LETTERS TO THE EDITOR

More on the reaction of C\textsubscript{6}K with water: influence of particle size
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Key Words—Potassium graphite, water.

The chemical and physical state of potassium intercalated within graphite has been of recent interest[1–4]. Based on the reaction of C\textsubscript{6}K with water, Schlügl and Bochim (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\textsubscript{6}K, Pretl and Fischer (PF) concluded that there was no more than 0.04 electron/K atom associated with potassium K\textsubscript{4} state; the electrons initially on the potassium metal are associated with graphite levels in C\textsubscript{6}K[2]. Since anions of aromatic hydrocarbons with K\textsuperscript{+} 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\textsubscript{6}K are in harmony.

The topochemical limitations cited by SB persisted to observed differences in chemistry due to particle size. The larger the particle, the less complete the C\textsubscript{6}K/H\textsubscript{2}O 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 coke treated at 1400°C. Following formation of C\textsubscript{6}K 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\textsubscript{6}K with water.

The calcined petroleum coke used to make C\textsubscript{6}K contained 91.40% C, 0.17% H, 0.31% S, 2.62 ppm V and 0.23% ash. X-ray diffraction showed discrete (002), (004), (100), (110) and (006) bands, with linewidth analysis of the (002) at δ = 346 pm (using a Scherrer constant of 0.9) indicating L\textsubscript{c} = 5600–5800 pm and of the (100) band at δ = 212 pm (Scherrer constant = 1.84) indicating L\textsubscript{c} = 5900 pm. The microanalysis and crystallite sizes are comparable to published values for 1400°C petroleum coke[9–10]. Natural polycrystalline graphites, such as SP-1 or UCP-1-100, show substantially larger crystallite sizes; we measure L\textsubscript{c} to be 45 nm for the SP-1 and 47 nm for the UCP-1-100 for analysis of the (002) peak (K\textsubscript{0} and K\textsubscript{2} were unresolved). Electron spin resonance of the coke showed a peak of derivative extremum width 2.54 mT, with derivative zero located at g = 2.019. The peak was anisotropic, with A = 2 and an apparent signal intensity of 2.7 × 10\textsuperscript{10} spins/gram (diluted in NaCl, 3T on weight basis). The particle size distribution was 85% larger than 250 μm, 14% between 65 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 coke 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\textsubscript{6}K which is golden in color[1–4].

The calcined petroleum coke was made to react with potassium metal at 72°C under He, conditions known to lead to C\textsubscript{6}K in the case of graphite[3,4]. The product solid developed a golden color, and ESR showed two new signals: 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\textsubscript{6}K at 346 pm and the absence of the initial (100) line at 346 pm, thereby demonstrating the presence of intercalation.

Under cover of helium, 3.048 g of the petroleum coke C\textsubscript{6}K, was reacted with 10 ml of deionized H\textsubscript{2}O, leading to gas evolution and a loss of the gold color. After filtration, with additional water used to rinse the solid, and drying (110°C, 50 μm H\textsubscript{2}O 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\textsubscript{6}K; 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\textsubscript{6}K 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\textsubscript{6}K was gone and the (100) and (004) lines were weak and diffuse. Electron spin resonance showed a single, narrow (0.014 mT) line at g = 2.0014 of apparent spin density 4 × 10\textsuperscript{14} spins/g. Wideline \textsuperscript{1}H NMR showed a narrow (0.014 mT) line at room temperature, and pulsed \textsuperscript{1}H NMR showed \textit{T}\textsubscript{1} values indicative of correlation times slightly to the high-temperature side of the \textit{T}\textsubscript{1} vs (temperature)\textsuperscript{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\textsubscript{6}K/H\textsubscript{2}O product, with a C/K atomic ratio of 49, contained far less potassium than any of the corresponding graphite C\textsubscript{6}K/H\textsubscript{2}O 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\textsubscript{6}K/H\textsubscript{2}O product (35.5 vs 5.94). If particle size were the most significant issue in potassium entrainment, the levels of K\textsuperscript{+} 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\textsubscript{6}K/H\textsubscript{2}O products existing only as hydrated KOH. The \textit{H} 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, corretting 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\textsuperscript{+} 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 coke[14]. It is thus interesting to note the ease of inter-
Concurrent carbon gasification in steam and carbon deposition in methane over chars

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Key Words—Carbon gasification, carbon deposition, methane, steam, chars.

Steam reforming of natural gas over a Ni-Al₂O₃ catalyst is a well known unit process. Nicked both catalysts CH₄ decomposition, producing carbon (a carbonaceous deposit), and gasification of this carbon with H₂O, producing CO and H₂. The H₂O/CH₄ ratio is adjusted such that carbon does not build up within the pore structure of the Al₂O₃ and thereby deactivate the catalyst.

Each inorganic species has a different specific activity for catalyzing the cracking of CH₄, on the one hand, and the gasification of carbon by steam, on the other hand. Likewise, carbons will have different activities for CH₄ 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 CO₂/CH₄ mixtures. Here we present results for the same chars in a H₂O/CH₄ 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 N₂. The Saran char contained <6 ppm C1 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 N₂ until the sample weight became constant. The sample was then cooled to reaction temperature (1173 K) and held for 30 min prior to introducing the desired reaction mixture, either wet N₂ or wet 80% N₂-20% CH₄. 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, H₂O/CH₄, was 0.12.

Table 1 presents selected physical property data on the chars. The Saran chars (SC and ASC) exhibit no molecular sieving of N₂ relative to CO₂. 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 H₂O/N₂ mixture vary by over a factor of 20 in going from the lignite char (LC) to the unactivated Saran char (SC). When CH₄ is added to the gas mixture, the dominant reaction for the lignite chars is still gasification, whereas for

<table>
<thead>
<tr>
<th>Sample</th>
<th>N₂ (77 K)</th>
<th>CO₂ (298 K)</th>
<th>Hg</th>
<th>He</th>
<th>Open Pore Volume, cm³/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC</td>
<td>871</td>
<td>932</td>
<td>1.16</td>
<td>2.18</td>
<td>0.404</td>
</tr>
<tr>
<td>ASC</td>
<td>1245</td>
<td>680</td>
<td>0.93</td>
<td>2.22</td>
<td>0.625</td>
</tr>
<tr>
<td>LC</td>
<td>31</td>
<td>420</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>ALC</td>
<td>17</td>
<td>470</td>
<td>--</td>
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</tbody>
</table>
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) rapid-
ly decreases until weight change occurs at a negligible
rate.
It is characteristic of chars, which have extensive apert-
ure-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 po-
rosity. 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 essen-
tially stopped. Carbon deposition at aperture surfaces,
where only a small fraction of the open pore volume origi-
nally existed, effectively restricted CH₄ 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 gasi-
fication in the H₂O/N₂ mixture and weight change in the
H₂O/CH₄/N₂ mixture. From differences in these rates, the
initial rate of carbon deposition in a dry N₂/CH₄ (20%) mix-
ture is estimated. Absolute ratios of carbon gasification
activity (in H₂O/N₂) to carbon deposition activity (in CH₄/
N₂) are then given in Table 2. It is seen that the Saran
chars have a distinctively greater activity for the cracking
of CH₄ to deposit carbon, whereas the lignite chars have
a distinctively greater activity for undergoing carbon gasi-
figation in steam. The ratio is expected to not only depend
upon the particular char and the H₂O to CH₄ ratio used
but also upon the absolute pressures of H₂O and CH₄ used.
Rates of carbon gasification in H₂O and carbon deposition
in CH₄ will have different pressure dependencies. Further,
H₂O produced from these reactions will, in turn, have
different inhibiting effects on the reactions.

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