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INFLUENCE OF ADDED ALKALINE SALTS ON HYDROGENATION KINETICS OF COAL

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ABSTRACT

This study investigates the catalytic coal hydrogenation reaction in the presence of various alkaline salts. The influence of several parameters (temperature, hydrogen pressure, salt content) was investigated. The experiments were carried out in a thermobalance under pressure. The exhaust gases were analysed by gas chromatography, and the coke residues examined by scanning electron microscopy.

The main conclusion that can be drawn from these investigations is that the presence of alkaline salts considerably increases the hydrogenation rate and yield of the analysed coals, in the efficiency order $K_2CO_3 > Na_2CO_3 > K_2SO_4 > KCl$.

INTRODUCTION

The parameters that influence direct hydrogenation kinetics of coal can be ranked in two categories. The external parameters: temperature, pressure, nature of the preliminary treatment, presence of a catalyst; and the factors inherent to the coal itself: rank, maceral composition, content and nature of the mineral matter, porosity.

This study investigates the influence of several alkaline salts (K_2CO_3, K_2SO_4, KCl and Na_2CO_3) on the hydrogenation rate and yield of low reactivity coals up to 900 °C and under 1–4 MPa.

LITERATURE REVIEW

Numerous studies have dealt with the catalytic influence of metals and salts on carbon and coal oxidation by steam, carbon dioxide and oxygen, at high temperature. Walker et al. [1] gasified under different atmospheres a lignite coke into which metals were introduced by ion exchange. McKee and Chatterji [2–5] studied the catalytic process, and described it as an oxida-

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tion/reduction cycle. The alkaline carbonates react with carbon at about 800 °C, under H_2O, CO_2 or in an inert atmosphere [6].

$$M_2CO_3 + 2C \rightarrow 2M + 3CO$$

The role of the metal obtained from that reaction is a matter of controversy. For some [7], the alkaline metal comes in between the lattice of the graphite. For others [8–10], the reaction yields C_nM complexes. Several authors [10–13] have listed the efficiency order of alkaline metals or salts during coal gasification by H_2O and CO_2. Finally, the EXXON carbon gasification proceeding by steam in the presence of K_2CO_3 should also be mentioned [14,15].

There has been little research into the influence of alkaline salts on the direct hydrogenation of coals at high temperatures, while other catalysts have been the subject of systematic studies. The influence of pyrite was examined by several researchers, whose works are listed in the bibliographical survey of ref. 16. Tamita and Tamai [17] studied catalytic carbon hydrogenation by transition metals. McKee [18] ranked metals into three categories: strong catalysts (Fe, Ni, Co), weak catalysts (Mn, Cr, Mo, V), and those that have no catalytic influence whatsoever (Zn, Ca, Cd, Pb, Ag).

Walker et al. [1] detected an important catalytic influence for Fe and Na, but a negligible one for K and Ca. Various catalysts, which were introduced into the coal by permeation of salts dissolved in a water solution, yielded more or less important results during hydrogenation. Gardner et al. [19] established the following order: $KHCO_3 \approx K_2CO_3 > ZnCl_2$.

EXPERIMENTAL

Samples

For the whole sequence of experiments, a Belgian variety of coal (Beringen) was selected which has a low reactivity rate with hydrogen, and whose characteristics are the following:

elemental analysis: C, 81.2; H, 1.5; O, 7.0; N, 15.0; S, 0.6 (wt%);
oxidized ash yield, 3.4 wt%;
reduced ash yield, 2.4 wt%;
volatile matter on dry, 29.4 wt%;
mineral matter on dry, 3.2 wt% consisting of:
basic ash: $CaCO_3$, 0.39%; $MgCO_3$, 0.08%; $CaSO_4$, 0.06%; Na_2CO_3, 0.17%; K_2CO_3, 0.03%;
acid ash: SiO_2, 1.02%; Al_2O_3, 0.63%; and
iron compounds: Fe_2O_3, 0.50%; FeS_2, 0.30%.

A given weight of coal, which had previously been dried and finely ground, was plunged into a water solution containing a well-defined quantity of an alkaline salt. The mixture was then properly dried, ground, homogenized and compacted into tablets. A fragment of about 100 mg of the tablet was taken to make an attempt at hydrogenation.

Procedure

The experiments were carried out in a thermobalance for use up to 1000 °C and under 5 MPa [20]. The temperature growth amounted to 10 °C min^{-1}. The sample was submitted to hydrogen pressure (1 l min^{-1}) from room temperature upwards. The loss in weight recorded as a function of temperature and time was compensated so as to reach the loss in weight corresponding to coal, while taking into account the decomposition of the salt, and the reaction with carbon of the CO_2 yielded by the carbonates. The loss in weight compensated as above, first as a function of temperature, then time at constant temperature, is expressed as the gasification yield

$$\theta = \frac{P_c}{P_i(1 - C)} \times 100$$

where P_c = compensated loss in weight, P_i = initial weight of coal, C = fraction of reduced ash contained in the coal.

Gases yielded by the reaction were analysed by gas chromatography. The solid residue was analysed by scanning electron microscopy (SEM) and X-ray diffraction.

RESULTS

A first series of experiments was carried out with samples containing 0, 5, 10, 15 and 20% K_2CO_3. They were heated up to 750 °C under 1 MPa of H_2 and maintained at that temperature for 100 min.

Table 1 shows the gasification yield, θ, of these samples. There is a very obvious increase of θ as a function of the K_2CO_3 content. These results are represented graphically by the curves of Fig. 1. Table 1 also shows the actual hydrogenation yield obtained by subtracting the content of volatile matter

TABLE 1

Hydrogenation under 1 MPa at 750 °C

% of K_2CO_3	θ(%)	θ − MV (%)
0	44.9	15.5
5	48.2	18.8
10	54.0	24.6
15	68.3	38.9
20	88.0	58.6

(29.4%) (θ – M.V.) from the gasification yield. It is worth noting that the hydrogenation of coal is actually nearly four times higher in the presence of 20% K_2CO_3 than for coal without any K_2CO_3.

Experiments in the presence of Na_2CO_3 yielded slightly inferior results. Experiments in the presence of KOH did not reveal any catalytic influence. The fact that at 750 °C, practically the whole of the KOH has entered the gaseous phase might account for this.

A series of experiments were also carried out at 750 °C with the addition of 15% K_2CO_3, but under pressures from 1 to 4 MPa. The results obtained are presented in Fig. 2, and they show that an increase in pressure facilitates hydrogenation, just as in the case of pure coal. The losses in weight, which slightly exceed 100% for pressures of 3 and 4 MPa, may be attributed to the volatilization of a certain quantity of K_2O. Indeed, an analysis of the residue by AAS reveals the presence of 60% of the original potassium only, while the other 40% has volatilized.

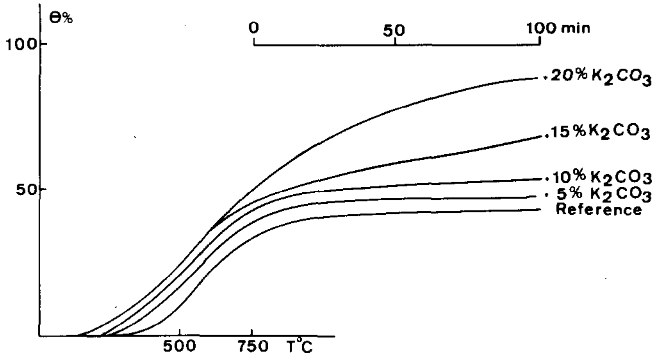

Fig. 1. Influence of the addition of K_2CO_3 on the hydrogenation yield of a variety of coal (750 °C, P_{H_2} = 1 MPa).

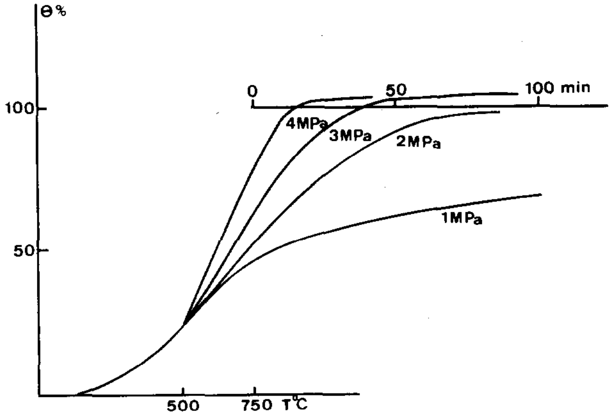

Fig. 2. Influence of pressure on the hydrogenation yield of a coal to which 15% K_2CO_3 was added (750 °C).

In a comparative view, the incorporation of 15% of several alkaline salts was studied in a series of experiments carried out at 800 °C and under 1 MPa of H_2. The results presented in Fig. 3 tend to show that gasification is highest with K_2CO_3.

Finally, the curves of Fig. 4 show the highest gasification yields under 1 MPa of H_2 in the presence of 15% K_2CO_3 for final temperatures varying from 750 to 900 °C.

Hydrogenation rate

Starting from the hydrogenation yield, it is possible to draw curves representing the hydrogenation rate (g g^{-1} min^{-1}).

$$(V_H)_{i+1} = \frac{\theta_{i+1} - \theta_i}{(t_{i+1} - t_i)\dfrac{100 - \theta_{i+1} + \theta_i}{2}}$$

where $(V_H)_{i+1}$ is the hydrogenation rate at time $i+1$ (g g^{-1} min^{-1}), θ_{i+1}

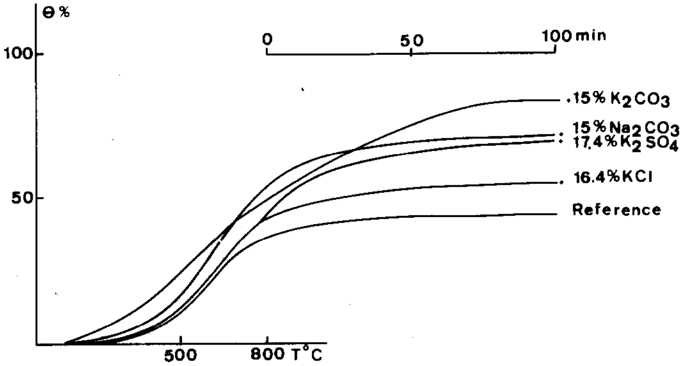

Fig. 3. Hydrogenation yield of a variety of coal at 800 °C and $P_{H_2} = 1$ MPa in the presence of various alkaline salts.

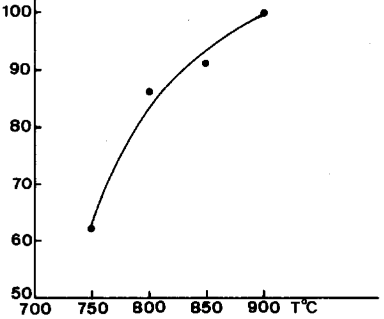

Fig. 4. Influence of temperature on the hydrogenation yield of a variety of coal to which 15% K_2CO_3 was added.

and θ_i are the hydrogenation yield at times $i+1$ and i (%), respectively, and t_{i+1} and t_i are times $i+1$ and i (min), respectively.

Figure 5 makes it possible to compare the curves obtained with pure coal and with coal to which 15% K_2CO_3 was added, for experiments carried out at 800 °C under 1 MPa. In the case of pure coal, one single maximum can be observed at about 500 °C, which corresponds to the volatilization of volatile materials.

For coal permeated with K_2CO_3, a second, more important peak appears at 800 °C, in addition to the first one. At the moment when this peak is recorded, about 50% of the K_2CO_3 that was introduced is decomposed, which indicates that hydrogenation kinetics are facilitated by the decomposition reaction, more than by the intrinsic presence of an alkaline salt.

Gas analysis

Since a considerable excess of H_2 has been used here, the other gases are therefore considerably diluted, which renders quantitative analysis by gas chromatography problematic. In addition to H_2, methane is the only gas to be detected from 500°C upwards whose content grows as a function of temperature. No CO can be detected. This is due to the well-known methanation reaction $CO + 3\ H_2 \rightarrow CH_4 + H_2O$ being catalyzed by K_2CO_3 (EXXON process). With the present experimental conditions, in which 100 mg of coal are treated with hydrogen in excess, there is a complete elimination of CO.

Analysis of the coke residue

SEM demonstrated the uniform repartition of salts permeated by means of the aqueous solution.

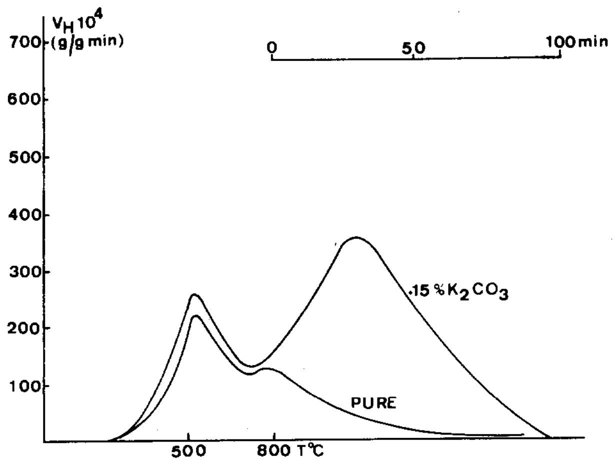

Fig. 5. Hydrogenation rate of a pure coal sample to which 15% K_2CO_3 was added, as a function of time and temperature up to 800 °C.

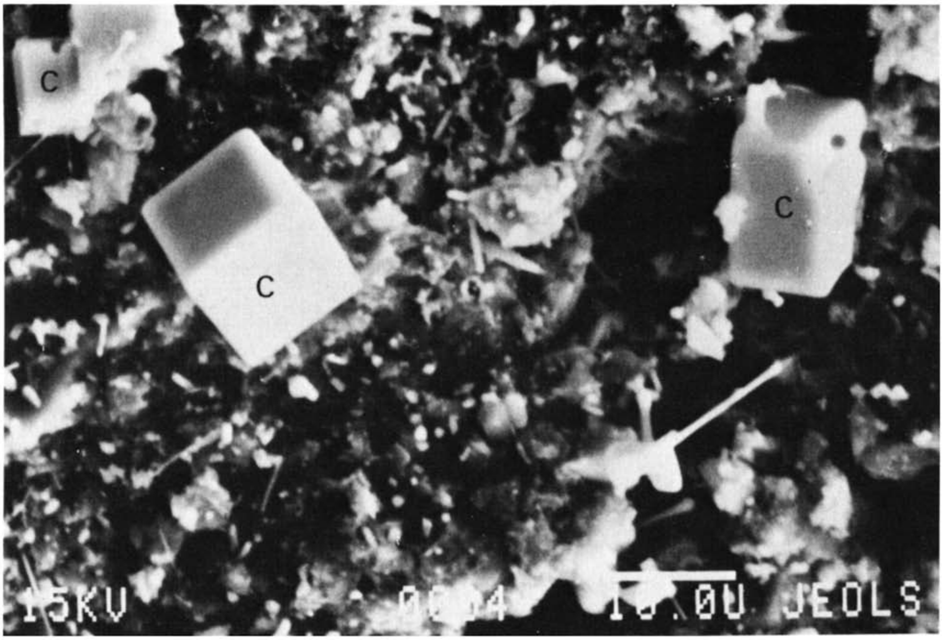

Fig. 6. SEM of the residue of a sample of coal enriched with KCl, after hydrogenation at 800 °C under 1 MPa (C = KCl).

The sample permeated with KCl displays cubic crystals of that salt after hydrogenation at 800 °C (see Fig. 6). X-ray diffraction analysis confirms the presence of KCl, whereas for the cokes obtained from coals enriched with K_2CO_3, the decomposition of the carbonate salt to K_2O is complete. The fact that KCl does not decompose under the present experimental conditions may account for its weak catalytic influence.

CONCLUSIONS

The whole set of results demonstrates that hydrogenation kinetics of low reactivity coal are influenced by alkaline salts in the efficiency order $K_2CO_3 > Na_2CO_3 > K_2SO_4 > KCl$, while KOH has no catalytic influence whatsoever.

It cannot be assumed that there is a proper catalytic reaction in the case of carbonates and sulfates, since it is rather the decomposition of these salts that influences hydrogenation kinetics. Their decomposition seems to play an important part in the hydrogenation process, which might be attributed to a substantial increase in porosity due to the decomposition of those salts at the most opportune moment.

Hydrogenation yield and rate are a function of pressure and temperature, and of the quantity of salt added.

In the case of the coal studied here, and for the very small quantities of coal involved, the presence of 15% K_2CO_3 makes it possible to obtain complete hydrogenation at 750 °C under 2.5 MPa H_2, instead of 900 °C and 4 MPa in the absence of salt.

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