy (FT-IR) of Ni-Al₂O₃ catalysts was recorded in the range of 400-4000 cm⁻¹ by a Nexus 870 FTIR spectrometer. Raman spectra of deposited carbon on used Ni-Al₂O₃-700 catalysts were measured by a Thermo Scientific DXR2 Raman Microscope equipped with a

2. SEM and TEM image of AACH rods.

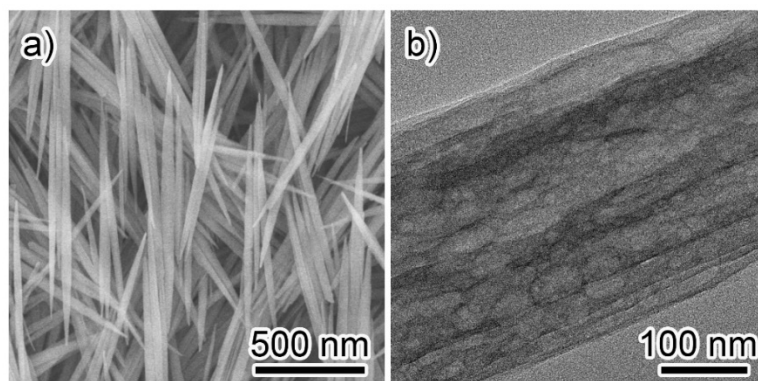


Figure S1. (a) SEM and (b) TEM image of AACH rods.

3. TEM images of porous Al_2O_3 rods calcined at 500 °C. $\text{NiO-Al}_2\text{O}_3$ calcined at 500,700 and 900 °C, respectively.

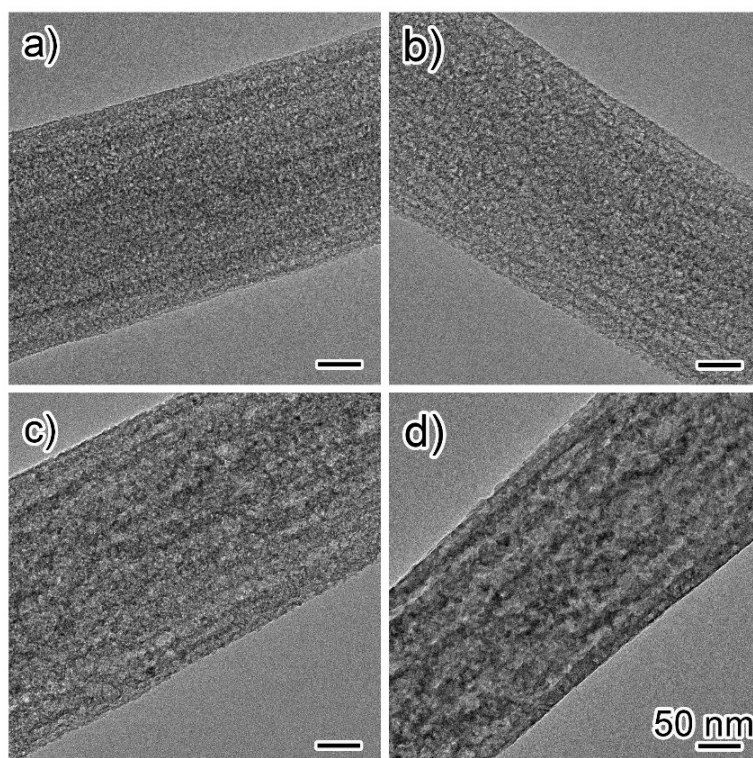


Figure S2. TEM images of (a) porous Al_2O_3 rods calcined at 500 °C. (b, c, d) $\text{NiO-Al}_2\text{O}_3$ calcined at 500, 700 and 900 °C, respectively.

4. Optical images of NiO-Al₂O₃ calcined at 500, 700 and 900 °C, respectively.

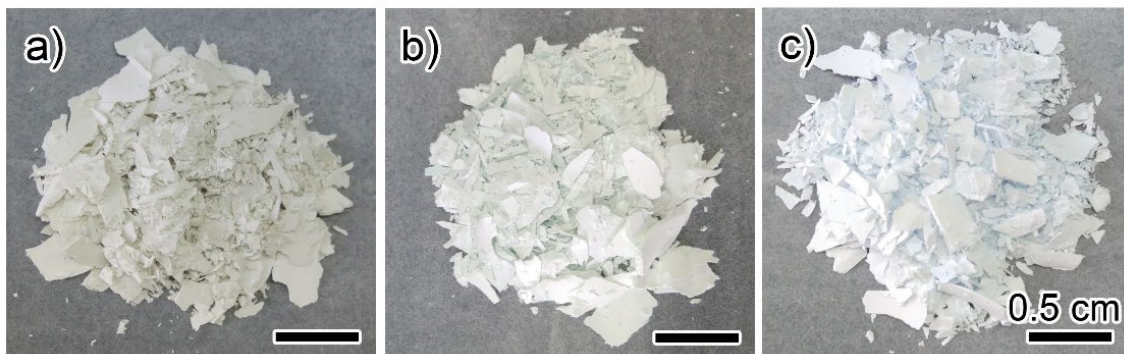


Figure S3. (a, b, c) Optical images of NiO-Al₂O₃ calcined at 500, 700 and 900 °C, respectively.

5. XRD pattern and TGA and DSC curve of AACH.

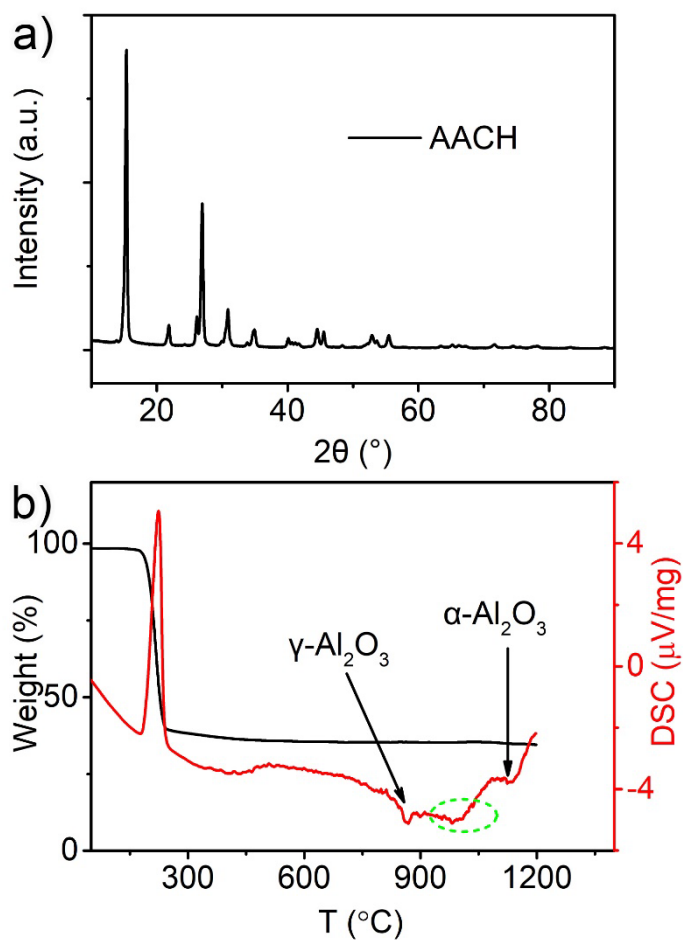


Figure S4. (a) XRD pattern and (b) TGA and DSC curve of AACH.

6. TGA analysis of Ni-Al₂O₃-500, Ni-Al₂O₃-700 and Ni-Al₂O₃-900 catalysts.

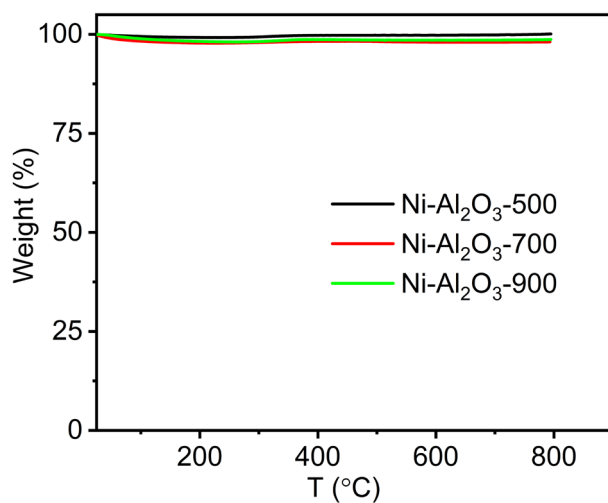


Figure S5. TGA analysis of Ni-Al₂O₃-500, Ni-Al₂O₃-700 and Ni-Al₂O₃-900 catalysts.

7. The conversions of CH₄ and CO₂ catalyzed by Ni-Al₂O₃-500 and Ni-Al₂O₃-900 catalysts.

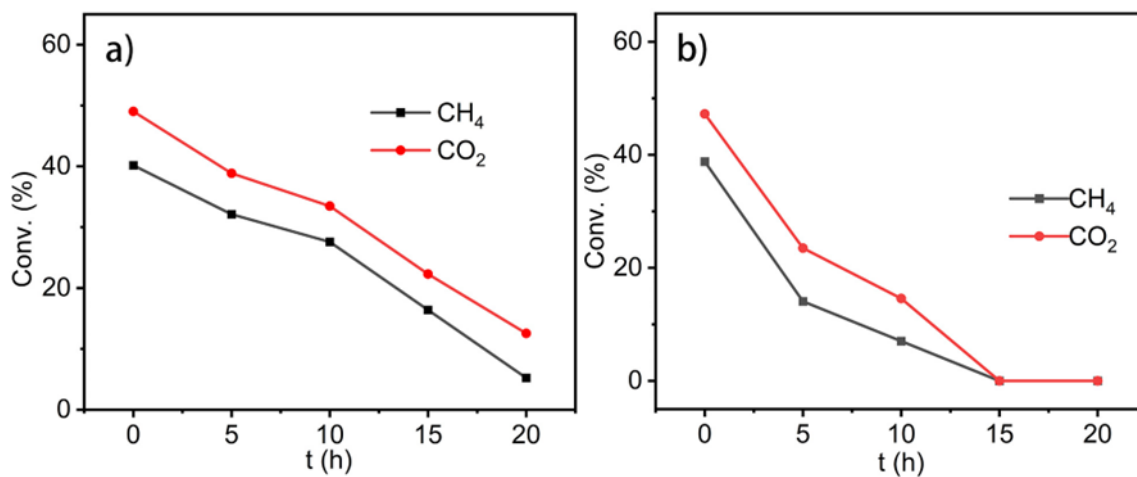


Figure S6. The conversions of CH₄ and CO₂ catalyzed by Ni-Al₂O₃-500 and Ni-Al₂O₃-900 catalysts.

8. TEM images of Ni-Al₂O₃-500, Ni-Al₂O₃-700 and Ni-Al₂O₃-900 catalysts after reaction for 6 hours.

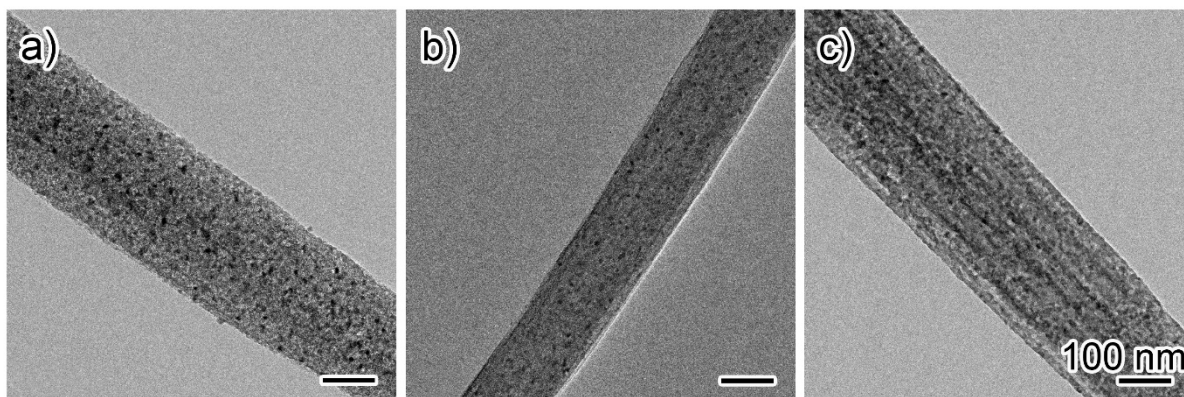


Figure S7. TEM images of (a) Ni-Al₂O₃-500, (b) Ni-Al₂O₃-700 and (c) Ni-Al₂O₃-900 catalysts after reaction for 6 hours.

9. Atom concentration of Ni-Al₂O₃-700 catalyst from EDS analysis.

Table S1. Atom concentration of Ni-Al₂O₃-700 catalyst from EDS analysis.

Element (%)	Weight (%)	Atomic (%)	Uncert (%)
O(K)	49.07	62.40	0.09
Al(K)	48.94	36.90	0.07
Ni(K)	1.97	0.68	0.01

10. The size and interplanar distance of Ni nanoparticles in three kinds of Ni-Al₂O catalysts.

Table S2. The size and interplanar distance of Ni nanoparticles in three Ni-Al₂O₃ catalysts.

Sample	Particle size (nm)	d-spacing (nm)
Ni-Al ₂ O ₃ -500	5.16	0.203
Ni-Al ₂ O ₃ -700	2.86	0.203
Ni-Al ₂ O ₃ -900	/	/

†The crystallite sizes were calculated from XRD data using the Scherrer equation and full width at half-maxima of (111) diffraction peaks from XRD patterns.

$$D = \frac{K\lambda}{\beta \cos\theta}$$

Where D=crystallites size (nm), K=0.94 (Scherrer constant), $\lambda=0.15406$ nm (wavelength of the X-ray sources), β =FWHM (radians), θ =Peak position (radians).

† The d-spacing was calculated from XRD data using Bragg's equation.

$$n\lambda = 2d\sin\theta \quad \text{or} \quad d = \frac{n\lambda}{2\sin\theta}$$

Where $\lambda=0.15406$ nm (wavelength of the X-ray sources), θ =Peak position (in radians), n=1 (order of diffraction), d=d-spacing (in nm). Both θ and β use radian data.

11. The Raman spectra of Ni-Al₂O₃-700 catalyst after long-term DRM reaction.

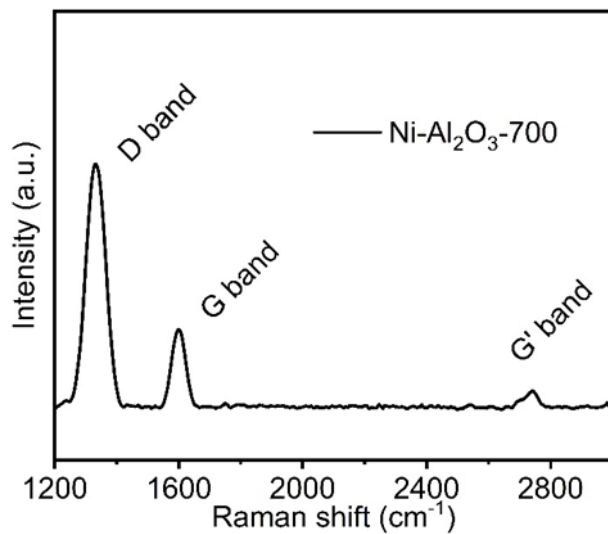


Figure S8. The Raman spectra of Ni-Al₂O₃-700 catalyst after long-term DRM reaction.

12. The FT-IR spectra of Ni-Al₂O₃-700 catalyst after long-term DRM reaction.

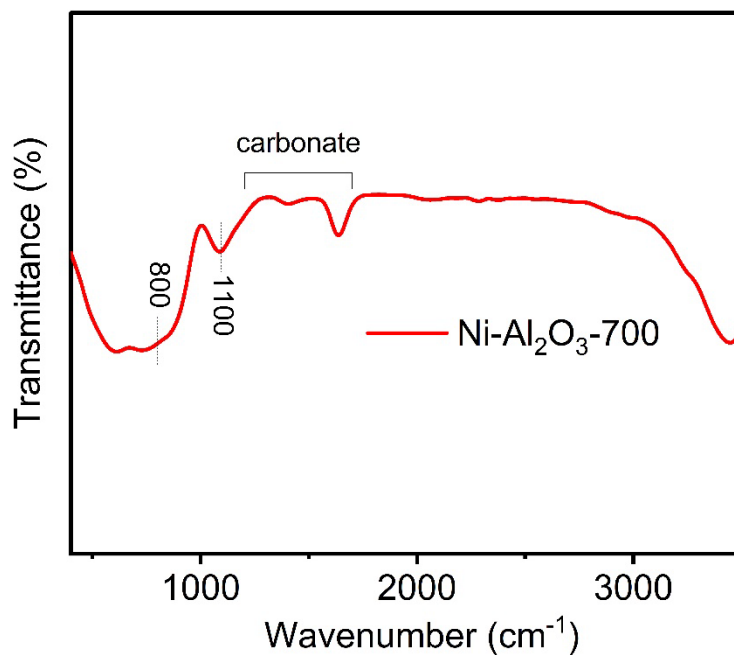


Figure S9. The FT-IR spectra of Ni-Al₂O₃-700 catalyst after long-term DRM reaction.

13. **Key words:** Ni nanoparticle, Al₂O₃ rod, Dry reforming of CH₄, stronger metal-support interaction (SMSI)

14. Comparison of TOF values‡ of CH₄ and CO₂ catalyzed by Ni-based catalysts in literature.

Table S3. Comparison of TOF values‡ of CH₄ and CO₂ catalyzed by Ni-based catalysts in literature

Ni-based catalyst	T (°C)	GHSV (L·g _{cat} ⁻¹ ·h ⁻¹)	TOF _{CH₄ ini.} (s ⁻¹)	TOF _{CO₂ ini.} (s ⁻¹)	Ref.
Ni-La-Mg-Al	600	24	0.013	0.017	Int. J. Hydrogen Energy 2018, 43, 19438–19450.
Ni-La ₂ O ₃ -Al ₂ O ₃	800	14.4	0.012	0.104	Int. J. Hydrogen Energy 2019, 44, 24510–24524.
Ni-Al ₂ O ₃	700	120	0.402	0.376	Chem. Commun., 2015, 51, 12044--12047
NiO-CaO-Al ₂ O ₃	750	30.3	0.340	0.353	ACS Catal. 2012, 2, 1331–1342
Ni-Ce-Al Oxide	700	18	0.131	0.135	ACS Catal. 2013, 3, 1638–1651
NiMgAl-LDH@m-SiO ₂	750	3.75	0.028	0.029	Chem. Commun., 2013, 49, 6770--6772
CoNi/Al ₂ O ₃ -CeZrO ₂	700	6	0.144	0.128	Ind. Eng. Chem. Res. 2015, 54, 3775–3787
Ni ₁₅ CeMgAl	800	24	0.023	0.023	Applied Catalysis B: Environmental 254 (2019) 612–623
Ni/ZrO ₂	750	25	0.075	0.083	Applied Catalysis B: Environmental 302 (2022) 120859
1.5CeO _{2-x} -NSNT	750	96	0.116	/	Applied Catalysis B: Environmental 277 (2020) 119278
Ni/CeO ₂	800	30	0.627	0.735	Applied Catalysis B: Environmental 268 (2020) 118387
RhNi-MgAl ₂ O ₄	600	18	0.256	0.310	International journal of hydrogen energy 48 (2023) 13890e13901
Ni-Al ₂ O ₃ -500	700	275	0.227	0.279	This work
Ni-Al ₂ O ₃ -900	700	275	0.230	0.287	This work
Ni-Al ₂ O ₃ -700	700	275	0.378	0.421	This work

‡ TOF values in literature and this work were calculated by the molar amount of converted CH₄/CO₂ and that of metal Ni. The TOF was calculated according to the following formulas, where the molar amount of gas (n) was calculated from its initial flow rate and conversion, and the molar amount of Ni was calculated by the mass of the catalyst, the weight percentage of Ni (wt%) from ICP-AES and its

molecular weight (M).

$$\begin{aligned} \text{TOF (CH}_4/\text{CO}_2) &= n (\text{CH}_4/\text{CO}_2) / [n (\text{Ni}) \times t] \\ &= [r (\text{CH}_4/\text{CO}_2)_{\text{in}} \times \text{Conv. (CH}_4/\text{CO}_2) \times t / 22.4] / [m (\text{cat}) \times \text{wt\% (Ni)} \times t / M (\text{Ni})]. \end{aligned}$$