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

Supplementary Information

1. Experimental Section

1.1 Sample preparation

We synthesized the Ni,Mo-containing phosphate by stirring an aqueous solution of $Ni(NO_3)_2·6H_2O$, $(NH_4)_6Mo_7O_{24}·4H_2O$ and $(NH_4)_2HPO_4$ with a molar ratio of Ni:Mo:P=1:1:1 at room temperature (RT) for 1 h. In order to dissolve the precipitate, a few drops of nitric acid were added in the solution. The solution was dried in air at 110 ^{o}C for overnight and then calcined in air at 500 ^{o}C for 3 h to form Ni,Mo-containing phosphate. The precursor for phosphide was prepared by mixing the Ni,Mo-containing phosphate with glucose solution and drying the resulting slurry at 110 ^{o}C for 12 h. The carbonization of precursor was carried out in a quartz reactor under a flow of Ar (50 ml min^{-1}). The temperature was raised linearly at a rate of 10 ^{o}C min^{-1} and kept at a given value (600-900 ^{o}C) for 1 h, followed by cooling to RT under Ar flow, and then passivated at RT in a flow of 1%O_2/Ar for 2 h.

In addition, the MoP sample was also prepared by traditional H_2-TPR method.[17] the Ni,Mo-containing phosphate was placed in a micro-reactor with an inner diameter of 10 mm. Then, a flow of pure H_2 (100 ml min^{-1}) was introduced into the system. The linear temperature program was as follows: the sample was fast heated from RT to 300 °C at a rate of 10 ^{o}C min^{-1} and then slowly heated from 300 to 850 °C at a rate of 1 ^{o}C min^{-1} before cooling to RT in a H_2 flow. Finally, the resulting sample was suffered from passivation process in a flow of 1%O_2/Ar for 12 h.

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. X-ray photoelectron spectroscopy (XPS) was carried out using a Kratos Axis ultra (DLD) equipped with Al Kα X-ray source. Surface atomic composition was estimated by calculating the integral of each peak using the sensitivity factor provided by the instrumental software. The spectra were analyzed by fitting the experimental curve to mixed Gaussiane Lorentzian peaks. The relative intensities of spin-orbit doublet peaks are given by the ratio of their respective degeneracy. The intensity ratios for the Ni $2p_{3/2}$-Ni $2p_{1/2}$, Mo $3d_{5/2}$-Mo $3d_{3/2}$ and P $2p_{3/2}$-P $2p_{1/2}$ doublets are 2/1, 3/2 and 2/1, respectively. Splittings of ~17.3, 3.1 and 1.0 eV are expected for the corresponding doublets. 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). Carbon content was determined by a Heraeus CHN-O-Rapid analyzer. Raman spectroscopy was carried out using a Horrba/Jobin-Yvon LABRAM-HR spectrometer with the 632.8 nm line of a helium-neon laser as excitation source. The thermogravimetric (TG) analysis was performed on a thermal analyzer (STA409C) under air atmosphere with a ramping rate of 10 ^{o}C min^{-1} from RT to 1000 ^{o}C. H_2-temperature-programmed reduction (H_2-TPR) experiments were carried out in a quartz tube micro-reactor. Before the H_2-TPR run, the sample (0.1 g) was heated from RT to 300 ^{o}C in Ar and maintained at this temperature for 30 min. After being cooled to RT, the sample was heated from 30 to 800 ^{o}C at a rate of 10 ^{o}C min^{-1} in a mixture of 10%H_2/90%Ar. The consumption of H_2 was monitored by a thermal conductivity detector.

1.3 Catalytic performance tests

Catalytic activities of phosphides for DRM were evaluated in a micro-reactor with an inner diameter of 10 mm at atmospheric pressure. Prior to the reaction, the NiMoP-Glu (prepared by glucose route) and NiMoP-H_2 (prepared by traditional H_2-TPR route) were preheated for 30 min in Ar at 900 ^{o}C and in H_2 at 850 ^{o}C, respectively, and then further cooled or heated to a given reaction temperature (800-900 ^{o}C) under an Ar flow. 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 20 ml min^{-1} (WHSV=12000 or 24000 cm^3 g^{-1} h^{-1}). The gas-phase products were analyzed by on-line gas chromatography (GC). The conversions of CH_4 and CO_2, and H_2/CO were defined respectively as follows: X_{CH4}(%)=(moles of CH_4 converted)/(moles of CH_4 introduced); X_{CO2}(%)=(moles of CO_2 converted)/(moles of CO_2 introduced); H_2/CO=(moles of H_2 produced)/(moles of CO produced). 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

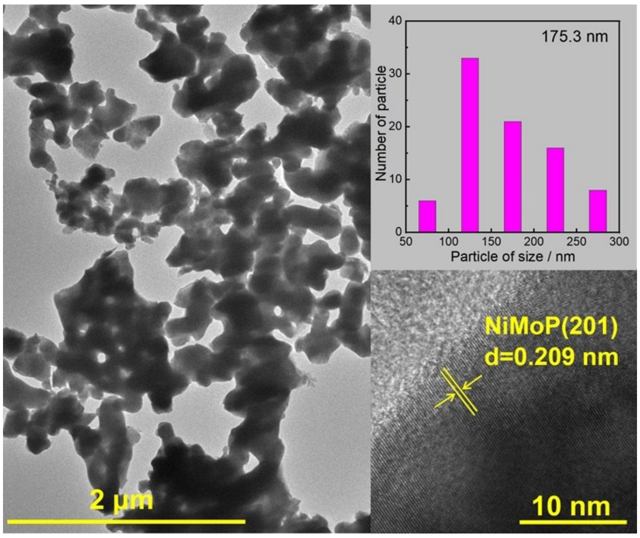

Fig. S1 TEM image of the NiMoP prepared by traditional H_2-TPR route. The insets show the particle size distribution and crystal lattice of NiMoP.

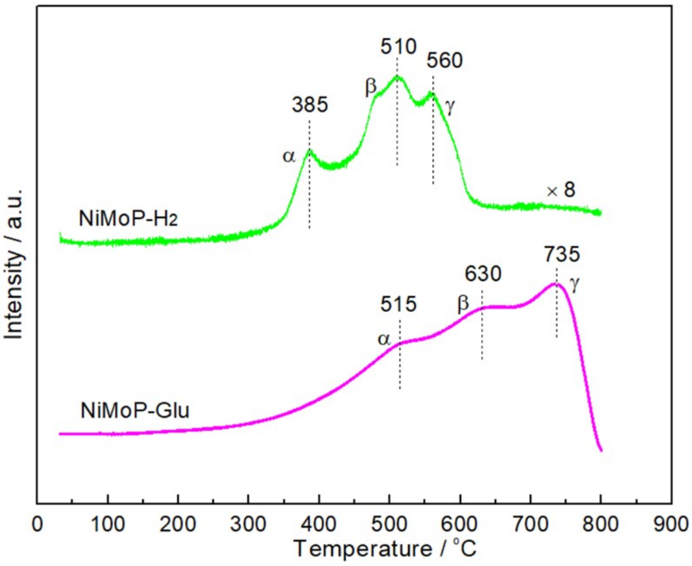

Fig. S2 H_2-TPR profiles of NiMoP catalysts

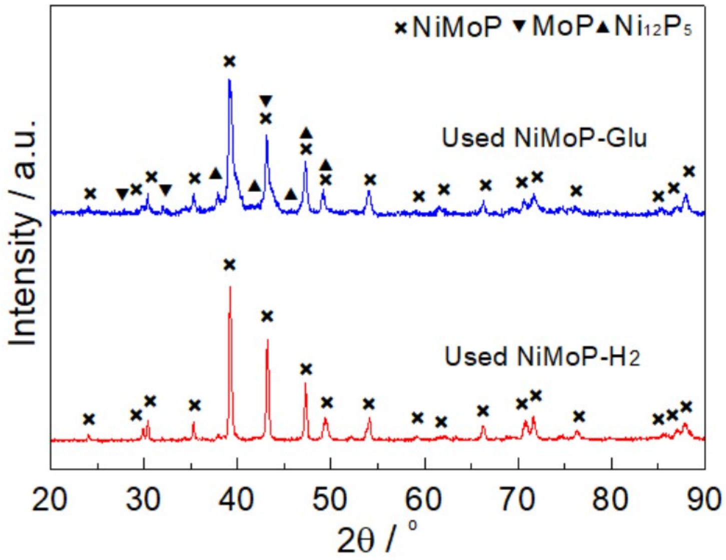

Fig. S3 XRD patterns of the used NiMoP catalysts in DRM. Reaction conditions: CH_4:CO_2=1:1, WHSV=12000 cm^3 g^{-1} h^{-1}, reaction pressure= 1 atm, reaction temperature= 850 °C; reaction time=30 h.