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Biomass to hydrogen-rich syngas via catalytic steam reforming of bio-oil

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ABSTRACT

Hydrogen-rich syngas production from the catalytic steam reforming of bio-oil from fast pyrolysis of pinewood sawdust was investigated by using $La_{1-x}K_xMnO_3$ perovskite-type catalysts. The effects of the K substitution, temperature, water to carbon molar ratio (WCMR) and bio-oil weight hourly space velocity (W_bHSV) on H_2 yield, carbon conversion and the product distribution were studied in a fixed-bed reactor. The results showed that $La_{1-x}K_xMnO_3$ perovskite-type catalysts with a K substitution of 0.2 gave the best performance and had a higher catalytic activity than the commercial Ni/ZrO_2. Both high temperature and low W_bHSV led to higher H_2 yield. However, excessive steam reduced hydrogen yield. For the $La_{0.8}K_{0.2}MnO_3$ catalyst, a hydrogen yield of 72.5% was obtained under the optimum operating condition ($T = 800$ °C, WCMR = 3 and $W_bHSV = 12\ h^{-1}$). The deactivation of the catalysts mainly was caused by coke deposition.

1. Introduction

Hydrogen is considered as a renewable energy carrier that can be used in internal combustion engines and fuel cells with very less pollution on the environment, especially without CO_2 emission [1]. Currently, hydrogen is mainly produced from a wide variety of fossil fuels such as coal, natural gas, petroleum by-products and waste. Hydrogen from renewable resources, such as biomass, exhibits a promising prospective [2]. Using biomass as renewable feedstock would strongly contribute to decreasing greenhouse gas emissions due to neutral CO_2 balance [3]. Three possible technologies that have been explored for hydrogen production from biomass are gasification [4], catalytic pyrolysis [5] and catalytic steam reforming of bio-oil [6,7]. The latter route involves biomass pyrolysis process, followed by bio-oil steam reforming process. Compared with raw biomass material, bio-oil has higher energy density which reduces storage and transport costs [8].

Pyrolysis is a process in which biomass is rapidly heated to 450–550 °C in the absence of oxygen [9]. Under this condition, bio-oil together with non-condensable gases and charcoal are produced. Generally, 70 wt.% (including water) of the biomass is converted into bio-oil [10]. Typical elemental analysis of bio-oil indicates 54–58 wt.% carbon, 5.5–7 wt.% hydrogen, 35–40 wt.% oxygen and about 0.2 wt.% nitrogen [11]. In the reforming process, the bio-oil can be supplied through oil pump without the problem of slag draining [12]. Bio-oil steam reforming could be categorized into those that use the whole bio-oil or its aqueous phase [13,14]. However, the energy conversion efficiency decreases when bio-oil aqueous fraction is catalytically reformed by the steam, due to the strict separation process [15]. Given all that, H_2 production from whole bio-oil is a viable option.

The use of a catalyst allows carrying out the bio-oil steam reforming process at a relatively lower temperature (500–800 °C) than that used in non-catalytic. Although Ni, Ru, or Rh based catalysts are of good performance, they suffer from the carbon deposits formed during the reaction [16]. Therefore, the development of effective catalysts has become an important challenge. Perovskites are mixed oxides with a general formula of ABO_3, where A-site is lanthanide metal and B-site is transition metal [17]. Perovskites have become attractive as catalyst material for reforming

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reaction due to their ability to retain the structure even at high temperatures, which prevents agglomeration of metal irons incorporated in their lattice [18]. As a result of smaller metal particle size, carbon formation is suppressed, thus leading to good activity and stability [19].

Partial substitution at A site by proper ions contributes to the formation of oxygen vacancies, which has an important function in hydrogen production. For example, substitution of Sr at A site exhibited higher catalytic performance than unsubstituted sample, while an opposite tendency was observed for Ca and Mg [20]. In our previous work [21], substitution of La^{3+} by K enhanced the oxygen mobility of sample, resulting in substituted sample with a better catalytic performance for H_2 production. Mn containing perovskite catalysts give excellent activity for total oxidation reactions. In addition, K substitution of La^{3+} make higher surface area of $LaMnO_3$. In the present study, $La_{1-x}K_xMnO_3$ perovskite-type catalysts were prepared, characterized and tested for high temperature bio-oil steam reforming using a laboratory scale fixed bed. The aim of this study is to investigate the performance of the $La_{1-x}K_xMnO_3$ catalysts in bio-oil steam reforming and compare it with the commercial catalyst (14 wt.% Ni/ZrO_2). The effects of K substitution, temperature, WCMR and W_bHSV on H_2 yield, carbon conversion and the distributions of products were also analyzed herein.

2. Methods

2.1. Materials

The bio-oil was obtained from fast pyrolysis of pinewood sawdust in a fluidized bed at our Lab (Tianjin Engineering Center of Biomass-derived Gas and Oil, Tianjin, China). The pyrolysis temperature of pinewood sawdust was about 550 °C. The elemental composition of bio-oil was analyzed using a vario Micro cube elemental analyzer (Table 1). Contents of carbon (C), hydrogen (H) and oxygen (O) are 47.27%, 6.98% and 45.54%, respectively. According to the elemental analysis in Table 1, molecular formula of bio-oil can be defined by $CH_{1.77}O_{0.722}$ (wet basis).

2.2. Catalysts preparation and characterization

The reagents used were $Mn(NO_3)_2{\cdot}4H_2O$ (Merck), KNO_3 (Aldrich), $La(NO_3)_3{\cdot}6H_2O$ (Strem) and citric acid (Merck). $La_{1-x}K_xMnO_3$ perovskite-type catalysts were prepared by sol-gel method. Firstly, metal nitrates were dissolved in deionized water. Followed, 10% (molar ratio) more citric acid over the theoretical value was added, stirred at 80 °C until a viscous gel was obtained. The gel was subsequently dried at 110 °C overnight and calcined at 900 °C for 5 h. Finally, all the samples were crushed and sieved with desired particle sizes.

The commercial reforming catalyst (14 wt% Ni/ZrO_2) was selected to provide a basis for comparison with self-prepared catalysts. The catalyst was characterized by a specific surface area of 16.33 $m^2\ g^{-1}$ and an average pore diameter of 354.82 Å.

The Brunauer-Emmett-Teller (BET) surface areas of catalysts were obtained by nitrogen adsorption at 77 K, evaluated using the BET equation on an automatic Quantachrome Aparatus, Autosorb-iQ-C. The effluent gas was analyzed by means of an on-line mass spectrometer (MS, Hiden QIC-20). X-ray diffraction (XRD) patterns were obtained by a DRON-3 diffractometer. The fourier transforms infrared (FTIR) spectra were recorded on a Shimadzu IR-Prestige-21 spectrometer in the range of 500–4000 cm^{-1}. The scanning electron microscope (SEM) images and surface elemental analysis were recorded on a Quanta 200 SEM system equipped with energy dispersive spectroscopy (EDS) detector.

2.3. Experimental apparatus and procedure

The schematic diagram of the fixed-bed reactor used for gasification studies was shown in Fig. 1. The maximum working temperature for the fixed-bed is 800 °C. Bio-oil (water) was supplied by a high-pressure pump. The reactor was purged with nitrogen (400 mL min^{-1}) for 20 min and then heated up to the desired temperature (600–800 °C). Afterwards, steam and bio-oil were introduced into the reaction system by the two high-pressure syringe pumps which could control their feed rates, when heaters were preheated to 350 °C. The gaseous mixtures flowed out and passed through the condenser where the condensable components were collected as liquid phase. Non-condensable gas was measured by bubble flow meter and was collected by gas-collecting bags. The collected gas was analyzed by Beifen GC-3420A (3 m Porapak Q column and 2 m 5A molecular sieve) equipped with a TCD and a FID. The contents of carbon deposition were tested by the carbon combustion method.

2.4. Methods of data processing

The catalytic performances of the catalysts were evaluated in terms of H_2, CO, CO_2, CH_4 and C_nH_m (C_2H_4, C_2H_6, C_3H_6 and C_3H_8) yields.

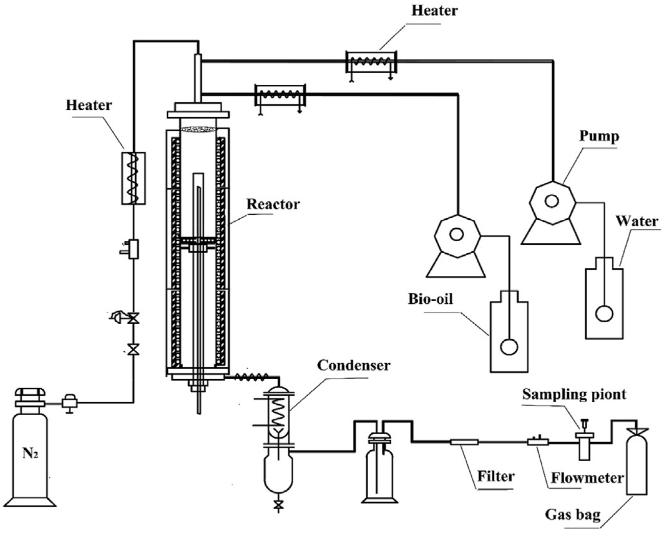

Fig. 1. The schematic diagram of bio-oil steam reforming.

Table 1
Ultimate analysis and several characteristics of the pinewood sawdust fast pyrolysis bio-oil.

Elements in bio-oil (wt. %)				H_2O (wt.%)	Ash (wt.%)	Density (kg m^{-3})	Calorific value (MJ kg^{-1})	pH	Kinematic viscosity at 20 °C ($mm^2\ s^{-1}$)
C	H	N	O[a]						
47.27	6.98	0.21	45.54	25.11	0.06	1150	16.24	2.6	60

[a] By difference.