INFLUENCE OF THE ATMOSPHERE IN THE CHEMICAL ACTIVATION OF WOOD.

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INTRODUCTION

A challenge in the adsorbent carbons field is the obtaining of materials, with given pore size distribution and specific surface properties, from low cost precursors and at low temperature. Chemical activation of wood by phosphoric acid appears to be an interesting process for reaching this target [1]. It is well known that phosphoric acid acts as an inhibitor of carbon oxidation [2], therefore it can play an important role in this procedure.

Usually carbons activated by phosphoric acid are prepared under mixture of gases such as oxygen, nitrogen, carbon dioxide and steam. The aim of the present work is to establish the influence of these different gases on the chemical and textural chracteristics of chemically activated carbons. Finally, mechanisms of the chemical activation by phosphoric acid will be proposed.

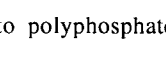
EXPERIMENTAL

The wood was ground below 20 µm and mixed with a 75% phosphoric acid aqueous solution in order to reach the following proportions: wood flour 25.6%, anhydrous P_2O_5 38.6% and H_2O 35.8%. The wood-acid mixtures were heated up to 480°C in a vertical furnace (Pyrox VK) under 20 l/min flow of various atmospheres (N_2, CO_2, and air). The heating conditions were a 30°C/h ramp and a 1 hour plateau at the final temperature. In the particular case of H_2O, the steam was introduced at 400°C with nitrogen as a carrier, the beginning of the pyrolysis being carried out only under nitrogen flow. Excess phosphoric acid was eliminated from the solid products by Soxhlet extraction using water as a solvent. The purifed chars were analyzed by ^{13}C NMR with magic-angle spinning (MAS) and ^{31}P NMR respectively at 90.5 and 145.7 MHz using a BRUKER MSL 360 spectrometer operating at 8.5 Teslas. For the microtextural determination, we used a Philips CM 20 Transmission Electron Microscope (TEM). Surface areas were measured by the BET method (N_2 or Ar adsorption at 77K) with a Sorptomatic 1900 from Carlo Erba Instruments, after heating the samples at 240°C under vacum.

RESULTS AND DISCUSSION

The carbonization yields were close to 45%, except for treatment under air for which it was only 30%. From the elemental analyses, it can be seen that the amounts of carbon, hydrogen, oxygen and residual phosphorus depend strongly on the nature of the atmosphere (Table 1). It is remarkable that the carbon content is higher with steam activation than with anhydrous atmospheres. The chars resulting from the steam activation are practically phosphorus free and contain the lowest oxygen amount. These data suggest that carbonization is promoted when activation proceeds under steam between 400 to 480°C. The more higher oxygen concentration for the sample treated under air is probably the consequence of carbon oxidation, even if P_2O_5 could partly inhibit this reaction [2].

Whatever the atmosphere, ^{13}C NMR magic-angle spinning (MAS) spectra show an unique band characteristic of aromatic rings, at about 125 ppm/TMS. An example is given on figure 1 in the case of a sample activated under nitrogen. Aliphatic carbons were not detected in the spectra whatever the atmosphere used, even in static conditions [3]. We can then conclude that the thermal treatment at 480°C allows the complete aromatization of wood in the presence of phosphoric acid.

The chemical shifts of the ^{31}P NMR spectra (figure 2) are expressed relatively to a 85% H_3PO_4 external standard. All the samples give a very weak band, at 0 ppm/H_3PO_4, which is attributed to excess phosphoric acid trapped in the microporosity and non-eliminated by Soxhlet extraction. The spectrum of the char obtained after steam treatment has a very weak signal/noise ratio. This is the confirmation of a very low phosphorus content, as deduced from elemental analysis (Table 1). The samples treated under anhydrous atmosphere present a main peak, at about 70 ppm/ H_3PO_4 (figure 2), which is attributed to phosphorus incorporated in the aromatic structure of the activated carbon, through P-C or P-O-C bonds. EDAX measurements coupled with TEM images confirm an homogenous dispersion of phosphorous and the absence of phosphorus pentoxide (P_4O_{10}) clusters. For a comparison, pure P_4O_{10} should give a ^{31}P NMR line at 54 ppm/H_3PO_4 [4]. However, the ^{31}P NMR spectrum of the sample prepared under air atmosphere presents an additional line at about 25 ppm attributed to polyphosphate groups  grafted on the surface of the active carbon. These groups could be formed owing to the oxidizing atmosphere.

For characterizing the development of the porous microtexture, argon and nitrogen adsorption isotherms were recorded at 77K. The data were analyzed with BET or Dubinin-Radushkevitch equations; the corresponding specific surface areas are given in table I. The nature of the atmosphere appears to be an important parameter governing the surface area and the development of porosity. The lowest specific surface areas were measured on chars formed with CO_2 or H_2O, in relation with a possible development of mesoporosity inside the microporous char, whereas nitrogen and air only develop microporosity.

Transmission Electron Microscopy showed that only the sample treated under steam is enough carbonized to give the contrasted lattice fringes imaging the aromatic layers profile. Polyaromatic basic structural units, formed of 2-3 stacked layers about 1 nm in diameter, were imaged. These units are strongly misoriented and the char microtexture is similar to crumpled

sheeps of paper [5]. The misorientation of these units is probably responsible for the microporosity detected by gas adsorption. Moreover, bright field images indicate that the "compacity" of the carbon particles is significantly more low with CO_2 and H_2O atmospheres; this well agrees with the development of a mesoporosity suggested by the gas adsorption data.

From all these results, it is likely that the Brönsted acid catalysis is responsible for the dehydration of wood at low temperature in the presence of phosphoric acid. One of the main components of wood is cellulose; therefore we suggest a dehydration mechanism similar to the one of alcohols (figure 3). At temperature higher than 300°C and in the case of anhydrous atmospheres, the phosphorus oxides are acting as Lewis acids and can form C-O-P bonds with the substrate. This is the reason for a low carbon content, and high amount of reticulating oxygen and phosphorus which favor a very important specific surface area [6]. In contrast, with steam injection at 400°C only Brönsted acids are formed, leading to an additional catalytic effect; consequently the carbonization is improved without phosphorus fixation (Table I).

CONCLUSION.

The atmosphere appears to have a strong influence on the chemical activation of wood in the presence of phosphoric acid. Important microporosity can be developed using either air or nitrogen. With steam, mesoporosity is also developed; the microporous area is consequently less important. These last chars present a great advantage, since they are not polluted by a large amount of residual phosphorus, and they could be very interesting in the field of food products. Using various atmospheres, a wide range of materials with various chemical properties and porosities could be obtained by the chemical activation process.

REFERENCES

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Table I- Elemental analyses and specific surface areas on the chars after Soxhlet extraction.

reference	C %	H %	O %	P %	S_{BET} m^2/g	S_{DR} m^2/g
air	66.7	1.7	24	1.5	2200	2950
N_2	68	2.4	15.4	4.5	2150	2750
CO_2	78	2.2	11.6	3.7	1500	2050
H_2O	88.2	2.2	5.1	0.8	1700	2300

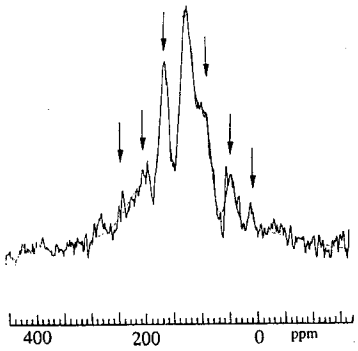

Figure 1. ^{13}C NMR-MAS spectrum of an activated carbon obtained after treatment of wood by phosphoric acid under nitrogen. The peaks labelled by arrows are rotation bands.

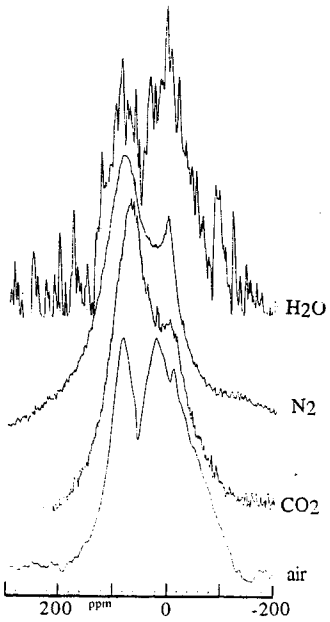

Figure 2. ^{31}P NMR spectra of the samples formed under different atmospheres. The reference for chemical shifts is 85% H_3PO_4 in water.

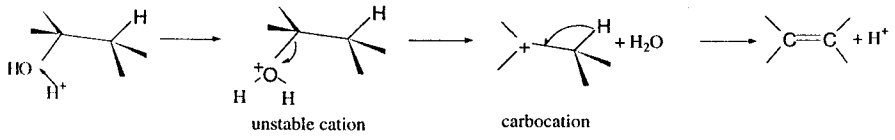

Figure 3. Dehydration mechanism of wood by acid catalysis.