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Catalytic reforming of tar during gasification. Part II. Char as a catalyst or as a catalyst support for tar reforming

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ABSTRACT

Char, char-supported catalysts and ilmenite were investigated for the steam reforming of biomass tar derived from the pyrolysis of mallee wood *in situ*. Special attention was given to the reforming of aromatic ring systems in tar. The results indicated that the char-supported iron/nickel catalysts exhibited much higher activity for the reforming of tar than the char itself. Ilmenite and the char-supported iron catalyst contained similar active phase but showed different tar reforming activities. Kinetic compensation effects demonstrated that the reaction pathways on the char-supported catalysts were similar but were different from those on ilmenite. The proprieties of support could play important roles for the activities of the catalysts and the reaction pathways on the catalysts. Char would not only disperse the catalysts but also interact with the catalysts to enhance their activity for the steam reforming of tar.

1. Introduction

Biomass gasification faces a number of technical challenges to become a commercial renewable energy technology. The most important one is the presence of tar in the gasification product gas. Catalytic reforming is commonly accepted as the best option that can convert tar into syngas efficiently. Many types of catalysts such as minerals [1–8] and Ni-based catalysts [9–15] have been tried to reform tar. Iron-based catalysts [8,16–19], having adequate catalytic activities but less prone to coke formation and cheaper than the Ni-based catalysts, show great promise for reforming tar during biomass gasification.

The functions of support are important for the activity of the catalyst. The support should be favourable for extending the life of catalyst by inhibiting the agglomeration of the active phases in the catalyst. Our recent review [20] has clearly indicated that the chars from the pyrolysis and gasification of low-rank coal and biomass could serve as support for a new class of cheap industrial catalysts with superior performance. Char itself also exhibits some activity for tar reforming with its reforming activity being influenced by pore size, surface area and AAEM contents of char [21–23]. The coke deposited on the char can block the pores and reduce the surface area to decrease its activity. However, the coke can also be consumed by gasification/reforming agents and gaseous products, such as steam, O_2, and CO_2, which would inhibit its deactivation by producing new pores [22,23]. Furthermore, char can act as a good support to disperse the active clusters at nanoscale following pyrolysis or partial gasification [20,24–26]. The char-supported catalysts would have low costs and be simply burned/gasified to recover the energy of the char without the need of often expensive regeneration after deactivation [20]. Hence, it is worthy to understand the catalytic activities of the char-supported catalysts on tar reforming and the functions of char during the catalytic steam reforming process.

In this study, char-supported iron/nickel and ilmenite catalysts are used for the steam reforming of biomass tar derived from the pyrolysis of mallee wood *in situ*. The performance of the catalysts on the steam reforming of biomass tar was studied under a wide range of operating conditions. The effects of support on the steam reforming of tar were investigated. The kinetic parameters have been calculated using a first-order kinetic equation and are discussed in terms of changes in the reaction pathways.

2. Experimental

2.1. Preparation of catalysts

A Victorian brown coal was used to prepare the catalyst. The main procedures for treating brown coal were acid washing and ion-exchanging [24–26]. Briefly, Loy Yang brown coal (Victoria, Australia) with a particle size range of 53–150 μm (Table 1) was washed with 0.2 M H_2SO_4 solution and de-ionised water to remove inherent metallic species (mainly, Na, Mg, Ca, Fe, etc.). These

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Table 1
Proximate and ultimate analyses of coal and biomass.

	Proximate analysis (wt.%)			Ultimate analysis (wt.%)					
	Ash[a]	Volatile matter[b]	Fixed carbon[b]	C[b]	H[b]	N[b]	S[b]	Cl[b]	O[b,c]
Brown coal	3.2	51.9	48.1	68.1	4.9	0.6	0.6	0.1	25.7
Mallee wood	0.9	81.6	18.4	48.2	6.1	0.15	0.01	0.04	45.5

[a] Dry basis.
[b] Dry and ash-free basis.
[c] By difference.

inherent metallic species are removed only for the purpose of fundamental investigation to ascertain the catalytic activities of each species although these species themselves could also act as tar reforming catalysts. The air-dried acid-washed coal that contains a negligible amount of inorganic species is termed as the H-form coal because all carboxylates (–COOM) have been turned into acids (–COOH). The H-form coal was ion-exchanged with 0.2 M $FeCl_3$ or $Ni(NO_3)_2$ solutions to load iron or nickel into the H-form coal, respectively. The treated coals are thus termed as the iron-loaded coal or the nickel-loaded coal.

The catalysts were prepared by pyrolysing and subsequently gasifying the H-form coal, the iron-loaded coal and the nickel-loaded coal at 800 °C in a one-stage fluidised-bed/fixed-bed quartz reactor [27]. Silica sand, ranging from 212 to 300 μm, was used as the bed material. The flow rates of feeding gas and fluidizing gas were each 1 L min^{-1}. The coal particles were fed into the reactor at a rate of around 300 mg min^{-1} through a water-cooled probe when the reactor had reached the target temperature. After the feeding process, the steam was injected into the reactor to start gasification that lasted for 10 min. An HPLC pump (Alltech 426) was used to supply water directly into the reactor at the required flow rate to make the steam concentration as 15 vol.% of the total gas fed into the reactor. Finally, the char samples were collected and used as the catalysts for the steam reforming of biomass tar in subsequent experiments. The iron content of the char-supported iron catalyst and the nickel content of the char-supported nickel catalyst, measured using ICP, were 2.34 wt.% and 0.88 wt.% on dry basis, respectively.

In some experiments, prior to being used for the steam reforming experiments, the char-supported iron catalyst was reduced at 600 °C *in situ* for 1 h using Ultra High Purity (>99.999%) hydrogen controlled by a mass flow controller (0.3 L min^{-1}).

In order to investigate the functions of the active phase and the support of the catalysts, ilmenite (TiWest Joint Venture, WA, 106–150 μm) and iron oxide (Sigma–Aldrich, Fe_3O_4, <5 μm) were also employed as catalysts for the steam reforming of biomass tar. The main components in the raw ilmenite were Fe_2O_3 and TiO_2 [8].

2.2. Steam reforming of biomass tar

A two-stage fluidised-bed/fixed-bed quartz reactor with three frits, modified from our earlier design [28], was used for the *in situ* catalytic steam reforming of biomass tar (Fig. 1a). The middle frit separated the reactor into two stages. Biomass was pyrolysed in the bottom stage and the product volatiles (tar) were reformed with steam and the catalysts in the top stage.

In the three-frit reactor (Fig. 1a), the gas flow rates used were so high for the char-supported catalyst particles (i.e. in the transport reactor region) that the particles were elutriated to form a thin bed underneath the top frit. The majority of the top stage was actually available for the complete mixing of steam and volatiles before they came into contact with the catalyst particles. However, when ilmenite and Fe_3O_4 were used as catalysts, their high density meant that these catalyst particles were only fluidised. There was concern that the volatiles and steam might not have well mixed before contacting with the catalyst particles in the lower part of the top stage. In order to ensure that steam and volatiles are well mixed before entering the catalyst bed, the three-frit reactor was modified into a four-frit two-stage fluidised-bed/fixed-bed quartz reactor [8] (Fig. 1b). The distance between the catalyst bed and the steam injection position of two reactors was the same (~30 mm) and the heights of the static catalyst bed were similar (1.0–1.5 mm). These conditions ensured that the gas residence time in the two reactors was comparable, allowing the direct comparison of the data obtained in these two reactors.

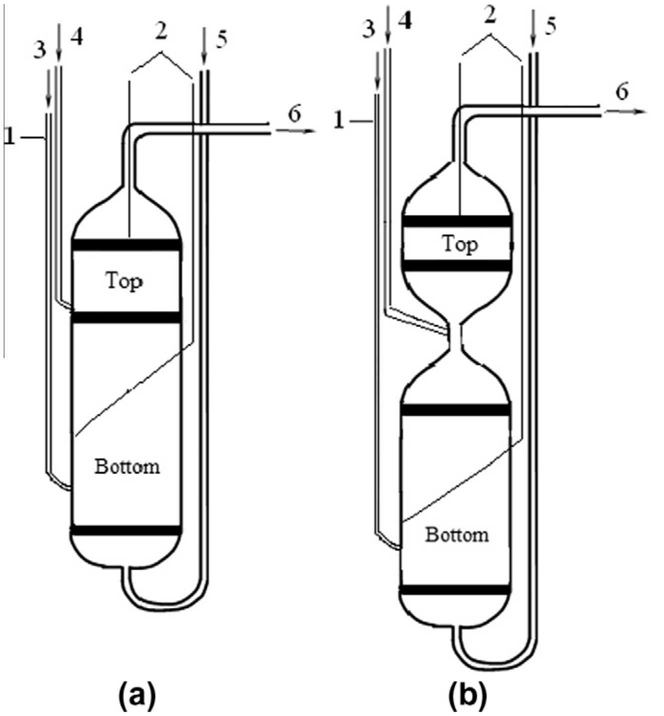

Fig. 1. A schematic diagram of the experimental set-ups for the steam reforming experiments. (a) Three-frit reactor [modified from Ref. [24]], (b) four-frit reactor [modified from Ref. [8]]. (1) water-cooled probe; (2) thermocouples; (3) biomass particles and argon; (4) steam; (5) argon; (6) gas outlet (to condenser).

Mallee wood (WA, Australia, Table 1) with a particle size range of 90–180 μm was dried at 105 °C for overnight prior to use. Silica sand (212–300 μm) was chosen as the fluidised-bed material in the bottom stage.

The catalysts were pre-loaded into the top stage before the reactor was heated up. The temperature of the top frit and the temperature distribution of the bottom stage were measured using two thermocouples for each reactor configuration (Fig. 1). The feeding gas flow rate was 1 L min^{-1}. The fluidising gas flow rate was varied in the range of 0.72–1.50 L min^{-1} to guarantee the same residence time at different reforming temperatures. The steam (15 vol.% of the total gas flow rate) was generated by feeding water directly into the reactor with a HPLC pump (Alltech 426). The biomass particles were fed into the reactor (at approximately 100 mg min^{-1}) through a water-cooled probe after the reactor had reached and stabilised at the target temperature. After the required amount of biomass had been fed into the reactor, the reactor was lifted out of the furnace immediately.

2.3. Sampling and analysis of tar

The details have been given in Part I of this series [8]. Briefly, a mixture of HPLC grade methanol and chloroform (1:4, vol) was