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Full Length Article

Effect of atmosphere on carbon deposition of Ni/Al_2O_3 and Ni-loaded on lignite char during reforming of toluene as a biomass tar model compound

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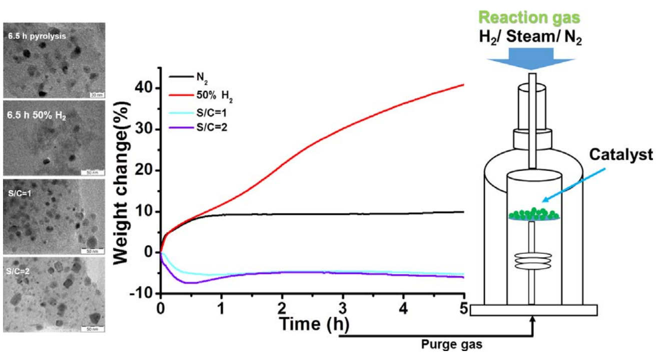
GRAPHICAL ABSTRACT



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ABSTRACT

Toluene as a model tar compound was used to study the effect of atmosphere on carbon deposition during biomass tar reforming. A novel Ni-loaded on lignite char (Ni/LC) and commercial Ni/Al_2O_3 was employed for stability evaluation in a thermogravimetric analyzer. The mechanism of coke formation under N_2, H_2 and steam with different steam/carbon (S/C) ratio were investigated during 5 h test. Nickel particle growth is the main reasons responsible for the deactivation of Ni-based catalysts for tar reforming. Steam remarkably suppressed the carbon deposition on Ni/Al_2O_3, especially in a high S/C ratio. Ni/Al_2O_3 exhibited high activity and stability for 5 h operation in S/C ratio of 2. H_2 significantly promoted the carbon deposition on Ni/Al_2O_3 and caused the catalyst deactivation within 0.5 h. Ni/LC exhibited great resistance to coke deposition under inert and H_2 reforming of toluene. The catalysts before and after catalytic cracking were characterized by X-ray diffraction and transmission electron microscopy to investigate the behavior of carbon deposition. Except for H_2 reforming, an obvious change of the Ni crystallite size (NCS) can be found after reforming for 5 h under all conditions used in this study. The NCS in Ni/LC was significantly increased with increasing time and S/C ratio, which should be partly responsible for the deactivation of the Ni/LC.

1. Introduction

Reforming of volatiles from biomass pyrolysis is an effective attempt to meet the goals of expanding the use of biomass [1]. It is considered as one of the most promising thermochemical technology that converts biomass into H_2-rich gas, which can be used as a fuel to generate electricity and feedstock for chemical synthesis processes. The major problem in biomass gasification is tar formation during the pyrolysis

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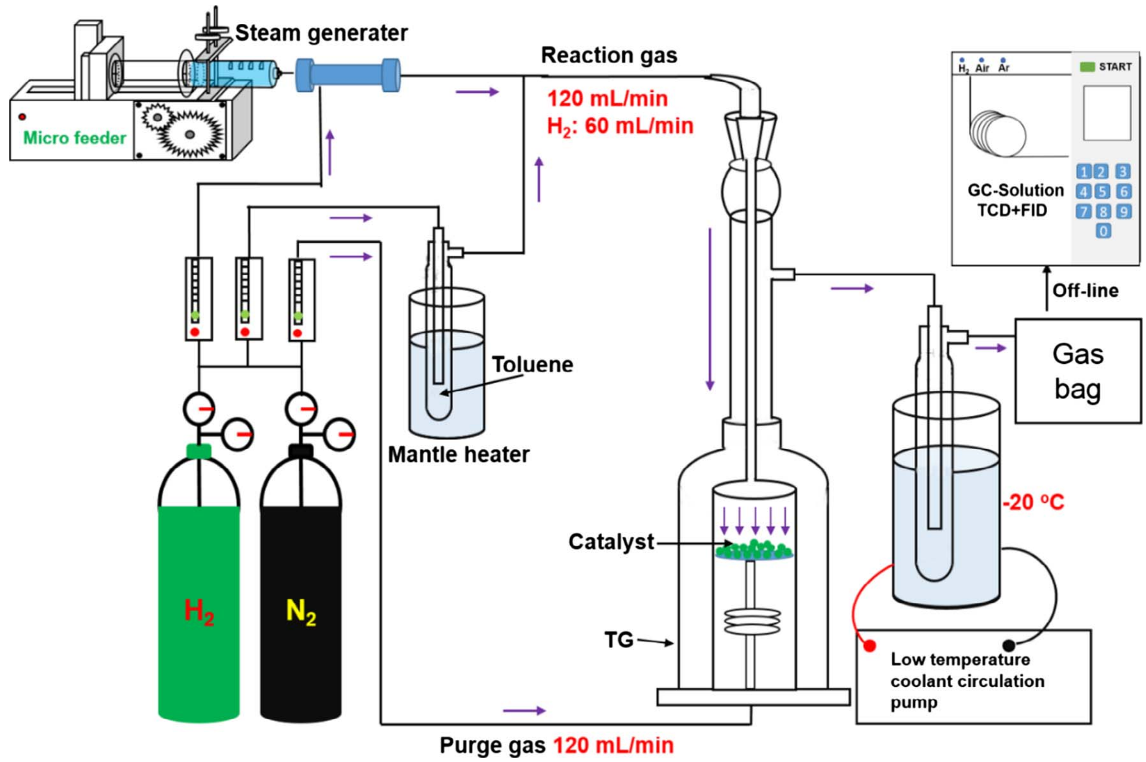

Fig. 1. Schematic diagram of catalytic set-up for TIR, THR and TSR.

process [2]. Tar can condense in pipes and filters then simultaneously cause the blockage and corrosion of engines and turbines [3,4]. The use of catalyst for biomass gasification is indeed promising to reduce the formation of tar [5]. Many kinds of catalysts were used for catalytic biomass gasification, such as Ni/Al_2O_3 [6], limonite ore [7], olivine [8], and HZSM-5 [9]. Among that, Ni-based catalyst was proved to be quite active for tar cracking [10–12]. However, Ni-based catalyst was easily sintered, active component lost, carbon deposit and phase transformed; which are responsible for its deactivation [13–16]. Carbon deposition was regarded as one of the main reasons responsible for the deactivation of Ni-based catalyst, which was produced from the catalytic cracking of different carbonaceous gases, such as CH_4, C_2H_4, and CO, over the active metal nickel [13,17].

In general, the catalytic activity of metal species significantly depends upon the support type. Different support has different interaction with metal, and the structure or electronic state of metal specie was changed [18]. There are many types of catalyst supports, such as Al_2O_3 [19], silica gel [20], zeolite [21], resin [22], activated carbon [23], and natural minerals [7,24,25]. Al_2O_3 is a commonly commercial catalyst, and is reportedly uneconomical and inactive at high temperatures of 800 °C [12,26,27]. Activated carbon was a universal resource, which can be obtained from biomass and coal substantially. We previously reported a novel catalyst for biomass gasification with dispersed metallic Ni particles in lignite char (Ni/LC) [28]. However, the lifetime and anti-coke deposition capability of the Ni/LC had not been well investigated yet. Although some literatures were reported about the lifetime and deactivation of the catalyst [29–32], but few work reported the effects of atmosphere and the steam/carbon (S/C) ratio on carbon deposition of Ni-based catalyst, especially the Ni/LC, during biomass gasification.

In this study, toluene was used as a biomass tar model compound to study the carbon deposition on Ni/LC catalyst and commercial Ni/Al_2O_3 catalyst. The effects of atmosphere, time and S/C ratio were investigated in a well-designed thermogravimetric analyzer.

2. Materials and methods

2.1. Materials

Loy Yang lignite (Victoria, Australia; 0.5–1.0 mm) was used for Ni/LC catalyst preparation. The proximate and ultimate analyses of Loy Yang lignite was as reported [33]. Ni/LC (Ni loading 19 ± 1 wt%) was prepared by ion exchange using lignite and nickel solution as reported previously [28]. A commercial Ni/Al_2O_3 (No. C13-4, Süd-Chemie Catalysts Japan, Inc., Ni loading 20 ± 2 wt%) was used for reforming experiments. All catalysts were crushed and sieved to 0.5–1.0 mm and stored in a vacuum container before use.

2.2. Instrument analysis

The gaseous products were analyzed with a Shimadzu GC-14B gas chromatograph, which equipped a thermal conductivity detector (TCD), flame ionization detector (FID) and methane converter to convert carbon oxides into detectable CH_4. A Sinku-Riko TGD7000 thermogravimetric analyzer (TG) was employed to determine the weight change of catalysts during reforming test. A Mac Science M03XHF X-ray diffraction (XRD) with Cu (λ = 1.54056 Å) Kα radiation at 40 kV and 30 mA was used to determine the characteristics of the catalyst before and after reforming, at a scanning speed of 1°/min from 10 to 110°. PDXL software and Scherrer equation was employed to analyze the XRD test data. A JEOL JEM-2010 transmission electron microscope (TEM) was employed for the catalyst characterization. Scion imaging analysis software was used to measure the Ni particle size (NPS) distribution. The catalyst after the experiment was finely pulverized and dispersed in ethanol with ultrasonic washer. After that, the solution was dropped on a grid of copper mesh and air dried. Observations were made at random places and image was obtained at a magnification of 50,000–15,000 times.