

## Research article

# Evolution of structure and activity of char-supported iron catalysts prepared for steam reforming of bio-oil



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## ABSTRACT

The aim of this study is to investigate the changes in iron phase, crystal size, surface area, and char structure/re-activity of the char-supported iron catalysts after them being used for bio-oil reforming. The catalysts were prepared under different conditions (varying in temperatures, gasification agents and iron concentrations) and then used to reform bio-oil under a fixed experimental condition at 800 °C. The results show that the catalysts prepared from the steam gasification of Fe-loaded coal were preferred in terms of catalytic performance. The X-ray diffraction analysis indicates that the iron phases in the fresh catalysts varied while the used catalysts nearly showed identical iron phase of magnetite (Fe<sub>3</sub>O<sub>4</sub>). The crystal iron particle in the catalysts would apparently increase after reforming when the initial iron phase was carbides (γ-Fe and/or α-Fe). The char structure of the catalysts was significantly affected by the 'volatile-char interactions' during reforming process. And the catalysts' surface area and reactivity in air were both reduced mainly due to the coke formation.

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## 1. Introduction

Biomass gasification is one of the most promising routes to produce syngas [1,2]. However, there are a number of technical barriers that need to be overcome to further develop a more advanced biomass gasification technology. The most challenging one is the presence of tarry by-products in the product gas, which has the potential to cause severe blocking and fouling problems in downstream applications and deactivate catalysts in the downstream synthesis process [3–5].

To date, numerous tar elimination techniques, such as thermal cracking, physical capture, catalytic reforming, plasma cracking etc., have been exploited [6,7]. Among these techniques, catalytic tar reforming has been believed widely as a technically and economically feasible method to convert tar into light gas [8–12]. Recently, char/char-supported catalysts, which have the below advantages: (i) inexpensive and easily available due to the easy and abundant production of char from coal/biomass pyrolysis; (ii) the spent catalyst can be directly/simple gasified/burned to recover the char's energy without any additional regeneration and disposal, have been widely reported as a promising medium to substantially reform/crack tar into light gases and coke [4,11,13–15]. It is a technically and economically interesting approach for gas cleaning.

Previous studies [11,16] pointed out the char loaded with some catalytically active species showed much higher reactivity for tar reforming than the char itself. The transition metal of iron is believed as an attractive catalytically active species of char-supported catalyst to reform tar during the gasification of biomass by reasons of its high economic feasibility, adequate catalytic activities and non-toxicity [16,17].

Numbers of literatures have reported the performance and activity of the char-supported iron catalysts (CSICs) [15,17–20], and the results show that the CSICs exhibit sufficient activity for tar reforming during gasification of biomass. Clearly, the activity of the CSICs is influenced significantly by the parameters such as char structure, char reactivity, catalytic species phase etc. These parameters further depend on preparation conditions (especially temperature and reactive atmosphere). However, only a few studies have been found to focus on the relationship between the above parameters changes and catalytic activity of CSICs. Min et al. [21] investigated the bio-char structure changes of the CSICs during steam reforming of tar, but the temperature and reactive atmosphere in catalysis preparation were not involved in. Further investigations focusing on the above aspects are vital to an in-depth insight into understanding the catalytic mechanism of the char-supported catalysts during the catalytic reforming process.

This study aims at investigating the evolution of char structure and catalytic species phase in the CSIC during bio-oil steam reforming. CSICs were firstly prepared under different temperature and reactive atmosphere. Following reforming tar/bio-oil, the changes in iron phase/crystal size, char physicochemical structure and char reactivity were

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examined to understand the relationship between the above parameters changes and catalytic performance of CSICs.

## 2. Experimental

### 2.1. Catalyst preparation

A sub-bituminous coal mined from Zhundong coalfield, which is the largest intact coalfield in China newly discovered in the east of Junggar Basin, Xinjiang, China, was firstly ground and sieved to the particle diameter of 106–150  $\mu\text{m}$ , and then air-dried in an oven at the temperature of 105  $^{\circ}\text{C}$  for 24 h used for this experiment. The proximate and ultimate analysis results and ash compositions of the coal sample are presented in Table 1.

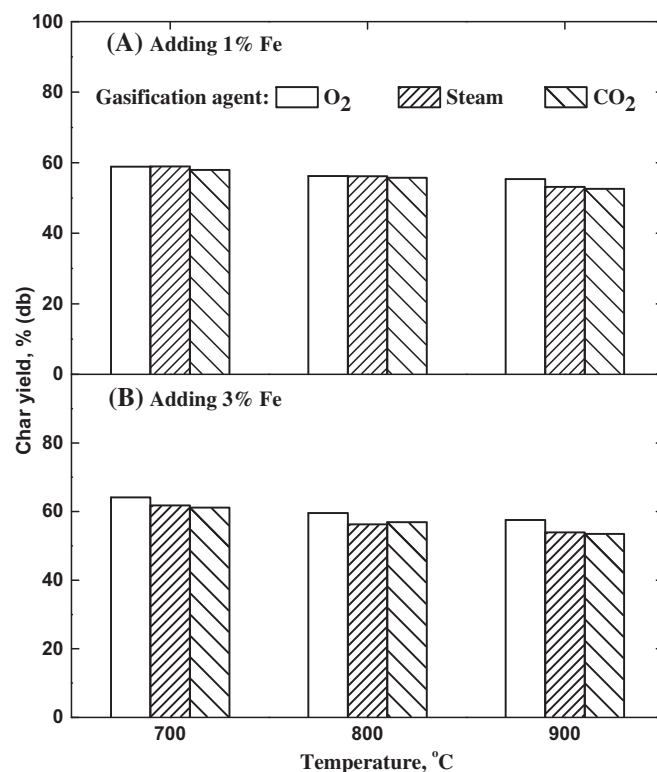
The sieved coal sample was added into a 0.2 M sulphuric acid solution (the ratio of coal and acid solution is 1:30 by mass) and stirred in a nitrogen atmosphere for 24 h to eliminate minerals influence in coal. Then it was filtered and washed by de-ionized water until the sulphate ion could not be found (by the method of barium ion titration). The solid residue was finally dried using an oven at 105  $^{\circ}\text{C}$  for 24 h. The pre-treated coal sample was free of inorganic minerals due to transformation of all carboxylates ( $-\text{COOM}$ ) into acids ( $-\text{COOH}$ ), and it is named as the H-form coal [17]. The H-form coal was then respectively ion-exchanged with 1 wt% and 3 wt%  $\text{FeCl}_3$  solution, and it is termed as the Fe-loaded coal.

The installation for slow pyrolysis of the Fe-loaded coal has been described elsewhere [22]. The detailed procedure was as follow: In each experiment, about 10 g of Fe-loaded coal was firstly loaded on quartz wool which was placed on the reactor's flaring. The nitrogen (flow rate of 500 ml/min, purity > 99.999%) was introduced into the reactor to eliminate impurities. Then the reactor was heated at 10  $^{\circ}\text{C}/\text{min}$  to the different desired temperature (700, 800 and 900  $^{\circ}\text{C}$ ), thereafter held for 15 min at the desired temperature with gasification agent supply of pure  $\text{CO}_2/30$  vol.% steam/0.15 vol.%  $\text{O}_2$ . After the 15 min holding time, the gas was switched to the nitrogen, and the reactor was moved out of the furnace to be naturally cooled down at ambient

**Table 1**  
The properties of the component coal and biomass.

Sample	Zhundong coal	Acid washed rice Straw [22]
Proximate analysis (wt%, air-dried basis)		
Moisture	12.47	6.22
Volatile matter	25.78	72.46
Fixed carbon	57.11	14.05
Ash	4.64	7.28
Ultimate analysis (wt%, dry and ash free basis)		
C	74.13	47.93
H	5.18	6.17
O <sup>a</sup>	19.64	44.88
N	0.55	0.91
S	0.49	0.12
Ash composition (wt%, normalized)		
$\text{Na}_2\text{O}$	6.02	0.23
$\text{MgO}$	6.51	0.52
$\text{Al}_2\text{O}_3$	7.75	0.63
$\text{SiO}_2$	17.22	94.01
$\text{P}_2\text{O}_5$	0.97	1.06
$\text{SO}_3$	13.49	0.86
$\text{K}_2\text{O}$	0.57	0.73
$\text{CaO}$	39.79	0.51
$\text{TiO}_2$	0.64	0.16
$\text{MnO}$	0.06	0.20
$\text{Fe}_2\text{O}_3$	6.96	1.08

<sup>a</sup> By difference.



**Fig. 1.** Char yields as a function of temperature under different gasification agents. A) using 1% Fe-loaded coal; B) using 3% Fe-loaded coal.

temperature. The prepared CSIC was finally collected and sealed in desiccators for the following reforming experiment use.

### 2.2. Reforming experiments

The bio-oil used in the current study was derived from fast pyrolysis of HCl washed rice straw (harvested at Wuhan area, Hubei province, particle size between 125 and 210  $\mu\text{m}$ ) at temperature of 500  $^{\circ}\text{C}$  with the similar procedure described elsewhere [23]. The only difference is that the tar traps were not filled with an adsorption solvent, and they were all cooled using dry ice bath ( $\sim -78.5$   $^{\circ}\text{C}$ ). The ultimate analysis results of the bio-oil are: C, 36.63; H, 7.67; N, 0.32; S, 0.03; O, 53.35 (wt%, O is calculated by difference). The water content and the high heating value are 31.53 wt% and 17.52 MJ/kg, respectively.

The bio-oil reforming was conducted in a laboratory-scale dual quartz reactor system which was used for pyrolysis/catalytic reforming of biomass/bio-oil in other studies [17,24]. Briefly, the bottom of the reactor was used as a fluidised-bed pyrolyzer while the top of the reactor acted as a fixed-bed reformer laying catalyst.

The syringe pump was used to control the feeding of oil (0.1 g/min) into the fluidised sand bed. Excess steam (feeding rate of 0.15 g/min water ( $\sim 250$  ml/min) controlled by a high performance liquid chromatography (HPLC) pump) was introduced at the middle of the dual reactors.

In each reforming experiment, accurately weighed  $1 \pm 0.05$  g of catalyst was pre-loaded in the top of the reactor, and this top part was always maintained at 800  $^{\circ}\text{C}$  during feeding of the bio-oil. The bottom part was kept at 500  $^{\circ}\text{C}$  in order to pyrolysis of the bio-oil. Thus, pyrolysis and reforming of bio-oil were performed simultaneously. The resulting tar was subsequently captured using three tar traps filled a mixture of methanol and HPLC-grade chloroform (1:4, by volume) cooled using dry ice bath in the downstream tar capture system, which was previously described elsewhere [23,25].

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