Supplementary Information

1. Experimental Section

1.1 Catalyst preparation and evaluation

We synthesized the $Ni_xMo_yP_1$ oxidic precursors by stirring an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and $(NH_4)_2HPO_4$ with a given molar ratio of Ni:Mo:P=x:y:1 (x,y=0, 0.3, 0.6 and 1) at room temperature (RT) for 1 h. In order to dissolve the precipitate, a few drops of nitric acid were added in the solutions. The solutions were dried in air at 110 °C for overnight to form $Ni_xMo_yP_1$ oxidic precursors. The synthesis of phosphides in CH_4-CO_2 and the reforming reaction were carried out in a fixed-bed micro-reactor with an inner diameter of 10 mm at atmospheric pressure. The $Ni_xMo_yP_1$ oxidic precursors (0.2 g) were heated under a flow of CH_4 and CO_2 (CH_4/CO_2 =1, 30 ml min^{-1}) from RT to 900 °C at a rate of 10 °C min^{-1} and then the temperature was kepted at 900 °C for 0-30 h. In addition, the $Ni_1Mo_1P_1$ oxidic precursors (0.2 g) were also heated under a flow of H_2 (30 ml min^{-1}) from RT to 650 °C at a rate of 10 °C min^{-1} and then the temperature was kepted at 650 °C for 2 h. Finally, the resulting sample was suffered from passivation process in a flow of 1%O_2/Ar for 12 h. Prior to the reaction, the catalyst prepared in H_2 was preheated to 900 °C under an H_2 flow and then a flow of CH_4 and CO_2 (CH_4/CO_2 =1, 30 ml min^{-1}) was allowed to pass through the catalyst. The conversions of CH_4 and CO_2, and selectivity of H_2 were defined as follows ($n_{i,in}$ = the initial molar fraction of component i in the feed, $n_{i,out}$

= the final molar fraction of component i in the gaseous effluent):

$$X_{CH4}(\%) = \frac{n_{CH_4,in} - n_{CH_4,out}}{n_{CH_4,in}} \times 100$$

$$X_{CO2}(\%) = \frac{n_{CO_2,in} - n_{CO_2,out}}{n_{CO_2,in}} \times 100$$

$$S_{H2} = \frac{n_{H_2,out}}{2(n_{CH_4,in} - n_{CH_4,out})} \times 100$$

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. SEM and TEM images were acquired using a scanning electron microscopy (SEM, Hitachi S-4800) and transmission electron microscope (Philips Tecnal 10). BET surface area of the samples was measured by a Nova 4200e (Quantachrome) instrument. CHN analysis was peformed using a Heraeus CHN-O-Rapid analyzer. H_2-TPR experiments were carried out in a quartz tube micro-reactor. The effluent gases were monitored by means of a GC thermal conductivity detector. Before each H_2-TPR run, the oxidic precursors (10 mg) was heated from RT to 120 °C in He and maintained at this temperature for 30 min. After being cooled to RT, the sample was heated from 30 °C to 1000 °C at a rate of 4 °C/min in a gas mixture of 10%H_2/Ar (80 ml min^{-1}). CO_2 and CH_4 dissociation studies were performed using a

flow of $2\%CO_2(2\%CH_4)/Ar$ (50 ml min^{-1}). Prior to the dissociation reaction, the sample was preheated to 900 °C under an H_2 flow and then the gas mixtures were allowed to pass through the sample. The change of CH_4 and CO_2 during reaction was monitored using gas chromatography (GC).
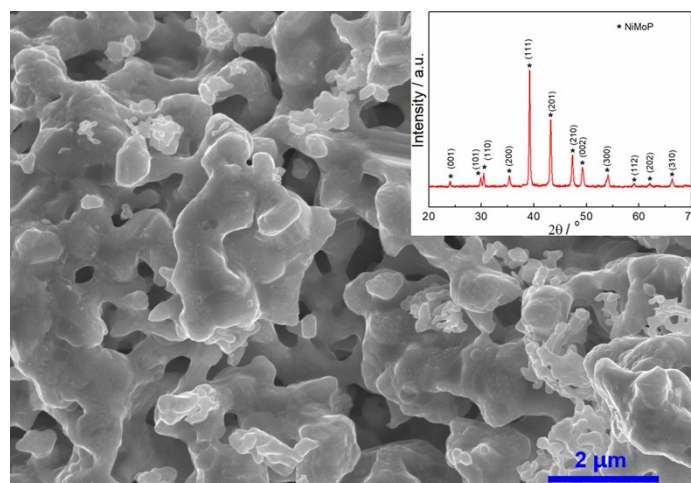
2. Results

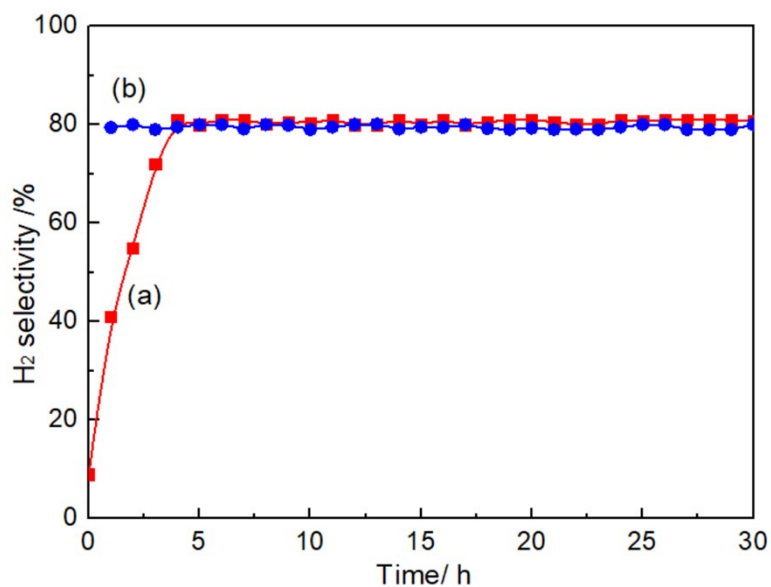Fig. S1 SEM image of H_2-NiMoP sample. The inset shows the XRD pattern of the sample.

Fig. S2 H_2 selectivity over the (a) $Ni_1Mo_1P_1$ precursors and (b) H_2-NiMoP in DRM. Reaction conditions: $CH_4:CO_2$=1:1, WHSV=9000 cm^3 g^{-1} h^{-1}, reaction pressure= 1 atm, reaction temperature=900 °C.
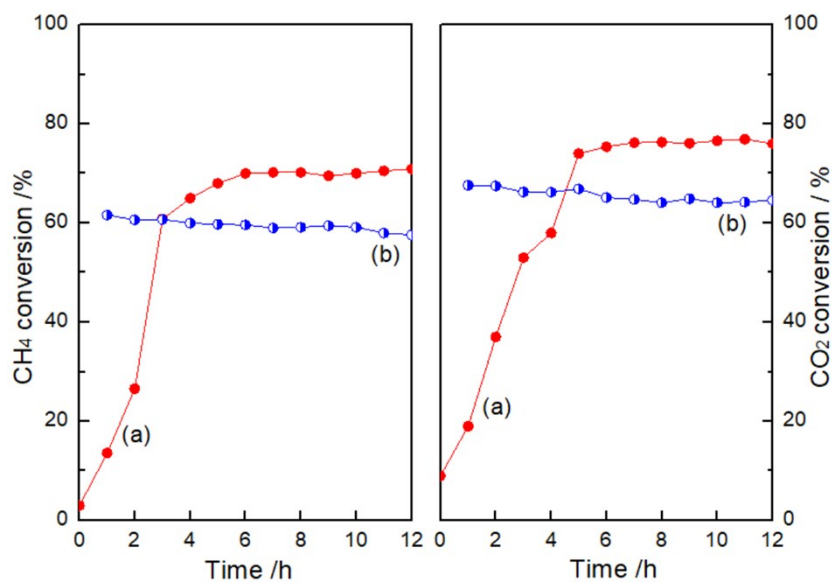
Fig. S3 CH_4 and CO_2 conversions over the (a) $Ni_1Mo_1P_1$ precursor and (b) H_2-NiMoP in DRM. Reaction conditions: CH_4:CO_2=1:1, WHSV=24000 cm^3 g^{-1} h^{-1}, reaction pressure= 1 atm, reaction temperature=900 °C.
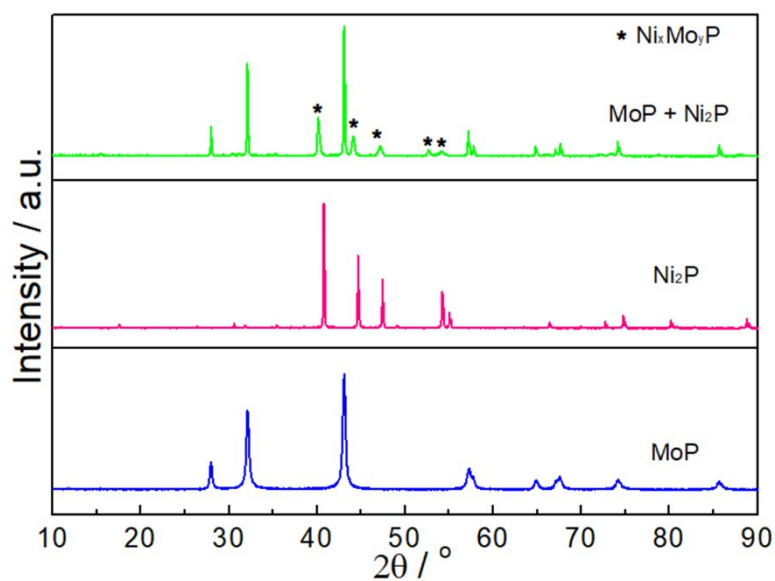

Fig. S4 XRD pattern of mechanical mixture of Ni_2P and MoP (Ni:Mo=1:1) treated in H_2 at 800 °C for 1 h. The patterns of Ni_2P and MoP are also shown for comparison.