Steam reforming of methanol for hydrogen production over nano-structured wire-like molybdenum carbide catalyst

Yufei Ma^a, Guoqing Guan^{a,b,*}, Patchiya Phanthong^a, Xiumin Li^a, Ji Cao^a,

Xiaogang Hao^c, Zhongde Wang^c, Abuliti Abudula^{a,b,*}

^a*Graduate School of Science and Technology, Hirosaki University, 3 Bunkyo-cho,*

Hirosaki, Aomori 036-8561, Japan

^b*North Japan Research Institute for Sustainable Energy, Hirosaki University, 2-1-3*

Matsubara, Aomori 030-0813, Japan

^c*Department of Chemical Engineering, Taiyuan University of Technology, Taiyuan*

030024, China

Corresponding authors: Tel.: +81-17-762-7756; fax: +81-17-735-5411.

E-mails: guan@cc.hirosaki-u.ac.jp (G. Guan); abuliti@cc.hirosaki-u.ac.jp (A. Abudula)

Abstract

Steam reforming of methanol over nanostructured wire-like molybdenum carbides, which were synthesized by direct carburization of aniline-intercalated molybdenum based organic-inorganic hybrid composite at different temperatures, were investigated in details. SEM and TEM images revealed that the obtained wire-like molybdenum carbide was composed of nano-particles (10-20 nm) and had microporous structure. These wire-like molybdenum carbides showed higher catalytic activity than those synthesized via the conventional temperature programmed reduction (TPRe) method. It is found that the wire-like molybdenum carbide synthesized at 675°C had higher surface area (93.2 m²/g) and showed more excellent catalytic activity and longer term stability. XRD results indicated that more α -MoC_{1-x} phase existed in this kind of molybdenum carbide. It indicated that an alternative high-performance molybdenum carbide catalyst can be easily obtained by adjusting the synthesis condition.

Keywords: Methanol; Hydrogen; Molybdenum carbide; Wire-like morphology; Organic-inorganic hybrid material; Catalytic activity; Long-term stability.

1. Introduction

Production of hydrogen via the steam reforming of methanol is considered as one of best ways for providing hydrogen for fuel cell in the future since liquid methanol with high energy density has no C-C bond, sulfur free, and is easily handled[1-3]. Steam reforming of methanol could be realized effectively at relatively low temperature in the presence of catalyst [4-6]. In the developing catalysts, molybdenum carbide is one of the possibly applicable catalysts[7-11]. Molybdenum carbide itself can be used directly for the steam reforming of methanol[12]. In order to promote its catalytic activity and improve its stability, it was loaded on other supports [13-15] or doped by some metals such as Pt, Ni, Co, Fe and Cu[16-19]. In our previous studies [16,17,19], Pt, Ni and Cu were doped on molybdenum carbide by carburization of metal doped molybdenum oxide via the temperature-programmed reduction (TPRe) method for the steam reforming of methanol. Due to the strong metal-support interaction between the doped metal and molybdenum carbide support, Pt doped molybdenum carbide exhibited high catalytic activity and 100% methanol conversion was reached at a reaction temperature as low as 200 °C while Ni doped molybdenum carbide showed a long-term stability and the methanol conversion kept at about 90 % for 50 h at 300 °C. XPS analysis indicated that the deactivation of molybdenum carbide in SRM reaction is due to the surface oxidation [16, 17, 19].

Traditional TPRe method for the preparation of molybdenum carbide has some disadvantages: (i) the flammable mixture of hydrogen and carbon-containing gases

including CH_4 , C_2H_6 , C_3H_8 and C_4H_{10} [20-22] are employed; (ii) complex and strict synthesis conditions such as the precise control of temperature heating rate ($1^\circ\text{C}/\text{min}$) and exact gas compositions and flow rates are necessary; (iii) large-scale production is impossible. Especially, molybdenum carbide produced from the TPRE method is always covered by the polymeric carbon species resulting from the carbon-containing gases so that some active sites are lost, reducing the catalytic activity. In general, the surface area of the obtained molybdenum carbide by this method is much low. Thus, new strategies for the synthesis of nano-structured molybdenum carbide are highly desired.

Recently, an effective and convenient route for the preparation of nanostructured molybdenum carbide via carburization of organic-inorganic hybrid amine-containing molybdenum based materials was proposed [23]. Using this route, it is possible to prepare a large amount of tunable nano-structured molybdenum carbide with high surface area and enriched porosity. It is found that the obtained molybdenum carbide catalysts with nanowire morphology had a good performance for the production of hydrogen from methanol decomposition [24]. In the present study, the same nanostructured wire-like molybdenum carbides were synthesized at different carburization temperatures and applied for the steam reforming of methanol at different temperatures. The effect of the carburization temperature on the catalytic performance and the long-term stability were evaluated and discussed in details. Physicochemical properties of the catalysts before and after the reaction were characterized by XRD, FT-IR, BET, TEM, SEM and EDS.

2. Experimental

2.1 Catalyst preparation

Nanostructured wire-like molybdenum carbides were prepared by following the method reported in the literature [24] with a minor modification. Firstly, MoO_x/aniline hybrid precursors (Mo₃O₁₀(C₆H₅NH₃)₂·2H₂O) was prepared as follows: 2.48 g of ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄·4H₂O, Konjundo Chem Lab, Japan) was dissolved in 40 ml of distilled water, followed by addition of 3.34 g aniline in it; then, 1 M HCl was added dropwise in the above solution with stirring at room temperature until the precipitate appeared; and then it was heated at 50 °C under stirring for 2.5 hours; the final product was filtrated, washed with ethanol and water until pH value=7, and dried at 50 °C in air overnight.

Carburization of the obtained MoO_x/aniline precursor was carried out in a fixed-bed quartz micro-reactor with an inner diameter of 10 mm. Firstly, air in the reactor was purged out by Ar (10 cm³/min) at room temperature for 4 h, and then heated to final carburization temperature (i.e., 675, 725 and 750 °C, respectively, in this study) with a ramping rate of 2 °C/min in Ar flow gas and a flow rate of 50 cm³/min, and remained at the final temperature for 5 h. As-obtained catalyst was cooled down to RT in the Ar flow and finally passivated in 1% O₂/Ar for 12 h at room temperature. The as-prepared catalyst is denoted as wire-Mo_xC_y-CT, where CT is calcination temperature (675, 725 and 750 °C). For comparison, molybdenum carbide sample was also prepared using the TPre method as reported in our previous studies [16, 17, 19]. The as-prepared catalyst is denoted as TPre-Mo₂C.

2.2 Catalyst characterization

Crystalline structure of the catalyst before and after the reaction was determined by X-ray diffraction (XRD 610, Shimadzu, Japan). The radiation used was CuK α and the operating potential was 30 kV with a current of 30 mA and a scanning rate 4°/min. BET (Brunauer-Emmett-Teller) surface area was measured through nitrogen adsorption at liquid-nitrogen temperature (77 K) using a Quantachrome NOVA 4200 surface area and pore size analyzer. The IR spectra were analyzed using FT-IR (JASCO 4200, USA). The microstructure and morphology were characterized with a scanning electron microscope (SEM, S-8000, Hitachi, Japan). Transmission electron microscope (TEM) images were obtained using a JEM-2100F transmission electron microscope JEOL operating at 200 kV.

2.3 Catalytic performance evaluation

Catalytic performance of as-prepared molybdenum carbide for the steam reforming of methanol (SRM) reaction was evaluated in a micro-reactor with an inner diameter of 6 mm. Prior to the reaction, the catalyst was pretreated with 15% CH₄/H₂ at 590°C for 2 h in order to reduce the surface oxide. The pretreated condition was chosen based on our preliminary experiments, which are not shown here. The total amount of the catalyst used was 0.4 g, and a weight hourly space velocity (WHSV) of 9000 cm³ g⁻¹ h⁻¹ was selected in this study. Methanol and water mixture with a molar ratio of 1:1 (13% CH₃OH-13% H₂O in Ar) was injected into the reactor with a

syringe pump. It was vaporized in a pre-heater containing ZrO₂ beads and carried by Ar gas flow. Catalytic performance was tested at different temperatures from 200 -400 °C and at atmospheric pressure. For comparison, the sampling was carried out after 1 hour reaction at each temperature. For stability test, the time-on-stream sampling analysis was performed every 1 hour during the reaction at 400 °C. Herein, a thermocouple was inserted in the catalytic bed for the reaction temperature control. A water-ice cold trap was set at the exit of the reactor to condense the unconverted methanol and steam. The products were analyzed using a gas chromatograph with TCD detector (Agilent 7890A GC system) and a gas chromatograph with FID detector (Shimadzu GC-2014). The outlet gas flow rate was determined by inner standard method, in which the flow rates of CH₄, CO, and CO₂ were calculated based on the flow rate of inner gas N₂ in the reaction system while that of H₂ was calculated based on the flow rate of inner gas He in the reaction system.

Performances of the catalysts were characterized in terms of methanol conversion. The methanol conversion was defined as the molar ratio of the gaseous carbon compounds (CH₄, CO, and CO₂) in the product stream to the feed methanol since only traces of other products such as C₂H₆, C₂H₄ and HCOOH in outlet gas and liquid were detected in this study. Methanol conversion was defined as:

$$X_{\text{CH}_3\text{OH}} = \frac{n_{\text{CO}} + n_{\text{CO}_2} + n_{\text{CH}_4}}{n_{\text{CH}_3\text{OH}}} \times 100\% \quad (1)$$

where n_{CO} , n_{CO_2} , n_{CH_4} , and $n_{\text{CH}_3\text{OH}}$ are the flow rates of CO, CO₂, CH₄ in the outlet products and methanol in the feed, respectively. The molar fraction of a product

component was defined as the molar ratio of this specific product to the total gaseous product.

3. Results and discussion

3.1 Physicochemical properties

Morphology, chemical composition and crystal structure of $\text{Mo}_3\text{O}_{10}(\text{C}_6\text{H}_5\text{NH}_3)_2 \cdot 2\text{H}_2\text{O}$ synthesized by aniline organic precursors are shown in Fig.

1. One can see that molybdate-aniline precursor showed uniformly wire-like morphology (Fig. 1 (a)) with a length of about 23 μm and a width of about 100-250 nm. EDS analysis (Fig. 1 (b)) indicated that the molybdate-aniline precursor consisted of Mo, C, N and O elements, but the signal of N element was weak. It might be due to that the concentration of N element in compounds is ultralow based on the chemical formula of $\text{Mo}_3\text{O}_{10}(\text{C}_6\text{H}_5\text{NH}_3)_2 \cdot 2\text{H}_2\text{O}$, in which the N element weight concentration is 4%. Furthermore, it is generally difficult to detect the light element such as N using EDS. Therefore, the chemical compositions were further confirmed by FT-IR. As shown in Fig. 1 (c), the bands at 3026 and 2918 cm^{-1} are attributed to the stretching vibration of C-H in benzene ring; the adsorption at 2584 cm^{-1} is ascribed to the stretching vibration of $-\text{NH}_3^+$; the bands at 1115 cm^{-1} is contributed to the stretching vibration of C-N; the bands at 1581 and 1494 cm^{-1} should be assigned to the vibration of the benzene ring; and the bands at 948 and 889 cm^{-1} should be contributed to the stretching vibration of Mo=O and Mo-O, respectively. These FT-IR results confirmed that molybdate-aniline precursor contained aniline and molybdenum oxide. All peaks in the XRD pattern (Fig. 1(d)) were in agreement with the characteristic diffraction

peaks of $\text{Mo}_3\text{O}_{10}(\text{C}_6\text{H}_5\text{NH}_3)_2 \cdot 2\text{H}_2\text{O}$.

Fig. 2 shows XRD patterns of the as-prepared freshTPRe-Mo₂C, wire-Mo_xC_y-CT(CT=675, 725 and 750 °C), and wire-Mo_xC_y-675°C after pretreatment under CH₄/H₂ at 590 °C. Herein, the peaks at 2θ of 34.8°, 38.4° and 39.8° are attributed to the presence of hexagonal β-Mo₂C phase with hcp crystal structure while the peaks at 2θ of 37.1° and 42.8 ° are attributed to cubic α-MoC_{1-x} phase with fcc crystal structure. For the fresh wire-Mo_xC_y-675 °C, the peak at 25.9° is attributed to molybdenum oxide (MoO₃). It should be noted that there are no peaks related to the metal molybdenum for all the as-prepared catalysts. These results indicated that the carbon and nitrogen atom in the organic precursor could reduce and carburize the molybdenum oxide. One can see that the fresh wire-like molybdenum carbides had two phases, i.e., α and β phases. With the increase in the carburization temperature, the peak intensity of the β phase was increased while that of the α phase was decreased, indicating that at higher temperature, the thermodynamically metastable α phase is easily transferred to the stable β phase. In general, thermodynamically metastable α-MoC_{1-x} is synthesized by nitrogenization of MoO₃ under ammonia atmosphere for the formation of Mo₂N at first and subsequently converting to α-MoC_{1-x} under the mixture of hydrogen and carbon containing gas during carburization process [25, 26]. Therefore, in the present case, it can be speculated that N atom in aniline could nitrogenize and reduce molybdenum oxide to Mo₂N at first, and then Mo₂N is carburized by C atom to α-MoC_{1-x}. On the other hand, based on Fig. 2, for the fresh wire-Mo_xC_y-675°C, MoO₃ existed. However, when the carburization temperature was

increased over 725 °C, pure molybdenum carbide pattern appeared. It is possible that the carburization temperature is too low to efficiently carburize all molybdenum oxide to molybdenum carbide at 675 °C. However, after the pretreatment under CH₄/H₂ at 590 °C, MoO₂ phase disappeared, indicating that the remained MoO₂ in the fresh wire-Mo_xC_y-675°C was easily carburized under the pretreatment atmosphere. For other samples, the XRD patterns after the pretreatment were almost the same as the fresh ones. The results were not shown here. In contrast, TPre-Mo₂C only contained the stable β phase.

SEM images of β-Mo₂C synthesized by the TPre method and the wire-Mo_xC_y-675°C are shown in Fig. 3 (a) and (b), respectively. Comparing with the image shown in Fig. 1(a), the wire-Mo_xC_y-675°C remained the wire-like morphology (Fig. 3 (b)) as the molybdate-aniline precursor. The wire length was about 8.5 μm, and the width is about 100-250 nm. Comparing with the organic-inorganic precursor, the width kept at the same, but the length became short. This might be due to the material broken during the carburization process at high temperature. In contrast, the β-Mo₂C synthesized by the traditional TPre method showed random large particle morphology (Fig. 3 (a)).

TEM images of β-Mo₂C synthesized by the TPre method and the wire-Mo_xC_y-675°C are shown in Fig. 3 (c) and (d), respectively. Obviously, the wire-like molybdenum carbide was composed of nano-particles with a size of about 10-20 nm, and these nanoparticles were connected with each other and thus, the wire-like molybdenum carbide had porous nanostructure, which could provide larger surface

area and more catalytic active sites. As shown in Table 1, the nano-structured wire-like molybdenum carbide had much higher surface area than that of Mo₂C synthesized by the traditional TPre method. However, it should be noted that with the increase in the carburization temperature, the surface area was decreased from 93.2 to 33.01 m²/g. It is possible that the particle sintering could occur at high carburization temperature, resulting in some nano-pore blocked. On the other hand, in general, comparing with β -Mo₂C, α -MoC_{1-x} showed higher surface area [27-29]. From the XRD patterns shown in Fig.2, one can see that with the increase in the carburization temperature, the peak intensity of the α phase decreased.

Fig. 4 schematically illustrates the synthesis process for the formation of the wire-like molybdenum carbide. Herein, the organic precursor served as the template to drive the molybdenum precursor to the wire-like morphology, and this morphology was maintained until the end of carburization process. It should be noted that the C and N atom in organic precursor served as the reducing agent which reduced molybdenum oxide and carburized molybdenum oxide to molybdenum carbide.

3.2 Catalytic performance

Catalytic performances of TPre-Mo₂C and wire-Mo_xC_y-CT (CT= 675, 725 and 750 °C) catalysts for the steam reforming of methanol were evaluated in details in a temperature range of 200 - 400 °C with a WHSV of 9000 cm³ g⁻¹ h⁻¹ and a steam-to-carbon molar ratio of 1. The results were expressed as the methanol conversion versus temperature. As shown in Fig. 5, it is found that the catalytic

performances of the wire-Mo_xC_y-CT (CT= 675, 725 and 750 °C) were higher than that of TPre-Mo₂C. As indicated in Table 1 and Fig. 3, it is possible that the higher surface area and nano-porous structure of the wire-like molybdenum carbide could provide more active sites for the steam reforming of methanol. Herein, it should be noted that the catalytic activity decreased as the wire-Mo_xC_y-CT was prepared at higher carburization temperature and the wire-Mo_xC_y-675 °C showed the highest methanol conversion at different reforming temperatures: the methanol conversion reached 30% at 200 °C and the highest methanol conversion was reached when the reaction temperature was increased to 350 °C. As indicated above, compared with other wire-Mo_xC_y, the wire-Mo_xC_y-675 °C had much higher surface area (93.2 m²/g), which could provide more active sites on the catalyst surface. Furthermore, it is possible that more α-MoC_{1-x} existed in the wire-Mo_xC_y-675 °C, which is more active than β-Mo₂C phase for the steam reforming of methanol [16, 30].

Fig. 6 shows the product compositions over TPre-Mo₂C and wire-Mo_xC_y-CT (CT= 675, 725 and 750 °C) corresponding to the results shown in Fig. 5. In all cases, H₂ and CO₂ are the two main products in the outlet gas, together with a small amount of CO and CH₄. In the present study, only traces of other products such as C₂H₆, C₂H₄ and HCOOH were detected for any catalyst. As we known, CO is a poison gas for fuel cell Pt-based catalysts and has to be removed or converted in a practical reforming process for the application of fuel cells. Herein, for TPre-Mo₂C, with the increase in the reaction temperature, the CO percentage increased from 0 to 10 %. In contrast, for the wire-Mo_xC_y-CTs, the CO percentage was

lower than 5% when the reaction temperature was in range of 200 to 400 °C. It is possible that the wire-Mo_xC_y-CTs provided higher surface area and more active sites for water gas shift (WGS) reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) as well. Several researches reported that WGS reaction could happen in SRM reaction over molybdenum carbide catalysts [13, 16, 17].

On the other hand, for all catalysts, one can see that with the increase in the reaction temperature, H₂ percentage decreased while CH₄ percentage increased to some extent. CH₄ is an unwanted by-product for the hydrogen production from SRM. In this study, the concentration of H₂ and CH₄ can be considered as the result of the competition reactions between the WGS and methanation ($\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$). One can see that more H₂ was obtained if the methanation reaction was hindered. Comparing with TPre-Mo₂C, the methane concentration was hindered when the wire-Mo_xC_y-675 °C catalyst was used.

3.3 Catalytic stability

Fig.7 shows the catalytic stability test results for TPre-Mo₂C and wire-Mo_xC_y-CT (CT= 675, 725 and 750 °C) catalysts at 400 °C. One can see that for TPre-Mo₂C catalyst, the methanol conversion rate was decreased rapidly from 100 % to 10 % in 9 h. In contrast, the catalytic stability was obviously enhanced when the wire-Mo_xC_y catalysts were used. With the decrease in the carburization temperature of the preparation of wire-Mo_xC_y, the catalytic stability performance increased. Especially, for the wire-Mo_xC_y-675 °C, the methanol conversion kept at about 95% in 12h,

suggesting that it is a very stable catalyst for the steam reforming of methanol. In contrast, for the wire-Mo_xC_y-725 °C and wire-Mo_xC_y-750 °C catalysts, the methanol conversions were decreased from 100 % to 70 % and 30 % in 12 h, respectively.

Fig. 8 shows the product compositions during the stability test related to Fig. 7. For TPre-Mo₂C catalyst, the outlet gas compositions were also unstable: CO percentage in the outlet gas increased from 5 % to about 20 % while CO₂ percentage decreased from about 23 to 10 % after 9 h reaction, and the H₂ percentage also decreased to some extent. In contrast, when wire-Mo_xC_y-CT catalysts were used, the stability of product compositions was enhanced obviously. Especially, over the wire-Mo_xC_y-675 °C (Fig. 8 (d)), the composition stability was very high: the CO₂ percentage remained at about 20 % and CO kept lower than 5 % after 12 h reaction.

Fig. 9 shows the XRD patterns of the spent catalysts after the stability test as indicated in Fig. 7. Herein, no peaks of MoO₃ and other molybdenum oxide appeared in the XRD patterns. In our previous studies [16,17,19], the deactivation of molybdenum carbide was confirmed to be due to the surface oxidation, but suggested that the oxidized layer should be only a few molecule layers, which is difficult to be detected by XRD. As the molybdenum carbide is in the reduce state, H₂O molecule could be easily adsorbed and dissociated on it. Moon et al. [21] reported that the deactivation of molybdenum carbide should be due to the Mo₂C transfer to MoO₃ with the reaction of H₂O in reactant during the WGS reaction. Here, as reported in our previous studies [16, 17, 19], the deactivation of catalyst should be also due to the oxidization of the molybdenum carbide surface by H₂O. However, it should be noted

that the stability of the wire-Mo_xC_y, could be enhanced to some extent due to the high surface area and more active sites.

4. Conclusions

Wire-like molybdenum carbide catalysts were synthesized by carburization of organic-inorganic hybrid materials under inert gas atmosphere at different temperatures, and applied for the steam reforming of methanol reaction at temperatures in the range of 200 – 400 °C. The following results were obtained:

- (a) XRD analysis indicated that the crystal structure of the obtained wire-like molybdenum carbide catalyst depended on the carburization temperature. α -MoC_{1-x} phase always appeared at a relatively low temperature, and with the increase in the carburization temperature, β -Mo₂C phase increased.
- (b) SEM and TEM images revealed that the obtained wire-like molybdenum carbides were composed of nano-particles (10-20 nm) and had porous structures.
- (c) These wire-like molybdenum carbides showed higher catalytic activity than those synthesized via the conventional temperature programmed reduction (TPRe) method. It is found that the wire-like molybdenum carbide synthesized at 675 °C had higher surface area (93.2 m²/g) and showed more excellent catalytic activity and longer term stability.

Acknowledgements

This work is supported by Japan Science and Technology Agency (JST), Japan and Aomori City Government. Ma thanks the State Scholarship Fund of China Scholarship Council (2012). P. Phanthonggratefully acknowledges the scholarship from Ministry of Education, Culture, Sport, Science, and Technology (MEXT) of Japan. The authors also thank Dr Yutaka Kasai at Aomori Prefectural Industrial Technology Research Center for their technical support on experiments.

References

- [1] Zhang XR, Wang LC, Yao CZ, Cao Y, Dai WL, He HY, Fan KN. A highly efficient Cu/ZnO/Al₂O₃ catalyst via gel-coprecipitation of oxalate precursors for low-temperature steam reforming of methanol. *Catal Lett* 2005; 102: 183-90.
- [2] Wu GS, Mao DS, Lu GZ, Cao Y, Fan KN. The role of the promoters in Cu based catalysts for methanol steam reforming. *Catal Lett* 2009; 130: 177-84
- [3] Sá S, Silva H, Brandão L, Sousa JM, Mendes A. Catalysts for methanol steam reforming-A review. *Appl Catal B Environ* 2010; 99: 43-57.
- [4] Yang L, Lin GD, Zhang HB. Highly efficient Pd-ZnO catalyst doubly promoted by CNTs and Sc₂O₃ for methanol steam reforming. *Appl Catal A Gen* 2013; 455: 137-44.
- [5] Men Y, Yang M. SMSI-like behavior and Ni promotion effect on NiZnAl catalysts in steam reforming of methanol. *Catal Commun* 2012; 22: 68-73.
- [6] Segal SR, Anderson KB, Carrado KA, Marshall CL. Low temperature steam reforming of methanol over layered double hydroxide-derived catalysts. *Appl Catal A Gen* 2002; 231: 215-26.
- [7] York AP, Pham-Huu C, Del Gallo P, Blekkan EA, Ledoux MJ. Comparative Effect of Organosulfur Compounds on Catalysts for the n-Heptane Isomerization Reaction at Medium Pressure: Mo₂C-Oxygen-Modified, MoO₃-Carbon-Modified, Pt/ γ -Al₂O₃, and Pt/ β -Zeolite Catalysts. *Ind Eng Chem Res* 1996; 35:672-82.
- [8] Shi C, Zhang A, Li X, Zhang S, Zhu A, Ma Y, Au C. Ni-modified Mo₂C catalysts for methane dry reforming. *Appl Catal A Gen* 2012;431:164-70.
- [9] Lee JS, Yeom MH, Park KY, Nam IS, Chung JS, Kim YG. Preparation and

benzene hydrogenation activity of supported molybdenum carbide catalysts. *J Catal* 1991;128:126-36.

[10] Brungs AJ, York AP, Claridge JB, Márquez-Alvarez C, Green ML. Dry reforming of methane to synthesis gas over supported molybdenum carbide catalysts. *Catal Lett* 2000; 70: 117-22.

[11] Blekkan EA, Pham-Huu C, Ledoux MJ, Guille J. Isomerization of n-heptane on an oxygen-modified molybdenum carbide catalyst. *Ind Eng Chem Res* 1994;33:1657-64.

[12] Széchenyi A, Solymosi F. Production of hydrogen in the decomposition of ethanol and methanol over unsupported Mo_2C catalysts. *J Phys Chem C* 2007;111:9509-15.

[13] Barthos R, Solymosi F. Hydrogen production in the decomposition and steam reforming of methanol on Mo_2C /carbon catalysts. *J Catal* 2007;249:289-99.

[14] Koós Á, Barthos R, Solymosi F. Reforming of Methanol on a K-Promoted Mo_2C /Norit Catalyst. *J Phys Chem C* 2008;112:2607-12.

[15] Lin SSY, Thomson WJ, Hagensen TJ, Ha SY. Steam reforming of methanol using supported Mo_2C catalysts. *Appl Catal A Gen* 2007;318:121-7.

[16] Ma Y, Guan G, Shi C, Zhu A, Hao X, Wang Z, Kusakabe K, Abudula A. Low-temperature steam reforming of methanol to produce hydrogen over various metal-doped molybdenum carbide catalysts. *Int J Hydrogen Energy* 2014; 39:258-66.

[17] Ma Y, Guan G, Phanthong P, Hao X, Huang W, Tsutsumi A, Kusakabe K, Abudula A. Catalytic Activity and Stability of Nickel Modified Molybdenum Carbide

Catalysts for Steam Reforming of Methanol. *J Phys Chem C* 2014; 118:9485-96.

[18] Setthapun W, Bej SK, Thompson LT. Carbide and Nitride Supported Methanol Steam Reforming Catalysts: Parallel Synthesis and High Throughput Screening. *Top Catal* 2008; 49: 73-80.

[19] Ma Y, Guan G, Hao X, Zuo Z, Huang W, Phanthong P, Kusakabe K, Abudula A. Highly-efficient steam reforming of methanol over copper modified molybdenum carbide. *RSC Adv* 2014, DOI: 10.1039/C4RA05673F.

[20] Nagai M, Matsuda K. Low-temperature water-gas shift reaction over cobalt-molybdenum carbide catalyst. *J Catal* 2006;238:489-96.

[21] Moon DJ, Ryu JW. Molybdenum carbide water-gas shift catalyst for fuel cell-powered vehicles applications. *Catal Lett* 2004; 92: 17-24.

[22] Bastos LC, Monteiro WR, Zacharias MA, da CruzGM, Rodrigues JAJ. Preparation and characterization of Mo/W bimetallic carbides by using different synthesis methods. *Catal Lett* 2008; 120: 48-55.

[23] Gao Q, Wang S, Tang Y, Giordano C. Preparation of organic-inorganic hybrid Fe-MoO_x/polyaniline nanorods as efficient catalysts for alkene epoxidation. *Chem Commun* 2012; 48:260-62.

[24] Gao Q, Zhang C, Xie S, Hua W, Zhang Y, Ren N, Xu H, Tang Y. Synthesis of Nanoporous Molybdenum Carbide Nanowires Based on Organic-Inorganic Hybrid Nanocomposites with Sub-Nanometer Periodic Structures. *Chem Mater* 2009; 21: 5560-62.

[25] Lee J, Volpe L, Ribeiro F, Boudart M. Molybdenum carbide catalysts: II.

- Topotactic synthesis of unsupported powders. *J Catal* 1988;112:44-53.
- [26] Jung KT, Kim WB, Rhee CH, Lee JS. Effects of transition metal addition on the solid-state transformation of molybdenum trioxide to molybdenum carbides. *Chem Mater* 2004;16:307-14.
- [27] Kojima R, Aika K. Molybdenum nitride and carbide catalysts for ammonia synthesis. *Appl Catal A Gen* 2001;219:141-7.
- [28] Bouchy C, Schmidt I, Anderson J, Jacobsen C, Derouane E, Derouane-Abd Hamid S. Metastable fcc α -MoC_{1-x} supported on HZSM5: preparation and catalytic performance for the non-oxidative conversion of methane to aromatic compounds. *J Mol Cataly A Chem* 2000; 163:283-96.
- [29] Tsuji M, MiyaoT, Naito S. Remarkable support effect of ZrO₂ upon the CO₂ reforming of CH₄ over supported molybdenum carbide catalysts. *Catal Lett* 2000; 69:195-8.
- [30] Ranhotra G, Bell A, Reimer J. Catalysis over molybdenum carbides and nitrides: II. Studies of CO hydrogenation and C₂H₆ hydrogenolysis. *J Catal* 1987; 108:40-9.

Figure captions

Fig.1(a) SEM image, (b) EDS pattern, (c) FT-IR spectra and (d) XRD pattern of MoO_x -aniline hybrid precursors.

Fig.2 XRD patterns of TPre- Mo_2C , fresh wire- Mo_xC_y -CT(CT= 675, 725 and 750 °C) catalysts and wire- Mo_xC_y -675°C after pretreatment.

Fig.3 (a) SEM image of TPre- Mo_2C , (b) SEM image of wire- Mo_xC_y -675°C and (c) TEM image of TPre- Mo_2C and (d) TEM image of wire- Mo_xC_y -675°C.

Fig.4 Schematic illustration of the synthesis of wire- Mo_xC_y from organic-inorganic hybrid material using aniline as organic precursor.

Fig.5 Catalytic activities over TPre- Mo_2C and wire-like molybdenum carbides with different carburization temperatures

Fig.6 Product compositions over wire-like molybdenum carbide catalyst (a) TPre- Mo_2C ; (b) wire- Mo_xC_y -750°C, (c) wire- Mo_xC_y -725°C and (d) wire- Mo_xC_y -675°C.

Fig.7 Time-on-stream testing of TPre- Mo_2C and wire-like molybdenum carbide catalysts at 400 °C.

Fig.8 Product compositions for stability test over wire-like molybdenum carbide catalysts (a) TPre- Mo_2C ; (b) wire- Mo_xC_y -750°C; (c) wire- Mo_xC_y -725°C and (d) wire- Mo_xC_y -675°C

Fig.9 XRD patterns of the spent catalysts after stability tests shown in Fig. 7.

Table 1 BET surface areas of wire-like molybdenum carbide catalysts.

Catalysts	$S_{\text{BET}}(\text{m}^2/\text{g})$	Catalysts	$S_{\text{BET}}(\text{m}^2/\text{g})$
Mo_2C	5.8	Mo_xC_y (725 °C) ^a	37.22
Mo_xC_y (675 °C) ^a	93.2	Mo_xC_y (750 °C) ^a	33.01

^a wire-like molybdenum carbide

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Graphical Abstract