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ON THE ROLE OF THE BOUDOUARD REACTION IN THE ISOTHERMAL REDUCTION OF IRON ORE BY CHAR AND GRAPHITE

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ABSTRACT

The kinetics of gasification of graphite and two types of char by carbon dioxide, as well as the kinetics of reduction of iron ore by these carbonaceous species were studied by thermogravimetry. Potassium carbonate was found to be more effective than sodium carbonate in catalysing both the Boudouard reaction and the reduction of iron ore. Although the activation energies of the reduction reactions were much lower than those of the corresponding gasification reactions, the reductants revealed the same order of activation energies in both types of reaction. It was shown that the Boudouard reaction played a predominant role in controlling the rate of the reduction reaction.

INTRODUCTION

There has been considerable interest in recent years in the reduction of iron oxides by solid carbon. Several papers on experimental work and mathematical modelling have been published [1–4]. Much of this interest has been stimulated by the development of the SL/RN process, which uses solid carbon as the reductant in the production of iron. The catalysis of this process by the addition of alkali salts has been investigated by numerous researchers [5,6]. It is also generally agreed that the reduction of iron oxide by carbon occurs through the gaseous intermediates CO and CO_2, i.e. via the Boudouard reaction. The latter reaction and its catalysis have received much attention in recent years [7–10]. Recognition of the catalytic influence of alkali-metal compounds dates back to the early work of Taylor and Neville [11].

Although it appears that this subject has been covered well enough in the literature, there still remains a lack of evidence to compare the Boudouard

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gasification reaction with the iron ore reduction reaction. The reason for this is that no attempt has been made to compare directly the rates of gasification of various forms of carbonaceous materials with the rates of reduction of iron ore by these materials. The purpose of this paper is therefore to compare the results obtained from the gasification of graphite and char with the results obtained from the reduction of iron ore by these carbonaceous species. The influences of particle size as well as alkali carbonate catalysts were investigated for both types of reaction.

EXPERIMENTAL

In general, two main techniques may be used for following the progress of gasification and reduction [12,13]: (1) measurement of the mass of the sample, either intermittently or continuously: (2) measurement of some change in the properties of the gas stream drawn from the reaction volume [14–16].

Materials

Graphite (maximum impurity level, 0.06%; particle size 100% < 106 μm), Coastal coal char (particle sizes 100% < 0.1 mm and 100% < 0.5 mm; ash yield 6.9 mass %) and Groothoekskag char (particle size 100% < 0.1 mm; ash yield 7.1%) were used in the gasification experiments. High purity CO_2 was used in the gasification of these carbonaceous species. Na_2CO_3 and K_2CO_3 were used as catalysts in some of these experiments.

Sishen Northmine iron ore (particle size < 0.1 mm) obtained from ISCOR Ltd. was used in the reduction experiments. The composition of the ore was determined as 97.10% haematite, 1.92% magnetite and 0.98% silica by mass. Commercial argon was used as an inert atmosphere during the reduction process. Before use, this argon was passed through a purification unit where water was removed by 98% H_2SO_4, $MgClO_4$ and $CaCl_2$; CO_2 was removed by NaOH-impregnated asbestos and oxygen was removed by titanium shavings at 600°C.

Apparatus

The gasification and reduction experiments were carried out in a thermogravimetric set up [17] comprising a continuous weighing and recording electronic balance mounted above a tube furnace of 50 mm internal diameter, which was heated by six silicon carbide elements and maintained at constant temperature by a Eurotherm on–off controller. The reaction mixture was placed in a small recrystallized-alumina crucible and connected to the weighing balance via a platinum support wire.

Procedure

Each sample was dried at 110°C for two hours before use. These samples were introduced into and removed from the water-cooled quenching chamber at the bottom of the furnace while the furnace tube was flushed for 5 min with either CO_2 or argon at a rate of 1.5 l min^{-1}. At this rate it was found that the kinetics were independent of the gas flow rate. The crucible was then raised quickly into the heating zone of the furnace.

During gasification experiments 1.00 g of the carbonaceous material and 0.10 g of either Na_2CO_3 or K_2CO_3 were used. In reduction experiments 0.75 g of iron ore, 0.25 g of the carbonaceous species and 0.15 g of either Na_2CO_3 or K_2CO_3 were used. These samples were mixed well before use.

The product gas from the reduction experiments was passed through a tube filled with NaOH-impregnated asbestos. This tube was weighed before and after each experiment in order to determine the concentration of CO_2 in the gas. Sodium and potassium carbonates were used in separate experiments to determine the additional CO_2 evolved from the decomposition of these catalysts [18,19].

TREATMENT OF DATA

In the gasification experiments the fractional conversion X was defined as

$$X = \frac{\text{mass loss of sample}}{\text{mass of carbon in sample}} \tag{1}$$

The fractional conversion X of iron ore during the reduction experiments was defined as

$$X = \frac{\text{mass of oxygen removed from sample}}{\text{mass of removable oxygen in sample}} = \frac{\Delta m M_{O_2}}{Zm}\left[\frac{\dfrac{P_{CO_2}}{P_{CO}} + \dfrac{1}{2}}{M_{CO_2}\dfrac{P_{CO_2}}{P_{CO}} + M_{CO}}\right] \tag{2}$$

where Δm = registered mass loss of sample, m = mass of ore in sample, Z = mass of removable oxygen per gram of ore, M = molecular mass, P_{CO_2} = partial pressure of CO_2 and P_{CO} = partial pressure of CO ($P_{CO_2} + P_{CO} = 1$). This definition of X is independent of the amount of carbon added to the ore, and is directly related to the amount of iron metal or carbide formed. In this study $Z = 0.2972$. The values of P_{CO} and P_{CO_2} could be determined from the composition of the product gas. From thermodynamic principles it was expected that P_{CO_2} would decrease sharply with an increase in temperature. Although these values could be calculated thermodynamically under equilibrium conditions, non-equilibrium conditions encountered in practice necessitated an experimental evaluation of P_{CO} and P_{CO_2}.

The initial slopes $\left.\frac{dX}{dt}\right|_{t=0}$ of the plots of fractional conversion versus time were used in the logarithmic form of the Arrhenius equation to estimate the activation energies for the different reactions:

$$\ln \left.\frac{dX}{dt}\right|_{t=0} = \ln A - \frac{E}{RT} \tag{3}$$

where A = the Arrhenius pre-exponential constant, E = activation energy, R = universal gas constant and T = absolute temperature. Linear regression was used to estimate the values of A and E for a specific reaction mixture.

RESULTS AND DISCUSSION

Gasification experiments

Figure 1 shows that the gasification behaviour of the two types of char differs widely from that of the graphite. This phenomenon may be explained by comparing the structural differences between chars and graphite.

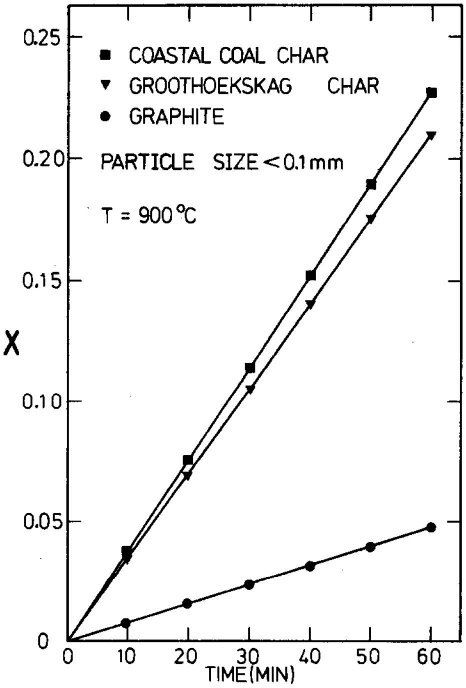

Fig. 1. Gasification of different carbonaceous species in an atmosphere of CO_2 at 900°C.

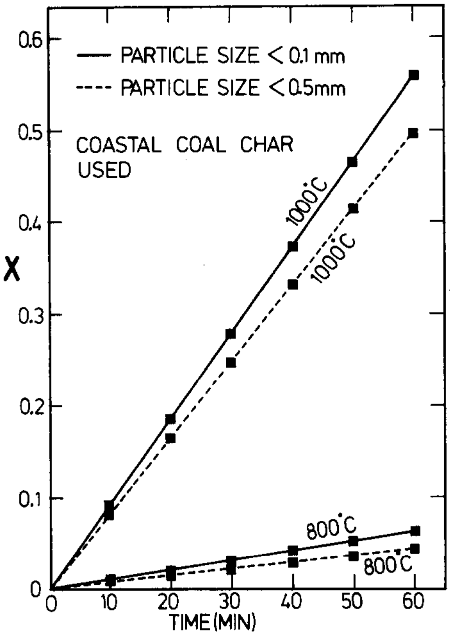

Fig. 2. Effect of particle size on the gasification of Coastal coal char in an atmosphere of CO_2.

Graphite is essentially pure carbon, while coal chars contain impurities, hydrogen and heteroatoms. In chars approximately 1 of every 5 atoms is a hydrogen and 1 of every 25 atoms is a heteroatom [20]. Furthermore, the ash content of the chars is significantly higher than that of the graphite. The molecular structure of graphite consists of extended basal planes of trigonal carbon atoms. However, this is an idealized single crystal structure, and graphite actually occurs in many forms and morphologies [21] and contains an assortment of edge dislocations. Nonetheless, the structure of graphite is irrefutably less complex than that of coal char. It is doubtful whether extensive basal planes of trigonal carbons are found in even the most ordered coal chars. In general, graphite is substantially less porous than coal chars [21]. McKee et al. [22] reported that BET surface areas are 20 to 100 times higher for chars than for graphite.

Figure 2 reveals an increase in gasification rate with a decrease in the particle size of Coastal coal char. Therefore, the Boudouard reaction is enhanced with an increase in the carbon surface area. This may be one of the reasons why porous chars are more reactive than non-porous graphite.

Figures 3 and 4 illustrate the effects of sodium carbonate and potassium carbonate on the gasification of graphite and Coastal coal char respectively. It is evident that K_2CO_3 is in both cases a more effective catalyst than Na_2CO_3 at all temperatures considered. This difference in catalytic activity

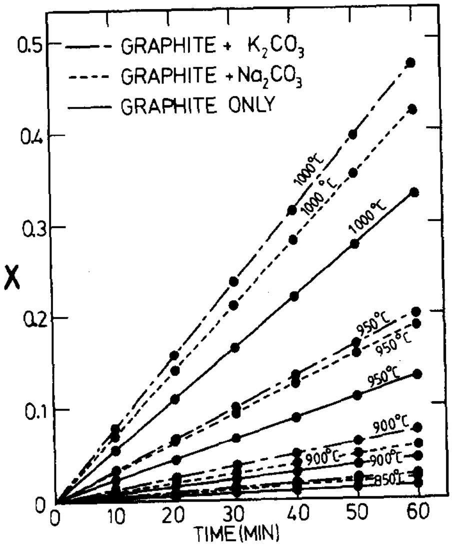

Fig. 3. Effect of catalysts on the gasification of graphite in an atmosphere of CO_2.

is also illustrated by the Arrhenius plots in Fig. 5. Table 1 shows that K_2CO_3 decreases the activation energy of gasification of both graphite and char to a greater extent than does Na_2CO_3. Furthermore, there seems to be a difference between graphite and coal char regarding the mechanism of catalysis. According to Table 1 Na_2CO_3 causes a decrease in the activation energy

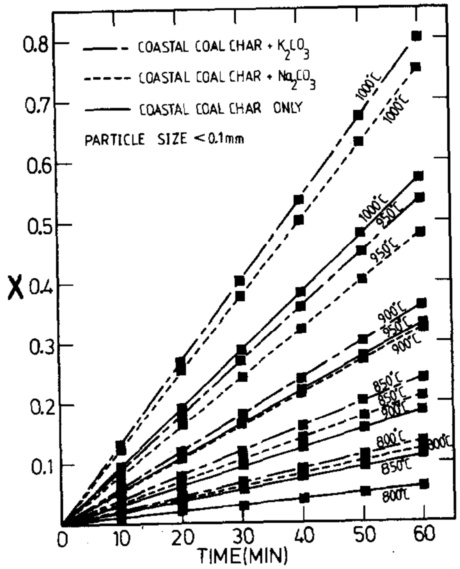

Fig. 4. Effect of catalysts on the gasification of Coastal coal char in an atmosphere of CO_2.

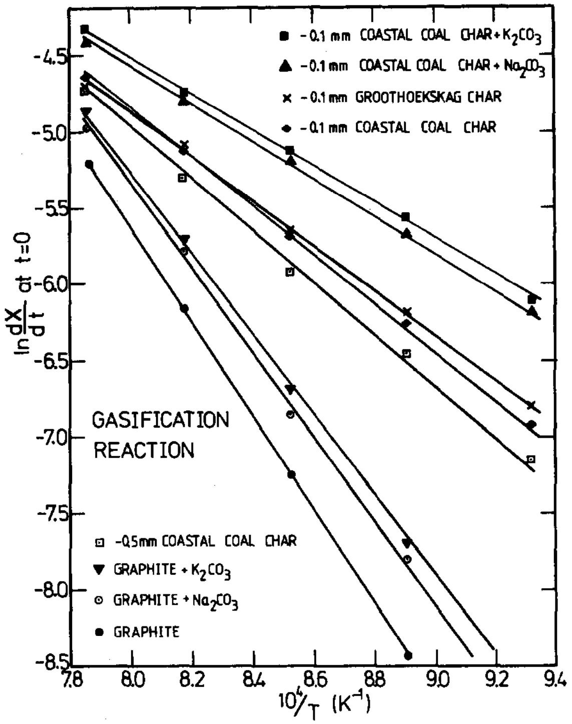

Fig. 5. Arrhenius plot of the rate of gasification of different carbonaceous species.

TABLE 1

Activation energies of gasification and reduction reactions

Carbonaceous species	E_1(kJ mol^{-1}) gasification	E_2(kJ mol^{-1}) reduction	$\frac{(E_1 - E_2)100}{(E_1)}$ (%)
Coastal coal char -0.1 mm + K_2CO_3	96.4	80.0	17
Coastal coal char -0.1 mm + Na_2CO_3	103.1	83.1	19
Groothoekskag char -0.1 mm	121.4	89.4	26
Coastal coal char -0.1 mm	134.7	101.8	24
Coastal coal char -0.5 mm	143.0	105.0	27
Graphite + K_2CO_3	217.8	133.0	39
Graphite + Na_2CO_3	231.1	139.3	40
Graphite	256.1	155.9	39

of gasification of coal char of 23%, and a decrease of only 10% in the case of graphite. The corresponding figures for K_2CO_3 are 28% and 15%.

Early workers in the field, such as Taylor and Neville [11], suggested that catalysis is caused by an increased adsorption of CO_2. Fox and White [23] believed that the rate-determining step is not chemical, but that the catalysis is due to an increase in the rate of external mass transfer. They proposed that Na_2CO_3 is reduced at the surface of the carbon and that the Na metal would, because of its high vapour pressure, evaporate into the bulk phase. After reaction with CO_2 the Na_2CO_3 is then drawn back to the surface. The Na_2CO_3 acts as a pump between the gas phase and carbon surface. McKee [24,25] proposed a kinetic cycle based on the chemistry of Fox and White [23]. Owing to the fact that graphite is essentially pure carbon, such a McKee cycle could form a mechanistic basis for the catalysed gasification of graphite.

Because coal chars contain not only carbon but also hydrogen and heteroatoms, it is unlikely that the McKee cycle is the only mechanism of catalysis in the case of chars. Spiro et al. [20] suggested a cyclic mechanism which explicitly includes the influence of residual hydrogen via alkali hydride catalytic intermediates. Thus, a hydride–hydroxide cycle may be operative besides the classic McKee cycle during the catalytic gasification of char. Although it cannot be proven, this mechanism may be used to explain the difference in gasification behaviour between graphite and coal char.

Reduction experiments

In Figs. 6 and 7 the equilibrium P_{CO_2}/P_{CO} values are plotted as a function of temperature for both the Boudouard reaction and the reduction of wüstite, which is the last stage in the reduction of haematite. The gas evolved from the reduction of Sishen iron ore by graphite or char revealed an average composition between the values for the reduction of wüstite and the Boudouard reaction. This composition will be closer to the value for the reaction which has the higher rate of reaction.

Figures 6 and 7 show that both chars yield lower CO_2 levels than does graphite, with Groothoekskag char giving the highest CO level of the uncatalysed reductants. In the case of both graphite and Coastal coal char the presence of Na_2CO_3 or K_2CO_3 shifted the gas composition towards the Boudouard equilibrium, with K_2CO_3 exerting the greater influence. Although the carbon–gas reaction is usually rate-limiting, these results indicate that reduction proceeds probably under mixed control where both the iron–gas and carbon–gas reactions influence the rate of reduction.

When comparing Figs. 1 and 8 it can be seen that the order of reactivity of the uncatalysed reductants is the same in both the gasification and reduction reactions. Figure 9 illustrates that a decrease in the particle size of the char enhanced the rate of reduction. This provides some further evidence

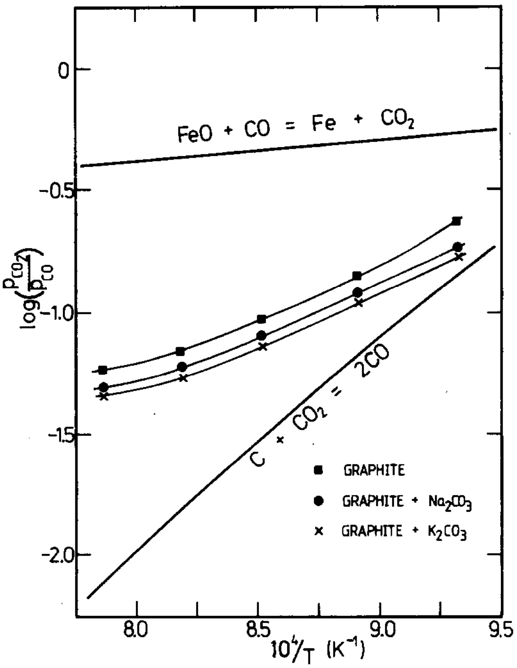

Fig. 6. Observed values of P_{CO_2}/P_{CO} ratios compared with equilibrium values for the reduction of Sishen iron ore by graphite.

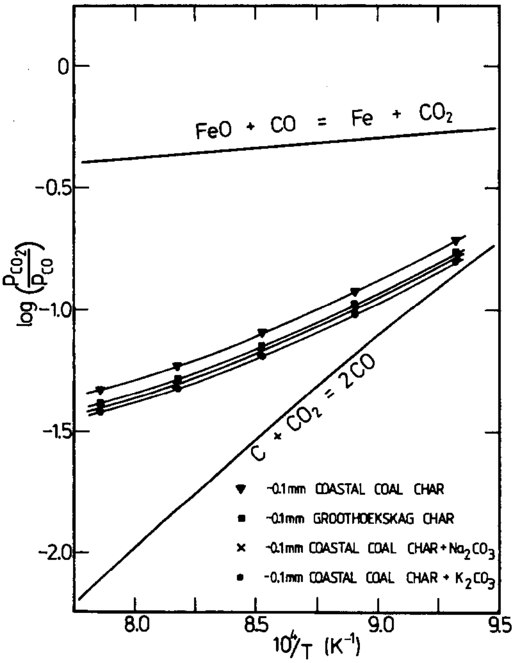

Fig. 7. Observed values of P_{CO_2}/P_{CO} ratios compared with equilibrium values for the reduction of Sishen iron ore by different chars.

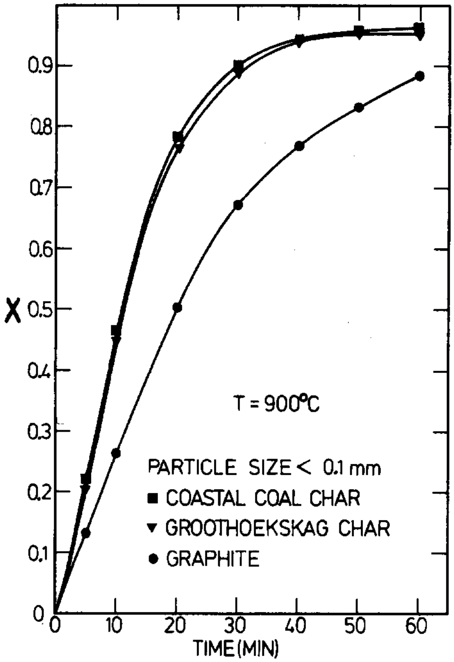

Fig. 8. The reduction of Sishen iron ore by different carbonaceous species at 900 °C.

that the Boudouard reaction plays a role in limiting the rate of reduction. Mookherjee et al. [26] and Rao [27] observed similar behaviour when using different particle sizes. The shape of the curves in Figs. 8 and 9 resembles those observed by Turkdogan and Vinters [28,29].

The catalytic influence of K_2CO_3 and Na_2CO_3 during the reduction of Sishen iron ore by graphite and Coastal coal char may be seen in Figs. 10 and 11 respectively. Similar to the trends observed in Figs. 3 and 4, it is evident that K_2CO_3 is in both cases a more effective catalyst than Na_2CO_3 at all temperatures considered. The Arrhenius plots in Fig. 12 further illustrate this difference in catalytic efficiency. Table 1 shows that K_2CO_3 decreases the activation energy of both the gasification and reduction reactions more than Na_2CO_3 does. Mookherjee et al. [26] also observed a decrease in activation energy when using Na_2CO_3 as catalyst during the reduction of haematite by char. The catalytic influences of K_2CO_3 and Na_2CO_3 are supported by the gas analyses given in Figs. 6 and 7. Szendrei and Van Berge [30] observed similar behaviour when using Na_2CO_3 as catalyst during the reduction of haematite by graphite, and surmised that K_2CO_3 would further increase the CO concentration.

Table 1 reveals that the activation energy of reduction is on the average 29% less than the activation energy for the corresponding gasification reaction for all the carbonaceous species investigated. It is noteworthy that

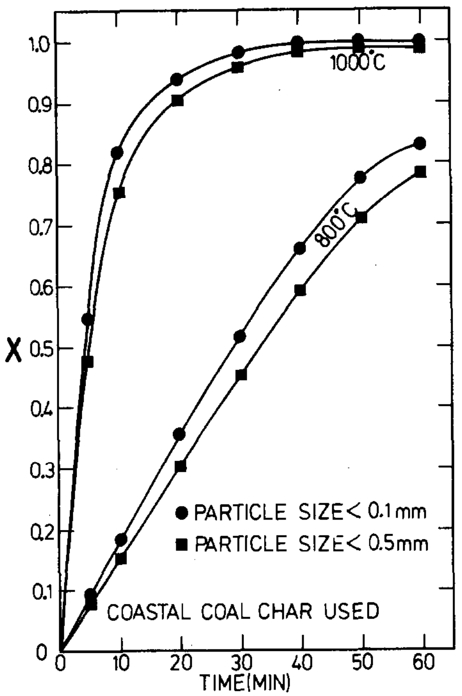

Fig. 9 Effect of particle size of carbon on the reduction of Sishen iron ore by Coastal coal char.

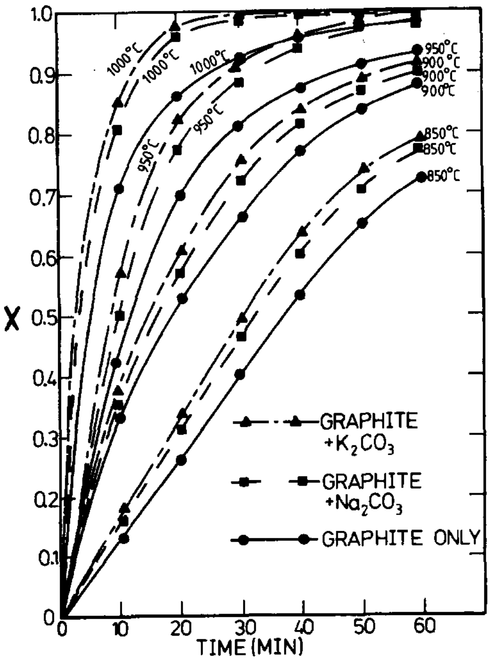

Fig. 10. Effect of catalysts on the reduction of Sishen iron ore by graphite.

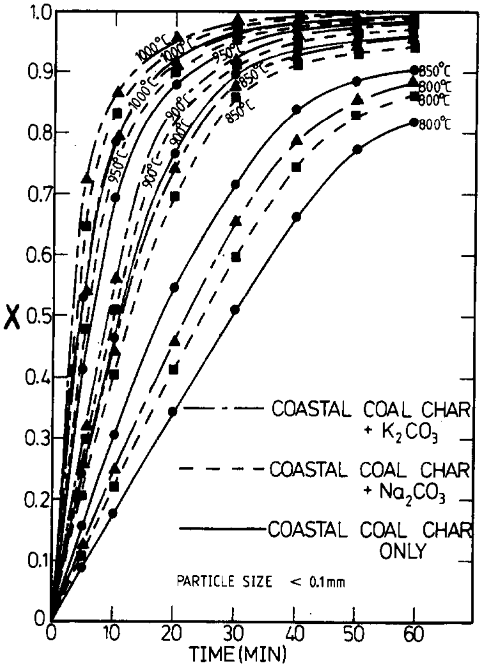

Fig. 11. Effect of catalysts on the reduction of Sishen iron ore by Coastal coal char.

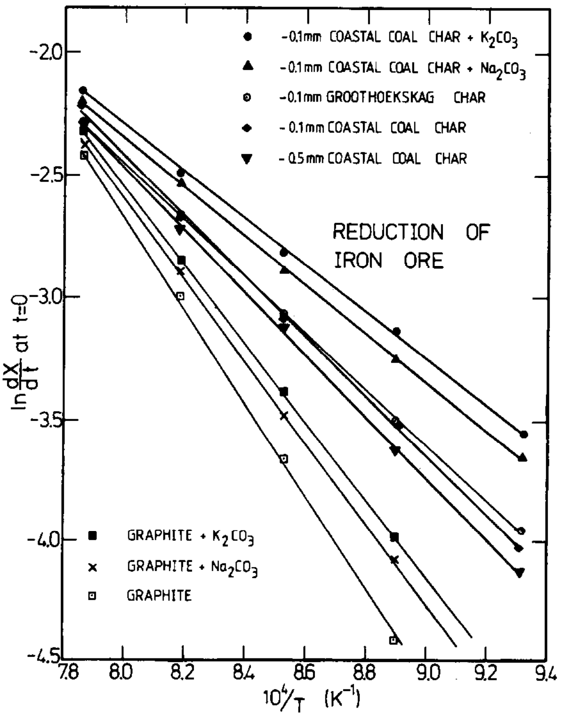

Fig. 12. Arrhenius plot of the rate of reduction of Sishen iron ore by different carbonaceous species.

this decrease in activation energy for the graphite with and without catalyst is more profound than that for the chars. Otsuka and Kunii [4] expected that the formation of metallic iron during the reaction could cause a decrease in the activation energy. However, Mookherjee et al. [26] investigated the reduction of haematite fines by a surrounding layer of char fines so that catalysis of the gas–carbon reaction by iron was not very likely.

A possible explanation for this phenomenon may be found in the work of Walker et al. [31], who concluded that the apparent activation energy is about half the true value when the reaction is controlled by both pore diffusion and chemical reaction. Von Bogdandy and Engell [32] confirmed these observations. Mookherjee et al. [26] merely speculated about the application of this theory to their results. During the reduction of iron ore a porous product layer may form around the unreduced cores of the particles. Here, inward diffusion of CO and outward diffusion of CO_2 will proceed through the porous layer. This may mean that the rate of reduction is controlled by pore diffusion as well as chemical reaction. The reduction reaction, where pore diffusion could be more significant than in the corresponding gasification reaction, would then be expected to be less dependent on temperature and therefore have a lower activation energy than the gasification reaction. As char has a higher porosity than graphite, it would be expected that the change in porosity from the gasification to the reduction reaction would be more severe in the case of graphite. This will mean that the decrease in activation energy for the char is lower than that for the graphite, as shown in Table 1.

Table 1 gives the activation energies for both gasification and reduction in ascending order. The carbonaceous species reveal the same order in both types of reaction, which provides further evidence that the Boudouard reaction plays a predominant role in controlling the rate of reduction.

CONCLUSIONS

(1) A decrease in the particle size of carbon increases both the rate of gasification and the rate of reduction.

(2) The activation energies of both gasification and reduction were decreased by the addition of either Na_2CO_5 or K_2CO_3. A concomitant decrease in the concentration of CO_2 in the product gas was observed. In all cases, K_2CO_3 was found to be a more effective catalyst than Na_2CO_3.

(3) The rate of gasification of char is much higher than that of graphite. Similarly, the rate of reduction of iron ore by graphite is much slower than when char is used.

(4) The apparent activation energy of reduction is on the average 29% less than the activation energy for the corresponding gasification reaction.

(5) In both gasification and reduction the carbonaceous reductants revealed the same order of activation energies. Evidence given in this paper shows that the Boudouard reaction plays a predominant role in controlling the rate of reduction.

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