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The Development and Research Prospect on Catalytic Coal Gasification

Xia Liu*, Yunbao Tu, Xiaoqing Xu, Zhongneng Liu

Sinopec Shanghai Research Institute of Petrochemical Technology, Shanghai 201208, China
liuxia.sshy@sinopec.com

Catalytic coal gasification has attracted much attention in both academic and industrial circles due to that it is considered as a key technology for coal efficient utilization, in terms of lower reaction temperature and higher heat efficiency as compared to the conventional coal gasification. In this paper, the development and the research on catalytic coal gasification are reviewed, including the mechanism, catalysts and applications. Four categories of intensively used catalysts, including alkali metal catalysts (i.e. K, Na), alkaline earth metal catalysts (i.e. Ca), transition metal catalysts (i.e. Fe), and compound metal catalysts as well as their composites are summarized in detail. Furthermore, process conditions, such as coal feed composition, gasification operating conditions, and amount of catalyst are also reviewed. Although catalytic coal gasification as a promising technology can overcome some operation difficulties for efficiently converting coal to target products (H_2, CH_4), there are still many unsolved problems remained, such as, how to find catalysts more effective, recyclable and cheaper, and how to balance the efficiency and economic cost of gasification process.

1. Introduction

In numerous utilization technologies of coal, the gasification is widely considered as an important industrial process for converting raw coal to more useful and cleaner carbon feedstock for power generation and syngas production (Akhlas et al., 2015). Coal gasification reaction involves complex heterogeneous physical and chemical changes that occur between coal and gaseous reactants. However, high temperature and high pressure operating conditions are required in the conventional coal gasification process, eg, 1,300 °C and 3 MPa in GE coal slurry gasification. These requirements increase the plant capital and operating cost considerably. It is necessary to develop more cost-effective coal gasification technology.

In last decades, catalytic coal gasification is becoming a more attractive way to produce hydrogen-rich and methane-rich syngas, compared with conventional gasification, which labelled a slow, highly endothermic reaction that requires high temperatures above 900 °C under certain pressure (Yuan et al., 2015). The r temperature of the catalytic gasification can be lowered to 704-815 °C through the utilization of the catalyst, which is more commercially desirable for the process. Furthermore, it can remarkably enhance the gasification reaction rate and elevate the gasification efficiency.

Generally, the overall reactions of catalytic coal gasification can be described by elementary Reaction (1)-(4):

Water-gas reaction: $C + H_2O \rightarrow CO + H_2$ +131.3 kJ/mol (1)

Boudouard reaction: $C + CO_2 \rightarrow 2CO$ +162.4 kJ/mol (2)

Water-gas shift reaction: $CO + H_2O \rightarrow CO_2 + H_2$ -41 kJ/mol (3)

Methanation reaction: $CO + 3H_2 \rightarrow CH_4 + H_2O$ -206.3 kJ/mol (4)

The main characteristics of catalytic gasification can be described as: (1) With catalysts loading, the activation energy of the gasification decreases and gasification reaction rate increases. The temperature of the steam gasification process can be lowered to 700 °C. (2) H_2 and CH_4 concentration is improved by taking advantage

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of the favourable reaction selectivity of catalysts loading. CH_4 could be increased to 20%-30% in the gasified syngas (Jing, 2016). (3) In overall reaction process, besides oxygen and air, the gasification agents could be CO_2, H_2, water steam, or mixture of H_2O and O_2, as utilizing CO_2 to react with coal is an effective way to realize reduced CO_2 emissions in the process.

Compared with the conventional entrained bed gasification technology, the catalytic coal gasification has lower reaction temperature, the higher thermal efficiency and selectivity to certain gas products, which is considered as the potential third generation of coal gasification technology.

2. Catalysts for catalytic coal gasification process

The catalytic activity is due to their ability to reduce the apparent activation energy. There is a wide acceptance that the presence of catalyst enhances the reactivity of coal gasification by increasing the amount of active intermediates on the carbon surface. The increase in the active surface area can be attributed to the interaction of catalyst with the solid carbon surface and to the resulting newly formed catalytic precursors (Hamilton, 1984). The precursors are capable of dissociating oxygen species containing gases (O_2, CO_2 and H_2O) and producing oxidized intermediates that participate in the redox reaction.

The catalytic mechanism involves an oxidation–reduction cycle with the intermediate formation of the hydroxide of the alkali metal (Jiang et al., 2017). As shown in Reaction (5), the alkali metals could be generated from the interaction between alkali carbonate and carbon. The intermediate formation is thought to be a highly reactive compound that acts as an oxygen carrier. It transfers the oxygen atom to the carbon surface where it reacts with the carbon substrate to form CO. For CO_2 gasification, the active intermediates are the free alkali metals and the metal oxides, as shown in Reactions Eq(6)-(8).

Under this mechanism, the alkali metal carbonate undergoes carbothermal reduction to metal by oxidation due to steam or CO_2, which reforms their carbonate.

$$M_2CO_3 + C \leftrightarrow M_2O + CO_2 + C \leftrightarrow 2M + CO_2 + CO \tag{5}$$

$$M_2CO_3 + 2C \leftrightarrow 2M + 3CO \tag{6}$$

$$M + CO_2 \leftrightarrow K_2O + CO \tag{7}$$

$$M_2O + CO_2 \leftrightarrow M_2CO_3 \tag{8}$$

Another important mechanism is the carbonate decomposed on carbon sites to form surface oxides (Sams and Shadman, 1986). Carbonate decomposed on carbon sites to form surface oxides. The mechanism is suggested in Reaction (9), where $(–CO_2M)_{(s)}$, $–(COM)_{(s)}$, $(–CM)_{(s)}$ represent the generalized sites with the fully oxidized, partial reduced, and the completely reduced. The catalytic gasification is aroused by CO_2 could be explained by Reaction (9), (10), including the oxidation and reduction reactions.

$$M_2CO_3 \xrightarrow{C} (-CO_2M)_{(s)} + (-COM)_{(s)} \xrightarrow{C} (-CK)_{(s)} + CO \tag{9}$$

$$(-COM)_{(s)} + CO_2 \longrightarrow (-CO_2M)_{(s)} + CO \tag{10}$$

Besides, alkali earth metals, transition metals such as nickel, iron, and other metals have been also used as catalysts to promote the gasification reaction of coal and other carbon-based sources. Recently, special attention has been given to co-feeding biomass.

Overall, salts and oxides of alkali metals, and alkaline earth salts, have been widely employed for the gasification of carbon materials due to their superior catalytic properties and relative low cost (Jiang et al., 2017). The types of catalyst used for catalytic coal gasification are shown in Figure.1.

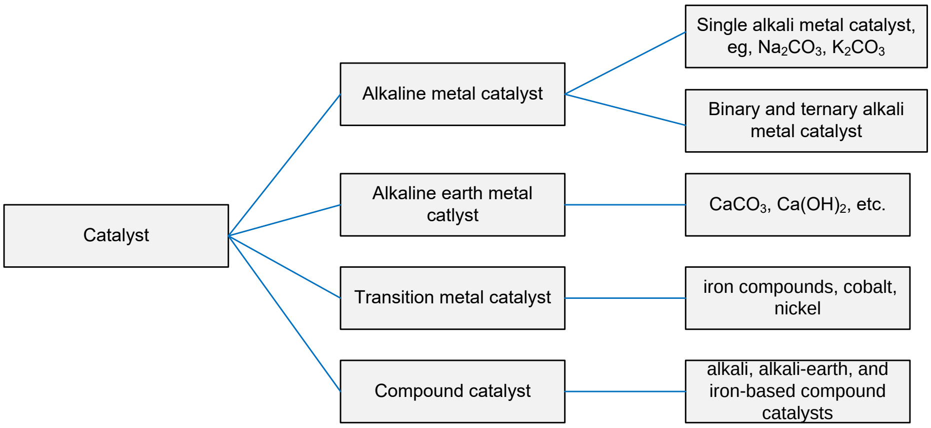

Figure 1: Types of catalyst used in catalytic coal gasification

2.1 Alkali metal catalyst

The early study on the gasification catalyst is focused on single alkali metal catalysts. When the activated carbon is gasified with CO_2, the catalytic activities are followed in order: Cs>Rb>K>Na>Li (Kapteijin, 1984). Li_2CO_3, Na_2CO_3, K_2CO_3 are used as the catalysts of steam gasification on lignite char, and the catalytic activities ranked as $Na_2CO_3>K_2CO_3> Li_2CO_3$ under same reaction temperatures (700-800 °C) with 3 wt.% catalyst loading (Kwon et al.,1989). Wang et al. (2015) provided the catalytic performance of Na_2CO_3 for high-aluminum coal gasification, with comparison of that of K_2CO_3, the catalytic action of Na_2CO_3 was better since its superior mobility and poorer volatility.

As the alkali metal carbonate in the same catalyst loading rates of steam gasification, Vamvuka (2012) tested the effect of different alkali catalysts on the conversion of waste paper, and the efficiency of these alkali metal catalysts found to be in the following order: $Li_2CO_3 > K_2CO_3 > CaCO_3 > Rb_2CO_3 > CaSO_4 > Cs_2CO_3 > Na_2CO_3$. These alkali metal catalysts increase reaction rates and lower the combustion temperature. Besides, it was found that sodium, potassium, and cesium carbonates were equally effective at typical gasification temperatures. As cheap disposable catalyst, alkali species (K, Na) are more catalytically active than alkaline earth species (Ca, Mg) during gasification.

Apart from single alkali salts, the binary and ternary alkali catalysts have been investigated with respect of their catalytic activity. McKee et al. (1985) observed that a Pittsburgh coal char containing a Li_2CO_3-Na_2CO_3-K_2CO_3 eutectic catalyst was at least an order of magnitude more reactive for steam gasification than the sample containing the same total concentration of K_2CO_3 alone. Similarly, on the same catalyst loading, in the CO_2 and char gasification process, Li_2CO_3-Na_2CO_3 eutectic catalyst and the Li_2CO_3-Na_2CO_3-K_2CO_3 had higher catalytic activity than single alkali carbonate, and the ternary eutectic catalyst was more effective than the binary one (Yeboah, et al. 2011).

2.2 Alkaline earth metal catalyst

Alkaline earth metal is important catalyst for gasification due to its low cost and getting easily from extensive sources, especially Ca-bearing minerals such as CaO, $CaCO_3$, and $Ca(OH)_2$ which have been widely investigated to improve hydrogen yields in last decade.

CaO can be used as a sorbent in CO_2 adsorption, which is with rapid initiation of the surface CO_2-CaO carbonation reaction that followed by the slow diffusion of CO_2 through $CaCO_3$ layers formed at the surface (Zhou, 2014). At the presence of steam, CaO reacts with H_2O to form $Ca(OH)_2$, which then reacts with CO_2 to form $CaCO_3$. These two reactions occur at relatively low temperatures and are not affected by the partial pressure of CO_2. Following the decrease in CO_2 partial pressure caused by CO_2 isolation, the water–gas shift reaction is driven forward, giving high H_2 yields in the coal or biomass gasification.

$Ca(OH)_2$ is usually produced by the calcinations of $CaCO_3$, followed by the subsequent hydration of the CaO formed. It is desirable to directly use $CaCO_3$ as the catalyst raw material owing its low cost. In the steam gasification of coal with $CaCO_3$ catalyst, TPD and XRD measurements demonstrated that calcium catalyst was initially present in the ion-exchanged form and as finely dispersed calcium species after pyrolysis. $CaCO_3$ was found to be effective as a catalyst raw material in the steam gasification, even at low catalyst loading (Murakami et al, 2014).

2.3 Transition metal catalyst

Transition metal is used as gasification catalyst including iron, cobalt, nickel compounds which have good catalytic effect on the steam gasification. In these transition metals, iron compounds catalyst attracted more interest because of their abundance, and low environmental impact compared with other transition metals.

The iron catalysts precipitated from aqueous solution of $FeCl_3$ that to catalyse the gasification of brown coal with CO_2 could lower the temperature at which the maximum rate of CO formation occurs by 130 - 160°C (Asami et al., 1996). $Fe(NO_3)_3$, $FeSO_4$, and $FeCO_3$ are also employed as the iron precursor. $Fe(NO_3)_3$ was less active than $FeSO_4$ during pyrolysis of a sub-bituminous coal with the same iron loading at 700 - 800 °C. For $FeCO_3$ used as a catalyst precursor in coal gasification with CO_2, the redox cycle is between metallic Fe and FeO catalysed the initial char gasification with CO_2. The catalytic iron species changed to FeO and Fe_3O_4 in the char gasification.

2.4 Compound catalyst

Pursuing higher gasification rates at relatively lower reaction temperatures, some alkali, alkali-earth, and iron-based compound catalysts, particularly potassium carbonate (K_2CO_3) based complex, have been trialled as catalysts for coal gasification.

In the steam gasification of coal char, the binary K_2CO_3-$Ca(OH)_2$ catalyst showed a synergic effect on promoting the gasification rate, whereas the catalytic activities of the Li_2CO_3-$Ca(OH)_2$ and Na_2CO_3-$Ca(OH)_2$ were worse than their respective alkali carbonates alone (Tang and Wang, 2015). The gasification characteristics of coal char with CO_2 under Cao and $Fe(NO_3)_3$ were studied by Chen etal.(2012), and it is found that the optimal mass addition of compound catalyst was 1 % Ca+2 % Fe, the catalytic intensity were 5.71, 1.65 and 2.04 times of raw coal char, single component catalyst of CaO and $Fe(NO_3)_3$. In addition, For K_2SO_4 and Na_2CO_3, the gasification rate could be enhanced by addition of iron salt. It is reported that the mixtures K_2SO_4-$FeSO_4$ and K_2SO_4-$Fe(NO_3)$ exhibited better catalytic activity than K_2CO_3 at 800 °C (Song and Kim, 1993).

3. The influence factors of catalytic gasification

In addition to metal catalyst discussed, there are also other factors which could have influence on the gasification efficiency, including quantity of coal, catalyst loading, operating condition of gasification.

The mineral components of coal including alkaline metal (K, Na) and alkaline earth metal (Ca) have catalytic activity for gasification. In the coal gasification, the low rank coal usually has higher gasification ratio. For catalyst K_2CO_3 loaded, the react ratio changes with coal ranks, as shown in Table 1, the higher coal rank, the higher catalytic efficiency in coal-based char gasification.

Table 1: Effect of potassium carbonate on carbon gasification by steam

Char source	Operating temperature (°C)	Content K_2CO_3 (wt%)	Ratio of rate Catalysed/uncatalysed	Reference
Lignite char	700	10	3.8	(Nzihou, et al., 2013)
Sub-bituminous char	700	10	7.5	(Nzihou, et al., 2013)
Bituminous char	700	10	16	(Nzihou, et al., 2013)
Anthracite char	800	10	25	(Nzihou, et al., 2013)
Sub-bituminous coal	700	10	20	(Kopyscinski, et al., 2014)

The catalyst loading also affects the gasification efficiency. At the low catalyst loading, the more catalyst addition, result in the higher of catalytic activity. However, as the catalyst addition exceeds the optimal amount value, the excess appear low dispersity on the surface, which decreased the active surface of the coal with catalyst. Yang et al. (2013) reported that the reactivity of lignite char increased linearly with catalyst loading up to a loading saturation level which was around 10 %, for both K and Ca.

Temperature and pressure of reaction are two main factors affecting gasification efficiency, which obviously influence reactive rate, carbon conversion and the components of the produced syngas. While the operating temperature of entrained bed gasifier is at range of 750 - 1,000 °C, the yield of H_2, carbon conversion rate both improved with the temperature increasing, which is confirmed by Popa and Fan (2013) that rate constants of coal char conversion with 900 °C was 3.4 - 3.7 times more than that of 700 °C.

4. Industrial application development

Catalytic gasification to synthetic natural gas (SNG) has been done a developmental effort by Exxon in the late 1970s to the early 1980s. Potassium carbonate (K_2CO_3) was employed in the Exxon pilot-scale coal gasification, which was demonstrated using a fluidized-bed gasifier in the late 1979 (Nahas, 1983). Exxon's catalytic coal gasification process was gasified coal with steam to produce a CH_4 and hydrogen. There were two steps included in this gasification process. Firstly, the coal underwent rapid devolatilization to yield coal char and numerous volatile products. The resulting char was catalytic gasified with steam and recycle gas to produce a mixture of CH_4, H_2, and CO_2. However, the high operating cost of catalyst recovery and the natural gas market contracted, continued developmental efforts stopped, resulting this technology could not proceed further.

In last decade, as the industrial development of coal-to-gas convention has drawn much attention, Great Point Energy from US has expanded on Exxon's developments and completed the 1 t/d pilot catalytic gasification study, the feedstock has extended with petroleum coke and biomass. The flowsheet of Bluegas™ gasification process is shown in Figure 2. The dried coal is mixed with catalyst in feedstock preparation step. The catalyzed coal is then dried and transported to a fluidized-bed gasifier. The catalyst promotes the hydrogasification/WGS/methanation reactions to produce CH_4 and CO_2 in gasifier. The produced syngas undergoes a series of steps to remove particulates, acid gases to recover the CH_4 product gas. The demonstration of their Bluegas™ technology was initially conducted at the Gas Technology Institute's (GTI) Flex-Fuel Test Facility in 2007. As the next stage of commercial development, Great Point Energy and China Wanxiang already have a \$1.25 10^9 partnership to build a synthetic natural gasification using the Bluegas™ hydro-methanation technology in China (NETL, 2017).

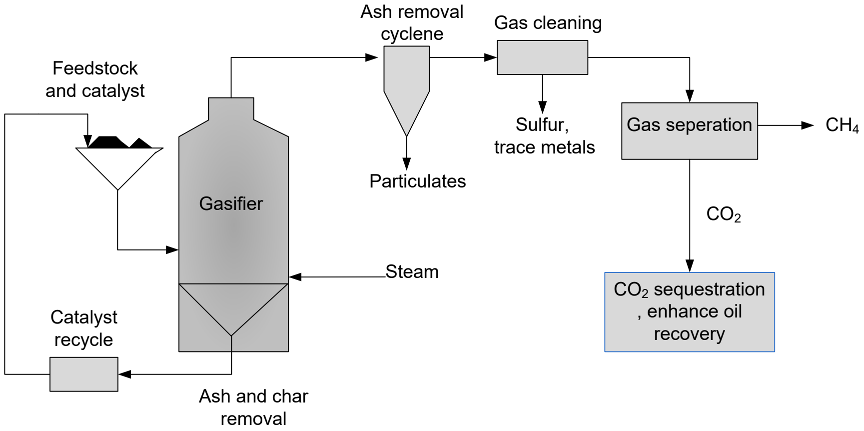

Figure 2: The flowsheet of Bluegas™ gasification process (NETL, 2017)

Although catalytic coal gasification has been developing for several decades, it has not been put into industrial application. One major reason is the poor recovery of the gasification catalyst, which is usually considered to be attributed to deactivation of the gasification catalyst resulting from the interaction between the catalyst and the mineral matters in the coal.

5. Conclusions

Catalytic gasification has a preference to other conventional gasification techniques due to its improved reaction activity and moderate operating conditions, especially for methane and hydrogen target production. A lot of work has been done to find the cheaper catalysts and improve the gasification scheme application more economically. The catalytic performance of alkali and alkaline earth metal salts on the goal gasification has been extensively investigated technically and in term of applications. With regard to improve the economics of catalytic gasification process and make it environmentally acceptable, recovery of the catalyst need to be used in catalytic gasification. The main process variables of catalyst recycle should to be considered, such as, solvent-to-coal ratio, mixing time, extraction temperature, pH, concentration, which are major factors affect the catalyst recovery efficiency. For further industrial application, the Heat Integration and Total Sites Integration tools (Klemeš, 2013), also should be considered to improve the gasification site energy efficiency.

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