Low-temperature steam reforming of methanol to produce hydrogen over various metal-doped molybdenum carbide catalysts

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ABSTRACT

Various transition metals (M = Pt, Fe, Co, and Ni) were selected to support on molybdenum carbides by in-situ carburization metal-doped molybdenum oxide (M-MoO_x) via temperature-programmed reaction (TPR) with a final temperature of 700 °C in a reaction gas mixture of 20% CH₄/H₂. XRD analysis results indicated that β-Mo₂C phase was formed in the case of Fe, Co, or Ni doping while α-Mo₂C phase was appeared with the β-MoC_{1-x} phase in the case of Pt doping. With the increase in Pt doping amount, more α-MoC_{1-x} phase was produced. As-prepared metal doped molybdenum carbides were investigated as alternative catalysts for the steam reforming of methanol. Comparing with the undoped molybdenum carbide such as β-Mo₂C, metal-doped one showed higher methanol conversion and hydrogen yield. It is found that Pt doped molybdenum carbide had the highest catalytic activity and selectivity among the prepared catalysts and methanol conversion reached 100% even at a temperature as low as 200 °C, and remained a long-time stability with a stable methanol conversion.

Keywords: Steam reforming of methanol; Molybdenum carbide; TPR method; Transition metal; Hydrogen production.

1. Introduction

In order to solve environmental problems, development of clean energy technology is becoming more and more important from now. Hydrogen is considered one of ideal and clean energy carriers. However, since it is difficult to store compressed hydrogen safely and economically, production of hydrogen using on-board reformers by the steam reforming of hydrogen carrier is required. Among the different liquid hydrogen carriers available, methanol has the greatest potential when comparing with other hydrocarbon fuels because it has many advantages: it is a liquid fuel at ambient condition with a low activation temperature, a high hydrogen-to-carbon ratio, but coke (without C–C bond) and sulfur free (no sulfur) [1-3]. Hydrogen can be produced from methanol by steam reforming, auto-thermal reforming, partial oxidation or even decomposition ways. Among these methods, the steam reforming of methanol (SRM) is considered the best way due to its high hydrogen yield. The SRM reaction can be expressed as:

In the case of using stoichiometric feed, only H₂ and CO₂ will be produced from the steam reforming of methanol theoretically. However, other gases such as methane and carbon monoxide are usually produced together with H₂ and CO₂ in the product stream, relying on the types of catalysts and the reaction conditions due to the following reactions [4-6].

Various catalysts have been developed for SRM reaction. Cu- and Pd-based catalysts are generally used because of their low CO production [4]. It is found that addition of Zn into the Cu-based catalyst can improve the Cu dispersion[5]. However, Cu-based catalysts have poor thermal stability when the reaction temperatures are over 300 °C due to the sintering of Cu, and they also are easily deactivated by H₂S contaminates and chloride in the reactant stream[6, 7]. Noble metal based SRM catalysts such as Pd/CeO₂, Pd/ZnO, Pd/Ga₂O₃, Pd/SBA-15, Au/Ce_{1-x}Zr_xO₂, Au/CeO₂, and Pd/Ga₂O₃ have also widely investigated and showed high activities at a temperature between 200-400 °C[8-14]. Recently, transition metal carbides such as tungsten carbide and molybdenum carbide have been attracted much attention because they show catalytic activities similar to those of noble metals in various reactions such as hydrogenation reactions, hydrocarbon isomerization, and methane and alcohol reforming [15-18]. Széchenyi and Solymosi prepared Mo₂C by the carburization of MoO₃ with C₂H₆/H₂ mixture and found that it is an effective catalyst for the decomposition of ethanol and methanol with a high thermal stability[19]. When Mo₂C was supported on carbon Norit, carbon nanotube, ZrO₂ and Al₂O₃, a higher catalytic activity than an unsupported catalyst was identified [1, 20-22]. Furthermore, when carbides are served as supports, they could stabilize the formation of small, flat metal

particles, leading to unique catalytic properties from the synergistic interaction of admetal particles and carbide substrates[23]. For instances, Lewandowski et al. dispersed Pt on the molybdenum carbide for simultaneous hydrodenitrogenation and hydrodesulfurization and found that the catalytic activity and stability were greatly enhanced when compared with the pure, non-modified one [24]. Griboval-Constant et al. supported Ru and Co on the molybdenum carbide for Fischer-Tropsch synthesis and also found the promotion effects[25]. However, in these studies, it should be noted that the metal was in fact supported on the passivated surface of the molybdenum carbide (i.e., oxide surface), but not on the carbide surface. In order to synthesize and characterize metal-doped carbide materials where the metals interact directly with the native surfaces of carbides, Schweitzer et al., directly deposited Pt onto the carbide surface using aqueous wet impregnation method, avoiding exposure of the carbide surface to O₂. When this catalyst was applied for water gas shift reaction, they found that it had high activity for this reaction due to the strong metal-carbide interactions and uniform Pt particle dispersion on the carbide surface[26]. When it was used for the SRM in the presence of 5ppm H₂S, a higher degree of tolerance to sulfur during SRM was found[27]. However, this method is very complex, and it cannot be used in practical process.

In the present study, a facile method was developed to support various metals on molybdenum carbide by in-situ carburization metal-loading molybdenum oxide (M-MoO_x) via temperature-programmed reaction (TPR) with a final temperature of

700 °C in a reaction gas mixture of 20% CH₄/H₂. The prepared catalysts were characterized using X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) surface area analyzer, Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) and applied for the SRM at different temperatures. The effects of Pt doping amount, weight hourly space velocity (WHSV) on the methanol conversion, hydrogen yield and selectivity were investigated. A long-time stability of as-prepared Pt-doped molybdenum carbide was also tested at different temperatures.

2. Experimental

For preparation of metal doped molybdenum oxide (M-MoO_x) (M: Pt, Fe, Co, and Ni), Firstly, aqueous solutions of (NH₄)₆Mo₇O₂₄·4H₂O mixed with H₂PtCl₆·6H₂O, Fe(NO₃)₃·9H₂O, Co(NO₃)₂·6H₂O, Ni(NO₃)₂·6H₂O, respectively, were stirred at 80 °C for 4 h, and then the resultant slurry was filtered out and dried at 110 °C for 12 h and finally calcined at 500 °C for 4 h in air. Carburization of M-MoO_x and the SRM reaction were carried out in the same fixed-bed quartz micro-reactor with an inner diameter of 8 mm. M-MoO_x powder was placed on a porous quartz plate in the micro-reactor, and then carburized in CH₄/H₂ (20 vol% CH₄) flow to M_xMo_yC with a successive temperature-programmed reaction (TPR) process [28,29]: the carburization temperature was raised from the room temperature (RT) to 300 °C in 1 h, and then increased to 700 °C at a rate of 1 °C /min, and subsequently kept at 700 °C for 2 h. As-obtained material was cooled down to RT in the CH₄/H₂ flow and finally passivated

in 1%O₂/Ar for 12 h. In this study, various metal doped molybdenum carbide with a same stoichiometric composition of M_{1.6}Mo_{98.4}C were prepared. Pt doped molybdenum carbides with stoichiometric compositions of Pt_{1.2}Mo_{98.8}C, Pt_{0.8}Mo_{99.2}C and Pt_{0.4}Mo_{99.6}C were also prepared. For comparison, MoO₃ powder was obtained by calcinations of (NH₄)₆Mo₇O₂₄·4H₂O at 500 °C for 4 h in air and then also carburized using the same method as the above to get β-Mo₂C catalyst.

The crystal structures of the catalysts before and after reactions were determined by X-ray diffraction (XRD 610, Shimadzu, Japan). The radiation used was CuKα and the operating potential was 30 KV, current 30 mA, and the scanning rate 4°/min. BET surface areas were measure at 77 K using a Bel-sorp 28SA automatic absorption instrument. The microstructure and morphology were characterized with a SEM (S-800, Hitachi, Japan). TEM images were obtained using a JEM-2100F transmission electron microscope JEOL operating at 200kV.

Catalytic performances of as-prepared pure molybdenum carbide and the metal loaded molybdenum carbide for the SRM were evaluated in the same 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 to reduce the surface oxide. The total amount of the catalyst used for the steam reforming of methanol was approximately 0.4 g. Two WHSVs, i.e., 9000 and 18000 cm³ g⁻¹ h⁻¹ were selected. Methanol and water mixture with a mole ratio of 1:1 was injected into the reactor with a syringe pump. It was vaporized in a pre-heater containing a ZrO₂ beads and carried by Ar gas flow. A cold trap was set at the

exit of the reactor in order to remove unconverted liquid hydrocarbons and steam prior to the analysis of the gas compositions in the product. The gases produced were analyzed using a gas chromatograph (Agilent 7890A GC system).

The performances of the as-prepared catalysts were characterized in terms of methanol conversion and hydrogen yield. The methanol conversion was defined as the molar ratio of the gaseous carbon compounds (CH_4 , CO , and CO_2) in the product stream to the feed methanol. The hydrogen selectivity was defined as the mole ratio of the produced hydrogen to the theoretical amount that could be produced from the feed methanol based on eq.(1). The mole fraction of a product component was defined as the mole ratio of this specific product to the total gaseous products.

3. Results and discussion

3.1. Characterization of fresh catalysts

Fig.1 shows the XRD patterns of $\beta\text{-Mo}_2\text{C}$ and various metal doped molybdenum carbide catalysts. The peaks at 2θ of 34.8° , 38.4° , 39.8° , 52.5° , 61.9° and 74.9° are attributed to the presence of hexagonal $\beta\text{-Mo}_2\text{C}$ (hcp crystal structure). The peaks at 2θ of 37.1° , 42.8° , 62.4° , 74.5° and 78.4° are attributed to $\alpha\text{-MoC}_{1-x}$ (fcc crystal structure). No peak corresponding to metal and its oxide was found for Fe, Co, and Ni doped catalysts, but a small peak corresponding to Pt was found in Pt doped catalyst with the increase in Pt doping amount (Fig.1b). Notably, as shown in Fig.1(a), using the present method, when Fe, Co, and Ni precursors were applied, $\beta\text{-Mo}_2\text{C}$ phase was formed in the

final catalysts during the temperature programmed reactions (TPRe) process. However, the doping of Pt resulted in the α -MoC_{1-x} phase appeared with β -Mo₂C phase, and with the increase in Pt doping amount, the peaks corresponding to α -MoC_{1-x} phase became more obvious, suggesting more α -MoC_{1-x} phase produced in the final catalyst. In general, the direct carburization of MoO₃ with CH₄/H₂ produces β -Mo₂C, which is a thermodynamically stable phase under the preparation conditions, but the carbide obtained via nitride (fcc γ -Mo₂N, produced from the TPRe of MoO₃ with NH₃) always has the metastable fcc α -MoC_{1-x} phase[30]. Jung et al. investigated the effect of various transition metals on the solid-state transformation of MoO₃ to molybdenum carbides in the CH₄/H₂ gas flow, and also found that the doping of Co or Cu resulted in the formation of hexagonal β -Mo₂C as in the absence of any transition metal while the doping of Pt or Pd produced cubic α -MoC_{1-x} phase[31]. It was proposed that the loading of Pt or Pd to MoO₃ could reduce the initial reduction temperature and the solid-transformation process become a topotactic transformation through a MoO_xC_y intermediate phase, leading to the formation of the metastable α -MoC_{1-x} phase. However, loading of some other transition metals such as Fe, Co and Ni in this study, MoO₂ and other suboxides other than MoO_xC_y could be formed as solid intermediates during the carburization, and in this case, two consecutive processes occurred: the reduction of MoO₃ to MoO₂ by H₂ at a relatively low temperature without involving CH₄, followed by the simultaneous further reduction and carburization of the intermediate MoO₂ to molybdenum carbide with a nontopotactic transformation route,

resulting in the formation of β -Mo₂C phase[30,31]. SEM images of β -Mo₂C, Pt_{1.6}Mo_{98.4}O, and Pt_{1.6}Mo_{98.4}C are shown in Figs.2 (a)-(c). As shown in Fig. 2(b), the morphology of MoO₃ was in platelet form. After carburization, the morphology of β -Mo₂C (Fig.2(a)) changed to agglomerated isotropic particles by breaking the platelet, and was completely different from the morphology of its parent MoO₃, indicating that the nontopotatic transformation was taken place during the carburization process. In the case of Pt_{1.6}Mo_{98.4}C, however, the morphology of some molybdenum carbides kept platelet form as their parent MoO₃ (Fig.2(c)), indicating that the topotatic transformation occurred during the carburization process. However, from the Fig. 2c, it should be noted that some agglomerated isotropic particles also existed, implying that the nontopotatic transformation also occurred during the carburization process in the presence of Pt. Insets of Figs 2(b) and (c) show TEM images of Pt_{1.6}Mo_{98.4}O and Pt_{1.6}Mo_{98.4}C. It is found that Pt particle size (ca. 13 nm) on the Pt_{1.6}Mo_{98.4}C catalyst (inset of Fig. 2(c)) maintained almost unchanged when compared with that on the surface of Pt_{1.6}Mo_{98.4}O (inset of Fig. 2(b)). It is possible that a strong metal-support interaction (SMSI) between the Pt and Mo_xC_y could trap the Pt particles, and prevent it to grow up.

BET surface area (S_{BET}) of the pure Mo₂C and metal modified molybdenum carbide catalysts are summarized in Table 1. One can see that Pt modified sample had the highest BET surface area (40 m²/g), approximately 4 times higher than the pure molybdenum carbide (10 m²/g). Comparing to the pure Mo₂C, the BET surface area

increased when metal was doped. This increase in surface area might be attributed to the lower temperature reduction of MoO_3 after metal doping [29, 31]. In general, the particle size should be determined by the mobility of the metal atoms, thus, low reduction temperature could limit the mobility and lead to smaller particles with high surface areas.

3.2. Performances of various metal doped catalysts

Fig.3(a) shows the effect of reaction temperature on methanol conversions for the SRMs over as-prepared $\text{M}_{1.6}\text{Mo}_{0.4}\text{C}$ ($\text{M}=\text{Fe}, \text{Co}, \text{Ni}$ and Pt) and $\beta\text{-Mo}_2\text{C}$ without metal doping under a WHSV of $9000 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$ and steam-to-carbon molar ratio of one. Since the SRM reaction is endothermic reaction which is generally more favorable at high temperatures, the methanol conversion increases with the increase in reaction temperature. Compared with the undoped $\beta\text{-Mo}_2\text{C}$, the metal doped catalysts showed higher conversion due to the synergistic interaction of the doped metal particles and the carbide substrate. Furthermore, Pt doped molybdenum carbide catalyst exhibited higher catalytic activity than other metal doped ones, and the methanol conversion reached 100% at a reaction temperature as low as 200°C at the beginning of reaction. However, for Fe, Co, and Ni doped catalysts, the similar conversion can be only found at a temperature over 300°C or higher. Also, it should be noted that the methanol conversion reached 60 % for $\text{Pt}_{1.6}\text{Mo}_{0.4}\text{C}$ catalyst even at a reaction temperature of 150°C , suggesting that Pt doped molybdenum carbide is a perspective catalyst for methanol

conversion at low temperatures. Fig.3(b) shows effect of Pt doping amount on the methanol conversion with the increase in temperature. The catalytic activity of $\text{Pt}_{0.4}\text{Mo}_{98.4}\text{C}$ decreased to some extent at a reaction temperature below 300 °C, but $\text{Pt}_{0.8}\text{Mo}_{99.2}\text{C}$ and $\text{Pt}_{1.2}\text{Mo}_{98.8}\text{C}$ showed a similar catalytic activity as that of $\text{Pt}_{1.6}\text{Mo}_{98.4}\text{C}$. It suggested that Pt doping amount could be reduced for a practical catalyst.

Fig.4 shows product compositions for the SRM over $\beta\text{-Mo}_2\text{C}$ and various metal doped molybdenum carbide catalysts at the same operation conditions as those in Fig.3. One can see that H_2 and CO_2 were the main components in the gas products, together with a small amount of CO and CH_4 . In this study, no other products such as dimethyl ether, methyl formate or ethane were detected from the SRM over any of the catalysts tested. It should be noted that the concentration of CO in the product was below 5 % for metal (Fe, Co, Ni, Pt) modified carbide catalysts while the CO content was over 10% at 400 °C, indicating that metal doping enhanced water gas shift (WGS, Eq.(3)) reaction over the molybdenum carbide surface. Several researches on WGS reaction also identified it [33, 34]. The WGS is a critical and important step in the removal of CO from reformat and often accompanies with the steam reforming reactions for the production of H_2 . CO is a poison for fuel cell catalysts and has to be removed or converted in a practical reforming process for fuel cell use. Therefore, it is meaningful to develop molybdenum carbide based catalysts for the SRM, WGS, and others for H_2 production.

CH_4 is another unwanted byproduct for the present study. CH_4 compositions in the

products as shown in Fig.4 were summarized in Fig.5. Compared with metal doped molybdenum carbide, it is obvious that more CH_4 was generated from the SRM over undoped $\beta\text{-Mo}_2\text{C}$ catalyst with the increase in reaction temperature, and the concentration was raised to approximately 13 % at 350 °C. Theoretically, the final H_2 percentage in the product should be the result of the competition among the SRM (Eq.(1)), WGS (Eq.(3)) and methanation (Eq.(4)) reactions. 1 mol methane production could result in a loss of 4 mol hydrogen. Therefore, it is expected that the methanation reaction can be hindered so that more hydrogen is extracted from steam as well as methanol in the SRM process. As indicated in Figs. 3 and 4, the methanation reaction was obviously hindered by the doping of metal. Especially, it should be noted that more hydrogen but less CH_4 were produced over Pt doped molybdenum carbide even at high reaction temperatures, indicating that the methanation reaction could be effectively hindered by the addition of Pt on molybdenum carbide.

Fig.6 shows effects of WHSV on the methanol conversion, H_2 selectivity and product distribution for the SRM over $\text{Pt}_{1.6}\text{Mo}_{98.4}\text{C}$ catalyst at different reaction temperatures. One can see that the increase of WHSV reduced the methanol conversion, especially at low reaction temperature. However, with the increase in WHSV, the concentration of CH_4 decreased while the H_2 selectivity increased, especially at high reaction temperatures.

3.3. Catalytic stability

Fig.7 shows the catalytic stability of β -Mo₂C and Pt_{1.6}Mo_{0.4}C used for the SRM at 200 and 400 °C for 20 h under a WHSV of 9000 cm³ g⁻¹ h⁻¹ and steam-to-carbon molar ratio of one. It is obvious that β -Mo₂C showed fast deactivation with the reaction time so that methanol conversion was lower than 10% after 10 h reaction even at a temperature of 400 °C. However, comparing with the β -Mo₂C, Pt_{1.6}Mo_{0.4}C showed a high long-term catalytic activity. One can see that the methanol conversion dropped from 100% to 60% during the initial reaction period (4 h) at a reaction temperature of 200 °C, but then maintained stable in the continuous reaction period, in which the methanol conversion kept at the 60% while the hydrogen production rate kept at 900 μ mol/g/min. The product distribution results also indicated that the product compositions were stable for 20 h, and the molar hydrogen composition kept at approximately 70 mol%. At a temperature of 400 °C, the reforming activity only suffered from an initial deactivation period where the methanol conversion dropped from 100% to 85%, and then a stable activity was maintained up to 20 h and the methanol conversion kept at approximately 85% with a hydrogen production rate of 1327 μ mol/g/min, suggesting that the stability of molybdenum carbide was greatly enhanced by addition of Pt. It should be noted that Pt was dispersed on Mo₂C and Mo₂C itself also provided active sites for the SRM. However, it is found that Mo₂C is easily deactivated in the SRM process as shown in Fig.7. It has been previously reported that the deactivation of Mo₂C is mainly caused by the oxidation of Mo₂C into inactive molybdenum dioxide[33], however, as shown in Fig.8, the XRD pattern of the spent

catalyst had no evidence of MoO_2 and other molybdenum oxide formation. Although the oxidation of the Mo_2C was not observed in the XRD pattern of spent catalyst, the surface oxidation should be possible for this reaction. The regeneration experiment for the used $\beta\text{-Mo}_2\text{C}$ indicated that the activity of deactivated catalyst recovered after it was treated at 15% CH_4/H_2 at 590 °C for 2 h. Furthermore, other reasons for the deactivation of Mo_2C such as coke formation on the catalyst surface should be also possible. On the other hand, as shown in Fig. 7, methanol conversion decreased only at the beginning of reaction for the Pt doped Mo_2C . According to the XRD results as shown in Figs. 1 and 8, it is found that the peak of $\beta\text{-Mo}_2\text{C}$ at 39.8° increased while the peak intensity of $\alpha\text{-MoC}_{1-x}$ decreased for the spent catalyst, suggesting that the unstable $\alpha\text{-MoC}_{1-x}$ transformed to the stable $\beta\text{-Mo}_2\text{C}$ during the beginning reaction time, resulting in the methanol conversion decreased to some extent. Furthermore, the surface area and catalytic activity of $\beta\text{-Mo}_2\text{C}$ are generally lower than those of $\alpha\text{-MoC}_{1-x}$. The decrease in methanol conversion at the beginning should be attributed to the phase transformation from $\alpha\text{-MoC}_{1-x}$ to $\beta\text{-Mo}_2\text{C}$. Other researchers also found the similar phenomena on the methane dry reforming over Mo_2C based catalysts[29, 35]. Other reasons for the conversion decreased such as coke formation on the catalyst surface should be also possible. Further study is necessary for this interesting phenomenon.

4. Conclusions

Steam reforming of methanol was performed on various transition metals ($\text{M} = \text{Pt}$,

Fe, Co, and Ni) doped on molybdenum carbides by in-situ carburization metal-doped molybdenum oxide (M-MoO_x) via temperature-programmed reaction (TPR) methods. Comparing with the undoped molybdenum carbide, metal-doped molybdenum carbides showed higher methanol conversion and hydrogen yield. Especially, Pt doped molybdenum carbide showed the highest catalytic activity and selectivity among the prepared metal doped catalysts and methanol conversion reached 100% even at a temperature as low as 200 °C, and remained a long-time stability at a temperature in the range of 200-400 °C. It is found that weight hourly space velocity had great effects on the methanol conversion and H₂ selectivity. XRD analysis results indicated that β -Mo₂C phase was formed in the case of Fe, Co, or Ni doping while α -Mo₂C_{1-x} phase was appeared with the β -Mo₂C phase in the case of Pt doping. With the increase in Pt doping amount, more α -Mo₂C_{1-x} phase was produced.

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Figure captions

Fig.1 (a) XRD patterns of metal doped molybdenum carbide catalysts; (b) XRD patterns of Pt doped molybdenum carbide with different doping amount

Fig.2 SEM morphology of (a) Mo_2C , (b) $\text{Pt}_{1.6}\text{Mo}_{98.4}\text{O}$, (c) $\text{Pt}_{1.6}\text{Mo}_{98.4}\text{C}$ with a magnification of 10000. Inserts in (b) and (c): Bright-field TEM photographs of Pt.

Fig.3 (a) Catalytic performances of metal doped molybdenum carbide for SRM reaction at different temperatures; (b) Catalytic performances of Pt doped molybdenum carbide with different doping amount

Fig.4 Product compositions for SRM reaction over as-prepared catalysts

(a) $\beta\text{-Mo}_2\text{C}$; (b) $\text{Fe}_{1.6}\text{Mo}_{98.4}\text{C}$; (c) $\text{Co}_{1.6}\text{Mo}_{98.4}\text{C}$; (d) $\text{Ni}_{1.6}\text{Mo}_{98.4}\text{C}$; (e) $\text{Pt}_{1.6}\text{Mo}_{98.4}\text{C}$; (f) $\text{Pt}_{0.8}\text{Mo}_{99.2}\text{C}$.

Fig.5 CH_4 composition in the product of SRM reaction over as-prepared catalysts showed in Fig.4.

Fig.6 (a) Effect of weight hourly space velocity on methanol conversion and H_2 selectivity; (b) Effect of weight hourly space velocity on product compositions

Fig.7 Time-on-stream testing of $\beta\text{-Mo}_2\text{C}$ and $\text{Pt}_{1.6}\text{Mo}_{98.4}\text{C}$ catalysts for SRM reaction at 200 and 400 °C

Fig.8 XRD patterns of the spent catalysts after the experiments shown in Fig.7

(a) $\beta\text{-Mo}_2\text{C}$ -400 °C; (b) $\text{Pt}_{1.6}\text{Mo}_{98.4}\text{C}$ -200 °C; (c) $\text{Pt}_{1.6}\text{Mo}_{98.4}\text{C}$ -400 °C

Table 1 BET surface areas of β -Mo₂C; Fe_{1.6}Mo_{98.4}C; Co_{1.6}Mo_{98.4}C; Ni_{1.6}Mo_{98.4}C; Pt_{1.6}Mo_{98.4}C

Catalysts	BET(m ² /g)	Catalysts	BET(m ² /g)
Mo ₂ C	10.2	Ni _{1.6} Mo _{98.4} C	19.3
Fe _{1.6} Mo _{98.4} C	18.3	Pt _{1.6} Mo _{98.4} C	40
Co _{1.6} Mo _{98.4} C	20.6		

Figure 1a

Figure 1b

Figure 2a

Figure 2b

Figure 2c

Figure 3a

Figure 3b

Figure 4a

Figure 4b

Figure 4c

Figure 4d

Figure 4e

Figure 4f

Figure 5

Figure 6a

Figure 6b

Figure 7a

Figure 7b

Figure 8