**Reaction intermediate species during the steam reforming of methanol
over metal modified molybdenum carbide catalysts**

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Abstract

To understand steam reforming of methanol (SRM) reaction pathways over the surfaces of various metal-modified molybdenum carbides, the reaction intermediate species generated during the SRM reaction are investigated by using a temperature programmed surface reaction (TPSR) approach, in which a mass spectroscopy is applied to detect the produced species on-line. It is found that the reaction temperature affects the formation of different intermediate species over different catalysts. At the temperature lower than 180 °C, SRM reaction proceeds over Cu modified molybdenum carbide surface through formic acid (HCOOH) intermediate pathway, but at the temperature over 180 °C, the reactions over pure β -Mo₂C, Ni, Cu and Pt modified molybdenum carbide surfaces proceed through methyl-formate (HCOOCH₃) intermediate pathway. It is expected that these findings can help us to understand the mechanism on SRM reaction over molybdenum carbide based catalysts.

Keywords: Steam reforming of methanol; Molybdenum carbide; Metal-modified molybdenum carbide; Reaction intermediate species; Mechanism.

1. Introduction

Compared with gaseous hydrogen storage, on-board hydrogen production by reforming liquid hydrogen carriers will be more potential for future commercialization. Steam reforming of methanol (SRM) is considered as one of the most favorable chemical processes for on-board hydrogen production because: (i) methanol is in liquid state at ambient condition; (ii) it has high hydrogen-to-carbon ratio; (iii) the activation of methanol can occur at low temperatures (200-400 °C); (iv) methanol is sulfur free and can be produced from biomass [1].

Various catalysts have been developed for the SRM [1-10]. Cu-based catalyst is widely used for SRM reaction due to its high activity and high selectivity at low temperature. However, this kind of catalyst is easy to be deactivated by thermal sintering [1-5]. Group 8-10 catalysts have also been developed for the SRM with high activity and stability, but their performances are generally affected by the support. Noble metals like Pt, Pd and Au supported oxides generally shows high activity, stability and selectivity [7-10], but their cost hinders their large scale applications. In our previous studies [11-14], metal-modified molybdenum carbide catalysts were prepared for low-temperature SRM reaction. It is found that the activation of methanol molecule can be promoted by the loading of metal (Fe, Co, Ni, Cu or Pt) on the molybdenum carbide, and water molecule

is mainly activated on molybdenum carbide surface itself. By adjusting the molar ratio of metal to carbide, the catalytic activity and stability can be tuned. Moreover, surface oxidation is usually the main reason for deactivation of carbide catalysts [11-25].

Three different reaction pathways for the SRM reaction over catalyst have been proposed in the literature [26-32]. The first one is the methanol decomposition to H₂ and CO followed by water gas shift (WGS) reaction (Pathway I, CO intermediate); the second one is methanol dehydrogenation to methyl-formate, which then further decomposed to H₂ and CO₂ (Pathway II); and the third one is the methanol dehydrogenation to formaldehyde followed by decomposition to final products (Pathway III). These three pathways are summarized as the followings.

Pathway I (CO intermediate):

Pathway II (Methyl formate intermediate):

Pathway III (Formaldehyde intermediate):

For the pathway I, CO is the primary product. Based on thermodynamic condition of WGS reaction, CO concentration should be at least equal to or higher than the H₂O concentration. However, Santacesaria and Carra [26] studied the SRM reaction over Cu-Zn catalysts in a continuous stirred-tank reactor (CSTR) using Langmuir-Hinshelwood model, and found that CO concentration was lower than the equilibrium concentration of WGS reaction. Luo and Asthagiri [27] applied density functional theory (DFT) to study the SRM reaction on Co (001) and Co (111) surface and found that CO cannot be obtained from the direct decomposition of methanol, but from the decomposition of CH₂O which is generated by methanol dehydrogenation. These results indicate that the pathway I is doubtful. For the pathway I, based on the diffuse reflectance infrared fourier transform (DRIFT) spectroscopic results, Frank *et al.* [28] found that methyl formate was the intermediate species in SRM reaction over Cu-based catalysts. Furthermore, according to plane-wave density functional theory, Lin *et al.* [29] considered that the methyl formate intermediate should be formed by a reaction between formaldehyde and methoxyl. Yi *et al.* [30] identified the pathway II occurring on the Au/CeO₂ surface via *in-situ* temperature

program surface reaction (TPSR) approach. For the pathway III, Takezawa and Iwasa [31] found that formaldehyde (HCHO) is an important intermediate involved in the SRM reaction over Cu and group VIII (Ni, Rh, Pd and Pt) metal based catalysts, where the HCHO intermediate was formed by dehydrogenation of methanol. This was also identified by other researchers [32,33], who found that CH₃OH is first dehydrogenated to HCHO followed by a nucleophilic attack of H₂O to form HCOOH, which is further decomposed to H₂ and CO₂ on Cu-Zn based catalysts. The calculation results based on density functional theory (DFT) also indicated that HCHO intermediate involves in the SRM reaction on Cu (111) and Pd (111) surface [34]. On Cu (111) surface, HCHO intermediate can be formed by dehydrogenation of methanol though the O-H bond scission at first and then, HCHO tends to react with hydroxyl by the dissociation of H₂O to form hydroxymethoxy, which is finally decomposed to CO₂. In contrast, on Pd (111) surface, HCHO intermediate can be formed via the C-H bond breaking at first and then, directly decomposed to CO and H₂. All these results indicate that for different catalysts, the intermediate species formed on their surfaces seems to be different. To understand the reaction pathway of SRM over metal-modified molybdenum carbide, in this study, the reaction intermediate species generated were investigated by using the TPSR approach, in which a mass spectroscopy was applied to detect the products on-line. The obtained

data were analyzed and discussed.

2. Experimental

2.1 Catalysts preparation

The catalysts were synthesized with the same procedure described in our previous studies [11-13]. In short, the molybdenum carbide (β -Mo₂C) was synthesized by carburizing molybdenum oxide (MoO₃) using temperature programmed reduction (TPR) method with 20% CH₄/H₂ mixture. Subsequently, the as-prepared fresh sample was passivated at room temperature using a 1% O₂/Ar gas mixture. For preparation of metal modified molybdenum oxide (M-MoO_x) (M: Pt, Cu, and Ni), Firstly, aqueous solutions of (NH₄)₆Mo₇O₂₄·4H₂O respectively mixed with H₂PtCl₆·6H₂O, Cu(NO₃)₂·3H₂O, Ni(NO₃)₂·6H₂O under stirring for 4 h at first, and then the mixture solutions were continuously stirred at 80 °C until dried. After continuously dried at 110 °C overnight, the samples were calcined in air at 500 °C for 4 h. The obtained M-MoO_x precursors were carburized using the same method as that for preparation of β -Mo₂C. It is found that Pt-Mo_xC_y with a Pt/Mo molar ratio of 1.6/90(Pt-Mo_xC_y(1.6)) [11], Ni-Mo₂C with a Ni/Mo molar ratio of 1.6/98.4 (Ni-Mo₂C (1.6)) [11,12], Cu-Mo₂C with a Cu/Mo molar ratio of 10/90 (Cu- Mo_xC_y(10)) [13] showed the highest activity and stability for each metal-modified molybdenum oxide. In this study, these three kinds of catalysts were for TPSR.

2.2 Temperature Programmed Surface Reaction (TPSR)

CH₃OH-TPSR and CH₃OH-H₂O-TPSR were respectively investigated in a quartz

micro-reactor with an inner diameter of 6 mm. 100 mg passivated molybdenum carbide based catalyst was loaded in the reactor. 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, and then the temperature was raised to 700 °C with a heating rate of 1°C/min under Ar flow (50 cm³/min), and remained at 700 °C for 2 h in order to remove the adsorbents on the catalyst surface, and finally the temperature was decreased to room temperature under Ar flow. TPSR was performed in 13% CH₃OH-Ar (50 cm³/min) or 13% CH₃OH-13% H₂O-Ar (50 cm³/min) gas flow, in which the reaction temperature was increased from the room temperature (RT) to 700 °C with a heating rate of 5 °C/min. The signal intensities of CO₂ (m/e=44), CO (m/e=28), CH₄ (m/e=15), H₂ (m/e=2), H₂O (m/e=18), CH₃OH (m/e=31), HCOOH (m/e=46) and HCOOCH₃ (m/e=60) were on-line monitored by mass spectroscopy (MS, BEL Mass, BEL Japan Inc.).

3. Results and discussion

3.1 Methanol decomposition pathway over β -Mo₂C surface

Fig.1 CH₃OH-TPSR profiles over β -Mo₂C catalyst surface.

As stated above, in this study, TPSR is used to study the interaction between the reactants and catalyst surface. As shown in **Fig.1 (a)**, for CH₃OH-TPSR over β -Mo₂C surface, one can see that the decomposition of CH₃OH starts at 205 °C, which is consistence with the result obtained in our previous study [11,12]. When the reaction temperature is increased to 420 °C, the methanol signal increases. This might be due to the coke formation from methanol dissociation at high temperature. Meanwhile, from **Fig.1 (b)**, one can see that small amounts of two intermediate species, formic acid (HCOOH) and methyl formate (HCOOCH₃), appear along with H₂, CH₄, CO₂ and CO. As reported by other researchers [28-32], for other kinds of catalysts, the surface of catalyst is always dominated by methoxy and formate groups, and methyl formate usually appears in the product spectrum at high methanol surplus. Moreover, the formed methyl formate can be further converted to formic acid (HCOOH), which can finally decompose to H₂ and CO₂. In this study, the results also indicate that the decomposition of methanol over β -Mo₂C catalyst surface also follows the methyl-formate (HCOOCH₃) intermediate species pathway, i.e., pathway II as indicated in eqs. (3)- (5). Here, the formation of formic acid can be attributed to the conversion of dioxymethylene (H₂COO) as following [30]:

Meanwhile, the formation of CO_2 and CH_4 in the outlet might be due to HCOOCH_3 decomposition, and another possibility is that CH_4 may be derived from *methanation*, from the generated CO_2 and H_2 (eq. (11)):

It should be noted that the temperature for CO formation is higher than that for other species. As such, CO may be also derived from the decomposition of HCOOCH_3 (eq. (12)), but it will compete with the formation of CO_2 and CH_4 (eq. (10)). The other possible way for CO formation may be from the reverse water gas shift reaction (eq. (13)).

3.2 SRM pathway over $\beta\text{-Mo}_2\text{C}$ surface

Fig.2 shows $\text{CH}_3\text{OH-H}_2\text{O-TPSR}$ profiles over $\beta\text{-Mo}_2\text{C}$ catalyst surface. One can see that the reaction starts at 210 °C, and with the reaction temperature increased to 410 °C, the signal of H_2O decreases sharply while that of H_2 increases, indicating that the $\beta\text{-Mo}_2\text{C}$

surface could be oxidized by water (eq. (14)) at high reaction temperatures ($> 400\text{ }^{\circ}\text{C}$).

Compared with **Fig.1**, one can find that the intensity of CO signal decreases by the addition of H_2O . This is due to WGS reaction (eq. (2)) occurring in the $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ system. On the other hand, based on **Fig.2 (b)**, it is obvious that only trace of HCOOCH_3 can be detected, but the intermediate species of HCOOH still remains relatively high. In contrast, as shown in **Fig.1(b)**, methyl formate can be easily detected in the case without steam. As such, it can be concluded that HCOOCH_3 can react with H_2O to generate HCOOH (eq. (4)). Here, methyl formate should be also the intermediate of methanol decomposition on the surface of catalyst, which could further react with H_2O in the reaction system. Therefore, for SRM reaction over $\beta\text{-Mo}_2\text{C}$ catalyst surface, methyl formate (HCOOCH_3) should be the intermediate species.

Fig.2 $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ -TPSR profiles over $\beta\text{-Mo}_2\text{C}$ catalyst surface.

3.3 SRM reaction pathway over metal-modified molybdenum carbide surface

Fig.3 CH₃OH-TPSR profiles over Ni-Mo₂C (1.6) catalyst surface.

Fig.4 CH₃OH-H₂O-TPSR profiles over Ni-Mo₂C (1.6) catalyst surface.

If compare **Fig.3** with **Fig. 1**, one can find that the start temperature for the methanol decomposition is decreased by modification of Ni on the molybdenum carbide catalyst surface, indicating that the dissociative adsorption of methanol molecule is enhanced by the loaded Ni metal, which is generally considered to be benefit for the hydrocarbon reforming reaction. On the other hand, if compare **Fig.4** with **Fig.2**, one can see that the SRM reaction also starts at lower temperature (175 °C) due to the modification of Ni on the molybdenum carbide catalyst surface. With the reaction temperature increased to high range (> 400 °C), there is no obvious decrease of water signal (**Fig.4 (a)**). Also, correlated with β -Mo₂C-TPSR results, it can be found that the intermediate species on Ni-Mo₂C (1.6) catalyst surface is almost the same as that on pure β -Mo₂C surface. Therefore, the SRM reaction pathway on Ni-Mo₂C (1.6) is similar to that on the pure β -Mo₂C catalyst surface.

Fig.5 Schematic illustration of SRM reaction on catalyst surfaces ((A) and (B): β -Mo₂C surface; (C) and (D): Ni-modified Mo₂C surface) *: adsorbed species.

Fig.6 Catalytic oxidation-reduction cycle over Ni-Mo₂C catalyst.

Based on our previous studies [11-14], the oxidation of Mo₂C with oxygen species is originated from the dissociation of H₂O on β -Mo₂C or metal-modified molybdenum carbide catalysts, and as such, the surface reaction mechanism can be assumed as illustrated in **Fig. 5**. As shown in **Fig.5** (A) and (B), the rates of water adsorption and activation over β -Mo₂C catalyst surface are fast due to the reduced property of the molybdenum carbide surface. It should be noted that water serves as the oxide reactant here. In contrast, methanol is a relatively more reduced reactant and thus, the rates of methanol adsorption and dissociation should be much slower than water dissociation on the molybdenum carbide surface. However, the reaction pathway during SRM reaction is still ambiguous. As shown in **Fig.5** (B), with the time on stream, the molybdenum carbide surface can be gradually oxidized by oxygen species from the dissociation of water molecule. Moreover, it should be noted that the surface oxygen species could hinder other reactant adsorption. However, when the metal such as Ni is loaded on the molybdenum carbide surface, Ni could accelerate the rate of methanol activation and dissociation and as a result, more reduced species i.e. CO* could be produced from methanol and the surface oxygen species generated from water could be reduced by CO* species, as shown

in **Fig.5** (C) and (D). In conclusions, the deactivation of β -Mo₂C catalyst during SRM reaction is due to that the reaction rate of water activation is faster than methanol dissociation. As such, the oxidized Mo species cannot be reduced by methanol. When metal such as Ni is loaded on the molybdenum carbide surface with suitable amount, the balance of oxidation and reduction rates can be achieved and an oxidation-reduction cycle shown in **Fig.6** could be established over it. That is why the activity and stability of molybdenum carbide are greatly promoted by doping some metals with proper amount.

Fig.7 CH₃OH-TPSR profiles over Cu-Mo₂C (10) catalyst surface.

Fig.8 CH₃OH-H₂O-TPSR profiles over Cu-Mo₂C (10) catalyst surface.

Figs. 7 and 8 shows CH₃OH-TPSR and CH₃OH-H₂O-TPSR profiles over Cu-Mo₂C (10) catalyst surface, respectively. One can see that the activation of methanol molecule over Cu modified molybdenum carbide catalyst starts at a temperature as low as 90 °C. Compared with the pure β -Mo₂C catalyst, the activation temperature is greatly decreased. This indicates that the dissociative adsorption of methanol molecule can be greatly enhanced by the modification of Cu. Here, methanol molecule is considered to be mainly

adsorbed on the Cu metal surface. On the other hand, as shown in **Fig.7(b)**, one can find that the methanol dissociation on the Cu-Mo_xC_y (10) catalyst surface has two stages: one is at the reaction temperature range of 90-180 °C; the other is the reaction temperature over 180 °C. Especially, in the first stage, only HCOOH intermediate species appears, indicating that the activation of methanol molecule can be enhanced at lower temperature due to the modification of Cu species. Based on our previous study [13], the high activity and stability should be attributed to the formation of Cu^I species on the catalyst surface, which was detected by XPS analysis and the Auger Cu LMM spectra.

Similar as shown in **Fig. 4**, the results in **Fig.8** indicate that the water signal has no significant decrease. As mentioned above, the oxidation-reduction cycle shown in **Fig.6** should be also existed on the Cu modified molybdenum carbide catalyst surface.

Fig.9 CH₃OH-TPSR profiles over Pt-Mo₂C (1.6) catalyst surface.

Fig.10 CH₃OH-H₂O-TPSR profiles over Pt-Mo₂C (1.6) catalyst surface.

Figs. 9 and 10 shows CH₃OH-TPSR and CH₃OH-H₂O-TPSR profiles over Pt-Mo_xC_y (1.6) catalyst surface, respectively. It is obvious that the methanol activation temperature

is decreased more (50 °C). This indicates that the methanol molecule can be dissociated on Pt modified molybdenum carbide catalyst even at near the room temperature. Our previous study also showed that Pt-Mo_xC_y (1.6) catalyst has high activity and stability for SRM reaction at low temperatures [14] and the results are consistence with those shown here. On the other hand, as shown in **Fig.10 (a)**, the water signal also has no significant decrease. This also indicates that the resistance of oxidation of molybdenum carbide has been enhanced by the modification of Pt. Furthermore, one can see that for the SRM reaction over Pt modified molybdenum carbide catalyst, methyl formate (HCOOCH₃) is also the intermediate species.

3.4 Reaction pathway

Table 1 The main features of β -Mo₂C, Ni-Mo₂C (1.6), Cu-Mo₂C (10) and

Pt-Mo₂C(1.6)

The main features of above catalysts can be summarized in Table 1. It shows that the metal modified Mo₂C catalysts have obviously improved when compared with the common β -Mo₂C in catalytic activity and stability. Based on these TPSR results, one can conclude that the reaction pathway over molybdenum carbide and metal modified

molybdenum carbide catalyst surface is the pathway II, i.e., through the methyl formate (HCOOCH_3) intermediate species route. However, the methanol dissociation on the $\text{Cu-Mo}_x\text{C}_y$ (10) catalyst surface has two stages: one is at the reaction temperature range of 90-180 °C; the other is the reaction temperature over 180 °C. Therefore, the reaction pathway can be summarized in the following 2 figures:

- (i) SRM reaction pathway (formic acid (HCOOH) intermediate pathway) over $\text{Cu-Mo}_x\text{C}_y$ (10) in the temperature range of 90-180 °C (**Fig.11**):

Fig.11 Schematic diagram of SRM reaction pathway over $\text{Cu-Mo}_x\text{C}_y$ (10) catalyst surface (90-180 °C).

- (ii) SRM reaction pathway (methyl formate (HCOOCH_3) intermediate pathway) over $\beta\text{-Mo}_2\text{C}$, $\text{Ni-Mo}_2\text{C}$ (1.6), $\text{Pt-Mo}_x\text{C}_y$ (1.6) and $\text{Cu-Mo}_x\text{C}_y$ (10) at a reaction temperature over 180 °C (**Fig.12**)

Fig.12 Schematic diagram of SRM reaction pathway over $\beta\text{-Mo}_2\text{C}$, $\text{Ni-Mo}_2\text{C}$ (1.6), $\text{Cu-Mo}_x\text{C}_y$ (10) and $\text{Pt-Mo}_x\text{C}_y$ (1.6) catalyst surfaces (>180 °C).

4. Conclusions

In this study, to understand the SRM reaction pathway over various metal-modified molybdenum carbide surfaces, reaction intermediate species generated during SRM reaction over the catalyst are investigated by using a temperature programmed surface reaction (TPSR) approach, in which a mass spectroscopy is applied to detect the products on-line. It is found that the reaction temperature affects the formation of different intermediate species over different catalysts. At the temperature lower than 180 °C, SRM reaction proceeds over Cu modified molybdenum carbide surface through formic acid (HCOOH) intermediate pathway, but at the temperature over 180 °C, the reactions over pure β -Mo₂C, Ni, Cu and Pt modified molybdenum carbide surfaces proceed through methyl-formate (HCOOCH₃) intermediate pathway. It is expected that these findings can help us understanding the mechanism on SRM reaction over molybdenum carbide based catalysts.

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Figure captions

Fig.1 CH₃OH-TPSR profiles over β -Mo₂C catalyst surface.

Fig.2 CH₃OH-H₂O-TPSR profiles over β -Mo₂C catalyst surface.

Fig.3 CH₃OH-TPSR profiles over Ni-Mo₂C (1.6) catalyst surface.

Fig.4 CH₃OH-H₂O-TPSR profiles over Ni-Mo₂C (1.6) catalyst surface.

Fig.5 Schematic illustration of SRM reaction on catalyst surfaces ((A) and (B): β -Mo₂C surface; (C) and (D): Ni-modified Mo₂C surface) *: adsorbed species.

Fig.6 Catalytic oxidation-reduction cycle over Ni-Mo₂C catalyst.

Fig.7 CH₃OH-TPSR profiles over Cu-Mo₂C (10) catalyst surface.

Fig.8 CH₃OH-H₂O-TPSR profiles over Cu-Mo₂C (10) catalyst surface.

Fig.9 CH₃OH-TPSR profiles over Pt-Mo₂C (1.6) catalyst surface.

Fig.10 CH₃OH-H₂O-TPSR profiles over Pt-Mo₂C (1.6) catalyst surface.

Fig.11 Schematic diagram of SRM reaction pathway over Cu-Mo_xC_y (10) catalyst surface (90-180 °C).c

Fig.12. Schematic diagram of SRM reaction pathway over β -Mo₂C, Ni-Mo₂C (1.6), Cu-Mo_xC_y (10) and Pt-Mo_xC_y (1.6) catalyst surfaces (>180 °C).

Table caption

Table 1 The main features of β -Mo₂C, Ni-Mo₂C (1.6), Cu-Mo₂C (10) and Pt-Mo₂C(1.6)

Table 1

	β -Mo ₂ C	Ni-Mo ₂ C (1.6)	Cu-Mo ₂ C (10)	Pt-Mo ₂ C (1.6)
Metal oxidation states		Ni ^{0*}	Cu ^{0*}	Pt ^{0*}
CH₃OH conversion(200 °C)**	3%	17%	64%	99%
Stability (h)	9	12	11	50
CH₃OH- TPSR reaction start temperature (°C)	205	175	90	120
CH₃OH-H₂O-TPSR reaction start temperature (°C)	210	175	180	150
Reaction intermediates	Formic acid and methyl formate	Formic acid and methyl formate	Methyl formate	Methyl formate

* Before test the catalysts were regenerated under 15% CH₄/H₂ gas flow.

** References [11-13].

Fig.1

Fig.2

Fig.3

Fig.4

Fig.5

Fig.6

Fig.7

Fig.8

Fig.9

Fig.10

Fig.11

Fig.12

Graphical Abstract