SURFACE GROUPS OF CARBON-COMPOSITE ADSORBENTS CHARACTERIZED BY PROTON AFFINITY DISTRIBUTION

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Introduction

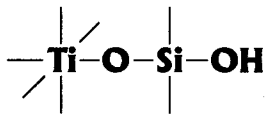
Active carbons are widely used as efficient adsorbents and ion exchangers for selective removal of contaminating substances of different origin from liquid and gas phases. Detailed knowledge of surface properties is necessary for the correct description and prediction of its adsorption behavior. In this paper a spectroscopic approach, namely, proton affinity spectra has been used to characterize qualitatively and quantitatively protolytic properties of surface groups of a carbon composite adsorbent denoted KAU-mod [1].

Experimental

The carbon composite adsorbent, KAU-mod, was obtained from oxidized fruit shell (apricot) active carbon KAUo by impregnation successively with solutions of titanium chloride and sodium silicate. After modification the adsorbent was extensively washed with distilled water until neutral pH. Samples were titrated in a constant ionic media (0.1 M NaCl) with 0.1 M NaOH solution using a fully automated system, Titrino 719 (Metrohm, Switzerland). Equilibrium conditions were controlled using in-house software (Labview). Proton affinity distributions (PAD) were calculated from the proton binding isotherms by solving the integral adsorption equation with a Langmuir kernel using CONTIN software [2].

Results and Discussion

Figure 1 shows that the proton binding isotherms for H-form and Na-form KAU-mod are shifted by 1.03 mmol/g. This value should be considered as the sodium ion loading on the KAU-mod: the isotherm for the Na-form merges with that for the H-form when the corresponding loading of sodium is subtracted. Figure 2 shows that the same information on surface groups may be obtained from either the H-form or the Na-form. The PAD of KAU-mod exhibits 4 peaks with pK values of 4.5, 6.4, 8.4 and 10.2. Most of these peaks may be explained by a linear combination of the PADs of the possible components (i.e., the oxidized carbon KAUo, and the individual oxides [3]: TiO_2 and SiO_2). The best fit result is shown in Figure 3 as a composite PAD (symbols) with the following contributions: KAUo=0.81, $TiO_2=6\times10^{-9}$ and SiO_2=0.17. These data clearly show that all of the peaks, except the peak at 8.4, are accounted for as additive components. It is not surprising that the contribution from TiO_2 is negligible. This is due to the fact that TiO_2 is deposited first, followed by the SiO_2 on top. The peaks at 4.0 and 6.1 may be assigned to carboxylic groups (–COOH), stemming from the oxidized carbon KAUo, while the peak at 10.2 is due to both phenolic groups (–OH) of KAUo and rehydration of siloxane groups yielding silanol groups (SiOH) of SiO_2. The peak at 8.4 may be in part explained by a contribution of phenolic and silanol groups; however the composite intensity is much lower than in the KAU-mod. This suggests that there should be another group that is absent in the PADs of the components, possibly a titanium-silicate group that is formed during synthesis, e.g.



References

[1] Puziy AM, Bengtsson GB, Hansen HS. J. Radional. Nucl. Chem. 1999; 240 (1):101-107.
[2] Puziy AM, Matynya T, Gawdzik B, Poddubnaya OI. Langmuir 1999; special issue devoted to ISSHAC-3.
[3] Contescu C, Popa VT, Miller JB, Ko EI, Schwarz JA. J. Catalysis. 1995; 157:244-258.

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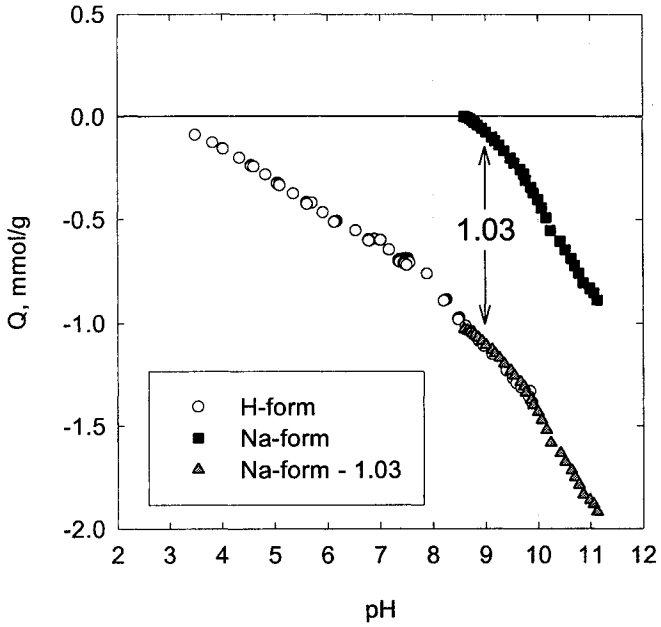

Figure 1. Proton binding isotherms for the H-form and Na-form of the KAU-mod

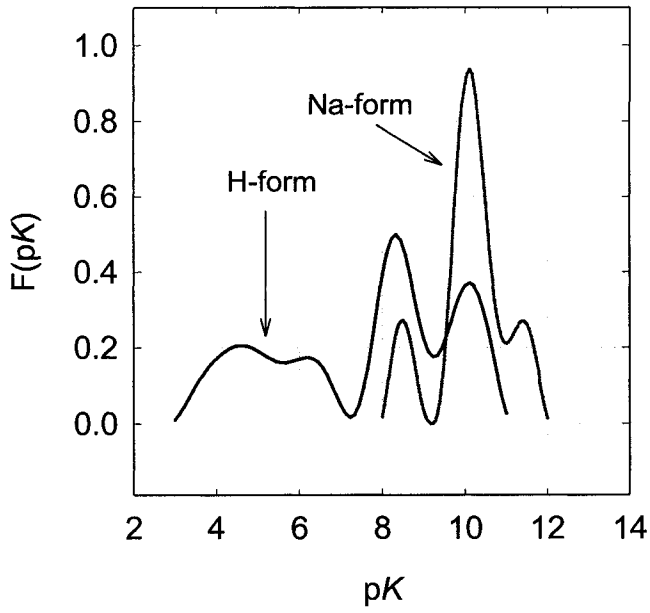

Figure 2. Proton affinity distributions calculated from proton binding isotherms for the H-form and Na-form of the KAU-mod

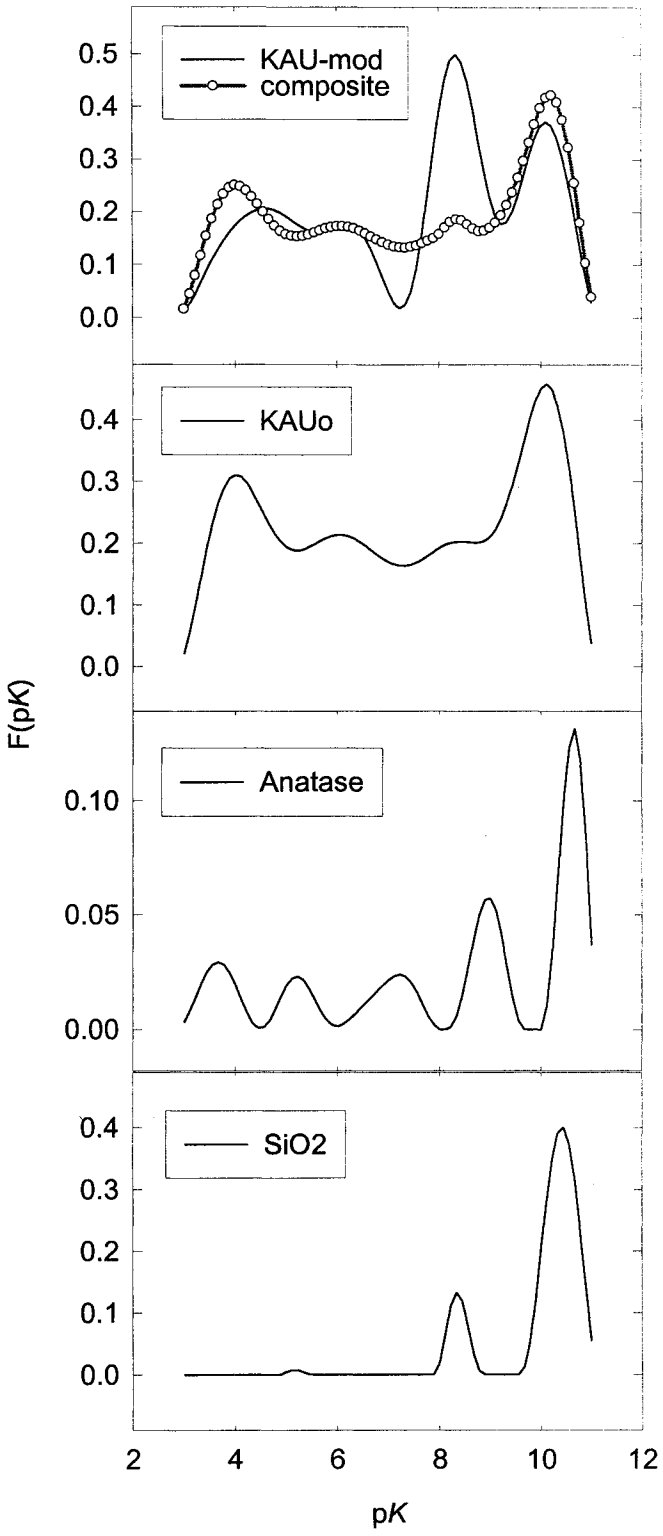

Figure 3. Proton affinity distributions of the KAU-mod and its possible constituents.