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WCl_6 chemical transformations occurring during pyrolysis and steam activation of coals + WCl_6 mixtures

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Different concentrations of WCl_6 have been added to three kinds of coking coals before their pyrolysis. The rank of the coal and mainly the volatile matters removed during the heat treatment are of great influence on the transformations of tungsten hexachloride. It first reacts with oxygen present in the starting coal to transform into $WO_{2.9}$ between ambient and 550°C. From 550°C to 750° the trioxide is reduced to WO_2 and a fraction reacts with Ca to form $CaWO_4$ as shown by X-ray diffraction. The total amount of W introduced in the initial mixture is recovered in the resulting green-coke and the total amount of chlorine is removed as HCl. After steam activation, WO_2 is oxidised into $W_{24}O_{68}$. © *2000 Kluwer Academic Publishers*

1. Introduction

For many years, the pyrolysis of coal in the presence of metal chlorides has been studied [1–4]. It has been shown that Lewis acids such as $ZnCl_2$, $AlCl_3$ and $FeCl_3$ can drastically influence the chemical reactions occurring during the coal (or coal tar pitch) carbonization [5–8]. It is well known that coal pyrolysis generates complex reactions depending on many parameters [9] and involving different transformations of the coal during the temperature increase. These transformations are accompanied by the removal of many volatile compounds such as H_2, CH_4, CO, CO_2 and also heavier tars [10–13]. It is generally admitted that the Lewis acid provokes an increase of the green-coke yield, a decrease of tar production and a great increase of H_2 production. In a recent paper, Alain *et al.* [14] have shown that the addition of 5 wt% of $FeCl_3$ increases by more than 20% the transformation rate of a coal tar pitch into green-coke.

One of the aims of such co-pyrolyses is to introduce the metallic heteroelement into the carbonaceous matrix of the green-coke which will then be activated to open its porosity. We have shown [15] that in the coal-$FeCl_3$ system, the so pyrolysed and activated mixtures present a homogeneous dispersion of the iron in the activated coke and are thus of interest for trapping sulfur compounds or for NOx reduction. According to the hetero-element, activated carbons can also be used as a catalyst support because of their high surface area [16, 17]. They are generally synthesized by direct impregnation of a salt in solution (Ni or Co nitrate for instance) in the active carbon which is then dried and heat treated [18, 19]. To decrease the number of steps (pyrolysis, activation, impregnation, heat treatment) we propose in this study to co-pyrolyse a mixture of coal + WCl_6 and then to activate it. Different kinds of coals have been selected as a function of their rank and in this paper we have observed during the different heat treatments the transformations of WCl_6 which is much more oxygen sensitive than $FeCl_3$ for instance.

We shall first study the influence of the coal rank and that of the final temperature pyrolysis on the WCl_6 transformations. The tungsten compounds will be charaterized before and after steam activation by X-ray diffraction, then by scanning and transmission electron microscopy.

2. Experimental

Three kinds of coking coals have been used in this study: one from a French mine (La Houve), one from Poland (Jastrzebie) and the last from USA (Pinnacle): their main characteristics are described in Table I: the coal of lowest rank is La Houve (it has the lowest carbon content and the highest content of volatile matter) and that of highest rank is Pinnacle (high carbon content and low content of volatile matter).

The mixtures were made by dry milling under nitrogen atmosphere for 15 minutes in a planetary ball mill (Fritsch Pulverisette 7) in a steel vial (50 cm^3) with seven steel balls (12.7 mm). Particle size of the mixture was lower than 40 μm.

Coal and tungsten chloride (Aldrich-purity >99.9%) mixtures were pyrolysed in a vertical open reactor under a stream of nitrogen as described elsewhere [7] at final temperatures comprised between 550 and 750°C.

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TABLE I Elemental analyses (wt%) of the three investigated coals

Coal	C (%)	H (%)	S (%)	Cl (ppm)	Moisture (%/dry)	Ash (%/dry)	Volatile matter (%/dry)
La Houve	75.4	5.01	0.96	0.23	2.5	5.1	37.2
Jastrzebie	81.9	4.7	0.6	0.08	1.2	6.9	28.5
Pinnacle	86.6	4.16	0.74	0.06		15.9	16.7

WCl_6 concentrations used for the mixtures were 2, 5 and 10 wt%. Heating rate was 5°C/min and soaking time at the final temperature 2 h. After cooling to room temperature, steam activation was performed as follows: the green-coke was heated to 800°C (5°C/min) under a flow of argon and steam activated (100% water vapor) at this temperature in a thermogravimetric apparatus up to a burn-off level of 50%.

Elemental analyses were carried out at the CNRS (Vernaison France). X-ray diffraction was performed with a curved detector associated with a rotating target X-ray generator (Rigaku-10 kW, with a Mo K_α source). The scanning electron microscope (SEM) was a 2500 Hitachi fitted with a dispersive X-ray spectrometer (EDS Quantum). The green-coke powder sample is deposited on a support which is then covered by a thin film of carbon. Transmission electron microscope (TEM) was a CM 20 Philips associated with a Electron Energy Loss Spectrometer (EELS). The sample is dispersed by ultrasound in an alcohol solution, then deposited on a copper grid and finally the alcohol is evaporated.

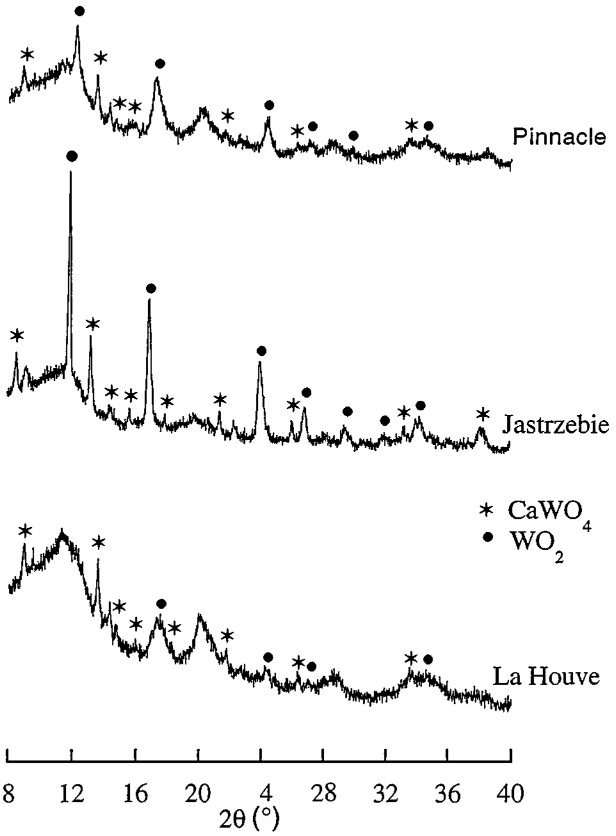


Figure 1 XRD patterns (Mo K_α radiation) of the green cokes obtained after pyrolysis of the three varieties of coal mixed with WCl_6 (10 wt%).

3. Results

The first experiments were realized by mixing 10 wt% WCl_6 with the three kinds of coal and these mixtures were then pyrolysed at 750°C. We describe in table 2 the green-coke yield (ratio of green-coke mass to initial mixture mass) of the three pyrolysed coals in the presence or absence of tungsten chloride. If we consider the raw coal, we see that the yield is higher when the coal rank is high (Pinnacle), which must be related to its lower volatile matter content (see Table I). The presence of WCl_6 does not significantly influence the green-coke yield if we do not take into account the tungsten mass in the green-coke and that of WCl_6 in the initial mixture. However, in a previous study [20], we have shown that in the coal-$MoCl_5$ system the pyrolysis mechanism was strongly modified according to the rank of the coal because of their different volatile matter contents and also their plastic phase range area.

TABLE II Green-coke yields of coal or coal + WCl_6 (10 wt%) after pyrolysis at 750°C

La Houve	La Houve+ WCl_6	Jastrzebie	Jastrzebie+ WCl_6	Pinnacle	Pinnacle+ WCl_6
65.2	65.1	77.2	77.9	85.1	84.1

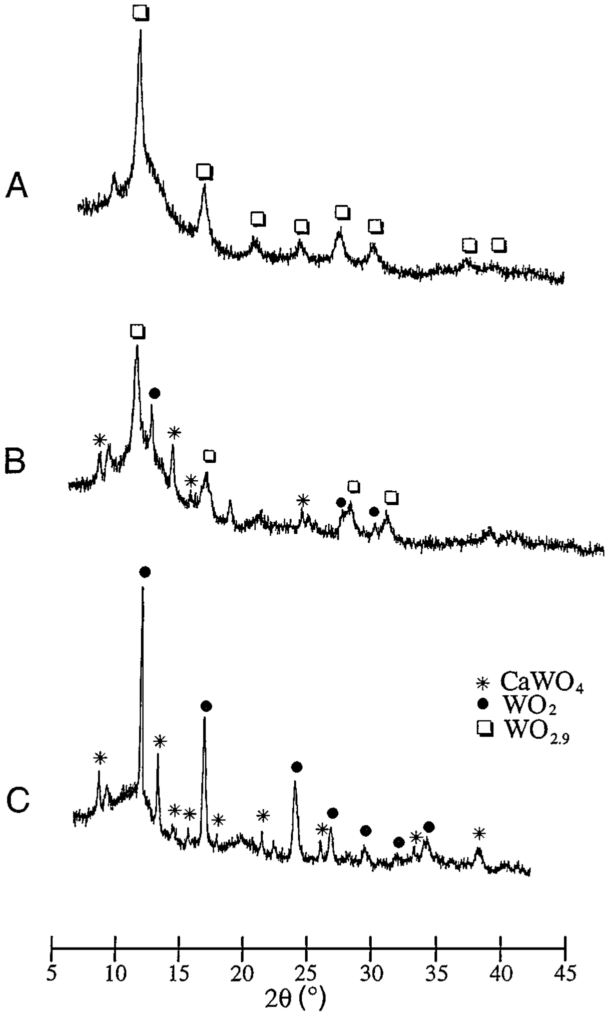


Figure 2 XRD patterns (Mo K_α radiation) of the green-cokes obtained after pyrolysis of the mixture Jastrzebie coal + WCl_6 (10 wt%) at 550°C (A), 650°C (B) and 750°C (C).

X-ray diffraction spectra of the green-cokes are presented in Fig. 1. Two crystallized phases can be identified whatever the initial coal: $CaWO_4$ (Scheelite) and WO_2 (tungsten dioxide) and no tungsten metal diffraction lines can be observed. This result is surprising if we consider the green-coke resulting from the pyrolysis of a mixture of coal + $FeCl_3$ [21]: in this case, αFe was the majority phase and no iron oxide was observed. However, we have to take into account that WCl_6 is very oxygen sensitive and can be easily transformed into tungsten oxide because of the oxygen content which is between 5 and 8% according to the coals used in this study. Moreover, because of the reducing atmosphere generated during pyrolysis, we shall see in the following that small tungsten metal particles have been characterized by TEM.

Whatever the green-coke, the intensities of the scheelite diffraction lines are independent of the nature of the coal. this is not the case if we consider WO_2: its diffraction lines are more intense and sharper in the case of the green-coke obtained from the pyrolysis of Jastrzebie coal. This suggests that this oxide is better crystallized as will be confirmed in the following by SEM. For comparison, Jolly [5] has also observed that in the pyrolysed coal-$ZnCl_2$ mixtures, ZnO was better crystallized when the coal was from an intermediate rank.

In the following, we shall try to explain the different steps of the transformation of WCl_6 into different oxides during pyrolysis with a final temperature comprised between 550 and 750°C, and for the above reasons, Jastrzebie has been chosen as initial coal.

3.1. Thermal transformations of WCl_6 during pyrolysis

The final pyrolysis temperature is an important parameter in explaining the physico-chemical mechanisms involved during the heat treatment of the mixture. For instance, the first removal of dihydrogen and methane occurs at 500°C and that of carbon mon(or di-)oxide at 600–650°C [6, 22]. In Fig. 2 are represented the X-ray diffractograms of the green-coke resulting from the Jastrzebie coal-WCl_6 10 wt% mixtures pyrolized at 550, 650 and 750°C.

TABLE III Elemental analyses (wt%) of green-cokes obtained after pyrolysis of coal + WCl_6 (at different concentration) at various final temperature

Jastrzebie	C	H	W	Cl
750°C				
10%	81,78	1,21	5,30	<0,20
5%	86,12	1,13	2,25	<0,20
2%	87,31	1,16	1,06	<0,20
650°C				
10%	81,31	1,78	5,32	<0,20
5%	84,33	2,08	2,90	<0,20
2%	86,44	1,80	0,65	<0,20
550°C				
10%	79,83	2,55	5,15	<0,20
5%	83,64	2,50	2,20	<0,20
2%	84,56	2,47	0,82	<0,20

At 550°C (Fig. 2A), diffraction lines allow identifying only one variety of tungsten oxide: $WO_{2.9}$ which crystallizes in the same space group as WO_3 (P4/nmm) but with a lack of oxygen. At 650°C (Fig. 2B), three phases are observed: $WO_{2.9}$ (with a decrease of the diffraction line intensity), WO_2 and $CaWO_4$. At 750°C (Fig. 2C), diffraction lines corresponding to $WO_{2.9}$ have disappeared and those corresponding to WO_2 and $CaWO_4$ are more intense. In a first step, the oxidation level of W is six then decreases to four when the

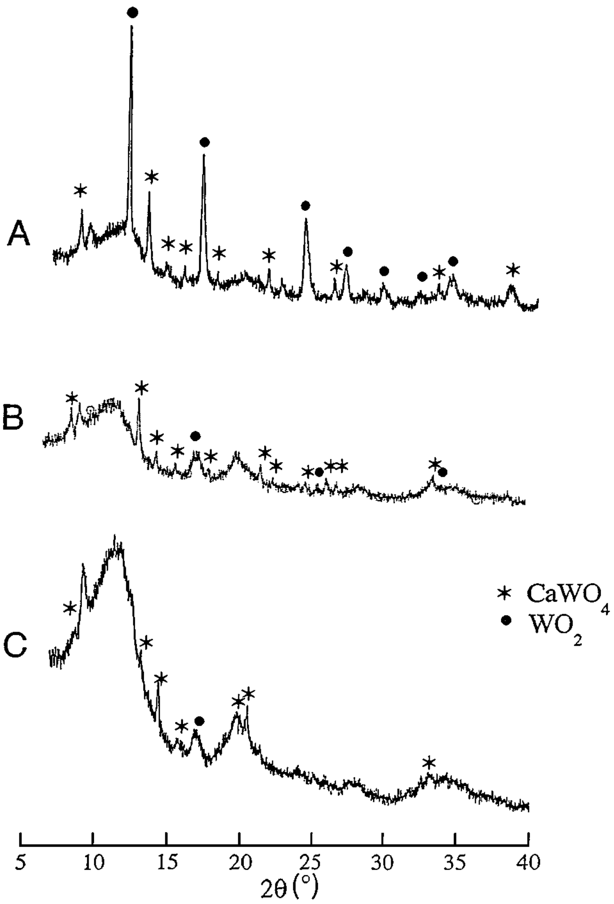


Figure 3 XRD patterns (Mo K_α radiation) of the green-cokes obtained after pyrolysis at 750°C of the mixture Jastrzebie coal + WCl_6 2% (A), 5% (B) and 10% (C).

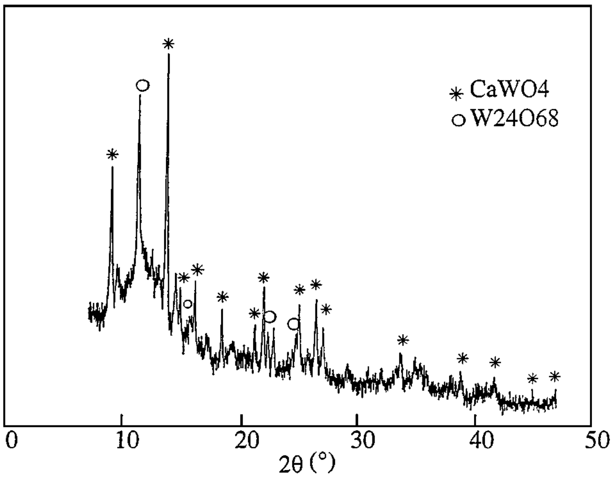


Figure 4 XRD pattern (Mo K_α radiation) of the green-cokes obtained after pyrolysis at 750°C of the Jastrzebie coal + WCl_6 (10%) mixture then steam activated at 800°C (burn-off level = 50%).

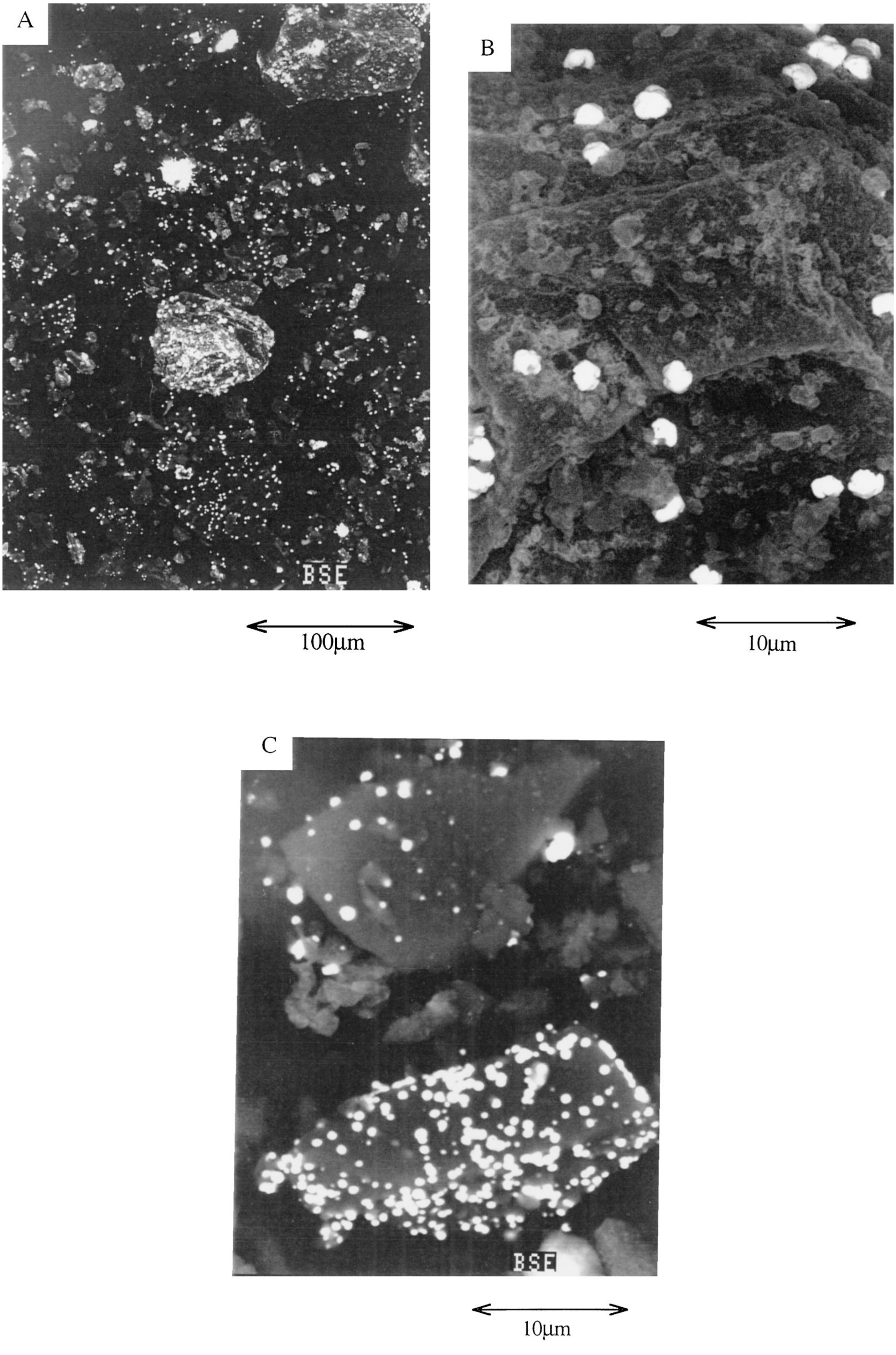


Figure 5 SEM micrographs of coal + WCl_6 (10 wt%) pyrolysed at 750°C. A: Jastrzebie: general view; B: Jastrzebie: WO_2 crystals are in white on the green-coke particle; C: Pinnacle: smaller WO_2 crystals.

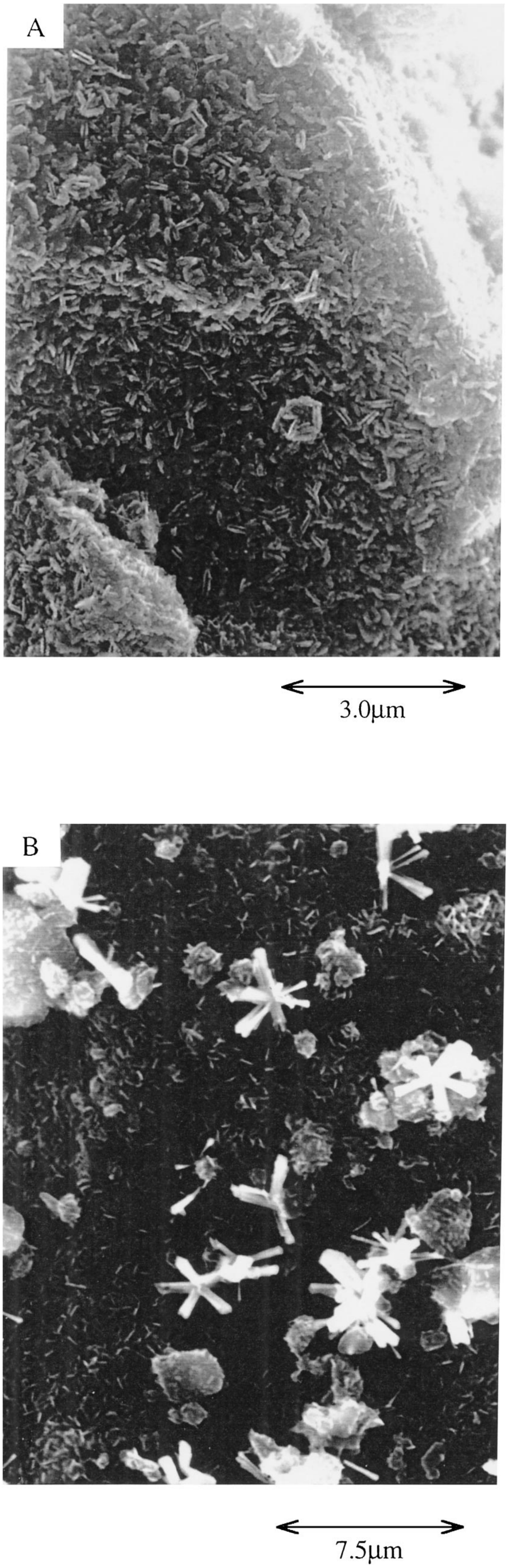


Figure 6 SEM micrographs of Jastrzebie coal + WCl_6 (10 wt%) pyrolysed at: A: 550°C, $WO_{2.9}$ crystals can be seen; B: 650°C: $WO_{2.9}$ and WO_2 star-like crystals.

temperature is increased from 550 to 750°C. At the same time, $CaWO_4$ appears (oxidation level VI) which results from the reaction of $WO_{2.9}$ with the calcium present in the initial coal.

In Table III, we present the elemental analyses of the green-cokes obtained after pyrolysis of the mixture at the three final temperatures. Carbon content increases with temperature and that of hydrogen decreases as typically observed during the pyrolysis of any coal. The tungsten content is rather stable (taking into account experimental analysis errors) and corresponds to the amount of tungsten introduced in the initial mixture as WCl_6. However, all chlorine is removed by 550°C.

4. Discussions

From ambient temperature to 550°C, tungsten hexachloride successively transforms upon heating into $WOCl_4$, WO_2Cl_2 and finally $WO_{2.9}$ because of the presence of oxygen in the coal; its oxidation level is always equal to six. At the same time, chlorine is removed as HCl which has been evidenced by acidimetric measurements. This experiment has shown that HCl removal occurs between 200 and 600°C with a maximal rate at 350°C. More than 90% of the chlorine initially introduced in the mixture as WCl_6 has been removed as HCl during pyrolysis and this observation agrees with its absence in the green-coke (see Table III).

We have carried out an experiment with the pyrolysis of a mixture of pure anthracene ($C_{14}H_{10}$) + WCl_6 (10 wt%) at 750°C to avoid the oxygen presence in the

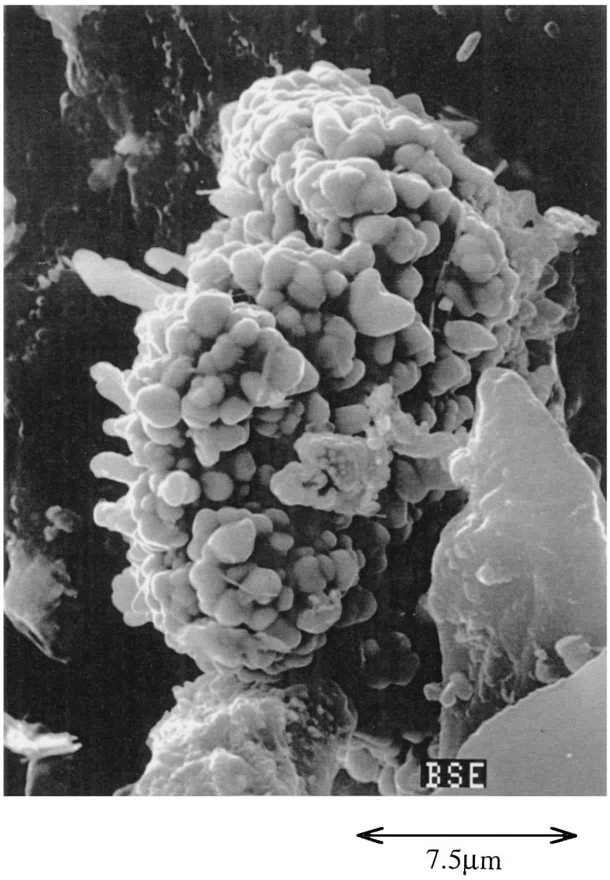
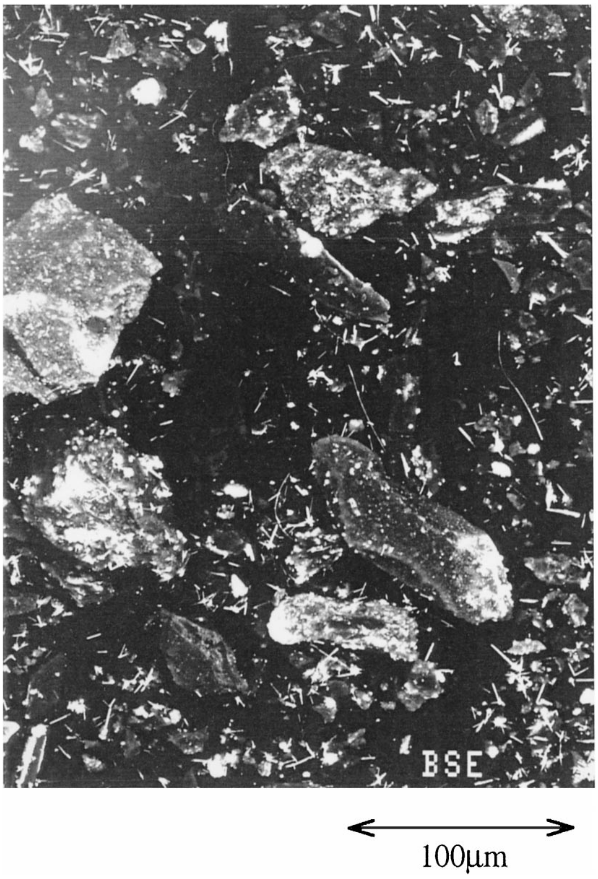
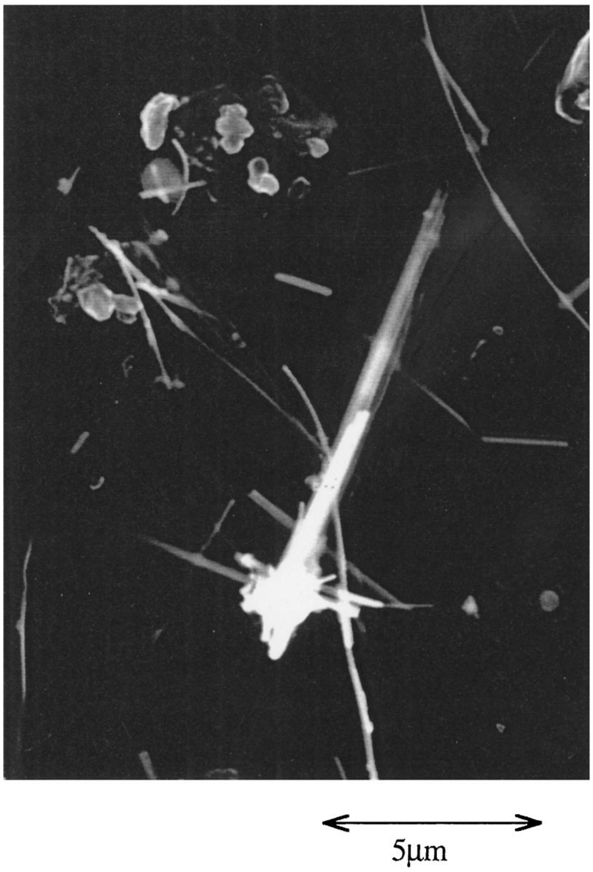


Figure 7 SEM micrograph of scheelite ($CaWO_4$) crystals.



(A)



(B)

Figure 8 SEM micrograph of Jastrzebie coal + WCl_6 pyrolysed at 750°C then steam activated at 800°C (burn-off = 50%). A: general view; B: $W_{24}O_{68}$ needle.

initial coal. The removal of HCl occurs in the same temperature range as in the case of the coal-WCl_6 mixture, but the tungsten is completely reduced to W(0) at 750°C. In the two cases (anthracene or coal), gases removed during the pyrolysis generate a reducting atmospher (H_2, CH_4, and also CO in the mixtures with coal). However, from 550 to 750°C, we have shown that $WO_{2.9}$ was reduced to WO_2 (the case of scheelite is different because of its high thermal stability and will be studied further). Elyuntin and Pavlov [23] have shown that WO_3 reduction in the presence of CO was very weak at 750°C: consequently, CO is not responsible for the reduction of $WO_{2.9}$ to WO_2. Schubert [24] and Zhengjï [25] have studied the WO_3 reduction by dihydrogen: they have shown that by 500°C the oxidation level of W(VI) decreases; their reactions [24, 25] can be written:

$$500^\circ\text{C}–575^\circ\text{C}: WO_3 \rightarrow WO_{2.9}$$

$$575^\circ\text{C}–650^\circ\text{C}: WO_{2.9} \rightarrow WO_2$$

(including a small temperature range near 575°C where $WO_{2.9} \rightarrow WO_{2.72}$) 650°C–725°C: Stability domain of WO_2.

These authors also identified a small amount of metallic tungsten in this last temperature range.

The limits of these temperature ranges can vary according to the dihydrogen pressure, and the reactions described by these authors were carried out with a dihydrogen stream of 3l/min. The compounds we have identified by X-ray analyses as a function of the pyrolysis temperature are the same as those indicated in ref [24, 25].

4.1. Formation of the scheelite ($CaWO_4$)

The scheelite observed at 650°C in the green-coke was rather unexpected at this temperature. Indeed, Flor *et al.* [26] have shown that the reaction between WO_3 and CaO giving $CaWO_4$ occurs only between 800 and 1000°C. However, Balarev and Nikolov [27] have studied the scheelite formation from WO_3 and calcium carbonate according to the following reaction:

$$CaCO_3 + WO_3 \rightarrow CaWO_4 + CO_2$$

After grinding and mixing the two initial compounds, they observed a beginning of CO_2 removal at 600°C, attesting to the scheelite formation. We have not tried to characterize the Ca compound in the initial coal because of the very low Ca content: for instance the CaO mass percentage in the La Houve coal ashes is 4% and the ash content in the coal is 5.1%, i.e., about 0.2% of CaO or 0.15% of Ca in the initial coal. Taking into account the molar mass of W and Ca, 0.67 wt% of W in the mixture will be needed to saturate the calcium, if we consider that the total amount of the calcium present in the coal will react with W. In this case, it will be necessary to introduce 1.44 wt% of WCl_6 into the mixture. The

Jastrzebie coal ash content is equal to 6.9%: in this case, about 2% of WCl_6 will be used for this reaction.

This hypothesis is confirmed by X-ray diffraction as can be seen in Fig. 3. Indeed, in the green-coke obtained after the pyrolysis of the coal + 2% WCl_6 mixture (Fig. 3C), the diffraction lines corresponding to the scheelite are the most intense and only a small diffraction line characterizing WO_2 is detectable. If the amount of WCl_6 is increased (Figs 3B and 3A with respectively 5 and 10% of WCl_6), the diffraction line

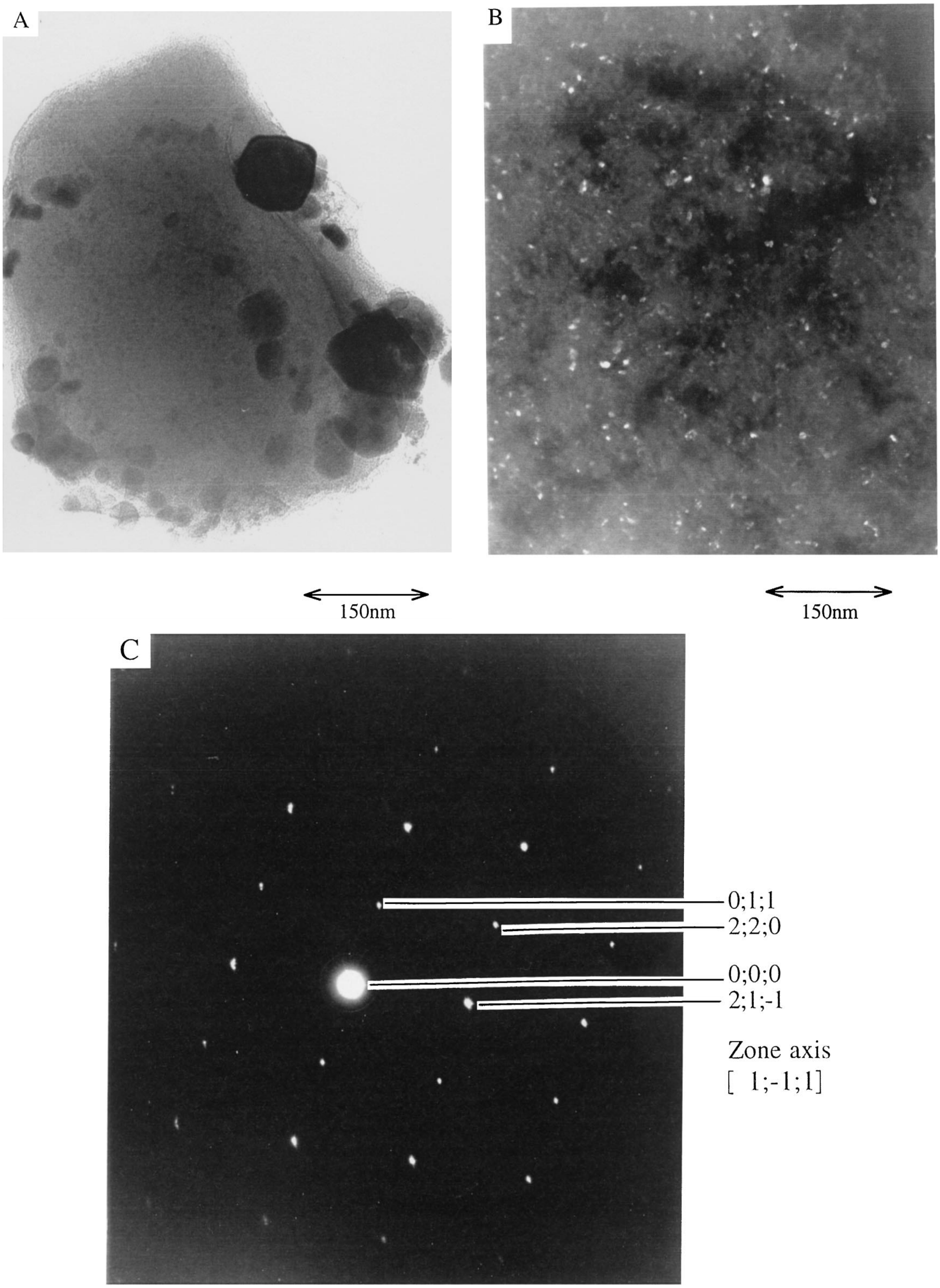


Figure 9 TEM micrographs of: (A) WO_2 particles, (B) WO_2 nanoparticles (dark field) and (C) WO_2 diffraction pattern with zone axis [1; −1; 1].

intensity corresponding to WO_2 increases in the resulting green-coke and that of scheeltie is rather stable, which agrees with our hypothesis.

4.2. Influence of steam activation

Steam activation allows opening the green-coke porosity and thus the accessibility of the tungsten active sites. This work was carried out in collaboration with the laboratory of Prof. T Siemieniewska in Wroclaw (Poland) and the porous texture of the green-coke before and after activation will be described in a forthcoming paper. The two main parameters of this treatment are the activation temperature (800°C) and the burn-off level (50%). Fig. 4 represents the diffractogram of a Jastrzebie coal + WCl_6 10% mixture pyrolysed at 750°C, then steam activated in the previously described conditions. Scheelite is always present in the so treated green-coke, but diffraction lines corresponding to WO_2 have disappeared. A new phase can be identified as $W_{24}O_{68}$ ($WO_{2.83}$): this oxidation of WO_2 is a consequence of the oxidizing atmosphere generated by the water vapor during activation. In a similar treatment, Begin *et al.* [28] have shown that αFe and FeS were oxidized into magnetite (Fe_3O_4) during steam activation. Further works will be made to study the catalytic properties of these activated green-coke.

4.3. Electron microscopy characterization

A more detailed study has been carried out by SEM and TEM to characterize at a micro (-nano) scale the green-cokes resulting from the pyrolysis of the mixtures of different coals with 10% of WCl_6.

4.3.1. SEM observations

Fig. 5A represents a mixture of Jastrzebie coal + WCl_6 carbonized at 750°C and shows the homogeneous dispersion of tungsten (in white) on the green-coke particles. On a larger scale (Fig. 5B) we observe the crystals of WO_2 at the surface of the green-coke and their size is close to 2 μm. Fig. 6A presents the same mixture pyrolysed at 550°C: the $WO_{2.9}$ particles are homogeneously distributed on this green-coke grain and have a stick shape. Their size are close to 0.3–0.4 μm. At 650°C (Fig. 6B) these $WO_{2.9}$ sticks gather to form "stars" which transform to WO_2 because of the reducing atmosphere generated during the pyrolysis. It seems that WO_2 growth occurs in several directions before transforming into crystals as can be seen in Fig. 5B.

Fig. 7 presents a particle of $CaWO_4$ (about 10 μm wide). In the green-coke resulting from the Jastrzebie coal, their diameter can reach a value greater than 25 μm. These particles are well crystallized and this is the reason why the corresponding X-ray diffraction lines are so sharp and intense.

It seems that the nature of the starting coal is of great influence as already described by X-ray diffraction. Thus, in Fig. 5C representing a (Pinnacle coal + WCl_6) mixture pyrolysed at 750°C , we can see that the WO_2 particle size (typically 0.5–1 μm) is much lower than in the case of Jastrzebie. This observation agrees with the presence of WO_2 diffraction lines which were more intense and sharper in the case of the Jastrzebie coal (Fig. 1).

After steam activation, we have shown by X-ray diffraction that WO_2 is transformed into $W_{24}O_{68}$. These particles are needle shape as already observed by Schubert [24] and Taskinen [29] and always homogeneously dispersed in the activated green-coke (Fig. 8A–B). Their length can reach values as high as 10 μm and the needles are twinned as confirmed by TEM observations (not represented here).

4.3.2. TEM observations

Fig. 9A represents some WO_2 particles: their size can vary from 10 nm to more than 0.1 μm. A diffraction pattern (zone axis [1; −1; 1]) of such a crystal has allowed confirming its space group ($P2_1/n$) and we have indexed three spots in Fig. 9C. However, the WO_2 particle size can also reach a nanometric scale as can be seen in Fig. 9B which is a dark field micrograph (WO_2 particles are black). Their diameter in this case is equal to 3–5 nm for the smallest, and these nanoparticles are characterized by some ring diffraction patterns not presented here. This observation is of a great interest in the final product which could present interesting catalytic propereties, providing of course that these active sites are accessible.

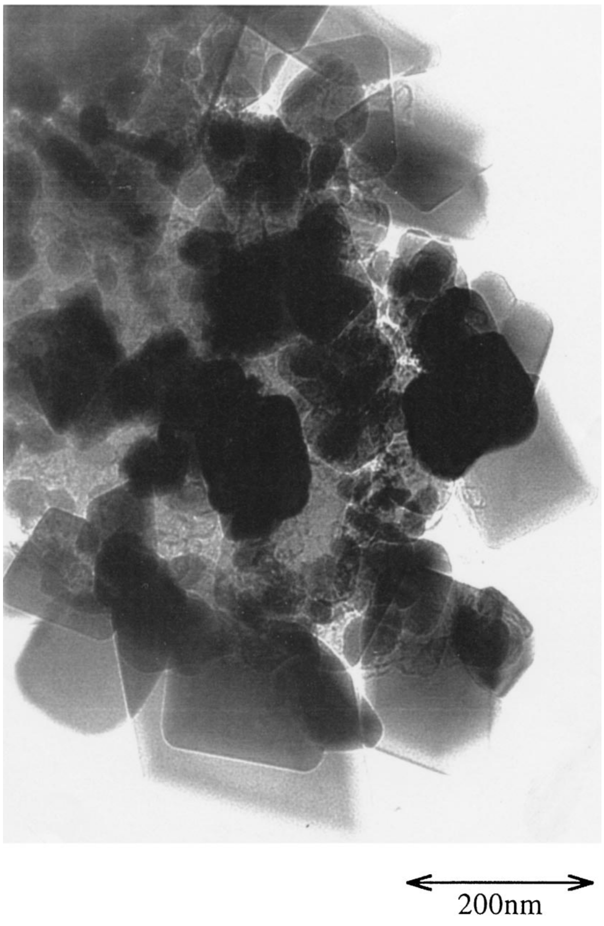


Figure 10 TEM micrographs of a $CaWO_4$ particle (A) and its diffraction pattern (zone axis: [18; −7; −1]).

A fraction of a $CaWO_4$ particle is also presented in Fig. 10A: we can see that it is made of many small crystallites. A diffraction pattern allows determining their space group ($I4_1/a$) which has been calculated according to the zone axis [18; −7; −1]. Three spots have also been indexed.

Many observations have been made by TEM and we have sometimes been able to identify some metallic tungsten particles (diameter close to 0.5 μm) in the green-coke pyrolysed at 750°C: this observation is in agreement with Schubert [24] and Zhengji [25] who indicate the presence of this metallic phase after WO_3 reduction at 725°C.

5. Conclusions

The pyrolysis of a mixture of coking coal + WCl_6 involves many reactions of the coal during its transformations in green-coke as it is well known. The rank of the coal and consequently the quantities of the different volatiles removed such as H_2, CH_4, CO... during the temperature increase are of great influence on the different transformations undergone by the tungsten hexachloride. Thus, we have shown that WCl_6 transforms successively into $WO_{2.9}$, then into WO_2 and $CaWO_4$ when the final temperature is increased. Tungsten hexachloride has a great affinity for oxygen and calcium present in the raw coal and this behaviour is very different from that of the coal + $FeCl_3$ system for which it has been shown that most of the iron chloride was reduced into metallic iron. After steam activation, WO_2 is oxidized into $W_{24}O_{68}$.

However, in all cases, the distribution of the metallic element is homogeneous in the final activated green-coke which presents a specific surface area greater than 800 m^2/g. The next step will be devoted to studying the catalytic properties of such compounds and the nanoparticles of tungsten might be very interesting if they are accessible of course.

Acknowledgements

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