

Electronic Supplementary Information

High Sintering-/Coke-Resistance Ni@SiO₂/Al₂O₃/FeCrAl-fiber Catalyst for Dry Reforming of Methane: One-Step “Macro to Nano” Organization via Cross- Linking Molecules

Ruijuan Chai, Guofeng Zhao,* Zhiqiang Zhang, Pengjing Chen, Ye Liu, and Yong Lu*

Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and
Molecular Engineering, East China Normal University, Shanghai 200062, China.

*Corresponding author. E-mail: ylu@chem.ecnu.edu.cn (Y.Lu); gfzhao@chem.ecnu.edu.cn(GZ).

Experimental Section

Catalyst preparation

Synthesis of microfibrrous-structured AlOOH/FeCrAl-fiber substrate

Briefly, the 3 dimensional (3D) FeCrAl-fiber network consisting of 15 vol% 22 μm FeCrAl-fiber and 85 vol% voidage was utilized as the substrate (purchased from Henan Xixiang Lier Filter Technology Co. Ltd., China). At first, circular chips punched down from their large felt were ultrasonically degreased in acetone for 10 min, thoroughly washed using deionized water, dried at 100 $^{\circ}\text{C}$ and calcined at 900 $^{\circ}\text{C}$ for 5 h. Then, NaAlO_2 (3.00 mmol) and $(\text{NH}_2)_2\text{CO}$ (2.25 mmol) were dissolved in 70 mL of distilled water. The solution was magnetically stirred for 10 min in air at room temperature and transferred into an autoclave pressure vessel. The FeCrAl-fiber chips (1.0 g) were then immersed in the solution and heated at 160 $^{\circ}\text{C}$ for 12 h. After hydrothermal process, the samples were washed using deionized water and dried overnight at 100 $^{\circ}\text{C}$ to obtain the AlOOH/FeCrAl-fiber. All salts (A.R. grade) and urea (A.R. grade) were directly used without further purification as received from Sinopharm Chemical Reagent Co. Ltd..

Synthesis of microfibrrous-structured Ni/Al₂O₃/FeCrAl-fiber catalyst

The microfibrrous structured Ni/Al₂O₃/FeCrAl-fiber catalyst was prepared by solvent-assistant incipient wetness impregnation with an acetone solution of nickel nitrate ($\text{Ni}(\text{NO}_3)_2$). The as-prepared AlOOH/FeCrAl-fiber substrate was directly impregnated with $\text{Ni}(\text{NO}_3)_2$ solution, followed by dried at 100 $^{\circ}\text{C}$ and calcined at 550 $^{\circ}\text{C}$ in air for 2 h as well as at 700 $^{\circ}\text{C}$ for 2 h in H_2 to obtain the Ni/Al₂O₃/FeCrAl-fiber

catalyst.

Synthesis of microfibrillar-structured Ni@SiO₂/Al₂O₃/FeCrAl-fiber catalyst

The microfibrillar structured Ni@SiO₂/Al₂O₃/FeCrAl-fiber catalyst was prepared by one-pot self-assembly method with the aid of cross-linking molecule 3-aminopropyltriethoxysilane (APTES). A certain amount of nickel acetylacetonate (Ni(acac)₂) and APTES with Ni:APTES of 1.0:1.8 was firstly added in the acetone at 60 °C. When the AlOOH/FeCrAl-fiber substrate was added into the solution of Ni²⁺-APTES complexes in an incipient impregnation manner, the silanisation reaction took place between the ethoxy (-O-CH₂-CH₃) groups of APTES and the surface hydroxyl (-OH) groups of AlOOH nanoarrays with leaving of ethanol, leading to the formation of Al-O-Si bonds serving as the mediator for linking core-shell nanosystems and microfibrillar-structured AlOOH/FeCrAl-fiber substrate. After 3 h, the Ni²⁺-APTES-grafted AlOOH/Al-fiber was obtained. Subsequently, some water is added into the system for hydrolysis of the rest -Si-O-CH₂-CH₃ to produce Si-O-Si bonds. After drying at 100 °C for 2 h, calcining at 550 °C for 2 h in air and subsequently being reduced at 700 °C for 2 h in H₂, the microfibrillar-structured Ni@SiO₂/Al₂O₃/FeCrAl-fiber catalyst was obtained.

Catalyst characterization

The actual loadings of Ni and Si were quantitatively determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on a USA Thermo IRIS Intrepid IIXSP ICP spectrometer. X-ray diffraction (XRD) patterns were obtained by a Rigaku Ultra IV diffractometer (Japan) using Cu K α radiation ($\lambda = 0.1542$ nm) at 35

kV and 25 mA in the 2θ scanning range of $10-90^\circ$ and scanning rate of $10^\circ \text{ min}^{-1}$. The surface morphology and cross-sectional structure of the samples were visualized by scanning electron microscope (SEM; Hitachi S-4800; Japan). The nano-scaled structure of the catalysts and the size of metal nanoparticles were characterized by transmission electron microscope (TEM; FEI-Tecnai G2F30; USA) operated at 300 kV. The porous structure of the sample was characterized by N_2 adsorption-desorption isotherms at liquid nitrogen temperature using a Quantachrome Autosorb-3B system (USA), and surface area, pore size distribution and total pore volume were analyzed by Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods. H_2 chemisorption was performed on a Quantachrome ChemBET 3000 (USA) chemisorption apparatus with a TCD detector. Sample of 0.15 g was reduced under the same reduction condition for DRM reaction followed by purging with N_2 for 30 min at the same temperature. After cooling down to 25°C under N_2 , successive doses ($250 \mu\text{L H}_2$ per time, five times) of H_2 were introduced into the N_2 stream through a calibrated injection loop until no further H_2 uptake was detected. And the surface Ni atoms per gram catalyst determined by H_2 chemisorption at 25°C by assuming H/Ni ratio of 1. Turnover frequency (TOF) of methane was calculated at $750-800^\circ\text{C}$ using a gas hourly space velocity of $140 \text{ L g}^{-1} \text{ h}^{-1}$ to control the methane conversion less than 15 %. The TOF of methane is defined as mole flow rate of methane converted moles of the active nickel (calculation based on the result of H_2 chemisorption). H_2 -temperature programmed reduction (H_2 -TPR) was performed on a TP 5080 multi-functional automatic adsorption instrument (Xianquan Industrial and Trading Co.,

Ltd.) with a thermal conductivity detector (TCD) and an online mass spectrometer (Proline Dycor, AMETEK Process Instrument, USA). Thermogravimetric analysis (TGA) for carbon deposition determination was carried out in 5% O₂/95% He flow on a Simultaneous Thermal Gravimetry-Differential Thermal Analysis/Differential Scanning Calorimetry (TG-DTA/DSC) Apparatus (High Temperature Platform 400, STA 449 F3 Jupiter, NETZSCH-Gerätebau GmbH), which was equipped with an online mass spectrometer (Proline Dycor, AMETEK Process Instrument, USA).

Catalyst test

DRM was performed in a fixed-bed quartz tube reactor (600 mm length by 16 mm inner diameter) at atmospheric pressure. Four circular chips of the FeCrAl-fiber-structured Ni@SiO₂ catalysts (0.80 g, including the mass of fiber) were packed layer-by-layer into the tubular reactor. The catalyst bed was then heated from room temperature to the reaction temperature ranged from 600 to 850 °C in He flow (20 mL min⁻¹) and a gas mixture of CH₄/CO₂ (1.0/1.1) was directly fed into the reactor continuously. The CH₄ and CO₂ were all controlled by the calibrated mass flow controllers. The product effluent after water condensation was analyzed by using an online-gas chromatograph equipped with thermal conductivity detector (TCD) and 2 m Shincarbon ST column (DIMKA). The CH₄/CO₂ conversions were calculated using standard normalization method on the base of carbon atom balance.

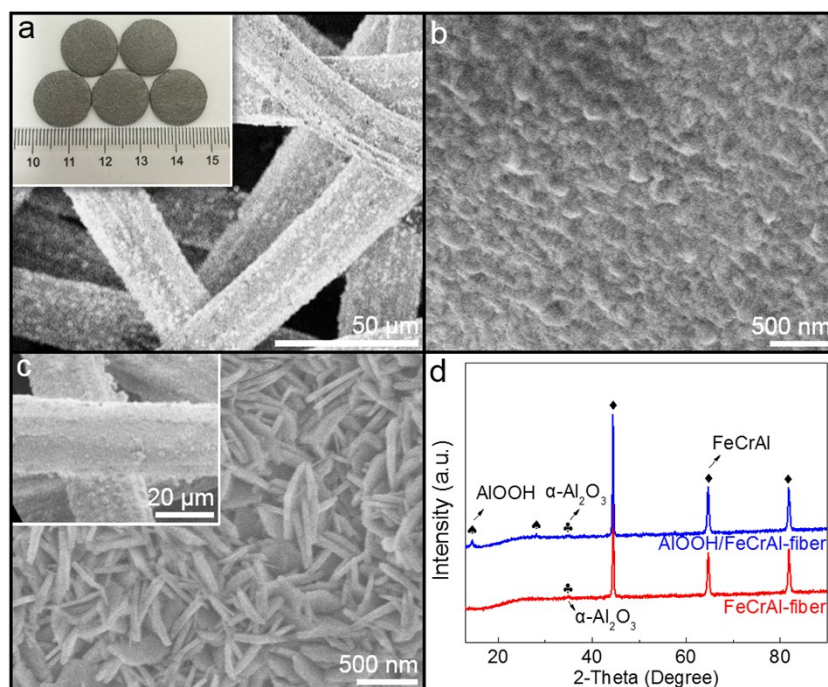


Fig. S1 Optical photograph (inset of a) and SEM image (a,b) of the FeCrAl-fiber support. (c) SEM image of the AlOOH/FeCrAl-fiber support. (d) XRD patterns of FeCrAl-fiber and AlOOH/FeCrAl-fiber supports.

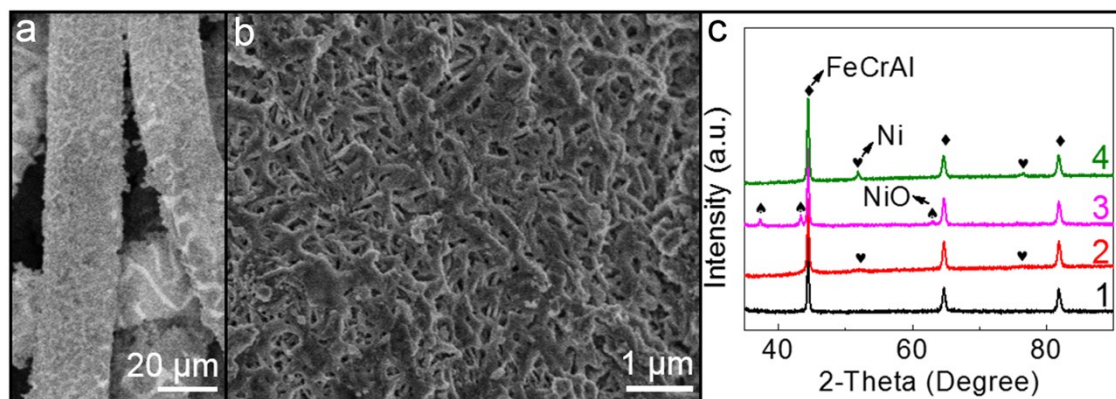


Fig. S2 (a,b) SEM images of the NiO@SiO₂/Al₂O₃/FeCrAl-fiber catalyst. (c) XRD patterns of the (1) NiO@SiO₂/Al₂O₃/FeCrAl-fiber, (2) Ni@SiO₂/Al₂O₃/FeCrAl-fiber, (3) NiO/Al₂O₃/FeCrAl-fiber, and (4) Ni/Al₂O₃/FeCrAl-fiber catalysts.

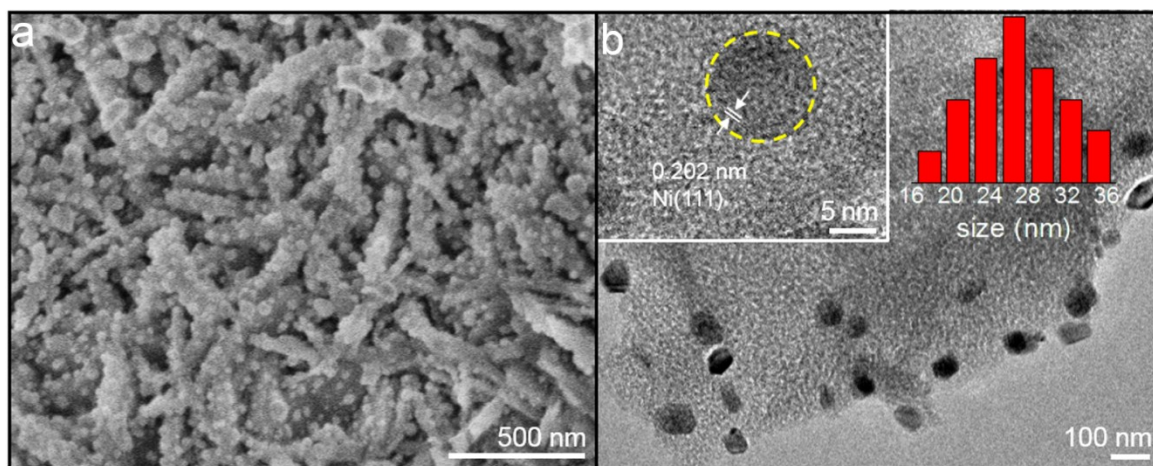


Fig. S3 (a) SEM, (b) TEM image, and (inset of b) Ni size distribution of the fresh reduced Ni/Al₂O₃/FeCrAl-fiber catalyst.

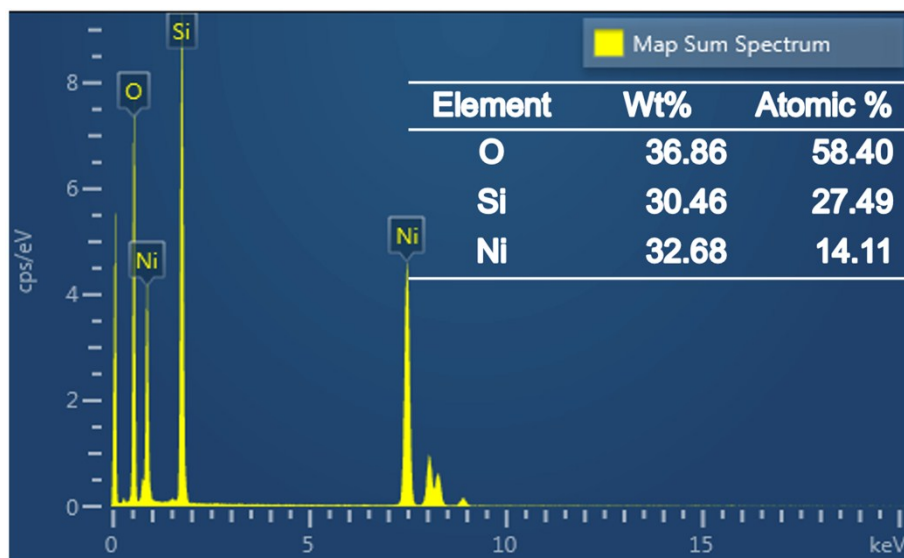


Fig. S4 TEM-EDS analysis of the Ni@SiO₂/Al₂O₃/FeCrAl-fiber catalyst.

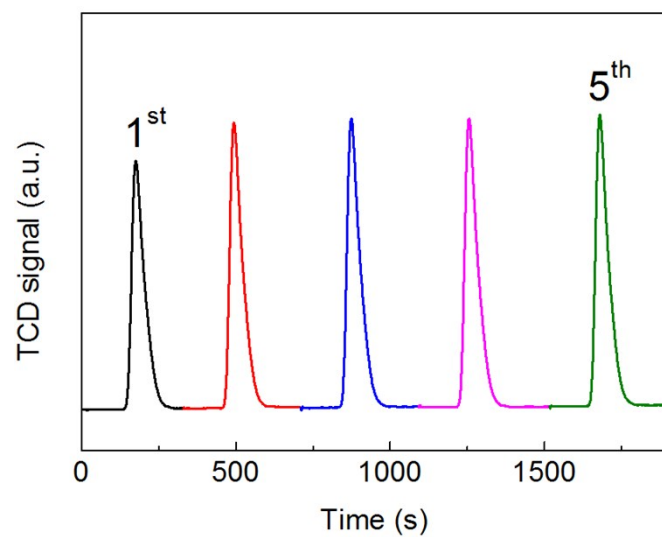


Fig. S5 H₂ pulse adsorption of the Ni@SiO₂/Al₂O₃/FeCrAl-fiber catalyst at 25 °C.

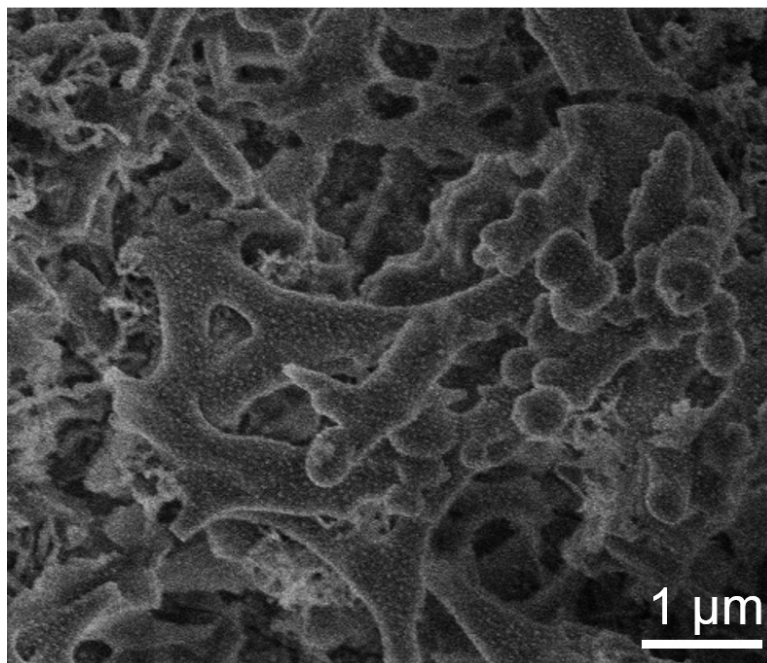


Fig. S6 SEM image of the used Ni@SiO₂/Al₂O₃/FeCrAl-fiber catalyst (after 500 h on stream).

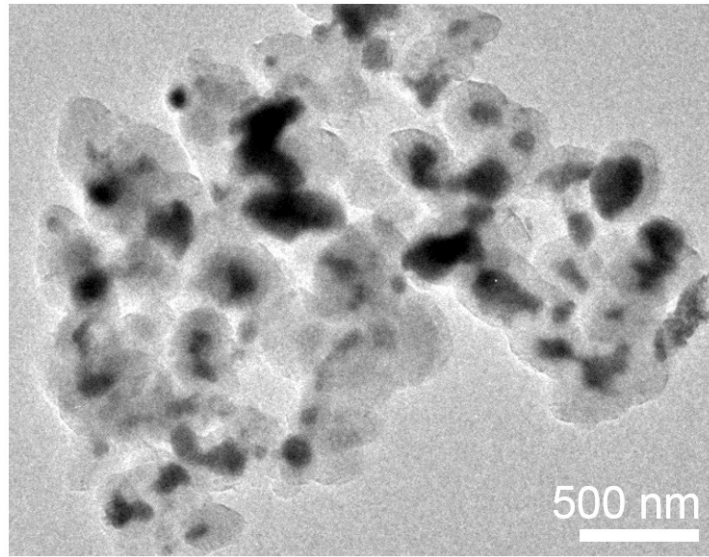


Fig. S7 TEM image of the 30-h tested Ni/Al₂O₃/FeCrAl-fiber catalyst.

Table S1 Comparison of TOF of methane among different studies

Catalyst	T (°C)	GHSV (L g _{cat} ⁻¹ h ⁻¹)	CH ₄ conversion (%)	Surface Ni exposure (μmol g _{cat} ⁻¹)	TOF (s ⁻¹)
Ref. [19]	700	1440	0.6	0.9	17
Ref. [20]	800	4	42	1.2	8.2
Ref. [21]	600	240	<20	43.9	4.1
Ref. [22]	750	50	-	17.7	0.8
Ref. [22]	750	50	-	20.9	0.8
This work	800	140	11.0	23	4.2
This work	750	140	9.3	23	3.5