

RELATIONSHIP BETWEEN CYCLIC VOLTAMMETRY AND TPD OF ACTIVATED CARBONS

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Introduction

Oxygen complexes on activated carbons, which largely determine their surface chemistry, have been studied for decades by a great variety of methods. However, the identification of surface oxygen functional groups remains unsolved, partly because of the lack of confrontation of data proceeding from different investigation fields [1]. This work presents an endeavor to correlate results obtained by TPD of carbon oxides with those obtained by cyclic voltammetry.

Experimental

Five activated carbons were studied (see Table 1). All carbons were studied as received except carbon Pl that was washed with distilled water. TPD experiments were carried out under vacuum (lower limit: 10^{-6} mm Hg or 10^{-4} Pa) at a heating rate of 10 K/min. CO₂ and CO evolutions were monitored (in separated runs) by means of a mass spectrometer. Sample masses were approximately 100 mg for CO₂ and 20 mg for CO determinations. Voltammetry measurements were performed with a three-electrode set up using carbon paste electrode as working electrode. The carbon paste consisted of high purity graphite powder (95 mg), activated carbon (5 mg) and 100 μ l of binder (1M HCl). Carbon F, which has a good electric conductivity, was used as a 1 cm thread from the fabric. The electrolyte was an aqueous solution of 1M HCl. The scanning rate was 2.5 mV/s. Reference was a calomel electrode. The chemical titration of superficial oxygen groups of activated carbons was performed by Boehm's method [2].

Results and Discussion

TPD showed a very broad spectrum of CO₂ between 300 and 1150 K composed of numerous poorly resolved maximums and shoulders. CO TPD spectra were simpler. They essentially exhibit one broad peak (see Figure 1). The maximum of this peak is located at about 900 K-950 K for carbons Pl and Ah, and at a rather high temperature (1200 K) for carbons Po, Pf and F. The total amounts of carbon oxides desorbed during TPD are also reported in Table 1.

Figure 2 shows the voltammograms of carbons Pl and Pf before TPD. For carbon Pl, three oxidation peaks and two reduction peaks are observed. Carbon Ah gave a very similar result. Peaks A1 and A2 are assigned to the oxidation of superficial oxygen groups. Peak A3 is assigned to the oxidation of carbon surface (or possibly of other superficial groups). Peak C3 results from the reduction of groups formed by oxidation A3, while peak C1 corresponds to the reduction of the groups formed by both oxidations A1 and A2.

For carbon Pf, only the peaks A3 and C3 were observed. The results obtained with carbons Po and F were quite similar. Peaks A1, A2 and C1 were not observed for these carbons.

After TPD, which removed most of the surface oxygen groups, the carbons Pl and Ah did not present the peaks A1, A2 and C1. Their voltammograms become quite similar to those of carbons Pf, Po and F (see Figure 3 for Pl and Pf).

No correlation was found between the CO₂ TPD profiles and voltammetry results. Nevertheless, the carbons that exhibit peaks A1, A2 and C1 were those that desorb CO at temperatures lower than 1100 K.

Now, there is a general agreement in assigning voltammetric peaks A1, A2 to the oxidation of hydroquinone groups [3]. Therefore, our results suggest that hydroquinone groups thermally decompose into CO between 800 and 1100 K. In contrast, CO producing groups that decompose above 1100 K do not undergo oxidations A1 and A2. A possible assignment of these groups should be isolated phenol or carbonyl groups.

Table 2 gives the results of surface titration by Boehm's method. The amounts of oxygen groups are much greater for carbons Pl and Ah than for the others. This result agrees with that of TPD (Table 1). It is noted that chemical titration, although it shows that carbons Ah and Pl contain the greatest amount of -OH groups, did not provide great differences between these amounts for the various carbons. In contrast, TPD showed, for the samples studied, clear differences in CO desorption temperatures that corresponded to different behaviors in voltammetry.

Conclusions

Activated carbons Ah and Pl showed voltammetric oxidation peaks at about 0.45 and 0.9 V and a

corresponding reduction peak at about 0.4 V. The same carbons presented a CO TPD peak at a temperature lower than 1100 K. These features might be related to the

presence of hydroquinone groups. The voltammograms of carbons F, Po and Pf did not exhibit these peaks. For these carbons, the CO TPD peak is located at about 1200 K.

Table 1. Activated carbons used and TPD results.

| Carbon | nomenclature | Surf. Area (m ² /g) | Amounts desorbed (μmol/g) | |
|-------------------------|--------------|--------------------------------|---------------------------|-----------------|
| | | | CO | CO ₂ |
| Aldrich | Ah | 1500 | 918 | 415 |
| Picabiol | Pl | 1100 | 1011 | 514 |
| Picactif | Pf | 1400 | 543 | 341 |
| Prolabo | Po | 1070 | 358 | 342 |
| Fabric (from cellulose) | F | 1500 | 621 | 271 |

Table 2. Results of titration by Boehm's method.

| Activated Carbon | HCl (meq/g) | COOH (meq/g) | COO (meq/g) | OH (meq/g) | C=O (meq/g) |
|------------------|-------------|--------------|-------------|------------|-------------|
| Graphite | 0.05 | 0.01 | 0 | 0.01 | 0 |
| Ah | 0.19 | 0.21 | 0.36 | 0.21 | 0.46 |
| Pl | 0.12 | 0.36 | 0.72 | 0.15 | 0.70 |
| Pf | 0.87 | 0.09 | 0.015 | 0.12 | 0.20 |
| Po | 0.62 | 0.18 | 0.01 | 0.08 | 0.23 |

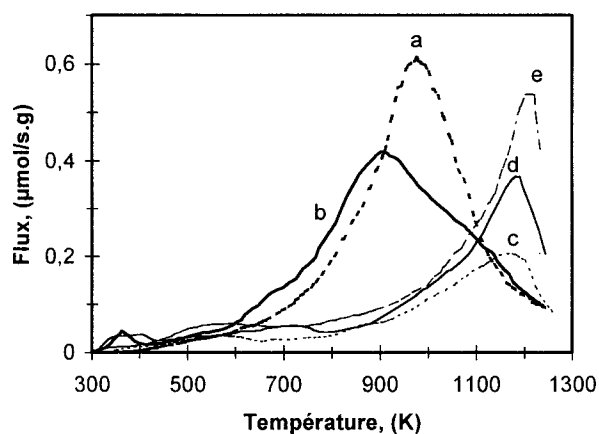


Figure 1. CO TPD : Pl (a), Ah (b), Po (c), Pf (d), F (e)

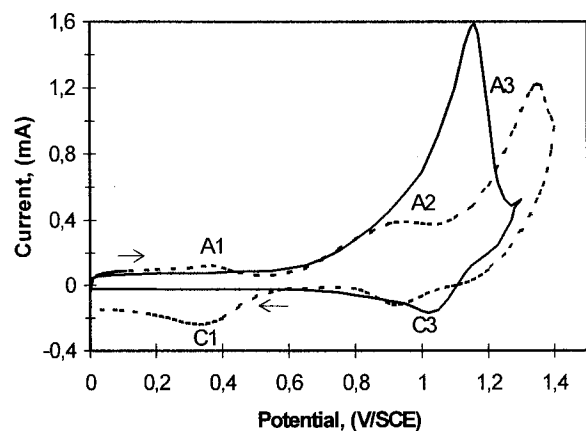


Figure 2. Cyclic voltammograms of Pl (---) and Pf (—) before TPD.

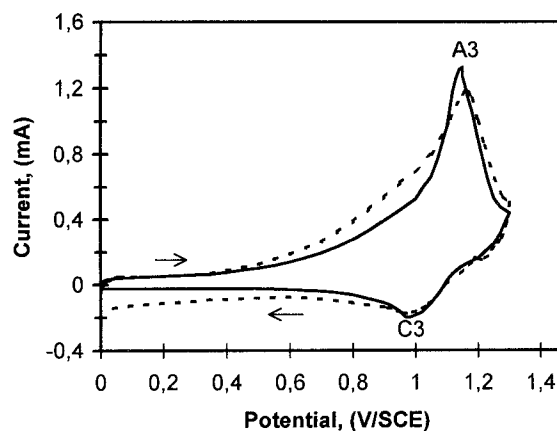


Figure 3. Cyclic voltammograms of Pl (---) and Pf (—) after TPD.

References

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