Catalytic steam reforming of cellulose-derived compounds using a char-supported iron catalyst

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ARTICLE INFO

ABSTRACT

This study aims to understand the mechanism for the removal of tar in the gasification of biomass with a char-supported iron catalyst. The pyrolysis of a pure cellulose sample and the following steam reforming of the pyrolysis products have been performed at temperatures from 500 to 850 °C. Our results indicate that tars are hard to be reformed without a catalyst. At low temperatures (<700 °C), compared with aromatic structural systems, the catalytic steam reforming showed better effects on the conversion of non-aromatics (e.g. sugars), particularly large molecules. Many aromatic ring systems can be formed at high temperatures (≥700 °C), and the catalyst was effective on reforming them with steam. The char structural features of a catalyst gave more information to understand the reactions that occurred on the catalyst.

1. Introduction

Biomass gasification is an attractive method to produce synthesis gas [1–3]. However, there are many obstacles that need to be resolved before this process can become a viable commercial renewable energy technology. One of the most significant problems is the existence of tar in the product gas [3,4]. Among many tar removal techniques, catalytic reforming is widely accepted as an efficient and economical option to convert tar into syngas [5–10].

Many catalysts have been investigated for tar reforming [4,5,11,12]. Dolomites were used for tar elimination with high activity and low cost. However, as a result of fragility, they are very soft and quickly eroded in fluidised beds [13]. Although zeolites and olivine are inexpensive, they can be deactivated easily by coke deposition [14]. Nordgreen et al. [15,16] used elemental and metallic iron as catalysts for tar reforming during gasification of biomass in a fluidised bed. However, iron can be deactivated rapidly by coke in the absence of hydrogen. With high activity for converting tar to syngas, Ni-based catalysts have been widely used in biomass gasification [4,5]. Nevertheless, Ni-based catalysts are expensive and hardly regenerated, limiting the use for industrial application [5].

Among these catalysts, the char or char-supported iron catalysts have shown adequate catalytic activities and have high economic feasibility for reforming tar during the gasification of biomass [12]. The further development of a tar reforming technology based on the char or char-supported catalysts requires a better understanding of the reactions involved. For example, the possible interactions among various

species in the bio-oil/bio-volatiles on the catalyst surface remain largely unknown. In particular, little is known about how these interactions might affect the notorious coke formation on catalyst surface, which could deactivate the catalyst [11,12,17,18].

Cellulose is one of the major chemical components of plant biomass, contributing a large portion of final products from the thermal treatments of biomass. For example, as a liquid product form the pyrolysis of biomass, bio-oil contains many cellulose-derived compounds such as aldehydes, ketones, acids, furfurals and anhydrosugars [19,20]. With well-defined chemical structure, cellulose has received much attention from studies on biomass utilisation. For example, the pyrolysis and/or gasification behaviour of cellulose has been a topic of intensive research to assist in understanding the corresponding behaviour of biomass [20–25]. However, insufficient knowledge exists about the catalytic steam reforming of cellulose-derived tar using a char-supported iron catalyst. This knowledge is non-negligible to understand the overall reactions occurring in the catalytic steam reforming of biomass/bio-oil using a char-supported catalyst.

Aromatic compounds, with single-ring to multiple-ring structures, constitute the tar from the gasification of biomass along with other oxygen-containing hydrocarbons [5,26,27]. These aromatic compounds, especially those with large aromatic structures, are more stable than other compounds in the tar, and prone to form large molecules such as coke during reforming. Therefore, the formation/evolution of various large/complex aromatic ring systems during the catalytic reforming process is especially important, requiring particular attention.

This study forms part of our ongoing efforts to understand the catalytic reforming of biomass/bio-oil tar using a char-supported iron catalyst. Cellulose was pyrolysed at 500 °C followed by the in-situ catalytic steam reforming using char-supported iron as a catalyst at different

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temperatures between 500 and 850 °C. Ultraviolet (UV) fluorescence spectroscopy was used to trace the evolution of aromatic ring systems during the reforming process. Gas chromatography–mass spectrometry (GC–MS) was used to quantify the evolution of light compounds in the tars. To gain further understanding of the roles played by the char-supported iron in the reforming process, the fresh and used catalyst char structures were characterised by Fourier transformed Raman spectroscopy.

2. Methodology

2.1. Catalyst preparation

The char-support iron was produced from pyrolysis of Fe-loaded brown coal. The detailed description of the catalyst preparation can be found elsewhere [18]. Briefly, the air-dried raw coal (Loy Yang brown coal from Victoria, Australia) was crushed and sieved to a size fraction ranging from 106 to 150 μm, and then was mixed in an aqueous solution of 0.2 M H_2SO_4 with a ratio of the acid solution to coal of 30:1 by mass and stirred in an argon atmosphere for 24 h to remove the metallic species in the coal. The slurry was then filtered and washed with de-ionised water until the pH value of the filtrates was constant (4.5–5.0). The air-dried acid-washed coal contains a negligible amount of inorganic species because all carboxylates (–COOM) have been turned into acids (–COOH), and it is termed as the H-form coal. The H-from coal was then impregnated with 1 wt.% Fe by ion-exchanging with an $FeCl_3$ solution to produce a Fe-loaded coal.

A modified one-stage fluidised-bed/fixed-bed reactor [28,29], heated with an external electrical furnace was used to prepare the catalysts at 800 °C. In each experiment, about 25 g of iron-loaded coal was firstly loaded into the quartz reactor followed by 15 min argon purging before it was heated at about 10 °C/min to the desired temperature with 0.5 L/min of argon flow. The reactor was then held for 15 min at the peak temperature with the supply of gasifying agent of 30 vol.% steam. At the end of 15 min, the reactor was lifted out of the furnace to be cooled down to room temperature with the argon flow. The fresh char-supported iron catalysts were then collected and stored in a freezer (about −10 °C) until required for the reforming experiments.

2.2. Pyrolysis/reforming experiments

The reforming of cellulose-derived compounds was conducted using a quartz reactor system previously used for pyrolysis of cellulose-derived compounds in another study for which the results were reported [30]. The difference in this study is the introduction of catalyst and steam to the process. Briefly, the bottom part of the reactor acted as a fluidised-bed pyrolyser whilst the top part was used as a fixed-bed catalytic volatile reformer. The cellulose (α-cellulose, Sigma-Aldrich) particles were entrained in a feeder with argon (1 L/min) and fed into the fluidised bed at 100 mg/min via the injection probe. Steam was injected at the middle part of the reactor, which was controlled by a high performance liquid chromatography (HPLC) pump. In any catalytic reforming experiment, a proper amount (about 1 g) of catalyst was pre-loaded into the top part of the reactor and the reforming section was conducted at different temperatures between 500 and 850 °C. The bottom part, where the cellulose pyrolysis took place, was kept at 500 °C. Tar was collected by a series of three tar traps containing a mixture of HPLC-grade chloroform and methanol (80:20 by volume) at the reactor outlet [11,12,30].

To study the effects of steam on the catalyst char structure alone, blank experiments were conducted. The only difference between the reforming experiment and blank experiment is the introduction of cellulose. In other words, all the experimental conditions were identical, except there was no feeding of cellulose during the blank experiment.

2.3. Characterisation of tar

2.3.1. UV-fluorescence spectroscopy

The UV-fluorescence spectra of tars were recorded using a Perkin-Elmer LS50B spectrometer. A detailed description about the configuration of the instrument and analysis method can be found elsewhere [30]. At the same concentration, the fluorescence intensity was multiplied by the tar yield to express the fluorescence intensity on the basis of 'per gram of cellulose' [11,30,31].

2.3.2. GC–MS analysis

Tars were analysed using an Agilent GC–MS (6890 series GC with a 5973 MS detector). A detailed description of the instrument and method can similarly be found elsewhere [30]. Briefly, 1 μL of the sample (be trapped in solution) was injected into the injection port set at 250 °C in a splitless configuration. Helium was used as a carrier gas. The column temperature was initially maintained at 35 °C for 3 min before increasing to 260 °C at a heating rate of 10 °C min^{-1}. The MS acquisition occurred after 5 min solvent delay. The peaks in the chromatogram were identified by the comparison with the standard spectra of compounds in the NIST library or on the retention times/spectra of known species injected. Some selected compounds were quantified by peak area integration. The integrated area was multiplied by a correction factor "mass of trapped solution/mass of cellulose fed" to express the area on the basis of "per gram of cellulose".

2.3.3. Spent catalyst washing

Spent catalyst (about 0.2 g) was mixed in a mixture of HPLC-grade chloroform and methanol (80:20 by volume) and stirred for 24 h. UV-fluorescence spectroscopy and GC–MS were used to determine species removed from the spent catalyst.

2.4. Char structures of catalysts

The structural features of fresh and used iron-char catalysts were characterised by using a Perkin-Elmer Spectrum GX FT-Raman spectrometer. A detailed description of the instrument and sample preparation can be found elsewhere [32–34]. In this study, the sample was diluted with IR grade KBr to a concentration of 0.5 wt.% and ground for 15 min to minimise the effects of concentration and particle size of char on the Raman intensity. The excitation laser wavelength was 1064 nm, the laser power was 150 mW and the spectral resolution was 4 cm^{-1} for all Raman spectra reported here. The diameter of the incidental laser spot was about 1 μm.

The Raman spectra, ranging from 800 to 1800 cm^{-1}, were deconvoluted into 10 Gaussian bands using the GRAMS/32 AI software, and a detailed discussion of the assignment of Raman bands can be found elsewhere [32 − 34]. Normally, the D band mainly represents the large aromatic ring systems (no less than 6 fused rings) in chars, whilst G_R, V_L and V_R bands mainly represent the 3–5 fused rings, methylene or methyl semicircle breathing of aromatic rings and methyl semicircle breathing of aromatic rings in chars, respectively. Thus, the ratio of $I_D/I_{GR + VL + VR}$ could express the ratio between large and small aromatic ring systems in chars. The G_L band mainly represents carbonyl groups. Therefore, the ratio of I_{GL}/I_{Total} was used to express the portion of carbonyl groups in the char.

3. Results and discussion

3.1. Tar yields from the pyrolysis, steam reforming and catalytic steam reforming of cellulose-derived compounds

Fig. 1 shows the tar yields from the pyrolysis and the reforming of cellulose as a function of the pyrolysis/reforming temperature in the top stage when the bottom stage was kept at 500 °C. As expected, all the tar yields decreased with increasing temperature because of the