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Steam reforming of bio-oil from coconut shell pyrolysis over Fe/olivine catalyst

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ABSTRACT

Catalytic steam reforming of coconut shell pyrolysis bio-oil over Fe/olivine catalyst was conducted in a fixed-bed quartz reactor. The effects of calcination temperature, iron loading, reaction temperature, steam to carbon ratio (S/C), bio-oil weight hourly space velocity (W_bHSV) on gas composition and carbon conversion were investigated. The results indicate that Fe/olivine has good activity for steam reforming of bio-oil, the couple $Fe^{2+/3+}/Fe^{2+}$ may be sufficiently efficient for C–C, C–O and C–H breaking. After steam reforming, most of the phenolics in pyrolysis oil are converted into light molecular compounds such as H_2, CO, CO_2, and CH_4. The H_2 concentration and carbon conversion were enhanced by increasing reaction temperature from 750 to 800 °C and the S/C from 1.5 to 2, but decreased with increasing calcination temperature. In the W_bHSV range of 0.5–0.6, the hydrogen concentration decreased obviously, whereas it decreased slightly by further increasing W_bHSV. The highest hydrogen concentration of 47.6 vol% was obtained among the catalysts tested, and the best carbon conversion was 97.2% over 10% Fe/olivine catalyst under the reforming conditions of temperature = 800 °C, W_bHSV = 0.5, S/C = 2.

1. Introduction

In recent years, energy shortage and environment problems caused by fossil fuel utilization have threatened the sustainable development of our society. As a kind of renewable sources, it is attractive to convert biomass into energy or chemicals using thermal–chemical technologies, such as pyrolysis for bio-oil, gasification for syngas, and hydrolysis for sugar [1–3]. Among these conversion processes, biomass pyrolysis for bio-oil production is an important technological route. The bio-oil can have a volumetric energy density up to ten times larger than biomass and is therefore more suitable for transport. However, the utilization of bio-oil is limited due to its high water content, low heating value, high viscosity and corrosiveness. Bio-oil catalytic steam reforming for hydrogen and syngas production provides a new route for utilization of bio-oil.

Up to now, considerable research effort has been devoted to the steam reforming of bio-oil. Published reports, however, indicate that the biggest bottleneck for hydrogen and syngas production via steam reforming of bio-oil in a large scale is the catalyst deactivation caused by carbon deposition [4–6]. Therefore, the exploration of effective catalyst is vital for steam reforming of bio-oil. It has been explored via reforming catalysts including the oxide catalyst, the Ni-based catalysts, and noble metal-loaded catalysts etc. Noble metals such as Ru, Rh and Pt are highly active elements for the reforming reaction [7,8], but high cost and limited availability of noble metals can decrease the applicability. Ni-based catalysts, such as Ni/Al_2O_3, Ni/CNTs, Ni/MCM-41, $Ni/Ru\text{-}Mn/Al_2O_3$, and $Ni–CeO_2/\gamma\text{-}Al_2O_3$ are commonly used because of their high reforming activities [9–11], which produce high yields of hydrogen-rich gas. The main drawback attributed to the use of Ni is its rapid deactivation by surface carbon deposits or sulfur poisoning, the cost and the environmental and safety measures derived from its toxicity. Iron-based catalysts, having adequate catalytic activities but less prone to coke formation and cheaper than the Ni-based catalysts, show great promise for reforming tar during biomass gasification [12], where correlative studies on steam reforming of bio-oil itself are very limited. Except for catalyst deactivation by carbon deposition, the mechanical strength of the catalyst is another important parameter to take into account because of attrition problem, especially in fluidized bed reactors [13]. The use of promoters, i.e. Ca, Mg, can improve catalyst resistance to attrition [13], however, it will increase operational complexity. As a natural mineral, olivine has the advantages of low cost and high attrition resistance. The addition of a variety of

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metals to olivine could improve its catalytic efficiency in steam reforming. Some researches have demonstrated that olivine activity, or more specifically olivine activation, depends on its iron oxide content [14]. The Fe/olivine catalysts are therefore of particular interest for steam reforming of bio-oil, for both economic and environmental reasons. Due to the complexity of bio-oil, although much of the literature has focused on bio-oil reforming, many of these studies have used model compounds such as acetic acid, glycerol, ethanol, m-cresol as the feed materials [11,15–19].

In this work, a series of the Fe/olivine catalysts were prepared and applied to the steam reforming reaction of the actual bio-oil. Effects of calcination temperature, iron loading content, reaction temperature, steam to carbon (S/C) ratio, bio-oil weight hourly space velocity (W_bHSV) on gas quality and carbon conversion were studied to optimize the catalyst activity.

2. Experimental

2.1. Preparation of bio-oil

The bio-oil used in this study was obtained from pyrolysis of coconut shell in an electrically heated rotary kiln at 450 °C, since the pyrolysis of coconut shells at 450 °C can obtain the maximum yield of liquid products [20]. After filtrating ash, the obtained liquid product was distilled under vacuum at 60 °C in a rotary evaporator to remove a part of water. The bio-oil appeared as a dark brown liquid. The residual water content in the bio-oil was 30.9% determined by toluene azeotrope method (ASTM D95-83). Ultimate analysis of the bio-oil showed that it contained 45.0 wt% carbon, 7.1 wt% hydrogen, 1.4 wt% nitrogen and 46.5 wt% oxygen (dry basis). The bio-oil can be described by molecular formula of $CH_{1.905}O_{0.774}$ according to elemental analysis. The nitrogen content in the bio-oil is negligible and thus not taken into consideration in the empirical formula.

2.2. Catalyst preparation

Natural occurring olivine from Yichang magnesium olivine institute, China, was used as catalyst support. The olivine was milled and sieved into size of 0.45–0.90 mm before experiments. The component analysis of the olivine is given in Table 1.

Fe/olivine catalysts were prepared by impregnating the olivine support using aqueous solution of $Fe(NO_3)_3{\cdot}9H_2O$ at room temperature for 12 h. The excess water was evaporated under vacuum by heating at 60 °C. After water evaporation, the samples were dried overnight at 105 °C and calcined at various temperatures (900, 1000 or 1100 °C) for 3 h in a muffle furnace. The concentration of the iron nitrate solution was modified in order to obtain Fe loading content of 5, 10, 15 and 20 wt%, respectively.

2.3. Reaction system

As shown in Fig. 1, the bio-oil steam reforming experiments were carried out in a fixed-bed quartz reactor. The quartz reactor with an inner diameter of 16 mm is heated by an electric tubular furnace. In each run, 2 g catalyst grains were placed in the middle of quartz tube and was supported by quartz wool. A K-thermocouple was employed to keep the catalyst bed at constant reaction temperature. Feeding rates of bio-oil and water were controlled by syringe pump (WZS-50F6). Bio-oil feeding rate of 1 g/h was adopted. To make the bio-oil and water flow through catalyst bed in the form of gaseous phase, a thin layer of quartz wool was placed on top of catalyst bed at the position where the reactor temperature was about 200 °C. N_2 was used as carrier gas at a flow rate of 40 ml/min. Reaction products were condensed through a condenser, and the condensable product was collected in a liquid receiver. After drying the gas product volume was measured by a soap bubble flowmeter.

Table 1
Chemical composition of olivine analysed by XRF.

Composition	MgO	SiO_2	Fe_2O_3	Al_2O_3	Cr_2O_3	CaO	NiO
Content (wt%)	51.8	36.5	9.14	0.9	0.6	0.4	0.4

2.4. Product characterization and data analysis

The evolved gases were off-line measured by a GC9790 gas chromatograph (Fuli, China) equipped with thermal conductivity detector (TCD) and flame ionization detector (FID). Main organic compounds in the bio-oil and liquid condensate collected after steam reforming were detected by a gas chromatograph/mass spectrometer (Agilent 7890A/5975C GC/MSD provided with HP-5MS column). Temperature programmed reduction (TPR) measurements were carried out for determining the reduction temperature of the different metallic phases present in the catalyst. 0.2 g catalysts were placed in a U-shaped quartz tube. The reducing gas mixture (5%H_2 + 95%Ar) passed through the reactor was heated from 100 °C to 950 °C with a slope of 10 °C/min. The fresh and used catalysts were analysed by powder X-ray diffraction (D/Max-2400, Rigaku). The diffraction spectra had been indexed by comparison with the JCPDS (Joint Committee on Powder Diffraction Standards) files. The crystallite size (d_{XRD}) was estimated using the Scherrer equation ($d_{XRD} = k\lambda/B\cos\theta$) derived from the Fe(311) reflection. The thermogravimetric analyse (TGA) was performed on a DTU-2 thermo-balance to determine the amount of carbon deposition on the catalysts' surface. Each sample was heated from room temperature to 900 °C with the rate of 10 °C/min in air.

Carbon conversion (X_c) is expressed as the percentage of carbon present in bio-oil converted to carbon-containing gaseous products (CH_4, CO, CO_2, C_2H_4, C_2H_6, C_3H_6 and C_3H_8).

$$X_c\ (\%) = \frac{\text{moles of carbon in the product gas}}{\text{moles of carbon in the feed}} \times 100 \quad (1)$$

The steam to carbon (S/C) ratio was defined as the number of moles of water fed to the moles of carbon in the feed (Eq. (2)). Note that the water present in the bio-oil, which was 30.9%, was considered in the formula.

$$\frac{S}{C} = \frac{\text{moles of water fed}}{\text{moles of carbon fed}} \quad (2)$$

The bio-oil weight hourly space velocity (W_bHSV) is defined by the formula given in Eq. (3).

$$W_bHSV\ (h^{-1}) = \frac{\text{mass flow rate of bio-oil}}{\text{mass of catalyst}} \quad (3)$$

Coke deposition is defined as the amount of coke deposited on the catalyst bed over the amount of catalyst used.

$$\text{Carbon deposition}\ (\%) = \frac{\text{weight of carbon deposition}}{\text{weight of catalyst}} \times 100 \quad (4)$$

3. Results and discussion

3.1. Stability test

In order to study the stability of the catalysts in the steam reforming of bio-oil, the activity of Fe/olivine catalyst was tested for 2 h, at operational conditions of Fe loading content = 5%,

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