



## Full Length Article

# Characteristics of $\text{Na}_2\text{CO}_3$ -catalyzed water-gas shift reaction under coal liquefaction conditions

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## ABSTRACT

The characteristics of  $\text{Na}_2\text{CO}_3$ -catalyzed water-gas shift reaction (WGSR) under coal liquefaction conditions were investigated. The reactivity of WGSR could be enhanced by improving water content and initial pressure of CO, owing to the reduced activation energy for WGSR in the high water density and subcritical state. The  $\text{Na}_2\text{CO}_3$  had a promoting effect on WGSR, and a synergistic effect between  $\text{Na}_2\text{CO}_3$  and water occurred obviously.  $\text{HCOONa}$  and  $\text{NaHCO}_3$  as intermediate products were generated for CO consumption, and subsequently decomposed into  $\text{CO}_2$  and  $\text{H}_2$ , which can be a hydrogen source further. A major catalyzed mechanisms in WGSR about intermediate products under coal liquefaction conditions was investigated preliminarily.

## 1. Introduction

Direct coal liquefaction process is an essential technology to transform coal into oil or other chemical products [1–3]. However, the utilization of lignite is limited in direct liquefaction, due to a large energy consumption for drying [4,5]. In view of this, some researchers thought the evaporated water could be potentially a hydrogen source, which could be utilized during the liquefaction reaction instead of expensive molecular hydrogen to liquefy lignite [6–12]. Fischer [7] pointed out that brown coal could be converted to ether-soluble products in a mixture condition of CO and water. Appell et al. [8] demonstrated the effectiveness of CO and water in the lignite liquefaction. Ross et al. [9,10] studied the liquefaction characteristic of an Illinois No. 6 coal in CO and water at 400 °C. Our previous investigation [12] also showed that the conversion and oil yield from Shengli lignite liquefaction under the system of syngas and complex solvent were obviously higher than those under the system of  $\text{H}_2$  and organic solvent. Therefore, it is considerable that using CO (or syngas) +  $\text{H}_2\text{O}$  as hydrogen sources is advantageous in lignite liquefaction processes.

The WGSR is widely suggested as a key reaction in lignite liquefaction under CO (or syngas) +  $\text{H}_2\text{O}$  system to produce active hydrogen to stabilize free radicals from coal [13–15]. There are many investigations only focused on WGSR [16–26]. Bianco et al. [14,17,22] proposed a mechanism about formation of formic acid as an intermediate in

WGSR. Melius et al. [23] predicted that an enhancement in the rate of WGSR occurred at high water density due to the generation of formic acid. Elliott et al. [27,28] explored WGSR in a two-phase system using high temperature, pressurized water, and alkali metal salts as potentially more effective homogeneous catalysts. Hodges et al. [29] investigated the degree of WGSR under CO and water system at 350 °C using alkali metals, and the highest CO conversion (89.0%) could be obtained in the presence of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ). Presently, the relevant investigations on WGSR with  $\text{Na}_2\text{CO}_3$  are not systematic enough, especially in WGSR under coal liquefaction conditions, and the process conditions and reaction process are still unclear. Therefore, a conventional lignite liquefaction environment was simulated without coal in this paper, and the effects of temperature, water contents, and initial CO pressure were studied on  $\text{Na}_2\text{CO}_3$ -catalyzed WGSR under coal liquefaction conditions. Meanwhile, the reaction path was investigated to obtain a further understanding of WGSR under coal liquefaction conditions, aiming at improving lignite conversion under CO (or syngas) +  $\text{H}_2\text{O}$  system.

## 2. Experimental

### 2.1. Materials

The used raw materials were deionized water, carbon monoxide

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### Nomenclature

WGSR	water-gas shift reaction
$n_{\text{CO}_2}$	production of $\text{CO}_2$ , mmol
$n_{\text{H}_2}$	production of $\text{H}_2$ , mmol
$n_{\text{CO}_c}$	consumption of CO, mmol
$X_{\text{CO}}$	conversion of CO, %
$n_i$	mole number of $i$ gas, mmol
$P_t$	pressure in reactor, MPa

$V_{\text{Gas}}$	volume of gas in reactor, L
$T$	temperature inside the reactor, °C
$C_i$	volume fraction of $i$ gas, %
$n_{\text{CO}}$	mole number of CO before reaction, mmol
$n'_{\text{CO}}$	mole number of CO after reaction, mmol

### Subscripts

$i$	gas components ( $\text{CO}$ , $\text{CO}_2$ , or $\text{H}_2$ )
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(99.99%), solvent, and catalyst. The tetralin was used as the solvent, and  $\text{Na}_2\text{CO}_3$  was used as the catalyst. All solvents and reagents were commercially pure chemical reagents and used as received without further purification.

### 2.2. Water-gas shift reaction experiment

The WGSR experiment was carried out in a 150 mL autoclave [30]. In each run, the liquefaction reactor was charged with 30 mL solvent, 10%–50% deionized water (volume ratio of deionized water to solvent), and 5 wt%  $\text{Na}_2\text{CO}_3$  (mass ratio of Na and solvent). Subsequently, the reactor was sealed and purged by  $\text{N}_2$  for six times before being pressurized to the desired initial pressure of CO, and then was heated to desired temperature. After the process was maintained for 60 min, the reactor was quenched quickly by cooling water to 25 °C, and the gaseous products were collected by an aluminum foil bag for composition analysis. After the solid-liquid mixture was taken out, and sample was stratified by centrifuge (rotating speed of 3000 r/min). The aqueous phase and the organic phase samples were segregated, and obtained using the glue head dropper, respectively. Subsequently, the recovered catalyst sample was rinsed with anhydrous ethanol and tetrahydrofuran, which was filtered and then dried under vacuum at 60 °C for 12 h. Finally, water phase, organic phase, and recovery catalyst samples were analyzed, respectively.

In this reaction, the productions of  $\text{CO}_2$  ( $n_{\text{CO}_2}$ , mmol) and  $\text{H}_2$  ( $n_{\text{H}_2}$ , mmol) were calculated according to Eq. (1), and the consumption ( $n_{\text{CO}_c}$ , mmol) and conversion ( $X_{\text{CO}}$ , %) of CO were calculated according to Eqs. (2) and (3), respectively.

$$n_i = \frac{V_{\text{Gas}}}{22.4} \times \frac{P_t}{0.101325} \times \frac{273.15}{T+273.15} \times C_i \times 1000 \quad (1)$$

$$n_{\text{CO}_c} = n_{\text{CO}} - n'_{\text{CO}} \quad (2)$$

$$X_{\text{CO}} = 1 - \frac{n'_{\text{CO}}}{n_{\text{CO}}} \quad (3)$$

where  $n_i$  (mmol) is the mole number of  $i$  gas ( $i = \text{CO}$ ,  $\text{CO}_2$ , or  $\text{H}_2$ ),  $P_t$  (MPa) is the pressure in reactor,  $V_{\text{Gas}}$  (L) is the volume of gas in reactor, and  $T$  (°C) is temperature inside the reactor.  $C_i$  (%) is the volume fraction of  $i$  gas, and which can be tested by a gas chromatography.  $n_{\text{CO}}$  (mmol) and  $n'_{\text{CO}}$  (mmol) are the mole numbers of CO before reaction and after reaction, respectively.

### 2.3. Analysis and characterization

#### 2.3.1. Gas chromatography

The concentrations of various gas components in gaseous phase were tested by a gas chromatography (GC 9790-II, Zhejiang Fu Li Analytical Instrument Co., Ltd.) equipped with a TDX-01 column (TCD for detecting  $\text{H}_2$ , CO, and  $\text{CO}_2$ ) and a Plot- $\text{Al}_2\text{O}_3$  column (FID for detecting  $\text{C}_1$ – $\text{C}_4$ ) [31].

#### 2.3.2. High performance liquid chromatography

The compounds in aqueous phase were analyzed by an Agilent 1260SL high performance liquid chromatography (HPLC) analyzer

equipped with an UV absorbance detector (210 nm) and a Shodex ionpak KC811 column, which was used to analyze the organic acids. The mobile phase was 0.003 M of  $\text{H}_2\text{SO}_4$  at flow rate of 1.5 mL/min, and the column temperature was kept at 50 °C. In addition, the concentrations of organic acids were calibrated using external standard method.

#### 2.3.3. X-ray diffraction

Physicochemical characterization of recovered catalysts was performed using X-ray diffraction (XRD produced by Rigaku Corporation), fitted with a Cu target and graphite monochromatic filter [32]. XRD analysis was performed using a Rigaku D/max-rA 12 kW X diffractometer at 40 kv and 100 mA. The diffraction patterns were obtained for  $10^\circ < 2\theta < 80^\circ$  with step size of  $0.02^\circ$ .

## 3. Results and discussion

### 3.1. The effect of temperature on WGSR

Fig. 1 shows the effect of temperature on WGSR without catalyst. It can be found that the CO consumption and  $\text{H}_2$  (or  $\text{CO}_2$ ) production increase with the increase of temperature. The CO consumption and  $\text{H}_2$  (or  $\text{CO}_2$ ) production increase slowly at the temperature range from 350 °C to 400 °C, and increase rapidly at the temperature range from 400 °C to 450 °C, indicating that high temperature is favorable to WGSR. Besides, the CO consumption is higher than the  $\text{H}_2$  (or  $\text{CO}_2$ ) production especially at the temperature range of 430 °C–450 °C, indicating that there are possibly some intermediate products in WGSR. Many literatures [17,22,33,34] had reported that the intermediate product in WGSR was mainly formic acid. Bianco et al. [17,22] thought that the  $\text{H}_2$  and  $\text{CO}_2$  productions were owing to the decomposition

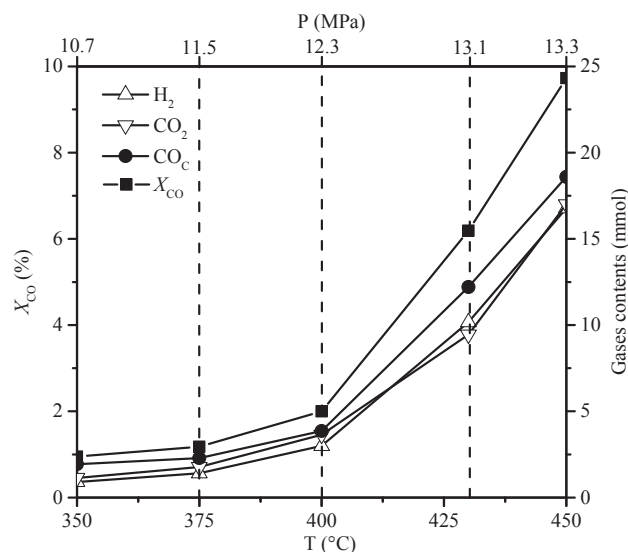


Fig. 1. Effect of temperature on WGSR without  $\text{Na}_2\text{CO}_3$  (Ratio of deionized water to solvent is 15%, initial CO pressure of 4 MPa).

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