Supplementary Information

1. Experimental Section

1.1 Catalyst preparation and evaluation

We synthesized the Ni$_x$Mo$_y$P$_1$ oxidic precursors by stirring an aqueous solution of Ni(NO$_3$)$_2$·6H$_2$O, (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O and (NH$_4$)$_2$HPO$_4$ 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$_x$Mo$_y$P$_1$ 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$_x$Mo$_y$P$_1$ 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 kept at 900 °C for 0-30 h. In addition, the Ni$_1$Mo$_1$P$_1$ 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 kept 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):

$$X_{\text{CH}_4}(\%) = \frac{n_{\text{CH}_4,\text{in}} - n_{\text{CH}_4,\text{out}}}{n_{\text{CH}_4,\text{in}}} \times 100$$

$$X_{\text{CO}_2}(\%) = \frac{n_{\text{CO}_2,\text{in}} - n_{\text{CO}_2,\text{out}}}{n_{\text{CO}_2,\text{in}}} \times 100$$

$$S_{\text{H}_2} = \frac{n_{\text{H}_2,\text{out}}}{2(n_{\text{CH}_4,\text{in}} - n_{\text{CH}_4,\text{out}})} \times 100$$

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 performed 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%CO₂(2%CH₄)/Ar (50 ml min⁻¹). Prior to the dissociation reaction, the sample was preheated to 900 °C under an H₂ flow and then the gas mixtures were allowed to pass through the sample. The change of CH₄ and CO₂ during reaction was monitored using gas chromatography (GC).

2. Results

Fig. S1 SEM image of H₂-NiMoP sample. The inset shows the XRD pattern of the sample.

Fig. S2 H₂ selectivity over the (a) Ni₁Mo₁P₁ precursors and (b) H₂-NiMoP in DRM. Reaction conditions: CH₄:CO₂=1:1, WHSV=9000 cm³ g⁻¹ h⁻¹, reaction pressure= 1 atm, reaction temperature=900 °C.
Fig. S3 CH₄ and CO₂ conversions over the (a) Ni₁Mo₁P₁ precursor and (b) H₂-NiMoP in DRM. Reaction conditions: CH₄:CO₂=1:1, WHSV=24000 cm³ g⁻¹ h⁻¹, reaction pressure= 1 atm, reaction temperature=900 °C.

Fig. S4 XRD pattern of mechanical mixture of Ni₂P and MoP (Ni:Mo=1:1) treated in H₂ at 800 °C for 1 h. The patterns of Ni₂P and MoP are also shown for comparison.