Steam reforming of biomass tar over calcined egg shell supported catalysts for hydrogen production

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Abstract

Calcined egg shell (CES) shows porous structure and exhibits alkaline property, which is expected to be applied for the adsorption and decomposition of biomass-derived tar. In this research, steam reforming of tar derived from cedar wood over CES was firstly investigated in a fixed bed reactor and found that CES had high catalytic activity for steam reforming of tar to produce hydrogen-rich gas. Then, iron, nickel, cobalt and copper were loaded on CES, more syngasespecially hydrogen gas was produced. Among them, copper loaded CES exhibited more enhanced catalytic activity. The optimum Cu loading amount on CES was found to be 1-2wt%, which resulted in the most amount of syngas and exhibited excellent reusability.

Keywords: *Biomass; Hydrogen production; Catalytic steam reforming; Egg shell;Copper.*

1. Introduction

Recently, biomass has gained great attention because of its renewability. Thermochemical conversion of biomass to gas, liquid and solid fuels is an effective way for utilization of biomass energy. Among the thermochemical conversion processes, gasification one can convert biomass into syngas, which can be used for the synthesis of methanol via catalytic reaction, the production of liquid fuels via Fischer-Tropsch synthesis process, and the generation of electricity via turbine, gas engine or fuel cell [1,2]. However, in the gasification process, a large amount of tar is generally cogenerated with syngas, resulting in gas-line blockage and even the system stopped suddenly in many cases. Therefore, it is necessary to reduce the tar generation and/or effectively remove it from the syngas.

To date, although some novel methods such as using gliding arc plasma [3,4] have been developed for the conversion of tar into syngas, most researches still focus on the catalytic steam reforming of tar, in which the key is to find high active catalysts with low cost. Alkali and alkaline earth metals (AAEM) such as Ca, Mg, K and Na, which are widely existed in natural resources such as biomass ash, biomass char, dolomite, and waste scallop shell have been found to have high catalytic activity for the tar reforming [5-9]. Besides, various transition metal catalysts such as Fe, Co and Ni and noble metal catalysts also show high catalytic activity [5,10-15]. To improve the catalyst

stability, some researchers mixed various transition metals or supported them on the porous materials [16-22]. Li et al. [23] supported Co on $\text{BaAl}_{12}\text{O}_{19}$ (BA) and found that Co/BA catalyst had significantly higher activity in tar reforming when compared with Co supported on Al_2O_3 , ZrO_2 , SiO_2 , MgO or TiO_2 . Because of the excellent CO_2 capture capability and low cost, CaO is applied as catalyst or catalyst support for tar removal. D'Orazio et al. [24] and Zamboni et al. [25] separately reported that the combination of Ni and Fe with $\text{CaO-Ca}_{12}\text{Al}_{14}\text{O}_{33}$ resulted in high catalytic activity for the steam reforming of tar and water gas shift reaction. Similarly, Ni loaded Mayenite was found to have high activity for conversion of biomass tar into hydrogen-rich gas in fluidized bed steam gasification process, and the conversion rate reached 90% at 800°C with a long-term stability [26]. Moreover, Ashok and Kawire reported that the addition of CeO_2 promoted the formation of Ni-rich surface in Ni/CaO- Al_2O_3 catalyst, which results in higher catalytic activity and carbon resistance [27].

In our previous studies [7-10], metal loaded on various low-cost resources such as waste scallop shell and biomass/coal char were successfully utilized for the steam reforming of tar derived from biomass to produce hydrogen-rich gas. Like waste scallop shell and biomass/coal char, egg shell is an abundant waste resource containing plenty of calcium element. In the present study, the calcined egg shell (CES) was used as catalyst and catalyst support for the steam reforming of tar. Various metals such as Fe, Ni, Co and Cu

were loaded on it to improve the catalytic activity, and the effect of metal loading amount on the catalytic activity was investigated. For the best obtained catalyst, its catalytic stability and reusability were also tested. It is expected to obtain a reliable and low-cost catalyst with high activity and long-term stability for the steam reforming of biomass tar.

2. Experimental

2.1 Biomass

In this study, cedar wood with a size of 1-2.8mm was used as biomass feedstock, which was dried at 110°C overnight before storage and further use. The final water content in it was about 8 wt%. The water-free element compositions by weight percentage of it were C 48.8 wt%, H 6.6 wt%, O 43.0 wt%, N 1.4 wt% and ash 0.2 wt%. Based on XRF analysis (Energy Dispersive X-Ray spectrometer EDX-800HS, Shimadzu), 0.8 wt% Fe_2O_3 , 50.68 wt% CaO , 4.1 wt% K_2O , and 0.04 wt% SrO were found in the ash.

2.2 Catalyst preparation and characterization

Egg shell was firstly washed several times and dried at 110°C for 24 h, and then, it was crushed and sieved to <250µm particle size before calcination in air at 900°C for 2 h. Based on the preliminary experiments, 1 wt% Fe-, Ni-, Co and 0.25-10 wt% Cu were respectively supported on the calcined egg shell (CES) by using the incipient wetness impregnation

method, in which a mixed aqueous solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Sigma-Aldrich Japan), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sigma-Aldrich Japan), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich Japan), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich Japan) was used. After impregnation and aging for approximately 2 h, the slurry was dried overnight at 110°C , and then, the dried powders were calcined in air at 650°C for 3 h. As a reference, commercial CaO (Nacalai Tesque Inc., Japan) was also used as the catalyst as well as the catalyst support.

Surface morphology of catalyst was characterized with a scanning electron microscope (SEM, SU8010, Hitachi, Japan) coupled with energy dispersive X-ray detector (EDX). The crystal structure of as-prepared catalyst was determined by using RIGAKU Smartlab X-Ray diffractometer (XRD) with Cu K_α radiation ($\lambda = 0.154 \text{ nm}$) generated at 45 kV and 200 mA.

2.3 *In-situ catalytic steam reforming experiment*

In this study, in-situ catalytic steam reforming of tar derived from cedar wood was performed in a fixed bed, which was illustrated elsewhere[10]. In short, about 0.6 g of cedar particle was put on the upper side of catalyst layer with a weight of 2.0 g, and a thin layer of quartz wool was used to separate them. As such, the tar derived from the cedar wood can be carried with a gas flow and enter the catalyst layer. During the experiment, 0.09 g/min of water was heated to about 250°C and carried by $50 \text{ cm}^3/\text{min}$ of Ar into the fixed bed reactor.

The reactor was heated to 650°C with a heating rate of 20 °C/min, and the pyrolysis of cedar wood and the steam reforming of tar derived from it were carried out at the same conditions. Thus, the tar derived from the pyrolysis of cedar was carried by steam-Ar gas flow and passed through catalyst layer, where the steam reforming of tar occurred. The outlet gas was cooled down by two ice-bath condensers and then filtered by a dry CaCl₂ column and collected in a gas bag. The reaction time was fixed at 2 h for each experiment. Agilent 7890A gas chromatograph system was used for the gas analysis.

3. Results and discussion

3.1 Catalyst characterization

Figure 1 shows XRD patterns of original egg shell and CES at different temperatures. Since CaCO₃ is the main component in egg shell, as shown in Fig.1, by calcining it at 800°C for 2 h, peaks of CaO and CaCO₃ can be simultaneously detected, indicating that a part of CaCO₃ has been transformed to CaO at this temperature. After calcined it in air at 900 °C for 2h, only the peaks of CaO can be observed, suggesting that all CaCO₃ in the egg shell has converted to CaO. From the TGA result of egg shell sample (Fig.2), at the decomposition temperature ranged around 100 to 550 °C, water and other organic protein molecules in egg shell structure are removed at first. Then, a significant weight loss (39 wt.%) is clearly observed at a temperature range of about 600 to 800 °C, resulting from the transformation

of the CaCO_3 to CaO with releasing of CO_2 . When the temperature is higher than 800°C , no significant mass decrease can be observed, indicating that most of CaCO_3 has transformed to CaO . In general, the thermal decomposition of pure CaCO_3 takes place at about $825\text{--}896.6^\circ\text{C}$. Therefore, in this study, the calcination temperature at 900°C is enough to transform egg shell to CaO as indicated in Fig.1. Otherwise, based on the measured XRD patterns, the crystallite sizes of CaO in CES obtained at 800 and 900°C are 82.8 and 106.9 nm, respectively, indicating that the crystallite size increases with the increase in calcination temperature. XRF analysis indicates that the compositions of CES are CaO 98.7 wt%, SO_3 0.8 wt%, K_2O 0.4 wt% and SrO 0.1 wt%.

Figure 3 shows SEM images of egg shell before and after calcination at 900°C . One can see that by calcined at 900°C , CES shows a macroporous structure on the surface (Fig. 3 (b)), which should be benefit for the catalyst as well as catalyst support. BET measurement indicates that the BET surface area is only about $3.834\text{ m}^2/\text{g}$ with a pore size of 4.21 nm .

3.2 Catalytic performance of CES

Figure 4 shows the gas yields by using CES as catalyst which are compared with the cases by using the commercial CaO and without catalyst. One can see that the gas yields increase obviously in the presence of catalyst. Generally, steam reforming of tar can be

expressed as[29, 30]:

At the same time, the water-gas shift (WGS) reaction will occur with the excess steam:

In addition, CH₄ is always detected, which should mainly come from the pyrolysis of biomass even without any catalyst. Here, it should be noted that the produced CO₂ could be reacted with CaO, which will result in the decrease of CO₂ partial pressure in the system and promote WGS reaction to go forwards. Moreover, the enhanced WGS reaction will decrease the CO partial pressure in the system, which could promote tar reforming reaction. That is why more H₂ and CO₂ and less CO are detected in the presence of CaO catalyst.

When compared with the case without catalyst, one can see that the hydrogen yield in the presence of CES increases 4.9 times, but only 3.7 times for the commercial CaO. For the commercial CaO, it is difficult to find macropore structure on it, and BET measurement indicates that its surface area is only 2.16 m²/g [28], which is also smaller than that of CES calcined at 900 °C. Although surface areas of both are not so high, the textural property of CES should be more benefit for the reaction. Furthermore, it should be noted that some other trace metal species in CES should also have some catalytic promoting effects on the reactions. As indicated above, besides CaO, little amounts of K₂O and SrO are also contained in CES. It has been proved that alkali metallic species such as K on CaO

can enhance the absorption of CO₂ and promote the WGS reaction[31-34].

3.2 Metal-loaded CES catalyst

In our previous work [7-10, 35-36], various metals were loaded on calcined scallop shell or commercial zeolite for the decomposition of the biomass-derived tar. It is found that the loading of metals on these supports can enhance the catalytic activity greatly. In this study, to investigate the effect of metal type on the catalytic activity, 1 wt% Ni, Co, Fe and Cu were respectively supported on CES at first for the reforming of tar. As shown in Fig.5, it can be seen that the doping of metal on CES obviously promotes the yield of H₂ while the yields of CO₂, CH₄ and CO are almost unchanged. It is reported that the tar could be adsorbed on metal crystallite sites as well as on CaO. Simultaneously, water molecules can be also adsorbed on CaO. As such, H₂ could be produced via dehydrogenation of adsorbed tar which could react with the back-spillover of labile –OH, H and –O species on the catalyst support as well as the metal active sites[37, 38]. It should be noted that H₂ yields in the presence of different metal loaded catalysts are different. The H₂ yield from nickel- or cobalt-loaded CES are almost the same, which is higher than that from iron-loaded one. It indicates that there are the different reforming activities for the steam reforming of tar by Ni, Co and Fe. Wang [39] and Ahmed [40] reported that metallic Ni catalyst has much higher reforming activity than metallic Fe. It is possible that Ni metal surface has higher activation

ability for cleavage of C-H and C-C bonds in the hydrocarbon molecules [10]. More interesting, compared with Ni, Co and Fe loadings, the highest H_2 yield is obtained in the case of Cu loading in this study. It indicates that Cu loaded CES could provide more active sites for the back-spillovers of labile $-OH$, H and $-O$ species on it for the steam reforming of tar.

3.3 Cu loading amount

To further understand the activity of Cu-loaded CES on the steam reforming of tar, the effect of Cu loading amount on the catalytic activity was investigated. 0.25, 1, 2, 5, and 10 wt% of Cu were supported on CES, respectively. Figure 6 shows the yields of H_2 , CO , CH_4 and CO_2 when different concentrations of Cu loaded CES are applied. One can see that 1-2 wt% Cu loading amount results in the maximum hydrogen yield. Figure 7 shows XRD patterns of CES with different Cu loading amounts. Only the peaks of CaO can be observed in the XRD pattern of un-doped CES. However, even a little amount of Cu (i.e., 0.25 wt%) is loaded on CES, the peaks of both CaO and $Ca(OH)_2$ appear. When the loading amount is higher than 1 wt%, the peaks of calcium copper oxide phase can be detected, and with the increase of Cu loading amount, the intensity of peaks corresponding to calcium copper oxide also increases, indicating the formation of larger calcium copper oxide particles on CES. It is considered that the formation of calcium copper oxide could stabilize Cu species

on CES and provide new active sites for the tar reforming. As a result, H₂ yield increases with the increasing of Cu loading amount from 0.25 wt% to 1 wt%. However, after the Cu loading amount is over 2 wt%, the H₂ yield gradually decreases to some extent. It is mainly due to the formations of larger particle of Cu and calcium copper oxide, which result in the decrease of active sites of the catalyst for contacting tar as well as steam. Herein, the Cu loading amount from 1 wt% to 2 wt% provides the most opportunity for tar to contact active sites. It is reported that Cu is less active for the steam reforming of hydrocarbons than Ni and Co when they are supported on other support [13]. It is possible that the activity of metal modified catalysts could be influenced by the loading amount and especially the interaction between the metal and support. It should be noted that the dispersion properties of metal species on different supports should be different, and some new phases could be generated because of the interaction. In the present study, the active sites should be mainly on Cu species and the new phases formed between Cu and support, i.e., Ca_{0.828}CuO₂ as shown in Fig.7.

3.4 Reusability of Cu-loaded CES

Figure 8 shows gas yields when 1wt%Cu/CES catalyst was reused for 5 cycles with regeneration by calcination of it in air at a temperature of 650°C for 3h. It is found that the gas yield, especially for H₂ yield, has almost no change and even increase a little more when

the catalyst is reused for 5 times, indicating that the catalyst has excellent reusability. Moreover, the regenerated catalyst shows a little higher catalytic activity, which should be caused by the following two possible reasons. On the one hand, it has been proved that the alkaline elements such as K contained in cedar wood can be evaporated and move to the catalyst layer with tar [10]. As such, with the increase of reuse cycle, more potassium could be fixed on the surface of catalyst, which will enhance the catalytic activity. On the other hand, it is reported that the presence of KFeO_2 in the Fe-based catalyst can maintain a high and long-term activity [33, 34]. Similarly, in this study, the formation of copper potassium oxide phase on the surface of CES should also be benefit for the maintaining of the high and long-term activity of Cu/CES catalyst.

4. Conclusions

Steam reforming of tar derived from cedar wood over CES as well as copper-loaded CES was investigated in a fixed bed reactor. CES showed a good catalytic activity for production of fuel gases, especially hydrogen gas from the tar reforming. Furthermore, loading of Fe, Ni, Co or Cu on CES resulted in higher catalytic activity. Especially, more fuel gases, especially H_2 , was produced when using Cu loaded CES. The optimum Cu loading amount on CES was found to be 1-2wt%, which produced the highest yield of fuel gases and also exhibited excellent reusability.

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Figure captions

Fig. 1 XRD patterns of egg shell calcined at different temperatures. Crystalline phases:

(●)CaCO₃; (◆)CaO;

Fig. 2 TGA profile of egg shell.

Fig. 3 Images of egg shell calcined at different temperatures. (a) SEM image of the surface of original egg shell; (b) SEM image of the surface of egg shell calcined at 900°C.

Fig. 4 Gas yield over different CES and commercial CaO at 650°C.

Fig. 5 Gas yields over CES loaded with different metals at 650 °C.

Fig. 6 Gas yields over CES loaded with different Cu loading amounts at 650 °C.

Fig. 7 XRD patterns of Cu/CES catalysts with different Cu loading amounts. Crystalline phases: (■) Ca_{0.828}CuO₂ (▲) Ca(OH)₂ (●) CaO

Fig. 8 Reusability of 1wt%Cu/CES catalyst for the steam reforming of tar derived from cedar wood.

Fig. 1

Fig. 2

Fig. 3

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Fig. 7

Fig. 8