

Novel fluoroalkylated and chlorofluorinated nanoporous carbons: synthesis and surface properties

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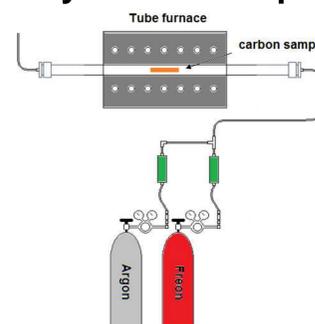
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In recent years, fluorine-containing carbons have been of considerable interest. The most promising fields of their applications are lithium battery electrodes and supercapacitors. Fluorination can also significantly affect the properties of the surface layer of the material, increasing its hydrophobicity and conductivity, which are important. Known methods of fluorination operate with potentially dangerous and toxic compounds: elemental fluorine, BrF₃, ClF₃, XeF₂, and the plasma of CF₄, CF₃I, and SF₆. Fluorination of carbon materials at high temperatures by fluorine-containing hydrocarbons (CHF) is a promising alternative as it requires no special treatment conditions, chemically aggressive and toxic substances and can be carried out using standard chemical equipment.

Nanoporous activated carbon BAU obtained by carbonization/activation of birch wood was used as the model carbon. The specific surface area (S_{BET}) of BAU is 663 m²/g, and the total pore volume (V_{tot}) of 0.380 cm³/g (Table 1). Modification of BAU with 1,1,1,2-tetrafluoroethane (F) and dichlorodifluoromethane (L) was carried out at 400, 500, 600, 700, and 800 °C in a stream of fluorinating agent diluted in argon.

Synthetic setup



Characterization of fluoralkylated and chlorofluorinated nanoporous carbons

Table 1. C.A. data and texture characteristics of BAUF and BAUL

Sample	Texture				C.A.	
	S_{BET} m ² /g	S_{micro} m ² /g	V_{tot} cm ³ /g	V_{micro} cm ³ /g	C_{F} mmol/g	C_{Cl} mmol/g
BAU	663	596	0.380	0.266	—	—
BAUF-400	760	719	0.431	0.314	0.17	—
BAUF-500	578	545	0.330	0.243	0.42	—
BAUF-600	219	194	0.128	0.084	1.86	—
BAUF-700	170	149	0.111	0.065	1.64	—
BAUF-800	91	73	0.073	0.032	1.44	—
BAUL-400	506	481	0.323	0.244	0.35	0.90
BAUL-500	472	438	0.309	0.226	0.80	2.41
BAUL-600	420	374	0.288	0.196	0.85	2.71
BAUL-700	184	158	0.203	0.117	0.76	2.38
BAUL-800	140	114	0.116	0.053	0.87	1.54

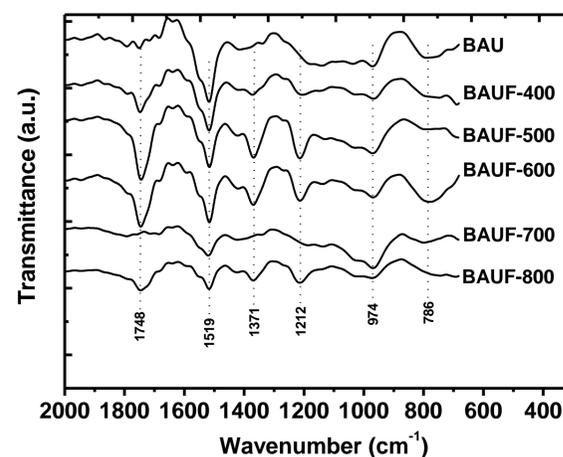


Fig. 1. FTIR ATR spectra for the BAUF

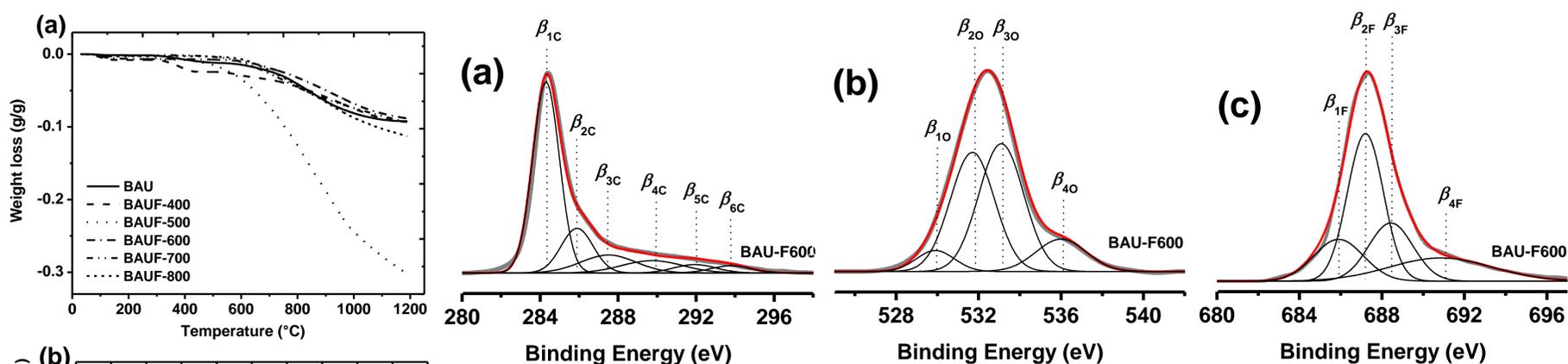


Fig. 2. Typical XP spectra of BAUF: (a) – C1s, (b) – O1s and (c) – F1s core level

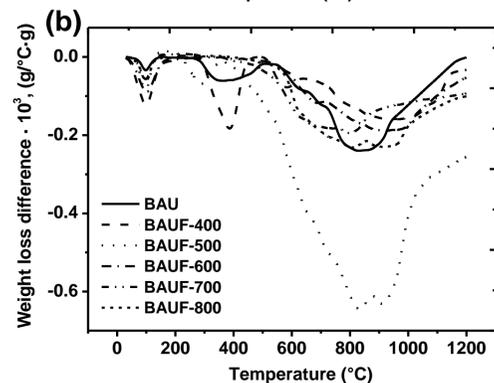


Fig. 3. TGA: (a) – TG and (b) – DTG curves for the BAUF

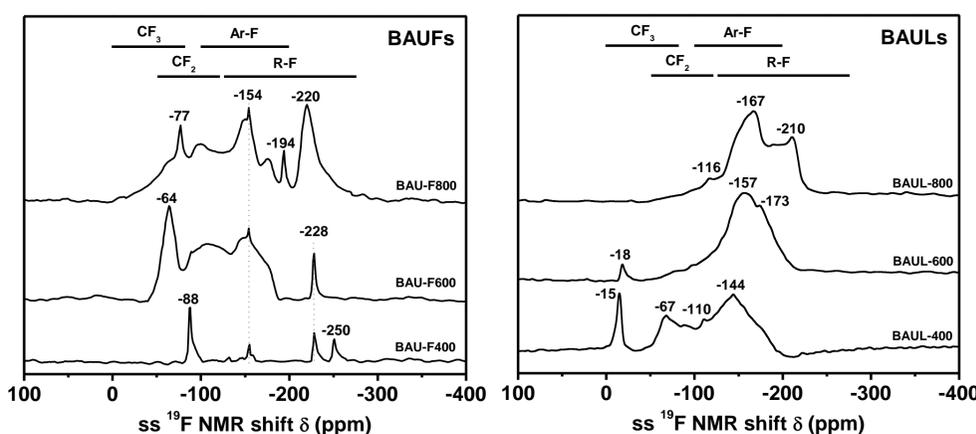


Fig. 4. 19F MAS NMR spectra for selected BAUF4 and BAUF5 samples.

Conclusion. We have demonstrated the temperature-differentiated addition of the F-containing groups by treating BAU with CHF(Cl). The treatment at 400 and 500 °C caused the formation of the carbon solids containing fluorine (chlorine). This fluorine includes in the fluoroalkyl groups or Cl and CCl₂ groups, and it can be added in small amounts at 400 °C. At 600 °C, the fluorine content is maximal over the studied range of the treatment temperature. Most of the high temperature fluorine is in a semi-ionic form. This form is like that of the fluorine attached by the treatment of the carbon surface with elemental fluorine. Further studies (starting from these interesting results) are currently underway aimed at tuning the treatment temperature to regulate the physicochemical parameters by changing the chemical nature of the grafted groups. Both CHF and products of the fluorine addition to the carbon matrix can form long-lived CF₂ biradicals at high temperatures. By migrating (laterally) across the damaged surface of the carbon matrix, they can interact with the conjugated π system and the surface radicals. By forming cross-links, they can bind individual graphene-like layers. In this way, the compaction and layer ordering can reduce the BET surface area at the expense of the advanced microporosity. In contrast to known fluorinated materials, here we reported fluoroalkylated ones. They are potential precursors for obtaining sulfur-containing functional materials by replacing the semi-ionic fluorine and chlorine for the sulfur-containing groups.

