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A SIMPLE NON-INVASIVE OPTICAL PYROMETRIC METHOD FOR PLOTTING TEMPERATURE–TIME PROFILES OF HIGH TEMPERATURE REACTIONS IN MICROWAVE OVENS

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Abstract

A simple optical pyrometric method is described, based on a photocell with red and blue filters calibrated by the disappearing filament technique. The method, which is cheap, non-invasive and reproducible, is used for measurement of the rate of heating of solid materials such as coke, CuO or Fe_3O_4 in a microwave oven.

All materials were heated under dinitrogen in a silica reaction vessel over 3 min in a 650 W oven. Coke (which contains graphitic phases) and magnetite heat smoothly to maximum temperatures of 1180 and 1050°C respectively. CuO heats erratically with plasma discharges from the surface, however when covered with a layer of coke the oxide heats smoothly achieving a maximum temperature of 1210°C. The observations are discussed.

Keywords: measurement, microwave, optical pyrometry, temperature

Introduction

Recent years have seen a growing interest, particularly within the chemistry community, in laboratory applications of microwave heating [1]. Although applications of microwave assisted acid digestion of geochemical and biochemical specimens prior to analysis is well established [2], recent applications have included the acceleration of organic reactions [3], of organometallic reactions [4] and applications to the heating of solids [5]. It is perhaps in the sphere of heterogeneous reactions involving solid components that the methodology shows most promise. A novel microwave method for the rapid pyrolysis of coal has for

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example been reported [6] and it is from developments of that work that the need for the system described in this short paper arose.

The measurement of temperature for a reaction mixture within the cavity of a microwave oven is not necessarily trivial. Whilst appropriately shielded and earthed thermocouples may be appropriate for some applications such as ashing, they were inappropriate for our pyrolysis system. Solutions based on fibre optic technology are available but tend to be expensive and, again, were inappropriate to our experiments. Since our reactions achieve high temperatures (>1100°C) we have developed a simple, cheap and effective use of non-invasive optical pyrometry for the measurement of temperature *vs.* time profiles.

Experimental

Reaction vessel

A pure silica reaction vessel fitted with an inlet for dinitrogen gas, which passes via a sintered glass pad into the reaction chamber, is fitted by means of a B19 joint to a spiral condenser cooled with solid CO_2 (which being non-polar is unaffected by microwaves). The condenser may be attached via the dinitrogen outlet line to a chain of further condensation vessels located external to the oven. Coal (0.5 g) is mixed with an appropriate 'receptor' of microwave energy [6] (3.0 g) and placed on the sintered glass pad, alternatively, as was the case with the development of the temperature measurement methodology, the receptor alone was introduced to the pyrolysis apparatus. The apparatus was placed in the cavity of a model MDS-81 microwave oven manufactured by CEM (N. C., U.S.A.) operating at 2.54 GHz and producing 650 W of microwave power on maximum setting. The contents of the reaction vessel were exposed to full microwave power for not less than three minutes.

Temperature measurement

A photocell containing blue and red filters was attached to a plotter which read voltage against time. The method was good to 1700–1750°C. Initially, calibration was achieved using a tungsten filament bulb through which variable current could be passed. The current/filament temperature calibration was achieved using the disappearing filament technique against standard flames. The bulb was then placed in the microwave oven to occupy a position equivalent to that of the reaction chamber of the pyrolysis apparatus. The filament was then fed with known currents to achieve known temperatures and thus provide a secondary calibration for the photocell. The method is considered accurate to ±10°C. Finally, the reaction vessel charged with a variety of receptors e.g. CuO,

Fe_3O_4, or coke was placed in the oven and subjected to microwave power. A voltage/time output was obtained from the photocell.

Results

Coke (metallurgical coke supplied by British Coal) shows a smooth temperature rise, e.g. Fig. 1, to a maximum value of 1180°C with the major temperature rise occurring between 1 and 2 minutes at a rate of 830 deg·min^{-1}.

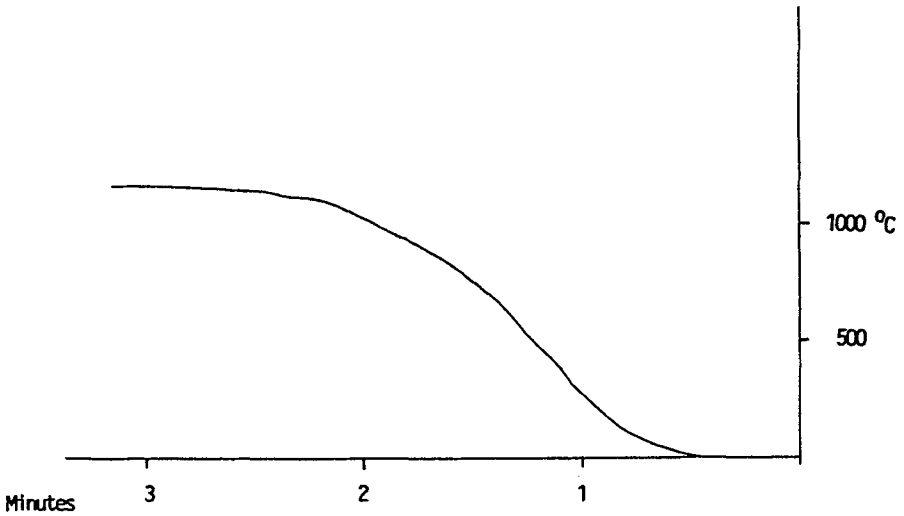

Fig. 1 Temperature *vs.* time profile for coke heated in a microwave oven

Fe_3O_4 (magnetite)

A smooth rise in temperature to a maximum value of 1050°C is seen similar to that for coke illustrated in Fig. 1. The maximum rise in temperature occurs between 0.7 and 1.0 mins at 1700 cm^{-1}.

CuO

This oxide produces interim flashes of light in the heating cycle which correspond to instantaneous temperatures of up to 1425°C, however if a layer of coke is placed on top of the CuO this erratic behaviour is virtually suppressed and a maximum temperature of 1210°C is reached (Fig. 2), at a maximum rate of 740 deg·min^{-1}.

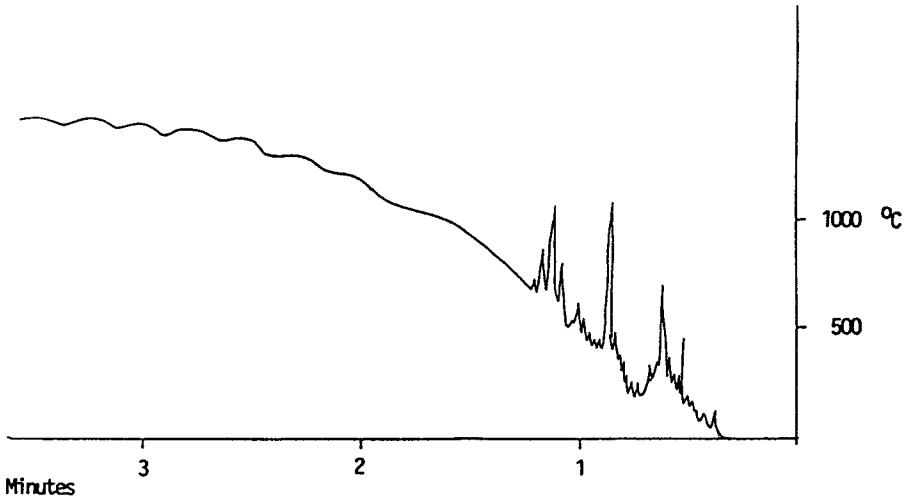

Fig. 2 Temperature *vs.* time profile for copper oxide (CuO), 3 g, covered with a layer of coke, 0.5 g, when heated in a microwave oven

Discussion

The method of temperature measurement which is based on well established methodology [7] works well and reproducibly in the new microwave context and should be generally applicable to high temperature reactions carried out in microwave ovens.

The ability of materials such as CuO and Fe_3O_4 to heat in a microwave oven has previously been remarked upon [1, 5], however our experimental conditions (heating under dinitrogen) allow the oxides to reach significantly higher temperatures. Thus for example 5–6 g samples of CuO and Fe_3O_4 have been found to heat to 701°C (0.5 min) and 510°C (2.0 min) in a 500 W oven [1, 5]. The differences are attributed to superior in our case.

Graphite, which is an electrical conductor will heat very rapidly in the microwave oven (e.g. ~1260 deg·min^{-1}), the ability of the metallurgical coke to function as a receptor is attributed to the presence of graphitic phases as revealed by X-ray powder diffraction analysis. Both the maximum temperature reached and the rate of heating are less than for graphite.

Magnetite, a stoichiometric oxide containing both Fe(II) and Fe(III) heats very smoothly under our experimental conditions. By contrast, the behaviour of CuO, a slightly non-stoichiometric compound, is both spectacular and erratic. The bright flashes of light which correspond to instantaneous high temperatures arise from plasma discharges at the surface. Once the material becomes very hot the behaviour becomes more calm. A simplistic explanation is that if va-

lence electrons are considered to be distributed in a band structure over the slightly non-stoichiometric $Cu(II)_{(1-x)}$ $Cu(I)_x$ $O_{(1-0.5x)}$ lattice, the hotter the material becomes, the greater the population of the conduction band and the better the oxide should function as a receptor. If a layer of coke was placed on top of the CuO, much more controlled behaviour was observed. This is attributed to the fact that, initially, coke functions as the main receptor and heats the oxide bed which then functions much more smoothly as a receptor at higher temperatures.

Mixtures of the receptors with coal provide a novel method of pyrolysis [6]. In general maximum temperatures achievable in the presence of coal are greater than with the receptors alone; the coal science implications of that observation will be discussed elsewhere.

The simple and cheap method of temperature measurement described here works well. Pyrometric methods do measure surface temperatures and there is a danger that bulk temperatures may differ. We believe that our experimental design is such that the temperatures recorded are characteristic of the whole specimen.

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Zusammenfassung — Es wird eine einfache optische pyrometrische Methode beschrieben, die auf einer Fotozelle mit Rot- und Blaufilter basiert und mit Hilfe der Kreuzfadentechnik kalibriert wurde. Diese kostengünstige und reproduzierbare Methode wurde zur Messung von Aufheizgeschwindigkeiten von Feststoffen, wie zum Beispiel Koks, CuO oder Fe_3O_4 in einem Mikrowellenofen verwendet.

Alle Substanzen wurden unter Stickstoff in einem Siliziumoxid-Reaktionsgefäß in einem 650 W Ofen für 3 Minuten lang erhitzt. Koks (mit einem Gehalt an grafitischen Phasen) und Magnetit werden gleichmäßig bis auf eine Höchsttemperatur von 1180 beziehungsweise 1050°C erhitzt.

CuO erhitzt sich sehr ungleichmäßig mit Plasmaentladungen an der Oberfläche, wird es jedoch mit einer Schicht Koks bedeckt, erhitzt sich das Oxid gleichmäßig bis auf eine Höchsttemperatur von 1210°C. Die Beobachtungen werden diskutiert.