

ACTIVATION OF MESO-CARBON MICROBEADS WITH KOH

Xuesong Chen and Brian McEnaney

Materials Research Centre, University of Bath, Bath, BA2 7AY, UK.

Introduction

Chemical activation by reaction between KOH and various carbon precursors is a very effective method for developing highly microporous activated carbons. KOH-activated carbons have been called super-activated carbons because of their very high nominal BET surface areas, in excess of $3000 \text{ m}^2 \text{ g}^{-1}$ [1]. KOH activated carbons were originally developed at the Amoco Corporation, USA. Further development work was carried out by the Andersen Development Company, USA and then by The Kansai Coke and Chemical Company, Ltd., Japan [2] (Maxsorb carbons). Originally, the carbon were produced by KOH activation of a petroleum coke. Subsequently, it has been shown that active carbons with significant porosity can be produced by KOH activation of a wide range of precursors, including bituminous coals [3, 4], wood [5] and phenol-formaldehyde resins [6]. Here, we present some results on the mechanisms of KOH activation of mesocarbon microbeads.

Experimental

The mesocarbon microbeads, MCB, were obtained from The Kawasaki Steel Corporation Japan. Some properties of the MCB are in Table 1. The MCB were pre-oxidised at $300 \text{ }^\circ\text{C}$ for 30 minutes.

Table 1. Some properties of the mesocarbon microbeads.

Property	Value
Toluene insolubles	97.5 wt%
Quinoline insolubles	91 wt%
Volatile matter	9.3%
Ash content	0.21 wt%
Mean particle size	$15.9 \mu\text{m}$
Maximum particle size	$40 \mu\text{m}$
Atomic C:H ratio	4.57

Manufacturer's data

KOH Activation of MCB. KOH flakes (BDH, UK) containing $\sim 15 \text{ wt}\%$ H_2O were ground to particles of size $<250 \mu\text{m}$ and then mixed uniformly with MCB in various ratios in the range $\text{KOH:MCB} = 1:10$ - $8:1$. The mixture was pressed into discs (25 mm diameter \times 10 mm thick) which were stored in a desiccator. The discs were heated at $2 \text{ }^\circ\text{C min}^{-1}$ in flowing helium (flow rate $1.0 \text{ dm}^3 \text{ h}^{-1}$) up to $400 \text{ }^\circ\text{C}$ and held at this temperature

for 2 h to remove water from the discs. The discs were then heated in flowing helium at the same rate to final temperatures in the range 750 - $850 \text{ }^\circ\text{C}$ and held at these temperatures for various times to achieve different extents of activation. After cooling the carbons were repeatedly washed in boiling distilled water to remove inorganic material until the water reached $\text{pH} \sim 7.0$, followed by further washing in an ultrasonic bath for 1 h. The samples were dried in an oven at $100 \text{ }^\circ\text{C}$ for 8 h. The degree of activation of the carbons, or fractional burn-off, BO, was given by

$$BO = \frac{\theta w_0 - w_1}{\theta w_0} \quad (1)$$

where w_0 and w_1 are the initial and final dry weights of the discs and θ is the fraction of MCB in the original discs.

BET surface areas were computed from N_2 adsorption isotherms at 77 K using a Micromeritics ASAP 2000M instrument. Micropore volumes (not considered here) were also obtained from the isotherms using the Dubinin Ashtakhov equation. Thermogravimetric analyses and evolved gas analyses were carried out using a Setaram TG-92 analyser coupled to a Spectramass Visa mass spectrometer. X-ray diffraction analysis was carried out using a Philips 1820 vertical goniometer.

Results and Discussion

Pre-Oxidation. The function of pre-oxidation is to rigidise the MCB by cross-linking with oxygen. Thermogravimetry shows that heating the MCB in air at $300 \text{ }^\circ\text{C}$ results in a weight gain of 2.5% due to pick up of oxygen. Heating MCB in nitrogen to $1000 \text{ }^\circ\text{C}$ gave a weight loss of 83% ; this increased to 87% for pre-oxidised MCB. The slightly higher weight loss after pre-oxidation can be accounted for by expulsion of oxygen as CO and CO_2 .

Activation by KOH. Figure 1 shows the BET surface area increases with initial KOH content up to a maximum of $\sim 3000 \text{ m}^2 \text{ g}^{-1}$ for a KOH:MCB ratio of $4:1$ and that burn-off, as defined by Equation (1), increases progressively with initial KOH content. The initial development of BET surface area with increasing KOH content reflects increased development of micropore volume. The decline in BET surface area at high KOH:MCB ratios is probably due to the enlargement of some micropores into mesopores with increased burn-off. Thus a KOH:MCB ratio of $4:1$ seems optimum for

development of microporosity in KOH activated MCB at 800 °C. Otowa *et al* [7] and Marsh *et al* [8] using petroleum coke as the precursor reached a similar conclusion.

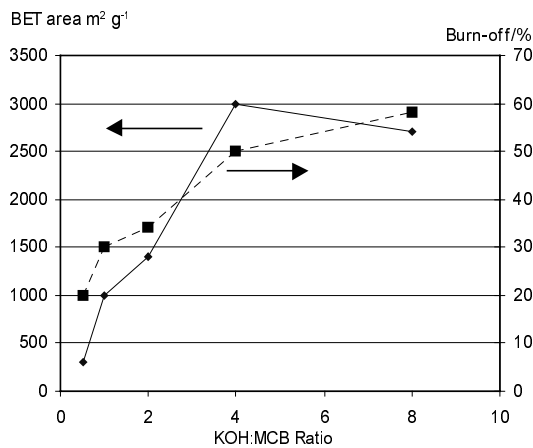


Figure 1. BET surface area and burn-off as functions of initial KOH:MCB ratio.

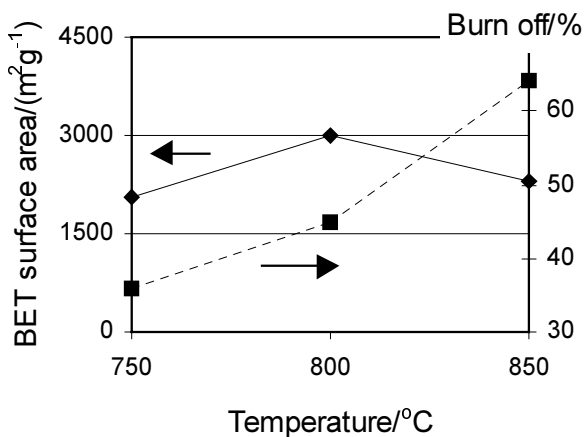


Figure 2. BET surface area and burn-off as functions of final heat treatment temperature.

Figure 2 shows the development of BET area as a function of final heat treatment temperature for a KOH:MCB ratio of 4:1 and a constant reaction time, 100 minutes. Once more, heat treatment at 800 °C yields the maximum BET surface area. Figure 2 also shows that the burn-off increases progressively with reaction temperature, indicating that the decrease in surface area at high reaction temperatures may be due to enlargement of micropores into mesopores at 850 °C.

Structural changes. Figures 3 and 4 show the X-ray spectra for the KOH-MCB material after heat treatment to 400 °C and 800 °C respectively. The shape of the spectrum for the material heated to 400 °C is

characteristic of carbon materials with a pre-graphitic structure. There is a prominent broad 002 peak at $2\theta \sim 25^\circ$ indicating parallel arrays of carbon layer planes and a smaller peak due to overlap of (100) and (101) reflections at $2\theta \sim 43^\circ$. This spectrum is similar to that found for mesocarbon microbeads thermally treated to 600 °C. The spectrum for the KOH-MCB material heat treated to 800 °C is dramatically different showing that the (002) peak is missing or obscured by strong small angle scattering extending out to large values of 2θ . These changes are consistent with destruction of much of the parallelism between carbon layer planes and the creation of extensive microporosity.

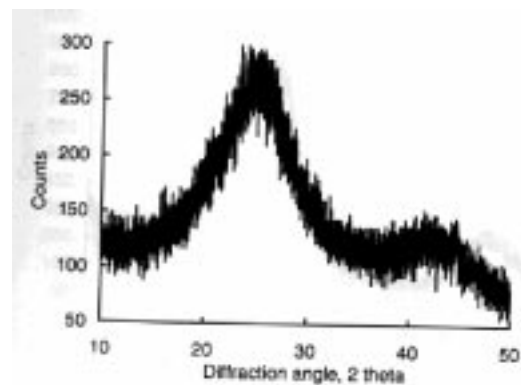


Figure 3. X-ray spectrum for KOH:MCB heat treated to 400 °C. KOH:MCB = 4:1.

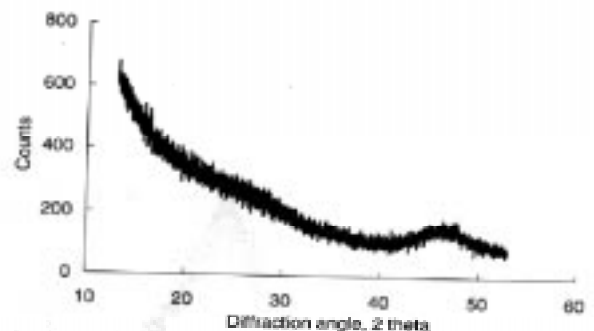


Figure 4. X-ray spectrum for KOH:MCB heat treated to 800 °C and 48% burn-off. KOH:MCB = 4:1.

Evolved gas analysis. The evolution of hydrogen from thermally treated MCB commences at ~ 400 °C and rises to a single maximum at ~ 700 °C, Figure 5. This is as expected for carbonisation of MCB. Evolution of H_2 from KOH-MCB commences at a lower temperature and shows two maxima at ~ 450 °C and ~ 750 °C. Evolution of CO_2 from KOH-MCB, Figure 6, is much more extensive than from the thermally treated microbeads. Finally, the evolutions of CO from thermally treated MCB and KOH-MCB are broadly similar up to ~ 700 °C, Figure 7. Thereafter, CO released from KOH-MCB is much more extensive. Thus, in summary, the evolved gas analyses indicate that the

KOH-MCB system is much more reactive than the thermally treated MCB.

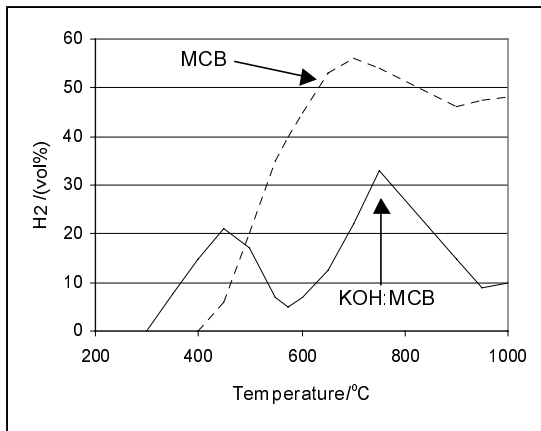


Figure 5. Evolution of H₂ from MCB (dashed line) and KOH-MCB (full line). KOH:MCB ratio = 4:1

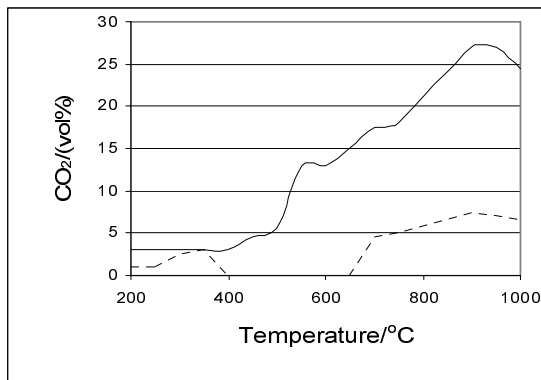


Figure 6. Evolution of CO₂ from MCB (dashed line) and KOH-MCB (full line). KOH:MCB ratio = 4:1

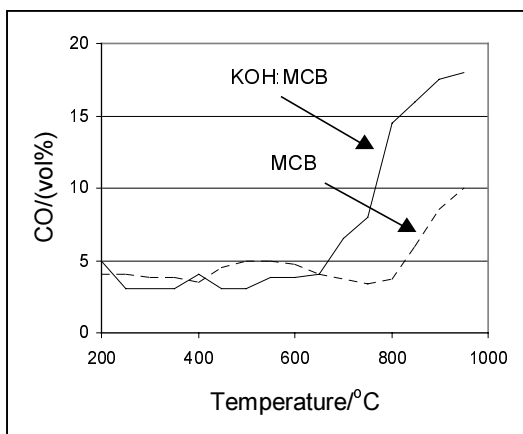
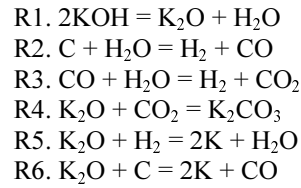


Figure 7. Evolution of CO from MCB (dashed line) and KOH-MCB (full line). KOH:MCB ratio = 4:1

Reaction mechanisms. The reactions taking place during the activation of carbons using KOH are

complex and incompletely understood. Ottawa *et al* [7] have proposed that the following reactions participate in the activation process.



In this work three additional reactions are also considered.

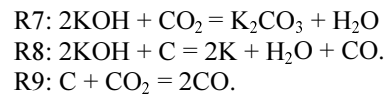


Table 2 shows standard free energy changes, ΔG° , for these reactions at 700 and 1100 K. These temperatures are close to the hold temperature for dehydration (400 °C) and the optimum final heat treatment temperature (800 °C).

Table 2. Standard free energy changes, $\Delta G^\circ/\text{kJ}$, for reactions in the KOH-C system.

Reaction	700 K	1100K
R1	167.19	144.87
R2	35.30	-22.03
R3	-13.04	0.15
R4	-278.85	-224.61
R5	106.89	16.58
R6	142.19	-5.45
R7	-111.63	-79.73
R8	309.38	139.42
R9	48.34	-22.18

On thermodynamic grounds, the dehydration of KOH to form K₂O (Reaction 1) is most unlikely to occur over the entire temperature range for KOH activation. There is much evidence for the formation of K₂CO₃ in the KOH-C system at intermediate temperatures; thermodynamics suggests that this occurs by carbonation of KOH (Reaction 7). Carbonation of K₂O (Reaction 4) is precluded, since Reaction 1 is unlikely to occur.

It is probable that the water gas shift reaction (Reaction 3) mediates the gas composition and may account for the early generation of H₂ in the KOH-MCB system, Figure 5. The gasification reactions of carbon by steam and/or carbon dioxide (Reactions 2, 9) become increasingly favoured thermodynamically as temperature increases and both reactions are catalysed by potassium salts. The evolved gas analyses, Figures 5, 7, suggest that Reaction 9 is the dominant gasification reaction at high temperatures, accounting for a

significant part of the increase in CO production at higher temperatures, Figure 7.

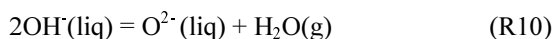
There is clear experimental evidence for the formation of metallic potassium at higher temperatures, but the reduction reactions that produce it are not clearly indicated on thermodynamic grounds. The reduction of KOH by carbon (Reaction 8) is unlikely to occur at 700 or 1100 K. The reduction of K₂O by carbon (Reaction 6) becomes thermodynamically favoured at 1100 K, but the reactions that form K₂O are not clear. Decomposition of K₂CO₃ at high temperatures by the reverse of Reaction 4 has been proposed as a source of K₂O, but this reaction (and the dehydration of KOH, Reaction 1) are not favoured on thermodynamic grounds. There is evidence that pure, solid K₂CO₃ is stable up to 1174 K when it undergoes melting.

A limitation of the simple thermodynamic analysis given above is that the solid and liquid reactants are assumed to be pure. KOH melts at 678 K to form an ionic liquid in which the thermodynamic activities of the dissolved components will not be unity as is assumed in Table 2. An ionic reaction scheme can be formulated that leads to the formation of metallic potassium.

The ionic melt forms at T = 678 K



The OH⁻ ions in alkali metal hydroxide melts undergo partial dissociation, the extent of dissociation increasing with increasing temperature [9]



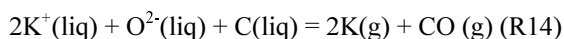
Alkali metal hydroxide melts also have a high affinity for CO₂ [9]



Dissolution of C into ionic melt may occur



The presence of dissolved C permits the reduction of K⁺ ions to form K at T~1100K



Once gaseous potassium is formed at T ~1100K insertion of the metal into the carbon can occur, leading to modification of the carbon microstructure, as proposed by others [1, 7]. The modification of the carbon structure following K insertion is not solely responsible for the development of microporosity. The evolved gas analyses Figures 5-7 suggest that carbon gasification also participates in micropore development.

The ionic mechanism proposed here may offer a basis for rationalising the effectiveness of different alkali metal salts as activating agents for carbons. For example, it is known that K₂CO₃ and Na₂CO₃ are much less effective activating agents than KOH and NaOH [8]. This may be partly because K₂CO₃ and Na₂CO₃ do not form ionic melts until T > 901 and 851 °C respectively. NaOH (m. pt 318 °C) forms an ionic melt at low temperatures, but is a less effective activating agent than KOH, possibly because metallic sodium is less effective than potassium at disrupting carbon structure. It would be interesting to use x-ray diffraction and other techniques to study the structural changes brought about by activation of carbon using different alkali metal salts.

Conclusions

Superactivated carbons (BET surface area ~3000 m²g⁻¹) can be produced by activation of mesocarbon microbeads using KOH. X-ray diffraction analyses show that the 'turbostratic' structure of the carbon is diminished or destroyed by the activation process due to insertion of metallic potassium into the carbon. Thermodynamic analyses suggest that the conventional mechanism for KOH activation, expressed in molecular terms, has some limitations. An alternative formulation expressed in ionic terms is proposed. The ionic mechanism may offer a rationalisation of the effectiveness of different alkali metal salts as activating agents.

References

1. Marsh H, Crawford D, O'Grady TM, Wennerberg A, Carbon 1982;20:419-426.
2. Otowa T, Nojima Y, Itoh M, In Extended Abstracts 'Carbon '94', Granada, Spain: Spanish Carbon Group, 1994. p. 808-809.
3. Verheyen V, Rathbone R, Jagtoyen M, Derbyshire F, Carbon 1995;33: 763-772.
4. Teng HS, Hsu LY, Ind. Eng. Chem. Res., 1999;38: 2947-2953.
5. Salame II, Badosz TJ, Ind. Eng. Chem. Res., 2000; 39: 301-306.
6. Teng H, Wang SC, Ind. Eng. Chem. Res., 2000;39: 673-678.
7. Otowa T, Shiraishi M, Tanibata R, Tanaka N, In Extended Abstracts 'Carbon '92', Essen, Germany: Deutsches Keramische Gessellschaft, 1992, p. 944-946.
8. Marsh H, Yang DS, O'Grady TM, Wennerberg A, Carbon 1984;22:603-611.
9. Claes P, Glibert J, In Lovering DG, Gale RJ, editors, Molten Salt Techniques, Vol. 1, New York: Plenum Press, 1983, p. 79-109.