Supplementary Information

1. Experimental Section

1.1 Sample preparation

The carbon nanotubes (CNTs, average outer diameter >50 nm, length 0.5-2 μm) used were multi-walled carbon nanotubes (purchased from Chengdu Organinc Chemicals Co. Ltd.). The Ni/Mo_2C/CNTs catalysts were synthesized by a simple and environmentally friendly carburization method according to our previous study.[16,18] This method did not require the passivation step for preparing Mo_2C. The Ni/Mo_2C/CNTs catalysts with different Ni/Mo molar ratios were prepared in two steps. In the first step, the precursors with theoretical loadings of 11.6 wt% Ni and a molar ratio of Ni/Mo=0.5, 1, 1.5 and 2 were prepared by two-step impregnation method with a Mo-first impregnation sequence. The first impregnation was followed by drying at 70 ℃ overnight and calcination at 350 ℃ in Ar for 1 h, and the second impregnation was followed only by drying at 70 ℃ overnight. In the second step, these samples were heated in a quartz reactor under a flow of Ar (50 ml min^{-1}). The temperature was increased linearly at a rate of 10 $^{o}C\ min^{-1}$ from room temperature (RT) to 850 ^{o}C, followed by cooling to RT under Ar flow. Then, the products were taken out for further use.

1.2 Sample characterization

X-ray diffraction (XRD) was conducted using an X-ray diffractometer (X'Pert Pro MPD) equipped with a Cu Kα source. BET surface areas of the samples were

measured by a surface area analyzer (NOVA4200). TEM images were acquired using a transmission electron microscope (Philips Tecnal 10). Methane temperature-programmed surface reaction (CH_4-TPSR) study was performed using a flow of 6%CH_4/Ar (50 ml min^{-1}). Prior to the reaction, the sample was heated to 850 ^oC under Ar, followed by cooling to RT under Ar, and then was heated under the reactant gas from RT to 850 ^oC at a rate of 10 ^oC min^{-1}. The evolution of gas-phase products during reaction was monitored using gas chromatography (GC).

1.3 Sample performance tests

Catalytic activities of Ni/Mo_2C/CNTs catalysts for DRM were evaluated in a micro-reactor with an inner diameter of 10 mm at atmospheric pressure. Prior to the reaction, the sample was preheated with Ar at 850 ^oC for 30 min. Then CH_4 and CO_2 mixture with a molar ratio of 1:1 was allowed to pass through the catalyst (60-80 mesh) at a flow rate of 40 ml min^{-1} (GHSV=60000 cm^3 g^{-1} h^{-1}). The exit gas stream from the reactor passed through a cold trap to remove water. The flow rates were measured with a soap bubble flow meter. The gas-phase products were analyzed by on-line gas chromatography (GC) equipped with a thermal conductivity detector and a TDX-01 (60-80 mesh) packed column (300 mm×2 mm i.d.). The external standard method was used to quantitative analysis. Linear relationship was obtained between values of peak area and volume concentration of gases in the range of 0.1-100 vol.%. The molar fraction for the products and reactants was determined on the basis of peak area-volume concentration curve and taken into account in the calculation of the conversion and product distribution. The conversions of CH_4 and CO_2, and selectivity

of H_2 were defined respectively as follows: CH_4 conversion (%)= (moles of CH_4 converted)/(moles of CH_4 introduced); CO_2 conversion (%)= (moles of CO_2 converted)/(moles of CO_2 introduced); H_2 selectivity (%)= (moles of H_2 produced)/(2× moles of CH_4 converted). When the test was over, the used sample was cooled to RT under Ar flow. Then, the used samples were taken out for further characterization.

2. Results

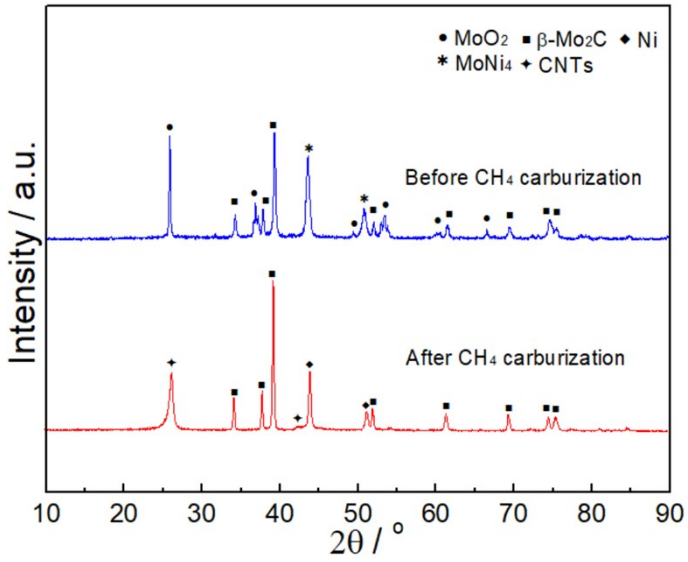

Fig. S1 XRD patterns of the sample contained $MoNi_4$ phase before and after CH_4 carburization.

Table S1 Comparison of DRM catalytic activity and stability for as-prepared and literature

reported Ni/Mo_2C catalysts.

Catalyst	Ni:Mo ratio	Temperature (°C)	GHSV ($cm^3\ g^{-1}\ h^{-1}$)	CH_4 conversion rate[b] ($mol\ g^{-1}\ h^{-1}$)	Catalytic stability (h)	Ref.
$Ni/Mo_2C/CNTs$	1:1	850	60000	0.96	36	This work
$Ni/Mo_2C/CNTs$	1:2	850	60000	0.98	22	This work
Ni/Mo_2C	1:2	850	18000	0.32	13	19
Ni/Mo_2C	1:5	850	3800[a]	0.07	2	22
Ni/Mo_2C	1:2	800	12000	0.22	23	27
Ni/Mo_2C	1:1	800	12000	0.21	4	27
$Ni/Mo_2C/La_2O_3$	1:2	800	12000	0.13	50	30
$Ni/Mo_2C/Al_2O_3$	1.6:1	700	20000[a]	0.04	5	7
$Ni/Mo_2C/SBA\text{-}15$	1:4	800	8000	0.17	180	24

[a] Unit is h^{-1}

[b] Calculated by the CH_4 conversion at the reaction time of 1 h.