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lignite char in 30% CO_2–70% N_2 and 40% CH_4–60% N_2 mixtures, respectively. As has been previously discussed[5], carbon deposition in chars from the cracking of methane essentially stops when only a fraction of the total pore volume in the char is filled. This has been attributed to a decrease in aperture size to an extent that methane no longer has access to the porosity within the cavities. However, it is possible in a CO_2–CH_4 mixture that the gasification of carbon atoms deposited from methane at aperture openings is sufficiently rapid that the rate of carbon deposition is not retarded. This is the situation which exists for the results shown in *Figure 1*. That is, curve (c) (open points) shows the experimental carbon weight loss *vs.* time plot for the mixture 30% CO_2–40% CH_4–30% N_2. The closed points on curve (c) were calculated, assuming that the initial rate of carbon deposition from the 40% CH_4–60% N_2 mixture continues throughout the run. That is, the cumulative carbon deposited, as calculated from the initial rate (estimated to be 2.2% weight gain/min), is subtracted from curve (a). Good agreement between the experimental and calculated results is seen.

In *Figure 2*, curves (a) and (b) show weight loss and weight gain plots for the Saran char in 30% CO_2–70% N_2 and 40% CH_4–60% N_2 mixtures, respectively. However, unlike the results shown in *Figure 1*, when the 30% CO_2–40% CH_4–30% N_2 mixture is passed over the char, a net weight gain is found, with the data points very close to that described by curve (b). The reason for this is that, whereas the rates of carbon deposition from methane are similar over the acid-washed lignite and Saran chars, the rate of gasification of the lignite char in CO_2 is considerably higher than that found for the Saran char. Similar results were found for these two chars when steam was substituted for CO_2. These results show the complexity of predicting changes in char weight in the presence of mixed gas systems. Inability to predict is caused by variations in carbon gasification and deposition rates affected by differences in: (1) the configuration of edge carbon atoms terminating crystallite basal planes, i.e. arm-chair and zig-zag[8], (2) the chemical and physical nature of inorganic impurities (catalysts) present[9], (3) extents of inhibition of the reactions by product hydrogen[10,11], and (4) the concentration of nascent sites.

Considering point (4), it is suspected that freshly deposited carbon has a 'super' reactivity to gasification and, conversely, that edge carbon sites newly exposed by gasification have 'super' catalytic activity to hydrocarbon cracking.

ACKNOWLEDGEMENTS

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Carbon deposition from methane over minerals

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Studies on carbon deposition from methane over a lignite char have been conducted[1]. Since deposition rates were more rapid over the raw char than the HCl-treated char, it was concluded that catalysis of methane cracking by some inorganic species occurred. Thus, we have studied the cracking of methane over different major minerals found in coals in a TGA unit at 900°C at a total pressure of 0.1 MPa in a flowing CH_4–N_2 mixture. The partial pressure of methane was 6.5×10^{-3} MPa. Prior to studying methane cracking at 900°C, the mineral sample (about 10 mg ground to –44 μm) was heated up in N_2 at 20°C/min and held at 900°C for 30 min. *Table 1* lists the minerals studied and reactions which they undergo upon heating in N_2 to 900°C[2].

Of all the minerals studied, only siderite and calcite were found to be precursors of catalysts for the cracking of methane. Gypsum was found to react with methane giving predominantly CaS and small amounts of $CaSO_4$ and CaO. No surface deposition of carbon was observed. In both N_2 and methane at 900°C, pyrite lost sulphur and was converted to triolite (FeS), but there was no evidence of either reduction of triolite to iron or of carbon formation. The cases of siderite and calcite can be considered in more detail.

Table 1 Minerals studied and their reactions upon heating to 900°C

Mineral	Chemical formula	Reactions
Kaolinite	$Al_4Si_4O_{10}(OH)_6$	Release of adsorbed water and dehydroxylation
Illite	$K_4(Al,Fe)_y(Mg,Fe)_wSi_xAl_yO_{10}(OH)_2$	Release of interlayer water and dehydroxylation
Calcite	$CaCO_3$	Decarbonation
Dolomite	$CaCO_3.MgCO_3$	Decarbonation
Quartz	SiO_2	Nil
Gypsum	$CaSO_4.2H_2O$	Dehydration
Rutile	TiO_2	Nil
Pyrite	FeS_2	Conversion to triolite
Siderite	$FeCO_3$	Decarbonation

Figure 1 Change in weight in a CH_4-N_2 atmosphere (O) followed by a H_2-N_2 atmosphere (●) for a run starting with a FeO sample derived from $FeCO_3$ at 900°C

Siderite

Upon heating in N_2 to 900°C, siderite loses CO_2 and is converted to FeO. In the CH_4-N_2 mixture, FeO is first reduced to iron within about 30 min, as seen in *Figure 1*. This is followed by a continuous increase in weight as carbon is deposited, at least up to 23 h. The maximum rate of weight increase was about 0.11 mg h^{-1} mg^{-1} starting weight of siderite. The deposited carbon can be completely gasified in a 10% $H_2-90\%$ N_2 mixture at 900°C, again yielding iron.

The carbon deposited over a 24 h period was characterized by X-ray diffraction, using silicon as an internal standard. Considering that it was only formed at 900°C, it was highly crystalline[3,4], having an interlayer spacing of 0.3371 nm and an average crystallite height, L_c, of 50 nm.

Calcite

Upon heating in N_2, calcite loses CO_2 in the temperature range 500–750°C producing CaO. In the CH_4-N_2 mixture at 900°C, a slow, continuous weight increase occurs. At the end o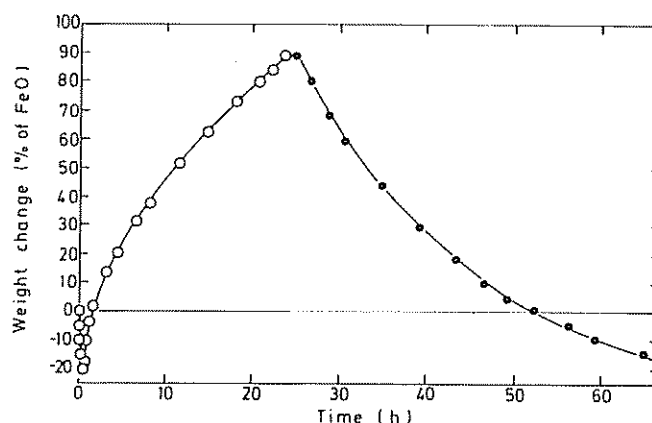f 3 and 15 h, it corresponds to about 3 and 11% of the starting weight of calcite, respectively. In contrast to the sharp (002), (100), (102), and (004) X-ray diffraction peaks found for the carbon deposited over iron (derived from siderite), only a very broad (002) diffraction peak was found for this carbon. This indicates that it has a very small crystallite size. X-ray diffraction peaks were also present for CaO.

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Mössbauer spectroscopic measurement of pyrite in coal*

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Process development and control for removal of pyrite (FeS_2) from coal requires techniques for the accurate measurement of the FeS_2 content. We report here the use of Mössbauer Spectroscopy (MS) as a simple, effective and relatively inexpensive monitor of pyrite in coal. In particular MS provides convincing evidence that the standard wet chemical technique for the determination of pyrite in coal (ASTM D 2492-68, reapproved 1974) can be inaccurate by up to 20%.

The ASTM method is based upon the assumption that pyritic iron in coal is insoluble in hydrochloric acid but soluble in nitric acid, and that the iron soluble in hydrochloric acid is also soluble in nitric acid. It follows that the difference $Fe(HNO_3) - Fe(HCl)$ should be equivalent to the pyritic iron. This then gives the pyrite sulphur in the coal. Such a procedure involves three potential problems.
(1) It neglects the possibility that some (extremely fine particle) FeS_2 in coal might be removed by the HCl;
(2) It is possible that some of the pyrite particles could be completely surrounded by the coal (even after crushing) in the test sample and might therefore not be removed by the nitric acid; and
(3) Many coals contain other iron-bearing minerals. Some of these might dissolve in hydrochloric acid but be only partly soluble in nitric acid. A discussion of the difficulties associated with problems (2) and (3) is given in Ref.1.

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