



Analysis of Non-Catalytic and Catalytic Steam Gasification of Hohhot Coal Char

BINGQING HONG, XINGJUN WANG, SHUPENG ZHAN and GUANGSUO YU*

Key Laboratory of Coal Gasification and Energy Chemical Engineering of Ministry of Education, Shanghai Engineering Research Center of Coal Gasification, East China University of Science and Technology, Shanghai 200237, P.R. China

*Corresponding author: Tel: +86 21 64252974; E-mail: gsyu@ecust.edu.cn; foxtown818@163.com

(Received: 21 November 2012;

Accepted: 1 July 2013)

AJC-13730

Steam gasification of Hohhot coal char, demineralized Hohhot coal char and several catalysts loaded samples including alkali, slaked lime and transition metal based compounds was performed under 700 °C and atmospheric pressure. A three-step steam gasification mechanism based on carbon-oxygen intermediate C(O) is proposed for the understanding of experimental data regarding both the kinetic behavior and reaction selectivity. The characteristics of reaction rate and the selectivity of CO, CO₂ and C(O) under the effect of different catalysts were discussed. It was found that the catalyst is more effective for the H₂O involved reaction steps which is probably due to the oxygen transfer function of catalyst from H₂O to carbon surface.

Key Words: Steam gasification, Catalytic performance, Reaction rate, Reaction mechanism.

INTRODUCTION

Catalytic steam gasification of coal/char has long received the bulk of research attention because of its kinetic advantages of mild operation condition and high efficient throughput of H₂^{1,2}. And the clarification of the mechanism of catalytic steam gasification has been the subject of numerous investigations³⁻⁶. Wood and Sancier⁷ have summarized to four reaction mechanisms including oxygen transfer mechanism, electrochemical mechanism, free radical mechanism and intermediate mechanism.

In order to explain the role of catalyst in coal/char gasification, the oxygen transfer mechanism has been put forward as early as in 1931. Later on the scholars have enriched and developed this mechanism furthermore. Hermann and Huttinger⁸ have adopted this mechanism to explain the catalytic mechanism of Fe on carbon steam gasification and suggested that there exists three different iron oxides surface compounds with different stability during Fe catalyzed steam gasification and the decomposition of water on Fe surface accelerates the transfer of oxygen from Fe to carbon surface. Later Miura *et al.*⁹ proposed the mechanism of the C(O) formation promoted by CaO. Meijer *et al.*¹⁰ put forward the C(O) intermediate mechanism to explain the gasification in another way. Based on the oxygen transfer mechanism and C(O) intermediate mechanism, Wang *et al.*¹¹ put forward a oxygen transfer and C(O) intermediate hybrid mechanism of carbon steam gasification catalyzed by potassium carbonate to explain the catalytic gasification rate and selectivity.

So far few researchers have discussed the characteristic of instantaneous release rate of steam gasification products. This paper chose Hohhot coal as the research object, for its considerable reserves in China, to explore the reaction mechanism and the performance of catalyst. A gas analyzer, which can determine the instantaneous contents of CO, CO₂, CH₄, C_nH_m (based on Infrared micro-flow technology) and H₂ (based on thermal conductivity technology) at the same time, combined with a flowmeter, were used to determine the instantaneous release rates of gas products *in situ*. The mechanism of steam gasification and the role of catalyst in the process were discussed based on the experimental data.

EXPERIMENTAL

Sample preparation: The Hohhot coal was crushed and pulverized to the particles with diameter sizes of less than 0.15 mm. The proximate analysis showed that the coal contained 12.9 % ash, 34.3 % volatile matter and 52.8 % fixed carbon on the dry basis. The ultimate analysis showed that the coal consisted of 72.8 % C, 4.0 % H, 1.1 % N and 0.6 % S, on the dry ash-free basis. The ash was composed of 46.18 % SiO₂, 19.83 % Al₂O₃, 4.37 % Fe₂O₃, 12.28 % CaO, 2.51 % MgO, 0.77 % Na₂O, 1.18 % K₂O, 11.10 % SO₃ and others. In order to eliminate the effect of minerals on the reactivity of samples, coal demineralization was conducted with two acids (HCl and HF), employing the method of Sun *et al.*¹². The proximate analysis showed that the demineralized coal contained 0.9 % ash, 33.3 % volatile matter and 65.8 % fixed carbon, on the

dry basis. The ultimate analysis showed that the coal consisted of 82.2 % C, 4.8 % H, 1.0 % N and 0.6 % S, on the dry ash-free basis. The catalyst was added to the demineralized coal using wet mixing method. The dry sample was ground and sieved to make sure the particle size is smaller than 0.15 mm and then placed in a desiccator in reserve. The catalyst loading is 10 wt % of coal which is calculated by the mass of metal.

Procedure: The experiments were carried out in a laboratory fixed-bed reactor. The inlet flowrate of nitrogen was fixed to 1 L/min. Once the inner temperature of reactor kept stable at the stated temperature and the pyrolysis gas production was negligible, the gas flow was shift to the mixture of nitrogen and steam, the flowrate of which was 2 L/min and the ratio was 1:1. The time point that the infrared gas analyzer detected any product gas was considered as the beginning of steam gasification. Preliminary experimental results indicated when the particle size was smaller than 150 μm and the steam flowrate was not less than 1 L/min, the influence of internal and external diffusion under atmospheric pressure has been basically eliminated.

RESULTS AND DISCUSSION

Instantaneous release rate: Fig. 1 illustrates the instantaneous gas release rates during the steam gasification of demineralized Hohhot coal char under 700 °C and atmospheric pressure. The instantaneous release rate v is defined as $v = \phi Q$, where v is the instantaneous release rate of product gas (mol/s), ϕ is the gas content (%) and Q is the instantaneous gas flowrate (mol/s).

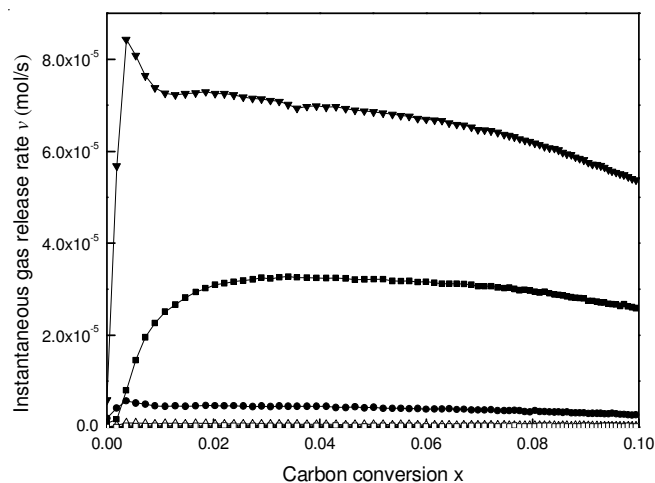


Fig. 1. Instantaneous release rate of demineralized coal char gasification
 ■: CO₂; ●: CO; ▼: H₂; ▲: CH₄; □: C_nH_m

As shown in Fig. 1, H₂ has the fastest release rate, followed by CO₂ and CO. Other gas components such as CH₄ and C_nH_m will not be discussed in this paper for their rare production. The instantaneous release rate curve can be generally divided into initial stage and stable stage. During the initial stage, the instantaneous release rates of H₂ and CO increase rapidly to the highest value and then decrease quickly to a relatively low value. In the stable stage, the instantaneous gas release rates decrease gradually without fluctuations. H₂ and CO are generated immediately after reactant steam flowing into the system,

while the generation of CO₂ exists a certain lag, therefore v_{CO_2} reaches its maximum value during the stable stage of v_{CO} and v_{H_2} .

According to the elements conservation principle, there exists a certain relationship among the production rate of the three main gas products. If the hydrogen and oxygen in the gasification products are from the water molecules only and the hydrogen and oxygen in water are transferred to the gas products merely without any residual in solid phase, the relationship of $\frac{v_{\text{H}_2}}{2v_{\text{CO}_2} + v_{\text{CO}}} = 1$ will then established considering only the three main product gases H₂, CO and CO₂:

In order to examine the above hypothesis, define the instantaneous molecular ratio N as $N = \frac{v_{\text{H}_2}}{2v_{\text{CO}_2} + v_{\text{CO}}}$ where

v_{H_2} , v_{CO_2} , v_{CO} represent the instantaneous release rate of H₂, CO₂ and CO, respectively.

Different catalysts [KOH, NaOH, Ca(OH)₂, Ni(NO₃)₂ and Fe(NO₃)₃] loaded samples, as well as raw and demineralized coal char were gasified with steam under 700 °C and atmospheric pressure. The instantaneous molecular ratios of these reactions are showed in Fig. 2. The calculated results indicate that the initial N values of all reactions are much larger than the hypothetical value 1. As the proceeding of steam gasification, the instantaneous molecular ratio N declines sharply to a value which is close to 1 and then keeps stable. The conclusion can be drawn from this phenomenon that during the initial stage, most hydrogen from H₂O is transferred to gas phase in the form of H₂ while a large amount of oxygen stays in the solid phase rather than be transferred to the gas phase. This part of oxygen is adsorbed by the surface carbon atoms to form a kind of carbon-oxygen intermediate which is expressed as C(O). When the reaction proceeds to the stable stage, the stable N values of all reactions are close to 1. Then it can be concluded that most of the hydrogen and oxygen from H₂O molecules are both transferred to the product gases. In fact,

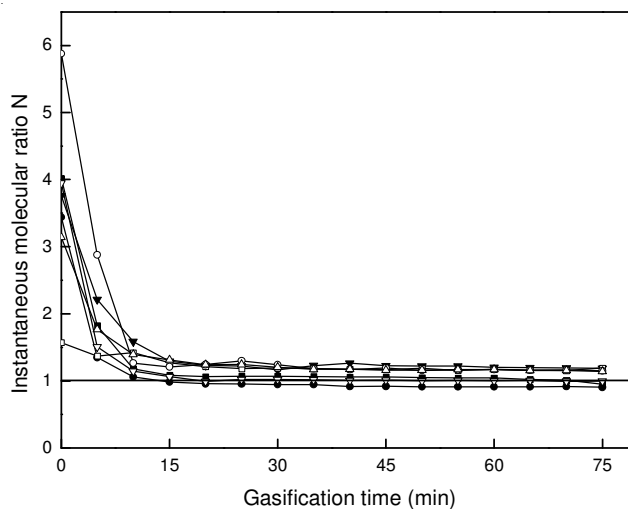


Fig. 2. Instantaneous molecular ratios of reactions catalyzed by different catalysts. ■: KOH; ●: NaOH; ▼: Ca(OH)₂; □: Ni(NO₃)₂; ○: Fe(NO₃)₃; ▲: Raw; ▼: Dem

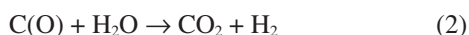
all the N values are slightly larger than 1 in the stable stage, indicating that part of oxygen from H_2O still remains in the solid phase during the stable stage.

Mechanism hypothesis of steam gasification: Based on the steam gasification mechanism proposed by Meijer *et al.*¹⁰ and Wang *et al.*¹¹ and considering only CO_2 , CO and H_2 as the reaction products, it is assumed that steam gasification process can be divided into the following three steps:

(1) H_2O molecules that spread to char surface are absorbed by the surface carbon atoms and then decomposes to H_2 and $C(O)$



(2) Part of the carbon-oxygen intermediates $C(O)$ react with H_2O molecules to produce H_2 and CO_2



(3) Part of the carbon-oxygen intermediates $C(O)$ desorbed from the surface as product CO



According to reactions (1-3), the following equations are established:

$$v_1 = v_{H_2} - v_{CO_2} \quad (4)$$

$$v_2 = v_{CO_2} \quad (5)$$

$$v_3 = v_{CO} \quad (6)$$

$$v_{C(O)} = v_{H_2} - (2v_{CO_2} + v_{CO}) \quad (7)$$

where v_1, v_2, v_3 are the reaction rate of reactions (1-3) separately.

Fig. 3 shows each step's reaction rate curve of demineralized coal char steam gasification under 700 °C and atmospheric pressure and the accumulation rate curve of $C(O)$ is showed in Fig. 4. During the initial stage, v_1 increases to the peak with great rate and then falls rapidly, v_2 and v_3 increase gradually from beginning. It illustrates that the initial rate of reaction (1) is very fast. The H_2 generated from reaction (1) spreads to the gas phase, but $C(O)$ accumulates quickly at the surface, leading to high concentration of $C(O)$ on interface which will restrain reaction (1) thus make the reaction rate fall rapidly. Meanwhile, the high concentration of $C(O)$ will promote reaction (2) and reaction (3). So v_2 and v_3 increase gradually during the initial stage. The fact that v_3 reaches its highest value prior to v_2 and then slightly decreases is due to the low surface concentration of H_2O which is mostly consumed by reaction (1). The low surface concentration of H_2O will restrict reaction (2). For this reason the generating rate of CO_2 is lower than CO at first. As the proceeding of the reaction, reaction (1) is gradually suppressed, the surface concentration of H_2O increases and reaction between $C(O)$ and H_2O is promoted. Then reaction (2) achieves a distinct advantage over reaction (3) in the competition that v_2 has been increased to a much higher level than v_3 during the initial stage. Once production rate and consumption rate of $C(O)$ are almost balanced, the steam gasification proceeds to the stable stage. In this stage, v_1, v_2 and v_3 decrease gradually and slowly for the reduction of active sites.

Catalyst effect on gasification rate and product selectivity: Supposing the catalytic steam gasification of coal char

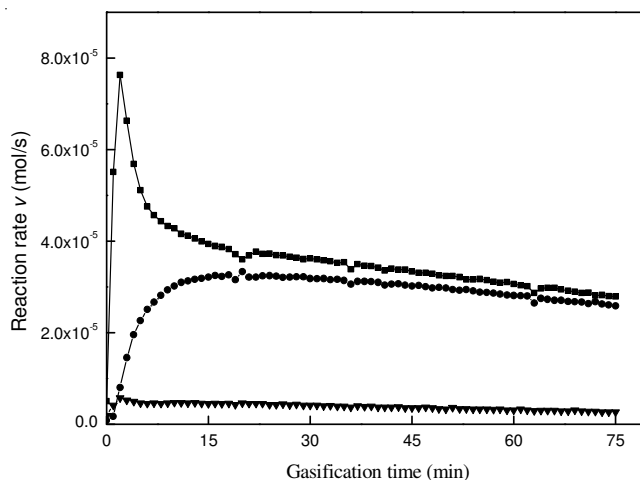


Fig. 3. Reaction rate of different steps of demineralized coal char gasification. ■: v_1 ; ●: v_2 ; ▼: v_3

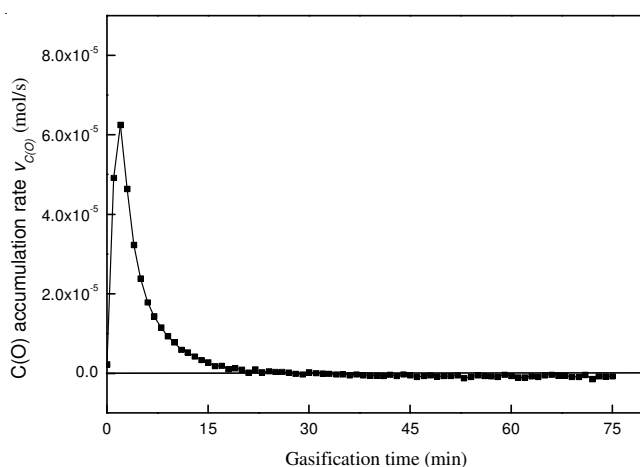


Fig. 4. $C(O)$ accumulation rate of demineralized coal char gasification

occurs according to the three reaction steps mentioned above, the catalyst influences on all the three reactions are investigated. In order to study the influence of different catalysts on reaction rate of each step, define the relative reaction rate ϕ as

$$\text{follows } \phi_1 = \frac{\bar{v}_1}{\bar{v}_{1,\text{dem}}}, \phi_2 = \frac{\bar{v}_2}{\bar{v}_{2,\text{dem}}}, \phi_3 = \frac{\bar{v}_3}{\bar{v}_{3,\text{dem}}}, \text{ where } \phi_1,$$

ϕ_2, ϕ_3 are the relative reaction rate of reactions (1-3), respectively, $\bar{v}_{1,\text{dem}}, \bar{v}_{2,\text{dem}}, \bar{v}_{3,\text{dem}}$, the average reaction rate of each step of demineralized coal char steam gasification at 700 °C and 0.1 MPa and $\bar{v}_1, \bar{v}_2, \bar{v}_3$ the average reaction rate of catalytic steam gasification under the same conditions.

Each step's relative reaction rate of raw coal char and catalysts catalyzed steam gasification are shown in Table-1. Overall, the catalytic activities are found to be the following order: $KOH > NaOH > Raw > Ca(OH)_2 > Ni(NO_3)_2 \sim Fe(NO_3)_3$. The effects of the catalysts adopted in this research have significant differences on different reactions. Most of the adopted catalysts have the best effect on reaction (2) and the worst on reaction (3). It indicates that the catalyst is more effective for the H_2O molecules involved reaction steps, which is probably due to the oxygen transfer function of catalyst from H_2O to carbon surface. Besides, the mobile nature of potassium (K)

TABLE-1
EFFECT OF DIFFERENT CATALYSTS
ON THE THREE REACTION RATES

	Raw	K	Na	Ca	Ni	Fe
ϕ_1	2.30	6.24	4.00	1.63	1.05	1.08
ϕ_2	3.58	7.52	6.20	1.66	1.19	1.03
ϕ_3	1.02	5.67	2.47	0.62	0.84	0.34

and sodium (Na)¹³⁻¹⁵ at high temperature in the presence of carbon makes them have better catalytic effect of the all three step reaction. The minerals in raw coal char have obvious catalytic effect too, while Ca, Ni, Fe have little catalytic performance on steam gasification. The ϕ_1 and ϕ_2 values of Ca, Ni, Fe catalyzed gasification are just above 1, while ϕ_3 values are even lower than 1 which indicates the catalysts will inhibit the desorption of C(O) instead.

The influence of catalyst on different reaction steps affects the selectivity of gas products greatly. In this paper the catalyst influence on the selectivity of carbon involved products CO₂, CO and the residual C(O) in solid phase is discussed. The respective selectivity of these products are defined as

$$S_{\text{CO}_2} = \frac{\bar{v}_2}{\bar{v}_1}, \quad S_{\text{CO}} = \frac{\bar{v}_3}{\bar{v}_1}, \quad S_{\text{C(O)}} = 1 - \frac{\bar{v}_2}{\bar{v}_1} - \frac{\bar{v}_3}{\bar{v}_1}, \quad \text{where } S_{\text{CO}_2},$$

S_{CO} , $S_{\text{C(O)}}$ are the selectivity of CO₂, CO, C(O), respectively.

The product selectivity of different catalysts catalyzed gasification is shown in Table-2. The demineralized coal char gasification has the highest selectivity of CO and the lowest selectivity of CO₂ illustrates that all catalysts are more favourable of reaction (2), on the other hand suppress reaction (3). Raw coal char gasification and Na catalyzed gasification have the highest selectivity of CO₂ indicates that Na is in favour of reaction (2). Ca(OH)₂ catalyzed and Fe(NO₃)₃ catalyzed reactions have the highest selectivity of C(O) which are even higher than demineralized coal char gasification indicates that Ca(OH)₂ and Fe(NO₃)₃ may react with the oxygen from H₂O molecules and form carbonate or complex oxides which will fix a few oxygen in solid phase.

TABLE-2
EFFECT OF CATALYSTS ON SELECTIVITY

	Dem	Raw	K	Na	Ca	Ni	Fe
S_{CO_2}	0.51	0.79	0.61	0.79	0.52	0.57	0.56
S_{CO}	0.24	0.11	0.22	0.14	0.09	0.19	0.10
$S_{\text{C(O)}}$	0.25	0.10	0.17	0.07	0.39	0.24	0.34

Dem = Demineralized

Conclusion

The reaction mechanism of steam gasification is supposed in three steps: (i) the H₂O molecules are absorbed by the surface carbon atoms and then decomposes to H₂ and C(O), (ii) a good quantity of C(O) reacts with H₂O molecules to produce H₂ and CO₂, (iii) a small quantity of C(O) desorbed from the surface as product CO. Part of oxygen from H₂O still remains in the solid phase after gasification. The effects of the catalysts have significant differences on different reactions. The catalysts are more effective for the H₂O involved reaction steps which is probably due to the oxygen transfer function of catalyst from H₂O to carbon surface.

ACKNOWLEDGEMENTS

This study is sponsored by National Key State Basic Research Development Program of China (973Program, 2010CB227000) and Fundamental Research Funds for the Central Universities.

REFERENCES

1. W.B. Hauserman, *Int. J. Hydrogen Energy*, **19**, 413 (1994).
2. J. Wang, K. Sakanishi, I. Saito, T. Takarara and K. Morishita, *Energy Fuels*, **19**, 2114 (2005).
3. D.W. Mckee, *Fuel*, **62**, 170 (1983).
4. W.Y. Wen, *Catal. Rev.*, **22**, 1 (1980).
5. H.Z. Cheng, Y.F. Zhang, G.J. Zhang and S.F. Song, *Asian J. Chem.*, **25**, 3179 (2013).
6. S.G. Chen and R.T. Yang, *Energy Fuels*, **11**, 421 (1997).
7. B.J. Wood and K.M. Sancier, *Catal. Rev.*, **26**, 233 (1984).
8. G. Hermann and K.J. Huttinger, *Fuel*, **65**, 1410 (1986).
9. K. Miura, K. Hashimoto and P.L. Silveston, *Fuel*, **68**, 1461 (1989).
10. R. Meijer, F. Kapteijn and J.A. Moulijn, *Fuel*, **73**, 723 (1994).
11. J. Wang, M.Q. Jiang, Y.H. Yao, Y.M. Zhang and J.Q. Cao, *Fuel*, **88**, 1572 (2009).
12. Q.L. Sun, W. Li, H.K. Chen and B.Q. Li, *Fuel*, **83**, 1787 (2004).
13. M. Matsukata, T. Fujikawa, E. Kikuchi and Y. Morita, *Energy Fuels*, **2**, 750 (1988).
14. T. Takarada, S. Ichinose and K. Kato, *Fuel*, **71**, 883 (1992).
15. T. Wigmans, R. Elfring and A.J. Moulijn, *Carbon*, **21**, 1 (1983).