The behavior of catalysts in hydrogasification of sub-bituminous coal in pressured fluidized bed

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HIGHLIGHTS

- CCHG in a pressured fluidized bed achieved 77.3 wt.% of CH_4 yield in 30 min.
- Co-Ca and Ni-Ca triggered catalytic coal pyrolysis and char hydrogasification.
- The reason for better catalytic performance of 5%Co-1%Ca was elucidated.
- Sintered catalyst blocked the reactive sites and suppressed coal conversion.
- Co-Ca made the catalyzed coal char rich in mesopore structures and reactive sites.
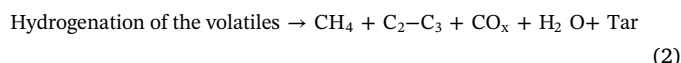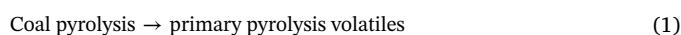
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ABSTRACT

The catalytic hydrogasification of the sub-bituminous coal was carried out in a lab-scale pressurized fluidized bed with the Co-Ca, Ni-Ca and Fe-Ca as catalysts at 850 °C and 3 MPa. The effect of different catalysts on the characteristics of gasification products was investigated, and the behavior of the catalysts was also explored by means of the X-ray diffraction (XRD), FT-Raman, Brunauer–Emmett–Teller (BET), etc. Experiment results showed that all the catalysts promoted the carbon conversion in the coal catalytic hydrogasification (CCHG), and the catalytic activity was in the order: 5%Co-1%Ca > 5%Ni-1%Ca > 5%Fe-1%Ca. Compared with the raw coal hydrogasification, the carbon conversion increased from 43.4 wt.% to 91.3 wt.%, and the CH_4 yield increased from 23.7 wt.% to 77.3 wt.% within 30 min after adding the 5%Co-1%Ca catalyst into the coal. Co-Ca and Ni-Ca possessed catalytic effect on both processes of pyrolysis of coal and hydrogasification of coal char in CCHG, by which the graphitization of the coal was suppressed and methane formation rate was significantly accelerated. Fe/Co/Ni-Ca could penetrate into the interior of coal during CCHG, making the catalytic production of CH_4 conduct in the pore structures. The activity difference of the catalysts was owing to the different ability of rupturing the amorphous C—C bonds in coal structure. The incomplete carbon conversion of the 5%Co-1%Ca loaded coal was due to the agglomeration of the catalyst and the blockage of the reactive sites by the sintered catalyst. This work will provide a straightforward method and reference data for the further industrial-scale production of 1.2 N m³ CH_4/kg–coal from CCHG by using pressured fluidized bed reactor.

1. Introduction

In recent years, the technology of low & middle rank coal-to-SNG (Substituted natural gas) has been fueled as a strategy to relieve the rapidly growing demand of natural gas in EU and Asia countries [1–3]. Coal hydrogasification is a clean and efficient way to produce SNG as well as hydrocarbon liquids (HCL) such as benzene, toluene, xylenes (BTX), phenol, cresols, xylenols and naphthalene (PCXN) [4–6], and it had been a subject of intensive research in 1970s and 80s due to the oil shortage crisis worldwide. However, no coal hydrogasification process has been commercially put into production. This is mainly owing to the high severities of hydrogasification conditions (900–1100 °C, 5–7 MPa) [1], low methane yield and inefficient coal conversion (50–60 wt.%) [7]. According to the pathways of coal hydrogasification [8] shown as follows:

$$\text{Coal pyrolysis} \rightarrow \text{primary pyrolysis volatiles} \tag{1}$$

$$\text{Hydrogenation of the volatiles} \rightarrow CH_4 + C_2\text{–}C_3 + CO_x + H_2O + \text{Tar} \tag{2}$$

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$$\text{Active carbon of coal char} + H_2 \rightarrow CH_4 + C_2\text{–}C_3 \qquad (3)$$

$$\text{Inert carbon of coal char} + H_2 \rightarrow CH_4 \qquad (4)$$

The limiting factor for the conversion of coal is that the reaction rate of step (4) is too slow [6].

The reactivity of coal char can be improved by adding the desirable catalysts, and the high conversion efficiency can be obtained under mild conditions (low temperature and H_2 pressure). Many works has been done on the catalytic effect of various compounds on hydrogasification [9–13]. The iron-group metals, such as Fe-, Co-, and Ni-compounds has been proved to be the very active hydrogasification catalysts with the addition of 2–5 wt.% in metal [14,15]. Matsumoto [16] reported that the catalytic activities of iron-group catalysts were in the order of Co > Ni > Fe. The activity patterns of them not only owed to the active hydrogen donating endowment [17], but also attributed to the interaction of metals with carbon in the coal/char lattice [18]. However, the iron-group metals were prone to be deactivated by sintering at high temperature and poisoning by sulfur in the reaction process [19,20]. To optimize the performance of the iron-group catalysts in the hydrogasification process, the addition of promoters were greatly advocated [21,22]. The use of alkaline-earth metal compounds as additive could increase the dispersion of iron-group metals on char surface and prevent them from poisoning [23–25]. Haga et al. [21] investigated the promoting effect of Mg, Ca, Ba, and Al salts on Ni-catalyzed hydrogasification. Interestingly, only Ca salt could promote the activity of nickel at high temperatures. This was due to the creation of reactive Ni-(O)-C species with the assistance of CaO above 700 °C [18]. The effect of iron-group metals accompanied with Ca on hydrogasification of pitch coke and activated carbon were also studied as a function of temperature up to 850 °C and pressure up to 3 MPa [9]. The Ca salt achieved the best promoting effect at the optimal reaction conditions of temperature 850 °C, pressure 3 MPa and metal loading of 1 wt.%. The activity of the bimetallic catalysts was in the order of: 5%Co-1%Ca > 5%Ni-1%Ca > 5%Fe-1%Ca.

Extensive researches reveal that the use of iron-group metals with calcium salts as co-catalysts possess profound catalytic performance on hydrogasification of model carbon materials such as active carbon, pitch coke and coal char. However, there remain some questions deserved to be further clarified, such as the reason for the activity sequence of bimetallic catalysts and the incomplete carbon conversion of coal/coal char. Furthermore, the previous works verified that the inert carbon of coal char can be easily converted in the presence of Fe-Ca, Co-Ca and Ni-Ca catalyst. Now, tracing back to the non-catalyzed coal hydrogasification process, it is therefore curious to know the catalytic performance and behavior of the aforementioned bimetallic catalysts on coal (bituminous coal) hydrogasification. It is known that coal hydrogasification process integrated pyrolysis of coal and hydrogasification of coal char [11], and raw coal has less ordered carbon structure than that of the coal char [26,27]. The additional interaction between catalysts and coal would led to a lower ordering of coal structural during pyrolysis [28], which may affect the reactivity of char generated after pyrolysis. Once the bimetallic catalysts could accelerate the

reaction rate of pathway (4) in coal hydrogasification process, it is feasible that the carbon conversion of coal and the yield of CH_4 could be significantly promoted.

Nevertheless, the attempts to improve the carbon conversion of bituminous coal and CH_4 yield through the method of CCHG are unsatisfactory till date. In our previous study [25], Ni-Ca catalyst was applied for sub-bituminous coal hydrogasification at 750 °C and 1 MPa. The results showed that the methane yield was 18.4 wt.% in 1 h. Jiang et al. [29,30] recently reported that the catalytic activity of Fe-Ca could be motivated only when the temperature was above 800 °C and pressure was above 3 MPa on char hydrogasification. The methane yield could reach 60–70 wt.%, but the reaction time was more than 6 h. In the practical industrial application process with the consideration of thermal efficiency and investment, high CH_4 yield is expected to be achieved in a short time. Although the CH_4 yield is low in Yuan's study [25], the coal can be fastly converted to 65–75 wt.% in 1 h. The limited catalytic effect of Ni-Ca in the study of Yuan may attribute to the low temperature and pressure. This arouses the authors' interests to further evaluate the activity of bimetallic catalysts on coal hydrogasification above 800 °C, 3 MPa with focus on the carbon conversion of coal, methane yield, and the effect of catalysts on the evolution of coal structure.

It is worthwhile to be concerned that the fluidized bed catalytic coal hydrogasification treats pulverized coal (below 5 mm) for methane production, which has the potential to act as a complement of Lurgi lump coal (6–50 mm) gasification in the coal-to-SNG plant [31]. In order to provide basic data for the industrial-scale production of SNG from CCHG, the pressured fluidized bed reactor is used in the study. This work is undertaken to study the catalytic behaviors of Fe-Ca, Co-Ca, and Ni-Ca on hydrogasification of sub-bituminous coal at temperature of 850 °C and pressure of 3 MPa. The CCHG is examined with regard to the distribution of gas-liquid-solid products, including the evolution profile of gaseous, liquid products and coal char. The reactivity and structures of the coal after reaction have been analyzed by pressurized thermo-gravimetric analyzer (P-TGA), TEM, XRD, Raman spectroscopy and BET to gain some insights into the behavior of catalysts in the process of CCHG. Furthermore, the crucial step and a probable reaction pathway in CCHG were also proposed.

2. Experimental

2.1. Material preparation

The sub-bituminous coal used in the CCHG experiments was obtained from Fugu, China. After being dried in vacuum at 105 °C for 2 h, the coal was crushed and sieved to 75–150 μm. The catalysts were loaded on the coal by the co-impregnation method. Briefly, a known mass of raw coal was impregnated into a solution containing predetermined amounts of $Fe(NO_3)_2 \cdot 9H_2O$ or $Ni(NO_3)_2 \cdot 6H_2O$ or $Co(NO_3)_2 \cdot 6H_2O$ and $Ca(NO_3)_2 \cdot 4H_2O$ with ultrasound at 50 °C for 1 h, and then dried at 50 °C in a water-bath to evaporate the water. Thereafter, the mixture was further dried in vacuum at 105 °C. The samples loaded

Table 1
Proximate and ultimate analyses of Fugu coal loaded with different catalysts.

Sample	Proximate analysis (wt.%, d)			Ultimate analysis (wt.%, daf)				
	VM	A	FC	C	H	N	S	O[a]
Raw coal	34.94	3.37	61.69	78.74	4.85	1.15	0.44	14.82
5%Fe-1%Ca	37.43	9.78	52.79	68.78	4.12	3.16	0.45	23.48
5%Co-1%Ca	38.86	9.51	51.63	70.06	4.38	2.60	0.47	22.49
5%Ni-1%Ca	37.50	9.02	53.48	69.15	4.61	2.84	0.45	22.94
R-raw coal	39.43	10.37	50.20	69.10	4.01	3.46	0.43	23.00

VM: volatile matter; A: ash; FC: fixed carbon; d: dried basis; daf: dry-ash free basis.
[a] By difference.