

Ni-modified β -Mo₂C catalysts effective for the dry reforming of methane at atmospheric pressure

Shaohua Zhang¹, Anjie Zhang¹, Yali Zhang¹, Chaktong Au², Chuan Shi^{1*}

¹Key Laboratory of Industrial Ecology and Environmental Engineering (MOE),
Dalian University of Technology, Dalian 116024, China

²Department of Chemistry, Hong Kong Baptist University, Hong Kong 999077, China

*corresponding author: chuanshi@dlut.edu.cn

Introduction

The DRM is attractive in terms of syngas production and industrial utilization. The catalysts for DRM processes are usually based on Group VIII metals. Among them, the nickel-based ones are commercially preferred due to the inherent availability and low cost of nickel. However, the problem with nickel-based catalysts is coke formation that leads to catalyst deactivation[1]. On the other hand, transition metal carbides show chemical properties similar to those of noble metals. Previous studies indicated that β -Mo₂C showed high thermal stability and good resistance to coking in the DRM [2]. However, the carbide catalysts deactivated rapidly due to oxidation by CO₂ at atmospheric pressure [3]. Herein, Ni modified β -Mo₂C catalyst were synthesized, which performed well in CH₄/CO₂ reforming at atmospheric pressure [4-7]. We summarized our recent work in the following aspects: (i) bi-functional catalysis of Ni-Mo₂C catalysts; (ii) in-situ synthesized Ni-Mo₂C catalysts ; (iii) influence of NiMoO_x precursors; (iv) La₂O₃ supported Ni-Mo₂C catalysts.

Materials and Methods

We prepared the NiMoO_x(CP) precursor by stirring an aqueous solution of (NH₄)₆Mo₇O₂₄·4H₂O and Ni(NO₃)₂·6H₂O at 80 °C for 4 h. The as-obtained NiMoO_x was filtered out and dried at 110 °C for 12 h and calcined at 550 °C for 4 h. Then NiMoO_x was carburized in CH₄/H₂ to Ni-Mo₂C following a series of TPR[4]. The Ni-Mo₂C bimetallic carbide catalysts with Ni/Mo molar ratios of 1/3, 1/2, and 1/1 are denoted hereinafter as Ni-Mo₂C (1/3), Ni-Mo₂C (1/2), and Ni-Mo₂C (1/1), respectively. Compared with NiMoO_x(CP) (Ni/Mo=1/2 is the optimized molar ratio), The NiMoO_x(MM)(Ni/Mo=1/2) precursor was prepared by mixing MoO₃ and NiO powder mechanically. In addition, the catalysts were characterized by XRD, XPS, CO₂-TPO and H₂-TPR techniques. Catalytic performance of the a series of the catalysts was evaluated at 800 °C atmospheric pressure.

Results and Discussion

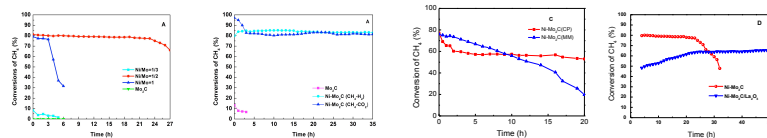


Figure A. Conversion of CH₄ over Ni-Mo₂C catalysts in CH₄/CO₂ dry reforming: CH₄/CO₂=1; F/W=12000 ml/g·h.

Figure B. Conversion of CH₄ over of catalysts: CH₄/CO₂=1; F/W=6000 ml/g·h.

Figure C. Conversion of CH₄ over Ni-Mo₂C(MM) and Ni-Mo₂C(CP) catalysts: CH₄/CO₂=1; F/W=15000 ml/g·h.

Figure D. Conversion of CH₄ over Ni-Mo₂C and Ni-Mo₂C/La₂O₃ catalysts; CH₄/CO₂=1; F/W=12000 ml/g·h.

The catalytic activity and stability are dependent on Ni/Mo molar ratio, stable catalytic performance could be achieved at a Ni/Mo molar ratio of 1/2. Characterization of the spent

samples revealed that the deactivation of Ni-Mo₂C (1/1) was due to coke formation whereas that of Ni-Mo₂C (1/3) was due to Mo₂C bulk oxidation. Only at a Ni/Mo molar ratio of 1/2, the catalytic oxidation–reduction cycle could be established.

The in-situ synthesized catalyst still exhibited stable activity at atmospheric pressure. Characterization and evaluation results indicate that the role of Ni is to facilitate CH₄ dissociation to generate active carbon and hydrogen species for the carburization of NiMoO_x.

The influence of NiMoO_x precursors on the catalytic behaviors of Ni-Mo₂C catalysts for CH₄/CO₂ reforming was investigated. Due to the formation of NiMoO₄(CP), molybdenum can be reduced at a temperature lower and nickel is better stabilized compared to that in form of NiO. With smaller Ni particles and higher CH₄ dissociation rate, Ni-Mo₂C(CP) performs better than Ni-Mo₂C(MM) in CH₄/CO₂ reforming.

In order to improve the dispersion and efficiency of the active components of Ni and β -Mo₂C, La₂O₃ supported Ni-Mo₂C catalyst was prepared. Though the catalyst's stability was greatly improved by such loading, it is interesting to find that Ni-Mo₂C/La₂O₃ changed its phase into Ni/La₂MoO₆ during the reaction, with only a small amount of β -Mo₂C left. With assistance of β -Mo₂C, better resistance of coke formation has been achieved.

Significance

Ni-Mo₂C catalyst is a typical bi-functional catalyst for CH₄/CO₂ dry reforming. The dissociation of CH₄ is catalyzed by Ni, while the activation of CO₂ takes place on β -Mo₂C. By regulating the molar ratio of Ni and Mo₂C, there is a matching of CH₄ dissociation and CO₂ activation rates. Thus, a catalytic redox cycle is established and the deactivation due to carbon accumulation or oxidation of β -Mo₂C could be avoided. The catalytic activity and stability are dependent on Ni/Mo molar ratio, stable catalytic performance could be achieved at a Ni/Mo molar ratio of 1/2.

Ni-Mo₂C catalyst could be in-situ synthesized through carburization of NiMoO_x in methane and carbon dioxide feed gas for dry reforming of methane (DRM) at atmospheric pressure. It is a simple and effective way to produce Ni-Mo₂C catalyst in CH₄-CO₂ for the DRM.

The important roles of NiMoO₄ as a precursor for the generation of Ni-Mo₂C by carburization are addressed for the first time.

Though the stability was greatly improved by loading, it is interesting to find that Ni-Mo₂C/La₂O₃ changed its phase into Ni/La₂MoO₆ during the reaction, with only a small amount of β -Mo₂C left. The catalytic role of β -Mo₂C as an important intermediate to participate the reaction was clarified.

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