

# Hydrogen production via steam reforming of bio-oil model compounds over supported nickel catalysts

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## Abstract

The steam reforming of four bio-oil model compounds (acetic acid, ethanol, acetone and phenol) was investigated over Ni-based catalysts supported on Al<sub>2</sub>O<sub>3</sub> modified by Mg, Ce or Co in this paper. The activation process can improve the catalytic activity with the change of high-valence Ni (Ni<sub>2</sub>O<sub>3</sub>, NiO) to low-valence Ni (Ni, NiO). Among these catalysts after activation, the Ce-Ni/Co catalyst showed the best catalytic activity for the steam reforming of all the four model compounds. After long-term experiment at 700 °C and the S/C ratio of 9, the Ce-Ni/Co catalyst still maintained excellent stability for the steam reforming of the simulated bio-oil (mixed by the four compounds with the equal masses). With CaO calcinated from calcium acetate as CO<sub>2</sub> sorbent, the catalytic steam reforming experiment combined with continuous in situ CO<sub>2</sub> adsorption was performed. With the comparison of the case without the adding of CO<sub>2</sub> sorbent, the hydrogen concentration was dramatically improved from 74.8% to 92.3%, with the CO<sub>2</sub> concentration obviously decreased from 19.90% to 1.88%.

## Key words

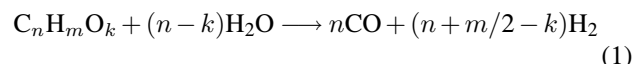
hydrogen production; bio-oil; model compounds; Ni catalyst; CO<sub>2</sub> capture

## 1. Introduction

Currently, hydrogen producing is mainly through steam reforming of fossil fuels containing nature gas, naphtha and coal. But due to the depletion of fossil fuels and the deterioration of the environment resulting from its utilization process, increasing attention is being paid to the development of clean and renewable energy [1]. Renewable biomass is recognized as an attractive alternative to fossil fuels, because of its rich reserves and neutral CO<sub>2</sub> emissions [2]. There are mainly two thermochemical processes to produce hydrogen from biomass, gasification and flash pyrolysis followed by steam reforming of the pyrolysis bio-oil. The latter was known as one of the more economically friendly methods for hydrogen production with the fairly mature pyrolysis technology and the easy transportability [3–9]. However, bio-oil is typically a complex mixture of low and high molecular weight oxygenated compounds, such as carbonxylic acids, alcohols, ketones, aldehydes and phenols [10–12]. So, it is difficult to directly perform the steam reforming of the entire bio-oil, and therefore, model compounds were often used to establish catalyst structure-activity correlations, such as ethanol, acetic acid, acetone, phenol, ethylene or the mixture of two or more

compounds [1,10,13–18].

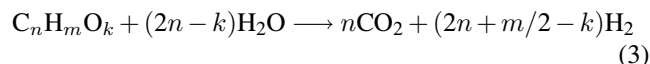
For the bio-oil, the steam reforming reaction is:



associated with the water gas shift (WGS) reaction:



Given the Equation (1) and Equation (2) happening successively, the overall reforming reaction can be represented as follows:



From the above equations, there is almost equivalent carbon dioxide with hydrogen in the final products of steam reforming, thereby limiting the hydrogen purity, with the concentration lower than 70% in the most researches [1,19–21]. On the other hand, as the WGS reaction is limited by the equilibrium, it is expected that the removal of CO<sub>2</sub> from the gas phase in the steam reforming process will displace the equilibrium to higher H<sub>2</sub> production [22]. Hence, the steam reforming process of bio-oil with in situ CO<sub>2</sub> capture was put forward. In the related studies, most of CO<sub>2</sub> sorbents were

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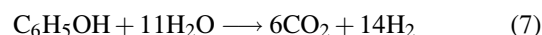
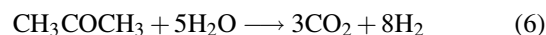
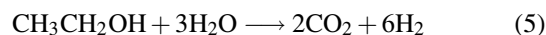
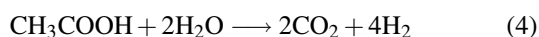
CaO-based substances [9,22–25]. And, the certain amounts of CO<sub>2</sub> sorbent, mixed with reforming catalysts, were often packed in a fixed bed reactor, and the results showed that the addition of CO<sub>2</sub> sorbents could obviously improve the hydrogen concentration before the adsorption capacity of CO<sub>2</sub> sorbents reached saturation [9,23,25]. However, the fixed amount of CO<sub>2</sub> sorbents limited the continuity of the SR process with high efficiency. Aimed to realize continuous CO<sub>2</sub> adsorption simultaneously with the reforming reaction, Chen and Ding et al. [26] put forward a new process of which the principle lied in the use of a combination of a packed catalyst bed and a moving bed for desorption. Microsized sorbent were pneumatically conveyed through the packed structure of the reforming catalysts by gaseous reactants or products for continuous CO<sub>2</sub> removal in the catalytic steam reforming process, and sorbent regeneration was carried out in the desorber for recycling. However, the real experimental studies of steam reforming of bio-oil or its model compounds in the above process have not been performed. To ensure microsized sorbent conveying through the catalytic bed, large-scale catalysts particles were required with bigger voidage of the bed structure.

Because of the high activity of Ni towards the C–C bond cleavage of oxygenated compounds and the lower prices of Ni and the Al<sub>2</sub>O<sub>3</sub> support, the Ni-Al<sub>2</sub>O<sub>3</sub>-based catalysts were widely studied in the steam reforming processes of bio-oil and compounds, but mostly with hundreds of microns or less in size [15,27–29]. Because of the limited activity of Ni and the strong acidity of alumina support, the Ni-based catalysts were often modified by the adding of some metals, such as magnesium, cobalt and ceria. The addition of Mg was found able to enhance both the steam adsorption capability and the stability of nickel against sintering [21]. The addition of Co was known to lead to relatively higher activities than Ni for the WGS reaction [30]. The addition of Ce were able to disperse the active metal efficiently and inhibit sintering, and as a promoter of carbon removal from metallic surfaces [31]. So, in this paper, various Ni-based catalysts supported on Al<sub>2</sub>O<sub>3</sub> particles with 3–5 mm in diameter modified by Mg, Ce and Co were prepared, and their catalytic activities were tested through the steam reforming of four model compounds (acetic acid, ethanol, acetone and phenol). Moreover, the most versatile catalyst was applied into the experiment of the steam reforming with in situ CO<sub>2</sub> capture.

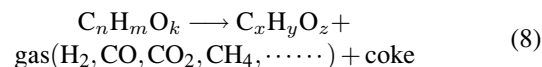
## 2. Experimental

### 2.1. Model compounds of bio-oil

In the present paper, the steam reforming processes of acetic acid, ethanol, acetone and phenol, as typical model compounds of bio-oil, were studied. For the four components, the overall steam reforming reactions are shown in the follows, for acetic acid, ethanol, acetone and phenol, respectively:



In the SR process, some side reactions also took place, such as thermal decomposition reaction (Equation 8) and (carbon) disproportionation reaction (Equation 9):



In the catalyst test experiments, ethanol, acetic acid and acetone were mixed with deionized water into the aqueous solution with the mole ratio of steam to carbon (S/C) of 6. Because of the limited solubility of phenol in water at room temperature, the aqueous solution of phenol was made up with S/C ratio of 12. In the experiment of catalytic steam reforming with in situ CO<sub>2</sub> capture, the four compounds were mixed with the equal masses, and then the mixture, called simulated bio-oil, was mixed with deionized water at S/C ratio of 9 into the aqueous solution as the feed of this experiment.

### 2.2. Catalysts preparation

Eleven nickel-based catalysts (Ni, Ni/Mg, Mg-Ni, Mg-Ni/Mg, Mg-Ni/Ce, Mg-Ni/Co, Ce-Ni, Ni/Ce, Ce-Ni/Mg, Ce-Ni/Ce and Ce-Ni/Co) supported on the Al<sub>2</sub>O<sub>3</sub> balls with 3–5 mm in diameter were prepared with the incipient wetness method. Mg, Ce and Co were as the auxiliary agent elements. The precursors used for Ni, Mg, Ce and Co metals were Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, respectively. For Ni, Ni/Mg and Ni/Ce, they were prepared with just one-time impregnation. For other catalysts, they were impregnated for two times. Mg or Ce metal was firstly impregnated to improve thermostability of the Al<sub>2</sub>O<sub>3</sub> carrier, and the mixed Ni and Mg or Ce or Co metals were then impregnated. In each impregnating process, the carrier particles were impregnated in the aqueous solutions of the precursors for 12 h and then were dried over night at 120 °C, and afterwards were calcined at 950 °C for 3 h. The nominal metal composition of the final catalysts was 10 wt% for Ni, 5 wt% for Mg and Ce in the first impregnation, and 5 wt% for Mg, Ce and Co in the second impregnation. Before the catalytic performance tests, these catalysts were activated at 600 °C in the atmosphere of H<sub>2</sub> (10% in N<sub>2</sub>) for 6 h.

### 2.3. Apparatus

Figure 1(a) shows a schematic illustration of the experiment apparatus of catalytic test. The experiments were conducted in a fixed-bed reactor made of stainless steel (06Cr25Ni20). The catalysts were placed in the middle of the

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