LETTERS TO THE EDITOR

More on the reaction of C_8K with water: influence of particle size

The chemical and physical state of potassium intercalated within graphite has been of recent interest[1–4]. Based on the reaction of C_8K with water, Schlögl and Boehm (SB) claimed that the intercalated potassium is equal in chemistry to metallic potassium, with observed deviations from this arising from topochemical limitations[1]. Based on an XPS analysis of the valence bands of C_8K, Preil and Fischer (PF) concluded that there was no more than 0.04 electron/K atom associated with potassium K($4s$) states; the electrons initially on the potassium metal are associated with graphite levels in C_8K[2]. Since anions of aromatic hydrocarbons with K^+ counter-ions react with water in a manner different from potassium metal[5–8], it is not clear that the SB and PF descriptions of C_8K are in harmony.

The topochemical limitations cited by SB pertained to observed differences in chemistry due to particle size, the larger the particle, the less complete the C_8K/H_2O chemistry. The crystallite size of their graphite specimens was presumably large. Herein, we discuss an alternative situation, that of large particle size and small crystallite size, as can be found in petroleum cokes treated at 1400°C. Following formation of C_8K and reaction with water, the resultant solid phase product contains less potassium than does material made from graphite of smaller particle size. This indicates that particle size is not the only variable involved in the outcome of the reaction of C_8K with water.

The calcined petroleum coke used to make C_8K contained 99.40% C, 0.17% H, 0.31% S, 2.6 ppm V and 0.22% ash. X-ray diffraction showed discrete (002), (004), (100), (110) and (006) bands, with linewidth analysis of the (002) at $d = 346$ pm (using a Scherrer constant of 0.9) indicating $L_c \cong 5600$–5800 pm and of the (100) band at $d = 212$ pm (Scherrer constant = 1.84) indicating $L_a \cong 5900$ pm. The microanalysis and crystallite sizes are comparable to published values for 1400°C petroleum cokes[9–10]. Natural polycrystalline graphites, such as SP-1 or UCP-1-100, show substantially larger crystallite sizes; we measure L_c to be 45 nm for the SP-1 and 47 nm for UCP-1-100 based on analysis of the (002) peak ($K\alpha_1$ and $K\alpha_2$ were unresolved). Electron spin resonance of the coke showed a peak of derivative extremum width 2.34 mT, with derivative zero located at $g = 2.0019$. The peak was anisotropic, with $A/B = 2$ and an *apparent* signal intensity of 2.7×10^{18} spins/gram (diluted in NaCl, 3/1 on weight basis). The particle size distribution was 84% larger than 250 μm, 14% between 63 and 250 μm, the remainder fines. This coke had been made by 1400°C calcination of a green coke of composition 95.43% C, 3.52% H and 0.25% S. Petroleum cokes formed in the heat treatment range 1250–2300°C have been reported to form intercalation compounds with potassium[11–13], and graphites of a variety of particle sizes form structurally well-defined C_8K which is golden in color[1–4].

The calcined petroleum coke was made to react with potassium metal at 110° under He, conditions known to lead to C_8K in the case of graphite[3,4]. The product solid developed a golden color, and ESR showed two new signals: of linewidth 1.03 mT at derivative zero 2.0020 (major) and of linewidth 0.05 mT at derivative zero 2.0028 (minor).

A second synthesis, involving only particles of size greater than 250 μm, led to similar results; furthermore, X-ray diffraction showed the presence of the (004) line of graphite C_8K at 540 pm and the absence of the initial (002) line at 346 pm, thereby demonstrating the presence of intercalation.

Under cover of helium, 3.048 g of the petroleum coke C_8K, was reacted with 10 ml of deionized H_2O, leading to gas evolution and to a loss of the gold color. After filtration, with additional water used to rinse the solid, and drying (110°C, 50 μm Hg vacuum), 2.392 g of black solid of composition 89.66% C, 5.94% K, 0.96% H and 3.26% O (total = 99.82%) were recovered. The liquid filtrate titrated 19.16 meq of acid, indicating a potassium balance of 101% (22.6 mmol K in C_8K; 3.6 mmol recovered in solid, 19.2 mmol in filtrate).

X-ray diffraction of this black solid showed it to be distinct from both the initial coke and the C_8K coke. The (002) line at 349 pm was 3.2 times broader than in the initial coke; the (004) line at 540 pm of the C_8K was gone and the (100) and (004) lines were weak and diffuse. Electron spin resonance showed a symmetric, narrow (0.014 mT) line at $g = 2.0027$ of apparent spin density 1.4×10^{18} spins/g. Wideline ^1H NMR showed a narrow (0.014 mT) line at room temperature, and pulsed ^1H NMR showed T_1 values indicative of correlation times slightly to the high-temperature side of the T_1 vs (temperature)$^{-1}$ minimum (298 K, 342 ms; 322 K, 566 ms; 350 K, 793 ms; see Ref. 4).

Although the petroleum coke had larger particle sizes than any of the graphites discussed in Ref. 4, its C_8K/H_2O product, with a C/K atomic ratio of 49, contained far less potassium than any of the corresponding graphite C_8K/H_2O products. Furthermore, with respect to a graphite of comparable particle size, such as sample "S 40" of SB[1], there is a factor of 6 differences in the level of potassium in the final C_8K/H_2O product (35.5 vs 5.94). If particle size were the most significant issue in potassium entrainment, the levels of K^+ in the petroleum coke should have been comparable to those of sample S 40 and greater than those of our graphites of smaller particle size.

Another aspect of the entrainment issue is the proposal by SB of potassium in the C_8K/H_2O products existing only as hydrated KOH. The ^1H data for the petroleum coke product are comparable to that reported for the graphite products in suggesting "free" water and distinct from the result for KOH monohydrate (linewidth of 1.4 mT at 298 K[3,4], 20 times broader!). Furthermore, correcting for the initial hydrogen content of the petroleum coke (3.64 mmol in 3.048 g), the atomic H/O ratio of the product is 3.9 (= 19.1/4.87), higher than the H/O ratio of the graphite specimens, and again suggesting the presence of water. Both of these observations are consistent with our model of hydrated K^+ rather than the SB proposal of hydrated KOH.

Another area of interest concerns structure/reactivity relationships. Lachter and Bragg have recently given evidence for the presence of interstitials in petroleum cokes[14]. It is thus interesting to note the ease of inter-

calation of potassium into our calcined coke, which shows $d(002)$ inequivalent to that of graphite, in light of work on other layered systems[15].

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Concurrent carbon gasification in steam and carbon deposition in methane over chars

Steam reforming of natural gas over a Ni–Al$_2$O$_3$ catalyst is a well known unit process. Nickel both catalyzes CH$_4$ decomposition, producing carbon (a carbonaceous deposit), and gasification of this carbon with H$_2$O, producing CO and H$_2$. The H$_2$O/CH$_4$ ratio is adjusted such that carbon does not build up within the pore structure of the Al$_2$O$_3$ and thereby deactivate the catalyst.

Each inorganic species has a different specific activity for catalyzing the cracking of CH$_4$, on the one hand, and the gasification of carbon by steam, on the other hand. Likewise, carbons will have different activities for CH$_4$ cracking and their interaction with steam. It is suspected that the activity of carbon surfaces is dependent upon the ratio of zigzag and arm chair to dangling carbon sites. We previously showed that two chars, containing widely different amounts of inorganic impurities, had sharply different activities for the cracking and gasification reactions in CO$_2$/CH$_4$ mixtures. Here we present results for the same chars in a H$_2$O/CH$_4$ mixture.

Chars were produced from a Montana lignite (PSOC-91)[1] and Saran (a copolymer of polyvinylidene chloride and polyvinyl chloride)[2] by heating them to 1273 K and soaking for 2 h in N$_2$. The Saran char contained <6 ppm Cl and ~100 ppm metallic impurities, primarily Fe and Si. Part of the Saran char was activated by reacting in 0.1 MPa of air at 698 K to a carbon burnoff of 63.8%. Part of the lignite char was washed with warm 10% (by volume) HCl; this reduced ash from 10.9% to 7.2%. The major inorganic elements in the lignite chars were Si, Al, and Ca.

A Fisher TGA unit, model 442, was used for the rate studies. About 3 mg of 40 × 100 U.S. standard mesh char were first heated to 1273 K in flowing dry N$_2$ until the sample weight became constant. The sample was then cooled to reaction temperature (1173 K) and held for 20 min prior to introducing the desired reaction mixture, either wet N$_2$ or wet 80% N$_2$–20% CH$_4$. In both cases, the water partial pressure was 2.3 kPa and the total pressure was 0.1 MPa. In the later case, the ratio, H$_2$O/CH$_4$, was 0.12.

Table 1 presents selected physical property data on the chars. The Saran chars (SC and ASC) exhibit no molecular sieving of N$_2$ relative to CO$_2$. This indicates the essential absence of very fine micropores or apertures[3]. In contrast, substantial sieving is noted for the lignite chars (LC and ALC) indicating that the microporosity is dominated by fine micropores approximately 0.4–0.5 nm in size[3]. For the Saran chars, SC and ASC, 46.8% and 58.1%, respectively, of the particle volumes were accessible to He.

Figure 1 presents the results. Gasification rates in the H$_2$O/N$_2$ mixture vary by over a factor of 20 in going from the lignite char (LC) to the unactivated Saran char (SC). When CH$_4$ is added to the gas mixture, the dominant reaction for the lignite chars is still gasification, whereas for

Table 1. Physical properties of chars

| Sample | Surface Areas, m^2/g | | Densities, g/cm^3 | | Open Pore |
	N$_2$ (77 K)	CO$_2$ (298 K)	Hg	He	Volume, cm^3/g
SC	871	932	1.16	2.18	0.404
ASC	1245	680	0.93	2.22	0.625
LC	31	420	---	---	---
ALC	17	470	---	---	---

Table 2. Rate data

Sample	Gasification Rate in H_2O/N_2, %/h	Initial Rate in $H_2O/CH_4/N_2$, %/h	Est. Init. Rate in CH_4/N_2, %/h	Gasification Rate / Deposition Rate
SC	-19	+60	+79	0.24
ASC	-45	+180	+225	0.20
LC	-440	-150	+290	1.52
ALC	-350	-190	+160	2.19

the Saran chars carbon deposition becomes dominant. In the former case, with carbon gasification being dominant, the initial large micropore surface area in the chars remains open; and thus gasification rates remain high as carbon burnoff proceeds. In the latter case, with carbon deposition being dominant, the initial, large micropore surface area in the chars is rapidly rendered inaccessible[4]. As a result, the rate of carbon deposition (and carbon gasification) rapidly decreases until weight change occurs at a negligible rate.

It is characteristic of chars, which have extensive aperture-cavity pore systems, to have their micropore volumes made inaccessible to gases long before their open pore volume is completely filled with deposited carbon[4]. For example, for Saran char SC, 46.8% of the particle volume is open porosity and 53.2% is solid and closed pore porosity. If deposited carbon were to fill all the open porosity

and have a density at least equal to that of the solid and closed pore volume, an increase in weight of 88% would be possible. However, a weight increase of only 5.5% was found, as seen in Fig. 1, before the weight increase essentially stopped. Carbon deposition at aperture surfaces, where only a small fraction of the open pore volume originally existed, effectively restricted CH_4 diffusion to the cavity surface and further carbon deposition.

An estimate of the ratio of carbon gasification to carbon deposition activity of the chars can be made. Table 2 lists estimates of the initial experimental rates of carbon gasification in the H_2O/N_2 mixture and weight change in the $H_2O/CH_4/N_2$ mixture. From differences in these rates, the initial rate of carbon deposition in a dry N_2/CH_4 (20%) mixture is estimated. Absolute ratios of carbon gasification activity (in H_2O/N_2) to carbon deposition activity (in CH_4/N_2) are then given in Table 2. It is seen that the Saran chars have a distinctively greater activity for the cracking of CH_4 to deposit carbon, whereas the lignite chars have a distinctively greater activity for undergoing carbon gasification in steam. The ratio is expected to not only depend upon the particular char and the H_2O to CH_4 ratio used but also upon the absolute pressures of H_2O and CH_4 used. Rates of carbon gasification in H_2O and carbon deposition in CH_4 will have different pressure dependencies. Further, H_2 produced from these reactions will, in turn, have different inhibiting effects on the reactions.

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Fig. 1. Weight change at 1173 K in various atmospheres over SC, O, ◉; ASC, ▽, ▼; LC, □, ▦ and ALC, △, ▲). Open symbols for H_2O/N_2, closed symbols for $H_2O/CH_4/N_2$.

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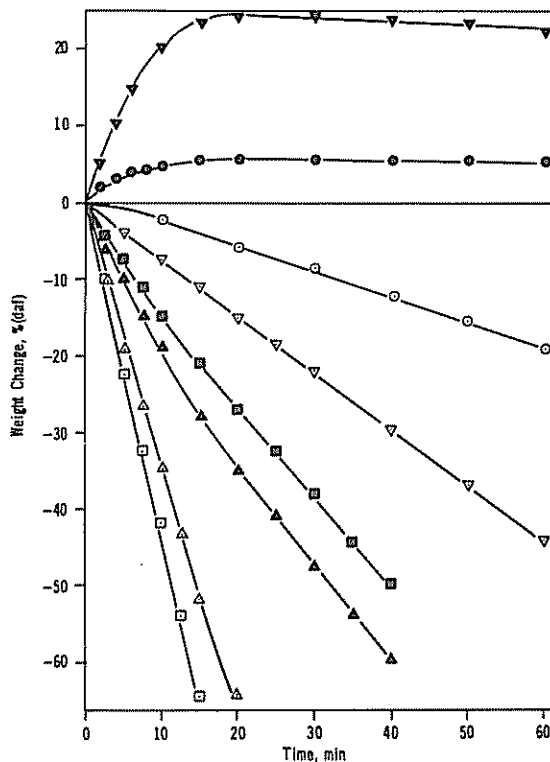†Present address: University of Alicante, Alicante, Spain.