

Steam reforming of carboxylic acids for hydrogen generation: Effects of aliphatic chain of the acids on their reaction behaviors

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ABSTRACT

The paper investigated the effects of molecular structures on the conversion of the carboxylic acids (formic acid, acetic acid, propionic acid and butyric acid) during the steam reforming reactions. In essence, molecular structures determined catalytic behaviors of the organics during the reforming reactions. The acids with a C–C bond were more stable than formic acid during the homogenous decomposition reactions. However, the steam reforming of formic acid was much easier than that of the heavier acids due to the absence of cracking of the C–C bond during reforming. The difficulty for reforming of the carboxylic acids increased with the increase of the length of the aliphatic carbon chain (from acetic acid to butyric acid). The carboxylic acids with a longer aliphatic carbon chain (propionic acid and butyric acid) also had a higher tendency towards coking than acetic acid and formic acid. The coke formed in steam reforming of formic acid was the lowest compared with other acids. The C–C bond and the number of C–C bond in the carboxylic acids affected the reactivity of the carboxylic acids, their tendencies towards the formation of coke and the properties of the coke. The coke had larger aromatic ring systems and oxygen-containing functionalities during steam reforming of acetic acid. The amorphous coke formed in reforming of acetic acid, while the fibrous coke formed during the reforming of the heavier carboxylic acids.

1. Introduction

Hydrogen is a clean energy carrier and a raw chemical feedstock with a wide application in the industries such as oil refinery, ammonia synthesis and etc [1–4]. In recent years, hydrogen has received additional attention due to its application in fuel cells such as proton exchange membrane fuel cells (PEMFCs), due to the high energy efficiency [5,6].

Currently, the annual output of H₂ derived from natural gas, petroleum and coal accounted for more than 95% of world-wide H₂ production [7–9]. Fossil fuels, however, are not sustainable and their use is associated with the emission of CO₂ and the pollutants such as NO_x and SO₂ [10]. In comparison, production of hydrogen from biomass does not have such issues as biomass is renewable, sustainable and carbon-neutral. Moreover, the generation of the NO_x and SO₂ pollutants could also be significantly reduced with biomass as the feedstock for hydrogen production.

The production of hydrogen from biomass involves mainly two steps. Firstly, biomass was pyrolysed to obtain bio-char and a condensable liquid named bio-oil [11–13]. Bio-oil was then further reformed with steam to

produce hydrogen [14]. Steam reforming of bio-oil involves a complicated reaction network, which is due to the complex composition of bio-oil [15]. Bio-oil generally contains carboxylic acids, aldehydes, ketones, sugars, sugar oligomers, phenolic and pyrolytic lignin [16,17].

The complexity of bio-oil makes the direct steam reforming of bio-oil rather challenging, which is due to the complex reaction behaviors of the organics in bio-oil during steam reforming, originating from their different structures and functionalities [18–23]. Among the various organics in bio-oil, carboxylic acids are one of the most important fractions with the typical concentration around 5 wt% in bio-oil [24]. Carboxylic acids in bio-oil also affect other components via catalyzing their polymerization during aging or heating of bio-oil [24–29]. Understanding the reaction behaviors of carboxylic acids during steam reforming could provide useful information for optimizing the process of steam reforming of bio-oil.

Although in many cases acetic acid is the main carboxylic acid in bio-oil [30,31], there are also many other acids in bio-oil, including formic acid, propionic acid, butyric acid and etc. These acids have different molecular structures from that of acetic acid, and are also expected to behave

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differently during steam reforming. Our previous study about esterification of the different acids in methanol has confirmed that molecular structures have a profound or intrinsic influence on reaction behaviors of the carboxylic acids with different molecular structures [32]. However, there are few study focusing on the effects of molecular structure of carboxylic acids on their reaction behaviors during steam reforming reactions.

In this study, we tried to establish the relationship between the structures and the reaction behaviors of the carboxylic acids during steam reforming reactions. Formic acid, acetic acid, propionic acid and butyric acid, which have different length of aliphatic carbon chain, were used as the reaction substrates. Ni/Al₂O₃, a typical catalyst for steam reforming, was used as the catalyst. Our results demonstrate that molecular structures of the carboxylic acids significantly affect their reaction behaviors during steam reforming. Formic acid, as a C1 acid, was very reactive, which could be converted via homogeneous dehydration (form CO and H₂O) or decarboxylation (form CO₂ and H₂). The homogeneous dehydration or decarboxylation of other acids was negligible in the absence of Ni/Al₂O₃ catalyst but was promoted over alumina carrier. As for the reactivity of the carboxylic acids during steam reforming, the shorter the aliphatic chain, the more reactive the acids towards hydrogen production. The tendency towards coke formation follows the similar rule.

2. Experimental

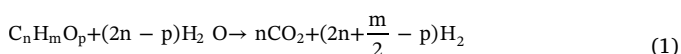
2.1. Catalyst preparation

Ni/Al₂O₃ catalysts were prepared via an traditional incipient wetness impregnation method with Ni(NO₃)₂·6H₂O as the precursor and Al₂O₃ as the support (277 m²/g, 30–45 mesh). Before the impregnation, the Al₂O₃ carrier was thermally treated in air at 600 °C for 5 h. A Ni(NO₃)₂·6H₂O solution (water as the solvent) was then prepared with a certain concentration of nickel to achieve a nickel loading of 20 wt% to Al₂O₃ support. After impregnation of the nickel precursors, the samples were dried at 105 °C for 10 h and then calcined at 600 °C for 4 h. NiO powder without support were prepared by calcination of the nickel nitrate hexahydrate purchased directly at 600 °C for 2 h.

2.2. Catalytic activity measurements

The catalytic tests were carried out in a fixed-bed reactor with 6 mm inner diameter. The experiments were performed at atmospheric pressure. Initially, 500 mg (volume = 0.43 mL, length = 1.5 cm) of catalyst was loaded and reduced in a 10% H₂ in N₂ (flow rate 40 mL/min) gas stream at 600 °C for 60 min. The reactor was then cooled down to the reaction temperature and the gas stream was switched to nitrogen, which was used as a carrier gas. The reactants with a given steam to carbon ratio (S/C) were fed into the reactor by a syringe pump. The residence time at each investigated temperature was 30 min. The gaseous products were analyzed by a gas chromatography (EWAI GC-4000A) equipped with a TCD detector. The liquid products were collected and analyzed by a liquid chromatography (SHIMADZU LC-20A). After the experiment, the sample was cooled in N₂ to room temperature and the catalyst samples were collected for further analysis. Reaction conditions were as follows: LHSV = 12.7 h⁻¹, P = 1 atm. GHSV changed versus temperature, 49317 h⁻¹ at 300 °C and 79848 h⁻¹ at 700 °C (including N₂).

The total reaction of the steam reforming of the carboxylic acids can be expressed by Eq. (1):



The conversion of a carboxylic acid was calculated according to the Eq. (2):

$$\begin{aligned} \text{Conversion}(\%) &= \frac{\text{Amount of acid in feedstock} - \text{amount of unreacted acid in residual}}{\text{Amount of acid in the feedstock}} \times 100\% \end{aligned} \quad (2)$$

The yield of H₂ was calculated by stoichiometric H₂ formation according to Eq. (3):

$$Y_{H_2}(\%) = \frac{\text{moles of } H_2 \text{ produced}}{(2n + \frac{m}{2} - p) \times \text{moles of acid fed}} \times 100\% \quad (3)$$

The yields of CO, CH₄ and CO₂ were calculated based on a carbon basis, as described in Eq. (4):

$$Y_{CO/CH_4/CO_2}(\%) = \frac{\text{moles of CO/CH}_4\text{/CO}_2 \text{ produced}}{n \times \text{moles of acid fed}} \times 100\% \quad (4)$$

2.3. Catalyst characterization

Temperature programmed reduction (TPR) experiments were carried out on a chemisorption analyzer (Vodo VDSorb-91i). The sample of 20.0 mg was packed in a U-tube reactor and the measurements were conducted at a ramping rate of 20 °C/min under the flowing mixture gas of 5 vol% H₂-Ar (20 mL/min) [30–32].

The phase detection was performed on an X-ray diffractometer (XRD, Bruker D8-Advance) equipped with a graphite monochromatized Cu Kα-radiation source (λ = 1.5406 Å) at a scanning rate of 10°/min in the range of 10–80° [33].

The thermogravimetry (TG) data was recorded with a Rigaku Corp equipment (model TG 812). During the analysis, 100 mg of sample was heated from 25 to 850 °C with a heating rate of 15 °C/min under an air flow (50 mL/min).

Temperature programmed oxidation (TPO) was conducted to evaluate the coke species by using PCA-1200 instrument. Prior to the TPO test, the sample was dried at 200 °C under high-purity Ar to remove absorbed water for 1 h. After that, the 20 mg catalyst loaded was heated to 800 °C at a heating rate of 15 °C/min under the flowing mixture gas of 5 vol% O₂-He (20 mL/min).

Element analysis (EA) was conducted to analyze the elemental composition of the coke depositing on the spent catalysts after steam reforming reactions by using Euro Vector EA-3000 element analyzer.

The carbon deposition on the surface of the catalyst was investigated on a Nicolet iS50 FT-IR Spectrometer equipped with a modified Harrick Praying Mantis DRIFT cell instrument. The details of the experiment were as follows. The powdered sample of ca. 100 mg was ground uniformly, then dried and degassed at 60 °C in vacuum oven for 12 h. After the pretreated, the sample was pressed into the cell for the in-situ IR characterization. During the test, the sample was heated from 25 to 800 °C at a ramping rate of 10 °C/min. Simultaneously, a vacuum pump was used to maintain vacuum. The spectra were recorded every 7 s during heating.

Raman spectroscopy of the spent catalysts was measured to analyze the aromatic ring structure of the coke formed by using a HORIBA LabRAM HR Evolution instrument.

The N₂ adsorption-desorption isotherms were measured at -196 °C in Pioneer SSA-6000 physical adsorption instrument.

Transmission electron microscope (TEM, JEOL2010) was used to observe the morphology of the coke on the spent catalyst.

3. Results and discussion

3.1. Catalysts characterization

The specific surface areas of the carrier and the reduced catalysts were measured by a BET method and the results were presented in Table 1 and Fig. 1, respectively. The surface areas of Ni/Al₂O₃ catalysts showed an obvious decrease compared with the carrier of Al₂O₃. The

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