

Supplementary Information

Interesting influence of Al₂O₃ on the catalytic stability of Co₂P, MoP and CoMoP catalysts for dry reforming of methane

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1. Experimental Section

1.1 Sample preparation

The unsupported oxide precursors were prepared by stirring an aqueous solution of Co(CH₃COO)₂·4H₂O, (NH₄)₆Mo₇O₂₄·4H₂O and (NH₄)₂HPO₄ with a given molar ratio of Co:Mo:P=x:y:1 (x=2, y=0; x=0, y=1; x=1, y=1) at room temperature (RT) for 0.5 h. The alumina-supported oxide precursors were prepared by the incipient wetness method using the solutions mentioned above and commercial Al₂O₃ (γ-Al₂O₃, 99.99%, purchased from Shanghai Macklin Biochemical Technology Co. Ltd.) with theoretical loading of 30 wt.% M (M=Co for Co₂P and M=Mo for MoP and CoMoP). All the oxide precursors followed by a long time drying at 110 °C and 3 h-calcination at 500 °C. The metal phosphides were prepared from unsupported and alumina-supported oxide precursors via H₂-reduction method described in our previous study.²⁴ The final

reduction temperatures were 850 °C for Co₂P and CoMoP phosphides, and 950 °C for MoP phosphides.

1.2 Sample characterization

X-ray diffraction (XRD) examinations were conducted using an X-ray diffractometer (X'Pert Pro MPD) with a Cu K α radiation. The BET surface areas were measured on a NOVA4200 instrument. Carbon content was determined using an elemental analyzer (Euro EA3000). The scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) element mapping images were obtained on Hitachi S-4800. The H₂-TPR analysis was performed in a quartz tube micro-reactor and the effluent gases were monitored using a thermal conductivity detector. Prior to the H₂-TPR run, the unsupported (0.05 g) and supported (0.1 g) oxide precursors were initially pretreated in Ar flow at 300 °C for 0.5 h. After being cooled to RT, the samples were heated from RT to 900 °C using 10%H₂/Ar (30 ml min⁻¹) at a rate of 4 °C min⁻¹. CO₂ (CH₄) dissociation study was performed with 6%CO₂(6%CH₄)/Ar mixture flowing at a rate of 50 ml min⁻¹. Before the dissociation reaction, the sample (0.1 g) was preheated at 850 or 900 °C under an H₂ flow for 0.5 h and then cooled to 800 °C in Ar. Then the gas mixture was allowed to pass through the sample. The change of CH₄ and CO₂ during reaction was monitored using gas chromatography (GC).

1.3 Catalytic performance tests

The DRM reaction was carried out in a fixed-bed flow system and the catalytic activity of catalyst was tested in a micro-reactor (id: 8 mm) at atmospheric pressure.

The feed gas consisted of 10 ml min⁻¹ of 50%CH₄ and 50%CO₂. The pretreatment process and gas detection device were similar to those in CO₂ (CH₄) dissociation study. The CH₄ conversion, CO₂ conversion and carbon balance 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):

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

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

$$B_C = \frac{(n_{\text{CO}_2,\text{out}} + n_{\text{CH}_4,\text{out}} + n_{\text{CO}_2,\text{out}})}{(n_{\text{CH}_4,\text{in}} + n_{\text{CO}_2,\text{in}})}$$

2. Results

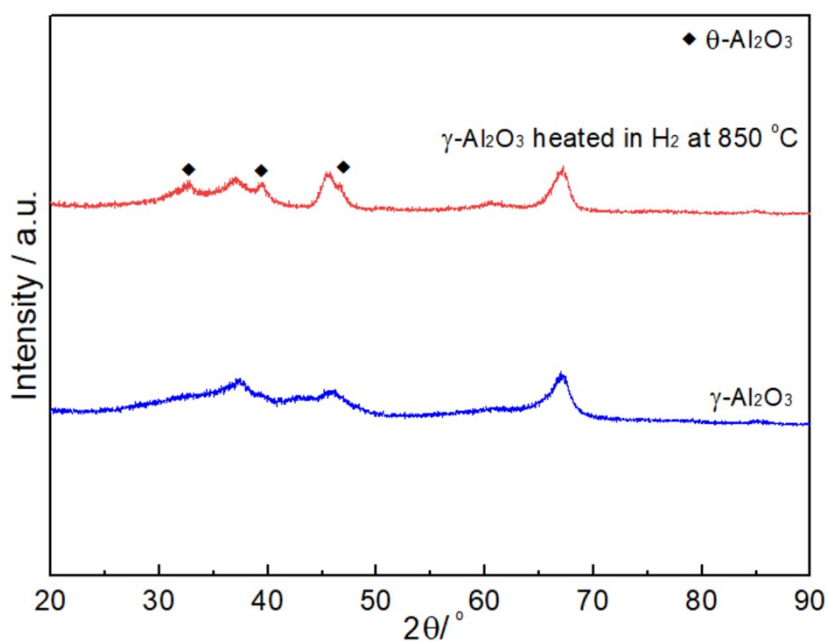


Fig. S1 XRD patterns of fresh γ -Al₂O₃ and the γ -Al₂O₃ heated in H₂ at 850 °C.

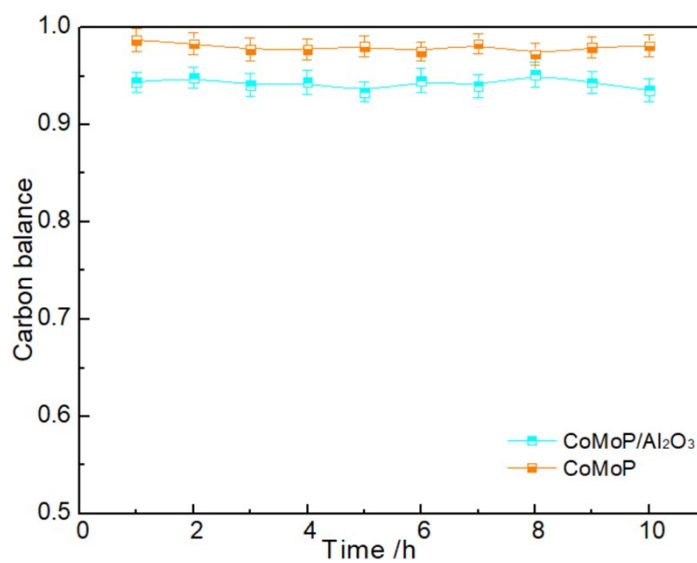
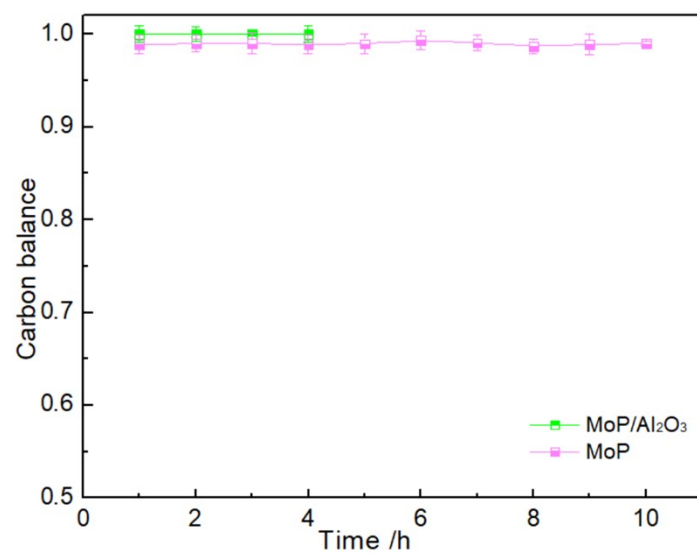
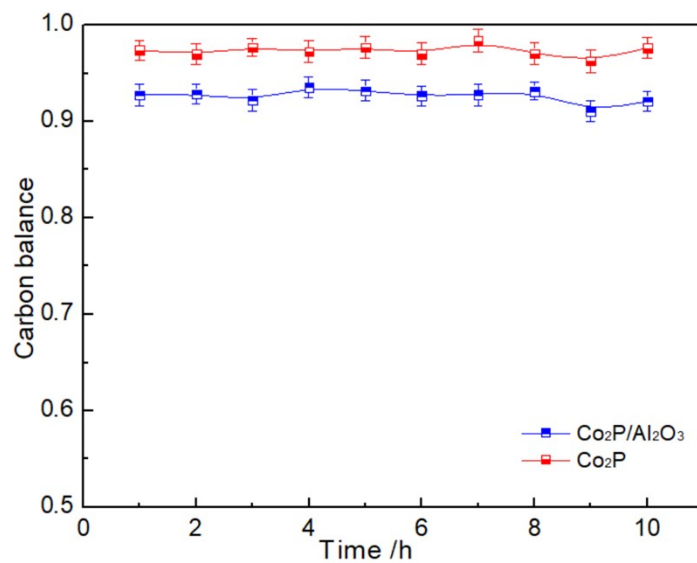


Fig. S2 Carbon balance value versus reaction time.

Table S1 CH₄ conversion rate and specific activity of phosphide catalysts for DRM.

Catalyst	CO chemisorption ($\mu\text{mol g}^{-1}$)	CH ₄ conversion rate		Specific activity	
		($\mu\text{mol g}_{\text{cat}}^{-1} \text{s}^{-1}$)		(s^{-1}) ^a	
		1 h	10 h	1 h	10 h
Co ₂ P	2.2	21.42	21.06	9.74	9.57
MoP	2.8	33.17	33.05	11.85	11.8
CoMoP	3.4	29.36	26.60	8.64	7.82
Co ₂ P/Al ₂ O ₃	31.3	33.40	33.54	1.07	1.07
MoP/Al ₂ O ₃	35.4	13.24	2.53 ^b	0.37	0.07
CoMoP/Al ₂ O ₃	36.8	31.00	29.77	0.84	0.81

^a(CH₄ conversion rate)/(chemisorbed CO)

^bCH₄ conversion rate at 4 h