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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 syngas especially 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 1–2 wt%, which resulted in the most amount of syngas and exhibited excellent reusability.

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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

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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, 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 Kawi 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.

Experimental

Biomass

In this study, cedar wood with a size of 1–2.8 mm 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.

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 <250 μm

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.

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 cm^3/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 CaCl_2 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.

Results and discussion

Catalyst characterization

Fig. 1 shows XRD patterns of original egg shell and CES at different temperatures. Since CaCO_3 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 CaCO_3 can be simultaneously detected, indicating that a part of CaCO_3 has been transformed to CaO at this temperature. After calcined it in air at 900 °C for 2 h, only the peaks of CaO can be observed, suggesting that all CaCO_3 in the egg shell has converted to CaO. From the TGA result of egg shell sample (Fig. 2), at the decomposition temperature ranged around 100–550 °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 600–800 °C, resulting from the transformation of the

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