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A THERMOCHEMICAL STUDY OF THE REACTIVE INTERMEDIATE IN THE ALKALI-CATALYZED CARBON GASIFICATION. I. X-RAY DIFFRACTION RESULTS ON THE ALKALI–CARBON INTERACTION

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ABSTRACT

Intercalation compounds of metallic potassium with graphite or activated carbon have been prepared and characterized by means of X-ray diffraction. The thermal stability of these compounds has been studied by quenching experiments and high-temperature X-ray diffraction (HTX). It is shown that potassium–carbon intercalation compounds are thermodynamically not stable at temperatures at which the alkali-catalyzed carbon gasification proceeds (950–1150 K). On the other hand, HTX-patterns exhibit a considerable interaction between K_2CO_3 and the activated carbon at the gasification temperatures. Interaction with Na_2CO_3 also takes place, but at much higher temperatures than with K_2CO_3. Increasing pretreatment temperatures of the activated carbon resulted in a decrease of the alkali–carbon interaction, whereas with graphite no interaction at all takes place. This indicates that surface groups on the carbon are the reactive sites for this interaction.

INTRODUCTION

The catalytic gasification of coal or char has been investigated for more than a century: the first patent dates are as early as 1867 [1]. Recently, the catalytic effects of alkalis, especially potassium salts like K_2CO_3, on the gasification rates have become of great technological interest. Although the catalytic reactions have been studied intensively since, the role played by the alkalis is not yet clearly understood. Several mechanisms have been proposed, in which redox systems with K_2CO_3 [2] or K_2O [3], C–O–K surface groups [4], and intercalates [5,6] have been suggested. These mechanisms, however, have rarely been based on thermochemical evidence obtained by experimental work. Here the results of such a study are presented. The first part deals with the thermal stability of potassium–carbon intercalation compounds at elevated temperatures (525–1125 K), and with the alkali–carbon interaction in mixtures of K_2CO_3 or Na_2CO_3 with graphite or

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activated carbon; the second part deals with the alkali vapour pressure over the alkali activated graphite or carbon. The proposed catalytic mechanisms will be discussed in the light of the results obtained.

EXPERIMENTAL

Intercalation compounds were prepared from metallic potassium and graphite or activated carbon, both pretreated at 2075 K for 1.5 h in purified argon. Stoichiometric amounts of carbon and potassium were mixed in an argon-filled glove box and heated overnight in sealed pyrex ampoules at 525 K. As the formation of the compounds is very slow at 525 K, they had to be homogenized in the glove box and heated again. The reaction products were characterized by means of X-ray diffraction, for which the samples were enclosed in small air-tight polyethylene bags. The X-ray powder diffraction patterns were recorded on film at room temperature in a Guinier camera (Enraf Nonius) using Cu K_α radiation ($\lambda = 0.15418$ nm), 1.5 h recording time and α-SiO_2 as an internal standard.

The thermal stability of the intercalation compounds has been determined by quenching experiments and in situ high-temperature X-ray diffraction (HTX). For the quenching experiments small amounts of the prepared compounds were packed in platinum foil to reduce the interaction between potassium metal and silica at the heating temperature and enclosed in evacuated silica ampoules. After heating a sample in a vertical furnace at a fixed temperature between 625 and 1025 K for a certain period of time (1, 5 or 20 h), the sample was cooled rapidly by dropping it in a Dewar vessel with iced water, placed below the furnace. The temperature path of the sample was measured with a Pt/Pt–10% Rh thermocouple which, also covered by quartz glass, was connected with the sample. This thermal quenching to the temperature of the iced water was accomplished in < 3 s. X-ray patterns of the quenched samples were taken, and the composition of a sample was obtained by comparing the diffraction lines with those of the model compounds.

The HTX-patterns were recorded in a Guinier–Lenné camera (Enraf-Nonius) using Cu K_α radiation. The intercalation compound with the highest potassium content (C_8K) was sealed in a polyethylene bag in the argon glove box and then mounted in the camera. The X-ray powder diffraction pattern was recorded on film as a function of the temperature of the sample in the camera. The heating rate of the sample was 10 K h^{-1} and in a separate experiment 5 K h^{-1}. The film speed was 5 mm h^{-1}. The sample was heated in vacuum ($< 10^{-3}$ Pa) from room temperature to 425 K to remove residual oxygen and water vapour from the furnace material. At 425 K the system was purged with helium and the sample was heated to the final temperature in a purified helium flow.

HTX-patterns were also taken of samples consisting of 30 wt% K_2CO_3 (K/C ratio = 0.075) or 23 wt% Na_2CO_3 (Na/C ratio = 0.068) mixed with Norit (RX extra) activated carbon. The influence of preheating the activated carbon on the alkali–carbon interaction was studied by heating the carbon at a temperature between 775 and 2075 K in purified argon. K_2CO_3 and Na_2CO_3 were dried at 575 K in argon before mixing with the preheated carbon samples in the glove box; the mixtures were enclosed in polyethylene bags. The heating sequence (first in vacuum, then in purified helium) of the samples in the apparatus was the same as with the intercalation compound.

RESULTS

Stability of the intercalation compounds

The X-ray patterns of samples with various C/K ratios heated at 525 K indicate the existence of discrete compounds at the compositions C_8K, $C_{24}K$, $C_{36}K$, $C_{48}K$, and $C_{60}K$; other compositions always contained mixtures of these compounds which can be discriminated by the 001-reflections at low glance angle [7,8]. The results of the quenching experiments with samples of the compositions C_8K and $C_{36}K$, prepared from graphite, are presented in Figs. 1 and 2. The X-ray patterns of the quenched samples indicate that with increasing temperature and increasing heating time the intercalation compounds decompose into compounds with a lower potassium content. In Fig. 1 it is apparent that C_8K loses potassium above 575 K; after 1 h at 1025 K all the potassium has been lost, graphite being formed. So the compound C_8K is positively not stable at gasification temperatures. $C_{36}K$ is stable to 675 K during heat-treatment for 1 h; above this temperature it

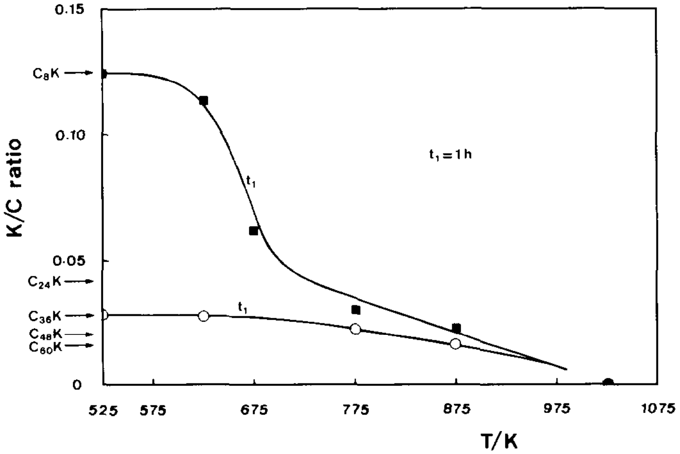

Fig. 1. Results of the quenching experiments with C_8K and $C_{36}K$; heating time 1 h.

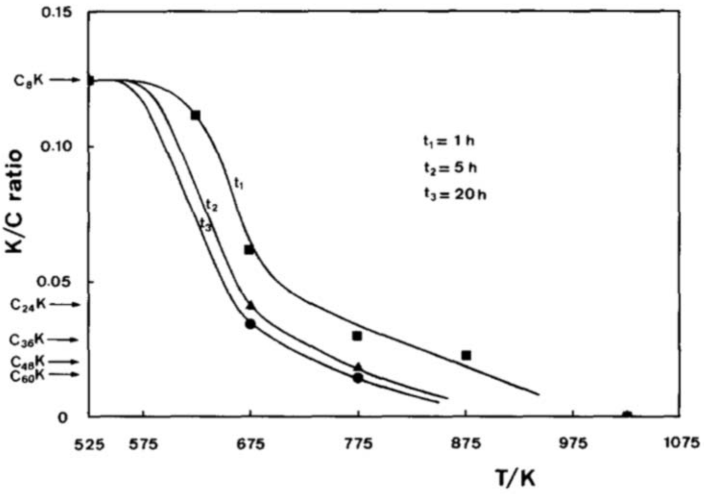

Fig. 2. Results of the quenching experiments with C_8K; heating times 1, 5 and 20 h.

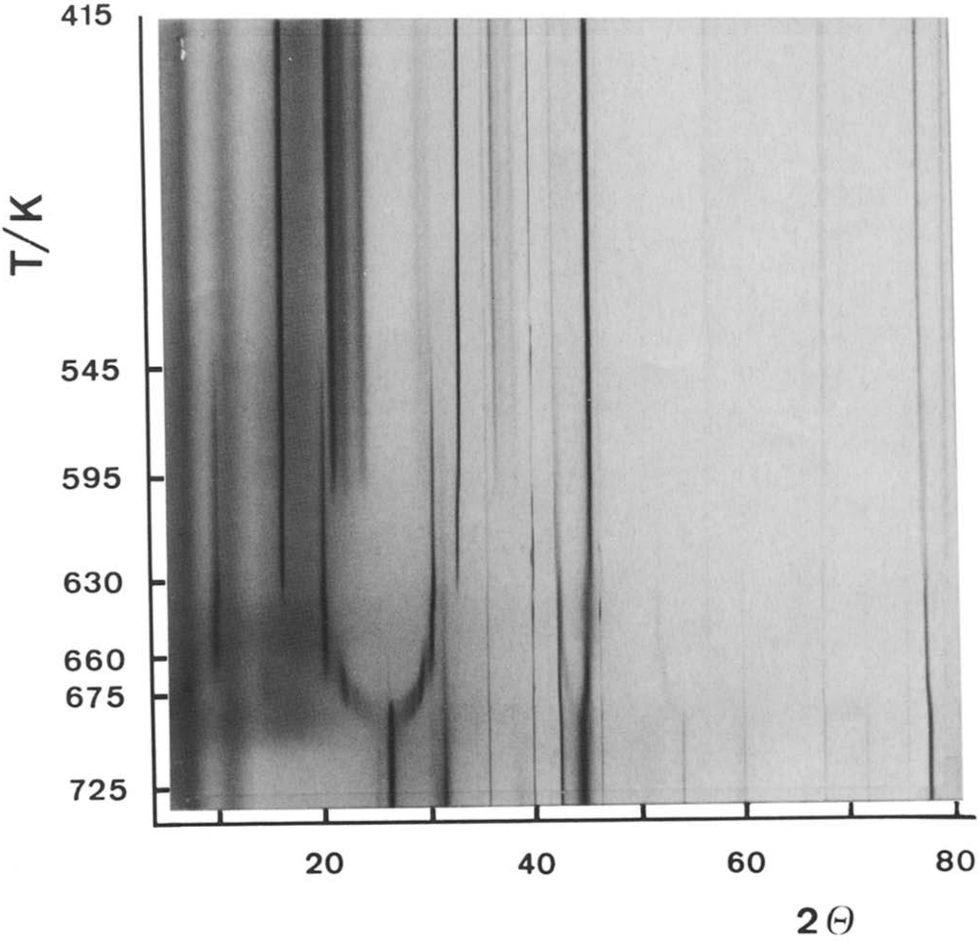

Fig. 3. HTX-pattern of C_8K; heating rate 10 K h^{-1}.

started to lose potassium gradually and at 1025 K again, as in the C_8K case, graphite was the stable compound. However, from Fig. 2 it appears that a sample of C_8K, heated for 1 h at a certain temperature, did not attain equilibrium. To achieve thermodynamic equilibrium the sample has to be heated for at least 5 h and preferably for at least 20 h. The same applies to the compound $C_{36}K$: heating of $C_{36}K$ at 875 K for 1 h yielded a mixture of $C_{48}K$ and $C_{60}K$ (Fig. 1), but heat-treatment at 875 K during 5 and 20 h resulted in complete loss of potassium from the samples (not in Figs. 1 or 2). It is, thus, concluded that above 875 K potassium–graphite intercalation compounds are thermodynamically not stable.

Quenching experiments with intercalation compounds, prepared from activated carbon (treated at 2075 K in argon for 1.5 h) showed the same

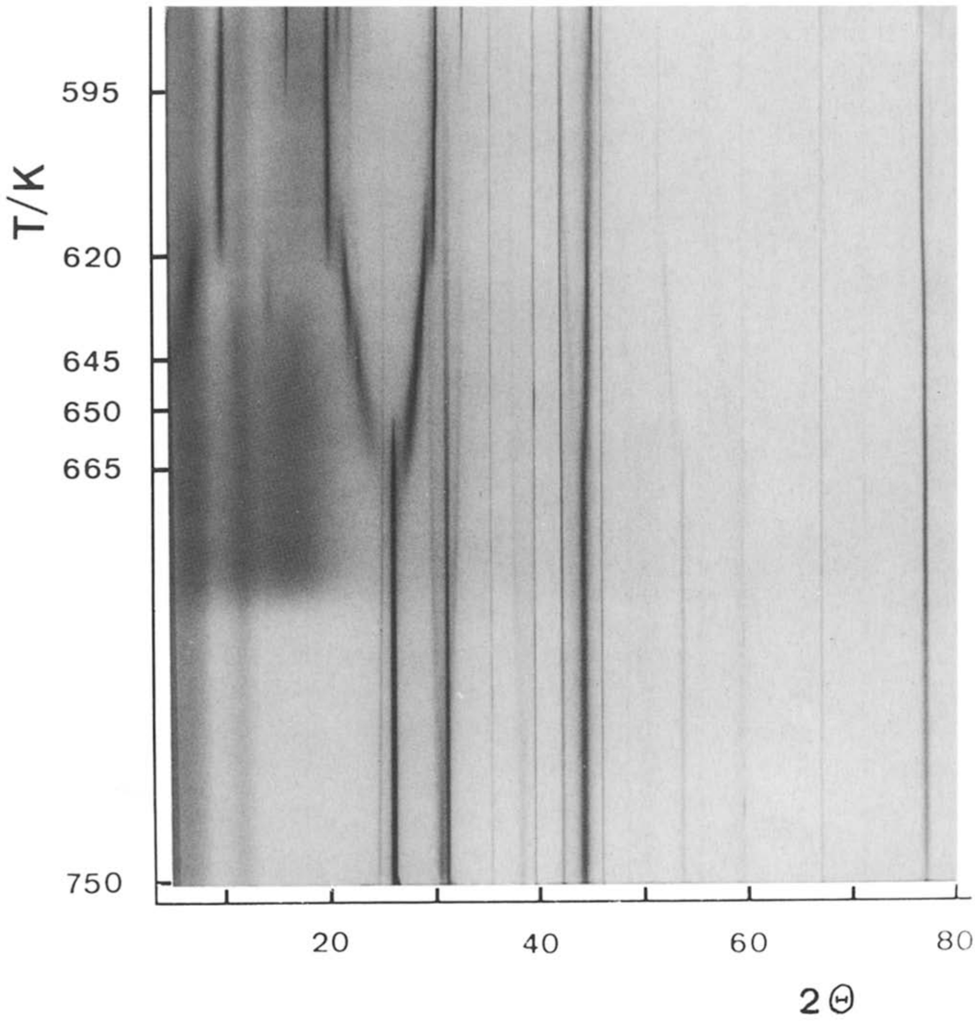

Fig. 4. HTX-pattern of C_8K; heating rate 5 K h^{-1}.

tendency as the experiments with the potassium–graphite samples. The intercalation compounds with activated carbon appear to be thermodynamically less stable than the compounds prepared from graphite.

The in situ HTX-pattern of the compound C_8K is presented in Fig. 3 (heating rate 10 K h^{-1}) and in more detail in Fig. 4 (5 K h^{-1}; separate experiment). The formation of the consecutive higher intercalation compounds (001-reflections at low glance angles), with increasing temperature until potassium has completely disappeared from the sample at about 665 K, and pure graphite is clearly visible. The fact that there is no continuous progress of the 001-reflections to the 002-reflection of pure graphite indicates that C_8K, $C_{24}K$, $C_{36}K$, $C_{48}K$ and $C_{60}K$ are all discrete compounds as concluded before. The temperature areas, in which the separate intercalation compounds are stable according to our HTX-experiments, are reported in Table 1.

From the above it is concluded that intercalation compounds are thermodynamically not stable at the temperatures at which the potassium catalyzed gasification of carbon proceeds (950–1150 K). It can, therefore, be assumed that such compounds will not play a role in the mechanism of the gasification reactions.

The alkali–carbon interaction, determined by means of HTX

To examine the alkali–carbon interaction other than intercalate formation, HTX-experiments were performed with mixtures of K_2CO_3 or Na_2CO_3 with activated carbon. Figure 5 shows the HTX-pattern of a non-pretreated mixture of 30 wt% K_2CO_3/70 wt% activated carbon. The heating rate was 25 K h^{-1}. At ~ 700 K the transition from monoclinic to hexagonal K_2CO_3 is visible. It is most remarkable that the K_2CO_3-reflections disappear at a much lower temperature than the melting temperature of pure K_2CO_3 (1163 K); all reflections have completely disappeared at 940 K with the exception of the Pt-reflections from the platinum sample holder. At 1010 K the carbon background disappears, probably by the oxidation of internally bound oxygen and by the (very low) oxygen partial vapour pressure in the purified helium flow. At the same time the K_2CO_3-reflections reappear with the same intensity as before. So hardly any or no potassium has been lost from the sample in the form of gaseous potassium metal, as would be the case during the carbothermic reduction of K_2CO_3. This would have been removed from

TABLE 1

Temperature areas in which the intercalation compounds are stable, starting from C_8K

Compound	C_8K	$C_{24}K$	$C_{36}K$	$C_{48}K$	$C_{60}K$
Temperature area (K)	up to 595	545–620	610–645	630–650	645–665

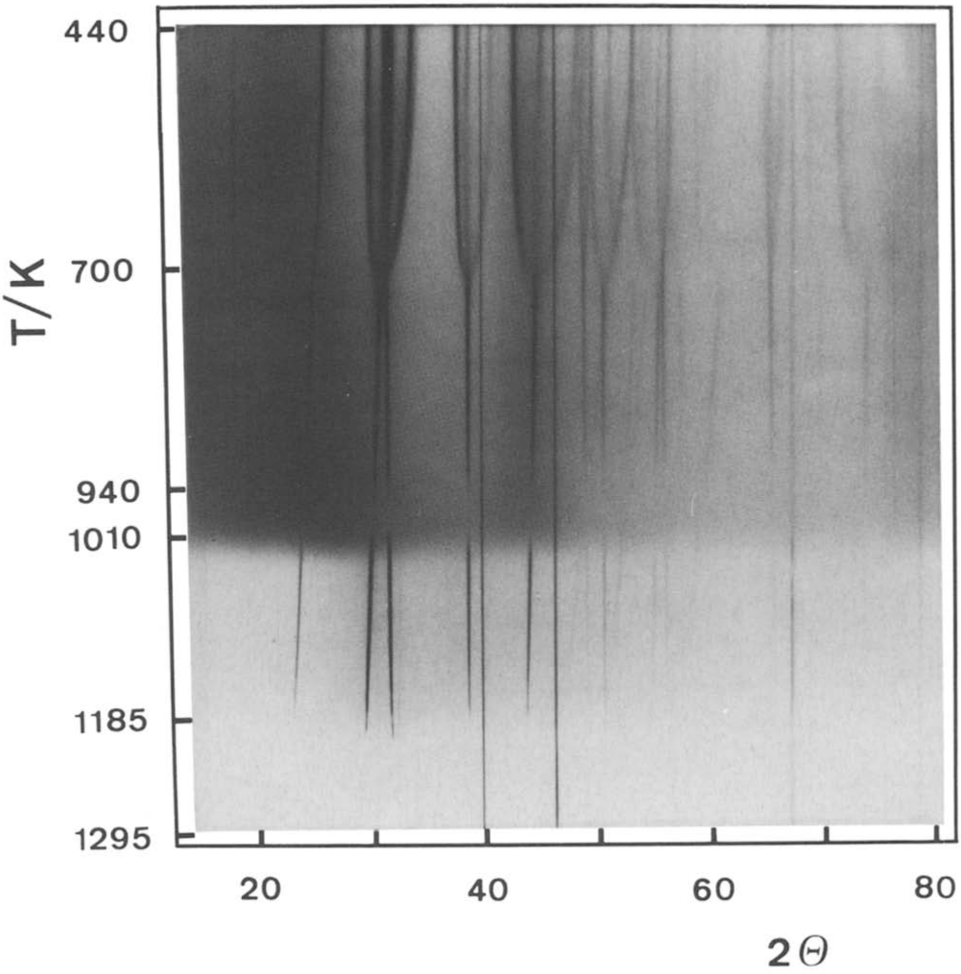

Fig. 5. HTX-pattern of a non-pretreated mixture of 30 wt% K_2CO_3/70 wt% activated carbon; heating rate 25 K h^{-1}.

the apparatus with the helium flow. Ultimately the K_2CO_3-reflections disappear again at the melting point of pure K_2CO_3.

In a separate experiment the disappearance of the K_2CO_3-reflections has been studied in more detail by applying a heating rate of 8 K h^{-1}, starting at 855 K; the result is shown in Fig. 6. It is clearly visible that the intensity of the K_2CO_3-reflections starts to diminish at 885 K and that the reflections have completely disappeared at 920 K. No new reflections have developed.

If the same experiment (heating rate 11 K h^{-1}, starting at 900 K) is carried out with a non-pretreated mixture of 23 wt% Na_2CO_3/77 wt% activated carbon, the carbon background disappears (again) at ~ 1000 K, but without anything happening with the Na_2CO_3-reflections; Na_2CO_3 shows the normal melting behaviour (melting point 1125 K). It is possible that the Na_2CO_3-reflections would have disappeared by the interaction with

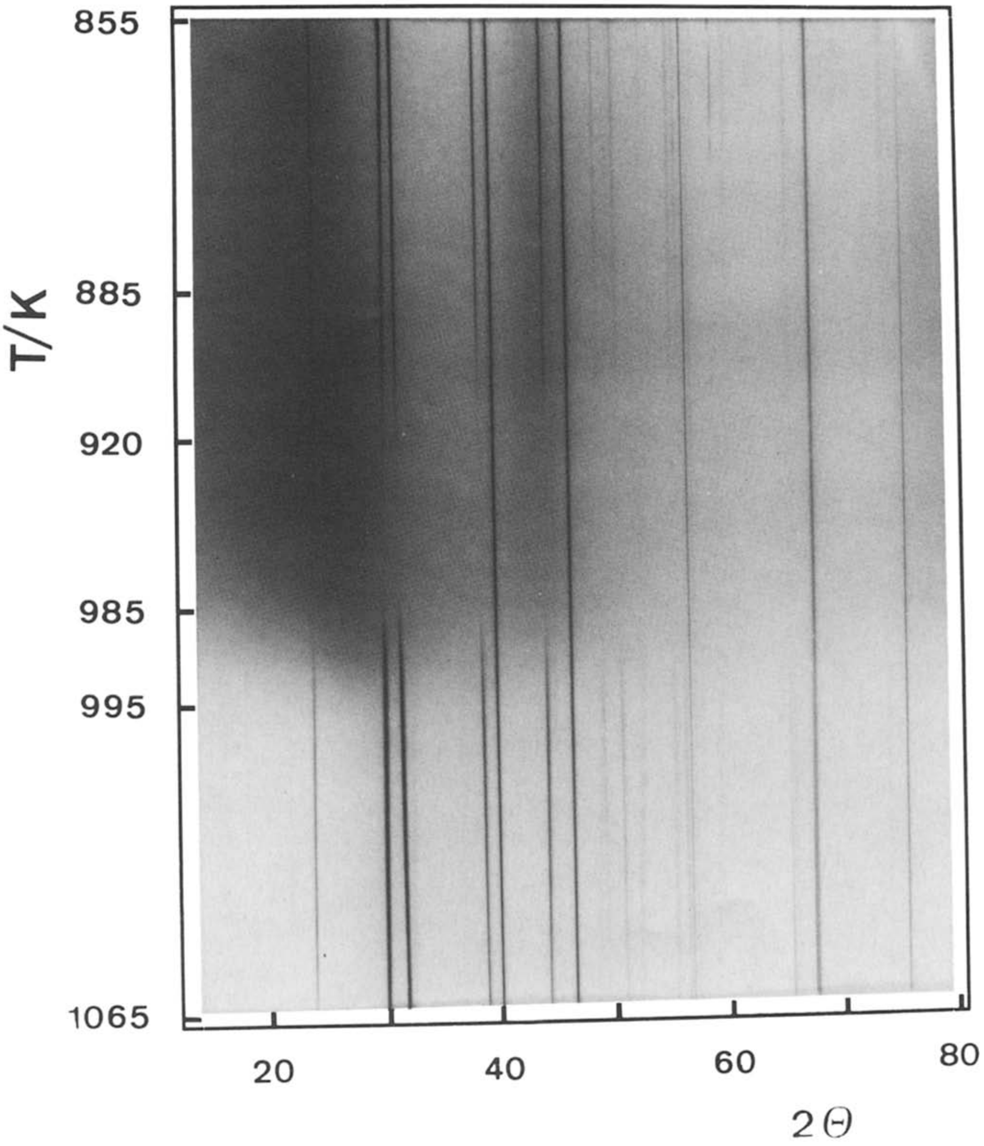

Fig. 6. HTX-pattern of a non-pretreated mixture of 30 wt% K_2CO_3/70 wt% activated carbon; heating rate 8 K h^{-1}.

the carbon at a temperature lower than the melting point of pure Na_2CO_3, but higher than 1000 K. However, above that temperature the carbon has already gone. Hence, the samples were pretreated so that the oxygen level in the system is much lower and, as a consequence, the activated carbon remains present up to temperatures higher than the melting point of Na_2CO_3 as well as of K_2CO_3. This has been attained by drying the K_2CO_3 and Na_2CO_3 at 575 K in argon, by pretreating the activated carbon at 1175 K in argon, and by transferring the samples into the apparatus under exclusion of

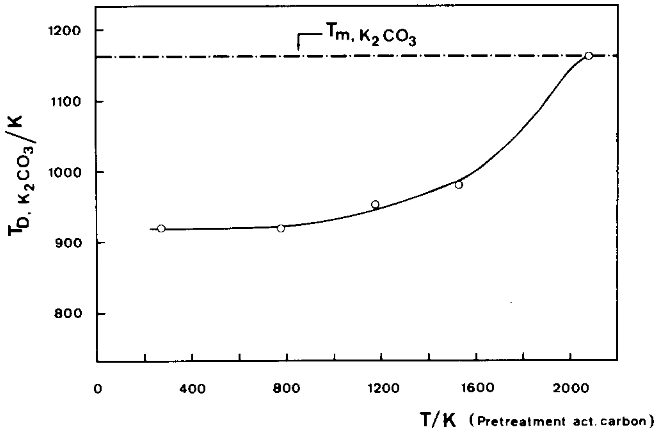

Fig. 7. Influence of the pretreatment temperature of the activated carbon on the potassium–carbon interaction. $T_d(K_2CO_3)$ = temperature at which the K_2CO_3-reflections have disappeared completely; T_m (K_2CO_3) = melting temperature of pure K_2CO_3.

oxygen and water vapour (polyethylene bags). For the K_2CO_3–C sample this treatment had the result that the K_2CO_3-reflections did not disappear at 920 K but at 955 K. For the Na_2CO_3–C sample the Na_2CO_3-reflections now disappeared at 1020 K, largely before the melting temperature of pure Na_2CO_3 was reached.

It is interesting to note that the K_2CO_3-reflections disappear at a much lower temperature (65 K) than the Na_2CO_3-reflections. This might be due to a higher potassium–carbon interaction and might explain the higher catalytic activity of K_2CO_3 compared to Na_2CO_3.

Likewise, the influence of the pretreatment temperature of the activated carbon on the disappearance of the K_2CO_3-reflections was examined; the results are plotted in Fig. 7. The value of T_d (K_2CO_3) increases with increasing pretreatment temperature of the activated carbon. What happens with the activated carbon as the temperature of pretreatment increases? Up to roughly 1300 K the activated carbon will lose oxygen and OH-groups from the surface of the carbon. Then, above 1300 K, graphitization of the carbon takes place which causes a dramatic decrease in the specific surface area of the carbon. Apparently, the disappearance of the K_2CO_3-reflections is caused by the presence of oxygen- and/or OH-groups on the carbon surface which, in turn, is related to the available surface area of the carbon.

CONCLUSION

No intercalation of the alkali metals with the carbon structure can be expected during the alkali-catalyzed carbon gasification. Nevertheless, an interaction of K_2CO_3 (and to a lesser extent of Na_2CO_3) with the activated carbon occurs, probably, via the functional groups on the carbon surface, under the formation of catalytic active sites for the gasification reactions. In Part II of this study the nature of this interaction will be discussed in more detail.

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REFERENCES

1 C.M. Tessi du Motay and C.R. Marechal, Brit. Pat., 2548 (1867).
2 D.W. McKee and D. Chatterji, Carbon, 16 (1978) 53.
3 S. Yokoyama, K. Miyahara, K. Tanaka, J. Tashiro and I. Takakuwa, Nippon Kagaku Kaishi, 6 (1980) 974.
4 C.A. Mims and J.K. Pabst, Prepr. Am. Chem. Soc., Div. Fuel Chem., 25 (3) (1980) 258.
5 W.Y. Wen, Adv. Catal., 22 (1980) 1.
6 T. Wigmans, Catalytic Gasification of Carbon; a Mechanistic Study. Thesis, Amsterdam, 1982.
7 W. Rudorff and E. Schultze, Z. Anorg. Chem., 277 (1954) 156.
8 D.E. Nixon and G.S. Parry, Brit. J. Appl. Phys., Ser. 2, 1 (1968) 291.