

# IMPROVEMENT OF THE ADSORPTIVE PROPERTIES OF ACTIVE COKES BY MILD OXIDATION IN AIR

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## INTRODUCTION

The adsorptive capacities of active carbons are essentially attributed to the internal surface area, porosity and surface reactivity (<sup>1</sup>). We described in this work active cokes obtained in one step in a rotary kiln starting from two different lignites. In order to improve their adsorption capacities, a mild oxidation is proposed and evaluated. The objective of this work is to explore the feasibility of the use of the active cokes for organic adsorption. The physical and the chemical effects of the oxidative treatment are discussed and connected to the modification of their adsorptive properties.

## EXPERIMENTAL

Two active cokes have been obtained in a rotary kiln at 973°K and 1063°K for respectively the samples called CL and PL. Mild oxidation in air has been realized in laboratory scale in a tubular oven. 5g of coke (200-630  $\mu\text{m}$ ) are introduced in a vertical glass reactor with a sintered glass under air. The heating rate was 293°K until 583 °K at 5°K/min following by 70 min to reach 598°K under a constant argon stream. 40 min of isotherm stage under air allows to perform oxidation.

Structural characterization : Gaseous adsorption isotherms were measured by adsorption of nitrogen (77°K) and by benzene. Pore size distribution are determined considering adsorption of benzene and CO<sub>2</sub> in order to divide total microporosity volume into ultra-micropore and micropore volume.

Adsorption experiments Adsorption of 4 nitrophenol (PNP) was conducted in aqueous phase in static mode. 0.1 g of active coke is added to 100 ml of distilled water and shaken during 3 hours to reach equilibrium. The concentration is determined by UV spectrophotometry at 317 nm.

Surface titration. To estimate the acidic and basic properties of each of the original and surface-modified active cokes, the method proposed by Boehm (<sup>2</sup>) was used.

## RESULTS AND DISCUSSION

### 1. Characterization of the active cokes

We choose the pyrolysis conditions in order to obtain the higher surface area. In this condition, it appears that

973°K and 1063°K allow to obtain the best surface development for respectively CL and PL (<sup>3</sup>). The obtained cokes are mostly different by their ashes content, about 24% for PL and 3% for CL.

### 2. Oxidation of the active cokes

After preliminary studies, we have performed the oxidation at 598°K during 40 min mainly for two reasons : i) in this range of temperature, oxidation of the surface sites is effective and lead to a wide range of oxygenated groups (<sup>4</sup>). ii) The kinetic formation of the oxygen groups is superior to the kinetic of degradation (<sup>5</sup>). Introduction of air at 593°K allows to obtain a continuously weight gain until 1%.

### 3. Titration of surface functional groups

The evolution of the acidic and basic character is evaluated using the classical Boehm titration. The repartition into four acidic groups (carboxylic acid (G I), lactone (G II), phenol (G III), carbonyl (G IV)) and one basic group (pyrone (G V)) is given figure 1. For both CL and PL, concentration in quite all acidic groups are increasing. The stronger evolution are observed for the carbonyl. Basic groups are both increasing for CLox and PLox after thermal oxidation. Basicity is generally attributed to the presence of pyrone groups (<sup>6</sup>). The basicity quantified by HCl included certainly the basic character of the ashes. Therefore, the difference between oxidized and non oxidized samples is representative of the appearance of basic organic group.

### 4. Evolution of porosity

The porosities of our samples are expressed in terms of ultramicroporosity (<0.4 nm), microporosity (0.4-2 nm), and mesoporosity (2-50 nm). The classification of the different porosities is given in table 1. CL and PL are rather microporous and ultra-microporous. The mild oxidation treatment leads to a clear evolution of the ultramicroporosity to the microporosity. This is demonstrated by the cumulated volume  $V_{u-mic}$  plus  $V_{mic}$  which remains constant. It should be noted that  $V_{meso}$  is practically not affected. Surface area has been calculated starting from the different volumes expressed in Table 2. The cross-sectional area of the benzene molecule was taken as 0.41 nm<sup>2</sup>. The obtained results are reported in table 2. It is clear that for all samples, the values of  $S_{mes}$  are small and contribute very little to the value of  $S_{mic+mes}$ .

Therefore, the rather high values of  $S_{mic+mes}$  are strongly related to the values of  $V_{mic}$ . The observed significant differences between the values of surface areas expressed as  $S_{BET}$  and  $S_{mic+mes}$  result from the fact, that in all benzene isotherms the effect of low-pressure hysteresis is visible.

#### 5. Adsorption of 4 nitrophenol (PNP)

The Freundlich equation is well adapted to describe equilibrium in aqueous phase (<sup>7</sup>). The constants  $k_f$  and  $n$  obtained by multiple linear regression of the logarithmic plot of the Freundlich expression are presented in table 3. The efficiency of the active coke PL is greater than CL. The adsorption is strongly increasing after oxidation (about 1.5 times more) and this is logically connected to the increasing of the BET surface area itself linked mainly to the micropores evolution. It should be noted that our oxidative treatment leads to an increase of the basic groups (see Boehm part), this could explained the increase of adsorptive capacity of the oxidized active cokes in our case and especially for PL char which presents a basic behavior (pH=9.9). Therefore, the ashes contents of PL and PL ox are very close, and the mild oxidation treatment cannot change drastically their chemical composition. This demonstrate that oxygenated surface groups improve sensibly the adsorption of the organic compounds.

The  $n$  values decrease after oxidation for both CL and PL until values near those obtained for commercial active carbon (<sup>4</sup>) (about 0.2). This evolution means that the adsorptive capacities per area surface unit for our cokes and active carbon are equivalent, however the BET surfaces are quite different. In good agreement with theory, the  $k_f$  (surface indicator) for PL and PL ox is higher than for CL, putting in evidence a more important microporosity accessible to PNP especially after the mild oxidation.

#### CONCLUSIONS

The initial adsorptive properties of an active coke can be strongly improve by a simple and short mild oxidation in air at about 600 K.

Our proposed oxidative post-treatment :

- i) introduce oxygen functional groups both acidic and basic characters.
- ii) allows to transform part of the ultra-microporosity into microporosity coupled to a moderate development of the mesoporosity;
- iii) contribute to strongly increase the adsorptive capacity of the organic compounds. These has been observed with PNP adsorption.
- iv) improve the adsorptive properties independently of the initial characteristics of the active cokes.

#### REFERENCES

- 1 Stoeckli F., Huguenin D. and Rebstein P.J., *J. Chem. Soc. Faraday Trans.* 1991, **87**, 1233
- 2 Boehm H.P., *Adv. Catal.*, 1966, **16**, 179

- 3 European report number 7220-EC/019, 1995
- 4 Krzton A., Heintz O., Petryniak J., Koch A., Machnikowski J., Zimny T. and Weber J.V., *Analisis*, 1996, **24**, 250
- 5 Marzet M., Farkhani B. and Baudu M., *Water Research*, 1994, **28**(7), 1609
- 6 Painter P.C., Starsenic M., Squires E. and Davis A.A, *Fuel*, 1983, **62**, 742
- 7 Freundlich H., *Z. Physick. Chem*, 1906, **57**, 385

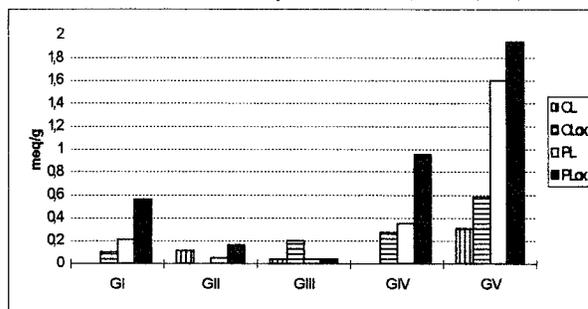


Figure 1 : concentration in functional groups for initial and oxidized active cokes CL and PL

Samples	Ultra-micro(a)	Micropores(b)	Mesopores
	$V_{u-mic}$ < 0,4 nm	$V_{mic}$ 0,4-2 nm	$V_{mes}$ (V total) 2-50 nm
CL	0,065	0,058	0,001
CL ox	<b>0,031</b>	<b>0,090</b>	<b>0,012</b>
PL	0,039	0,140	0,049
PLox	<b>0,018</b>	<b>0,165</b>	<b>0,052</b>

Table1: Parameters characterising the porosity of active cokes

a) The value of  $V_{u-mic}$  was calculated as difference between  $V_0$  (from DR equation applied to carbon dioxide adsorption isotherm at 25°C) and  $V_{mic}$  (from evaluation of the benzene desorption isotherm at 25°C).

b) the value of  $V_{mic}$  was calculated from the benzene desorption isotherm at 25°C, as difference between the Gurvitsch volume (taken at  $P/P_0 = 0.96$ ) and  $V_{mes}$ .

CL	40	160	1	161
CLox	110	249	7	256
PL	290	387	18	405
PLox	400	456	20	476

Table 2: Surface evolution of the active cokes in  $m^2/g$

	$n$	$k_f \cdot 10^3$	R
CL	0.34	16.3	0.98
CLox	0.23	35	0.97
PL	0.45	180	0.96
PLox	0.23	150	0.96

Table 3: Freundlich isotherm constants for PNP adsorbed on active cokes

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