Effects of electric current upon catalytic steam reforming of biomass gasification tar model compounds to syngas

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ABSTRACT

Electrochemical catalytic reforming (ECR) technique, known as electric current enhanced catalytic reforming technique, was proposed to convert the biomass gasification tar into syngas. In this study, Ni–CeO$_2$/γ-Al$_2$O$_3$ catalyst was prepared, and toluene was employed as the major feedstock for ECR experiments using a fixed-bed lab-scale setup where thermal electrons could be generated and provided to the catalyst. Several factors, including the electric current intensity, reaction temperature and steam/carbon (S/C) ratio, were investigated to reveal their effects on the conversion of toluene as well as the composition of the gas products. Moreover, toluene, two other tar model compounds (benzene and 1-methylnaphthalene) and real tar (tar-containing wastewater) were subjected to the long period catalytic stability tests. All the used catalysts were analyzed to determine their carbon contents. The results indicated that the presence of electric current enhanced the catalytic performance remarkably. The toluene conversion reached 99.9% under the electric current of 4 A, catalytic temperature of 800 °C and S/C ratio of 3. Stable conversion performances of benzene, 1-methylnaphthalene and tar-containing wastewater were also observed in the ECR process. H$_2$ and CO were the major gas products, while CO$_2$ and CH$_4$ were the minor ones. Due to the promising capability, the ECR technique deserves further investigation and application for efficient tar conversion.

1. Introduction

Gasification is one of the most promising technologies to utilize biomass materials [1–3]. It can convert solid biomass mainly into a combustible H$_2$&CO-rich gas product which can be further used in power generation or synthesis applications [4–6]. However, the formation of tar during the gasification process is a critical problem that hinders the large-scale application of gasification technique, because the presence of tar will bring many negative effects to process equipment.

Catalytic steam reforming is an effective method to convert tar compounds to permanent gases in the presence of steam and proper catalysts [7–9]. Till now, various catalysts have been tested for catalytic steam reforming of tar or model compounds, such as dolomite and olivine [10–12], nickel based catalysts [13–15] and

noble metal based catalysts [16–18]. Among these catalysts, nickel based catalysts have been confirmed to be promising for tar reduction [13–15], and also capable for methane reforming and water gas shift reaction, allowing the adjustment of the H$_2$/CO ratio in syngas.

However, exorbitant reforming temperature and quick catalyst deactivation are two serious challenges that hinder the application of catalytic steam reforming technique. Hence, it is very essential to develop new catalytic steam reforming techniques and optimize the nickel based catalysts. Recently, a novel ECR technique was proposed to treat bio-oil for hydrogen production [19–23]. In the ECR process, an electrified wire was embedded in the catalyst layer, and synchronously providing thermal electrons to the catalysts. The research confirmed that the ECR process could improve catalytic efficiency and lower catalyst deactivation as compared with traditional steam reforming process [22]. Currently, the ECR technique has not been applied to treat the biomass gasification tar or related model compounds.

The objective of this work is to apply the ECR technique to convert the tar and its model compounds into syngas, investigating the effects of electric current on the catalytic steam reforming process.

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Hence, a newly designed lab-scale setup was established to perform the ECR experiments. An electrified Ni–Cr wire was installed in the catalyst bed, to generate thermal electrons for the ECR process. Three tar model compounds (toluene, benzene and 1-methylnaphthalene) and real tar (tar-containing wastewater) were selected for experiments, and toluene was used as the major feedstock. Toluene and benzene were selected because they were the major tar components, 1-methylnaphthalene was selected because it represented large compounds in the real tar [24], while tar-containing wastewater was obtained from the wet scrubbing system of a biomass gasification plant. The ECR experiments were conducted using the Ni–CeO$_2$/γ-Al$_2$O$_3$ catalyst, to investigate the effects of several factors on the conversion and product distribution of the three tar model compounds and tar-containing wastewater.

2. Experimental

2.1. Materials

The feedstock employed in this study included three tar model compounds (toluene, benzene and 1-methylnaphthalene) and real tar (tar-containing wastewater). The tar-containing wastewater was a mixture of real tar and water, obtained from the wet scrubbing system of a biomass gasification plant around Beijing. Its elemental composition was analyzed by a Vario Macro Cube Elemental Analyzer. The results were C 2.7 wt%, H 11.1 wt%, N 0.2 wt%, S 0.1 wt% and O 85.9 wt% (by difference).

2.2. Catalyst preparation and characterization

Nickel supported on γ-Al$_2$O$_3$ doped with CeO$_2$ (Ni–CeO$_2$/γ-Al$_2$O$_3$) catalyst was prepared by one step incipient wetness impregnation method using nickel nitrate as the nickel precursor and cerium nitrate as the cerium oxide precursor [13]. Typically, 14.9 g nickel nitrate hexahydrate and 7.6 g cerium nitrate hexahydrate were impregnated to 94.0 g γ-Al$_2$O$_3$ with 12 h ultrasonic treatment. Afterwards, the slurry was dried at 105 °C for 12 h in air. Finally, the solid was directly calcined in situ in the mixture of nitrogen and hydrogen before the ECR experiments, to obtain the Ni–CeO$_2$/γ-Al$_2$O$_3$ catalyst with good reducibility, metal dispersion, and high surface area [25]. The nickel and CeO$_2$ loadings of the Ni–CeO$_2$/γ-Al$_2$O$_3$ catalyst were both fixed at 3 wt%.

Nitrogen physical adsorption measurement of the catalyst was performed at 77 K using the Quantachrome Autosorb-iQ physical adsorption instrument. The Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods were used to calculate the specific surface areas and pore volumes. The X-ray diffraction (XRD) patterns were recorded on a Rigaku Rotaflex diffractometer equipped with Cu Kα radiation source (λ = 0.15406 nm). Moreover, all the used catalysts were analyzed by a Vario Macro Cube Elemental Analyzer to determine the contents of carbon deposited on them.

2.3. Experimental setup and operation procedure

The lab-scale fixed-bed ECR setup is shown in Fig. 1. The setup was composed of three systems: the feeding system, the reaction system and the testing system. The feeding system consisted of two gas cylinders (H$_2$ and N$_2$), two mass flow meters, a syringe pump for toluene and a peristaltic pump for water. The reaction system consisted of two quartz reactors (an upper one and a bottom one), two electric heating furnaces and an electric current controller. The testing system consisted of a condenser (ice-cooled) and an on-line gas chromatography analyzer (MICRO GC 3000,

INFICON, USA). The two pumps in the feeding system were used to inject water and toluene (or other two tar model compounds and tar-containing wastewater) with stable flow rates into the upper quartz reactor of the reaction system. The S/C ratio (mole ratio of steam to carbon in toluene or other tar model compounds) could then be calculated based on the feeding rates. The injected water and toluene (or other two tar model compounds and tar-containing wastewater) were evaporated in the upper quartz reactor (i.d. 32 mm) and reacted in the bottom quartz reactor (i.d. 32 mm). In the upper reactor, some quartz wool was fixed in it. In the bottom reactor, an electrified Ni–Cr wire (resistance: 15 Ω) entwined around a U-shaped quartz tube was installed in it. The catalyst (2.4 g uncalcined catalyst in each experiment) was placed above some quartz wool and embedded uniformly around the Ni–Cr wire. When the current was switched on, thermal electrons would be generated and provided to the catalyst. The two quartz reactors were heated by the two heating furnaces, and the temperatures inside the two quartz reactors were measured by thermocouples which were calibrated before the ECR experiments.

Two series of toluene reforming experiments were carried out, i.e., the ECR experiments and the common catalytic reforming (CCR) experiments. During each ECR experiment, the calcination was firstly conducted on the uncalcined catalyst in the H$_2$ and N$_2$ mixture (50%/50%) of 120 mL/min. The catalyst was heated from room temperature to 800 °C at 2 °C/min, and then kept at 800 °C for 6 h, obtaining the Ni–CeO$_2$/γ-Al$_2$O$_3$ catalyst (around 2.2 g). The temperature of the catalyst was measured by a thermocouple. Afterwards, only N$_2$ was fed as the carrier gas, and the electric current was switched on. Water and toluene were then injected into the upper quartz reactor which was kept at 300 °C. The feeding rates of toluene (g), H$_2$O (g) and N$_2$ (g), based on the gas phase state at 25 °C, were 1.94 mL/min, 27.2–68.1 mL/min and 106.3–147.2 mL/min, respectively. The toluene feeding rate was constant, and the total feeding rate of the H$_2$O and N$_2$ was also constant. Hence, the toluene concentration in the gas flow was fixed at 45 g/Nm^3 (1.1 vol.%) [26]. The H$_2$O feeding rate varied to ensure the S/C ratio ranging from 2 to 5. The N$_2$ feeding rate was adjusted based on the H$_2$O feeding rate, to ensure the constant total flow rate. The space time ($w_{cat}/F_{toluene}$) was 19 kg$_{cat}$ h/m^3, defined in terms of the Ni–CeO$_2$/γ-Al$_2$O$_3$ catalyst weight divided to the volumetric flow rate of the toluene vapor at 25 °C [27]. These parameters represented severe reaction conditions for the reforming process, which facilitated the performance evaluation of the ECR technique. The catalytic temperature varied in the range of 500–800 °C. The gas products from the bottom reactor firstly passed through the ice-cooled condenser where the liquid compounds (un-reacted toluene and water) were condensed and collected. After the subsequent drying by the CaCl$_2$ column, the non-condensable gases were analyzed by the online gas chromatograph. Four detection modules were installed in the gas analyzer, to allow the measurement of the N$_2$, H$_2$, CO, CO$_2$ and C$_1$–C$_3$ hydrocarbons. The gas analysis started when the experiment reaching steady state. Each ECR or CCR test lasted for 4 h, and each gas analysis was accomplished in 2.8 min. Hence, around 85 measurements were obtained in each test. When the 4 h test finished, the water and toluene were not injected, and the electric current was switched off. The N$_2$ was still fed to cool the catalyst and quartz reactor to room temperature, preventing the oxidization of the catalyst and the char formed on it by air. In the final step, the used catalyst was collected and analyzed to determine the carbon content. The CCR experiments were performed in the similar way, with the only difference that the electric current was shut off (i.e., I = 0 A).

After the 4 h reforming tests of toluene under different reaction conditions, stability tests up to 24 h were performed on toluene and other two model compounds (benzene and 1-methylnaphthalene) at the catalytic temperature of 800 °C,