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

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ABSTRACT

Catalytic steam reforming of tar derived from Japanese cedar pyrolysis was investigated over a prepared biomass char supported molybdenum carbide (Mo_2C/BC) catalyst in a fixed-bed reactor. Mo_2C/BC was prepared by in-situ solid state reaction, and characterized by XRD and SEM to study the effects of carburization temperature and Mo loading amount on Mo_2C formation. The results show that Mo_2C/BC catalyst was successfully prepared at a relatively low carburization temperature of 800 °C and the initial Mo loading amount for the preparation of this catalyst should be lower than 30 wt.%. The Mo_2C/BC showed a good catalytic activity for the steam reforming of tar derived from biomass. In the case of Mo_2C/BC with a Mo loading of 20 wt.%, the highest H_2 yield was obtained, which is about 5 times higher than that of non-catalytic test. Mo_2C/BC could be a promising catalyst in steam gasification of biomass to remove tar and produce H_2-rich gas.

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

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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 CO_2 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 Mo_2C 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 Mo_2C which is covalently anchored to carbon supports, and found that active catalysts (Mo_2C) 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 Mo_2C based catalysts. Herein, Mo_2C/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.

Experimental

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%, SO_3 10.47%, SiO_2 6.83%, P_2O_5 6.45%, K_2O 4.01%, Fe_2O_3 0.80% and SrO 0.04%. Ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) was purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan) and used directly.

Biomass char supported Mo_2C (Mo_2C/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 cm^3/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 Mo_2C 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 Mo_2C/BC catalyst, the spent catalyst was recarburized in Ar atmosphere at temperature of 800 and 900 °C, separately, using the same procedure as a carburization of Mo_2C/BC catalyst.

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)