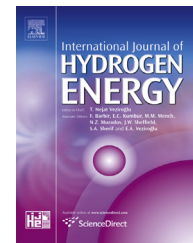


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Catalytic steam reforming of bio-oil model compounds for hydrogen production over coal ash supported Ni catalyst

Shurong Wang^{a,*}, Fan Zhang^a, Qinjie Cai^a, Xinbao Li^a, Lingjun Zhu^a, Qi Wang^b, Zhongyang Luo^a

^a State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, China

^b College of Metrological Technology and Engineering, China Jiliang University, Hangzhou 310018, China

ARTICLE INFO

Article history:

Received 17 September 2013

Received in revised form

27 November 2013

Accepted 30 November 2013

Available online 4 January 2014

Keywords:

Hydrogen
Reforming
Coal ash
Bio-oil
Acetic acid
Phenol

ABSTRACT

The development of a high performance and low cost catalyst is an important contribution to clean hydrogen production via the catalytic steam reforming of renewable bio-oil. Solid waste coal ash, which contains SiO₂, Al₂O₃, Fe₂O₃ and many alkali and alkaline earth metal oxides, was selected as a superior support for a Ni-based catalyst. The chemical composition and textural structures of the ash and the Ni/Ash catalysts were systematically characterized. Acetic acid and phenol were selected as two typical bio-oil model compounds to test the catalyst activity and stability. The conversion of acetic acid and phenol reached as much as 98.4% and 83.5%, respectively, at 700 °C. It is shown that the performance of the Ni/Ash catalyst was comparable with other commercial Ni-based steam reforming catalysts.

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1. Introduction

With the depletion of fossil fuels and the deterioration of the environment, increasing attention is being paid to the development of clean and renewable energy. Biomass-based hydrogen is an attractive energy source, widely used in fuel cells and internal combustion engines. There are two thermochemistry methods for the production of hydrogen from biomass. One is by biomass gasification, and the other is via catalytic steam reforming of biomass pyrolysis oil (also called bio-oil). The combination of the high yield of bio-oil and its

easy transportability makes the process of hydrogen production by steam reforming of bio-oil more economical [1–4]. Therefore, considerable research effort has been devoted to the steam reforming of bio-oil to hydrogen since the 1990s. However, bio-oil is a mixture of hundreds of components, including low and high molecular weight oxygenated compounds, such as carboxylic acids, aldehydes, ketones, alcohols and phenols [5,6]. Thus, model compounds are often used to establish catalyst structure–activity correlations. Carboxylic acids and phenols are two major chemical families in bio-oil, whose concentrations are in the range of 17–32% and 28–52%, respectively [7–11]. Acetic acid (HOAc) is the main carboxylic

* Corresponding author. Tel.: +86 571 87952801; fax: +86 571 87951616.

E-mail address: srwang@zju.edu.cn (S. Wang).

acid, while phenols contain phenol (PhOH) and its derivatives like guaiacol, 2,4-dimethyl-phenol and vanillin. Therefore, HOAc and PhOH were selected as the model compounds to represent carboxylic acids and phenols, respectively.

Ni–Al₂O₃-based catalysts have been widely used in the reforming of bio-oil because of the high activity of Ni towards the C–C bond cleavage of oxygenated compounds and the strong acidity of the Al₂O₃ support [3,4,12–14]. Furthermore, adding alkali (K, Na) and alkaline earth metals (Mg, Ca) can significantly promote the stability of the catalyst by increasing the water adsorption on the surface [15–17]. For example, a commercial catalyst (G1-50, BASF) for naphtha steam reforming consisted of 20% NiO, 32% Al₂O₃, 11% MgO, 16% CaO, 14% SiO₂, and 7% K₂O [18]. Iwasa et al. [19] studied the influence of the addition of various alkali metals on the Ni incorporated mesoporous smectite-like material on the performance for HOAc reforming. It was found that 1% K promoted the reduction of Ni species incorporated in the smectite, yielding more metallic Ni species and enhancing the conversion of HOAc dramatically.

Solid waste coal ash, generated from coal-fired power stations, is a complex mixture consisting of many oxides such as SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, K₂O, and Na₂O. Generally, SiO₂ is the most abundant component in the ash, followed by Al₂O₃ and Fe₂O₃. After combustion at high temperature, up to 1500 °C, coal ash has highly stable physical and chemical properties. The traditional treatment of coal ash is to use it for construction materials or just for landfill. It is regrettable that the ash, with its metallic compounds and stable properties, is not used further. Fortunately, more and more studies have been carried out to explore its utilization as a catalyst or catalyst support for reactions such as methane reforming, waste gas cleaning and petroleum hydrocracking [20]. However, no work has been reported regarding its use for bio-oil catalytic steam reforming.

It is of considerable interest to discover if a catalyst, made from coal ash as the support and with Ni as the active component, can provide high performance in the steam reforming reaction of bio-oil for hydrogen production. Furthermore, with the utilization of low cost coal ash, the economics of bio-oil catalytic reforming can be improved dramatically. In the present work, we choose HOAc and PhOH as typical bio-oil model compounds. Our objective is to combine the utilization of waste coal ash and the clean production of hydrogen by renewable bio-oil steam reforming.

2. Experimental

2.1. Catalyst preparation

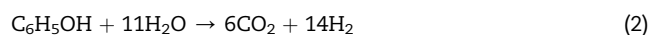
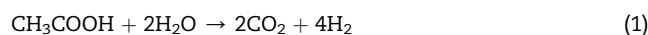
Coal ash was produced from a representative Chinese brown coal (produced in Yunnan Province, China) according to the standard coal ash manufacturing process. Coal powder was calcined at 815 °C for 2 h in air at a heating rate of 15 °C/min and then cooled to room temperature. This coal ash was chosen as the catalyst support. The catalyst with 15 wt% Ni loading was prepared by wet impregnation. Ni(NO₃)₂·6H₂O (7.4 g) was added to 50 ml ethanol and stirred at ambient temperature until fully dissolved (0.5 mol/L). Then 10 g coal

ash was added to the solution. The suspension was stirred for 2 h, followed by heating to 80 °C with stirring until the ethanol had completely evaporated. After evaporation, the sample was dried at 110 °C overnight and then calcined for 3 h at 815 °C. The calcined sample was crushed and sieved to 40–60 mesh. The prepared coal ash, and the Ni loaded catalyst are denoted as Ash and Ni/Ash, respectively.

2.2. Catalytic activity test

The catalytic activity test was carried out in a continuous-flow fixed-bed reactor. In each experiment, 1 g catalyst was sandwiched with quartz wool and packed in a quartz tube reactor with an inner diameter of 8 mm. A thermocouple was placed at the center of the catalyst layer to monitor the reaction temperature. The liquid feedstock was fed into the reactor by using a syringe pump at a weight hourly space velocity (WHSV) of 4 h⁻¹. The steam to carbon molar ratio (S/C) was initially maintained at 9.2, and then declined to 7.5, 5, 2.5 and 1. Prior to the reaction, the catalyst was reduced using hydrogen (50 ml/min) at 800 °C for 2 h at a heating rate of 10 °C/min. The experimental data were obtained after 2 h on-stream.

The overall reactions of HOAc and PhOH reforming are shown in Eqs. (1) and (2) and the stoichiometric yield (% stoi.) of H₂, and the conversion are defined by Eqs. (3) and (4):



$$\text{H}_2 \text{ yield(stoi)} = \frac{\text{moles of H}_2 \text{ obtained}}{\text{moles of H}_2 \text{ in stoichiometric potential}} \times 100\% \quad (3)$$

$$\text{Conversion} = \frac{\text{moles of carbon in the product gas}}{\text{moles of carbon in the feed}} \times 100\% \quad (4)$$

2.3. Catalyst characterization

The Brunauer–Emmett–Teller (BET) surface area (S_{BET}) and other textural properties were measured by N₂ adsorption–desorption. N₂ adsorption–desorption isotherms were recorded at 77 K using a Tristar 3000 apparatus. Before the measurement, the samples were degassed at 573 K for 3 h. The specific surface area was calculated based on the multipoint Brunauer–Emmett–Teller (BET) method. Powder X-ray diffraction (XRD) patterns were recorded on a PANalytical X'Pert PRO X-ray diffractometer with a Cu-K_α radiation source operating at 40 kV and 30 mA. The crystallite size was calculated according to the Scherrer equation. The chemical composition of the ash was analyzed by an energy dispersive X-ray emission spectrometer (EDX, GENESIS-4000 X).

Transmission electron microscopy (TEM) images were obtained using a Philips Tecnai G²F30 instrument. The surface morphologies were observed by scanning electron microscopy (SEM, FEI Model SIRION-100). H₂ temperature programmed reduction (H₂-TPR) analysis was carried out on an AutoChem

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