

# TEXTURAL MODIFICATION OF A COMMERCIAL ACTIVATED CARBON BY TRANSIENT OXIDATIVE TREATMENTS : EXPERIMENTS AND MODEL

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## Introduction

Many various industrial and domestic applications are based on the use of activated carbons as adsorbent. The performances of those processes have been proved to be linked to the textural characteristics of the involved carbonaceous material. Therefore, extensive efforts have been recently devoted to develop new methods of pore size tailoring and storage capacity enhancement. Among those techniques, a transient method based on successive molecular oxygen chemisorption step followed by thermal decomposition of the formed oxygen-containing groups has shown to lead to very regular pore size widening of 1 or 2 Å per cycle depending on the material origin [1,2]. Simultaneously, the specific microporous volume ( $W_o$  cm<sup>3</sup>×g<sup>-1</sup>) of the tested activated carbons were enhanced of 25% to 30%.

In the present paper, a commercial activated carbon, namely the *NORIT RB2*, widely used in industrial applications, has been submitted to such treatments. In the series of modified activated carbons, textural characteristics of particular interest, in term of industrial and academic point of view, have been obtained.

## Experimental

### *Porous structure characterizations*

The porosity characterization of those materials was proceeded by conventional nitrogen adsorption isotherms at 77 K on samples of 0.2 g following outgasing at 523 K for 24 h and under a residual vacuum of less than 10<sup>-4</sup> Pa.

The microporosity has been characterized following to the Dubinin's theory. On the Dubinin-Radushkevich (D-R) plots of the modified adsorbents, experimental curves present two linear parts which evidences the existence of two microporous domains. From each of those two linear parts, were estimated both the specific microporous volume  $W_o$  and the average micropore sizes  $L_o$  [1].

The  $S_{BET}$  value was calculated using the BET theory and the external surface  $S_{ext}$  from the Sing's  $\alpha$  plot (with black carbon Vulcan 3 as a reference).

As the experimented solids have low external surface areas ( $S_e < 20\text{-}25 \text{ m}^2 \times \text{g}^{-1}$ ), the specific total pore volume ( $W_t$ ) has been estimated directly from the gas amount adsorbed at relative pressure of  $p/p_s = 0.95$ .

#### *Activated carbon*

The experimented commercial adsorbent is the as-received *RB2*, provided by *NORIT*, the textural characteristics of which are gathered in Table 1.

$L_o$ (Å)	$S_{\text{BET}}$ ( $\text{m}^2 \times \text{g}^{-1}$ )	$W_o$ ( $\text{cm}^3 \times \text{g}^{-1}$ )	$W_t$ ( $\text{cm}^3 \times \text{g}^{-1}$ )
8.1	1063	0.40	0.43

Table 1. textural characteristics of the raw activated carbon *RB2*.

This initial activated carbon has been submitted to 12 successive textural modification treatments leading to a series of homologous activated carbons of gradual increase in mean pore size and microporous specific volume while their surface chemistry and carbonaceous structure are kept unchanged.

#### *Textural modification technique*

Pore size widening cycles have been managed by transient successive molecular oxygen chemisorption step (under air at 473 K during 8 hours) followed by thermal decomposition of the formed oxygen-containing groups (under nitrogen at 1173 K during 2 hours) [1,2]. This treatment was proceeded in a conventional laboratory-scale tubular furnace with the sample held on a nickel basket.

Each activated carbon obtained at the end of each cycle (oxidative and pyrolysis steps) has been referenced *RB2Cn*, *n* being the corresponding number of cumulated cycles. At the end of each cycle, the whole sample contained in the basket was weighted and a 1 g sample withdrawn for analysis.

## **Results and Discussion**

#### *Mean pore size*

According to the two linear domains evidenced on their Dubinin-Raduschkevich experimental curves, the series of modified *RB2* present two distinct microporous domains characterized by two respective mean pore sizes  $L_{o1}$  and  $L_{o2}$ .

On the Figure 1 are illustrated the evolutions of those two mean pore sizes with respect to the number of oxidative cycles.

Like in the case of previous other activated carbons submitted to the same procedure [1,2], gradual linear increases of the mean pore sizes are observed on the first cycles. Nevertheless, this linear behaviour concerns the 7 first cycles in the case of the *RB2* while it concerned only the 4 or 5 first cycles in the previous study.

Considering each of the two observed microporous domains, slopes of 1.6 Å and 2.2 Å per cycle were observed for  $L_{o1}$  and  $L_{o2}$  respectively. This difference in slope can be explained by the difference in nature of the corresponding porosities [3,4]. As a matter

of fact, the oxidative treatments are known to concern only the peripheral carbon atoms at the edge of the graphene layers present within the activated carbon edifice. Therefore, only pore nature involving at least one edge of BSU (basic structural unit) can be concerned by such treatment and the corresponding pore size widening depends on the number of edge involved in the pore walls.

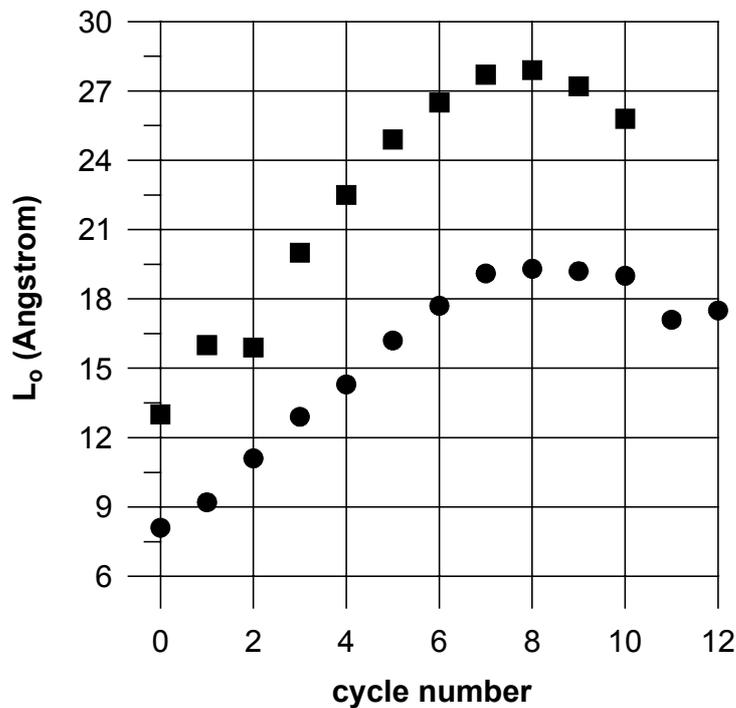


Figure 1. Mean pore size evolutions of the modified RB2 versus cycle number (●) narrowest microporous domain  $L_{o1}$ , (■) larger microporous domain  $L_{o2}$

According to the nanomorphology model recently proposed [3,4], activated carbons porosity can be considered as composed of different kinds of pores depending on the involved walls. Three characteristic pore models were validated : the pore composed by the volume available between two adjacent BSU faces (the so-called slit-like pore), the pore composed by the volume available between an edge and a face of two adjacent BSU (the edge/face model) and the pore between two adjacent BSU edges (the edge/edge model). Each oxidative cycle is responsible for the withdrawal of the peripheral carbon atoms situated at the edge of the BSUs. This effect leads to different increases in porosity depending on the type of pore : the edge/edge pore model leads to a pore size increase twice of that observed for edge/face model. This theoretical difference in pore behaviour is well illustrated by the present experimental slopes of the modified RB2.

Moreover, for a same value of mean pore size, two different pore morphologies do not present the same potential of adsorption. According to the corresponding carbon atom density, face/face pores should be much more active than edge/face which should be much more active than edge/edge ones.

During the isotherm measurement process, the porosity  $L_{o1}$  is the first filled by the gas and presents smaller mean values than  $L_{o2}$ .

#### *Specific microporous volume*

The respective evolutions of both the total specific porous volume and the specific microporous volume have been gathered in Fig. 2 with respect to the number of oxidative cycles.

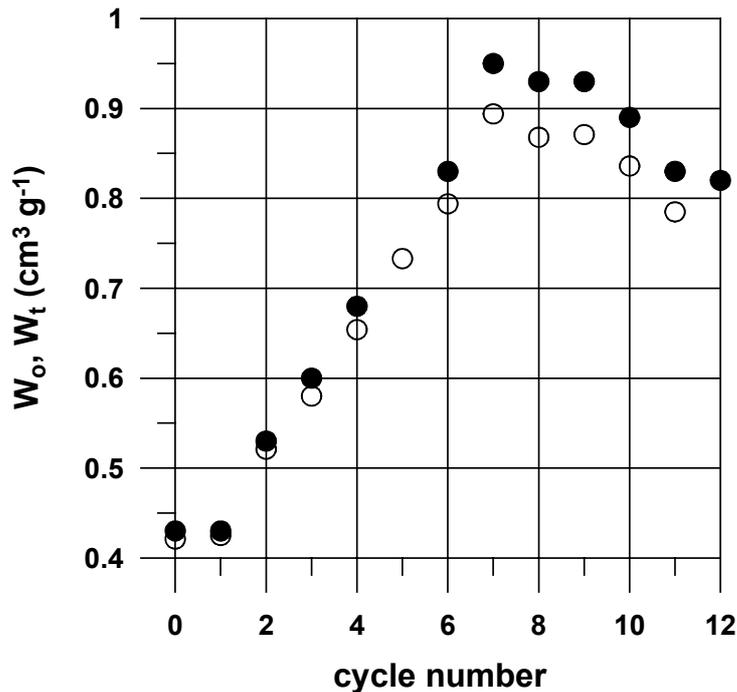


Figure 2. Total microporous volumes of the modified RB2 versus cycle numbers (●) total porous volume, (○) microporous volume.

Each cycle, from the second to the seventh, is responsible for linear increases on both specific volumes. According to the  $W_o$ , this increase is three times more important than those previously observed on other activated carbons submitted to the same transient procedure [1,2].

The pore size widening observed in Fig.1 is linked to a simultaneous increase in whole specific microporous volume  $W_o$  of 109% (from 0.43 to 0.90  $\text{cm}^3 \times \text{g}^{-1}$ ).

This result illustrates a particular behaviour of the RB2 activated carbon with respect to the oxidative cycles especially interesting for adsorption capacity enhancement needed for gas storage processes like  $\text{CH}_4$ ,  $\text{CO}_2$  or  $\text{H}_2$ .

This being achieved by the use of heat, air and nitrogen instead of chemical agent like KOH (usually needed for high capacity adsorbent elaboration), this method is of great interest with respect to environmental and cost considerations.

The total and microporous volumes are very similar on the first cycles but the former one progressively presents slightly higher values than the second, indicating the formation of meso and macro porosity formation. According to those results, the textural

modification method is proved to lead to homogeneous activated carbons. This advantage of the method is inherited from the separation of the oxidative and carbonization steps abolishing the diffusion/reaction competition phenomenon within the particle.

The following cycles, from the 7<sup>th</sup> to the last one, lead to a decrease in porous volumes. This effect, already observed on the TA90 [1,2] activated carbon, is due to a too extensive erosion of the carbonaceous structure by the oxidative treatments.

#### *Specific BET surface area*

The BET specific surface areas of the series of modified *RB2* have been illustrated in Figure 3 with respect to the number of oxidative cycle.

Considering the 7<sup>th</sup> first cycles, the BET surface area increases very linearly with a slope of  $132.6 \text{ m}^2 \times \text{g}^{-1}$  per cycle. At the 7<sup>th</sup> cycle, the initial BET surface value of the commercial *RB2* has been increased of 80%. This result is of particular interest for processes in which activated carbons of high BET surface are needed. The developed series of adsorbents could be also of great interest for studies concerning activated carbon as catalysis support.

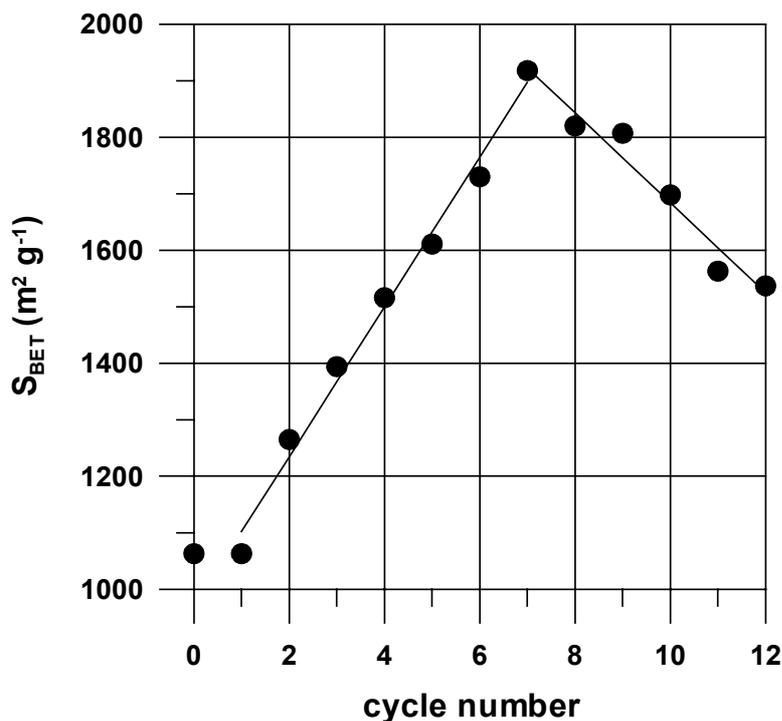


Figure 3. Specific BET surface area of the modified *RB2* versus cycle numbers

The last following cycles, from the 8<sup>th</sup> to the 12<sup>th</sup> one, lead to a decreasing linear behaviour with a slope of  $-79.57 \text{ m}^2 \times \text{g}^{-1}$  per cycle. Again, this behaviour has to be linked to a too extensive structural erosion of the material.

## Conclusions

The microporous characteristics (mean pore size, specific porous volumes and BET specific surface) of the commercial activated carbon *NORIT RB2* have been modified by successive widening cycles composed of an initial molecular oxygen sorption step followed by a carbonization step under nitrogen. The obtained series of adsorbents have been characterized by nitrogen and carbon dioxide isotherms.

According to the two linear regimes evidenced on their Dubinin-Raduschkevich experimental curves, the series of modified *RB2* present two distinct microporous domains characterized by two mean pore sizes  $L_{o1}$  and  $L_{o2}$ . Corresponding gradual and linear mean pore size evolutions of 1.6 Å and 2.2 Å per cycle respectively were observed linked to a simultaneous increase in whole specific microporous volume  $W_o$  of 109% (from 0.43 to 0.90 cm<sup>3</sup>×g<sup>-1</sup>) and BET surface increase of 80%.

Such series of adsorbents of common origin and same surface chemistry but gradual textural parameter evolutions present a high interest for academic studies concerned by adsorption mechanisms and porosity modelization. Moreover, they present also a wide potential for the optimization of adsorption processes in various fields as gas storage, gas separation and purification as well as water treatment.

## References

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