

ACTIVATED CARBON PREPARED FROM ANTHRACITES AFTER CHEMICAL TREATMENT

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Introduction

Among a wide range of precursors of activated carbons, anthracites are of interest for their abundance, low cost, high carbon content and already existing micropores. Physical activation either with CO_2 or with steam has been successfully used for the production of activated carbons from anthracites^{1,2}. Low reactivity and low accessibility of the pores however complicate the physical activation process. Therefore, we proposed the application of a low temperature chemical modification prior to physical activation³. The objective of this work is to analyse the effects of this anthracite pretreatment before activation with carbon dioxide.

Experimental

The experiments were performed with anthracite from La Mure (France). All the samples have been demineralized using a HCl/HF treatment. For the chemical modification, HClO_4 and $\text{Mg}(\text{ClO}_4)_2$ were used. In order to study the effect of water rinsing on activation process of chemically modified anthracite, some samples have been washed with distilled water until neutral pH. After chemical pretreatment, the anthracite was filtered and freeze-dried to remove the excess of acid and water. All the samples (2g) were submitted to the thermal shock at 850°C , followed by an activation with CO_2 (flow rate 400 ml/min) at the same temperature in a tubular furnace, during different residence times to obtain the activated carbons with 10-80% burn-off. In this way, four different series were prepared from:

1. *IC*: raw anthracite;
2. *AC*: anthracite chemically modified by HClO_4 ;
3. *AWC*: anthracite chemically modified by HClO_4 and washed with water;
4. *SC*: anthracite chemically modified by $\text{Mg}(\text{ClO}_4)_2$.

Nitrogen adsorption measurements at 77K were carried out with a Sorptomatic 1900 (Carlo Erba Instruments). The BET equation was used to determine the specific surface area. The Dubinin-Raduskhevich, B.J.H. and Horvath-Kawazoe methods were applied to determine the

pore volume of micro and mesopores and the pore size distribution. Thermal decomposition of the pretreated anthracite was studied with a home made thermogravimetric apparatus consisting essentially of a Setaram microbalance type MTB 10^{-8} connected with a Pyrox oven type VL30 and with a Baltzers multichannel mass spectrometer type QMS420 for the analysis of evolving gases. The determination of different types of functional groups and impregnating species has been undertaken by spectroscopic methods: X ray photoelectron spectroscopy (XPS) and Fourier Transform Infrared (FTIR) spectroscopy. An Escalab MK2 (VG Instrument) apparatus equipped with a X ray aluminum source (K_α radiation) and a Nicolet spectrometer in the $4000 - 400 \text{ cm}^{-1}$ range with a resolution 16 cm^{-1} were used to realise these measurements.

Results and Discussion

Gas adsorption. One of the effects of chemical modification by HClO_4 is the noticeable reduction of activation time. The gasification rates of series *AC* and *AWC* are essentially equal ($3.2\% \text{ h}^{-1}$) and greater than gasification rates of series *SC* ($2.3\% \text{ h}^{-1}$) and of raw anthracite ($1.8\% \text{ h}^{-1}$) under using conditions of CO_2 activation. There is a linear relationship between the BET surface area of all activated anthracites and burn-off. Gasification with carbon dioxide developed surface area and porosity to a maximum at about 60-65% burn-off (Table 1).

Chemical modification of raw anthracite has a direct influence on the final pore size distribution. The evolution of the micro/mesopores ratio during activation and pore size distribution in the resulting activated carbons (at 50% burn-off) may be summarized for the four series as follows:

1. *IC*: during activation micropores are slowly opened; mesopores are scarcely developed. Resulting activated carbon mainly consists of micropores; for 50% burn-off meso/micro = 0.18;

2. *AC*: rapid creation of narrow micropores during the step of thermal shock (10 min at 850°C), followed by their destruction and widening during activation. Resulting activated carbon consists of well-balanced micro and mesopores; for 50% burn-off meso/micro = 0.40;

3. *AWC*: there is creation of micro and mesopores during activation. Resulting activated carbon mainly consists of micropores: for 50% burn-off meso/micro is only 0.25;

4. *SC*: increasing mesoporosity is created during stage of chemical modification, micropores are scarcely developed. Resulting activated carbons are highly mesoporous, however with a low total pore volume. For 50% burn-off meso/micro = 0.64 and 2.5 for $Mg(ClO_4)_2$ /anthracite ratio 1:1 and 2:1, respectively.

Table 1. Specific surface area and pore volume of activated carbons.

References	Burn-off, %	S_{BET} m ² /g	V_{total} cm ³ /g	V_{micro} cm ³ /g	V_{meso} cm ³ /g
<i>IC</i>	55	865	0.47	0.54	0.10
<i>AC</i>	65	1600	0.86	0.61	0.30
<i>AWC</i>	65	1240	0.66	0.71	0.18
<i>SC</i>	50	785	0.34	0.25	0.16

*Data for 24h activation with CO₂ at 850°C

Such differences during activation are caused by the modification of the internal and external surfaces during stage of chemical pretreatment.

XPS and IR data. Chlorine is present in a consequent amount in all the pretreated samples. The Cl 2p core level signal is composed of two contributions which are attributed to chlorine bound to aromatic carbon (201.5eV) and to chlorine inside the perchloric acid (209eV). The main difference between the HClO₄ pretreated anthracite, washed one and Mg(ClO₄)₂ treated lies in the distribution of these two contributions. In the case of the HClO₄ treated anthracite, the Cl (in HClO₄)/ Cl (reacted) ratio is 0.5, whereas it is 0.4 in the case of the washed sample. For Mg(ClO₄)₂ treated anthracite chlorine is only bound to carbon.

The Cls and O1s core level signals also show different behaviour of chemically modified samples. After fitting, peaks could be attributed to C-C, C-O bonds without remarkable difference for all the pretreated samples, and C=O, O-CO bonds more important in the case of HClO₄ treatment. There are negligible C=O peak, no O-CO peak and noticeable presence of water (despite the freeze-drying) in the case of Mg(ClO₄)₂ treatment. Last could be due to a high hygroscopic effect of the incorporated chemicals. These results were confirmed by IR data, according to which a peak at 1730 cm⁻¹ corresponds to ester and (or) lacton groups.

TGA analysis. The total weight loss of pretreated anthracite at 850°C could be attributed to the thermal desorption of incorporated chemicals and water. However, as it can be seen on the mass spectrometry curve, there is a release of carbon dioxide during the thermal treatment. It results from the reaction of incorporated chemicals with carbon at low temperature and from O-CO surface functional groups outgassing at high temperature.

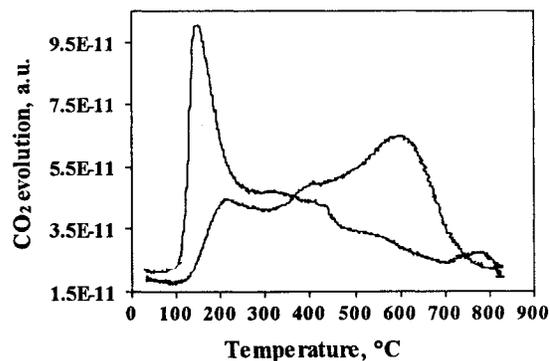


Figure 1. CO₂ evolution for anthracite chemically modified by HClO₄ (1), for the same sample washed by water (2).

IR, XPS and TGA data on pretreated anthracite thus prove the effectiveness of the chemical pretreatment through which the reagent was well introduced inside the anthracite microtexture and was also reacted to some extent with carbon. During activation the incorporated chemicals play a double role: (i) they increase the accessibility of inner surface of anthracite for CO₂ by creation of numerous channels in the anthracite macrotexture; (ii) they occupy a volume which inhibits the construction of the particle during the heat treatment, thus leaving porosity when they evolve by gasification. Both effects cause the well-balanced micro- and mesoporosity of activated carbon.

The chemicals can also oxidize anthracite during the stage of chemical modification. This reaction appears to be more important for the Mg(ClO₄)₂ pretreatment and responsible for the creation of mesoporosity of the activated carbon obtained.

Conclusions

Chemical modification clearly affects the reactivity of anthracite and it has a strong influence on the textural properties of the activated carbons obtained. The detailed analysis indicates that activated carbons from chemically modified anthracites have a well-balanced micro and mesoporosity in the case of pretreatment by HClO₄, and mainly mesoporosity in the case of Mg(ClO₄)₂ treatment. BET surface area as high as 1600 m²/g and a total pore volume close to 1cm³/g were obtained after CO₂ gasification of a pretreated anthracite for 24 h at 850°C.

References

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