**Hydrogen production by steam reforming of biomass tar over biomass char
supported molybdenum carbide catalyst**

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23 **Abstract**

24 Catalytic steam reforming of tar derived from Japanese cedar pyrolysis was investigated over a
25 prepared biomass char supported molybdenum carbide (Mo₂C/BC) catalyst in a fixed-bed reactor.
26 Mo₂C/BC was prepared by in-situ solid state reaction, and characterized by XRD and SEM to
27 study the effects of carburization temperature and Mo loading amount on Mo₂C formation. The
28 results show that Mo₂C/BC catalyst was successfully prepared at a relatively low carburization
29 temperature of 800 °C and the initial Mo loading amount for the preparation of this catalyst
30 should be lower than 30 wt.%. The Mo₂C/BC showed a good catalytic activity for the steam
31 reforming of tar derived from biomass. In the case of Mo₂C/BC with a Mo loading of 20 wt.%,
32 the highest H₂ yield was obtained, which is about 5 times higher than that of non-catalytic test.
33 Mo₂C/BC could be a promising catalyst in steam gasification of biomass to remove tar and
34 produce H₂-rich gas.

35 **Keywords:** Biomass; Tar reforming; Molybdenum carbide; Biomass char; Catalytic activity.

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1. Introduction

Nowadays, energy and environmental issues are two common concerns that should be managed simultaneously. At present, although fossil fuels such as oil, coal and natural gas are the major energy sources for global energy requirement, they are finite and will be depleted eventually, and also the major cause for global warming due to the emission of greenhouse gas during combustion of fossil fuels. According to the two issues stated above, considerable efforts have been made to develop or find the alternative fuels that can solve both the mentioned problems. Hydrogen has been proposed as one of the most promising energy carriers in the future due to its cleanliness and high-energy yield. However, approximately 96% of hydrogen is produced from fossil fuels, mainly by steam reforming of natural gas. In such cases, a significant amount of CO₂ is released during the hydrogen production [1,2]. Biomass gasification is a promising way to produce hydrogen or synthesis gas, which is a high value gaseous product and can be applied in fuel cells for power generation or production of liquid fuels [3-7]. Biomass is renewable, abundant and carbon neutral. Nevertheless, the major problem of biomass gasification is the formation of tar, which is a complex mixture of aromatics and undesirable products. Tar can remain liquid at room temperature, causing plugging, fouling and corrosion in the equipment downstream [8-12]. Therefore, tar removal step from the syngas is imperative before syngas applications. There are several methods to reduce the tar content in raw fuel gas by

physical and chemical processes. Among them, catalytic steam reforming is a very attractive technique for tar removal since it can remove tar effectively and simultaneously convert tar into useful gaseous products (H_2 and CO) [13-16].

Many kinds of catalysts have been developed for catalytic conversion of tar. Noble metal catalysts such as Ru, Rh, and Pt showed high catalytic activity in the steam reforming of tar with high sulfur resistance and long term stability [17,18]. However, noble metals are expensive, making them not be used in the conventional process. Ni-based catalysts have been used extensively for biomass tar conversion because of their high tar destruction activity. However, the main limitation of nickel catalysts is the rapid deactivation, caused by carbon formation on the catalyst surface [19-21]. Moreover, other metal catalysts like Co, Fe, Zn, and Cu have also been investigated in steam reforming of tar and showed higher catalytic activity than Ni catalyst in some cases. Although other metal catalysts exhibit a good performance in steam reforming of tar, they are still deactivated easily by sulfur or high heavy tar content [1,22-24].

In recent years, molybdenum carbide (Mo_2C) has been reported to have high catalytic activity similar to precious metals in various reactions such as methanol reforming, hydrogenation reactions, water gas shift, and methane reforming [24-28]. Especially, the raw materials for synthesis of Mo_2C are abundant and inexpensive. Generally, metal carbide catalysts could be prepared through pyrolysis, self-propagating high temperature synthesis and direct carburization

at high temperature up to 2000 °C. However, these methods require very specialized high temperature equipment, gadget and facilities [29]. In order to reduce the production cost of such catalysts, several methods have been developed for the preparation of metal carbide at relatively low temperature. For instance, Mordenti et al. [30] have reported that the formation of Mo₂C phase at low temperature (1000 °C) was obtained by reaction between the transition metal oxide and high specific surface activated carbon. Chen et al. [31] studied the synthesis of Mo₂C which is covalently anchored to carbon supports, and found that active catalysts (Mo₂C) can be produced by solid-state reaction of original biomass (soybean) and ammonium molybdate at relatively low temperature (800 °C). In this work, we tried to use carbon in original biomass as the carbon source and find a simple preparation method to prepare Mo₂C based catalysts. Herein, Mo₂C/cedar char catalysts were prepared by in-situ solid state reaction. The obtained catalysts were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and BET surface area measurements, and then tested their catalytic activities for the steam reforming of tar derived from biomass pyrolysis. The effects of Mo loading amount and carburization temperature on the formation of molybdenum carbide and their catalytic activities were investigated and discussed.

2. Experimental

2.1. Materials and catalyst preparation

In this study, cedar wood (with particle size of 1.0-2.8 mm) was used as the carbon sources. It was dried in an oven at 105 °C before storage and further use. The water content of the dried cedar wood was 8.0 wt.%. The water-free compositions by weight percentage were C 48.8%, H 6.6%, O 43.0%, N 1.4%, and ash 0.6%. From XRF analysis, the main compositions in ash by weight percentage were CaO 50.68%, SO₃ 10.47%, SiO₂ 6.83%, P₂O₅ 6.45%, K₂O 4.01%, Fe₂O₃ 0.80% and SrO 0.04%. Ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄·4H₂O) was purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan) and used directly.

Biomass char supported Mo₂C (Mo₂C/BC) catalyst was prepared by the following procedures: (1) dried cedar was directly impregnated by wet impregnation method with an aqueous solution of ammonium heptamolybdate of appropriate concentration to load 5-30 wt.% on initial Mo basis; (2) the slurry was dried at 110 °C overnight; (3) the solid mixture was carburized in a vertical tube furnace with a 50 cm³/min Ar flow from room temperature (RT) to the desired temperatures and then held for 2 h. The carburization was performed at the temperature range of 600-800 °C. Ar was kept purging through the reactor when the reactor was cooled down to room temperature before storage and further use. To evaluate the effect of carburization temperature on the Mo₂C formation, ammonium heptamolybdate deposited dried cedar (initial Mo loading amount of 10 wt.%) was carburized at different carburization

temperatures of 600, 700 and 800 °C, separately. The samples were heated at rapid rate from room temperature to the final carburization temperature and held at that temperature for 2 h. For regeneration of the as-prepared Mo₂C/BC catalyst, the spent catalyst was re-carburized in Ar atmosphere at temperature of 800 and 900 °C, separately, using the same procedure as a carburization of Mo₂C/BC catalyst.

2.2. Characterization of catalyst

XRD analysis was conducted using a XRD 610 (Shimadzu, Japan) to determine the crystal structure of the as-prepared catalyst. The morphology of as-prepared catalyst was characterized using a SEM (SU6600, Hitachi) equipped with energy dispersive spectrometer (EDS). Catalyst surface areas and pore volumes were measured using BET sorption isotherm method (Quantachrome NOVA 4200e, USA)

2.3. Catalytic activity test

Catalytic activity in the steam reforming of tar was tested in a down-flow fixed-bed reactor with an internal diameter and a length of 18 and 350 mm, respectively. The experimental setup was described in details in our previous study [32]. 0.6 g of cedar powders and Mo₂C/BC catalyst with different amounts were introduced into the reactor and separated with a layer of

quartz wool. The height of catalyst bed was kept constant about 8 cm for all experiments. The reactions were carried out at atmospheric pressure. Reaction temperatures were chosen in the range of 550-750 °C. Heating rate was fixed at 20 °C/min. Water with a flow rate of 0.09 g/min was introduced using a peristaltic pump into a steam generator (250 °C) at first, and then was carried to the reactor by argon gas with a flow rate 50 cm³/min. The produced gases were passed through two cooling baths under 0 °C and a dry cylinder with CaCl₂ particles, and collected using a gas bag. The gas compositions were analyzed using an Agilent 7890A gas chromatograph system. The carbon content in the remained char was estimated by using Vario EL cube elemental analyzer. The heavy tars were collected in the bottle with acetone, and then the water and acetone were evaporated at 100 °C for 24 h in an oven, and the remained heavy tars were weighed.

For the catalytic system, the gas production yield (Y_{bio}) from the gasification of cedar and the catalytic steam reforming of tar derived from cedar was calculated as follow:

$$Y_{bio} = Y_{total} - Y_{cat} \quad (1)$$

where Y_{total} is the gas production yield in the catalytic system (consisting of the gas production yield from the gasification of cedar, the catalytic steam reforming of tar derived from cedar and the gasification of catalyst itself) while Y_{cat} is the gas production yield when catalyst itself was gasified at the same condition.

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149 3. Results and discussion

150 3.1. Characterization of the as-prepared molybdenum carbides

151 3.1.1. Effect of carburization temperature

152 As stated above, Mo₂C/BC catalysts were prepared by in-situ solid state reaction from dried
153 cedar and ammonium heptamolybdate. As shown in Fig. 1, it can be seen that at a low
154 carburization temperature, i.e., 600 °C, only molybdenum oxide (MoO₂) phase was observed. As
155 the temperature was increased to 700 °C, it is found that the signal of MoO₂ phase decreased and
156 the signal of Mo₂C began to appear. When the temperature was increased to 800 °C, the XRD
157 pattern shows the peaks of pure Mo₂C, indicating that Mo₂C was successfully prepared by in-situ
158 solid state reaction of dried cedar and ammonium heptamolybdate. All these results indicate that
159 the minimum carburization temperature for Mo₂C formation is 800 °C under the conditions
160 selected in this work.

161 According to the XRD results, as the Mo₂C formation pathway reported in literatures
162 [33,34], the carburization steps for Mo₂C/BC catalyst were illustrated in Scheme 1. Ammonium
163 heptamolybdate should be decomposed to MoO₃ (Mo⁶⁺) at the lower temperature step and then,
164 the generated MoO₃ (Mo⁶⁺) is continuously reduced to MoO₂ (Mo⁴⁺). Thereafter, MoO₂ (Mo⁴⁺) is
165 continuously reduced to metallic molybdenum and further transformed into Mo₂C at the high

carburization step. Especially, the use of dried biomass instead of pure carbon materials (such as biomass char) as the carbon source in this study could promote the Mo_2C formation and reduce the carburization temperature. This is due to the reducing gases such as CO and H_2 , which are produced during biomass pyrolysis. These can provide reduction atmosphere to reduce the molybdenum oxide, leading to the formation of Mo_2C more easily. Furthermore, carbon monoxide and methane are considered as reduction and carburizing gases, respectively, for metal carbide preparation [30]. For comparison, we had ever used cedar char as the carbon source, and found that the carburization temperature should be increased to over $900\text{ }^\circ\text{C}$ in order to obtain pure Mo_2C supported on char (as shown in Fig. 2).

3.1.2. Effect of Mo loading amount

In order to investigate the effect of Mo loading amount on the Mo_2C formation, dried cedar was impregnated with an aqueous solution of ammonium heptamolybdate with different contents in the range of 5-30 wt.% on Mo basis. The samples were carburized at a temperature of $800\text{ }^\circ\text{C}$ for 2 h and characterized by XRD. Fig. 3 shows the XRD patterns of carburized products prepared under different Mo loading amounts. It is found that pure Mo_2C phase can be obtained at initial Mo loading amount below 30 wt.%, and the signals of Mo_2C phase increased with the increase in Mo amount due to the formation of better-crystalline Mo_2C particles. However,

further increased initial Mo loading amount to 30 wt.%, the XRD pattern showed two different crystalline phases (1) a main Mo₂C phase, and (2) traces of MoO₂ phase. It is indicated that due to the excess of Mo loading amount in this experiment, some Mo could still remain in the oxidation state. Similar results were also reported by Guil-López et al. [34], who investigated the influence of the Mo-loading on the crystalline Mo-phases during the carburization processes. Their results revealed that at high Mo-loading amount, the carburization of the molybdate precursor was not complete and a higher carburization temperature was required to fulfill Mo-carbide formation. Therefore, based on the XRD results, the initial Mo loading amount for Mo₂C/BC catalyst in this study should be lower than 30 wt.% at which well-crystalline Mo₂C was generated in this one-step solid-solid carburization process at relatively low carburization temperature of 800 °C.

The BET surface area and pore volume of the as-prepared Mo₂C/BC catalyst with different initial Mo loading amount are given in Table 1. It can be seen that the surface area and pore volume of the samples decreased with increasing of Mo loading amount. However, all catalysts have high surface areas, which are benefit for the catalyst. Scanning electron microscope (SEM) equipped with energy dispersive spectrometer (EDS) was also used to explore the morphology of the Mo₂C/BC catalysts. Fig. 4 shows the SEM images and the EDS mapping image of ammonium heptamolybdate deposited dried cedar (initial Mo loading amount of 20 wt.%) after

carburization at 800 °C for 2 h. It indicated the existence of Mo with good dispersion on the surface of the as-prepared catalyst.

3.2. Catalytic activity of Mo₂C/BC catalyst

Three main ways which can enhance the biomass gasification rate and increase the hydrogen production yield are always considered. That is, (1) using steam gasification instead of partial oxidation, (2) increasing reaction temperature, and (3) catalyst assistance [35]. In the present study, the catalytic activity tests of the as-prepared Mo₂C/BC catalysts toward tar steam reforming were performed in a fixed-bed reactor with different conditions. In general, when tar cracking is performed in the presence of steam, the general steam reforming reaction can be expressed as following:

and the produced CO could react further with excess steam and is converted to CO₂ and H₂ by water-gas shift (WGS) reaction:

Fig. 5 shows the yield (Y_{bio}) of each gas, which was calculated by Eq. (1), from catalytic steam gasification of biomass using Mo₂C/BC catalysts with different initial Mo loading amounts. Here, the experiments were performed at a reaction temperature of 650 °C with a water flow rate of

0.09 g/min at room temperature. Results were compared to those obtained from non-catalytic system. It is found that significant changes in the gas production yields due to the presence of catalyst, especially for H₂ and CO₂. According to Eqs. (2) and (3), the results can be explained by the fact that biomass tar is decomposed first over the catalyst to gaseous components such as CO and H₂ and then, the produced CO reacts further with excess steam by water-gas shift reaction, leading to high H₂ and CO₂ yields.

For different initial Mo loading amounts, the results showed that Y_{bio} increased with increasing of Mo loading amount at the beginning, and decreased slightly with Mo loading amount higher than 20 wt.%. According to the results of surface area measurements and crystallite size calculations of the as-prepared catalysts with different initial Mo loading amounts as shown in Table 1, surface area of the as-prepared catalyst decreased and crystallite size of the as-prepared catalyst increased obviously when the initial Mo loading amount was increased to 30 wt.%. This may be due to the sintering of metal particle during carburization, resulting in the decrease of surface area of the as-prepared catalyst and the catalytically active sites. This may be one of the reasons for the decrease in the gas production yield at high Mo loading amount. Another possible reason may be the existent of MoO₃, which is not successfully transforming to Mo₂C and has not active in steam reforming reaction [36,37], covered the active sites of Mo₂C, also leading to the decrease of the catalytically active sites. In the case of initial Mo loading

amount of 20 wt.%, the highest H₂ yield was obtained and about 5 times higher than that of non-catalytic system.

Fig. 6 shows the effect of weight ratio of catalyst to biomass on the gas production yields from catalytic steam gasification of biomass. Here, the experiments were performed at a reaction temperature of 650 °C with a water flow rate of 0.09 g/min at room temperature. The height of catalyst bed was kept constant at 8 cm by mixing the silica with catalyst. The results revealed that the catalyst to biomass ratio had a great influence on the gas production yields, especially for H₂ yield. With the increase in the weight ratio of catalyst to biomass, the H₂ yield increased obviously when compared to the yield of other gases. Moreover, the CO yield decreased greatly at 3.3 weight ratio of catalyst to biomass. This may be due to the strong influence from the water-gas shift reaction. As reported in many literatures [27,38,39], Mo₂C is also highly active for this reaction. Therefore, in order to obtain the H₂-rich gas product, the weight ratio of catalyst to biomass should be higher than 3.3 in this study.

Generally, the product gas compositions and carbon conversion in the gasification process strongly depend on the reaction temperature [40]. In the present study, in order to evaluate the effect of reaction temperature on the catalytic activity of Mo₂C/BC catalyst at the initial Mo loading amount of 20 wt.% in steam reforming of tar, the reaction temperature was varied from 550 to 750 °C but the steam flow rate remained at a constant rate of 0.09 g/min. The results are

presented in Fig. 7. It is found that gas production yield increased sharply with the increasing of reaction temperature, especially for H₂, and then decreased slightly when the reaction temperature was higher than 650 °C. On the one hand, higher temperature can enhance both steam gasification and the Boudouard reactions by providing the energy for endothermic gasification reactions, resulting in more volatiles and gas release. Moreover, high temperature also favors cracking and reforming of tar leading to an increase in the gas production yield [41-43]. On the other hand, at high temperature, Mo₂C might be oxidized to MoO₂ and/or MoO₃, which is not active in steam reforming reaction, by steam and produce CO₂ via the following reactions, respectively [36]:

Darujati et al. [36] also reported that the Mo₂C was oxidized to MoO₂ at temperature about 600 °C when the carbide was exposed to either steam or CO₂. This may be the reasons for the decrease in the gas production yield at high temperature. Fig. 8 shows the XRD patterns of the as-prepared catalysts with initial Mo loading content of 20 wt.% before and after the reaction at a temperature of 650 °C. As can be seen, after the reaction, a peak corresponding to MoO₂ appeared and the intensity of the carbide peak decreased obviously, indicating that some Mo₂C

was oxidized to MoO₂ during the reaction, leading to decreasing of catalytic activity. Based on these results, the optimum reaction temperature of Mo₂C/BC catalyst for steam reforming of tar in this experiment was approximately 650 °C at which the highest gas production yield was obtained.

Table 2 shows the heavy tar amount collected from the experiments and the calculated tar amount by carbon balance in non-catalytic and catalytic steam gasification of cedar.

Herein, the tar reduction is defined as:

$$\% \text{ tar reduction} = (A/B) \times 100 \quad (7)$$

where A (g) is the weight difference between heavy tar collected in a non-catalytic and a catalytic system while B (g) is the weight of heavy tar collected in a non-catalytic system. According to the heavy tar amount, it is found that the as-prepared Mo₂C/BC catalyst showed a potential to remove the heavy tar in biomass gasification and the % tar reduction was found to be 99.0%. However, comparing with the calculated tar amount, the % tar reduction was found to be only 19.1%. This may be due to some of tar or light tar is difficult to be collected. Therefore, it can be assumed that the as-prepared Mo₂C/BC catalyst has a good efficiency for the removal of heavy tar, which can cause many problems more easily than light tar, in biomass steam gasification process under the conditions selected in this work.

3.3. Stability and reusability of $\text{Mo}_2\text{C}/\text{BC}$ catalyst

Fig. 9 shows gas production yields when the as-prepared catalysts with initial Mo loading content of 20 wt.% was used again with and without regeneration for the steam reforming of biomass tar. In the case of without regeneration, the gas production yields decreased slightly due to parts of Mo_2C were oxidized to MoO_2 by steam during the reaction, but MoO_2 has no active for the steam reforming reaction [36,37]. On the other hand, the carbon deposition on the catalyst surface due to the cracking of tar molecules could also decrease the catalytic activity of the catalyst. Therefore, in order to remain its catalytic activity, the spent catalyst should be regenerated before reuse again. In this study, in order to regenerate the deactivated $\text{Mo}_2\text{C}/\text{BC}$ catalyst, a try was performed to re-carburize it in Ar atmosphere at different temperatures and the results are shown in Fig. 8. From the XRD patterns, it can be seen that pure Mo_2C phase can be only obtained when the spent catalyst was re-carburized at a temperature above 900 °C for 2 h in Ar atmosphere. As mentioned above in section 3.1.1, in the case of when using cedar char as a carbon source, the carburization temperature should be also increased above 900 °C in order to obtain pure Mo_2C supported on char. Therefore, the spent catalyst was regenerated by re-carburized at a temperature above 900 °C for 2 h in Ar atmosphere and its catalytic activity is shown in Fig. 9. It is found that the gas production yield exhibited a little bit higher than the original one, indicating that the catalytic activity of the spent catalyst can be recovered when

MoO₂ was re-carburized into Mo₂C. In addition, a part of alkali and alkaline earth metallic species could be moved from the biomass with tar and deposited on the catalyst, resulting in its activity promoted to some extent [44]. From these results, it is suggested that the as-prepared catalysts exhibited good catalytic activity and reusability.

4. Conclusions

The findings of the present study can be summarized as follows:

- 1) Mo₂C/BC catalyst was successfully prepared by in-situ solid state reaction using original biomass as the carbon source. Pure Mo₂C phase was achieved at relatively low carburization temperature of 800 °C and the initial Mo loading amount lower than 30 wt.%.
- 2) The as-prepared Mo₂C/BC catalyst exhibited a good catalytic activity for the steam reforming of heavy tar to produce H₂ and easily regenerated. In the case of 20 wt.% of initial Mo loading amount, the highest H₂ yield was obtained and about 5 times higher than that of non-catalytic system.
- 3) Reaction temperature had a significant effect on the gas production yield. The optimum reaction temperature of Mo₂C/BC catalyst for steam reforming of tar in this experiment was found to be 650 °C.

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458 **Table captions**

459 **Table 1.** Surface area, pore volume and crystallite size of the as-prepared catalysts with different
460 initial Mo loading amounts.

461 **Table 2.** Tar amount from steam gasification of biomass at reaction temperature of 650 °C.

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463

464 **Figure captions**

465 **Fig. 1** XRD patterns of carburized products at different carburization temperatures.

466 **Fig. 2** XRD patterns of carburized products at different carburization temperatures when using
467 cedar char as carbon source.

468 **Fig. 3** XRD patterns of carburized products at different Mo loading amounts (Carburization
469 reaction temperature = 800 °C).

470 **Fig. 4** SEM (a,b) and EDS mapping (c) photographs of Mo₂C/cedar char catalyst (Mo loading
471 amount = 20 wt.%; carburization reaction temperature = 800 °C).

472 **Fig. 5** Effect of Mo loading amount on gas production yields (Reaction temperature = 650 °C).

473 **Fig. 6** Effect of the catalyst to biomass ratio on the gas production yields (Reaction temperature
474 = 650 °C).

475 **Fig. 7** Effect of reaction temperature on gas production yield.

476 **Fig. 8** XRD patterns of Mo₂C/BC catalysts with Mo loading content of 20 wt.% (Reaction
477 temperature = 650 °C).

478 **Fig. 9** Stability and reusability of Mo₂C/BC catalysts with Mo loading content of 20 wt.% for
479 steam reforming of biomass tar (Reaction temperature = 650 °C).

480 **Scheme 1** Proposed formation process of biomass char supported Mo₂C catalyst by in-situ solid
481 state reaction.

Table 1. Surface area, pore volume and crystallite size of the as-prepared catalysts with different initial Mo loading amounts.

Initial Mo loading amount (wt.%)	Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Crystallite size ^a (nm)
5	422.0	0.231	24.2
10	362.3	0.201	24.6
15	323.4	0.198	25.4
20	317.8	0.193	25.7
30	247.1	0.169	29.9

^a Crystallite size of Mo₂C is estimated using the Scherrer formula.

Table 2. Tar amount from steam gasification of biomass at reaction temperature of 650

°C.

System	Heavy tar amount (g for 0.6 g biomass)	Calculated tar amount by carbon balance (g for 0.6 g biomass)
Non-catalytic	0.1715	0.1778
Catalytic ^a	0.0017	0.1438

^a Mo loading amount = 20 wt.%.

Figure-1

(1) Lower temperature:

(2) Higher temperature:

Figure-2

Figure-3

Figure-4

Figure-5

Figure-6

Figure-7

Figure-8

Figure-9