Fuel 187 (2017) 128–136

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Catalytic reforming of toluene and naphthalene (model tar) by char supported nickel catalyst

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HIGHLIGHTS

- Char supported nickel catalysts were prepared for model tar reforming.
- Effect of nickel precursors and hydrazine on catalysts' performance were studied.
- Char with nickel nitrate precursor was more effective than char with nickel acetate.
- The presence of naphthalene affected reforming of toluene.

ARTICLE INFO

Article history:
Received 10 May 2016
Received in revised form 22 August 2016
Accepted 12 September 2016
Available online 21 September 2016

Keywords:
Char
Catalyst
Tar reforming
Gasification

ABSTRACT

The purpose of this study was to utilize gasification derived char as a catalyst support for tar removal. Red cedar char collected from downdraft bed gasification was chemically activated into activated carbon and impregnated with nickel acetate and nickel nitrate. The effects of nickel salts precursor, nitric acid treatment of support and reduction of nickel in hydrazine medium on catalyst performance were studied. It was found nickel nitrate was a better nickel precursor than nickel acetate for preparation of char supported nickel catalyst. The catalyst impregnated with nickel nitrate was found more active in steam reforming of toluene than the catalyst impregnated with nickel acetate. TEM results indicated that nickel particle size of the catalyst impregnated with nickel nitrate was much smaller than that of the catalyst impregnated with nickel acetate. Toluene showed higher removal efficiency than naphthalene. The presence of naphthalene decreased the toluene removal.

1. Introduction

Gasification, a biomass thermochemical conversion technology, converts biomass into synthesis gas (syngas), a mixture of primarily carbon monoxide, carbon dioxide and hydrogen. The produced syngas can further be used as a feedstock for hydrocarbon fuels production through the Fischer–Tropsch synthesis (FTS) process, which produces hydrocarbons of different lengths. Syngas can also be used as an alternative to natural gas fuel for hydrogen or power production. However, biomass-generated syngas cannot be used directly because it contains high concentration of tars which are a mixture of several aromatic compounds. The components of biomass tars can be categorized into five classes: undetectable, heterocyclic, light aromatic hydrocarbons (LAH), light polyaromatic hydrocarbons (LPAH) and heavy polyaromatic hydrocarbons (HPAH) [1].

The tars must be removed prior to utilization of syngas [2,3] because tars cause a lot of equipment problems, such as condensation on facility leading to fouling [3]. The environmental legislation also requires removal of toxic aromatic compounds from syngas. Wet scrubbing, catalytic conditioning and high temperature thermal cracking are three major syngas cleaning methods. Catalytic conditioning is of the most promising because of its high conditioning efficiency. In addition, catalytic conditioning of syngas tars can increase syngas H_2/CO [1,4,5] that is, typically, inadequate (<1) for the FTS (about 2.0) and other syngas conversions [6].

Recently, biochar, one of the byproducts of biomass gasification, was reported as a potential catalyst for tar removal [7]. The catalytic activity of char for tar elimination can be related to its high pore size, surface area, and ash/mineral content. Char can also be activated into activated carbon and used as a support for preparing metal catalysts [8,9]. When used as a catalyst support, activated carbon has unique properties, such as its stability in both acidic

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http://dx.doi.org/10.1016/j.fuel.2016.09.043
0016-2361/

and basic media, the possibility of easy recovery of precious metals supported on it and the possibility of tailoring both its textural and surface chemical properties [10,11].

Pretreatments to the carbon support can significantly affect the properties and performance of the carbon-based catalysts. High surface area, acid groups and oxygen-containing functional groups on the surface play an important role in catalyst reactivity of biochar. The metal dispersion ratio and metal–carbon interactions also affect the reactivity of carbon supported metal catalysts. Several studies have confirmed that pre-treatments of activated carbon increase metal dispersion ratio, support surface area and surface functional group, thus, influence its reactivity [12,13]. Pre-treatment includes acid treatment of carbon with various acids (H_2SO_4, HNO_3) and reducing agents (hydrazine and $NaBH_4$). Acid treatment can increase surface oxygenated groups on the activated carbon, and thus increase its catalytic activity [12,14–16]. Aksoylu et al. [12] studied the effect of HNO_3 treatment on Pt/carbon catalyst performance in the benzene hydrogenation reaction. The results showed that HNO_3 treatments not only led to increase in oxygen bearing groups on the exterior and interior surfaces of the activated carbon, but also enhanced dispersion of Pt. The catalyst activity test showed that the treated catalyst exhibited higher efficiency as compared to the untreated catalyst [14]. Besides acid treatment, hydrazine treatment has also been widely used in catalyst preparation as a reducing agent of metallic catalyst. Treating the catalyst with reducing agent produces nanoparticle metal catalyst with small average particle size and high dispersive ratio [13,17,18]. Wojcieszak et al. [13] compared the properties of hydrazine treated catalysts (reduction of nickel by aqueous hydrazine) and classically prepared catalysts (without the hydrazine treatment) and found that the hydrazine reduction process improved metal dispersion and catalyst efficiency.

Nickel based catalysts have been widely used in tar reforming [19–22]. Świerczyński et al. [23] found that the nickel based catalyst was very effective in reforming of tars. Michel et al. [20] compared performances of olivine-based catalysts for steam reforming of methylnaphthalene (MNP) as a model tar compound. The results showed that conversion efficiency of MNP to CO/H_2 with olivine alone (4%) was much lower than that with Ni/olivine (30%).

The objective of this study was to develop novel char based catalysts. Red cedar-derived char was used as a precursor for making activated carbon support material for nickel. The effects of pretreatment method and precursor on the catalytic performances were studied: the first type of catalyst was prepared by mild oxidation of activated carbon (support) with nitric acid and reduction of impregnated nickel acetate or nickel nitrate with hydrogen; the second type of catalyst was prepared by reduction of nickel acetate with hydrazine. The properties of char based catalysts were evaluated using TEM, XRD and N_2 isotherms, and the catalysts' performances were tested in steam reforming of toluene and naphthalene (model tar compounds). Toluene was used as light monoaromatic model tar compound. Naphthalene was used as light polyaromatic model tar compound because high molecular weight compounds, such as naphthalene, are difficult to crack and have not been studied extensively.

2. Materials and methods

2.1. Materials

The char for making catalysts in this study was produced from gasification of eastern red cedar in a unique downdraft gasifier as described in previous study [24]. The resulting biochar contained 66.4% C, 1.9% H and 0.2% N on dry basis [24]. The gasification temperature was around 900 °C [24]. $Ni(NO_3)_2 \cdot 6H_2O$, $Ni(CH_3COO)_2 \cdot 4H_2O$ ($\geqslant$99.0%) and hydrazine anhydrate (50–60%) were purchased from Sigma Aldrich (St. Louis, MO, USA). The KOH was purchased from Fisher Scientific (Pittsburgh, PA, USA).

2.2. Activated carbon preparation

Chemical activation is a widely used activation method for making activated carbon [25,26]. This method uses chemicals such as KOH and NaOH as an activator to develop pores. In our study, char was mixed with KOH and soaked for 2 h. The mixture was dried in an oven overnight at 105 °C. The dried mixture was then placed in a fixed-bed tubular reactor and activated. The reactor was first heated to 300 °C and held at this temperature for 2 h to prevent carbon loss from char. For carbonization, the temperature was then raised to 800 °C and char was activated at this temperature for 1.5 h under nitrogen flow of 200 ml/min. After carbonization, the char was washed with deionized water until the pH of leaching water reached 7. The activated carbon prepared using this method contained 79.03% C, 1.92% H, and 0.51% N on dry basis.

2.3. Catalyst synthesis

The activated carbon was treated with 30 vol.% HNO_3 before loading nickel. Activated carbon was loaded in a round bottom flask equipped with a thermometer and reflux condenser. The flask was immersed in a water bath at 70 °C. The activated carbon suspension was stirred continuously using a magnetic stirrer bar. After 1.5 h acid treatment, activated char was filtered from the suspension into a funnel and washed with deionized water until pH of the filtered solution reached neutral. The acid soaked char was then dried in an oven at 105 °C overnight. The activated carbon treated with acid contained 69.18% C, 1.04% H, and 0.56% N on dry basis. The dried acid treated activated char was the wet impregnated in a solution of nickel acetate or nickel nitrate. The concentration of the nickel acetate solution was calculated before impregnation in order to achieve 10 wt.% nickel loading. The mixture was ultrasonicated for 3 h and kept in a vacuum desiccator for 16 h. The soaked samples were then dried in the oven at 105 °C and denoted as Ni-AC-N (activated char loaded with nickel nitrate) and Ni-AC-A (activated char loaded with nickel acetate).

To study the effect of hydrazine reduction on catalyst properties, Ni-AC-A was further treated with hydrazine using a method reported in literature [13]. The catalyst precursor was soaked in a 2.0 M hydrazine solution for reduction. The reduction of nickel catalyst precursor was performed in a 250 ml three necked flask that was immersed in a hot water bath. The reaction flask was fitted with a reflux condenser, a thermometer and a gas tubing for using helium to purge the air out of the flask. The mixture of nickel catalyst precursor and hydrazine solution was stirred at 80 °C for 4 h. After reduction, the catalyst was filtered and the excess hydrazine left in catalyst was washed off with deionized water. The catalyst was then dried in an oven at 105 °C before test and denoted as Ni-AC-AH.

2.4. Catalyst activity test

2.4.1. Steam reforming of toluene

The catalytic reforming tests were performed in a fixed bed reactor with a 1/2 in. inner diameter. One layer of quartz wool was kept beneath the catalyst (particle size of 0.3–0.6 mm and weight of 0.25 g) for support and one layer of quartz wool was kept above the catalyst. The catalyst was reduced in 200 ml/min hydrogen (50% hydrogen, 50% nitrogen) flow at 350 °C for 3 h before testing. During testing, 150 ml/min nitrogen controlled by mass flow controller (Burkert, Charlotte, NC, USA) was introduced into the reactor. The water and toluene were injected into evaporator by