Experimental and simulated investigation of chemical looping combustion of coal with Fe$_2$O$_3$ based oxygen carrier

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Abstract

Reaction of Fe$_2$O$_3$ oxygen carrier (OC) with a Chinese bituminous coal was experimentally investigated using thermogravimetric (TGA)-differential thermal analysis (DTA) and then thermodynamically simulated based on the minimization of Gibbs free energy, with focuses on the effect of both oxygen excess number $\Phi$ and the inclusion of inert support Al$_2$O$_3$ to Fe$_2$O$_3$. TGA-DTA investigation indicated that sufficient supply of Fe$_2$O$_3$ was beneficial to the full conversion of PDS with its characteristic temperatures shifted to lower temperature, but the inclusion of Al$_2$O$_3$ to Fe$_2$O$_3$ hindered the reaction of Fe$_2$O$_3$ with PDS at the final reaction stage. And thermodynamic simulation of the reaction of PDS with Fe$_2$O$_3$ at $\Phi=1$ revealed that at the temperature of interest for chemical looping combustion (CLC) 900$^\circ$C, full conversion of PDS was reached and increasing oxygen excess number $\Phi$ was beneficial to promote the sufficient conversion of PDS as well as to reduce more Fe$_2$O$_3$ to Fe$_3$O$_4$. But the inclusion of Al$_2$O$_3$ to Fe$_2$O$_3$ resulted in the interaction between the reduced Fe$_2$O$_3$ with Al$_2$O$_3$ to FeAl$_2$O$_4$ and hindered the full regeneration of the reduced Fe$_2$O$_3$ with air.

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1. Introduction

Chemical looping combustion has received increasing attention and intensive research for its verified advantages in the effective separation of CO\textsubscript{2} from the flue gas without big cost penalty. Considering more CO\textsubscript{2} emitted from coal combustion than other anthropogenic activities, and thus research on the chemical looping combustion of coal would be greatly meaningful to control CO\textsubscript{2} from coal combustion.

Full conversion of coal to CO\textsubscript{2} and H\textsubscript{2}O was the key to determine the CO\textsubscript{2} separation cost and the overall efficiency of the total CLC system to capture CO\textsubscript{2}. The amount of oxygen carrier supplied was considered as one of the crucial factors to correlate the full conversion of coal\cite{1}. Meanwhile, inert support was also the necessary part of oxygen carrier (OC) to sustain the good reactivity of active metal oxides and the mechanical integrity of OC without abrasion and fragmentation over multicyclic reaction of OC with coal and then with air\cite{2}. And thus, in this research, the reaction of a Chinese bituminous coal with Fe\textsubscript{2}O\textsubscript{3} OC was experimentally investigated by TGA-DTA, and further thermodynamically simulated using HSC software, with focuses on the effect of both oxygen excess number and the introduction of inert support Al\textsubscript{2}O\textsubscript{3} to Fe\textsubscript{2}O\textsubscript{3} on the PDS transformation, Fe\textsubscript{2}O\textsubscript{3} conversion and the interaction of the reduced Fe\textsubscript{2}O\textsubscript{3} with Al\textsubscript{2}O\textsubscript{3}.

2. Experimental Procedures

2.1. Materials and characterization

The Chinese coal selected was a Pingdingshan bituminous coal, abbreviated as PDS. The original samples were firstly dried at 105\textdegree}C overnight, then ground and sieved to the desired size in 63-106 μm. The characteristics of PDS, including both its proximate and ultimate analysis and ash analysis, could be found out elsewhere in our previous study\cite{3}.

Besides the coal sample, Fe\textsubscript{2}O\textsubscript{3} OC was synthesized by the novel sol-gel combustion synthesis (SGCS) method with hydrated nitrates and urea as the precursors. The detailed procedure of SGCS and the characterization of the formed oxides were elaborated elsewhere. Similarly, after grinding and sieving, the oxides in 63-106μm were used. Finally, the as-prepared coals were evenly mixed with the synthesized oxides at the designed mass ratio (as descried in section 2.3) in a laboratory mortar.

2.2. Experimental methods

The reaction characteristics of the synthesized Fe\textsubscript{2}O\textsubscript{3} with PDS were investigated using Netzsch STA 409 C (Germany). The mixture of coal with Fe\textsubscript{2}O\textsubscript{3} at different mass ratio was heated from ambient to 850\textdegree}C with duration of 10 min to ensure the sufficient conversion of PDS. Pure CO\textsubscript{2} atmosphere was used throughout for the reaction of PDS with Fe\textsubscript{2}O\textsubscript{3} without special emphasis and the flow rate was fixed as 100 ml/min and the total mass for the mixture of PDS with Fe\textsubscript{2}O\textsubscript{3} was fixed around 15 mg.

2.3. Definition of oxygen excess number Φ for PDS

Sufficient supply of OC is very important to the full conversion of coal in the CLC system. The method of coal mass balance was adopted to determine the amount of Fe\textsubscript{2}O\textsubscript{3} to be introduced into the CLC system. Firstly, from the proximate and ultimate analysis of PDS in Table 1, the weight fractions of hydrogen and oxygen in the moisture were deducted. If 1 kg of coal sample were used, the content of different atoms (including C, H, O, N, S) contained in PDS could be determined and the relative chemical
formula was represented as \( \text{C}_\alpha \text{H}_\beta \text{S}_\gamma \text{O}_\delta (\text{N}_2)_\nu \). Supposing the reduced counterpart of \( \text{Fe}_2\text{O}_3 \) was \( \text{Fe}_3\text{O}_4 \) when PDS being fully converted, the reduction reaction of \( \text{Fe}_2\text{O}_3 \) with PDS could be depicted below in Eq. (1).

\[
\begin{align*}
\text{C}_\alpha \text{H}_\beta \text{S}_\gamma \text{O}_\delta (\text{N}_2)_\nu + 3(\alpha + \beta/4 + 2\gamma - \delta/2) &\text{Fe}_2\text{O}_3 &\rightarrow \nonumber \\
2(\alpha + \beta/4 + 2\gamma - \delta/2) &\text{Fe}_3\text{O}_4 &+ \alpha \text{CO}_2(g) + \beta/2\text{H}_2\text{O}(g) + \gamma\text{SO}_2(g) + \nu\text{N}_2(g) \end{align*}
\]

From Eq.1, the theoretic stoichiometric oxygen needed for the full conversion of coal is \( 3(\alpha + \beta/4 + 2\gamma - \delta/2) \). Supposing the realistic oxygen contained in OC was \( Y(O) \), then the oxygen excess number \( \Phi \) was determined below:

\[
\Phi = \frac{Y(O)}{3(\alpha + \beta/4 + 2\gamma - \delta/2)}
\]

In Eq. (2), \( \Phi = 1 \) referred that the \( \text{Fe}_2\text{O}_3 \) OC provided just met the requirement of the full conversion of PDS. According to the aforementioned method, the relative chemical formula of PDS of 1 kg could be depicted as \( \text{C}_{35.1}\text{H}_{20.2}\text{N}_{1.45}\text{S}_{0.13}\text{O}_{16.8} \). Then, based on Eq. (2), if \( \Phi = 1 \), the mass ratio of \( \text{Fe}_2\text{O}_3 \) to PDS was determined as 38.2, and then if \( \Phi = 0.5 \) and 1.5, the mass ratio of \( \text{Fe}_2\text{O}_3 \) to PDS would be 19.1 and 57.3, respectively.

2.4. Thermodynamic simulation of the reaction of PDS with \( \text{Fe}_2\text{O}_3 \) OC

In order to better understand the lattice oxygen transfer and coal evolution, the equilibrium calculation of the reaction of PDS with \( \text{Fe}_2\text{O}_3 \) was conducted based on the minimization of the total Gibbs free energy with the HSC-Chemistry software 4.1. According to the characteristics of PDS, including its proximate and ultimate analysis as well as ash analysis, a complex reaction system with 376 species in total was established. Noteworthy is that in this equilibrium simulation, PDS was considered to consist of the main matrix elements (such as C, H, N, S and O) as well as various minerals. And seven categories of compounds were involved for the minerals inherent in PDS, including various oxides, species of hydroxyl-based, carbon-based, sulfur-based, silicon-based, aluminum-based and titanium-based, which were more realistic than other equilibrium simulations.

3. Results and Discussion

3.1. Experimental investigation of the effect of oxygen excess number \( \Phi \)

From Figure 1 (a) and (b), after dehydration below 300°C, the characteristic temperatures at the second stage for the reaction of PDS with \( \text{Fe}_2\text{O}_3 \) were found to decrease from 613°C at \( \Phi = 0.5 \) to 611°C at \( \Phi = 1 \) and then to 608°C at \( \Phi = 1 \), and similarly, at the third stage, the characteristic temperature \( T_{m3} \) was also shifted to lower temperatures with the increase of \( \Phi \), possibly due to the easier access of the gaseous products to \( \text{Fe}_2\text{O}_3 \) provided.

Furthermore, from Figure 1(b), at the second reaction stage for PDS with \( \text{Fe}_2\text{O}_3 \) under \( \text{CO}_2 \), heat needed was decreased with \( \Phi \), and the integral areas at this stage were found to be 31.5 at \( \Phi = 0.5 \), similar to 32.11 at \( \Phi = 1 \), but when \( \Phi \) was further increased to 1.5, the integral area at the second reaction stage was greatly decreased to 13.56 \( \mu \text{V.s/mg} \), possibly due to far less coal added for the total mass fixed as 15mg. Different behavior for the heat flow was found at the third reaction stage of PDS with \( \text{Fe}_2\text{O}_3 \) under \( \text{CO}_2 \) atmosphere, integral area was increased from 35.72 \( \mu \text{V.s/mg} \) at \( \Phi = 0.5 \) to 58.78 \( \mu \text{V.s/mg} \) at \( \Phi = 1 \), but when \( \Phi \) was further increased to 1.5, the integral area was 50.17 \( \mu \text{V.s/mg} \), approaching 58.78 \( \mu \text{V.s/mg} \) at \( \Phi = 1 \). Overall, though excess supply of OC \( \text{Fe}_2\text{O}_3 \) was beneficial to its reaction with PDS, but greater amount of \( \text{Fe}_2\text{O}_3 \) added than the full conversion of PDS will lead to the cost penalty and thus was not economical.
3.2. Experimental investigation of inert support $\text{Al}_2\text{O}_3$ on the reaction of PDS with $\text{Fe}_2\text{O}_3$

Inert support is also the necessary part to sustain structural integrity and high reactivity of OC during many cycles of reactions in CLC system. $\text{Al}_2\text{O}_3$ was widely used and adopted as an example in this research. And the experimental results were presented in Fig. 2.

From Fig. 2(a) and 2(b), when a certain fraction of $\text{Al}_2\text{O}_3$ was introduced to $\text{Fe}_2\text{O}_3$, the characteristic temperature $T_{m2}$ at the second stage was decreased from 611°C for the reaction of PDS with $\text{Fe}_2\text{O}_3$ to 573°C for the reaction of PDS with $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, due to the increased surface area and optimized pore size distribution of $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ than $\text{Fe}_2\text{O}_3$, but at the third reaction stage, the characteristic temperature $T_{m3}$ was directed to a later period due to the hindrance effect of $\text{Al}_2\text{O}_3$ at this reaction stage [7]. Furthermore, from Figure 2(b), there similar three endothermic regions for the reaction of PDS with $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ to that with $\text{Fe}_2\text{O}_3$. Of course, the decreased integral areas at the three stages for PDS to react with $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ than to react with $\text{Fe}_2\text{O}_3$ were due to less than PDS added with the inclusion of $\text{Al}_2\text{O}_3$ support for the total 15 mg experimental sample.

3.3. Thermodynamic simulation of PDS with $\text{Fe}_2\text{O}_3$

Full conversion of PDS into $\text{CO}_2$ and $\text{H}_2\text{O}$ during its reaction with $\text{Fe}_2\text{O}_3$ was very important to $\text{CO}_2$ capture in the fuel gas. In order to obtain deep insight into the reaction of PDS with $\text{Fe}_2\text{O}_3$, thermodynamic simulation was further conducted.

3.3.1. PDS transformation during its reaction with $\text{Fe}_2\text{O}_3$

Firstly, from Fig. 3(a) for C species transformation of PDS during its reaction with $\text{Fe}_2\text{O}_3$ at $\Phi=1$, $\text{CO}_2$ was dominant with its fraction no less than 90% throughout the whole reaction process. And both $\text{CO}_2$ and CO were increased with temperature at 400-600°C and then their fractions kept stabilized, but on the contrary to CO and $\text{CO}_2$, C and $\text{CH}_4$ fractions sharply diminished to zero at 400-600°C due to the disintegration of the carbon matrix of PDS with enhanced temperature and full conversion of $\text{CH}_4$ with $\text{Fe}_2\text{O}_3$ OC.

Furthermore, from Fig. 3(b) for the evolution of various H species of PDS, it could be observed that the main H-containing products was $\text{H}_2\text{O}$, resulting from the reaction of H species inherent in PDS with $\text{Fe}_2\text{O}_3$, and its fraction was fastly increased with temperature from 79.8% at 400°C to 98.6% at 1100°C; meanwhile, less than 10% $\text{H}_2$ was also produced especially at lower temperatures than 500°C, mainly due to the gasification of PDS char with $\text{H}_2\text{O}$ produced into $\text{H}_2$. 

Fig. 1. Effect of excess number on the reaction of PDS with $\text{Fe}_2\text{O}_3$ under CO$_2$ atmosphere

Fig. 2. Effect of inert support $\text{Al}_2\text{O}_3$ on the reaction of PDS with $\text{Fe}_2\text{O}_3$ under CO$_2$ atmosphere
Finally, in terms of S species evolution from PDS, according to Fig.3(c), below 600°C, the main two sulfur species were FeS and H2S, which resulted from the reduction of pyrite (FeS2) in PDS with H2; and then at 600-800°C, H2S dominated and its fraction was firstly increased and then fastly decreased with temperature; finally, above 800°C, the full oxidization of various sulfur species (including H2S and COS) occurred and SO2 fraction was remarkably increased. Especially at the temperature window of CLC interest 900-1000°C, SO2 fraction nearly increased towards 100%, which indicated the sulphur involved in PDS was almost completely converted to SO2.

3.3.2. Effect of oxygen excess number \( \Phi \) on the conversion of PDS and Fe2O3

The amount of OC supplied was considered as one of the determined factors to the full conversion of coal. Effect of oxygen excess number \( \Phi \) on the conversions of PDS with Fe2O3 at the realistic temperature of CLC 900°C was studied, and the related simulated results are shown in Fig.4(a) and (b), respectively. From Fig.4(a), it could be found that conversion of PDS to CO2 and H2O was rapidly increased with the Fe2O3 supplied. At \( \Phi=0 \), i.e., no Fe2O3 was provided, CO2 and H2O fractions from PDS pyrolysis approached zero, but with more Fe2O3 introduced and \( \Phi \) increased, PDS conversions to CO2 and H2O were also increased. Meanwhile, from Fig.4(b), at \( \Phi=0 \), more than 80% Fe species in PDS was reduced to elemental Fe, but with \( \Phi \) increasing, more Fe3O4 was obtained, especially when \( \Phi \) was bigger than unity, more than 10% Fe2O3 was left, although some FeO still existed. Overall, sufficient supply of Fe2O3 more than the theoretical \( \Phi=1 \) is necessary to full conversion of PDS and sustain iron oxides with not less than valence of Fe3O4.

3.3.3 Effect of inert support Al2O3 on the evolution of Al species

Inert support was the necessary part to sustain OC with good performance over cyclic reactions with coal and air. Effect of Al2O3 on the evolution of Al species during the reaction of PDS with Fe2O3 was exemplified, as shown in Fig.5.

From Fig.5(a), although the main Al species for PDS with Fe2O3 was Al2SiO5, but when some fraction of Al2O3 was introduced into Fe2O3, the main Al species was changed to FeAl2O4 and its fraction was found to decrease with temperature due to more FeO produced at low temperatures and further interaction with Al2O3 introduced\(^{[5]}\). Obviously, the interaction of Al2O3 with the deeply reduced Fe2O3 counterpart than Fe3O4 would hinder the full regeneration of the reduced Fe2O3 with air.
4. Conclusions

The reaction of Fe₂O₃ with PDS was experimentally studied using TG-DTA and further thermodynamically simulated. Relevant conclusions are reached below.

(1) Experimental investigation indicated that sufficient supply of Fe₂O₃ was beneficial to the full conversion of PDS with its characteristic temperatures shifted to lower temperature, but the inclusion of Al₂O₃ to Fe₂O₃ hindered the reaction of Fe₂O₃ with PDS at the final reaction stage;

(2) Thermodynamic simulation of PDS with Fe₂O₃ at Φ =1 indicated that CO₂ and H₂O fractions increased with temperature but FeS, H₂S and SO₂ dominated below 600°C, 600-800°C and then above 800°C, respectively;

(3) Increasing oxygen excess number Φ promoted the sufficient conversion of PDS to CO₂ and H₂O as well as benefited to reduce more Fe₂O₃ to Fe₃O₄;

(4) Inclusion of Al₂O₃ to Fe₂O₃ resulted in the interaction between the reduced Fe₂O₃ with Al₂O₃ to FeAl₂O₄, which was detrimental to full regeneration of the reduced Fe₂O₃ with air.

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