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The effect of calcium aluminates on the coke analogue gasification

Apsara S. Jayasekara, Brian J. Monaghan*, Raymond J. Longbottom

PYRO metallurgical Group and School of Mechanical Materials Mechatronics and Biomedical Engineering, University of Wollongong, Northfield Ave, Wollongong, NSW 2522, Australia



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ABSTRACT

The gasification rate in CO₂ of the coke analogue containing calcium oxide was studied using analogues doped with alumina (corundum), calcium aluminates (CA6, CA, C3A) and lime minerals. The coke analogue is a laboratory material with simplified carbon structure that has a mineral component with a particle size, size distribution and mineral dispersion that can be controlled. The main focus of this study was to quantitatively assess the effect of calcium in the mineral on the analogue's reactivity. The analogues were reacted with CO₂ isothermally in the temperature range of 1173–1623 K. It was found that the reaction rate increased with increasing CaO activity/number of moles of Ca in the mineral. The relative reaction rates (from lowest to highest) of the analogues doped were alumina, CA6, CA, C3A and lime. The relative apparent activation energies of the gasification from lowest to highest was lime, C3A, CA, CA6 and alumina.

1. Introduction

Metallurgical coke is a key reagent used in blast furnace iron production. It is the fuel for the furnace, the source of reductant for the iron ore and aids control of permeability in the furnace [1]. Coke is a complex material, composed of different forms of carbonaceous materials, minerals and has an intricate pore structure. It also is inherently heterogeneous with respect to most metrics used to characterise it.

The mineral component of metallurgical coke is of the order 10–12 mass% and comprises of elements such as O, Si, Al, Fe, Ca, S, Mg, K, Ti and Na [2–4]. Though less common, the minerals may also contain P, Mn, C, H, N, Ba, Sr, F and Cl [5]. Minerals containing oxides of alkalis [3,6–9] and transition metals [2,3,7,10,11] can increase coke gasification/ reactivity. Calcium-bearing minerals are of particular interest in coke/coal studies. It has been shown to be particularly mobile in coal and coke [12–15] and significantly affects coke reactivity. Well-known calcium-containing minerals in coke are oldhamite (CaS), fluorapatite (Ca₅(PO₄)₃F), akermanite (Ca₂Mg(Si₂O₇)) and diopside (MgCaSi₂O₆) [16].

When exposed to high temperatures and reactive atmospheres, the inherent complexity and heterogeneous nature of coke make it difficult to isolate the effects of specific components on coke behavior and reaction kinetics [17–19]. To overcome the complexity and heterogeneity issues associated with studying the reactivity of metallurgical coke, a coke analogue has been developed. The mineral component in the analogue can be controlled with respect to phase, composition, particle size and dispersion throughout the analogue. This analogue has

previously been used in studies to distinguish the relative reactivities of coke analogues doped with different minerals [18,20], the dissolution rate of coke in liquid iron [19,21,22], kinetic mechanistic studies of reaction in CO₂, isolating specific CaO/lime [15] effects on the coke analogue reactivity and demonstrating it had similar gasification reaction behaviour to that of metallurgical coke [23,24].

The focus of this investigation was to assess the effects of calcium added as a simple oxide or as a calcium aluminate on the gasification kinetics of the coke analogue in CO₂. Three calcium aluminates, CaO·6Al₂O₃ (CA6), CaO·Al₂O₃ (CA) and 3CaO·Al₂O₃ (C3A), lime (CaO) and alumina (Al₂O₃) were used to represent the mineral (ash) component of the analogue. The choice of minerals was a compromise, dealing with minerals of some relevance to metallurgical coke but less complex than those found in metallurgical coke. This simplified mineral component of the analogue allowed the focus of the effects of Ca and Al oxides/minerals on coke reactivity in the absence of interference from other components such as Mg, F and PO₄³⁻ that have been identified to also have effects on coke gasification.

2. Experimental

Coke analogue samples were reacted with CO₂ in a thermogravimetric analysis (TGA) set-up (Fig. 1) to assess the effects of selected minerals on the coke gasification kinetics.

Five different coke analogue batches were prepared using either a calcium aluminate (CA6, CA or C3A), Al₂O₃ or CaO. The minerals were added to give a constant concentration of 0.1 mol cations/100 g in the

* Corresponding author.

E-mail address: monaghan@uow.edu.au (B.J. Monaghan).

Nomenclature

X	Carbon conversion
R_C	Initial apparent reaction rate, $\text{g g}^{-1} \text{s}^{-1}$
T	Temperature, K
dt	Reaction time, s
W_0	Initial mass of the sample, g
W	Mass at time t , g
dW	Mass change during the reaction, g

analogue and were sieved prior to the addition to give a constant particle size range of 38–53 μm . Experiments were carried out for 2 h isothermally in the temperature range of 1173–1623 K.

The calcium aluminates were chosen based on the Al_2O_3 -CaO binary system (Fig. 2). The choice of minerals allowed the evaluation of the specific effects of CaO as a separate phase and of CaO bonded/complexed within a mineral.

2.1. Reaction rate measurements

An unreacted coke analogue sample was weighed and placed in the furnace hot zone on an alumina pedestal suspended from a balance. This was then heated at 10 K/min to the desired temperature under Ar flowing at 1 L/min. Once the reaction temperature was reached, the gas was changed from Ar to CO_2 and set at a flow rate of 4.5 L/min. The changing over of the gas was defined as the start of the experiment. The flow rate was chosen/ established to ensure the reaction kinetics were independent of gas flow (i.e. eliminate gas film diffusion control) [23]. The gases used were 99.99% pure and passed through ascarite and drierite prior to entering the TGA. When running with Ar, the gas was also passed through Cu turnings at 573 K to minimise oxygen entering the furnace.

The recorded weight change during the reaction as measured by the TGA was used to calculate the carbon conversion, X (Eq. (1)), and initial apparent reaction rate, R_C (Eq. (2)).

$$X = \frac{W_0 - W}{W_0} \quad (1)$$

$$R_C = \frac{1}{(1-X)} \frac{dX}{dt} \quad (2)$$

2.2. Preparation of coke analogue

The coke analogue was prepared using carbonaceous materials (laboratory grade graphite, phenol-formaldehyde resins (Bakelite and

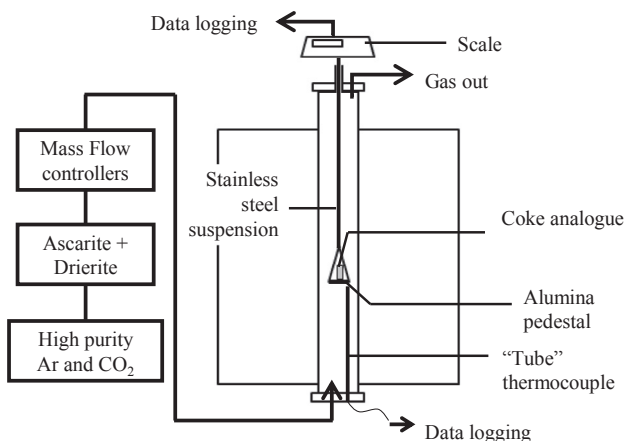


Fig. 1. A schematic diagram of the TGA set up used for reactivity experiments.

Novolac resin in propylene glycol) and hexamethylenetetramine (HTMA)) and minerals (CA6, CA, C3A, alumina or lime). The ingredients were mixed and pressed to form a cylinders of ~ 30 mm height and 18 mm diameter samples. These cylindrical samples were then cured for 24 h in an oven at 443 K and then fired in a two-stage process. In stage 1, the analogue was fired at 1273 K for 1 h. In stage 2, the analogue was fired at 1473 K for 1 h.

A fired coke analogue sample from each batch was cross-sectioned, mounted in epoxy resin, polished and carbon coated for SEM analysis. The CA6, CA, C3A and lime doped coke analogue samples were treated as water sensitive and prepared using, water-free alcohol based polishing lubricants. These samples were used in optical porosity and SEM/EDS characterisation.

The initial porosity of all the coke analogue samples was measured using an optical porosity method (detailed elsewhere [20]). The initial porosities of the samples (10–500 μm pore diameter range) prior to the gasification in the TGA were in a narrow range of 30–33%. This technique had a pore diameter lower limit of ~ 10 μm . It is desirable to maintain the initial porosities in a narrow range to minimise the effect of porosity on the measured analogue reactivity. This should aid elucidation of the specific effects of mineralogy on reactivity.

2.3. Preparation of the mineral phase

High purity (+99.9%) laboratory grade Al_2O_3 and CaCO_3 powders obtained from Sigma Aldrich were used in the production of the mineral phases.

The calcium aluminates were prepared by mixing Al_2O_3 and CaCO_3 powders in appropriate proportions and fired to produce pellets of calcium aluminates. CaCO_3 was used instead of CaO to overcome issues associated with CaO moisture absorption, allowing accurate weighing of the carbonate. The powders were first mixed with 500 ml of deionised water to make a slurry. They were then filtered using a 75 mm Büchner funnel and a Filtech 2850 – 70 filter paper equivalent to Whatman #6 (pore size 3 μm). The resulting filter cake was then oven dried at 373 K for 24 h. Deionised water (2 mass%) was added as a binder to the dried filter cake prior to pressing into pellets. Approximately 8 g of the mixture was pressed in a 25 mm diameter steel die under a 1.3×10^{-8} Pa pressure. The pellets were then fired in a

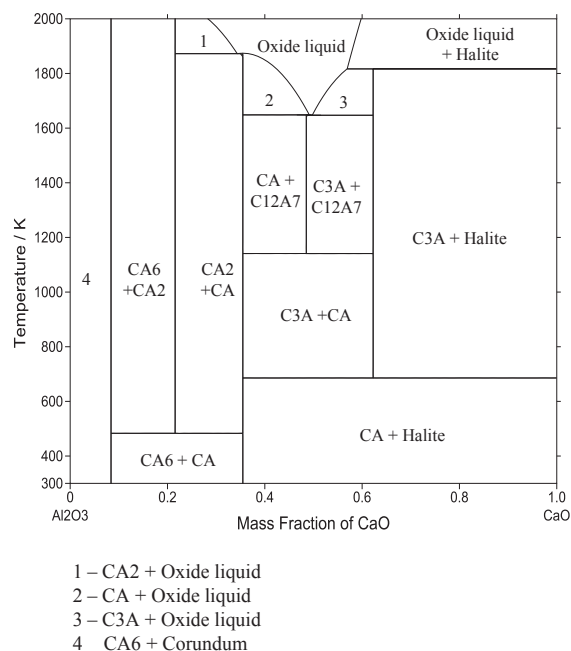


Fig. 2. A phase diagram of the Al_2O_3 – CaO binary system (from MTDATA [28]). The dashed lines represent single-phase calcium aluminates.

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