

CARBON AND SULFUR CONVERSION OF HIGH-SULFUR ORGANIC WASTE IN THE ENHANCED CHEMICAL LOOPING GASIFICATION

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ABSTRACT

When sulfur in petroleum coke (petcoke) converts to H₂S instead of SO₂, it is the resource which can be recovered by Claus process. Chemical looping gasification (CLG) is capable of achieving petcoke conversion and sulfur recovery. To simultaneously overcome the obstacles of low gasification reactivity and improve H₂ and H₂S production, hematite modified by K as oxygen carrier (OC) was involved in the high-sulfur system to investigate the effect on sulfur conversion via batch fluidized bed in petcoke CLG process. K enhanced H₂ generation beyond expectation because K not only improved the petcoke gasification but also enhanced the steam oxidation of deep reductive OC. Especially when using 10%KNO₃-hematite, H₂ yield increased by 3.9 times as compared to 0%K, with the carbon conversion efficiency of 99.92% in the 22nd minute. The sulfur fate had been originally studied using K-modified hematite OC. H₂S was the main phase of sulfur release and the high H₂ yield also assisted H₂S production. Introducing K contributed to in-situ sulfur capture forming K-Fe-S compounds in the OCs due to the deep reduction of Fe. 10%KNO₃-hematite exhibited excellent cyclic stability with a H₂ volume fraction more than 65% in 21 cycles.

INTRODUCTION

Petroleum coke (petcoke) is the main by-product of industrial coking process, and its production has been dramatically increasing along with the over-exploitation and the poor quality of crude oil. Fuel-grade petcoke is considered as an alternative to coal due to high cost-effectiveness, little ash, and heating value [1]. However, high-sulfur content contributes to environmental degradation due to the sulfur pollutant, which is also a limit to petcoke utilization. Therefore, it is necessary to innovate the technology of petcoke usage environmentally and economically to provide the market with opportunities for demand growth.

Gasification is a cleaner method of carbonaceous material conversion to generate syngas with less heavy metal and SO_x pollution, as compared to combustion. Syngas with abundant H₂ and CO can be used for industrial chemicals. H₂ is widely known as a potential energy and the amount of H₂ also determines the further applications of the gaseous products and the calorific value of syngas. Moreover, petcoke mainly generates H₂S instead of SO₂ during the gasification atmosphere, which is widely used as feedstock to recover sulfur by mature Claus process with a substantial economic income. If the sulfur-containing gas product is H₂S, sulfur is no longer pollution, but resource. But the reactivity of petcoke gasification is dampened by its high graphitization structure, low porosity, and little alkali/alkaline earth metal (AAEM) content [2]. AAEM was always employed to enhance the gasification reactivity of petcoke and H₂ yield, and H₂ ratio was up to 60% of syngas especially at just 750 °C in steam gasification by prompting char gasification and water-gas shift reactions [3-6]. But K vaporization significantly limited the increase of reaction rate [7]. The alkali and transition metal such as K and Fe had synergistic catalytic effects on char gasification [8, 9] as well as H₂ yield [2] at the presence of steam. However, the dispersion of Fe on carbon surface caused agglomeration and sulfur poisoning during gasification, which was the primary reason of catalyst deactivation [9-11]. The application of expensive catalysts brought out some unfeasible problems in practice [12].

Chemical looping gasification (CLG) is a promising and green technology for solid fuel conversion in which oxygen carrier (OC) substitutes molecular oxygen sources with less SO_x and NO_x, originated from Chemical looping combustion [13]. Metal oxide as OC supplies lattice oxygen instead of pure oxygen to achieve the operating cost reduction [14]. Furthermore, OC as catalyst circulates between gasification reactor and air reactor, so the waste of expensive catalysts and equipment corrosion caused by

catalysts such as K, may be averted, compared with catalyzed gasification. Meanwhile, OC also acts as the heat source at the expense of combustible gases and provides heat during OC regeneration in AR. CLG could provide more extra heat to obtain the heat balance by contrast, when catalyzed gasification has the similar conditions.

In terms of the advantages of CLG, the investigation of OC becomes particularly important. Fe-based OCs were generally adopted for different chemical looping technologies due to the non-toxicity and abundant source [15-19]. However, Fe-based CLG process also encountered two difficulties, consisting of the low reaction rate between OC and solid fuel [20]. Potassium with movability between char and OC increased the reactivity of iron oxides as well as char gasification synergistically, thus improving the reduction rate [17, 21-24]. The K-Fe-O composites in OC inhibited the volatilization of K. They proposed that the low-ash coal contributed to inhibiting the loss of K [20, 25]. Gu [26] prepared K_2CO_3 -modified hematite to accelerate char gasification and water-shift reaction. Besides, the iron oxides system had low tendency to generate sulfide or sulfate at any sulfur-containing gas concentration or operation temperature [27, 28]. In conclusion, considering the advantages and behaviors of catalysts in traditional gasification and OCs in CLG as described above, introducing K to Fe-based OC is an effective and economical approach to utilize the low-ash petcoke for enhancing the gasification rate, OC reactivity, and H_2 production. However, Fe-based OC modified by K has not been involved in the sulfur-containing system.

Accordingly, this research aimed at enhancing H_2 and H_2S production by promoting the reactivity of OC reduction and petcoke gasification during CLG process to improve the value-increment utilization. The performance based on K-modified hematite OC was detailed investigated in the sulfurous CLG via a batch fluidized bed, such as the enhancement of OC reactivity and petcoke gasification. The releases of SO_2 and H_2S were rival and intricate, so sulfur fate had been originally studied when K-modified hematite OC was employed. Furthermore, the multicycle operations were proposed to test the durability of OC. And the catalytic and competitive effects of K on petcoke gasification and OC reactivity were discussed.

MATERIAL AND EXPERIMENT

Material preparation

Wet-impregnation method was used to prepare several different K-modified hematite samples. A certain amount of KNO_3 was dissolved in deionized water. 100 g of dry hematite in the size range of 0.3-0.4 mm was accurately weighed and then was added to the prepared solution thoroughly. The addition amount of potassium was set to 0.3%, 3%, 10%, and 15%

respectively, according to the mass ratio of metal atom mass to hematite. The mixture was vigorously stirred and evaporates in the water bath of 80 °C with a magnetic stirring rotor until the sample becomes slurry. After drying, the paste mixture was put in a muffle furnace to heat up to 950 °C in 4h, and calcined at this temperature for 4.5h. Finally, the OCs were screened to the size range of 0.3-0.4 mm for spare. The elemental contents of the bulk prepared OC samples were analyzed by X-ray Fluorescence Spectrometer (XRF-1800, SHIMADZU, Japan). The surface morphology and elemental analyses of the OC samples were examined by HITACHI SU3500 scanning electron microscopy combined with energy-dispersive X-ray spectroscopy (SEM-EDX).

Industrial high-sulfur petcoke from China Yangzi Petrochemical Co., Ltd was considered as fuel in the experiments. The proximate and ultimate analyses of petcoke were summarized in Table 1. Before the tests, the lumps of petcoke were crushed, and particles of 0.1-0.3 mm were screened out. The small size was favorable for increasing gasification rate of petcoke.

Table 1. Proximate and ultimate analyses of petcoke

Proximate analysis	(wt.%, ad)
M	0.76
V	12.98
FC	85.87
A	0.39
Ultimate analysis	(wt.%, ad)
C	85.24
H	3.82
O	2.44
N	1.29
S	6.06

Experiment procedure

In order to evaluate the performance of K-modified hematite OC in petcoke CLG, the experiments were conducted in a batch fluidized bed as illustrated in Fig.1. The reactor tube was made of quartz with an inner diameter of 32 mm and a height of 600 mm, in the middle of which the porous plate was settled. And the tube was heated up to the desired temperature of 900 °C by electric furnace. In the single test, before adding OC (36 g) from the top, the oxidation atmosphere was the mixture of O_2 (100 ml/min STP) and N_2 (2 L/min STP) to fully oxidize the synthetic OC. The gasification experiment started from introducing petcoke (0.75 g) when the bed materials were exposed to the stream of N_2 (1 L/min STP) and steam (1 ml/min) at 900 °C. Stable steam was transported by the constant flow pump (TBP-50 A) and generated by the heating tape of 120 °C. The conditional gases (CO , CO_2 , CH_4 and O_2) were collected by sample bags after condensation, drying and filtration. The conditional

gases were analyzed by off-line gas analyzer (Emerson NGA2000), and the sulfurous gas products (H_2S and SO_2) were on-line analyzed by MRU Vario plus. The mass of fuel and OC were reduced by 1/3, and N_2 (5 L/min STP) diluted the outlet gases before the on-line analyzer to meet the range requirement of H_2S and SO_2 concentration when detecting sulfurous gases. The factors, including K adding amount, K source, which affect carbon and sulfur conversion were tested by the single experiment. Each single experiment was repeated for at least twice, and the average results were shown.

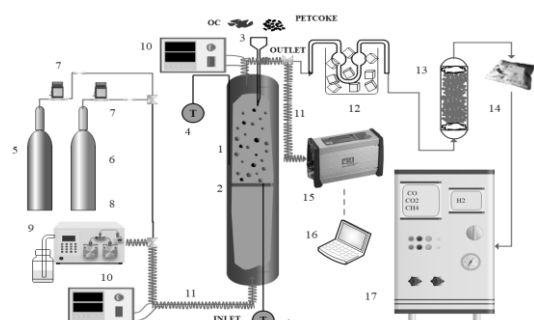


Fig.1 Scheme of batch fluidized bed experimental apparatus

Multicycle experiments were conducted under oxidizing and gasification atmosphere to simulate the actual situation of CLG. The reacted solid fuel petcoke and the reduced OC underwent complete oxidation. Between gasification and oxidation stage, the residual gas in the reactor was purged with N_2 (2 L/min STP). After the atmosphere alters to a mixture of N_2 and steam, petcoke was added from the hopper at the top of reactor by opening the valve once more, and the next cycle of reduction process started.

RESULTS

Effect of K on carbon and hydrogen conversion

The influences of hematite with different K amounts on gas generation rate in outlet gas and carbon conversion efficiency within 60 minutes of the petcoke CLG process were evaluated in Fig.2. The CH_4 product was low and the change was neglected, so it was omitted. H_2 was always the main gasification product of CLG based on petcoke. With the increase of K loading from 0% to 10%, H_2 production also increased from 0.81 Nm^3/kg to 3.18 Nm^3/kg ; when the loading continued to increase to 15%, it slightly decreased to 2.74 Nm^3/kg because of the enhanced oxidation effect of OC modified by K. With the increase of potassium loading, CO decreased, and CO_2 became the second largest gas product only to H_2 . The extremely small existence of K just promoted the generation rates of CO, CO_2 and H_2 slightly. When K loading increased from 3% to 15%, the yields of CO_2 and H_2 were opposite to

CO. This was the competitive and combined effect of potassium promoting char gasification (R1), water-shift reaction (R2), reductive reactivity of OC (R3-R4). The change of gas products may be ascribed to the slight sintering when the potassium loading was 15%. In terms of the relative fraction of effective syngas (CO and H_2), it increased slightly when loading trace K, but it decreased by 9.61% with 3%K. The relative fraction of CO and H_2 increased with the K adding amount increasing from 3%K to 15%K. In the view of the comprehensive consideration of effective syngas concentration and gas generation rates, 10%K was the best K-modified hematite for petcoke CLG process in this work. The carbon conversion efficiency was presented in Fig.2(b) when using different K adding amount. The carbon conversion efficiency reached 73.44%, 77.42% and 97.02% respectively after the experiment lasted for 60 min when K loading was 0%, 0.3% and 3%. Petcoke was almost completely converted, and the carbon conversion efficiency sharply reached 99.92% at 36th minute and 22th minute in the case of 10%K and 15%K loading on hematite. As a conclusion, the increase of K adding amount accelerated the carbon conversion rate, effectively shortening the reaction time, and petcoke would be thermally converted to gas products sharply.

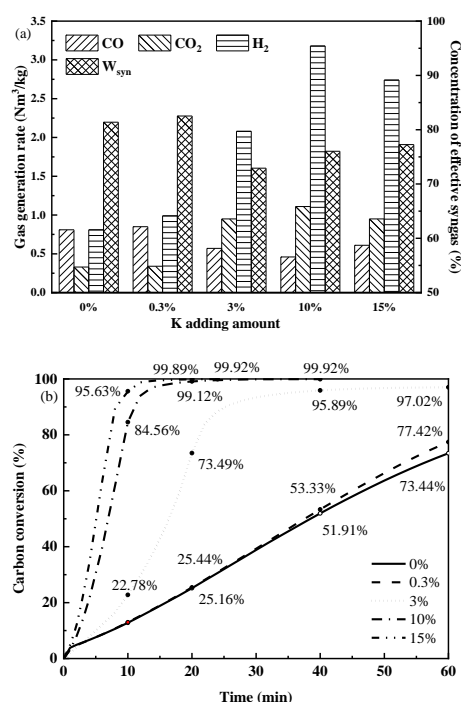
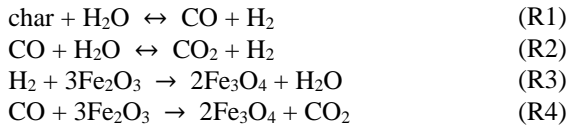


Fig.2 Effect of K adding amount to hematite on (a) gas generation and (b) carbon conversion at 900 °C



To analyze the mechanism of CLG performance based on K-modified hematite, the X-ray diffraction (XRD) patterns of the fresh and reacted OC samples with 0%K, 0.3%K, and 10%K were shown in Fig.4. The main phase of fresh hematite and 0.3%K-hematite was Fe_2O_3 , without obvious characteristic peak of K-containing phases. It verified the conclusion that the gas generation rate and carbon conversion rate were similar in the conditions of 0%K and 0.3%K. In the hematite with 10%K, some different phases besides Fe_2O_3 were found, mainly $\text{K}_2\text{Fe}_{22}\text{O}_{34}$. With the formation of various kinds of $\text{K}_2\text{O}-x\text{Fe}_2\text{O}_3$, the reactivity of modified hematite was enhanced [29], along with the gas generation rates and carbon conversion efficiency in the CLG process of petcoke, which was consistent with the conclusion above. Fe_3O_4 and Fe_2O_3 were the main components in the reductive OCs of none and 0.3%K loading on hematite after reactions, while the peak of Fe_2O_3 could not be detected when hematite was loaded with 10%K. Although potassium ferrite had Fe_2O_3 after reaction, the peak intensity also implied the decreasing amount of Fe_2O_3 , and K_3FeO_2 was detected which consisted of Fe in the valence state of +1. These indicated that the reduction degree of Fe_2O_3 in OCs was evidently deepened by introducing K. Therefore, it was speculated that $\text{K}_2\text{O}-x\text{Fe}_2\text{O}_3$ were the main phases in OCs to promote the reactivity of OCs, thereby improving the performance of petcoke CLG process.

Sulfur fate in the petcoke CLG based on K-modified hematite

The impact factors such as K adding amounts and potassium sources were investigated to explore the sulfur conversion of the petcoke CLG based on K-modified hematite. Fig.4 showed the release of sulfur-containing gases (SO_2 and H_2S) with different K adding amounts (3%, 10%, and 15%) and different potassium sources (K_2CO_3 and KNO_3) when the CLG based on K-modified hematite lasted for 1200 s. SO_2 increased with K loading amount, because more K loading amount represented the high reactivity in gasification and more oxygen transformation capacity until the sintering endurance. Organic sulfur is the main form of sulfur in petcoke, which is usually combined with carbon matrix [30]. The effect of K on carbon conversion can be used for reference in the sulfurous CL system. The OC modified by K provided the lattice oxygen for char gasification [31], significantly promoting the conversion of carbon and sulfur. The K-Fe-O phases of superior catalytic activity was

attributed to the weakened bonding strength and the elongated bonding length by the introduction of K. In the initial stage, there was a single SO_2 concentration peak with a value greater than 50 ppm. When 15% KNO_3 was added, the SO_2 concentration peak had already exceeded 100 ppm. When the potassium salt adding was 3%, 10% and 15%, the time without SO_2 observed was 36 s, 36 s, and 60 s, respectively. SO_2 was generated not only directly by volatile matter releasing, but also from the oxidation of H_2S and fresh K-modified hematite OC.

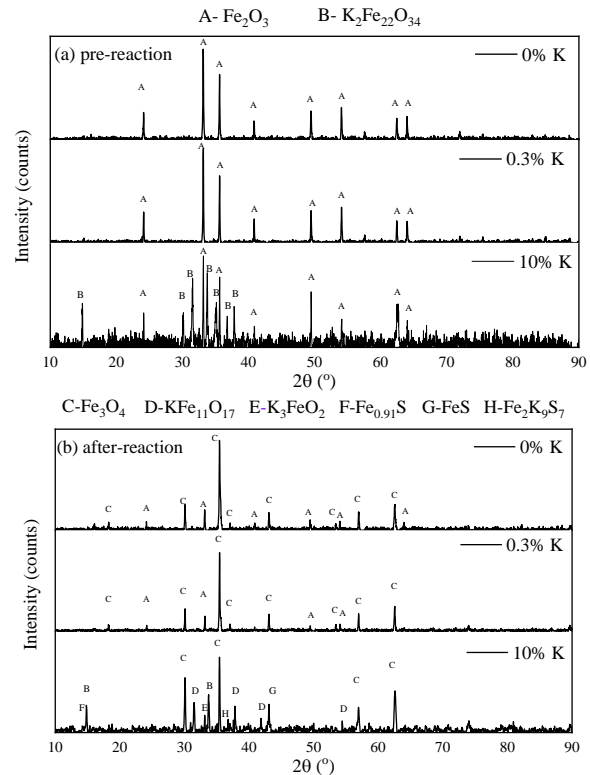


Fig.3 XRD patterns of (a) pre- and (b) after-reaction OC samples

In terms of H_2S releasing, it was always the main sulfurous component because the atmosphere of CLG including H_2 and H_2O was reductive and more conducive to producing H_2S instead of SO_2 . The curves of H_2S appeared the two-bell shape obviously. The first peaks of H_2S appeared in approximately 10 s of the initial reaction, and the H_2S peak values above 800 ppm were much higher than those of SO_2 . The H_2S peak value was even as high as 973 ppm using 15% KNO_3 -hematite. For the case of 10%K and 15%K, the time observing the highest H_2S concentration in the char gasification stage was prior to the case of 3% KNO_3 -hematite. H_2S and SO_2 generation both were improved by adding more K on hematite. The gasification reactivity of petcoke was enhanced by the

catalytic influence and the lattice oxygen supply amount. H_2 from the coke gasification played a decisive role on providing the ample hydrogen atmosphere, to react with organic sulfur and generate H_2S [32]. When the source of K changed from KNO_3 to K_2CO_3 with the same amount, SO_2 and H_2S in the case of K_2CO_3 released more intensely than using KNO_3 -hematite. The above experimental data showed that the effect of promoting the release of SO_2 and H_2S using K_2CO_3 was better than KNO_3 during the reaction, and the reaction rate also became faster.

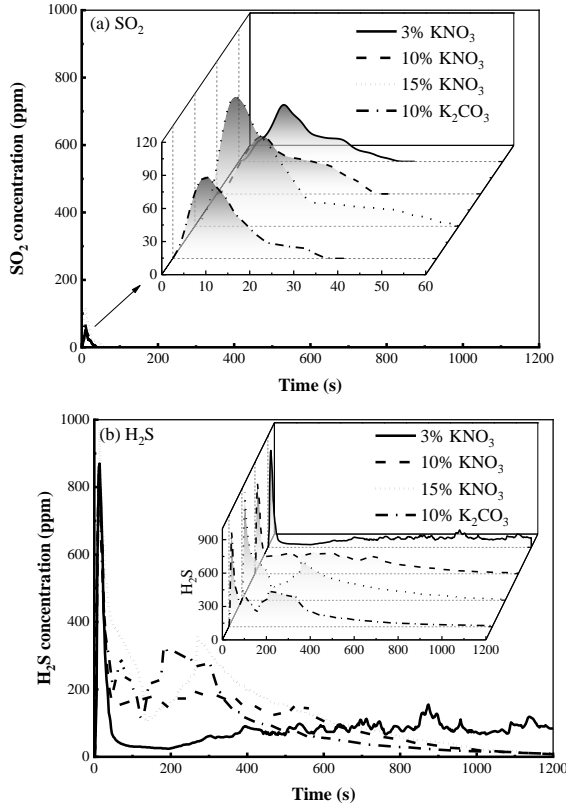


Fig.4 Effect of K amount and sources on (a) SO_2 and (b) H_2S concentration

The sulfur conversion of petcoke consisted of releasing in gas phases and capturing in solid phases of OC. The gases had been analyzed, and the sulfur-containing compositions in the reacted OC were detected by XRD (Table 2). It was found that no major phase of S-containing composition was detected, and just some trace phases such as Fe_xS_y were in the hematite OC without K and with 0.3% KNO_3 . When the K adding amount reached 10%, Fe_xS_y and K-Fe-S were observed as major phases, and diverse minor phases including K-S, K-S-O and K-Fe-S were generated, thus K improving the sulfur adsorption on OC. Fe-based OC had been proven to be susceptible to sulfur after being reduced beyond Fe_3O_4 [33]. Moreover, the regeneration

10% KNO_3 -hematite with Fe_2O_3 , $K_2Fe_{22}O_{34}$, and some sulfur-containing phases such as $Fe_{0.91}S$, $KFe(SO_4)_2$ were also analyzed. Sulfate of K and Fe was detected in the major phases of regeneration OC besides Fe_xS_y . Sulfide could convert to sulfate in the oxidizing atmosphere and reductive Fe was easily sulfurized than Fe_2O_3 when K was added to hematite.

Table 2. Sulfur-containing phase composition in reacted OC

	Major phase	Minor/Trace phase
0K	-	Fe_3S_4 , FeS
0.3% KNO_3	-	FeS, FeS_2
10% KNO_3	$Fe_{0.91}S$, FeS, KFe_2S_3	$Fe_2K_9S_7$, FeS_2 , $K_3Fe_2S_4$, $KFe(SO_4)_2$, K_2S_5 , $K_2S_4O_6$
R-10% KNO_3	$KFe(SO_4)_2$, $Fe_{0.91}S$	$K_2S_4O_6$, $K_2S_3O_{10}$, $K_3Fe_2S_4$, FeS ₂ , $Fe_2K_9S_7$

Cyclic performance of K-modified hematite in CLG process

From the results above, it was found that 10% KNO_3 -hematite OC showed better performance in carbon conversion efficiency, gas generation rate and effective syngas ratio. It was significant to evaluate the OC stability of 10% KNO_3 -hematite in a successive 21 redox cycles at high temperature 900 °C and high sulfur atmosphere. Fig.5 demonstrated that the volume fraction of H_2 fluctuated between 65% and 67%. The volume fraction of CO_2 was just higher than 23% in the first two cycles, which decreased in oscillations and rebounded up to 22%. CO volume fraction was fluctuating upward following by a downward trend. In the early two cycles, the carbon conversion efficiency reached 99.9% in 30 minutes; with the increase of cycles, it decreased to 97.1% and showed a rebound growth from 15th cycle. But the difference of volume fraction was small, indicating the successive performance of 10% KNO_3 -hematite OC was stable in CLG tests.

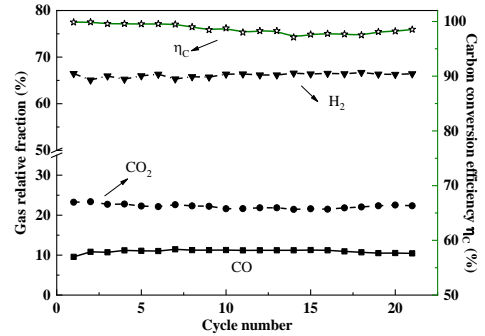
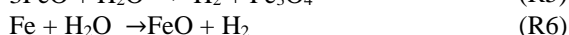
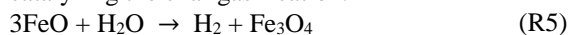


Fig.5 Redox performance of 10% KNO_3 -hematite OC

DISCUSSIONS

H₂ not only is the vital gasification production, but also provides advantageous condition to H₂S. It is interesting to note that the H₂ production yield exceeded the theoretical yield of the complete gasification of carbon in the petcoke when using 10%K-hematite as OC. H₂ generation had two routes, one of which was from carbon gasification. The above results showed that the petcoke gasification was enhanced after introducing K to hematite, so higher H₂ yield generated when there was higher carbon conversion in the case of adding K. However, the excess portion of H₂ was from the reduction of H₂O by reductive state of iron [34, 35]. The adding of K deepened the reductive state of oxygen carrier, so more H₂ was generated according to the reactions (R5-R6). Consequently, H₂ yield was enhanced by the synergies of introducing K to hematite on carbon gasification and reductive OC, which could promote the competitiveness of petcoke CLG, as compared to the case of adding K to petcoke of a major effect on catalyzing the char gasification.



The addition of K also had dual influences on sulfur fate: the sulfur conversion enhancement of petcoke due to driving the lattice oxygen and catalysis by K. Especially, HS or S radical was positive to form H₂S in the ample H₂ using K-modified hematite in petcoke CLG process. Another aspect was to absorb sulfur in OC through sulfides when Fe-based OC was deeply reduced after introducing K. Alkali was beneficial to in-situ sulfur capture through the formation of compounds containing K and S, which agreed with the finding of Furusjö [36]. For the large-scale OC production in the future, the most cost-effective and feasible method would be the utilization of natural hematite modified by potassium salts by mechanical mixing and impregnation [33, 37]. According to the performance of petcoke CLG based on K-modified hematite as OC, it was concluded that the adding of potassium promoted the fuel conversion including C, H and S. The tripartite mechanisms of K affecting the petcoke CLG performance was summarized in Fig.6.

CONCLUSION

- Introducing K had an evident enhancement on H₂ generation from improving petcoke gasification and partial oxidation of deepened reductive Fe by steam. Especially for the best case of 10%KNO₃-hematite, H₂ production increased by 3.9 times and carbon conversion efficiency dramatically increased by 26.48% with a sharp conversion rate in comparison with the iron ore.
- H₂S was the major sulfur-containing gas with the assistant of high H₂ yield using K-modified

hematite. The dual functions of K to sulfur fate were accelerating the sulfur conversion via char-S gasification, and in-situ sulfur capture through the formation of K-Fe-S compounds in OCs.

- 10%KNO₃-hematite exhibited excellent cyclic stability with a H₂ volume fraction more than 66% and a carbon conversion efficiency over 98% after 21 cycles. The catalyzed char gasification due to migration of K to petcoke, the pores formation because of migration from surface to inner and the generation of K-Fe-O contributed to the enhancement of C, H, and S conversion during the sulfurous CLG process.

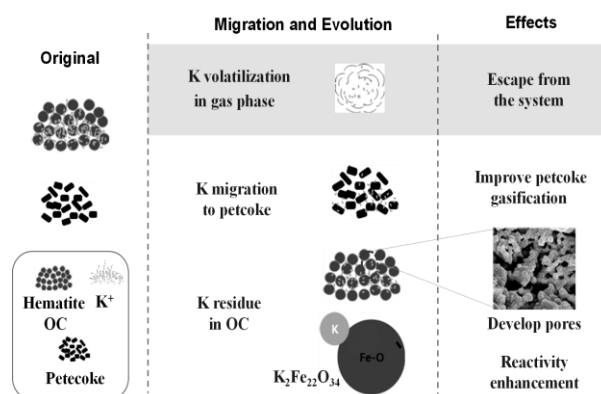


Fig.6 Schematic diagram of the mechanism of K to affect the CLG process

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