Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information

1. Experimental Section

1.1 Catalyst preparation

The carbon nanotubes (CNTs) used were multi-walled carbon nanotubes (purchased from Chengdu Organinc Chemicals Co. Ltd.). And more information regarding the CNTs was listed in Table S1. The Mo_2C nanoparticles supported by CNTs were prepared in two steps. In the first step, two kinds of precursors for Mo_2C/CNTs with theoretical loadings of 30 wt% Mo were prepared by incipient wetness impregnation method and mechanical mixing method, respectively. The former was prepared via stirring CNTs in an aqueous solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, followed by sonicating for about 30 min, and then dried in air at 70 ^oC for overnight. The latter was prepared by mixing $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and CNTs powders mechanically. In the second step, these precursors 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 ^oC min^{-1} from room temperature (RT) to 850 ^oC, followed by cooling to RT under Ar flow. Then, the products were taken out for further use. In addition, unsupported Ni(Co)/Mo_2C and CNTs supported Ni(Co)/Mo_2C catalysts were also obtained in this study. The unsuppored samples were prepared based on the method reported before.[28] In the case of the CNTs supported samples, their precursors with theoretical loadings of 30 wt% Mo and a ratio of M:Mo=1:2 (M=Ni or Co) were prepared by two-step impregnation method with a Mo-first impregnation sequence and the carburization procedures were similar to those for the Mo_2C/CNTs mentioned above.

Table S1 The detailed information regarding the carbon nanotubes provided by the company.

Index	Value
Purity (wt%)	>98
Inner diameter (nm)	5-15
Outer diameter (nm)	>50
Length (μm)	<10
Specific surface area (m^2 g^{-1})	>60
Tap density (g cm^{-3})	0.18
True density (g cm^{-3})	~2.1
The content of metal impurity: Fe, Ni, Co, Zn, Mg, Cu, Al, Ca, Cr, Mo, Mn, Na (ppm)	≤200, ≤1000, ≤100, ≤100, <500, <100, <100, <1000, <50, <50, <50, <500

1.2 Catalyst characterization

X-ray diffraction (XRD) was conducted using an X-ray diffractometer (X'Pert Pro MPD) equipped with a Cu Kα source. X-ray photoelectron spectroscopy (XPS) was carried out using a Kratos Axis ultra (DLD) equipped with Al Kα X-ray source. The binding energies (±0.2 eV) were referenced to the C 1s peak at 284.8 eV due to adventitious carbon. 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). Raman spectroscopy was performed using a Horrba/Jobin-Yvon LABRAM-HR spectrometer with the 632.8 nm line of a helium-neon laser as excitation source. Carbon dioxide temperature-programmed oxidation (CO_2-TPO) and methane temperature-programmed surface reaction (CH_4-TPSR) studies were performed using a flow of $5\%CO_2(2\%CH_4)/Ar$ (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 Catalyst performance tests

Catalytic activities of carbides 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 (H_2) at 850 ^oC (650 ^oC) for 30 min. Then CH_4 and CO_2 mixture with a mole ratio of 1:1 was allowed to pass through the catalyst (60-80 mesh) at a flow rate of 30 ml min^{-1} (WHSV=18000 cm^3 g^{-1} h^{-1}). The products were analyzed by on-line gas chromatography (GC). The conversions of CH_4 and CO_2, selectivity of H_2 and carbon balance 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); carbon balance (%)=(moles of CO_2 in products + moles of CH_4 in products + moles of CO produced)/(moles of CO_2 introduced+ moles of CH_4 introduced).

2. Results

Table S2 Textural properties of Mo_2C/CNTs samples obtained in this study.

Sample	S_{BET} (m^2 g^{-1})	D_P (nm)	V_P (cm^3 g^{-1})
Mo_2C-in-CNTs	75.2	52.26	0.98
Mo_2C-out-CNTs	66.0	53.57	0.81

S_{BET}=BET surface area; D_P=Average pore diameter; V_P=Total pore volume.

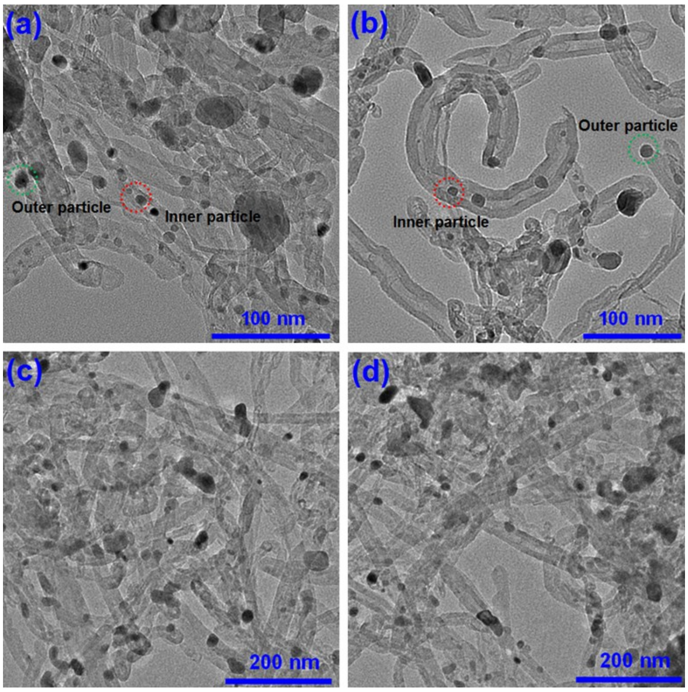

Fig. S1 TEM images of Mo_2C-in-CNTs (a-b) and Mo_2C-out-CNTs (c-d).

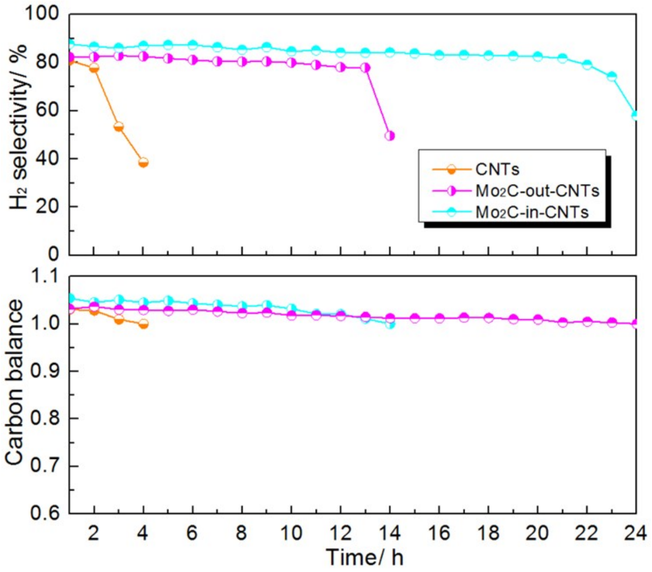

Fig. S2 Lifetime study of Mo_2C-out-CNTs and Mo_2C-in-CNTs catalysts in DRM (T=850 ^{o}C, P=1 atm, CH_4/CO_2=1, WHSV=18000 cm^3 g^{-1} h^{-1}).

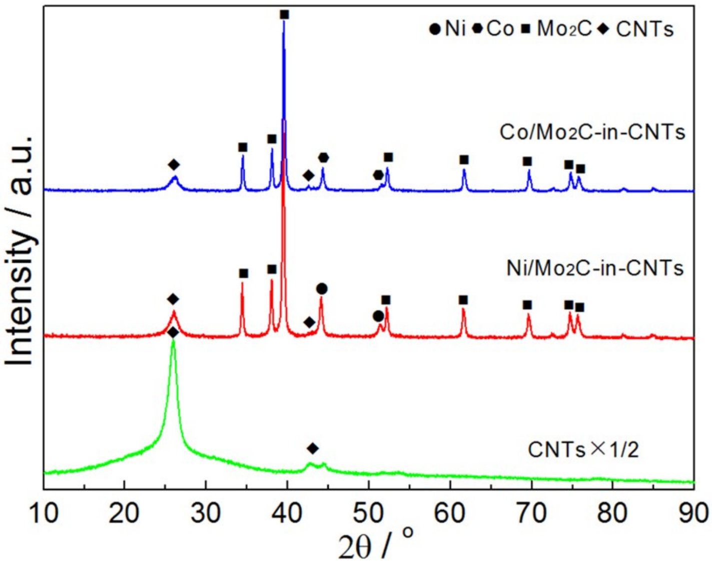

Fig. S3 XRD patterns of Ni/Mo_2C-in-CNTs and Co/Mo_2C-in-CNTs samples as well as CNTs support for comparison.

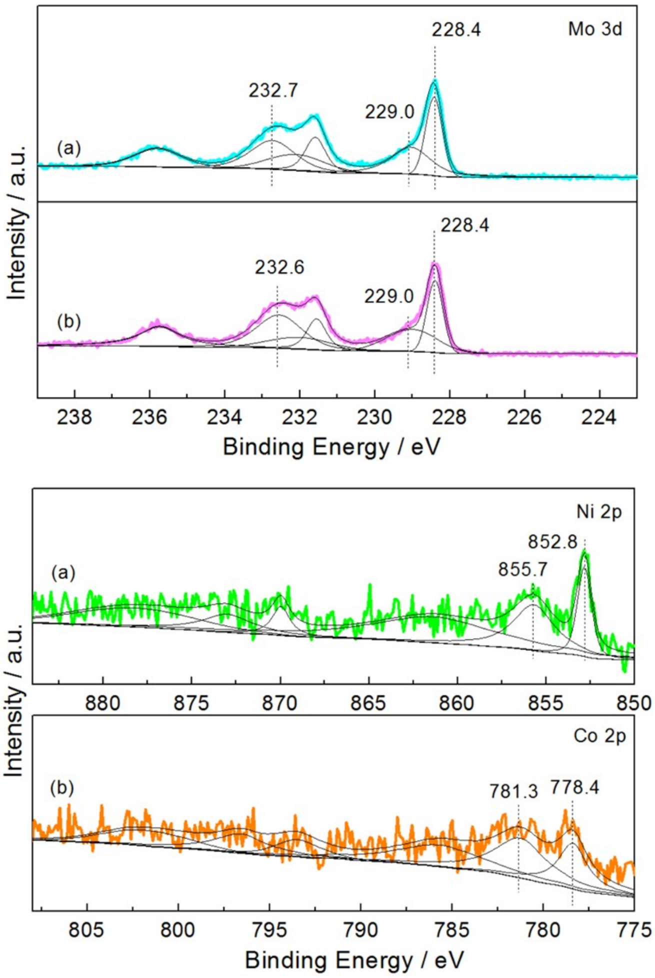

Fig. S4 XPS spectra of Mo 3d, Ni 2p and Co 2p (a) Ni/Mo_2C-in-CNTs; (b) Co/Mo_2C-in-CNTs.

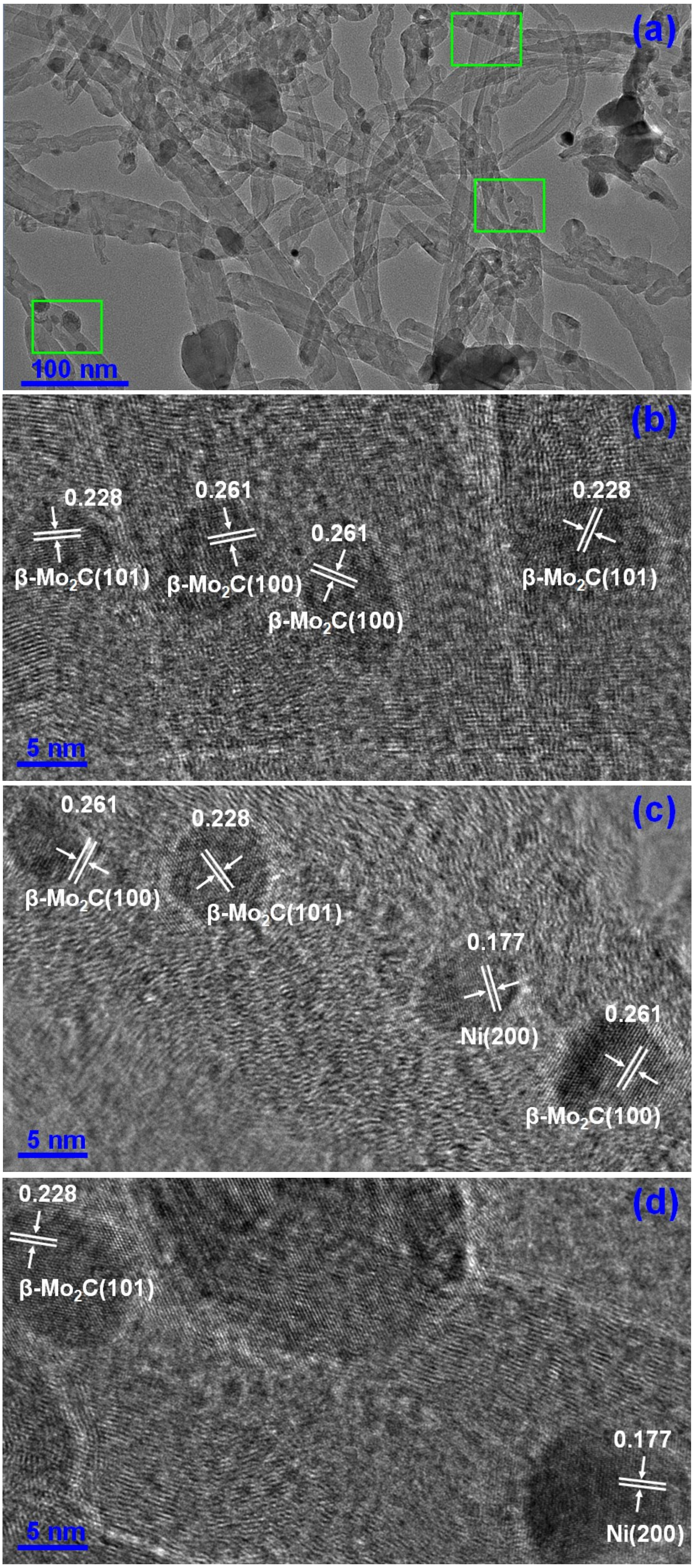

Fig. S5 TEM image of Ni/Mo$_2$C-in-CNTs (a) and corresponding HRTEM images (b-d).

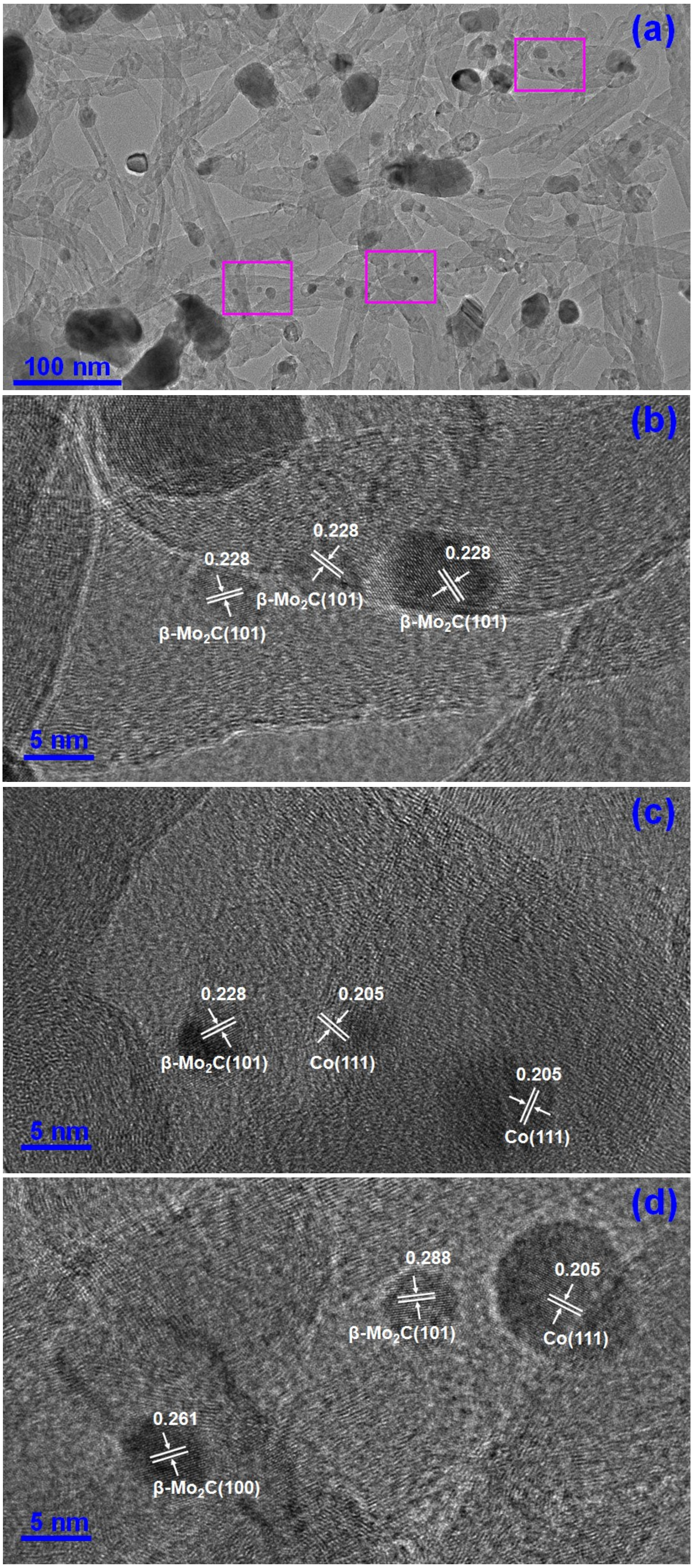

Fig. S6 TEM image of Co/Mo_2C/CNTs (a) and corresponding HRTEM images (b-d).

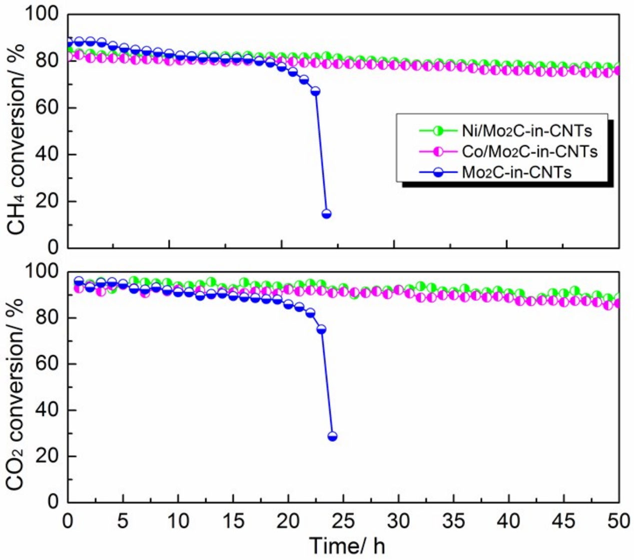

Fig. S7 Lifetime of Ni(Co)/Mo_2C-in-CNTs in DRM as well as that of Mo_2C-in-CNTs for comparison (T=850 °C, P=1 atm, CH_4/CO_2=1, WHSV=18000 $cm^3\ g^{-1}\ h^{-1}$).