



## Full Length Article

# Promoted catalysis of calcium on the hydrogasification reactivity of iron-loaded subbituminous coal



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## HIGHLIGHTS

- Ca facilitated the dispersion of metallic Fe in coal char.
- Ca and Si formed  $\text{Ca}_3\text{SiO}_5$  to promote the reduction of iron oxide to iron metal.
- Ca species existing as  $\text{CaO}(\text{COO})$  could release  $\text{CO}_2$  which react with  $\text{Fe}_3\text{C}$ .
- $\text{Fe}(\text{O})\text{-C}$  triggered hydrogasification and maintained the high dispersion of Fe.

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## ABSTRACT

The calcium as a promoter in iron-catalyzed hydrogasification of sub-bituminous coal was studied to examine the catalytic activity of the Fe-Ca dual systems at  $\text{H}_2$  pressure 0.1–3.0 MPa, temperature 650–750 °C. Experimental results showed that the yields of light aromatic hydrocarbons (LAHs) and methane (synthetic natural gas, SNG) could be greatly improved at a given ratio of calcium-iron. Maximum yields of light aromatic hydrocarbons, 3.38 wt% (2.47 wt% of BTX and 0.34 wt% of naphthalene) were achieved using 5% Fe + 1% Ca dual catalysts at the catalyzed hydrogasification conditions of 750 °C and 1.0 Mpa. Analyses of coal chars were investigated to explain the promoted catalysis. The calcium promoted the reduction of iron oxide to active metallic iron, the increased dispersion of iron by calcium was found to result from the enhanced iron-calcium interaction, which was monitored through the carbon dissolved into iron to form  $\text{Fe}_3\text{C}$ . The rate of iron-catalyzed hydrogasification increased with time during the isothermal mode, the added calcium accelerated the catalytic activity increase and converted the oxygen, aromatic contents in oil and coal char to the formation of  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$ , BTX, PCXN and  $\text{CH}_4$ .

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## 1. Introduction

Coal hydrogasification is an attractive technique for coal conversion with the goal of producing more methane (synthetic natural gas, SNG) and/or light aromatic hydrocarbon liquids (LAHs) consisting of benzene, toluene and xylenes (BTX), phenol, cresol, xylenols (PCX) and naphthalene, so it is being paid great attention by researchers worldwide [1–13]. The yields of methane and LAHs products depend on  $\text{H}_2$  pressure, temperature, residence time and  $\text{H}_2/\text{coal}$  (wt%/wt%) [2]. The light aromatic hydrocarbon liquid products show maximum value at a certain temperature level (800–850 °C) [4,5]. Methane yield shows maximum value at a certain  $\text{H}_2$  pressure up to 7 MPa [6]. However, the coal hydrogasification has some difficulties such as the need for high temperature and  $\text{H}_2$  pressure, low  $\text{H}_2$ -coal interaction reactivity, low gas and

light aromatic hydrocarbons yields, and unattractive investment prospects [7].

Coal catalytic hydrogasification has attracted increasing attention because a catalytic hydrogasification process can decrease the reaction temperature and  $\text{H}_2$  pressure, increase the carbon conversion and reaction rate. Thus, many researchers have been studied the catalytic effect of various substances (alkali and transition metal compounds). It is generally known that nickel catalyst is the most effective catalyst for hydrogasification. A pitch coke [14,15] was impregnated with nickel nitrate and some additives (Mg, Ca, Ba and Al) and gasified in an atmospheric hydrogen, to investigate the possibility of promoting nickel catalyzed hydrogasification by the addition of foreign components, the calcium acted as a promoter for nickel had a marked influence on the catalytic activity, and it became a maximum carbon conversion at a given ratio of calcium to nickel [16–18,19]. However, the use of expensive nickel would not be feasible in practice. Consequently, the use of a cheaper, ampler, and high activity catalyst is necessary

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for the development of catalytic hydrogasification process, iron catalyst was attractive as an substitute for nickel catalyst [20], and the iron catalyst sources from industrial wastes was the most prospective alternatives [21].

Iron has been studied as a hydrogenation catalyst for hydrogasification and attracted attention. Haga et al. [16,17] had reported that hydrogasification of carbon (pitch coke, activated carbon and coal char) catalyzed by the iron metal was greatly promoted by the added calcium, which was not a catalyst for hydrogasification. The degree of promotion increased with increase in the amount of added Ca, temperature, and H<sub>2</sub> pressure. Hydrogasification of iron-loaded Australian Loy Yang brown coal by adding urea, Ca(OH)<sub>2</sub> and NH<sub>3</sub> was carried out at a low temperature of 600 °C under atmospheric H<sub>2</sub> pressure, the degree of iron dispersion evaluated from the size became higher in the order of Fe + NH<sub>3</sub> > Fe + Ca(OH)<sub>2</sub> > Fe + urea, the iron catalyst prepared by adding urea showed the largest activity for the hydrogasification [22]. Calcium formed calcium iron oxides [23], inhibiting the reduction of iron oxide to iron metal with catalytic activity at low temperatures (<700 °C). However, The calcium iron oxides such as Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> [24,25], reducible at high temperature (>700 °C), were beneficial for the formation of active metallic iron. Iron and calcium cations might be octahedrally coordinated to range of oxygen functional groups, such as O<sup>2-</sup>, OH<sup>-</sup>, H<sub>2</sub>O and -COO<sup>-</sup>, in coal structure [26], which essentially provided atomic-level dispersion and, consequently, leads to high activity for the gasification of brown coal by steam. The calcium made the Fe<sub>3</sub>O<sub>4</sub> disperse well on coal and prevented sulfur poisoning [27]. Thus, the promotion of iron catalyzed steam coal gasification by added calcium was observed in the reactions.

The Fe + Ca dual catalyst systems were highly active on hydrogasification. But the studies were mostly carried out utilizing simpler or purer model carbon (petrol coke, activated carbon), biomass (wood char) and coal char than coal, coal is a complex heterogeneous material with a wide range of chemical and physical properties, and catalysis in coal hydrogasification is seriously influenced by coal characteristics. Therefore, it seems important to see whether or not the iron-calcium catalyst works effectively for coal hydrogasification. The calcium additive in hydrogasification of iron-loaded coal have been rarely reported for product distributions including the yields of oils, water, gas and light aromatic hydrocarbon liquids (LAHs) such as benzene, toluene and xylenes (BTX). In this paper, we reported the additive effect of calcium for iron-loaded Chinese sub-bituminous coal during the coal catalyzed hydrogasification. The calcium loading on iron-loaded coal hydrogasification is examined with respect to product distributions, gas evolution profile, light aromatic hydrocarbon liquids and the coal char to further elucidate the role of Ca promoter on iron-catalyzed hydrogasification of coal. The iron dispersion and iron-carbon interaction in the coal hydrogasification process are also discussed.

## 2. Experimental

### 2.1. Materials

Two Chinese subbituminous coal (Wangjiata [19] and FuGu) were tested in the catalytic hydrogasification. However, the cat-

alytic activity of iron-calcium-loaded Wangjiata coal was not obvious increase compared with raw coal, this can be determined by two factors: (1) the iron content (18.30%) was very higher in the ash preventing the iron catalyst from being loaded onto Wangjiata coal, the ash composition analysis of samples were shown in Table 2; (2) A yellow color of iron nitrate was observed on the Wangjiata coal but not on the surface of FuGu coal after the impregnation and drying indicated a significant influence of the surface area of coal on the dispersion of Fe catalyst. Similar phenomena appeared in the literature [17]. Consequently, the FuGu coal was used in the iron-calcium-loaded coal hydrogasification. The iron-calcium-loaded coal with a particle size range of 75–150 μm was utilized in this work. The specimen was dried in vacuo at 105 °C for 2 h before each experiment. The proximate and ultimate analyses of the coal were shown in Table 1. The iron catalyst and calcium promoter were loaded onto coal by impregnation with iron and calcium nitrate aqueous solutions and mixed by ultrasound for 45 min, which were followed by removed water at water-bath (40–60 °C) and dried the mixture in vacuum (100–105 °C). The coal loaded iron catalyst alone and co-loaded iron catalyst and calcium promoter were denoted as 'Fe' and 'Fe-Ca', respectively. The iron catalyst and calcium promoter loading are defined as the nominal weight percentage of each metallic element relative to raw coal, irrespective of the working state of the Fe-Ca dual catalysts.

### 2.2. Fixed-bed reactor

The catalytic hydrogasification of iron loaded sub-bituminous coal was performed in the pressurized fixed-bed reactor, as described previously [19]. The pressurized fixed-bed reactor (40 mm inner diameter and 1200 mm in length) made of stainless steel. The porous plate located at the bottom of the reactor supported the bed materials (the coal and catalyst). Three electric furnaces were used to supply the heat needed in the reaction zone independently. Two tar traps connected in series were cooled with ethane-diol/ice. The connecting pipe between the top of reaction and the ethane-diol/tap was kept at approximately 400 °C by a electric heating sleeve to avoid condensation of the tar. The n-hexane was filled in ice-trap to capture the light aromatic hydrocarbons (LAHs). The gaseous products were collected with a gas bag for analysis. The reaction zone was purged with nitrogen at a flow rate of 3.5 L/min to eliminated air and then pressurized to 1.0, 2.0, 3.0 MPa at ambient temperature, subsequently, three electric furnaces were used to heat the reactor to final temperature at a heating rate of 30 °C/min, H<sub>2</sub> substituted for N<sub>2</sub> at the same flow rate to introduce into the reactor to begin the catalytic hydrogasification reaction until the H<sub>2</sub> purity was equivalent to 99.99%.

### 2.3. Hydrogasification experiment condition and product analysis

The experimental conditions of the catalytic hydrogasification were the same as in the previous work [19]. Coal catalyzed hydrogasification was performed in a hydrogen flow. The experimental conditions were set as follows: a static bed height of 800 mm; heating rate 100 °C/min; temperature (650 °C–750 °C); hydrogen

**Table 1**  
Proximate and ultimate analyses of the FuGu coal.

Proximate analysis (wt%, d)			Ultimate analysis (wt%, daf)				
VM	A	FC	C	H	N	S	O <sup>b</sup>
31.60	7.92	60.48	77.54	5.65	1.41	0.38	15.02

VM: volatile matter; A: ash; FC: fixed carbon; d: dried basis; daf: dry ash free basis.

<sup>b</sup> By difference.

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