Supplementary Information

First comparison of catalytic CO_2 reduction to CO over molybdenum carbide, nitride and phosphide catalysts

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1. Experimental Section

1.1 Sample preparation

The carbon nanotubes (CNTs) used were multi-walled carbon nanotubes, purchased from Chengdu Organic Chemicals Co. Ltd. And more information regarding the CNTs was listed in Table S1. Firstly, the oxide precursors for molybdenum carbide, nitride and phosphide catalysts were prepared by impregnating CNTs with an aqueous solution of $(NH_4)_6Mo_7O_{24}·4H_2O)$ and $(NH_4)_2HPO_4$ (only for phosphide) with a 60 wt% Mo loading and a 1:1 Mo:P molar ratio, followed by sonicating for about 30 min, and then dried in air at 80 °C for 4 h. Secondly, these precursors were heated from room temperature (RT) to

700 $^{\circ}$C at a rate of 10 $^{\circ}$C min^{-1} under H$_2$ or NH$_3$ (150 ml min^{-1}) and maintained at this temperature for 2 h, followed by cooling to RT, and then passivated in a 1%O$_2$/Ar flow for 2 h. The resulting samples were denoted as carbonized Mo/CNTs, nitrided Mo/CNTs and phosphorized Mo/CNTs, respectively.

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,	≤200, ≤1000, ≤100, ≤100, <500,
Co, Zn, Mg, Cu, Al, Ca, Cr, Mo, Mn,	<100, <100, <1000, <50, <50, <50,
Na (ppm)	<500

1.2 Sample characterization

X-ray diffraction (XRD) was carried out from 10 to 90 $^{\circ}$ with a step-size of 0.2 $^{\circ}$ and a counting time of 2 s 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. Samples were introduced directly, by a fast entry lock system, into the XPS analytical chamber. The binding energies (±0.2 eV) were referenced to the C 1s

peak at 284.8 eV due to adventitious carbon. The assignments of the peaks were carried out by using the values in the references reported in the text. The N_2 adsorption-desorption isotherms were measured on a Nova 4200e instrument at -196 °C. Before the measurement, the sample was degassed at 300 °C for 6 h under vacuum. The specific surface area was calculated by a multipoint Braunauer-Emmett-Teller method. The morphologies of the samples were characterized by transmission electron microscopy (TEM, Philips Tecnal 10). The samples for TEM observations were prepared by dispersing a dry powder on a lacey-carbon coated 200 mesh Cu TEM grids. CO-temperature programmed desorption (CO-TPD) experiments were carried out in a quartz tube micro-reactor. Prior to the CO-TPD process, 0.1 g of catalyst was heated from RT to 700 °C in H_2 or NH_3 and maintained at this temperature for 30 min. After being cooled to RT in He flow, a stream of 10%CO/He was introduced into the system for 20 min. After CO adsorption, the gas flow was switched to He (30 ml min^{-1}) to remove physically adsorbed CO on catalyst surface 30 min. Finally, the sample was heated from RT to 900 °C at a rate of 10 °C min^{-1} in He (30 ml min^{-1}), and then was held at 900 °C for 30 min. The effluent gases were monitored by means of a GC thermal conductivity detector.

1.3 Catalytic performance tests

Catalytic activities of catalyst for RWGS were evaluated in a micro-reactor with an inner diameter of 8 mm at atmospheric pressure. Prior to the reaction, the sample was preheated in H_2 or NH_3 at 700 °C for 30 min. Following the

pretreatment, a gas mixture (H_2:CO_2=2:1) was allowed to pass through the catalyst. The gas-phase products were analyzed by on-line GC. The conversion of CO_2 and the selectivities of CO and CH_4 were defined as follows:

CO_2 conversion (%)=([CO_2]$_{in}$ - [CO_2]$_{out}$)/([CO_2]$_{in}$) ×100

CO selectivity (%)=([CO]$_{out}$)/([CO]$_{out}$ + [CH_4]$_{out}$) ×100

CH_4 selectivity (%)=([CH_4]$_{out}$)/([CO]$_{out}$ + [CH_4]$_{out}$) ×100

2. Results

Fig. S1 The catalytic stability of carbonized, nitrided and phosphorized Mo/CNTs in the RWGS reaction (CO_2/H_2=1/2, WHSV=36000 cm^3 g^{-1} h^{-1}, P=1 atm, T=350 °C).
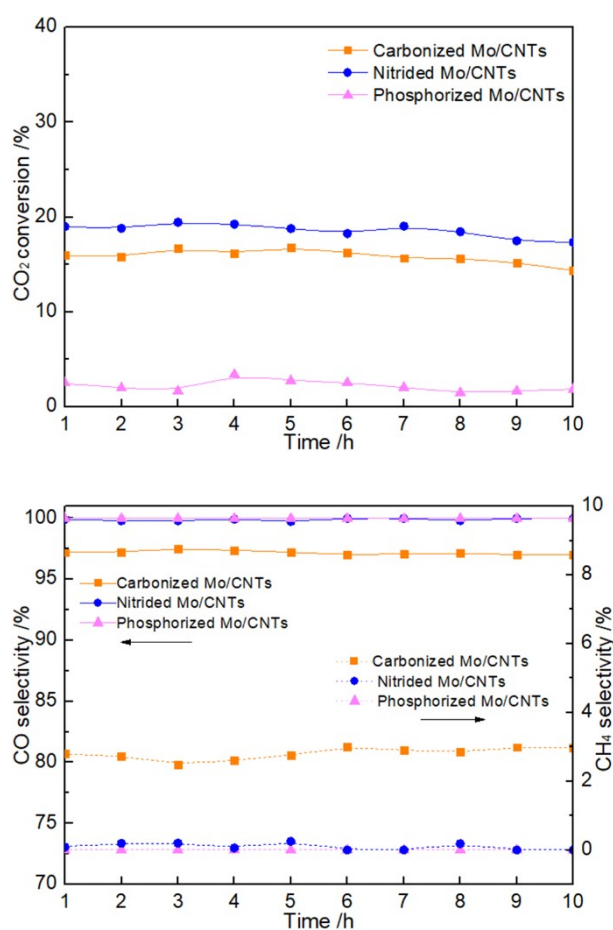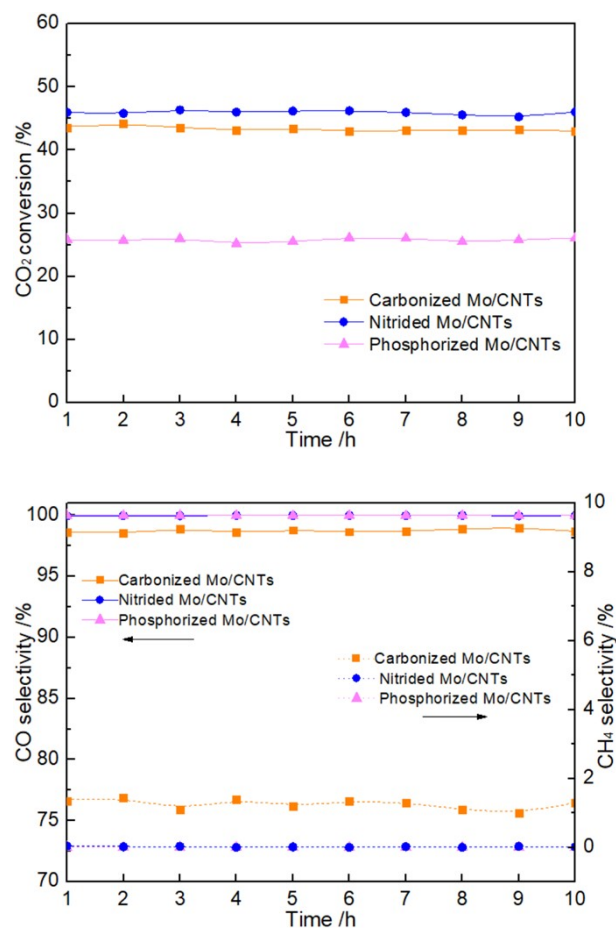
Fig. S2 The catalytic stability of carbonized, nitrided and phosphorized Mo/CNTs in the RWGS reaction ($CO_2/H_2=1/2$, WHSV=36000 cm^3 g^{-1} h^{-1}, P=1 atm, T=550 ^oC).
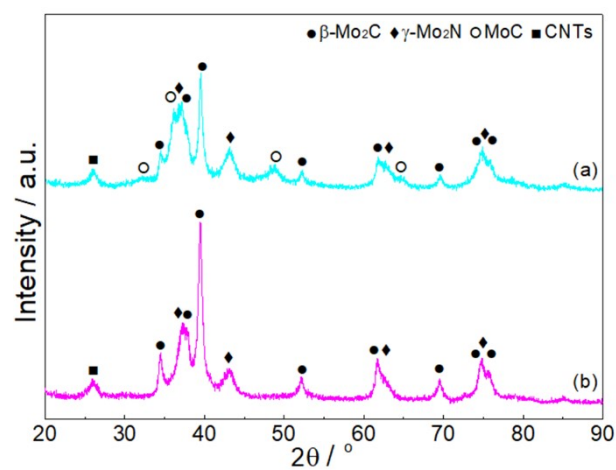
Fig. S3 XRD patterns of (a) used nitrided Mo/CNTs in the RWGS reaction ($CO_2/H_2=1/2$, WHSV=300000 cm^3 g^{-1} h^{-1}, P=1 atm, T=600 ^oC, t=1 h) as well as (b) fresh sample for comparison.

Table S2 Comparison of CO_2 conversion rate and CO selectivity for the nitrided Mo/CNTs and literature reported catalysts.

Catalyst	H_2:CO ratio	Temperature (^{o}C)	WHSV (cm^3 g^{-1} h^{-1})	Rate ($\times$ 10^{-5} mol$_{CO2}$ g$_{cat}^{-1}$ s^{-1})	CO selectivity (%)	Reference
Nitrided Mo/CNTs	2:1	300	300000	4.1	100	this work
	2:1	400	300000	14	100	this work
	2:1	500	300000	34.4	100	this work
	2:1	600	300000	51.5	100	this work
Cu/β-Mo$_2$C	2:1	300	300000	7.3	96.5	23
	2:1	600	300000	47.7	99.2	23
Co/β-Mo$_2$C	2:1	300	36000	1.41	98.1	30
Cu-Zn-Al	2:1	500	300000	26.1	100	23
Pt-Al$_2$O$_3$	1.4:1	400	12000	0.16	N/A	46
Pt-TiO$_2$	1.4:1	400	12000	0.47	N/A	46
Cu-Al$_2$O$_3$	1:9	500	12000	0.9	100	47
Ni-CeO$_2$	1:1	400	120000	6.69	77	48