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A THERMOCHEMICAL STUDY OF THE REACTIVE INTERMEDIATE IN THE ALKALI-CATALYZED CARBON GASIFICATION. II. ALKALI METAL VAPOUR PRESSURES

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ABSTRACT

Alkali metal vapour pressure measurements over mixtures of K_2CO_3 or Na_2CO_3 and graphite or activated carbon have been performed at elevated temperatures (925–1125 K) in an inert atmosphere. With graphite the values of the alkali metal vapour pressures are independent of the alkali/carbon ratio and correspond to the carbothermic reduction of the carbonates to the metals.

In the presence of activated carbon, however, the values are a function of the alkali/carbon (M/C) ratio and increase with increasing M/C ratio until a surface saturation value is reached at which the alkali metal vapour pressure corresponds with the value for the carbothermic reduction reaction. The deviation of the pressure from the value at the surface saturation value is indicative for an alkali–carbon interaction. This interaction is stronger for potassium than for sodium. Preheating the activated carbon at increasing temperatures (1275, 1675 or 1875 K) in an inert atmosphere shows a decreasing alkali–carbon interaction, while the surface saturation value is reached at a lower M/C ratio.

The results can be explained by the formation of alkali–oxygen sites on the carbon surface which could act as the reactive intermediates in the alkali-catalyzed carbon gasification.

INTRODUCTION

In part I of this study [1] it was concluded from the high-temperature X-ray diffraction experiments with mixtures of K_2CO_3 or Na_2CO_3 and activated carbon that an interaction occurs between the two physically mixed components at the gasification temperatures (925–1125 K). This interaction is stronger with potassium than with sodium. Since the interaction decreases with increasing pretreatment temperature of the activated carbon it was suggested that the alkali–carbon interaction might take place via the functional groups on the carbon surface [1]. As an alkali–carbon interaction should manifest itself in the alkali–metal partial vapour pressure of the

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system, these vapour pressures above mixtures of K_2CO_3 or Na_2CO_3 and activated carbon or graphite with different alkali/carbon ratios have been measured in an inert atmosphere in the temperature range 925–1125 K. The influence of outgasing the activated carbon at different temperatures in an inert atmosphere on the alkali metal vapour pressure has also been studied. The measured values were compared with those calculated under the assumption that no interaction had taken place [2,3], according to the following reaction

$$M_2CO_3(s) + 2C(s) \rightleftarrows 3CO(g) + 2M(g)$$

where M = Na or K.

EXPERIMENTAL

K_2CO_3 (Baker, 99.9%) or Na_2CO_3 (Baker, 99.5%), both dried at 575 K in argon, were added to graphite (Merck) or activated carbon (Degussa Eponit 114 N, an acid-washed activated carbon, containing < 0.8 wt.% ash) in an argon glove box by dry mixing and grinding in a mortar. The graphite was preheated at 2075 K, and the activated carbon at 475, 1275, 1675 and 1875 K for 2 h in purified argon. Specific surface areas of the carbon samples were determined according to the BET method by adsorption with nitrogen at 77 K.

The vapour pressure apparatus was of the transportation type [4]. The parts to be heated were made of stainless steel, the remaining parts were of quartz glass. The sample (2–4 g carbonate/carbon) was placed in a platinum boat and isothermally heated at a temperature between 925 and 1125 K in an atmosphere of purified argon. During the heating of the sample from room temperature to the temperature of measurement (0.5 h) the argon gas flows countercurrently through the sublimation tube. After 1.5 h equilibrium was attained ($\Delta T < 1$ K) and the direction of the argon flow was reversed. A velocity of the argon flow was taken such that it was saturated with the alkali metal vapour (~ 50 ml min^{-1}). The alkali metal sublimes in the cooler part of the sublimation tube. After the experiment the argon flow was again reversed, and the furnace was cooled rapidly. The sublimation tube was then flushed with distilled water at room temperature under vacuum. The hydroxide solution formed was outgased with nitrogen and titrated with a 0.100 N HCl solution. The volume of argon gas, with which the alkali metal was transported, was measured with a calibrated gas meter.

RESULTS

The measured alkali metal partial vapour pressures for the K_2CO_3-containing samples (p_K) are listed in Table 1, and those for the Na_2CO_3-con-

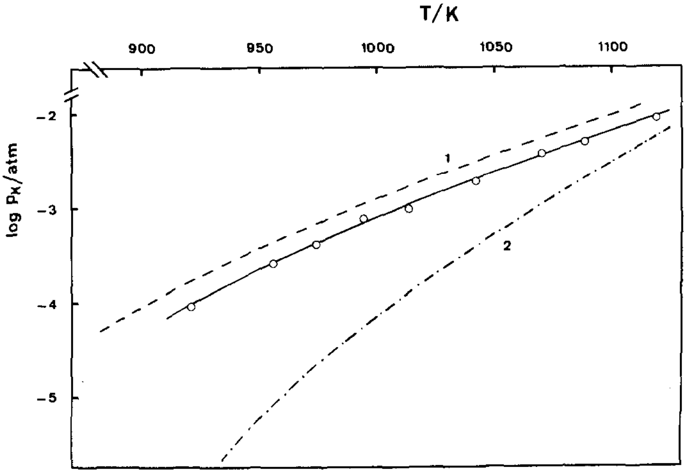

Fig. 1. Comparison between the calculated and measured potassium metal vapour pressures. (1) Calculated curve for an inert atmosphere; (2) calculated curve for an inert atmosphere with $p_{CO_2} = 10^{-4}$ atm; (○) measured values for the 50 wt.% K_2CO_3/graphite samples.

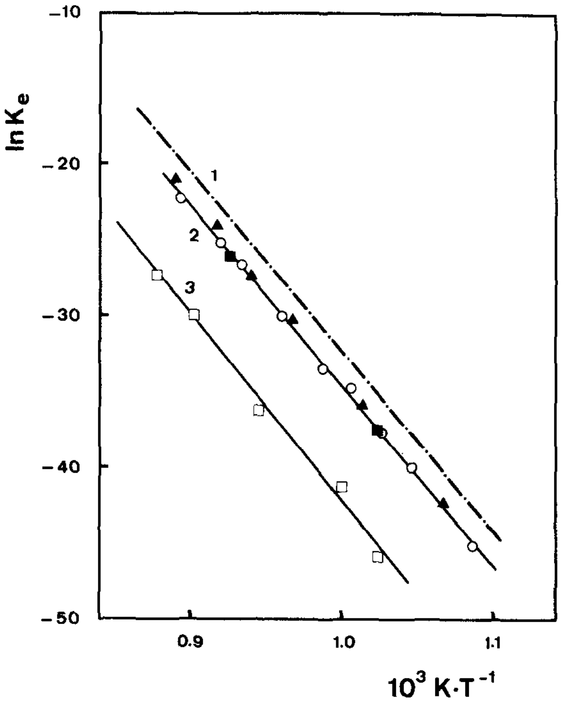

Fig. 2. Ln $K_e = p_K^2 p_{CO}^3 \equiv 3.375 p_K^5$ as a function of the reciprocal value of the temperature. (1) Calculated line according to the carbothermic reduction reaction; measured values for (○) 50 wt.% K_2CO_3/graphite samples; (▲) 50 wt.% K_2CO_3/activated carbon samples; (■) 20 wt.% K_2CO_3/graphite samples; (□) 20 wt.% K_2CO_3/activated carbon samples.

TABLE 1

Vapour pressure measurements for the K_2CO_3-containing samples

Wt.% K_2CO_3	K/C ratio of sample	Lab. temp. (K)	Ar gas volume (10^3 m^3)	Total press. (atm.)	Sample temp. (K)	T^{-1} (10^3 K^{-1})	K_{subl} [a] (10^3 mol)	p_K [b] (atm.)	ln K_e [c]
K_2CO_3/graphite (2075 K for 2h)									
50	0.174	296.2	16.935	0.989	1013.5	0.987	0.666	9.56×10^{-4}	−33.5
50	0.174	295.3	4.436	0.997	1088.5	0.919	0.931	5.07×10^{-3}	−25.2
50	0.174	297.0	6.320	0.989	1070.5	0.935	0.992	3.81×10^{-3}	−26.6
50	0.174	296.4	20.406	0.986	994.0	1.006	0.644	7.67×10^{-4}	−34.7
50	0.174	292.7	51.995	0.995	974.0	1.027	0.877	4.15×10^{-4}	−37.7
50	0.174	297.7	14.880	1.015	1042.0	0.960	1.183	1.94×10^{-3}	−30.0
50	0.174	293.5	62.192	1.013	955.5	1.047	0.681	2.64×10^{-4}	−40.0
50	0.174	291.4	288.654	0.994	920.5	1.086	1.094	9.07×10^{-5}	−45.3
50	0.174	296.2	2.237	0.990	1119.5	0.893	0.839	9.04×10^{-3}	−22.3
25	0.058	296.1	52.508	1.004	977.5	1.023	0.852	3.95×10^{-4}	−38.0
20	0.043	296.3	4.041	0.980	1080.0	0.926	0.686	4.11×10^{-3}	−26.3
20	0.043	296.0	51.131	0.999	975.5	1.025	0.865	4.11×10^{-4}	−37.8
15	0.031	295.9	54.157	0.991	978.0	1.022	0.933	4.18×10^{-4}	−37.7
K_2CO_3/activated carbon (dried at 475 K)									
50	0.174	296.0	14.917	1.001	1089.0	0.918	3.936	6.37×10^{-3}	−24.1
50	0.174	296.1	15.381	0.996	1032.5	0.969	1.127	1.78×10^{-3}	−30.4
50	0.174	296.2	4.966	1.000	1064.5	0.940	0.661	3.23×10^{-3}	−27.5
50	0.174	292.8	208.423	0.995	937.0	1.067	1.366	1.57×10^{-4}	−42.6
50	0.174	293.3	53.259	0.998	985.5	1.015	1.279	5.89×10^{-4}	−36.0
50	0.174	295.8	3.009	1.001	1124.5	0.889	1.289	1.03×10^{-2}	−21.2
20	0.043	296.7	11.437	0.994	1108.5	0.902	0.916	1.95×10^{-3}	−30.0
20	0.043	296.7	5.717	0.995	1138.0	0.879	0.747	3.17×10^{-3}	−27.5
20	0.043	296.2	208.197	0.997	996.0	1.004	1.741	2.03×10^{-4}	−41.3
20	0.043	295.7	49.536	1.008	1059.0	0.945	1.098	5.38×10^{-4}	−36.4

20	0.043	295.5	80.809	1.007	977.5	1.023	0.262	7.87×10^{-5}	−46.0
35	0.094	295.9	71.229	0.991	979.5	1.021	0.982	3.35×10^{-4}	−38.8
27.5	0.066	295.7	59.319	0.995	975.5	1.025	0.392	1.61×10^{-4}	−42.5
15	0.031	296.0	229.212	0.989	978.5	1.022	0.380	4.03×10^{-5}	−49.4
10	0.019	295.8	205.587	0.985	979.0	1.021	0.057	6.77×10^{-6}	−58.3
K_2CO_3/activated carbon (1275 K for 2 h)									
14.7	0.030	290.9	207.360	1.010	978.5	1.022	0.575	6.63×10^{-5}	
18.7	0.040	292.6	54.240	1.003	980.0	1.020	0.246	1.09×10^{-4}	
22.3	0.050	293.7	59.730	1.015	972.0	1.029	0.419	1.69×10^{-4}	
28.7	0.072	294.3	72.275	1.000	980.0	1.020	0.727	2.43×10^{-4}	
31.5	0.080	293.9	58.510	1.024	981.0	1.019	0.611	2.52×10^{-4}	
36.5	0.100	294.1	59.690	1.019	979.5	1.020	0.708	2.87×10^{-4}	
K_2CO_3/activated carbon (1675 K for 2 h)									
7.9	0.015	288.8	217.080	0.997	980.5	1.020	0.215	2.35×10^{-5}	
13.8	0.028	293.5	212.470	0.979	981.0	1.019	1.336	1.52×10^{-4}	
18.3	0.039	295.7	140.340	0.985	981.5	1.019	1.150	1.99×10^{-4}	
28.7	0.062	296.2	51.210	1.000	981.0	1.019	0.456	2.17×10^{-4}	
42.0	0.126	294.4	51.640	1.011	979.0	1.021	0.519	2.43×10^{-4}	
46.0	0.149	294.9	52.310	0.998	980.0	1.020	0.530	2.45×10^{-4}	
52.2	0.190	295.6	60.670	0.978	981.0	1.019	0.722	2.88×10^{-4}	
K_2CO_3/activated carbon (1875 K for 2 h)									
12.6	0.025	294.4	202.705	1.005	981.0	1.019	1.104	1.32×10^{-4}	
18.7	0.040	295.0	56.785	1.013	981.0	1.019	0.545	2.32×10^{-4}	
25.6	0.060	296.0	58.570	1.017	980.0	1.020	0.681	2.82×10^{-4}	
31.5	0.080	296.5	60.755	1.013	983.0	1.017	0.721	2.89×10^{-4}	
40.8	0.119	296.0	49.915	0.983	980.0	1.020	0.550	2.68×10^{-4}	
47.1	0.155	296.3	50.575	1.002	980.5	1.020	0.610	2.94×10^{-4}	

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[a] K_{subl} = amount of potassium metal sublimed during experiment.

[b] p_K = potassium metal vapour pressure.

[c] K_e = equilibrium constant $p_K^2\, p_{CO}^3 \equiv 3.375\, p_K^5$.

TABLE 2

Vapour pressure measurements for the Na_2CO_3-containing samples

Wt.% Na_2CO_3	Na/C ratio	Lab. temp. (K)	Ar gas volume (10^3 m^3)	Total press. (atm.)	Sample temp. (K)	T^{-1} (10^3 K^{-1})	Na_{subl} (10^3 mol)	p_{Na} (atm)	ln K_e
Na_2CO_3/graphite (2075 K for 2 h)									
40	0.151	292.8	207.732	0.997	942.5	1.061	1.044	1.21×10^{-4}	−43.9
40	0.151	294.3	51.559	0.988	1020.5	0.980	1.749	8.19×10^{-4}	−34.3
40	0.151	295.1	3.440	0.981	1118.0	0.895	1.082	7.57×10^{-3}	−23.2
40	0.151	294.9	11.436	0.994	1063.5	0.940	1.077	2.28×10^{-3}	−29.2
40	0.151	292.9	208.533	1.013	930.0	1.076	0.607	6.99×10^{-5}	−46.6
16	0.043	295.9	56.228	1.007	978.0	1.022	0.804	3.47×10^{-4}	−38.6
12	0.031	295.1	51.335	0.995	977.5	1.023	0.707	3.34×10^{-4}	−38.8
Na_2CO_3/activated carbon (dried at 475 K)									
40	0.151	295.3	10.567	0.998	1069.5	0.935	1.329	3.04×10^{-3}	−27.8
40	0.151	294.3	50.321	0.998	988.5	1.011	0.980	4.71×10^{-4}	−37.1
40	0.151	292.6	299.226	1.001	922.5	1.084	0.758	6.08×10^{-5}	−47.3
40	0.151	294.9	3.285	1.003	1111.5	0.900	0.878	6.43×10^{-3}	−24.0
40	0.151	295.7	127.803	1.011	958.0	1.044	1.032	1.96×10^{-4}	−41.5
40	0.151	294.0	53.731	1.008	1015.0	0.985	1.726	7.75×10^{-4}	−34.6
16	0.043	296.9	51.391	1.014	1048.5	0.954	2.892	1.37×10^{-3}	−31.7
16	0.043	296.9	209.654	1.016	951.0	1.052	0.674	7.84×10^{-5}	−46.1
16	0.043	296.6	51.343	1.015	1015.5	0.985	1.406	6.67×10^{-4}	−35.3
16	0.043	296.8	17.245	1.003	1072.0	0.933	1.760	2.48×10^{-3}	−28.8
16	0.043	295.3	57.218	1.004	999.5	1.001	0.950	4.03×10^{-4}	−37.9
16	0.043	295.9	3.362	1.007	1123.0	0.890	1.013	7.27×10^{-3}	−23.4
16	0.043	296.6	74.325	1.012	978.0	1.022	0.503	1.65×10^{-4}	−42.3
24	0.071	296.2	186.682	1.007	977.5	1.023	2.701	3.52×10^{-4}	−38.5
12	0.031	296.3	79.869	1.001	977.5	1.023	0.295	8.98×10^{-5}	−45.4
9	0.022	295.3	167.921	0.997	978.5	1.022	0.287	4.14×10^{-5}	−49.2

taining samples (p_{Na}) in Table 2. Saturation experiments indicated that the accuracy of the measured vapour pressures is within 10%.

In Fig. 1 the measured values for the graphite samples containing 50 wt.% K_2CO_3 have been compared with those calculated from the JANAF thermochemical Tables for the equilibrium

$$K_2CO_3(s) + 2C(s) \rightleftarrows 3CO(g) + 2K(g)$$

in an inert atmosphere. It appears that the measured values are somewhat lower (~ 30%) than the calculated ones. This deviation can be explained by the formation of some CO_2, besides CO, due to the Boudouard equilibrium ($2CO \rightleftarrows C + CO_2$). Hence, the calculated p_K's at the partial CO_2 pressure over the sample equal to 10^{-4} atm * are also included in Fig. 1. It thus appears that small amounts of CO_2 considerably decrease the alkali metal vapour pressure.

In Fig. 2 the calculated and measured alkali vapour pressures for the 50 wt.% K_2CO_3/graphite samples are repeated, but now expressed as ln K_e (equilibrium constant $K_e = p_K^2 p_{CO}^3 \equiv 3.375\ p_K^5$, if $p_{CO} = 1.5\ p_K$) as a function of the reciprocal value of the temperature. This has also been done for the

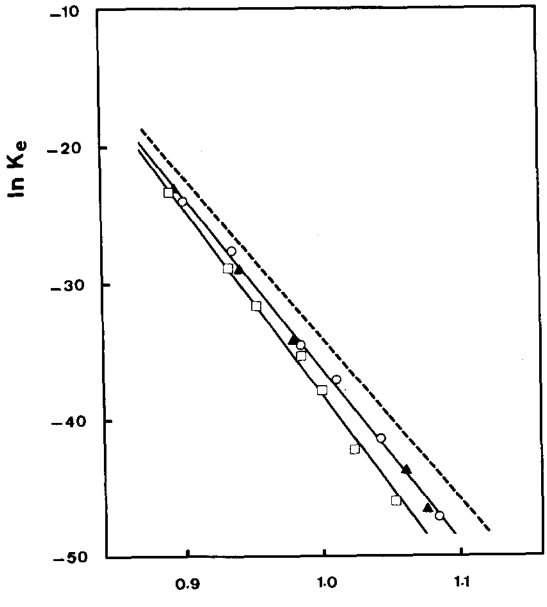

Fig. 3. Ln $K_e = p_{Na}^2 p_{CO}^3 \equiv 3.375\ p_{Na}^5$ as a function of the reciprocal value of the temperature. (- - - - - -) Calculated line according to the carbothermic reduction reaction; measured values for (○) 40 wt.% Na_2CO_3/graphite samples; (▲) 40 wt.% Na_2CO_3/activated carbon samples; (□) 16 wt.% Na_2CO_3/activated carbon samples.

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* Throughout this paper 1 atm = 101.325 kPa.

activated carbon (dried at 475 K in purified Ar) samples containing 50 wt.% K_2CO_3. It is obvious that the values of ln K_e (as well as the p_Ks) are equal for both systems at a certain temperature. In other words: at the given K/C ratio (0.174) the carbothermic reduction of K_2CO_3 to potassium metal takes place independent to the nature of the carbon.

However, decreasing the K/C ratio to 0.043 (20 wt.% K_2CO_3) results in a distinction between graphite and activated carbon. With graphite the potassium vapour pressure is independent of the K/C ratio, while in the case of activated carbon it decreases by a factor of 4–5.

The Na_2CO_3-containing samples show the same tendency as the samples with K_2CO_3, however, the dependence of the sodium vapour pressure on the Na/C ratio with C = activated carbon is less pronounced (see Fig. 3).

The relation between the alkali metal vapour pressure and the alkali/carbon ratio of both the graphite and the activated carbon samples has been studied in more detail at ~ 980 K. For potassium the influence of preheating the activated carbon at different temperatures in a purified argon atmosphere on the potassium vapour pressure has also been investigated. The results for potassium are shown in Fig. 4.

The potassium vapour pressures of the samples with activated carbon, dried at 475 K (specific surface area: 760 m^2 g^{-1}), depend strongly on the K/C ratio and converge at increasing K/C ratio towards the vapour pressure corresponding to the carbothermic reduction of the carbonate to the metal (corrected for some CO_2 production). This "surface saturation" value

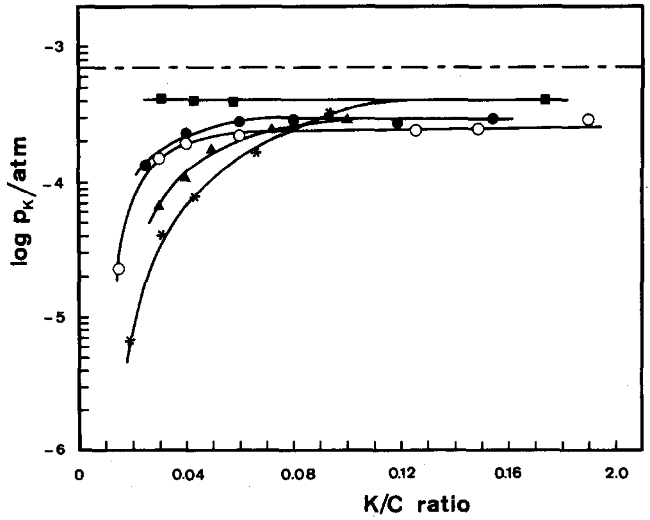

Fig. 4. Potassium metal vapour pressure as a function of the K/C ratio of the sample at 980 K. (- — - - — -) Calculated line according to the reaction $K_2CO_3(s)+2C(s) \rightleftarrows 3CO(g)+2K(g)$; (∗) C = activated carbon predried at 475 K; (▲) C = activated carbon preheated at 1275 K for 2 h; (○) C = activated carbon preheated at 1675 K for 2 h; (●) C = activated carbon preheated at 1875 K for 2 h; (■) C = graphite preheated at 2075 K for 2 h.

is reached at a K/C ratio of about 0.12. Preheating the activated carbon at increasing temperature (1275, 1675 and 1875 K for 2 h) in purified argon results in a smaller deviation from the saturation plateaus at the low K/C ratio's. The appearance of the lower plateaus in these last three cases is probably due to a somewhat higher oxygen level in the transportation apparatus during these experiments. The specific surface area of the activated carbon was not changed after temperature treatment at 1275 K, however, heat treatment at 1675 and 1875 K decreased the specific surface area to 340 and 260 m^2 g^{-1}, respectively.

As found before, the potassium vapour pressures of the graphite-containing (specific surface area: 8.1 m^2 g^{-1}) samples are independent of the K/C ratio at 980 K and correspond to the carbothermic reduction of potassium carbonate.

X-ray diffraction at room temperature in an inert atmosphere of the graphite samples after the overflow experiments still shows the carbonate reflections, whereas in the activated carbon samples, which yield a potassium vapour pressure lower than the saturation value, the carbonate reflections are absent on the X-ray diagrams after the experiments. These activated carbon samples, originally loaded with K_2CO_3 (the same holds for Na_2CO_3) are pyrophoric at room temperature; when exposed to air the alkali carbonate reflections in these samples appear again on the X-ray diagrams. This implies that potassium (sodium) was still present on the carbon surface.

In Fig. 5 the results for sodium are compared with those for potassium. The results are clearly similar, except that for sodium the partial vapour pressure which corresponds to the carbothermic reduction is reached at an alkali/carbon ratio about twice as low as in the case of potassium. Also the

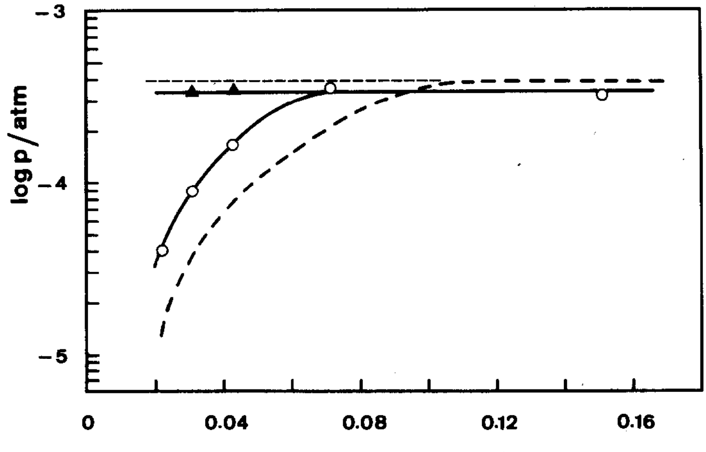

Fig. 5. Comparison between potassium and sodium of the alkali metal vapour pressures at 980 K as a function of the M/C ratio with C = activated carbon, predried at 475 K. (- - - - - -) Potassium (from Fig. 4); (○) sodium/activated carbon; (▲) sodium/graphite.

deviation from the plateau value with decreasing Na/C ratio is smaller, indicative of a weaker interaction between sodium and the carbon surface as compared with potassium.

DISCUSSION

The existence of an alkali–carbon interaction can be shown by a deviation of the alkali metal partial vapour pressure from the value which corresponds to the carbothermic reduction of the alkali carbonate to the metal. This implies that the carbothermic reduction reaction as proposed by McKee and Chatterji [5] can only be important in the alkali-catalyzed gasification of graphite but not in the carbon (or coal) gasification.

Wood et al. [6,7] also found, from mass spectrometric vapour pressure measurements, a strong chemical interaction between the alkali carbonate salt and the carbon. They suggested that a discrete chemical compound is formed in which oxygen has an essential role and proposed a non-stoichiometric oxide that contains an excess of the metal as ions. At the gasification temperatures (925–1125 K) this oxide phase could be melted and distributed as a liquid film over the carbon surface. The film would serve as the oxygen transfer medium between the gaseous reactant (H_2O or CO_2) and the carbon [6].

The picture obtained from the present observations is different because a discrete chemical compound would give a discrete alkali metal vapour pressure. From the experiments with pre-dried activated carbon, potassium (and sodium) could be bound at the carbon surface, its activity being a function of its concentration until the K/C ratio reaches a surface saturation value. This value is in good agreement with the saturation value for the gasification rate, showing an analogous increase with increasing alkali/carbon ratio, as reported by Mims and Pabst [8]. They proposed the formation of alkali surface salt complexes such as surface phenoxide groups: $>C-O^{-}-K^{+}$, indicating that oxygen plays an important part in the alkali/carbon interaction. In part I of this study [1] it was suggested that this oxygen originates from the functional groups on the carbon surface. The results described here indicate that this is only partially true because even after high temperature preheating of the activated carbon an alkali/carbon interaction still exists, however decreasing. So after removing most of the functional groups from the carbon surface at 1275 K, carbon active sites are still present or are created, which can bind potassium, probably via the oxygen of the carbonate itself. Preheating the activated carbon at 1675 or 1875 K will deactivate part of the carbon active sites via recombination and recrystallization, resulting in a decrease in the specific surface area. Therefore, the surface saturation value will be reached at lower alkali/carbon ratios with increasing pretreatment temperature but the deviation from the saturation value at decreasing alkali/carbon ratios will also be reduced. It is surprising, however, than even after heat treatment at 1675 K the deviation of the potassium vapour pressure from the saturation plateau is large for K/C ratios lower than ~ 0.03. These results indicate the existence of strong potassium-binding sites which are difficult to remove during heat treatment in an inert atmosphere. The number of these sites is too large to be explained by the ash content of the activated carbon (< 0.8 wt.% ash).

Mims and Pabst [9] showed the existence of O- and possibly C-anionic sites on the carbon surface, which can bind alkali atoms, by methylation of these sites with $^{13}CH_3I$ at room temperature. They reported that their results indicate that the number of sites per alkali atom is smaller for sodium than for potassium. This agrees with the results given in Fig. 5, indicating a lower surface saturation value for sodium compared with potassium ($M/C = 0.07$ for Na versus 0.12 for K). From these results, a lower catalytic activity of sodium for the carbon gasification reactions is made clear, although the cause of this phenomenon is not yet well understood.

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