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Biomass to hydrogen-rich syngas via steam gasification of bio-oil/biochar slurry over $LaCo_{1-x}Cu_xO_3$ perovskite-type catalysts

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ABSTRACT

$LaCo_{1-x}Cu_xO_3$ (x = 0, 0.1, 0.2, 0.3) perovskite-type catalysts were prepared, characterized and tested for hydrogen-rich syngas production from steam gasification of bio-oil/biochar slurry (bioslurry). The effects of the Cu-substitution, temperature, water to carbon molar ratio (WCMR) and bioslurry weight based hourly space velocity (W_bHSV) on the hydrogen (H_2) yield were investigated. The results showed that the activity of $LaCoO_3$ was improved by Cu-substitution. $LaCo_{0.9}Cu_{0.1}O_3$ exhibited the best performance and gave higher H_2 yield and higher carbon conversion than that of non-catalytic process and also that of commercial 14 wt% Ni/ZrO_2. Coke deposition could be depressed by higher temperature, higher WCMR or lower W_bHSV, while higher temperature and lower W_bHSV made for higher H_2 yield. 2 was deemed to be the optimum WCMR. A maximum H_2 yield of 75.33% and a maximum carbon conversion of 80.42% were obtained at 800 °C with a combination of WCMR = 2 and W_bHSV = 15.36 h^{-1}.

1. Introduction

Hydrogen as a kind of renewable and clean energy carrier has recently attracted increased attention [1]. To achieve sustainable low-carbon hydrogen production, thermochemical conversion of biomass or biomass derived fuels is deemed to be the ideal option [2]. However, biomass is widely dispersed and of low volumetric energy density and poor grindability, high logistic cost would be a major constraint that impedes biomass utilization for hydrogen production [3]. Via flash pyrolysis, biomass decomposes into gas, bio-char and bio-oil [4]. Mixing bio-char into bio-oil can generate a bioslurry fuel, which has high volumetric energy density and can be readily transported and stored [5]. The use of bioslurry makes it possible for hydrogen production from biomass on a large scale [6].

Introducing steam as a gasifying agent in biomass gasification process would be beneficial to both hydrogen yield and biomass conversion [7]. Catalyst addition favors tar cracking, steam reforming reaction (SRR) and water gas shift reaction (WGSR) and lowers the reaction temperature leading to higher hydrogen yield [8,9]. Conventional catalysts are noble metal and transitional metal based catalysts, which are of excellent catalytic activity, but they have problems with high cost, sintering or/and carbon deposition. Therefore, efforts should be made to develop cheap, simple and effective catalysts.

Perovskite-oxide-type (ABO_3) catalysts arouse wide concern among researchers owing to their good activity and stability at moderate high temperatures [10–14]. ABO_3 catalysts with highly dispersed metal particles are reported to have functions in breaking C–C bonds, decomposition and dehydration, resulting in high H_2 production from carbon-containing material [15]. Moreover, the lattice oxygen in perovskite structure is conducive to suppressing coke deposition in SRR [16,17]. Perovskites containing both Cu and Co seem to be good candidates for the catalytic steam gasification of bio-oil/biochar slurries. Since Cu-based and Co-based perovskites are found to be very active for the oxidation of hydrocarbons, as well as for reactions of SR and WGS [18–20]. In this article, sol–gel $LaCo_{1-x}Cu_xO_3$ (x = 0, 0.1, 0.2, 0.3) perovskite-type catalysts were prepared, characterized and evaluated in steam gasification of bioslurry process. The present study aims at hydrogen production from steam gasification of bioslurry over $LaCo_{1-x}Cu_xO_3$ perovskite-type catalysts and compares it with that of non-catalytic process and that of commercial 14 wt% Ni/ZrO_2. The H_2 yield, carbon conversion and the distributions of gaseous products were examined as a function of Cu-substitution, temperature, WCMR and W_bHSV.

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2. Methods

2.1. Materials

A bioslurry with 90 wt% bio-oil and 10 wt% biochar was selected as the feedstock as investigated by our previous work (Table 1) [21]. Prior to preparing the bioslurry, the biochar was first ground to fine particles by milling and then sieved to the size below 25 μm. On the basis of the elemental composition shown in Table 1, the average molecular formula of bioslurry can be established as $CH_{1.451}O_{0.768}$.

2.2. Catalysts preparation and characterization

$LaCo_{1-x}Cu_xO_3$ catalysts were prepared by sol–gel method. The required amount of metal nitrates was dissolved in deionized water under mechanical stirring. Then, 5% excess citric acid over the theoretical value was added to the aqueous solution. The reaction mixture was evaporated at 80 °C until reaching gel formation. The gel was then dried overnight at 100 °C, followed by calcination at 850 °C for 5 h in air. All catalysts used in this work were crushed and sieved to a particle size range of 230–325 μm.

The commercial 14 wt% Ni/ZrO_2 with an average pore diameter (PD) of 354.82 Å and a specific surface area (SSA) of 16.33 $m^2\ g^{-1}$ was tested as a reference.

The BET surface areas and H_2 temperature programmed reduction (H_2–TPR) of catalysts were evaluated on Quantachrome Aparatus (Autosorb-iQ-C). X-ray diffraction (XRD) patterns were measured on a D/MAX-2500 diffractometer. The fourier transforms infrared (FTIR) spectra were registered by using a Vertx-70 FTIR spectrophotometer. The scanning electron microscope (SEM) images were obtained using a Quanta 200 SEM equipment.

2.3. Apparatus and steam gasification tests

The experiments were performed in a continuous flowing system using a fixed-bed reactor (Fig. 1). The reactor had a height of 785 mm and a diameter of 51.5 mm. 3 g of catalyst was used in each test. Before each test, the reactor was swept with N_2 until the catalytic bed was heated up to the scheduled temperature. Then after, bioslurry (0.768–3.702 g/min) and water (1.704–4.297 g/min) were introduced into the reactor by a pump. The yield of products in gas was measured with a bubble flowmeter. The gas phase products were analyzed by Beifen GC-3420A equipped with TCD using porapakQ and 5A columns. The contents of carbon deposition were examined gravimetrically by combustion method under air flow using TGA/DSC1 thermobalance, with a heating rate of 10 °C min^{-1} up to 800 °C.

2.4. Data analysis

The theoretical H_2 yield from bioslurry used here was 0.152 g $H_2\ g^{-1}_{bioslurry}$ calculated by Eq. (1). The yield of H_2 (Y_H) and yields of carbon containing gas were defined by Eqs. (2) and (3), respectively. The coke deposition (Y_c) and carbon conversion (E_c) were defined by Eqs. (4) and (5), respectively. WCMR and W_bHSV were defined by Eqs. (6) and (7), respectively.

$$CH_{1.451}O_{0.768} + 1.232H_2O \xrightarrow{\text{catalyst}} CO_2 + 1.958H_2 \quad (1)$$

$$Y_H\ (\%) = \frac{\text{moles of hydrogen produced}}{1.958 \times \text{moles of carbon fed}} \times 100\% \quad (2)$$

$$\text{Gas yield}\ (\%) = \frac{\text{moles of gas produced}}{\text{moles of carbon fed}} \times 100\% \quad (3)$$

$$Y_c\ (\%) = \frac{\text{weight of coke deposited on the catalyst bed}}{\text{weight of bioslurry fed}} \times 100\% \quad (4)$$

$$E_c\ (\%) = \frac{\text{moles of carbon in the product gas}}{\text{moles of carbon fed}} \times 100\% \quad (5)$$

$$\text{WCMR} = \frac{\text{moles of total water fed}}{\text{moles of carbon fed}} \quad (6)$$

$$W_bHSV\ (h^{-1}) = \frac{\text{mass flow rate of bioslurry}}{\text{mass of catalyst}} \quad (7)$$

3. Results and discussion

3.1. Characterization

3.1.1. XRD and BET

The XRD patterns of all $LaCo_{1-x}Cu_xO_3$ catalysts (Fig. 2) confirm the formation of the rhombohedral $LaCoO_3$ perovskite structure (JCPDS card Nos. 48-0123). No reflection lines for La_2O_3, Co_3O_4 and CuO are observed, indicating the successful substitution by Cu in the perovskite lattice. However, a small shift of the characteristic peak to lower 2θ values is observed for substituted samples. This can be explained by the difference in ionic radii between cobalt and copper, which causes changes in unit cell of perovskite lattice [22]. Similar phenomena have been reported in other literature [23].

The crystallite sizes (d_{XRD}) of $LaCo_{1-x}Cu_xO_3$ are calculated by the Scherrer equation using peaks at around $2\theta = 33.2°$. The characteristics of $LaCo_{1-x}Cu_xO_3$ catalysts including d_{XRD}, SSA, pore volume (PV) and PD are summarized in Table 2. The crystallite sizes are varied from 53.9 nm to 77.7 nm. The catalysts prepared in this work have SSA values between 2.10 and 4.27 m^2/g, which correspond well with values reported by other researchers [24]. The catalysts own mesopores with PD values between 26.86 and 44.75 nm. The PV values are found to be in between 0.0028 and 0.0096 $cm^3\ g^{-1}$.

3.1.2. Morphological properties

Fig. 3 shows SEM images of $LaCo_{1-x}Cu_xO_3$ catalysts. As observed, particles of each sample show irregular shapes. $LaCoO_3$ and $LaCo_{0.9}Cu_{0.1}O_3$ own the largest and the smallest particle sizes, respectively, which is consistent with the analyses from XRD. However, the average particle sizes obtained here (80–190 nm) are larger than those obtained from XRD results, which could be attributable to agglomeration and sintering of particles [25]. Moreover, agglomeration and sintering can also result in a decrease in SSA values, which are in accordance with results of BET surface area analyzed above, especially for $LaCo_{0.8}Cu_{0.2}O_3$ and $LaCo_{0.7}Cu_{0.3}O_3$.

3.1.3. FTIR spectra

Fig. 4 presents FT-IR spectra of $LaCo_{1-x}Cu_xO_3$ catalysts. The absorption bands appeared at around 425, 558 and 610 cm^{-1} suggest the formation of rhombohedral perovskite-type structure. Two bands at 558 and 610 cm^{-1} belong to Co–O stretching vibrations in CoO_6 octahedron (v_1), while 425 cm^{-1} can be attributed to a Co–O bending vibration (v_2) [26]. Further, vibration bands upshift toward higher wavenumber attributing to Cu-substitution in $LaCoO_3$ [27]. These results clearly support the XRD results.

3.1.4. TPR

H_2–TPR profiles of $LaCo_{1-x}Cu_xO_3$ catalysts are displayed in Fig. 5. As seen, two reduction peaks are observed in each H_2–TPR