

[Supporting Information]

## ***In-situ* growth of carbon nanotubes on Ni/MgO: A facile preparation of efficient catalysts for the production of synthetic natural gas from syngas**

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### **1. Experimental**

The Ni/MgO catalysts were prepared by modified co-precipitation under low saturation method. The metal nitrate aqueous solution was obtained by dissolving 9.3 g Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 17.9 g Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (all in A. R. grade) in 50 mL deionized water. An aqueous solution of NaOH and Na<sub>2</sub>CO<sub>3</sub> with a molar ratio of 4:1 (1.6 mol/L and 0.4 mol/L, respectively) was used as precipitant. The precursor of mixed oxide was prepared by simultaneously adding these two solutions mentioned above very slowly to a container under continuous stirring at room temperature, while the pH of the mixed solution was held at 10 ± 0.2 by controlling the dropping rate. After aging for 12 h at 90 °C, the precipitate was washed with deionized water until the filtrate was neutral, and then it was dried at 110 °C for 12 h. The Ni/MgO catalyst was then obtained by calcining the precipitate at 450 °C in air for 5 h, named p-Ni/MgO. The Ni content of Ni/MgO catalyst was 40 wt%.

The *in-situ* growth of CNTs on Ni/MgO catalyst was prepared by chemical vapor deposition (CVD) using CO as carbon source. Firstly, 100 mg of the prepared Ni/MgO catalyst, diluted with 500 mg of quartz sand (both of 40 ~ 80 mesh), was reduced at 600 °C for 5 h in a gas flow of 5%H<sub>2</sub>-95%Ar (30 mL min<sup>-1</sup>), and then switched to pure CO stream (99.9%, 30 mL min<sup>-1</sup>) for *in-situ* growth of CNTs. In order to get rid of amorphous carbon, the catalyst was calcined in a gas flow of 5%H<sub>2</sub>-

95%Ar at 550 °C for 2 h. After cooling to 200 °C, the prepared catalysts could be used for syngas methanation directly. The prepared catalysts were named as i-Ni/MgO-CNTs catalysts.

For comparison, catalysts containing CNTs were also prepared by co-precipitation method of the same procedure as Ni/MgO catalysts. The CNTs were obtained from i-Ni/MgO-CNTs catalysts, which were purified in concentrated nitric acid at 120 °C for 5 h, and then washed with deionized water until the filtrate was neutral, following by dried at 110 °C for 12 h. Two CNTs-containing catalysts, noted as p-Ni/MgO-CNTs and p-Ni/CNTs, were prepared, wherein, the p-Ni/MgO-CNTs catalyst had the essentially same composition with i-Ni/MgO-CNTs, and the Ni content of p-Ni/CNTs catalyst was 40 wt%.

The X-ray diffraction (XRD) patterns were conducted on a Rigaku D/MAX-rC X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda=0.15418$  nm). The tube voltage was 35 kV and the current was 15 mA. The crystal size of the catalyst was calculated using the Debye-Scherrer equation. Nitrogen adsorption-desorption isotherms were measured by static N<sub>2</sub> physisorption at 77 K using a Micromeritics TriStar II 3020 surface area and pore analyzer. All samples were outgassed and evacuated at 250 °C for 2 h before adsorption. The specific surface area was determined according to the Brunauer-Emmett-Teller (BET) method. The average pore diameter and pore size distributions were evaluated by the Barrett-Joyner-Halenda (BJH) method using the desorption branch of isotherms. The pore volumes were evaluated at a relative pressure (P/P<sub>0</sub>) of 0.99. Hydrogen temperature-programmed reduction (H<sub>2</sub>-TPR) experiments were performed on a Micromeritics Autochem II 2920 instrument. Prior to the H<sub>2</sub>-TPR test, 50 mg calcined catalyst was pretreated in a quartz U-tube reactor at 450 °C for 1 h under a gas flow of Ar to remove physically adsorbed impurities. And then the H<sub>2</sub>-TPR experiments were carried out in a gas flow of 5%H<sub>2</sub>-95%Ar (30 mL min<sup>-1</sup>) with the temperature elevated from 50 °C to 900 °C at a rate of 5 °C min<sup>-1</sup>. The outlet gas was passed through a 5A zeolite trap to remove moisture and then the hydrogen consumption rate was monitored by a thermal conductivity detector (TCD). Raman spectra were obtained using a Renishaw inVia Raman microscope with excitation wavelength at 532 nm in a back scattering configuration. The surface

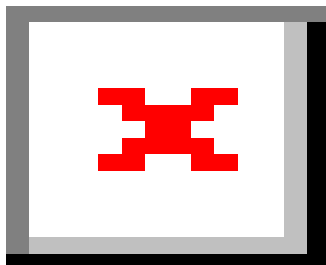
morphologies of the catalysts were observed using FESEM (JEOL JSM-6700F). Transmission electron microscopy (TEM) micrographs were obtained on a JEM-2100 apparatus operated at 200 kV. The catalyst samples were ultrasonically dispersed in ethanol at room temperature for 30 min. The as-obtained solution was dropped onto the copper grid for TEM. The contents of C was measured by elemental analyzer (Vario EL III).

The evaluation of Ni catalysts for syngas methanation was carried out in a continuous flow fixed-bed reactor equipped with a quartz tube. Prior to the reactivity measurements, 100 mg of the catalyst, diluted with 500 mg of quartz sand (both of 40 ~ 80 mesh), was reduced at 600 °C for 5 h in a gas flow of 5%H<sub>2</sub>-95%Ar (30 mL min<sup>-1</sup>) and then the temperature was lowered to 200 °C. The syngas methanation was performed in the feed gas of V(H<sub>2</sub>)/V(CO)/V(CO<sub>2</sub>)/V(N<sub>2</sub>) = 75/15/5/5 at a weight hourly space velocity (WHSV) of 40000 mL g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> under atmospheric pressure. The outlet stream was monitored by an online gas chromatograph (GC2060, Shanghai RAMI Instrument Co.; Ltd) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The TCD was equipped with a TDX-01 packed column (1 m in length) and the FID with a Porapak Q-S packed column (2 m in length), respectively. After two hours of steady-state operation at each temperature, the concentrations of CO, CO<sub>2</sub> and N<sub>2</sub> (N<sub>2</sub> as an inner standard) were analyzed by the TCD, and the concentrations of CH<sub>4</sub> and other C-containing hydrogenated products were determined by FID. The conversion of CO and total conversion of CO and CO<sub>2</sub> were determined by the N<sub>2</sub> internal standard. The carbon-based selectivity for CH<sub>4</sub> selectivity was calculated by an internal normalization method. And the yield of CH<sub>4</sub> was calculated by multiplying the value of total conversion of CO and CO<sub>2</sub> and CH<sub>4</sub> selectivity.

## **2. Effects of growth time on i-Ni/MgO-CNTs-n catalysts**

The i-Ni/MgO-CNTs-n catalysts were characterized by N<sub>2</sub> physisorption, SEM, XRD and Raman spectra. As seen in Fig. S1, the CNTs growing among Ni/MgO particles were about 40 ~ 60 nm in diameter. The amount of CNTs in the catalysts

increased with growth time increasing from 5 to 20 min. Carbon content of fresh catalysts could serve as references of CNTs content, seen in Tab. S1.



**Fig. S1** SEM images of the fresh prepared i-Ni/MgO-CNTs-*n* catalysts and the fresh reduced Ni/MgO catalyst. (a: i-Ni/MgO-CNTs-5; b: i-Ni/MgO-CNTs-7.5; c: i-Ni/MgO-CNTs-10; d: i-Ni/MgO-CNTs-12.5; e: i-Ni/MgO-CNTs-15; f: i-Ni/MgO-CNTs-20; g: Ni/MgO.)

**Tab. S1** Carbon content of *in-situ* growing CNTs on Ni/MgO Catalysts

Catalysts	Growth time (min)	Carbon content (%)
i-Ni/MgO-CNTs-5	5	11.7
i-Ni/MgO-CNTs-7.5	7.5	16.4
i-Ni/MgO-CNTs-10	10	22.2
i-Ni/MgO-CNTs-12.5	12.5	26.0
i-Ni/MgO-CNTs-15	15	29.0
i-Ni/MgO-CNTs-20	20	36.5

As shown in Fig. S1 and Tab S1, the contents of CNTs increase with increasing of reaction time. The Ni particle surface is finite, more and more Ni particles will be covered with CNTs during the CNTs growth. To a certain growth time, part of Ni particles may be encapsulated entirely by CNTs, resulting in worse “low-temperature superiority”. Therefore, as the growth time further increasing to more than 10 min, i-

Ni/MgO-CNTs-*n* (*n*>10) catalysts show worse "low-temperature superiority" activities than that of i-Ni/MgO-CNTs-10.

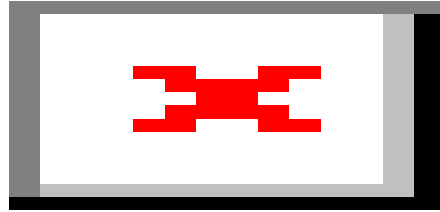
Fig. S2(a) showed the XRD patterns of the i-Ni/MgO-CNTs-*n* catalysts and the Ni/MgO catalyst. There was a group of characteristic peak at 26.1°, except the two groups of peaks attributed to Ni ( $2\theta = 44.3^\circ$ ,  $51.8^\circ$ ,  $76.2^\circ$ , JCPDS No. 01-087-0712) or MgO phase ( $2\theta = 37.0^\circ$ ,  $42.8^\circ$  and  $62.1^\circ$ , JCPDS No. 01-075-0447). Previous studies suggested that the XRD pattern of CNTs was close to that of graphite with (002) peak of  $2\theta = 26.5^\circ$ , but the peak of CNTs, weakened and broadened, shift from  $26.5^\circ$  to  $26.1^\circ$ . The diffraction peak at  $26.1^\circ$  of i-Ni/MgO-CNTs-*n* catalysts was attributed to CNTs. The peak intensity of CNTs increase with increasing growth time.

**Tab. S2** Textural properties of i-Ni/MgO-CNTs-*n* catalysts and the fresh reduced Ni/MgO catalyst

Catalysts	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$V_{\text{P}}$ ( $\text{cm}^3 \text{g}^{-1}$ )	$D_{\text{P}}$ (nm)
Ni/MgO	54.5	0.13	7.1
i-Ni/MgO-CNTs-5	83.9	0.22	8.8
i-Ni/MgO-CNTs-7.5	87.9	0.23	8.9
i-Ni/MgO-CNTs-10	92.1	0.29	11.7
i-Ni/MgO-CNTs-12.5	90.6	0.31	11.0
i-Ni/MgO-CNTs-15	95.4	0.33	12.8
i-Ni/MgO-CNTs-20	106.2	0.40	13.4

Raman spectra is one of the most effective method for CNTs characterization. In Raman spectra, CNTs shows a strong peak around  $1580 \text{ cm}^{-1}$  noted as G band (Graphite band), which is related to the C-C vibration of the  $\text{sp}^2$  orbital structure, and a strong peak around  $1350 \text{ cm}^{-1}$  noted as D band (Disorder band), which is contributed to the disorder-induced vibration of C-C bond. In Fig. S2(b), Raman

bands at 1580 and 1345  $\text{cm}^{-1}$  could be assigned to the CNTs Raman features of *i*-Ni/MgO-CNTs-*n* catalysts. In addition, the ratio of  $I_D/I_G$  of the catalysts was between 1.0 and 1.2, which was very close to each other, indicating that the graphitization extents of CNTs showed relatively uniform with different growing time.



**Fig. S2** XRD patterns (a) and Raman spectra (b) of the fresh prepared *i*-Ni/MgO-CNTs-*n* catalysts and the fresh reduced Ni/MgO catalyst. (a, *i*-Ni/MgO-CNTs-5; b, *i*-Ni/MgO-CNTs-7.5; c, *i*-Ni/MgO-CNTs-10; d, *i*-Ni/MgO-CNTs-12.5; e, *i*-Ni/MgO-CNTs-15; f, *i*-Ni/MgO-CNTs-20; g, Ni/MgO)

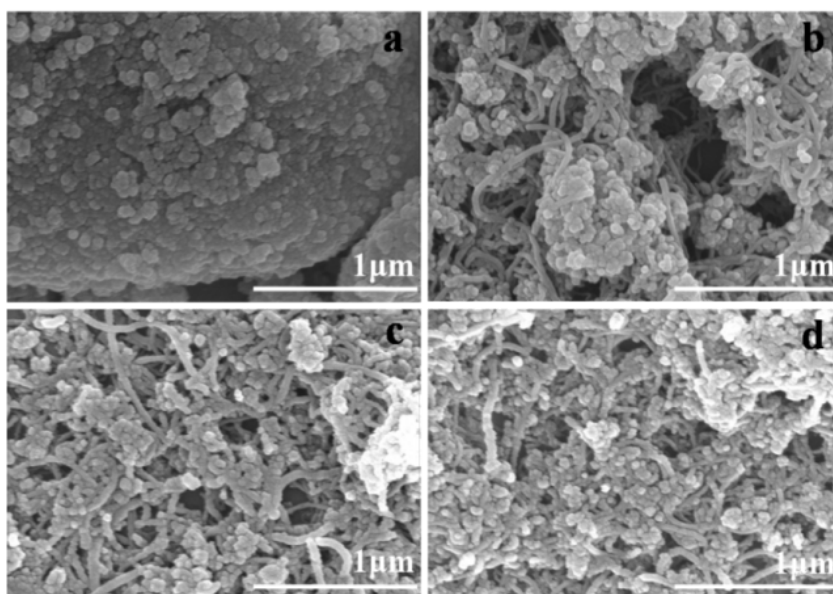
### 3. Effects of preparation method on Ni-based catalysts

**Tab. S3** Textural properties of Ni-based catalysts prepared by different methods

Catalysts	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$V_{\text{p}}$ ( $\text{cm}^3 \text{g}^{-1}$ )	$D_{\text{p}}$ (nm)
p-Ni/MgO	54.5	0.13	7.1
p-Ni/CNTs	118.9	0.45	13.2
CNTs	230.0	0.42	6.8
<i>i</i> -Ni/MgO-CNTs	92.1	0.29	11.7
p-Ni/MgO-CNTs	110.7	0.30	9.4

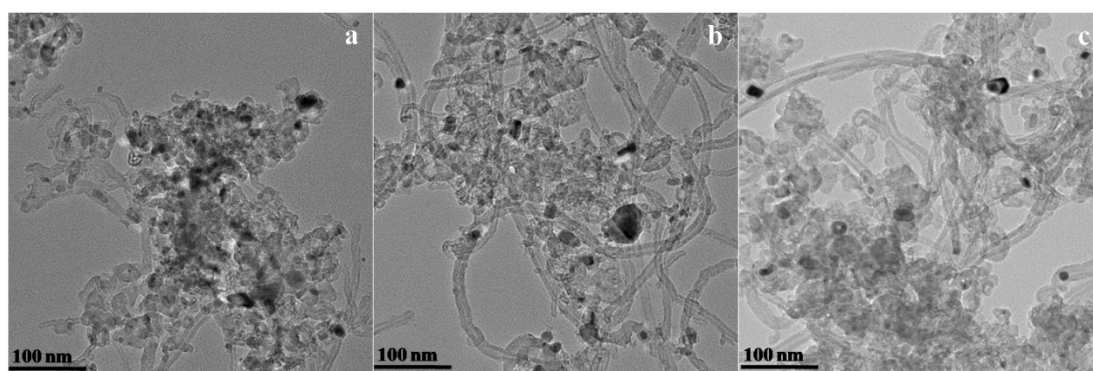
The surface properties of the catalysts prepared by different method and purified CNTs were list in Tab. S3 according to the  $\text{N}_2$  physisorption characterizations. The specific surface area of p-Ni/MgO catalyst without CNTs was only  $54.5 \text{ m}^2 \text{g}^{-1}$ , but after *in-situ* growth CNTs on Ni/MgO catalyst, the  $S_{\text{BET}}$  increased to  $92.1 \text{ m}^2 \text{g}^{-1}$ . Pure

CNTs showed large  $S_{\text{BET}}$  of  $230.0 \text{ m}^2 \text{ g}^{-1}$ , and might be responsible to the comparatively large surface area of catalysts containing CNTs.



**Fig. S3** SEM images of Ni catalysts prepared by different method: a, p-Ni/MgO; b, i-Ni/MgO-CNTs; c, p-Ni/MgO-CNTs; d, p-Ni/CNTs.

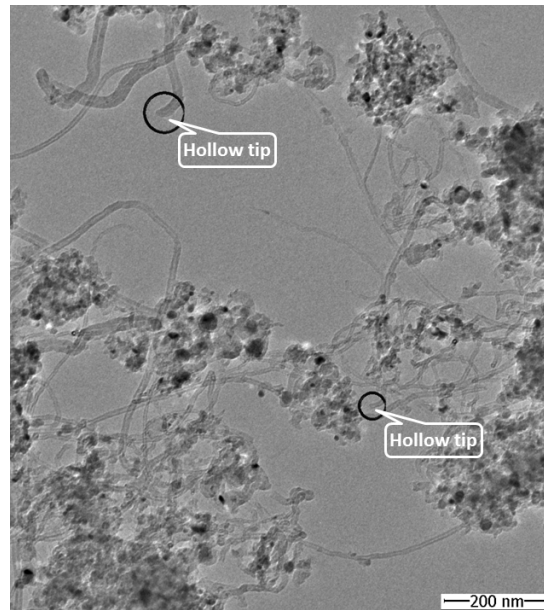
As can be seen from Fig. S3, the SEM images of the p-Ni/MgO catalyst showed that the particles over the catalyst was compactly stacking. For i-Ni/MgO-CNTs catalyst, CNTs *in-situ* grow between Ni/MgO particles, and result in porous construction among the particles.



**Fig. S4** TEM images of Ni catalysts prepared by different method: a, i-Ni/MgO-CNTs; b, p-Ni/MgO-CNTs; c, p-Ni/CNTs.

Fig. S4 shows the TEM images of the i-Ni/MgO-CNTs, p-Ni/MgO-CNTs and p-Ni/CNTs catalysts.

The hollow tip shown in Fig. S5 implies that the *in-situ* growth of the CNTs on Ni/MgO catalyst using CVD method was attributed to the base-growth model.



**Fig. S5** TEM image of CNTs *in-situ* growth on Ni/MgO using CVD method