

## Electronic Supplementary Information

# Endogenous growth of 2D AlOOH nanosheets on 3D Al-fiber network via steam-only oxidation in application for forming structured catalysts

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## Experimental Section

### Preparation of Al-substrates@ns-AlOOH(or $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) and catalysts

#### *Preparation of Al-fiber@ns-AlOOH and Al-fiber@ns- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>*

The 3D Al-fiber network consisting of 10 vol% 60- $\mu$ m Al-fiber (99.9 wt% purity) and 90 vol% voidage was utilized as the substrate, which was taken from Shanghai Xincui Net-structured Material Co. Ltd. (China). The typical preparation of this unique composite involved two simple steps. Firstly, five circular chips (about 1.0g) punched down from their large felt were ultrasonically degreased in analytically pure acetone for 10 min and etched in 10 mL NaOH (0.1 wt%) aqueous solution for 2 min to remove original barrier oxide layer and thoroughly washed using deionized water without special attention to deoxidization until no Na<sup>+</sup> was detected. Secondly, the pretreated substrates were packed layer-by-layer into a quartz tube in steam flow at 120-600 °C for 0.5-72 h and dried at the same temperature for 2 h in N<sub>2</sub> flow. The obtained samples were denoted as Al-fiber@ns-AlOOH.

The Al-fiber@ns- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> composites can be obtained by calcining the as-made Al-fiber@ns-AlOOH samples at 600 °C in air for 2 h.

#### *Preparation of other Al-substrates@ns-AlOOH*

All the other Al-substrates, namely Al powders (40~325 mesh), Al wires (1.2 mm), Al tubes (3 mm o.d., 2 mm i.d. and 10 mm o.d., 8 mm i.d.), Al foam (30 PPI), Al foils and Al microchannel, were firstly etched in NaOH (0.1 wt%) aqueous solution and treated with steam at 120 °C for 6 h, subsequently dried at 120 °C for 2 h in N<sub>2</sub> and the Al-substrates@ns-AlOOH were obtained.

### ***Preparation of the Al-fiber@ns-AlOOH@Pd catalyst***

The as-prepared Al-fiber@ns-AlOOH was directly impregnated with a toluene solution of palladium acetate (Pd loading of 0.3 wt%) by an incipient wetness impregnation method, subsequently dried at 100 °C for 2 h and calcined in air at 300 °C for 2 h to obtain Al-fiber@ns-AlOOH@Pd. Furthermore, in order to investigate the effect of hydroxyl on the catalyst performance, the Al-fiber@ns-AlOOH was calcined at different temperatures to tune the hydroxyl contents prior to loading Pd.

### ***Preparation of Pd/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst***

For reference, Pd/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst was also synthesized with the same preparation method as for the Al-fiber@ns-AlOOH@Pd catalyst.

### ***Preparation of Al-fiber@ns- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>@FeMnK catalyst***

The as-made Al-fiber@ns-AlOOH was calcined at 600 °C in air for 2 h to form the Al-fiber@ns- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, which was firstly modified by 10 wt% K with a nitrate aqueous solution using a wet impregnation method. Then the Al-fiber@ns- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>@FeMnK was also prepared by a wet impregnation method using different precursors of Fe and Mn, and the Fe and Mn loadings were both 10 wt%. Impregnated catalysts were dried at 100 °C for 12 h and finally calcined at 300 °C for 2 h.

### ***Preparation of Al-tube@ns- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>@Ni catalyst***

The Al-tube@ns-AlOOH (4 mm length, 3 mm o.d., 2 mm i.d.) was obtained by steam-only oxidation in steam flow at 120 °C for 6 h and dried at the same temperature for 2 h as 3D Al-fiber network without any change. The as-made Al-tube@ns-AlOOH substrate was calcined at 600 °C for 2 h to form Al-tube@ns- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> which was then wetly impregnated with an

aqueous solution of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  corresponding to NiO loading of 15 wt%. The impregnated samples were dried at 100 °C for 12 h and subsequently calcined at 450 °C for 2 h.

### **Catalyst characterization**

The catalysts were characterized using scanning electron microscopy (SEM, Hitachi S-4800; Japan), transmission electron microscopy (TEM, FEI TECNAI G<sup>2</sup> F30 instrument at 300 kV; USA), X-ray diffraction (XRD, Rigaku Ultima IV, Cu K $\alpha$ ; Japan), Fourier transform infrared (FTIR, Nicolet Nexus 670; USA) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES; ICP Thermo IRIS Intrepid II XSP; USA). Specific surface area was determined from N<sub>2</sub> adsorption isotherm at -196 °C using standard Brunauer-Emmett-Teller (BET) theory. The pore size distribution was determined using the Barrett-Jovner-Halenda (BJH) method. The adhesion of samples was measured by thermal shock tests which were conducted by keeping them at 600 °C for 10 min, followed by quenching them in water at room temperature. After such thermal shock process was repeated 10 times, the weight loss was measured. The mechanical strength of samples was evaluated using ultrasound tests by immersing the samples into petroleum ether and exposing to ultrasound at 200 W for 4 h. After the samples were dried at 150 °C for 2 h, the weight loss was measured. CO chemisorption was performed on a Quantachrome ChemBET 3000 chemisorption apparatus with a thermal conductivity detector (TCD) to measure the metal dispersion of catalysts. 100 mg of the catalyst was reduced by 50 mL/min 10 vol% H<sub>2</sub> in Ar at 150 °C for 2 h and purged in He by 90 mL/min at the same temperature for 1 h. After cooling down to 35 °C in He, the CO gas pulses were carried out until the pulse area didn't change. The adsorption

stoichiometry (expressed as  $\text{CO}_{\text{ad}}/\text{Pd}$ ) was assumed to be one. Temperature programmed desorption (TPD) technique was employed to study the Hydroxyl desorption behavior of the Al-fiber@ns-AlOOH, using a Tianjin XQ TP-5080 chemisorption instrument with a thermal conductivity detector (TCD). The sample of 100 mg packed into a quartz tube reactor was purged in He by 40 mL/min at 150 °C for 1 h and subsequently heated to 600 °C at a temperature ramp rate of 10 °C/min.

## **Reactivity tests**

### ***CO oxidative coupling to DMO***

Catalyst testing in the CO oxidative coupling to DMO was carried out in a fixed-bed quartz tubular reactor equipped with a thermocouple in the middle of the catalyst bed. Catalyst loading was 0.80 g if not specified. The reactant gases (10 vol%  $\text{CH}_3\text{ONO}$ , 14 vol% CO and 76 vol%  $\text{N}_2$ ) were passed through one quartz tube (760-mm length by 16-mm inner diameter and 20-mm outside diameter) at low gas hourly space velocity (GHSV, for example, 3000  $\text{L kg}^{-1} \text{h}^{-1}$ ) and the other quartz tube (760-mm length by 8-mm inner diameter and 20-mm outside diameter) at high GHSV (for example, 60000  $\text{L kg}^{-1} \text{h}^{-1}$ ). Prior to the reaction, the samples were in-situ activated at 200 °C for 2 h in the feed gas. The catalytic test was carried out at 110-170 °C and under 0.1 MPa. The composition of the reactants and products was analyzed online by a gas chromatograph (GC) equipped with a TCD connected to a ShinCarbon ST packed column (DIKMA) and a flame ionization detector (FID) connected to an Innowax 20 m capillary column (DIKMA).

The conversion of CO and the selectivity of DMO were calculated as the following formulas:

$$\text{Conversion of CO}(\%) = 1 - \frac{A_{CO_{out}} \div A_{N_{2out}}}{A_{CO_{in}} \div A_{N_{2in}}} \times 100\%$$

$$\text{Selectivity of DMO}(\%) = \frac{A_{DMO}}{A_{DMO} + f \times A_{DMC}} \times 100\%$$

Where  $A_{CO_{in}}$  and  $A_{CO_{out}}$  are the peak areas of CO at the inlet and outlet,  $A_{N_{2in}}$  and  $A_{N_{2out}}$  are the peak areas of N<sub>2</sub> at the inlet and outlet, respectively.  $A_{DMO}$  and  $A_{DMC}$  are the peak areas of dimethyl oxalate and dimethyl carbonate and  $f$  is the relative correction factor of dimethyl carbonate to dimethyl oxalate.

TOF values were calculated as the following equation:

$$\text{TOF} = \frac{\text{Productu Molecules}}{\text{Active Sites} \times \text{Time}} = \frac{\frac{F_{CO}}{V_m} \times X_{CO} \times S_{DMO}}{\frac{m_{cat} \times w_{Pd}}{M_{Pd}} \times D}$$

Where  $F_{CO}$  is the volume velocity of CO,  $V_m$  is molar volume of gas,  $X_{CO}$  is the conversion of CO,  $S_{DMO}$  is the selectivity of DMO,  $m_{cat}$  is the weight of catalyst,  $w_{Pd}$  is the actual Pd loading measured by ICP-AES,  $M_{Pd}$  is the Pd molar weight,  $D$  is the Pd dispersion measured by CO chemisorption.

### ***Catalytic VOCs combustion***

The catalytic VOCs combustion on Al-fiber@ns-AlOOH@Pd catalysts was performed on a fixed-bed quartz tube reactor (600-mm length by 8-mm inner diameter) under atmospheric pressure. The catalyst used in testing experiments was 0.20 g. A gaseous mixture (1 vol% CH<sub>4</sub> or 1000 ppm other VOCs in air) was employed as feedstock. The effluent gas was quantitatively analyzed online by an HP 6850 gas chromatograph equipped with a TCD connected to Porapak Q and MS 5A parallel capillary columns (DIKMA).

The conversions of VOCs, namely, methane, ethane, ethylene, methanol, and methyl formate were calculated as the following formula:

$$Conversion(\%) = \frac{f \times A_{CO_2out}}{n \times A_{VOCout} + f \times A_{CO_2out}} \times 100\%$$

Where  $f$  is the relative correction factor of  $CO_2$  to the VOC,  $n$  is the carbon number of the VOC and  $A_{CO_2out}$  and  $A_{VOCout}$  are the peak areas of  $CO_2$  and the VOC at the reactor outlet.

The other conversion of VOCs, namely, toluene and formaldehyde were calculated as the following formula:

$$Conversion(\%) = 1 - \frac{A_{VOCout} \div A_{N_2out}}{A_{VOCin} \div A_{N_2in}} \times 100\%$$

Where  $A_{VOCin}$  and  $A_{VOCout}$  are the peaks area of the VOC at the reactor inlet and outlet,  $A_{N_2in}$  and  $A_{N_2out}$  are the peaks area of  $N_2$  at the inlet and outlet, respectively.

### ***Fischer-Tropsch to low olefins (FTO)***

The FTO reaction over the Al-fiber@ns- $\gamma$ - $Al_2O_3$ @FeMnK catalysts was carried out in a fixed bed stainless steel reactor with an internal diameter of 8 mm. Catalyst of 0.50 g was activated with 10% $H_2$  in  $N_2$  (50 ml/min) at 400 °C for 2 h at atmospheric pressure. Then, such activated catalyst was cooled down to the reaction temperature and the gas flow was switched to a  $H_2/CO/N_2$  mixture (6: 3: 1) with fast increasing the pressure to appointed values. All post-reactor lines were heated to 200 °C to prevent product condensation. The effluent gas was quantitatively analyzed on-line using an Agilent GC 7820 with a TCD and a Shimadzu GC2014 gas chromatography with a FID connected to a 30 m HP-PLOT/Q capillary column. The CO conversion (%) was calculated by an internal standard method with  $N_2$  as standard.

The hydrocarbons distribution (wt%) towards the individual components (i) on was calculated according to the same principle:

$$S_i(\%) = \frac{A_i \times f_i}{\sum A_i \times f_i} \times 100\%$$

Where  $S_i$  is the selectivity of the individual components,  $A_i$  is the peaks areas of the individual components and  $f_i$  is the relative correction factor of the individual component to benzene.

### ***Hydrogenation of CO to methane***

The hydrogenation of CO to methane was performed in a fixed-bed quartz tube reactor (600 mm length by 16 mm inner diameter) under atmospheric pressure. The catalyst loading was 4.50 g. Prior to the reaction, the catalyst was pre-reduced in  $H_2$  flow at 550 °C for 2 h. A mixture of  $H_2/CO$  (3/1) was preheated to the desired temperature and then fed into the reactor continuously. The  $H_2$  and CO were all controlled by the calibrated mass flow controllers. The product effluent was analyzed by using an online-gas chromatograph equipped with a TCD and 2 m Shincarbon ST column (DIMKA). No coke was found on the catalyst during the reactivity test. The CO conversion and methane selectivity were calculated using standard normalization method on the base of carbon atom balance and defined as follows:

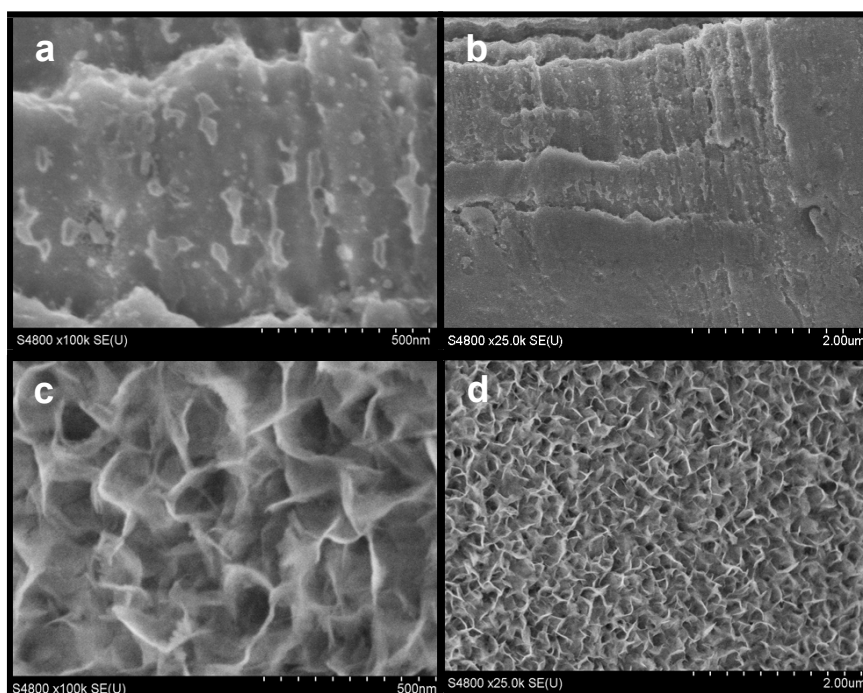
$$\text{Conversion of CO}(\%) = \frac{V_{CO,in} - V_{CO,out}}{V_{CO,in}} \times 100\%$$

$$\text{Selectivity of } CH_4(\%) = \frac{V_{CH_4,out}}{V_{CO,in} - V_{CO,out}} \times 100\%$$

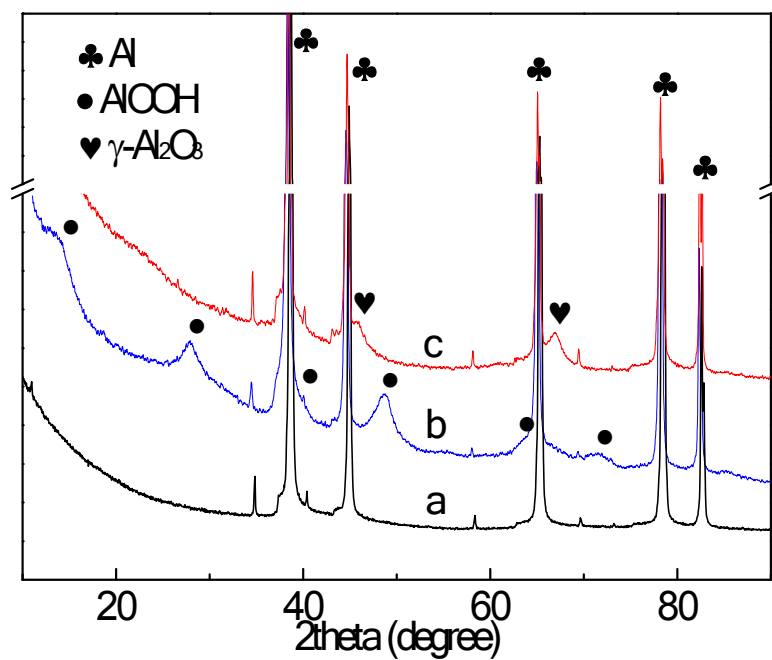
Where  $V_{i,in}$  and  $V_{i,out}$  are the volume flow rates of species i (i = CO or  $CH_4$ ) at the inlet and outlet (mL/min), respectively. Moreover, the  $V_{CO,in}$  equal to the sum of  $V_{CO,out}$ ,  $V_{CH_4,out}$  and  $V_{CO_2,out}$  because no other carbon containing materials were detected and neglect of carbon



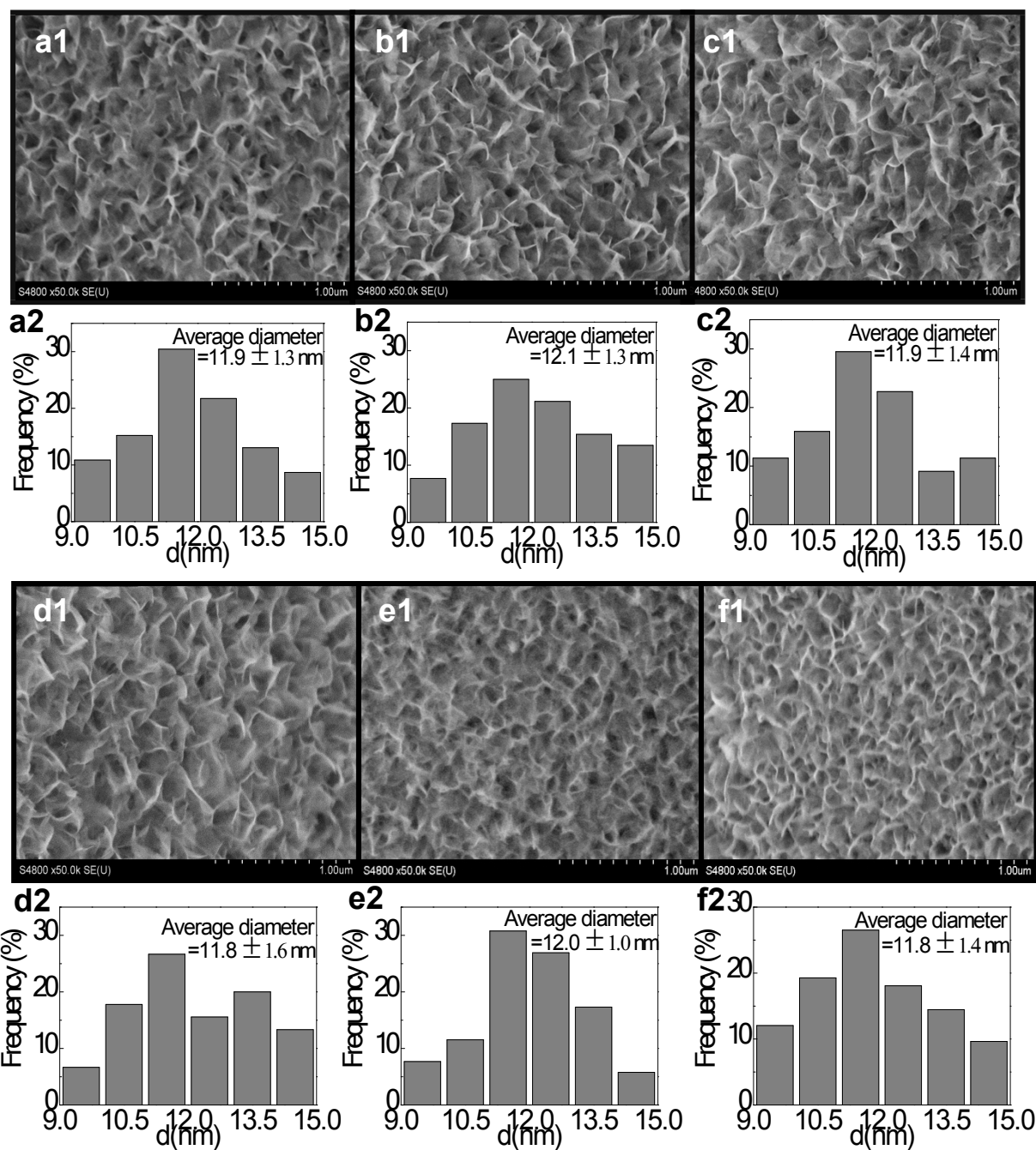
deposition.



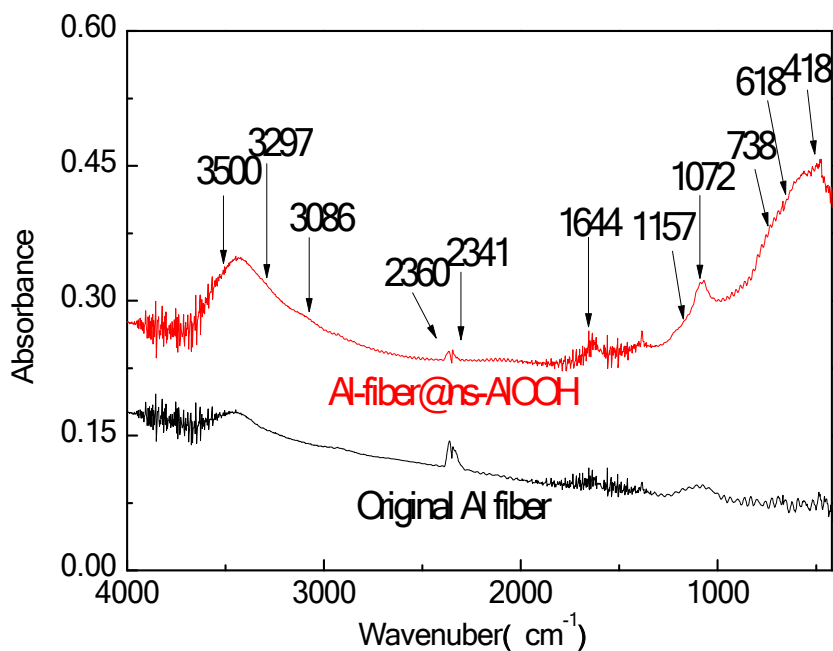
**Fig. S1** High-magnification SEM images of a,b) original Al-fiber without steam-only oxidation; c,d) Al-fiber after steam-only oxidation in steam flow at 120 °C for 6 h and subsequent calcination at 600 °C for 2 h.



**Fig. S2** XRD patterns of a) original Al-fiber without steam-only oxidation; b) Al-fiber after steam-only oxidation in steam flow at 120 °C for 6 h; c) Al-fiber after steam-only oxidation in steam flow at 120 °C for 6 h and subsequent calcination at 600 °C for 2 h (the XRD samples are prepared by scratching AlOOH and Al off the 3D Al-fiber network to increase the intensity).

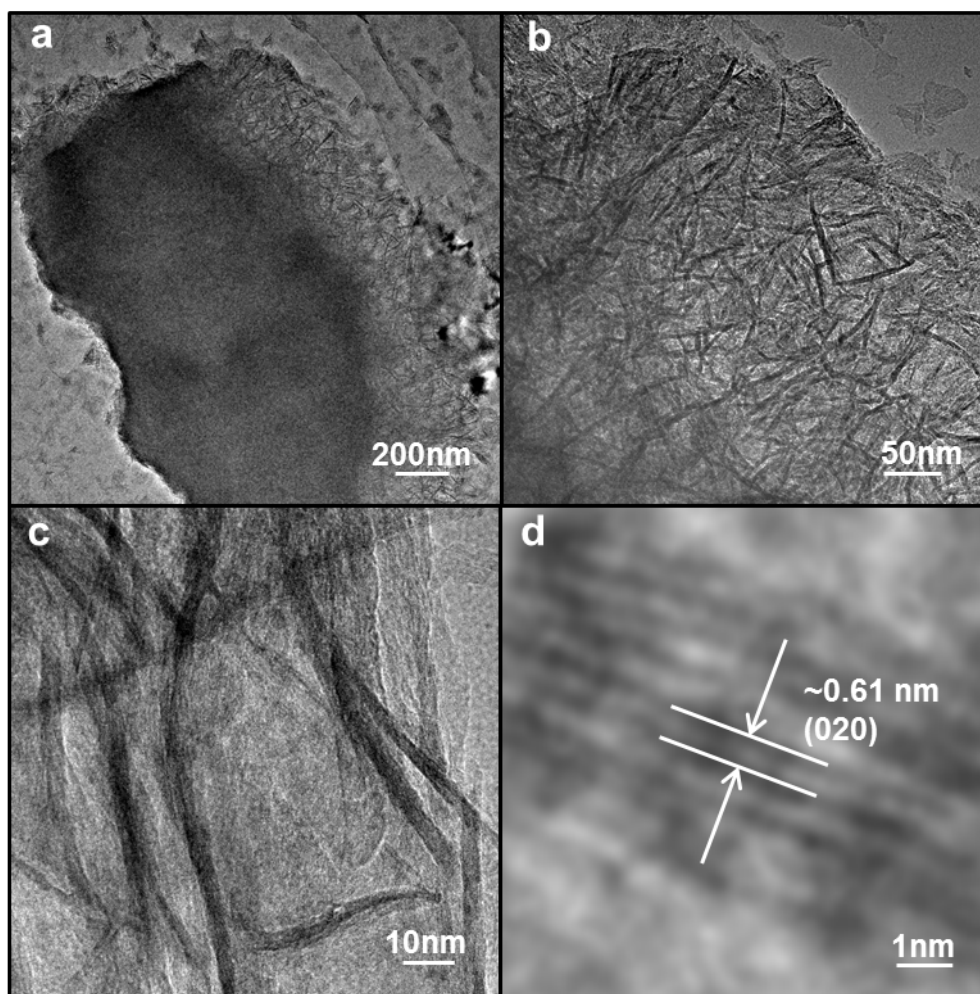


**Fig. S3** High-magnification SEM images and ns-AlOOH thickness distribution (determined by SEM images) of Al-fiber in steam flow for 6 h at 120 °C a1,a2), 300 °C b1,b2) and 600 °C c1,c2) and at 120 °C for 0.5 h d1,d2), 12 h e1,e2) and 72 h f1,f2).



**Fig. S4** FTIR spectra of original Al fiber and Al-fiber@ns-AIOOH after steam-only oxidation in steam flow at 120 °C for 6 h (the FTIR samples are prepared by scratching AIOOH and Al off the 3D Al-fiber network to increase the intensity).

The FTIR spectra of Al fiber before and after steam-only oxidation are shown in Fig. S4. It can be seen that the FTIR spectra of original Al fiber and Al-fiber@ns-AIOOH are clearly different from each other. In Fig. S4, the band at about 3297 and 3086  $\text{cm}^{-1}$  are ascribed to symmetric and asymmetric stretching vibrations in (Al)OH groups. The intensive band at 1072  $\text{cm}^{-1}$  and shoulder at 1157  $\text{cm}^{-1}$  are respectively attributed to the symmetric and asymmetric bending vibrations in (Al)OH groups. The band at about 738  $\text{cm}^{-1}$  is assigned to the angle bending in (Al)OH groups. The band at about 618 and 418  $\text{cm}^{-1}$  are attributed to the angle bending and angle deformation in (OH)-Al-O.<sup>S1,S2</sup> In addition, the band at 3500 and 1644  $\text{cm}^{-1}$  can be attributed to the adsorbed water and band at 2360 and 2341  $\text{cm}^{-1}$  can be attributed to the adsorbed  $\text{CO}_2$ .



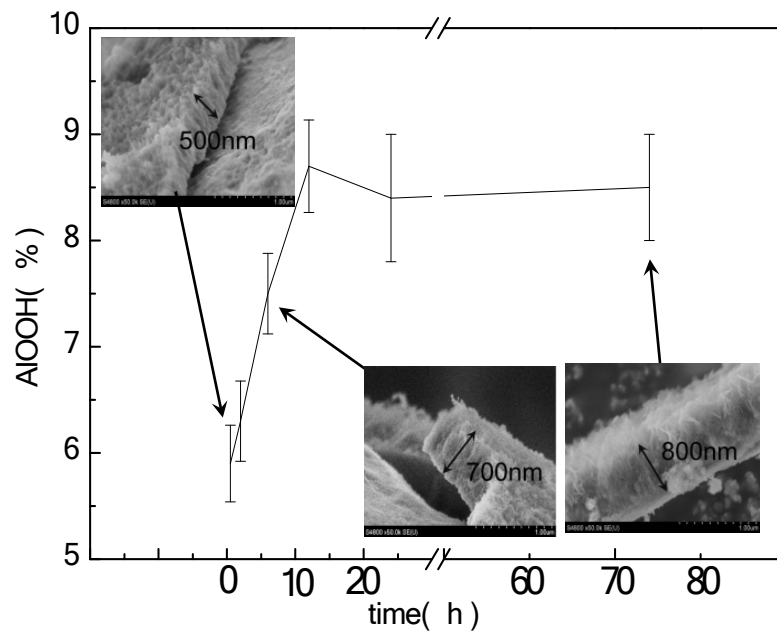
**Fig. S5** a,b) TEM images and c,d) HRTEM images of Al-fiber@ns-AlOOH after steam-only oxidation in steam flow at 120 °C for 6 h.

The TEM images (Fig. S5a,b) and HRTEM image (Fig. S5c) display that ns-AlOOH is disorderedly stacked on the Al-fiber. The HRTEM image (Fig. S5d) further displays lattice spacing of about 0.61 nm corresponding to the (020) planes (0.61 nm) of ns-AlOOH. The main (020) planes of ns-AlOOH is related to the nanosheets structure, which is consistent with the reported literatures.<sup>S1,S3</sup>

**Table S1.** Textural properties of Al-fiber@ns-AlOOH with the calcination temperature <sup>a</sup>.

Temperature (°C)	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )
No calcination	13.1	0.018
300	12.5	0.019
600	10.1	0.020

<sup>a</sup> Al-fiber after steam-only oxidation in steam flow at 120 °C for 6 h and subsequent calcination at different temperatures.



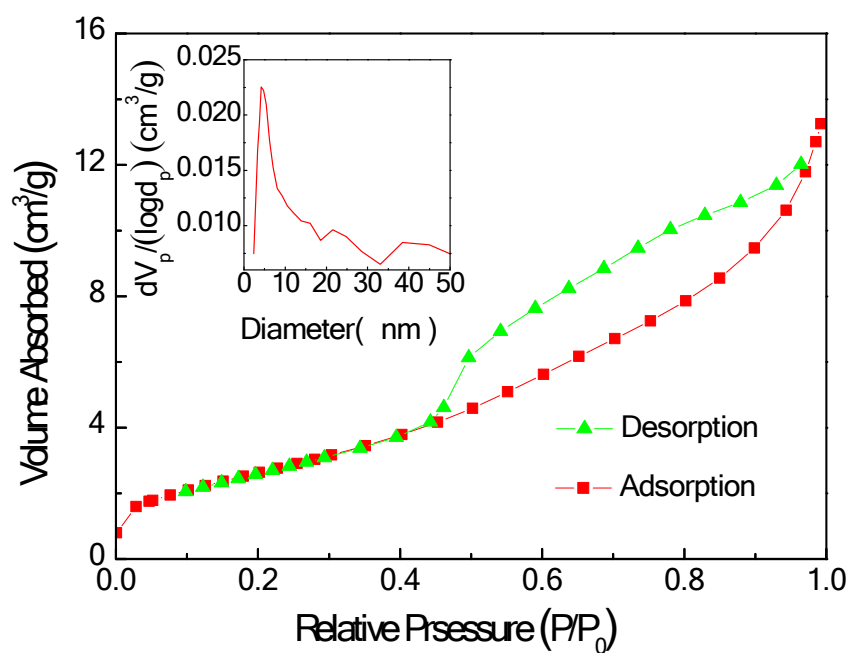
**Fig. S6** Relation between the weight increase and steam-only oxidation time for formation of ns-AlOOH on Al-fiber in steam flow at 120 °C ranged from 0.5 h to 72 h.



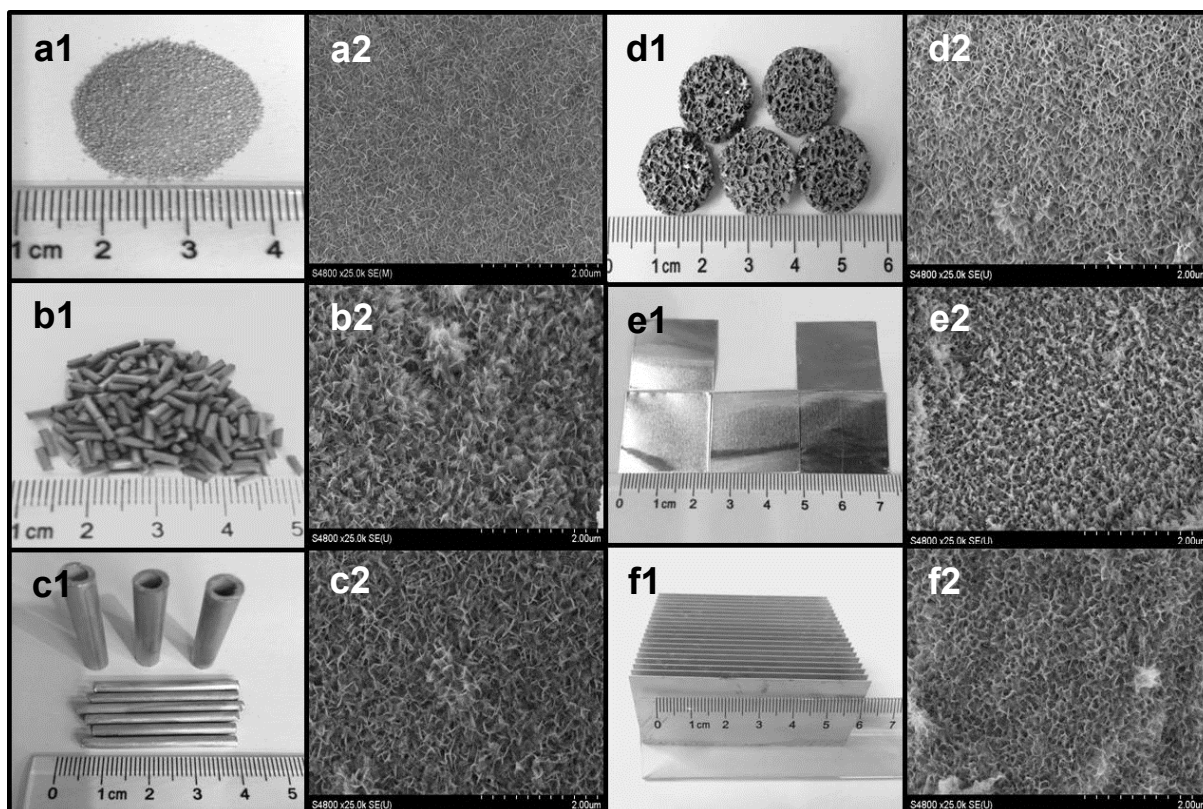
**Table S2.** Weight increase of Al-fiber on steam for 12 h at different temperatures.

Temperature (°C)	120	300	600 <sup>a</sup>
AlOOH (wt%)	8.7	5.0	4.4

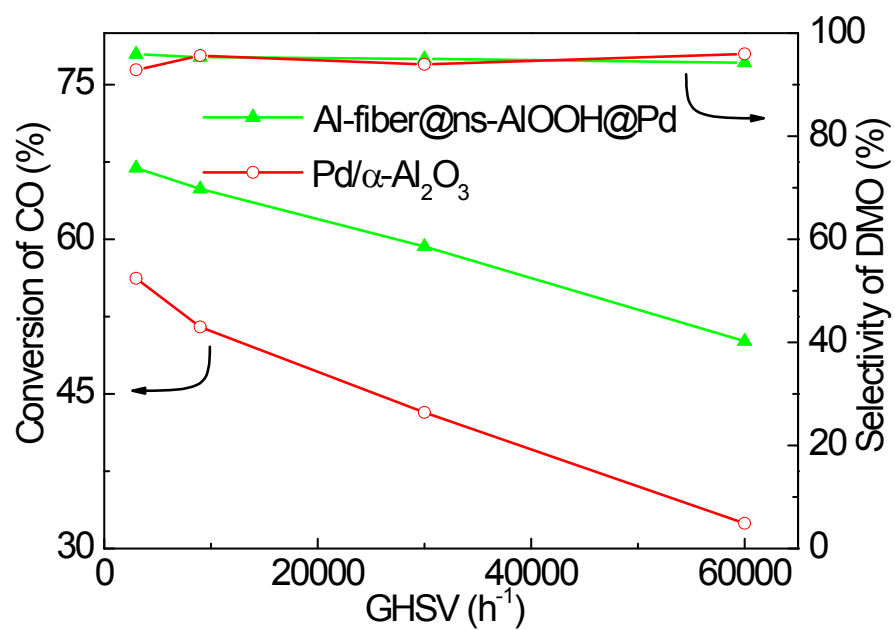
<sup>a</sup> The weight increase of ns- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> on Al-fiber was converted into ns-AlOOH multiplied by a coefficient of 1.18.



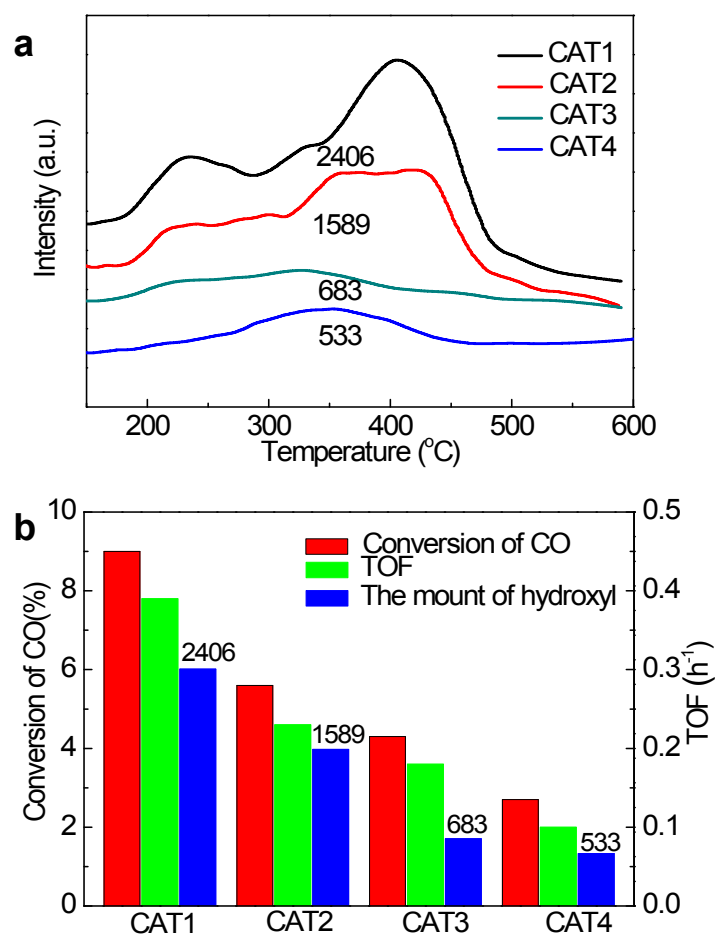
**Fig. S7** N<sub>2</sub> adsorption-desorption isotherm for Al-fiber after steam-only oxidation in steam flow at 120 °C for 6 h and subsequent calcination at 600 °C for 2 h (insert: Barrett-Joyner-Halenda (BJH) mesopore size distribution calculated by the adsorption isotherms).



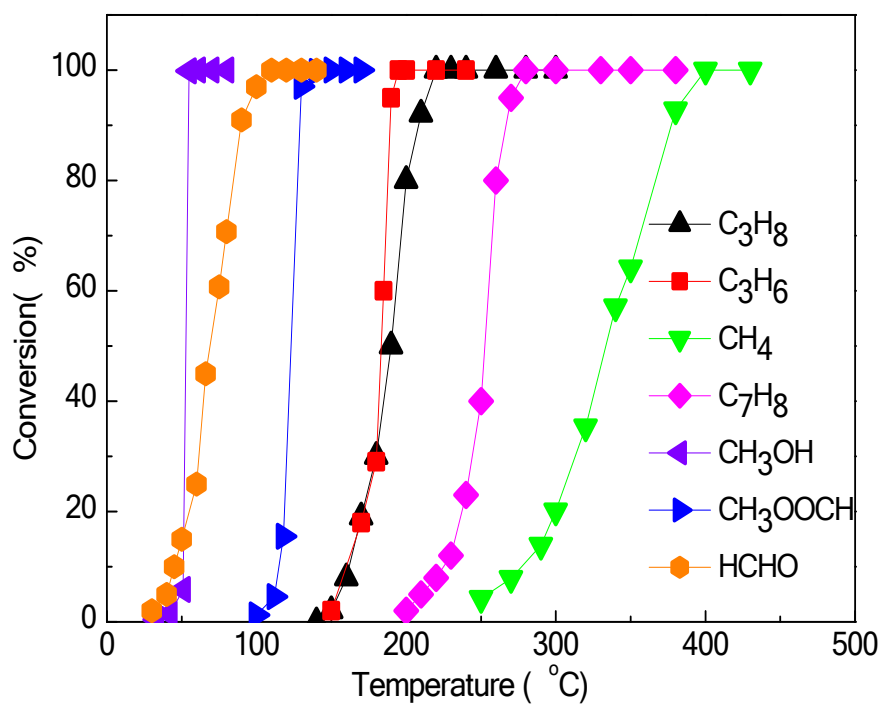
**Fig. S8** The macroscopic photographs and high-magnification SEM images of Al particles a1,a2), Al wires b1,b2), Al tubes c1,c2), Al foams d1,d2), Al foils e1,e2) and Al microchannels f1,f2) after steam-only oxidation in steam flow at 120 °C for 6 h.



**Fig. S9** Conversion and selectivity for CO oxidative coupling to DMO against GHSV at 150 °C. Other conditions: 0.80 g catalyst for GHSV of 3000 and 9000 h<sup>-1</sup>, 0.08 g catalyst for GHSV of 30000 and 60000 h<sup>-1</sup>, CO/CH<sub>3</sub>ONO volume ratio of 1.4, 0.1 MPa.



**Fig. S10** a) The TPD profiles of dehydroxylation (the data are the peak areas) and b) the relationship between the OH contents and catalytic performance on the Pd/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (CAT4) and Al-fiber@ns-AlOOH@Pd catalysts prior to loading Pd with different calcination temperature: CAT1: no calcination, CAT2: 300 °C for 2 h, CAT3: 600 °C for 2 h. Other conditions: 0.08 g catalyst, GHSV = 60000 h<sup>-1</sup>, CO/CH<sub>3</sub>ONO volume ratio of 1.4, 0.1 MPa.

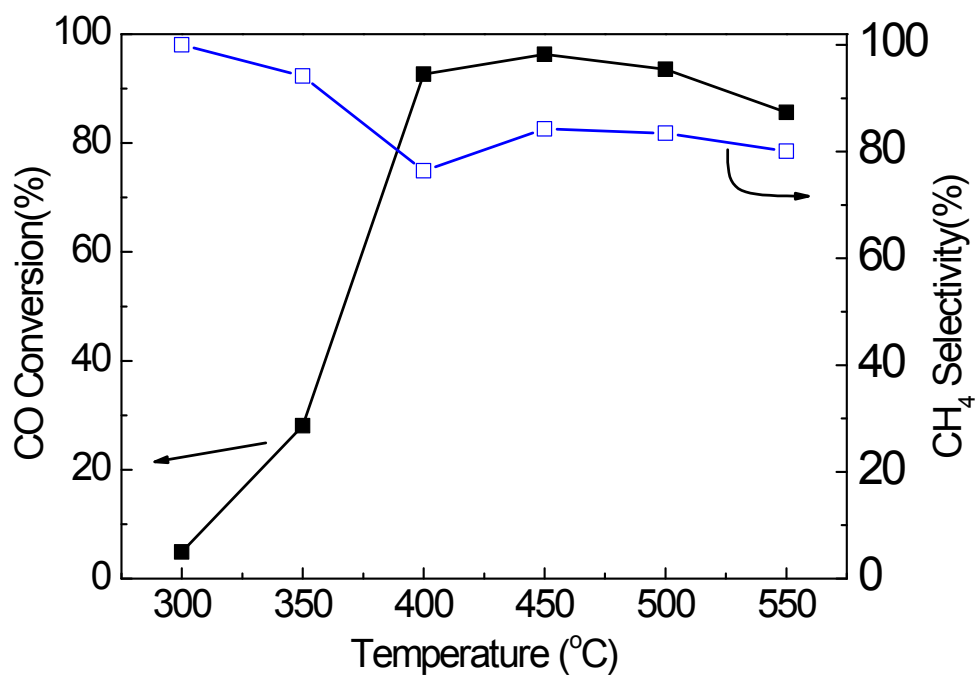


**Fig. S11** Conversions of different VOCs as a function of temperature over the Al-fiber@ns-ALOOH@Pd catalyst. Other conditions: 0.20 g catalyst, GHSV = 72L g<sup>-1</sup> h<sup>-1</sup>, 1 vol% CH<sub>4</sub> in air and 1000 ppm other VOCs in air.

**Table S3.** The effect of different Fe and Mn precursors on catalytic performance of Al-fiber@ns- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>@FeMnK for the Fisher-Tropsch to olefins.

Catalyst	CO Conv.(%)	CO <sub>2</sub> (% CO Conv.)	Hydrocarbon distribution (wt%)				
			C1	C2=C4=	C2-C4	C5+	O/P
CAT-1	80.9	32.7	17.6	38.8	9.7	33.9	4.0
CAT-2	89.0	31.8	17.0	39.7	9.3	34.0	4.3
CAT-3	92.5	29.7	16.5	39.4	9.3	34.8	4.3
CAT-4	83.7	30.4	17.6	38.6	9.5	34.3	4.0

CAT-1: Fe(NO<sub>3</sub>)<sub>3</sub>, Mn(NO<sub>3</sub>)<sub>2</sub> and KNO<sub>3</sub>; CAT-2: Ammonium ferric citrate, Mn(NO<sub>3</sub>)<sub>2</sub> and KNO<sub>3</sub>; CAT-3: Fe(NO<sub>3</sub>)<sub>3</sub>, Mn(CH<sub>3</sub>COO)<sub>2</sub> and KNO<sub>3</sub>; CAT-4: Ammonium ferric citrate, Mn(CH<sub>3</sub>COO)<sub>2</sub> and KNO<sub>3</sub>. Reaction conditions: 0.50 g catalyst, T = 350 °C, P = 4 MPa, GHSV = 10 L g<sup>-1</sup> h<sup>-1</sup>, H<sub>2</sub>/CO = 2, data taken after 20 h when reaction state remains steady.



**Fig. S12** Effect of reaction temperature on the catalytic performance of Al-tube@ns- $\gamma$ - $\text{Al}_2\text{O}_3$ @Ni for the hydrogenation of CO to methane. Other conditions: 4.50 g catalyst, GHSV =  $2500 \text{ h}^{-1}$ ,  $\text{H}_2/\text{CO} = 3$ , 0.1 MPa.



## Reference

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