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Investigate the kinetics of coke solution loss reaction with an alkali metal as a catalyst based on the improved genetic algorithm

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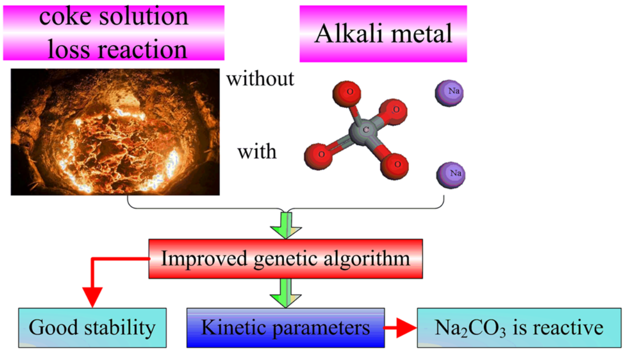
Abstract The kinetics of coke solution loss reaction with and without sodium carbonate were investigated under the reaction atmosphere of carbon dioxide. The variables of gas flow rate and coke particle size were explored to eliminate the external and internal diffusion, respectively. Then, the improved method combining with the least square and the genetic algorithm was proposed to solve the homogeneous model and the shrinking core model. It was found that the improved genetic algorithm method has good stability by studying the fitness function at each generation. In the homogeneous model, the activation energy with and without sodium carbonate was 54.89 and 95.56 kJ/mol, respectively. And, the activation energy with and without sodium carbonate in the shrinking core model was 49.83 and 92.18 kJ/mol, respectively. Therefore, it was concluded that the sodium carbonate has the catalytic action. In addition, results showed that the estimated conversions were agreed well with the experimental ones, which indicated that the calculated kinetic parameters were valid and the proposed method was successfully developed.

Graphical Abstract



Keywords Coking · Kinetic · Improved genetic algorithm · Alkali metal · Catalyst

1 Introduction

Coke is extensively applied to metallurgy, and widely used as raw materials in many fields such as calcium carbide, foundry industry and chemical engineering (Manning and Fruehan 2001; Wang et al. 2007; Gielen and Taylor 2009). Therefore, coke plays an important role in many industries. During the last three decades, there are increasing interests in those factors that influence the gasification rate of coke (Hijiriyama et al. 1983; Zamalloa and Utigard 1995; Eatough et al. 2007; Grigore et al. 2008; Pusz et al. 2010; Zhou et al. 2010). Further, the reaction between carbon in coke and carbon dioxide is also gasification, and so-called coke solution loss reaction (Wang et al. 2016), which is the main reason leading to fragmentation and pulverization of coke in the middle and lower part of blast furnace (Wang

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et al. 2017). Therefore, it is believed that the coke reactivity is the core of above investigations. Because it might clarify the quantitative relationship between chemistry reaction rate and each physical factor, to provide a guiding significance in reaction optimum conditions selection and reactors design.

Some kinetic models (Miura and Silveston 1989; Belkbir et al. 2004; Nakagawa et al. 2004; Wang et al. 2009) have been reported to study coke gasification reaction with steam and CO_2 in reactive temperature (1248–1323 K). Zhang et al. (2006) investigated the procedure of anthracite chars with steam and CO_2 at 0.02–0.1 MPa and 1193–1323 K. They applied homogeneous model and shrinking core model to verify experimental data. Moreover, it was proved that two models well described experimental results. Therefore, the mentioned models are often used for describing the kinetic behavior of coke solution loss reaction.

Among above mentioned investigations, there is not any material as a catalyst. Furthermore, it is a known fact that addition of a range of alkali and alkaline earth metals on the substance based on carbon could enhance the efficiency of gasification. Ueda et al. (2011) studied the catalytic effect of an alkaline earth metal compound on gasification of bitumen coke in a fluidized bed reactor. Furimsky et al. (1986) used a lignite ash containing Ca, Mg, Ba, Fe, and Ni oxides as catalyst with both delayed and fluid cokes from Alberta oil sands in a fixed bed reactor. Watkinson et al. (1989) studied the addition of potassium carbonate to oil sand coke in a fluidized bed. However, the reactant in those investigations is the coke based on petroleum. Kinetic behaviors of coke solution loss reaction using alkali and alkaline earth metals as a catalyst is rarely published.

For solving above kinetic models, the accuracy of the estimated result is dependent on the calculated method. The common and reliable method is regression analysis on the basis of statistics theory, such as least square method (LS) (Axelsso 1980, 1987). However, it is difficult to solve the aforementioned models because the kinetics equations are nonlinear in most cases. Therefore, some intelligent algorithm for example the genetic algorithm (GA) (Chan et al. 2009; Delavar et al. 2010), simulated annealing, and particle swarm optimization was developed to calculate the parameters of the kinetic model in recent years. Among those methods, the GA has been widely applied to solve the problem (Mitra and Mitra 2012). In addition, fitting of nonlinear models relies on non-trivial assumptions. And, users are required to carefully ensure and validate the entire modeling. Moreover, parameter estimation is carried out using some variant of the least squares criterion involving an iterative process. Thus, researchers need to have a clear understanding of the model, its parameterization and data considered, and knowledge of model diagnostics procedures and so on (Baty et al. 2015). Therefore, the GA toolbox in MATLAB was performed to obtain initial kinetic parameters, which might deeply understand model, parameterization and diagnostics procedures and so on. To improve the computational accuracy, the least square method was also used to re-estimate the parameters.

Based on above considerations, the reactive behavior of the blast furnace coke under CO_2 as reaction atmosphere was investigated with and without sodium carbonate as a catalyst in the temperature range of 1073–1623 K. Then, two classical kinetic models were employed to describe the kinetics of coke solution loss reaction. Furthermore, kinetics parameters were estimated using the GA method combined with LS.

2 Experimental and calculation method

2.1 Materials

The raw coke material was the blast furnace coke, which came from Ma-steel Coking Plant. The catalyst was the reagent grade (>99.8%) sodium carbonate (Na_2CO_3) from Shanghai Hongguang Chemical Plant. A Cahn Thermax 700 thermogravimetric analyzer was used to conduct the coke solution loss reaction experiments. The protective atmosphere and the reactive atmosphere were provided with a purity >99.999% nitrogen gas and a purity >99.99% carbon dioxide, respectively, from Ma-steel Coking Plant.

2.2 Coke sample preparation

The raw coke material is the blast furnace coke, which came from Ma-steel coking plant. Proximate analysis and basic properties parameters are listed in Table 1.

Before the kinetic experiment, it is needed to eliminate the influence of external and internal diffusion. Four different gas flows, 150, 140, 120 and 100 mL/min, were carried out in experiments to remove the external diffusion. And, coke samples were ground by a pestle and mortar and sieved into four size ranges: 0.3–0.4, 0.2–0.3, 0.075–0.2 and <0.075 mm to eliminate the internal diffusion.

2.3 Adsorption of catalyst

In our work, the reaction temperature was quickly heated to 1173 K with the rate of 20 K/min. Sodium carbonate was

Table 1 Proximate analysis and basic properties parameters of coke

M_{ad}	V_{daf}	A_d	$S_{t,d}$ (%)	MSI (%)	SSI (%)	PRI (%)
0.41	2.43	13.07	0.52	62.9	94.1	24.8

decomposed into sodium oxide in 1017 K. At this time, sodium oxide is a gas state, and partly raised with gas flow to low temperature zone in the blast furnace. After that, sodium oxide was cooled down and adsorbed on the surface of coke. Adsorption metal oxide is a catalyst in the process of coke solution loss reaction. Considering the cycle enrichment of alkali metals in blast furnace, the salt of Na_2CO_3 was selected as a catalyst, and added with the quantity (0, 0.5, 1, 2 and 3% based on mass) to the sieved coke particles. Then, a few droplets of water (1.0 ml) were placed in those mixtures. At 373 K temperature, those waters were evaporated.

2.4 Coke solution loss experiments

Coke solution loss experiments were implemented by using a Cahn Thermax 700 thermogravimetric analyzer. A coke sample (10 mg) was placed in a crucible of the furnace under nitrogen gas and dried at 378 K for 1 h. Then, the sample was heated up with the rate of 20 K/min. When the desired temperature was reached, N_2 was replaced by CO_2. And the reaction temperature was kept constant until no evident weight loss was observed. Finally, the reaction system was cooled under N_2 flow to room temperature.

2.5 Calculation method

The least square combined with genetic algorithm (LS-GA) was developed to estimate the kinetic parameters as showed in Fig. 1. The initial kinetic parameters were calculated by the GA method. Based on those initial values, parameters were further optimized using the LS method. The proposed LS-GA procedure worked through the following steps:

Step 1: Construct the objective function. The kinetics parameters were established by optimization. The objective function was described as

$$\min \psi(K) = \left[\sum_{m=1}^{P}\left[x_j^*(t_m, K) - x_j(t_m)\right]\right]^2 \tag{1}$$

where K is the kinetics parameter, P the experimental point number, t_{m} the reactive time, $x_j^*(t_m, K)$ described the calculated values of the experimental molar fraction, $x_j(t_m)$ described the carbon conversion, ψ is the value of the objective function.

Step 2: Population size. The population size was set to 20.

Step 3: Initial population. The population type was set to be a double vector, and a random initial population with a uniform distribution was created using the uniform function.

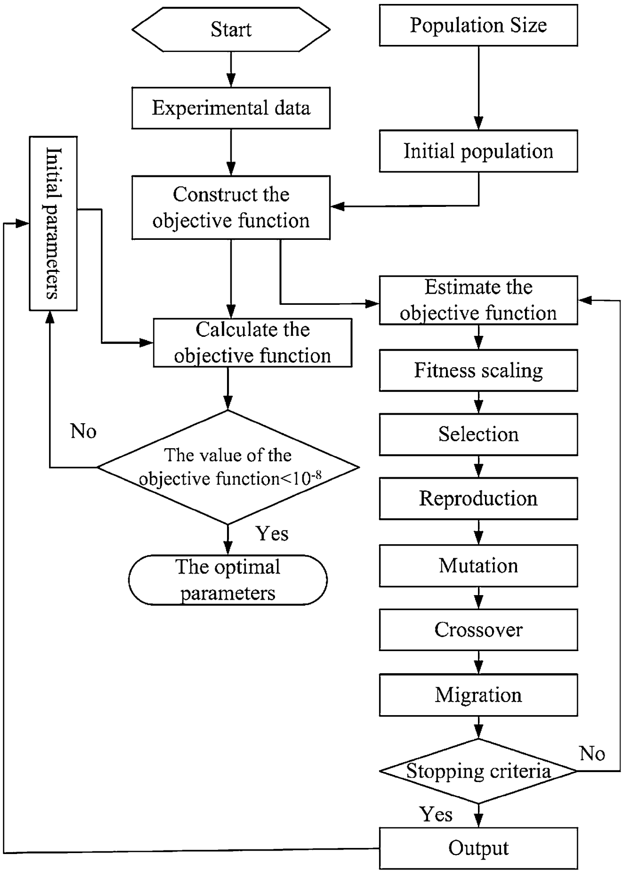

Fig. 1 Flow chart of the LS-GA

Step 4: Estimating the objective function value. Based on the experimental data, the objective function value was calculated.

Step 5: Fitness scaling operator. The rank function was used for the fitness scaling operator, which could scale the raw scores based on the rank of each individual. The fitness scaling operator converted raw fitness scores to values in a range that was suitable for the selection function.

Step 6: Select operator. The selection operator chose parents for the next generation based on their scaled values from the fitness scaling operator. The stochastic uniform was applied for the selection operator.

Step 7: Reproduction operator. The reproduction operator determined how the genetic algorithm creates children at each new generation, where the elite count was set to 2, and crossover fraction was equal to 0.8. The elite count specified the number of individuals, which were guaranteed to survive to the next generation. The crossover fraction specified the fraction of the next generation.

Step 8: Crossover operator. The crossover operator combined two individuals, or parents, to form a new individual, or child, for the next generation. The scattered function was used as a crossover function. The scattered function created a random binary vector.

Step 9: Mutation operator. The mutation operator made small random changes in the individuals in the population, which provided genetic diversity and could the GA to search a broader space (Beasley et al. 1993; Johnson and Rahmat-Samii 1997). The Gaussian function was introduced for the mutation operator. The average amount of mutation is controlled by scale and shrink. In this case, scale and shrink were both set as 1.0.

Step 10: Migration operator. The migration operator was the movement of individuals if population size was set to be a vector of length greater than 1. The best individuals often replace the worst individuals. The direction function was used to control the migration.

Step 11: Stopping criteria. The stopping criteria operator determined what caused the algorithm to terminate. The specified the maximum number of iterations was equal to be 100. Function tolerance, tall generations and stall time limit were set as 0.000001, 50, and 20, respectively.

Step 12: Estimating the kinetic parameters. The kinetic parameters obtained by GA were set as the initial kinetic parameters. Then, the kinetic parameters were obtained by the LS method that was solved using the lsqnonlin function in Matlab. If the objective function value was greater than 10^{-8}, the initial kinetic parameters were afresh set as the results obtained from the LS method. Then, the NLS method was newly carried out until the objective function value was less than 10^{-8}.

3 Results and discussion

3.1 Elimination of coke samples diffusion

3.1.1 *Influence of gas flow rate*

Preliminary experiments were performed to study the effect of external diffusion by varying the gas flow rate with the other variables constant, including 100, 120, 140 and 150 mL/min. And the load of a catalyst and the particle size of coke samples used in this experiment were 0.309 mg and 0.075–0.2 mm, respectively. As showed in Fig. 2a, the conversion of carbon was increased with the increasing gas flow rate. And as it can be seen in Fig. 2b, the conversion of carbon with 120, 140 and 150 mL/min at 12000 s was respectively 73.38%, 71.13% and 69.85%, which was indicated that there was no obvious change among those conversions when the gas flow rate was equal to or greater than 120 mL/min. Therefore, the gas flow rate with 150 mL/min was employed in our experiment.

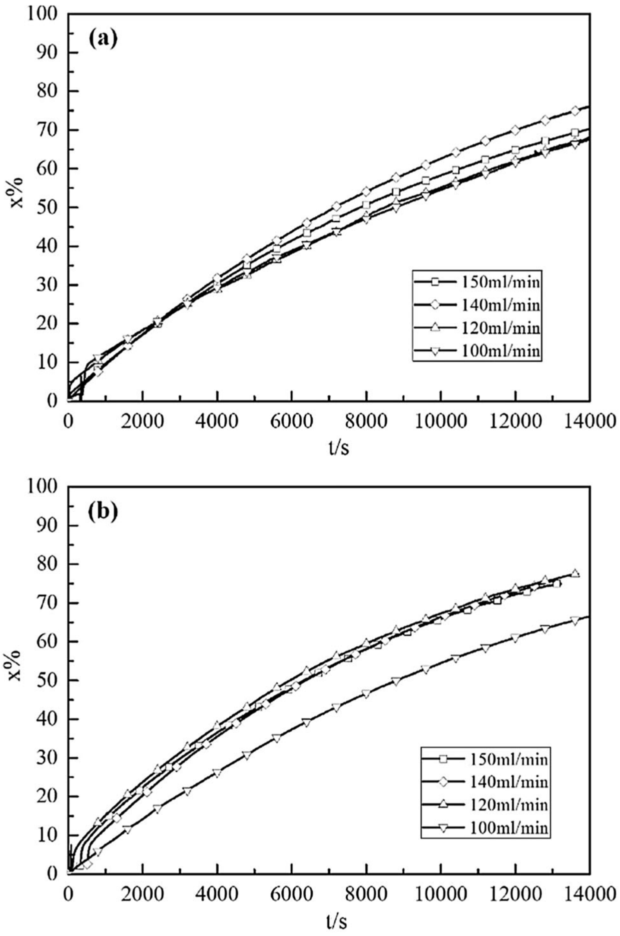

Fig. 2 Variation of carbon conversion with time at different gas flow rate in **a** raw coke samples and **b** samples adsorbed Na_2CO_3

3.1.2 *Effect of coke particle size on reaction conversion*

The coke was sieved into four size groups: (I) <0.075 mm, (II) 0.075–0.200 mm, (III) 0.200–0.300 mm, and (IV) 0.300–0.400 mm. Experiments were carried out at the gas flow rate with 150 mL/min. The results of carbon conversion with different particle size were presented in Fig. 3a, b. As shown in Fig. 3a, the conversion of carbon was increased with decreasing coke particle size. However, when reaction time was greater than 12,050 s, the conversion of size (II) was greater than the one of (I) in Fig. 2b.

Furthermore, it was reported that the fine coke particle size range from 0.038 to 0.053 mm was adopted in kinetics investigation (Semagina et al. 2011). Therefore, the coke particle size of (I) was implemented in our work.

3.1.3 *Effect of loaded catalyst quantity*

In addition, the effect of catalytic salt on the carbon conversion rate was shown in Fig. 4. It was found from Fig. 4 that carbon conversion rates were nearly equal to zero in

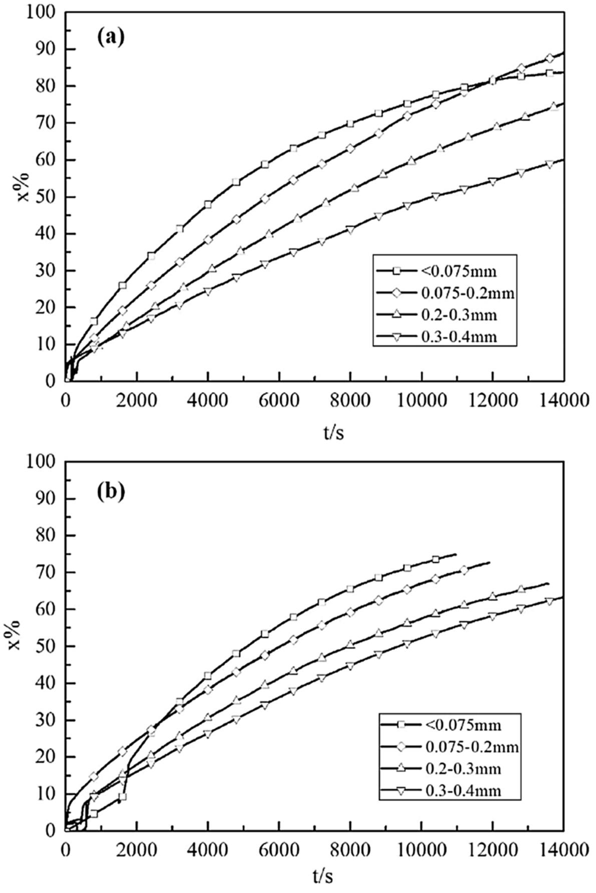

Fig. 3 Variation of carbon conversion with time at different particle size in **a** raw coke samples and **b** samples adsorbed Na_2CO_3

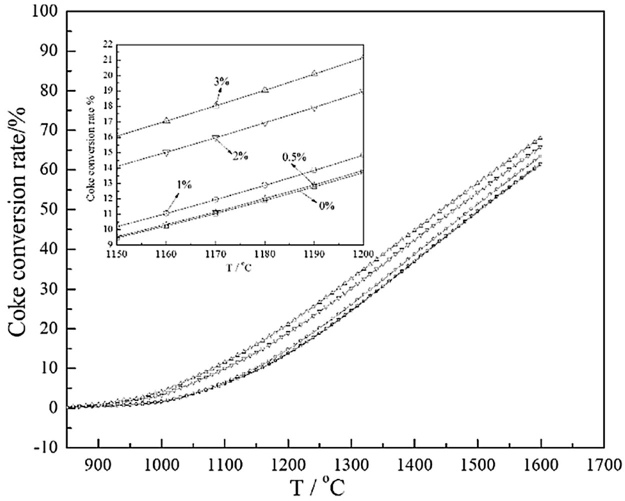

Fig. 4 The effect of catalytic salt on the carbon conversion rate

the range of temperature from 1073 to 1273 K. The reasons for the phenomenon was that trace amounts of secondary volatile ran away from a reactive system. When the temperature was greater than 1273 K, the coke solution loss reaction initiated, which resulted in the carbon conversion rate obviously increasing. It was also noticed from Fig. 4 that the carbon conversion rate was raised by increasing catalytic salt loaded quantity. Because the maximum of carbon conversion rate was under condition of 3% salt loaded quantity, the coke with 3% catalytic salt loaded quantity was selected as example to study the kinetics of coke solution loss reaction.

3.2 Kinetic modeling

3.2.1 Kinetic model

Generally, a kinetic expression for the reaction rate is written as Eq. (2)

$$\frac{dx}{dt} = k(T)f(x) \tag{2}$$

where $k(T)$ is reaction rate constant, T is temperature, $f(x)$ describes the changes in physical or chemical properties of coke during the reaction processes. In addition, the reaction rate constant can be expressed by the Arrhenius equation:

$$k(T) = Ae^{-\frac{E}{RT}} \tag{3}$$

where A and E are the pre-exponential factor and activation energy, respectively.

In our work, the homogeneous model and shrinking core model were adopted to investigate the coke solution loss reaction, respectively. The homogeneous model (Ishida and Wen 1971) assumes that reaction takes place throughout the whole volume of the coke particle, and reaction surface area linearly decreases with conversion, as described in Eq. (4).

$$\frac{dx}{dt} = k(1-x) \tag{4}$$

The shrinking core model (Manning and Fruehan 2001) assumes that the reaction occurs at an external surface of the coke particle, and gradually moves inside, leaving an ash layer behind. The space leaving inside of particle constitutes the porous network. The model is described as:

$$\frac{dx}{dt} = k(1-x)^{2/3} \tag{5}$$

To satisfy the need of LS method, above two equations were modified as follows:

$$-\ln(1-x) = kt \tag{6}$$

$$3\left[1-(1-x)^{1/3}\right] = kt \tag{7}$$

3.2.2 Stability of calculation method

The GA method was introduced in the above method. Because there is the random search procedure in a GA

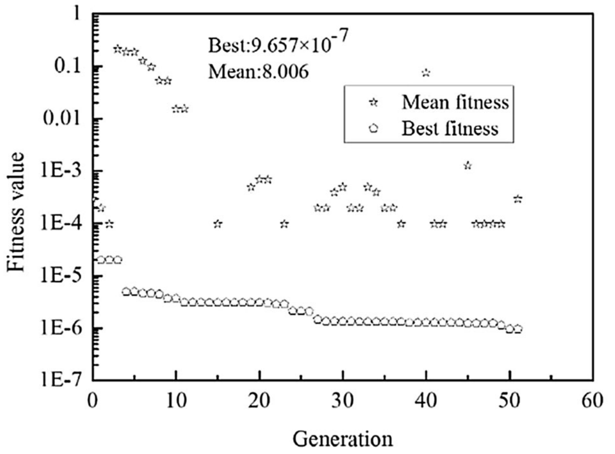

Fig. 5 The best and mean values of the fitness function at each generation

method, the method stability based on GA algorithm is poor. Thus, the stability of improved GA method is important in application. Therefore, the stability of the above mentioned method was investigated, as showed in Fig. 5.

The best and the mean values of the fitness function at each generation were shown in Fig. 5, respectively. The points at the bottom of the plot denoted the best fitness values, while the points above them denoted the averages of the fitness values in each generation. The best and the mean values in the current generation were also numerically displayed at the top of Fig. 5, respectively. It was concluded that the best fitness value was improved rapidly in 15th generations before, when the individuals were far from the optimum. The best fitness value improved more slowly to near 1.2866×10^{-6} after the 30th generation, whose populations were closer to the steady point. Hence, the improved GA method in our work has good stability.

3.2.3 Kinetic parameters

Based on the above improved method, the relationships between carbon conversion and reaction time using the

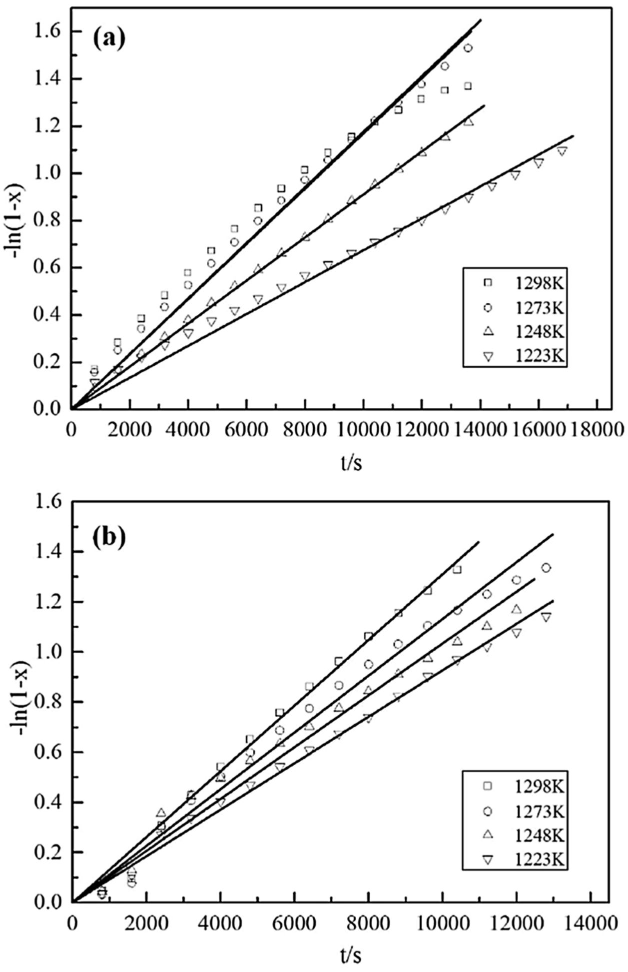

Fig. 6 Homogeneous model for **a** raw coke samples and **b** samples adsorbed Na_2CO_3 at different temperatures

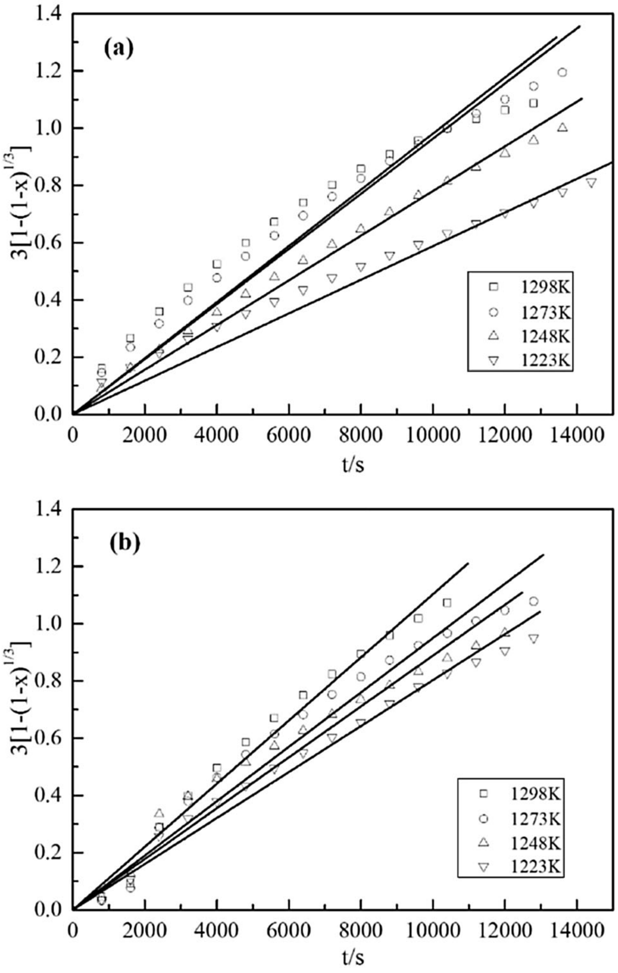

Fig. 7 Shrinking core model for **a** raw coke samples and **b** samples adsorbed Na_2CO_3 at different temperatures

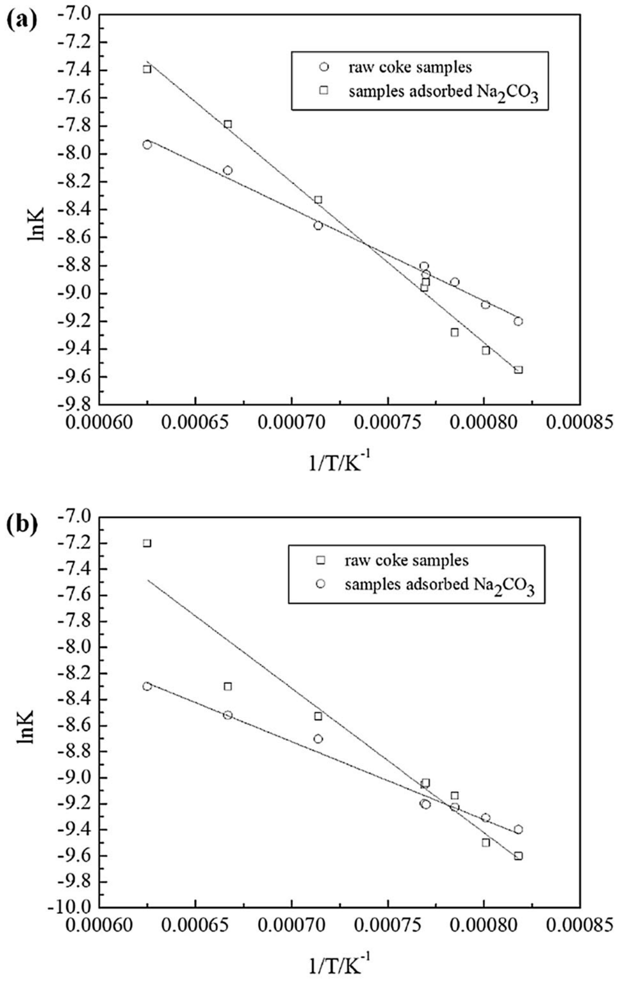

Fig. 8 Arrhenius plots for **a** the homogeneous model and **b** the shrinking core model during gasification in CO_2 at different temperatures

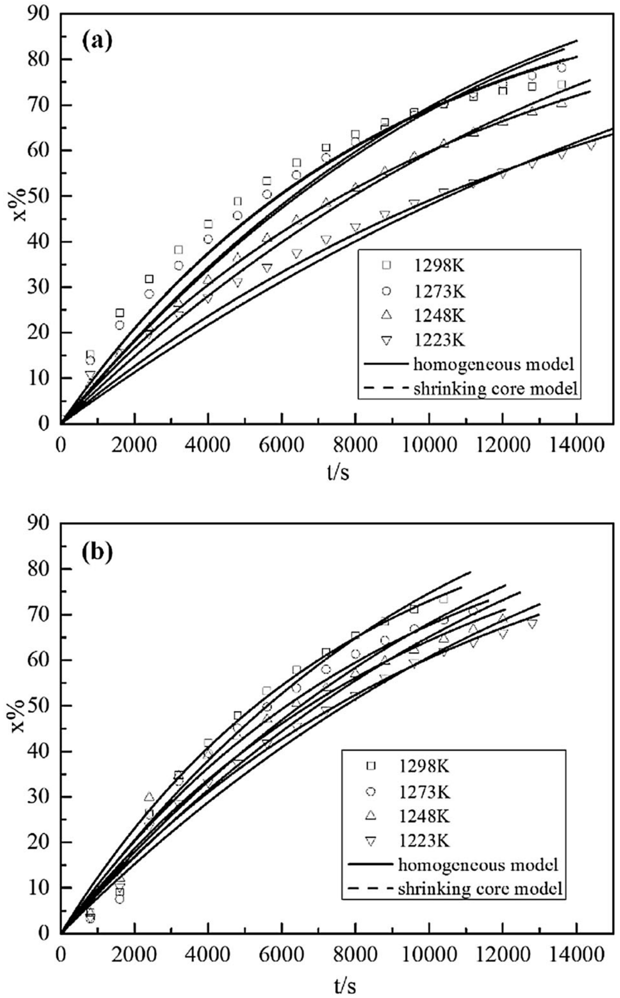

Fig. 9 Comparison between **a** raw coke samples and **b** samples adsorbed Na_2CO_3 experimental data and those predicted by the models

homogeneous model and the shrinking core model were estimated in experiment with and without the catalyst. Then, the relationships using the estimated and experimental values were exhibited in Figs. 6 and 7, respectively.

The scattered symbols expressed the experimental data. And, the lines were calculated values that were estimated with the LS-GS method. Obviously, both of them agree very well, indicating that calculated values are acceptable.

The relation of reaction rate constant and temperature was showed in Fig. 8. It was seen from Fig. 8 that the data from kinetic model was agreed with the experimental one, indicating that estimated values were available. Then, kinetic parameters were calculated by using Arrhenius Law, and listed in Table 2. It was found that activation energy with Na_2CO_3 as a catalyst was lower than the one without Na_2CO_3 in both kinetic models. Therefore, it was suggested that Na_2CO_3 has a catalytic action.

Moreover, the kinetic model was verified by comparing the estimated data with the experimental ones, as shown in

Table 2 Kinetic parameters of coke samples for the homogeneous model and the shrinking core model

Sample	Activation energy E (kJ/mol)	Pre-exponential A (s^{-1})		
	Homogeneous	Shrinking core	Homogeneous	Shrinking core
Raw coke samples	95.56	92.18	0.8548	0.5656
Samples adsorbed Na_2CO_3	54.89	48.83	0.0230	0.0108

Fig. 9. From Fig. 9, it can be seen that both homogeneous model and shrinking core model give a good fit to experimental data. Those results indicated that the estimated kinetic parameters are valid.

4 Conclusions

The kinetics of coke solution loss reaction with and without sodium carbonate were investigated with CO_2 as a reaction atmosphere using the thermogravimetric analyzer. In the primary experiment, two variables (gas flow rate and coke particle size) were studied. As the results showed, 120 mL/min is sufficient to avoid the external mass diffusion, and the internal diffusion is negligible when the particle size is lower than 0.075 mm. The improved method combined the least square with the genetic algorithm was implemented to solve the homogeneous model and the shrinking core model. By investigating the fitness function at each generation, it was found that the improved genetic algorithm method has good stability to solve two models. Based on estimated reaction rate constant, kinetic parameters were obtained using the Arrhenius Law. In the homogeneous model, the activation energy with and without sodium carbonate was 54.89 and 95.56 kJ/mol, respectively. And, the activation energy with and without sodium carbonate in the shrinking core model was 49.83 and 92.18 kJ/mol, respectively. Therefore, it was obvious that Na_2CO_3 has a catalytic action during coke solution loss reaction. The estimated carbon conversions obtained from two models with the LS-GA method agreed well with experimental datum, indicating that the calculated kinetic parameters were valid and the method combined the least square with the genetic algorithm was successfully developed.

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