

Nanoporous Activated Carbon Chlorofluorination with Dichlorodifluoromethane for the Production of Surface Precursors

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Objectives: Previously, we showed the fluoroalkylation of Norit 830W with asymmetric tetrafluoromethane and pentafluoroethane in the gas-phase, in the temperature range 400–800 °C [1, 2]. However, the total fluorine content in the samples obtained under the stated conditions is 0.11–1.44 mmol/g only. The Fluocar® F materials [2] prepared at 450 °C are effective materials for supercapacitor electrodes. In this work, we report the results of the patented gas-phase treatment [2] of nanoporous activated carbon in dichlorodifluoromethane. Using Norit 830W activated carbon, as an example, we have shown that dichlorodifluoromethane can interact with the carbon material in the gas phase at 400–800 °C.

Methods: All preparation and characterization methods are briefly reported in [1].

Table 1. C.A. data and texture characteristics of 830WR12

Sample	Parameters			
	F, mmol/g	Cl, mmol/g	BET Surface area, m ² /g	Total Porosity, cm ³ /g
830W	0	0	1254	0.63
400	0.21	1.11	1035	0.57
500	0.86	2.23	990	0.50
600	0.96	2.87	901	0.45
800	0.62	1.94	856	0.50

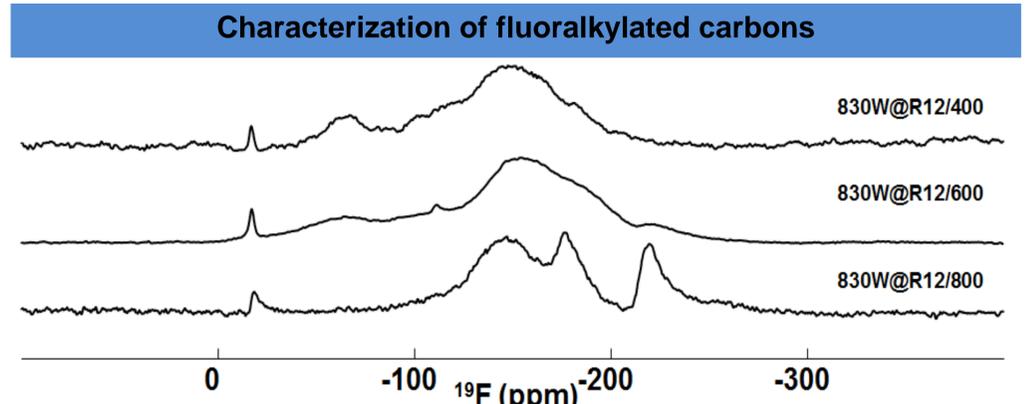


Fig. 1. ¹⁹F NMR spectra for selected 830WR12 samples

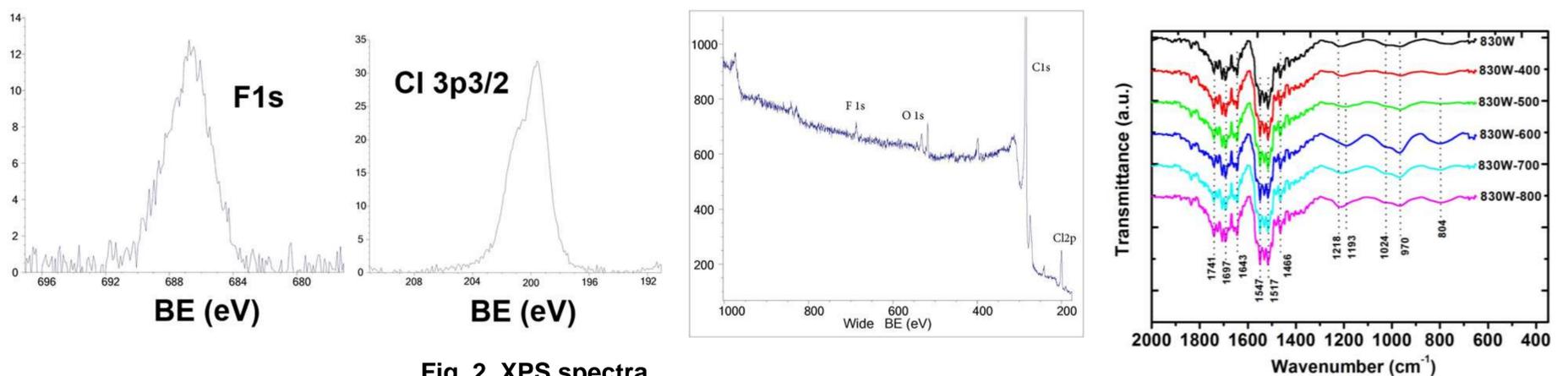


Fig. 2. XPS spectra

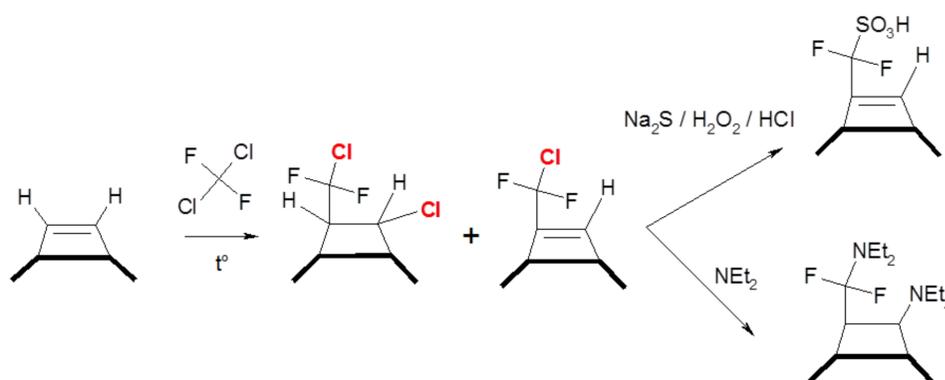


Fig. 4. Schema of pyrolytic addition of CCl_2F_2 , catalytic hydrolysis and oxidation and amination.

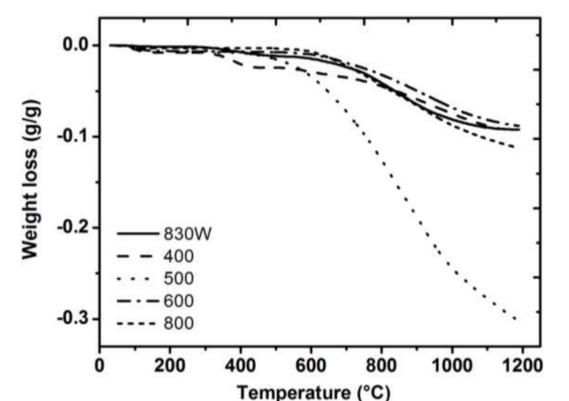


Fig. 3. ATR (upper) and TG (lower)

Results: Fluoroalkylation of Norit 830W with R12 is optimal at 600 °C. Here, the total fluorine and chlorine reach maximal values with medium shortage of porosity. ¹⁹F MAS NMR spectra (Fig. 1) showed wide variety of surface groups presented on the scheme of pyrolysis addition, which are confirmed also by ATR spectra, by bands at characteristic wavenumbers. TG showed minimal weight loss for prepared samples which have high thermal resistance. By treatment with R12, chlorine atoms easily bind to C surfaces, which increases their Lewis acidity but decreases their Brønsted acidity due to resonance from the aromatic rings. A binding energy of ~200.5 eV is indicative of chlorine atoms covalently bonded to sp² C as reported for organo chlorine compounds. The high-resolution Cl 2p peak (Fig. 2) arises from two major components: inorganic chlorine (binding energy 200 eV), from chlorine bonded to aromatic sp² C atoms, the F 1s spectra show the presence of C-F bond at 688.7 eV.

Conclusion. The fluorinated and chlorinated carbons contain 0.21–1.0 mmol/g of fluorine and 1.11–2.0 mmol/g of chlorine. The mechanisms of fluorochlorination are proposed, and the features of materials obtained at different temperatures are discussed. The obtained samples were studied by XPS, low-temperature adsorption of argon, thermogravimetry, solid-state ¹⁹F MAS NMR, FTIR ATR, chemical analysis, mass spectrometry, and some additional physicochemical methods. Fluorinated chlorine samples show relatively high loading with halogens, both fluorine and chlorine, and based on their texture, structural, chemical, and thermochemical characteristics, we can assume that such materials can serve as very efficient precursors for the production of carbon super acids containing –CF₂SO₃H groups, and which are analogs of the classic Nafion® H super acid material, which is widely used for the production of proton exchange membranes and in acid catalysis (see the schema, Fig. 4).

References:

- [1] Fluocar is registered trademark of US #5,479,088 and Ukraine #213,198
- [2] Method of fluorochlorination is patented: UA110301, WO2016072959, and US10000382 patents