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# Effect of additives on the properties of nickel molybdenum carbides for the tri-reforming of methane

Hanbo Zou<sup>\*</sup>, Shengzhou Chen, Jiangnan Huang, Zhaohui Zhao

Department of Chemistry and Chemical Engineering, Guangzhou University, Guangzhou 510006, China

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## ABSTRACT

A series of NiMo carbides modified with different additives were prepared with the temperature programmed reduction method. Characterization and catalytic properties for the tri-reforming of methane were performed. It was found that the presence of nickel species in NiMo series carbides stimulated the dissociation of methane and supplied the active carbon for the carburization process. La-promoted NiMo carbide could prevent the aggregation of small particles, facilitate the topotactic transformation of Mo<sub>2</sub>C species and inhibit the carbon deposition, which were benefit for the excellent catalytic performance. Ce and Co additives deteriorated the activities of NiMo carbides to some extent due to the larger particle size. Mg favored the coke generation and decreased the surface area and pore volume of NiMoC–Mg carbide. The addition of K suppressed the carburization process of molybdenum oxide species and caused the phase transformation of active  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to less active  $\theta$ -Al<sub>2</sub>O<sub>3</sub>. Mg and K modified NiMo carbides, especially the latter, showed a dramatic decrease in the redox ability for the tri-reforming of methane. The oxidation of carbidic species, the agglomeration of small particles and the carbon deposition decreased the catalytic activities of NiMo series carbides for the tri-reforming of methane.

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## Introduction

Syngas, a mixture of CO and H<sub>2</sub>, plays a significant role in the chemical industry as an important feedstock for many desirable chemical processes, such as Fischer–Tropsch reaction, hydroformylation, ammonia synthesis. Syngas is typically produced by the gasification or pyrolysis of carbonaceous materials. In recent decades, three well-known methane processes, namely partial oxidation of methane (POM), dry reforming of methane (DRM) and steam reforming of methane (SRM), have been widely used for the syngas generation. Tri-reforming of methane (TRM), namely a combination of the above-mentioned three reactions in a reactor, has attracted

considerable attentions due to the high efficiency, low carbon deposition, desired H<sub>2</sub>/CO ratio and good utilization of CO<sub>2</sub> [1]. Nickel catalysts, such as Ni/La–Ce–O [2], Ni–Mg/ $\beta$ -SiC [3], Ni/SiO<sub>2</sub> [4], Ni–CeO<sub>2</sub> [5] have been regarded as the promising catalyst for TRM. However the stability of nickel catalysts at high temperatures and the coke generation are the main obstacles for their widespread applications. In order to improve the performance of nickel catalysts, some precious metal promoted nickel catalysts were investigated for TRM. Rh–Ni bimetallic catalysts supported on zeolites exhibited the methane conversion of 97.04% and 96.42% for the tri-reforming of model biogas, respectively [6]. Jiang et al. examined the thermal distribution in the catalyst bed for TRM over

<sup>\*</sup> Corresponding author. Fax: +86 20 39339685.

E-mail address: [zouhb@gzhu.edu.cn](mailto:zouhb@gzhu.edu.cn) (H. Zou).

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Pt modified Ni/MgO catalysts and found that the temperature profile of the catalyst bed depended on the preparation method of these catalysts [7].

Transition metal carbide, such as Mo<sub>2</sub>C or WC, is proposed as a possible substitute for noble metals due to its low cost and superior performance in the methane reforming. Most of the reported Ni–Mo<sub>2</sub>C catalysts were used in the dry reforming of methane instead of TRM. It has been well demonstrated that nickel modified molybdenum carbides displayed the enhanced activity and stability compared to the corresponding monometallic carbides [8,9]. Mo<sub>2</sub>C–Ni/ZrO<sub>2</sub> catalyst was used for the steam-CO<sub>2</sub> bi-reforming of methane and it was found that the modified Ni/ZrO<sub>2</sub> with 0.5wt%Mo<sub>2</sub>C loading exhibited higher catalytic performance [10]. There are very few researches on the carbide for the tri-reforming reactions. Jiang et al. have published that high activity can be obtained for the carbide catalysts for the tri-reforming of methane and the activities of carbide catalysts decrease as follows: MoC > WMoC > WC [11]. The objective of this work is to synthesize a series of promoted NiMo carbides and study the effects of different additives on their catalytic performance for TRM.

## Experimental

### Catalyst preparation

The NiMo oxidic precursors were prepared by impregnation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with the mixed aqueous solution containing the appropriate amounts of nickel nitrate, ammonium heptamolybdate and other additives (La, Ce, Mg, K, etc) nitrate for 24 h. The mass ratios of Mo and Ni to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> carrier were 0.3:1 and 0.15:1, respectively. The loadings of the additives were 1wt. %. The impregnated samples were dried overnight at 120 °C and then calcined at 500 °C for 4 h.

As-prepared oxidic precursors were then carburized using 20 vol. % CH<sub>4</sub> in hydrogen with a flow rate of 40 mL min<sup>-1</sup>. The carburization temperature was ramped from room temperature to 300 °C by 10 °C min<sup>-1</sup>, and then increased from 300 °C to 700 °C at 1 °C min<sup>-1</sup>, finally held at 700 °C for 2.5 h. The obtained un-modified and modified NiMo carbide catalysts were designated as NiMo–C and NiMoC–X, respectively, where X referred to the additive. For comparison, monometallic carbides, Mo–C/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ni–C/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, were prepared by impregnation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with the aqueous solution of ammonium heptamolybdate and nickel nitrate, respectively. The resulting oxidic precursors were then calcined and carburized as mentioned above.

### Characterization of the catalysts

X-ray diffraction (XRD) analysis was performed on the XD-3 diffractometer with Cu K $\alpha$  radiation, operating at 36 kV and 20 mA with the scanning rate of 4° min<sup>-1</sup>. SEM analysis was carried out on the LEO-1530VP scanning electron microscope at the voltage of 10 kV.

X-ray photoelectron spectroscopy (XPS) patterns were measured on the Kratos AXIS Ultra DLD spectrometer. The operated atmosphere was in 5 × 10<sup>-9</sup> torr vacuum with the

monochromatized Al K $\alpha$  X-rays (1486.6 eV). The binding energies (B.E.) of Mo 3d and C 1s were analyzed using the Shirley and linear baseline correction, respectively. The Mo3d spectra were deconvoluted using a mixed 50% Gaussian/50% Lorentzian function. The intensity ratio and the double line separation between Mo 3d<sub>3/2</sub> and 3d<sub>5/2</sub> doublets were set 2:3 and 3.2 eV, respectively.

The surface area and the pore size were determined by N<sub>2</sub> adsorption at –196°C using the Micromeritics ASAP 2020M analyzer. Prior to N<sub>2</sub> adsorption measurement, the samples were degassed at 250 °C for 3 h. Thermal analyses were performed with a TA SDT Q600 instrument from 50 °C to 850 °C at 10 °C min<sup>-1</sup> in air atmosphere.

### Catalytic activity test

The catalytic experiments of TRM were tested with 1.0 g catalyst in a continuous-flow fixed-bed quartz reactor heated by the tube furnace. H<sub>2</sub>O was injected with a micro-pump for liquids, whereas CH<sub>4</sub>, O<sub>2</sub> and CO<sub>2</sub> were fed by mass flowmeters. They were mixed in an evaporator at 393 K to achieve the feed stream containing CH<sub>4</sub>, O<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>O with the ratio of 1.00:0.16:0.39:0.30 at a flow rate of 4600 mL h<sup>-1</sup>. The outlet gas was cooled down in a condenser. The dry effluent streams was analyzed by the online gas chromatography (Shimadzu, GC-2014) equipped with TDX-01 column, using argon as the carrier gas. The reactor was heated to the reaction temperature at the rate of 2 °C min<sup>-1</sup>, and then at least five successive data points were recorded at every reaction temperature after the reaction reached equilibrium. The average of these data points was used to evaluate the conversions of CH<sub>4</sub> and CO<sub>2</sub> as well as the yields of CO and H<sub>2</sub>.

## Results and discussion

### Reactivity of molybdenum carbides for TRM

The catalytic performance of various NiMo carbides for TRM was displayed in Figs. 1 and 2. It was seen that the activities of NiMo–C catalyst at low temperatures were poor. The conversions of CH<sub>4</sub> and CO<sub>2</sub> were below 7% at 650 °C, but upon further heating to 800 °C they could reach 91.1% and 90.2%, respectively. The doping of La was benefit to TRM at lower temperatures. CH<sub>4</sub> and CO<sub>2</sub> conversions for NiMoC–La carbide could reach 84.8% and 75.2% at 750 °C, respectively, and the yields of H<sub>2</sub> and CO were the highest among the NiMo-series carbides below 750 °C. The dopants of Ce and Co were detrimental to the activities of NiMo carbides below 800 °C, but the inhibitory effect became weaker above 800 °C. Other additives, namely Mg and K, especially the latter, caused a dramatic decrease in the CH<sub>4</sub> and CO<sub>2</sub> conversions. The maximum CH<sub>4</sub> conversion for NiMoC–K was only 17.4% at 850 °C, but CO<sub>2</sub> conversion as well as the yields of CO and H<sub>2</sub> were negligible below 850 °C.

### Physical and chemical characterizations

The XRD patterns of the fresh and spent NiMo carbides were given in Figs. 3 and 4. It was shown that for fresh Mo–C/ $\gamma$ -

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