Performance of Metal Compound Catalysts for Coke Gasification Reaction[#]

Liangguo Lyu [1], Yuanpei Luo [2], Shengping Zhang [3], Fei Dai [4*]

1 Laboratory of Distributed Energy System and Renewable Energy, Institute of Engineering Thermophysics, Chinese Academy of Sciences; Inner Mongolia University of Science & Technology

2 Xi'an Jiaotong University

3 Department of Thermal Science and Energy Engineering, University of Science and Technology of China

4 Laboratory of Distributed Energy System and Renewable Energy, Institute of Engineering Thermophysics, Chinese Academy of Sciences

(Corresponding Author: daifei@iet.cn)

ABSTRACT

With the excessive use of fossil energy and concern for environmental protection, coal coke gasification as an clean means of energy utilization has received widespread attention worldwide. Coal catalytic gasification is an effective way to realize clean coal utilization. The catalytic gasification technology of coke and CO_2 has the advantages of low reaction temperature, small energy consumption and low CO_2 emission. In this study, the catalytic effect of alkali metals, alkaline earth metals, transition metals and rare earth on the reaction between coke and CO_2 was investigated by using a self-made gas-solid reaction device. It was concluded that in the gasification reaction between coal coke and CO_2 at 1173K, the performance of K_2CO_3 catalyst was the best. Under the condition of wet mixing, the conversion rate of K_2CO_3 was 98.8%, and $\tau_{50\%}$ was 40.6min. The metal compound catalyst of Ca, Fe in wet mixing and dry mixing conditions had little effect on the coal coke -CO_2 gasification. Thus, K and Ce was kinds of efficient catalyst and will be used as a promising catalyst for coal char CO_2 gasification.

Keywords: coke; gasification reaction; alkali metal; alkaline earth metal; transition metal; rare earth; CO_2

NONMENCLATURE

Abbreviations	
DLIET	Distributed Laboratory of the Institute of Engineering Thermophysics
g	gram
h	hour
m	mass
mm	millimeter

1. INTRODUCTION

Coal is the main fossil resource and energy in China, but pollutants originating from coal combustion have considerably harmed the ecological environment and human health.[1] Although the proportion of coal has declined year by year with the adjustment of energy structure, it still accounts for 55.3% of the total energy consumption in 2023.[2] In order to achieve the goal of '2030 carbon peak and 2060 carbon neutrality', the clean, efficient and low-carbon utilization technology of coal will occupy an extremely important position in the future energy. Coal gasification technology is an efficient, clean and low-carbon coal utilization technology.[3] Gasification reaction of coal char and CO_2 can realize the utilization of CO_2, then the CO product can be further used for chemical industry. Conventional gasification techniques do not use catalysts and the operating temperature is generally higher than 1273K. Conventional coal gasification process is completed in a reactor, which requires pure O_2 as the gasification agent. The air separation device for oxygen production is imported. The composition of gasification syngas is complex and needs to be purified, thereby restricting its development and utilization. The air separation unit and the syngas purification unit have the disadvantage of high energy consumption, resulting in the decrease energy system efficiency.[4]

Hongguang Jin proposed that coal grading gasification reaction was carried out to generate the path of H_2, CO and CO_2 formation. The complex reactions were decoupled into three processes: Coal-Coking, Coal Char-CO_2 gasification to produce CO, CO conversion to produce H_2 and CO_2, respectively. Three-Step Method could obtain hydrogen-rich pyrolysis gas and CO, achieving the classification and directional conversion of coal hydrocarbon components, and to realize the directional enrichment of CO and impoverishment of CO_2.[5] That method could reduce the energy level difference of gasification reaction. Through the selection and control of the gasification reaction path, the

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irreversible loss of the reaction process itself could be lessened. In addition, since the gasification method used CO_2 as the gasification agent rather than pure oxygen, a large amount of air separation power consumption were avoided, thereby improving the overall efficiency.[6] In the three-step method, coal coke-CO_2 gasification was the core of the method. Utilization of catalyst in char-CO_2 gasification could effectively reduce the reaction temperature, shorten the gasification time, and regulate the components of gaseous production, thereby lowering the energy consumption. Equipment requirements of the gasification reaction was simplified. [7-9] At the same time, the efficiency of coal char-CO_2 gasification could be improved and the composition of directional gas could be optimized. Process flow was shortened by the method. Economy of coal gasification industrial production was upgraded [10].

Many studies have been carried out to date. It found that alkali, alkaline earth metal, transition metal, rare earth (K, Ca, Fe, Ce, etc.) are the most commonly used as catalysts for coal gasification, due to their relatively low cost and acceptable catalytic performance. [11] Among alkali metal catalysts, K and Na catalysts have become the most common catalysts in the study of coal catalytic gasification due to their high activity and selectivity to some products. McKee found that K^+ was in continuous reduction and oxidation process in coal gasification reaction. Potassium contributed to the transfer and circulation of oxygen in coal gasification.[12] Kopyscinski revealed that the use of K_2CO_3 could effectively reduce the reaction temperature, and K_2CO_3 was activated to-COK or-CK surface complex at 700℃ in N_2 atmosphere.[13] Wang et al. studied the role of $Ca(OH)_2$ in the supercritical water gasification of low rank coal. $Ca(OH)_2$ was beneficial to the extraction of volatile substances from coal and the decomposition of volatile substances into small molecule gases, while reducing the amount of residual carbon. In addition, the use of calcium catalyzed the gasification of coal, the production of H_2 and CH_4 increased.[14] Yu found that Fe-based catalysts helped to increase the steam gasification rate of coal and reduce the reaction temperature. Compared with iron-free catalysts, iron-based catalysts could significantly increase the yield of H_2 in the generated gas.[15] Rare earth elements had unpaired 4 f orbitals and lanthanide shrinkage properties, showing unique physical and chemical properties. Zhang found that compounds of rare earth element were adopted as catalysts for the decomposition of organic compounds. Mesoporous CeO_2 completely catalyzed the degradation of benzene at 260°C.[16] These studies aroused our great interest, but there are still obvious deficiencies. Although the alkali metals, alkaline earth metals, transition metals and rare earth elements had been found the effect of catalyzing

coal gasification, increasing the gasification reaction rate of coal to a certain extent. Alkali metals, alkaline earth metals and transition metal reduced the gasification reaction temperature and could be regulated the composition of the product gas directionally. But there were still obvious deficiencies. For example, there are few studies on the reaction of coke and CO_2 with alkali metals, alkaline earth metals, transition metals and rare earth elements. In paper the performance of alkali metal, alkaline earth metal, transition metals and rare earth on the reaction of the same coal char and CO_2 at 1173K were investigated, revealing the reaction mechanism.

2. MATERIAL AND METHODS

2.1 xperimental Apparatus

For the coal coke and CO_2 gasification experiment, the fixed bed reactor shown in Figure 1 was used. The system was mainly composed of gas flow control system, electric heating system, gas analysis and collection system.
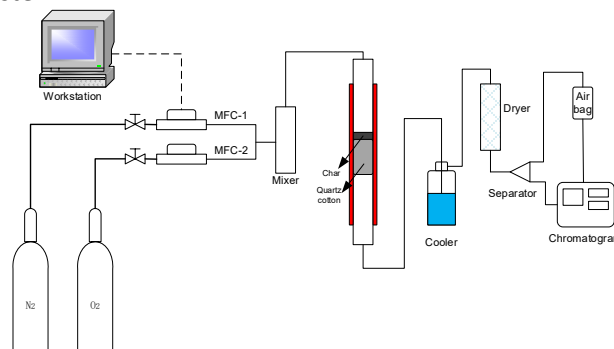
Fig. 1 Schematic Diagram of Fixed Bed Reactor

The coal coke used in the experiment was the coal char produced by the Distributed Laboratory of the Institute of Engineering Thermophysics (DLIET). The protective gas was N_2(purity 99.99%). The reaction gas CO_2(purity 99.99%) was produced by Langfang Anci District Changhong Gas Co., Ltd. K_2CO_3, CeO_2, CaO, and Fe_2O_3 were analytical reagents (produced by Tianjin Beichen Fangzheng Reagent Factory).

2.2 Methods

K_2CO_3, CeO_2, CaO, and Fe_2O_3 catalysts were added to the gasification reaction of coal coke and CO_2, respectively. Catalyst (m=0.5g) and coal char (m=4.5g, average coke particle size for 0.575mm) were added by dry mixing and wet mixing. The wet mixing method was mixing the catalyst and coal char in pure water. It was agitated for 12h by magnetic stirrer, and dried to obtain the reactant. Coke was placed in the reaction tube at quartz cotton. The reactants were heated from room temperature to 1173K in N_2 atmosphere, and kept for 1h. The N_2 atmosphere was switched to CO_2 atmosphere (80ml/ min), and the reaction gas was collected every 10

minutes. 20 bags of gas samples were collected for 3 hours. The concentrations of CO_2 and CO components were measured by Agilent chromatograph, and carbon conversion rate was calculated by CO concentration. The time required for the carbon conversion rate to reach 50% in the reaction $\tau_{50\%}$ was used as the catalyst performance index to judge the catalyst performance.[7]

The microstructures of the post-reaction solid residues from coal char were characterized by scanning electron microscopy (SEM), XRD analysis. For SEM, a ZEISS instrument with a magnification of 10×, an operating voltage of 10.0 kV, and a working distance of 7 mm was used to observe the morphological changes in the carbon matrix and pore structure before and after the coke reaction. The mineral composition of coke samples was determined using an X-ray diffractometer (XRD).
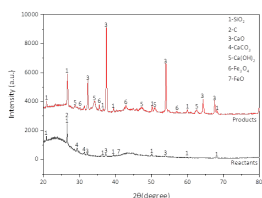
3. RESULTS

3.1 Raw coal char
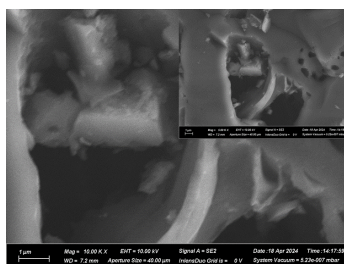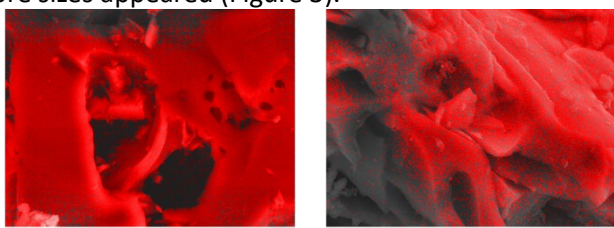

Fig. 2 XRD diffractograms of char samples

Fig. 3 SEM images of raw coal char

The raw coal char was prepared by the (DLIET). Figure 2 shows Si, Ca, Fe of metal element existed in char samples. The surface morphology obtained by SEM characterization showed that the surface of the coal char reactant was rough and uneven, and pores with different pore sizes appeared (Figure 3).


a. Raw coal char reactant

B. Raw coal char product

Fig. 4 EDS image of C element

Figure 4 (a) shows that carbon element existed in the whole raw coal char. Carbon element of reaction production distribution was smaller than that of char-CO_2 reactants. Figure 4 (b) illustrated without the addition of catalyst, the product of gasification appeared residual char, while the reaction of coal char with CO_2 at 1123K for 3h. Coal char does not react completely.

3.2 CO product of char-CO_2 gasification with the different catalysts
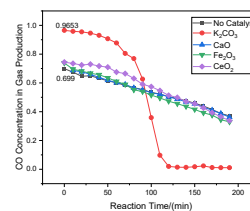
a. Dry mixed
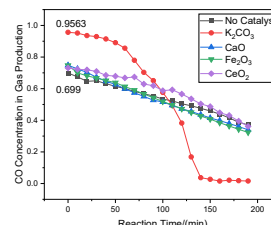
b. Wet mixed

Fig. 5 CO produced

Compared with the catalyst-free coke-CO_2 gasification, Figure 5 shows the gasification performance was improved when K_2CO_3 and CeO_2 catalysts were loaded. The catalyst increased the concentration of CO at the early stage of the reaction, and the concentration of CO began to decrease as the reaction proceeds in Figure 5 (a), (b). Figure 5 (a) shows that CO concentration in the produced gas increased from 69.90 % without catalyst to more than 96.53% within potassium carbonate (dry mixed), and maintained for nearly 60 min. Figure 5 (b) shows that CO concentration in the produced gas increased from 69.90 % without catalyst to more than 95.63% within potassium carbonate (wet mixed), and maintained for nearly 60 min. It could be concluded that K had a good catalytic effect on char-CO_2 gasification. At 90-150 min, compared with K_2CO_3, CeO_2 as a catalyst could still maintained a high gasification rate. It could be seen from Figure 5 that the addition of CaO/Fe_2O_3 to coal char-CO_2 was consistent with the trend of CO concentration in the char-CO_2 reaction without catalyst.

3.3 Effect of catalyst on gasification rate of coal coke
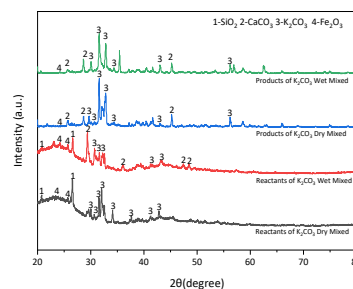
3.3.1 K_2CO_3 Catalyst

Fig.6 XRD diffractograms of K_2CO_3 added to char samples

Figure 6 shows Si, Ca, Fe,K of metal element existed in char samples.

a. Reactants (Dry mixing)   b. Products (Dry mixing)

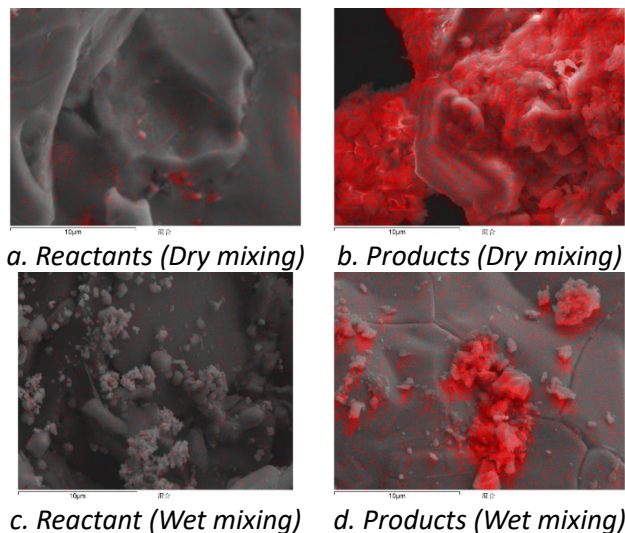c. Reactant (Wet mixing)   d. Products (Wet mixing)

Fig. 7 EDS image of K element

It was seen from Figure 7 that K element was on the surface of coal char after dry mixing and wet mixing of coal char with K_2CO_3. The coal ash after the reaction of coal char with CO_2 contained K element.
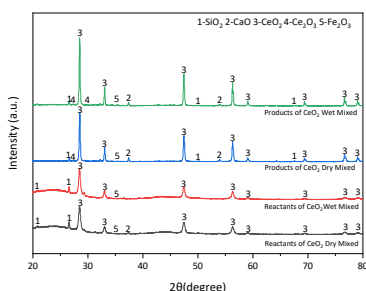
3.3.2 CeO_2 Catalyst

Fig.8 XRD diffractograms of CeO_2 added to char samples

Figure 8 shows Si, Ca, Fe, Ce of metal element existed in char samples.

a. Reactants (Dry mixing)   b. Products (Dry mixing)

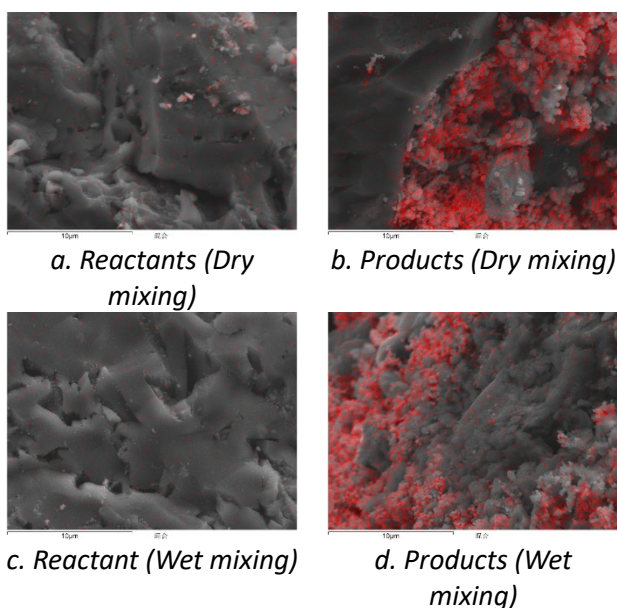c. Reactant (Wet mixing)   d. Products (Wet mixing)

Fig. 9 EDS image of Ce element

Through Figure 9, it was confirmed that Ce was distributed on the surface of char after dry mixing and wet mixing of coal char with CeO_2. The coal ash after the reaction of coal char with CO_2 contained Ce element.
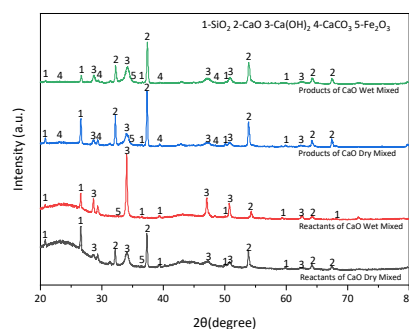
3.3.3 CaO Catalyst

Fig. 10 XRD diffractograms of CaO added to char samples

Figure 10 shows Si, Ca, Fe of metal element existed in char samples.

a. Reactants (Dry mixing)   d. Products (Wet mixing)

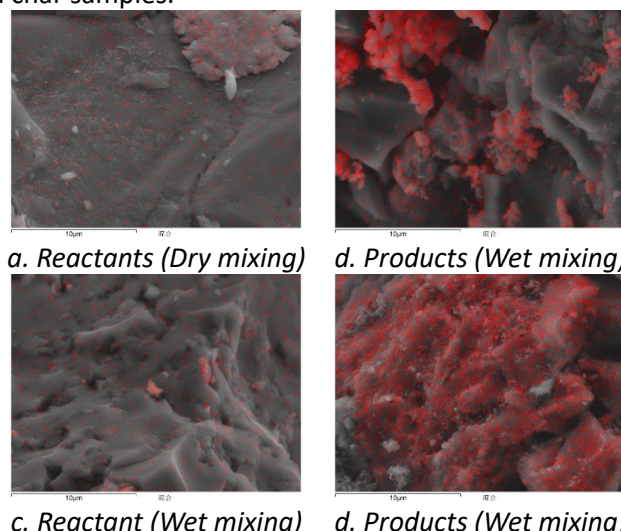c. Reactant (Wet mixing)   d. Products (Wet mixing)

Fig. 11 EDS image of Ca element

It was found from Figure 11 that Ca element was distributed on the surface of coal char after dry mixing and wet mixing of coal char with CaO. The coal ash after the reaction of coal char with CO_2 contained Ca element.
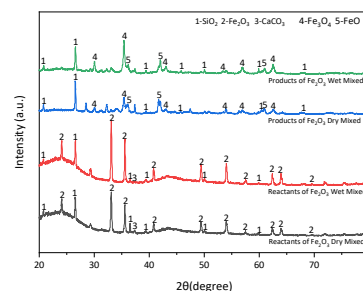
3.3.4 Fe_2O_3 Catalyst

Fig. 12 XRD diffractograms of Fe_2O_3 in samples

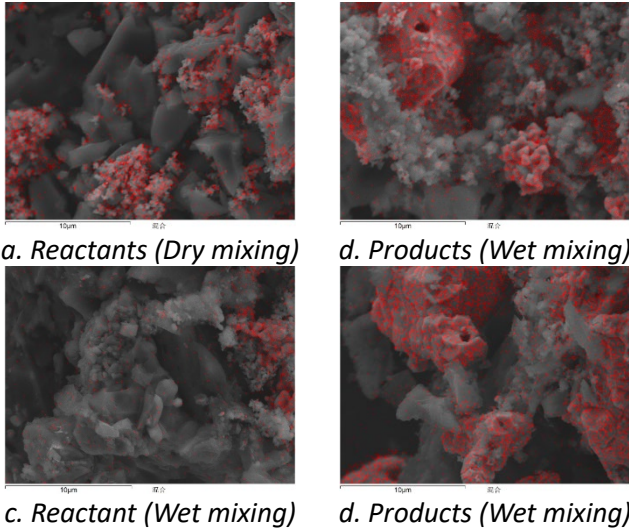Figure 12 shows Si, Ca, Fe of metal element existed in char samples.

a. Reactants (Dry mixing)   d. Products (Wet mixing)

c. Reactant (Wet mixing)   d. Products (Wet mixing)

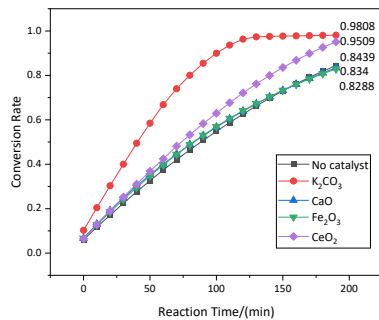Fig. 13 EDS image of Fe element

It was found from Figure13 that Fe element was distributed on the surface of coal char after dry mixing and wet mixing of coal char with Fe_2O_3. The coal ash after the reaction of coal char with CO_2 contained Fe element.

4.   DISCUSSION
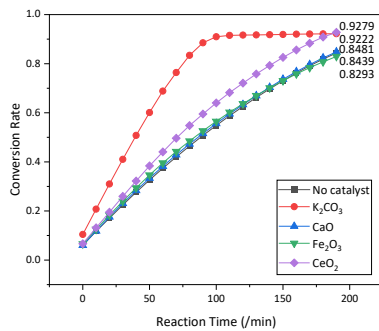
a. Dry Mixed

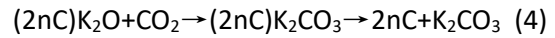b. Wet Mixed

Fig.14 Coal char conversion rate

Figure 14 (a) shows under dry mixing condition of K_2CO_3 and char, the carbon conversion rate of char-CO_2 was 92.22 %, $\tau_{50\%}$ was 39.2 min. Figure 14 (b) illustrates under wet mixing condition of K_2CO_3 and char, the carbon conversion rate of char-CO_2 was 98.8%. $\tau_{50\%}$ was 40.6 min.

After the addition of catalyst, the gasification reaction effect of char-CO_2 was significantly enhanced

and more CO was obtained. This possible explanation is that Wen[17] proposed the reaction mechanism of C-CO_2 catalyzed by K_2CO_3:

$$K_3CO_3+C \rightarrow 2K+3CO \qquad (1)$$
$$2K+2nC \rightarrow 2CnK \qquad (2)$$
$$2CnK+CO_2 \rightarrow (2CnK)OCO \rightarrow (2nC)K_2O+CO \quad (3)$$
$$(2nC)K_2O+CO_2 \rightarrow (2nC)K_2CO_3 \rightarrow 2nC+K_2CO_3 \quad (4)$$

The mechanism of C-CO_2 reaction catalyzed by alkali metal was suitable to be explained by oxygen transfer theory[18]. Alkali metal salts were first reduced with carbon bond energy, and then oxidized by an oxidizing atmosphere, so that the catalytic gasification of char was realized by a cyclic redox reaction. The experimental results of catalyst was manufactured by dry mixing and wet mixing. Under the same conditions, the reaction rate of char-CO_2 after impregnation was significantly faster than that of dry mixing, which indicated that there was more potassium attached to char particles through impregnation, and there were more active sites, and the reaction effect was better.[19]

Figure 14 (a) shows under dry mixing condition of CeO_2 and char, the carbon conversion rate of char-CO_2 was 92.79 %, $\tau_{50\%}$ was 70.7 min. Figure 14 (b) illustrates under wet mixing condition of CeO_2 and char, the carbon conversion rate of char-CO_2 was 95.09%. $\tau_{50\%}$ was 73.6 min. The gasification efficiency of char-CO_2 was improved with CeO_2 of catalyst, and the effect of wetted catalyst was better than that of dry mixing. The contact between the catalyst components in the dry mixing method was more dependent on physical collision and electrostatic force, resulting in the uneven distribution of the active components. The wet mixing method was to mix the catalyst with coal char in the liquid phase, involving steps such as dissolution and precipitation. The catalyst and coal char were obtained by drying. That method could obtain more uniform and better dispersed reactants. CeO_2 belonged to fluorite type oxide semiconductor, which had excellent oxygen storage and released ability. The oxygen atoms on the surface and bulk lattice of CeO_2 could directly participate in the reaction and be consumed, and formed oxygen vacancies, which were supplemented by active oxygen species such as O_2^-, O^-, O_2^- and O_2^{2-}. Therefore, CeO_2 had a strong catalytic ability and was often employed as a catalyst[20]. In Boudouard reaction, CeO_2 could absorb oxygen in the CO_2 atmosphere to form CeO_{2-x} (oxygen-deficient cerium oxide). When the Boudouard reaction required oxygen, CeO_{2-x} would release oxygen to provide the coal char produced CO needed in the reaction. Oxygen storage and release cycle could stabilize the redox balance during the reaction and promoted the reaction. The surface of cerium oxide might provide active sites, which was conducive to the adsorption and activation of CO_2 and coal coke. These active sites might reduce the energy

barrier of CO_2 reduction, promote the formation of carbon-carbon bonds, increase the contact opportunities between them, and accelerate Boudouard reaction. The oxygen species of CeO_2 (such as O_2^-, O^-) on the surface of ceria could be directly involved in the reduction of CO_2. The active oxygen species promoted the decomposition of CO_2 molecules, thereby generating CO.

It could be seen from Figure 14 that the addition of CaO/ Fe_2O_3 to coal char for gasification reaction with CO_2 was consistent with the trend of C conversion rate in the above-mentioned char-CO_2 reaction without catalyst. Conversion rate of C was much lower than that of K_2CO_3 and CeO_2. The reason was that the coal char itself contained Fe and Ca elements, which had played a catalytic role in the char-CO_2 reaction(Figure10 and Figure 12). Therefore, the addition of CaO and Fe_2O_3 as catalysts in the experiment had no significant effect.

The metal compound catalyst of Fe, Ca in wet mixing and dry mixing conditions had little effect on the reaction between coke and CO_2. K_2CO_3 and CeO_2 as catalysts could improve the kinetic performance of coke-CO_2 gasification to a certain extent, and the migrations of catalyst characteristics in reactions were different, resulting in different catalytic effects in different gasification stages. On the whole, the order of catalytic performance was: K_2CO_3 > CeO > CaO / Fe_2O_3.

5. CONCLUSIONS

A series of metal compound catalysts added coal char produced by DLIET. With CO_2 gasification were investigated by fixed-bed reactor, XRD and Sem-Eds respectively. The catalytic performances of K_2CO_3 were best. Under the condition of wet mixing, in the reaction of coke with CO_2 gasification. Conversion rate of K_2CO_3 was 98.8%, $\tau_{50\%}$ was 40.6min. K_2CO_3 in the coal coke and CO_2 gasification reaction mechanism was the electron promotion effect, the change of surface physical properties, to provide intermediate reactants. The coal char itself contained Fe and Ca elements, which had catalytic effect on coke-CO_2 gasification. The order of catalytic performance was: K_2CO_3 > CeO_2 > CaO / Fe_2O_3. The effect of wetted catalyst of Ce was better than that of dry mixing. Metal compound catalyst of K, Ca, Fe in wet mixing and dry mixing conditions had little effect on the reaction between coke and CO_2. In conclusion, reactive differences and the competitive effect of metal compound catalyst in coal coke-CO_2 gasification had been described from a perspective, which might provide potential theoretical support for the selection of clean utilization of coal technologies.

DECLARATION OF INTEREST STATEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. All authors read and approved the final manuscript.

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