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▶ **To cite this version:**

Romuald van Riet, Eder Amayuelas, Peter Lodewyckx, Michel H. Lefebvre, Conchi Maria Concepcion Ovin Ania. Novel opportunities for nanoporous carbons as energetic materials. Carbon, 2020, 164, pp.129-132. 10.1016/j.carbon.2020.03.061 . hal-02612620

HAL Id: hal-02612620
https://hal.science/hal-02612620

Submitted on 6 Nov 2020

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Carbon 164 (2020) 129–132

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Letter to the editor

Novel opportunities for nanoporous carbons as energetic materials

A B S T R A C T

A novel energetic material based on nanoporous carbons as main ingredient is herein reported for the first time. Prepared by filling the pores of nanoporous carbons with an oxidizer, its energetic character is demonstrated. The decomposition of the oxidizer confined in the nanopores of the carbon renders a material capable to sustain a detonation. The energetic character -temperature and reactivity- seems to be promoted by the nanoconfinement of the salts. The safety properties of such materials are in line with the requirements for application as high explosives or propellants.

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Energetic materials (EM) are those capable of rapidly releasing energy through a chemical reaction. Although plenty of materials show such ability to release energy, only a few combine it with adequate physicochemical, thermal and mechanical properties that allow their use in civilian and military applications as high explosives, propellants or pyrotechnic formulations [1]. Most in service and currently produced EM's suffer from serious drawbacks such as hazardous ageing (e.g., nitrocellulose), soil and water pollution (e.g., RDX) or high toxicity (e.g., TNT, lead azide). We herein report new horizons for EM's based on nanoporous carbon as primary component, which nanopore structure is filled with an oxidizer. Because of the high pore volume of nanoporous carbons, an oxygen balance near stoichiometry (i.e. the amount of oxygen required for a complete combustion of the fuel atoms, expressed in wt.%) can be obtained at a nanometer scale, which confers excellent energetic properties to the composite material. Furthermore, mechanical robustness is provided by the carbon skeleton itself [2]. Other porous materials (e.g., porous silicon [3], metal organic frameworks [4]) filled with oxidizers have been studied as EM's, however practical applications are strictly limited to specific pyrotechnic formulations. In contrast, when nanoporous carbon is used as fuel, the scope of potential applications can be extended to high explosives or propellants. To demonstrate the energetic character of composites based on nanoporous carbons, two commercially available carbons were selected: Norit C (CC, Cabot Norit, USA) and F5001 (FC, Blücher, Germany). They were chosen based on their differences in porosity (Fig. 1), composition and surface chemistry. CC is a hydrophilic functionalized carbon (ca. 13 wt% oxygen), whereas FC is hydrophobic with low functionalization (ca. 0.5 wt % oxygen). Additional characterization of the carbons composition, surface chemistry and hydrophobicity is shown in the SI (e.g., TPD-MS, water physisorption, elemental analysis, Figs. S1 and S2, Tables S1 and S2).

Experimental details for the preparation of the composites can be found in the SI. To infiltrate the oxidizers, the equilibrium adsorption capacities in saturated aqueous solutions at 20 °C were initially evaluated (Fig. 1). Data showed that the equilibrium uptake is one order of magnitude too small to reach the stoichiometric mixture needed for complete combustion. To increase the loading, a second infiltration method was carried out using supersaturated solutions of the salts. The uptakes increased for all the salts (Fig. 1), reaching values in line with those expected for energetic properties for $NaClO_4$ [1]. The reason for a higher infiltration of $NaClO_4$ in both carbons still remains unclear, but it may be attributed to the hydration state of the adsorbed salt. Based on their thermodynamic stable forms, $NaClO_4$ is most likely adsorbed as $NaClO_4 \cdot H_2O$, while the other salts are adsorbed in their anhydrous form. This would require all the solvent to be expelled from the pores, thus the growth rate of the adsorbed phase is slowed down. The homogenous nucleation could compete with the growth, thereby limiting the achievable uptake.

XRD patterns of the composites based on $NaClO_4$ confirmed that the salt crystallized inside the pores of the carbons (Fig. 1). A higher number of reflections was obtained for composite CC/$NaClO_4$ (despite its lower salt content), indicating that the differences in the porosity or surface chemistry of the carbons affect the crystallization. The oxygen balance of composites CC/$NaClO_4$ and FC/$NaClO_4$ was close to stoichiometry (ca. −21, −11 wt%, respectively), while the values for the composites prepared with NH_4ClO_4 and KNO_3 were smaller than −100% for both carbons (values for common EM's range from −70 to 0 wt% [1]). Additional confirmation that the oxidizer is retained in the nanopores of the carbons was provided by gas adsorption (Fig. 1), as inferred in the low pore volumes after filling with $NaClO_4$ (these values were lower than for the physical mixtures). The visual inspection of the samples also confirmed this (Fig. S3); despite the high salt loadings, the composites and the carbons look alike, with no evidences of salts crystallized on the external surface. The largest decrease in pore volumes was obtained for CC/$NaClO_4$, prepared with the carbon of hydrophilic character. Gas adsorption data showed that $NaClO_4$

https://doi.org/10.1016/j.carbon.2020.03.061
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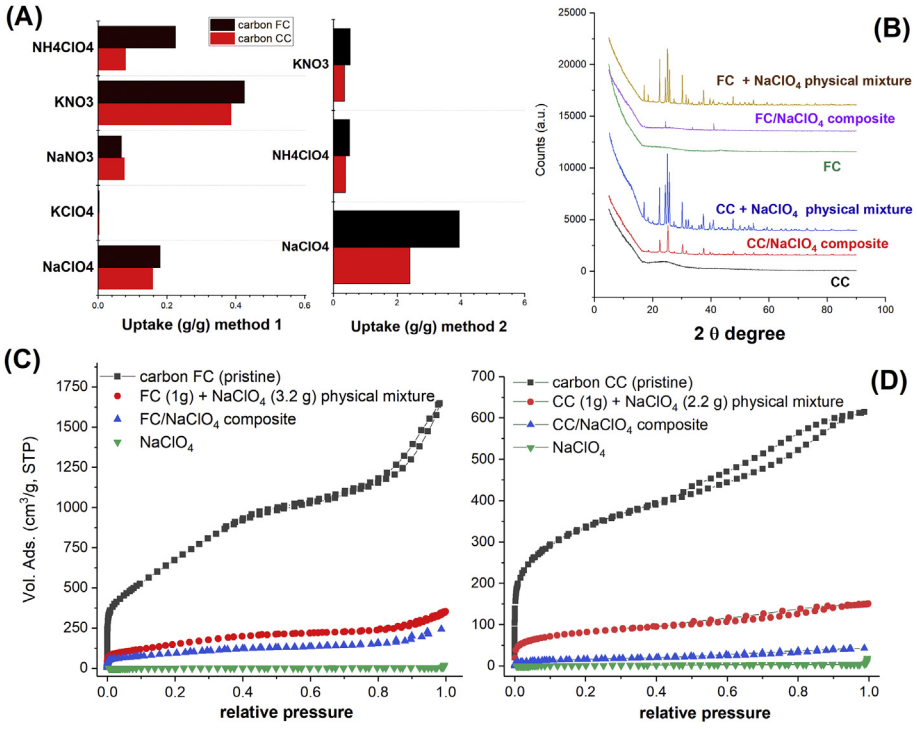


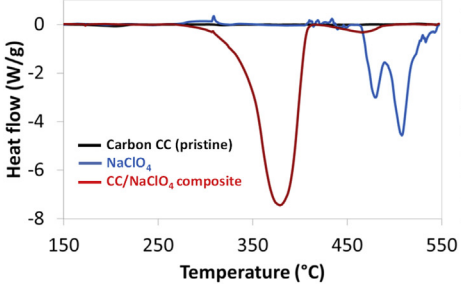
Fig. 1. (A) Salt loadings obtained upon two different infiltration methods (details in SI); (B) XRD of the pristine carbons, the physical mixtures and the composites with $NaClO_4$ (salt loadings of 2.2 and 3.2 g/g for CC/$NaClO_4$ and FC/$NaClO_4$, respectively); (C,D) Equilibrium N_2 adsorption-desorption isotherms at −196 °C of selected samples. (A colour version of this figure can be viewed online.)

is retained throughout the whole porous structure, with ca. 80% of the salt inside micropores and mesopores. The remaining 20% would be located in the macropores. The pore size distributions confirmed a modification in the fraction of pores in the composites beyond a mass dilution effect of the physical mixtures (Fig. 1, Table S3, Table S4, Fig. S4). Similar conclusions can be drawn for composites prepared with other salts (Fig. S6, Table S5).

The energetic character of the composites was explored by differential scanning calorimetry (DSC) in high pressure sealed stainless steel crucibles. For safety reasons, DSC were carried out on 1 mg of sample. Fig. 2 illustrates the DSC curves of CC/$NaClO_4$ compared to the pristine carbon and the bare oxidizer. The onset temperature of decomposition of the carbon/oxidizer composite observed in the DSC curves was much lower than that of unconfined $NaClO_4$. This suggests that the thermal decomposition of the oxidizer is promoted by the confinement in the pores. The same behaviour was observed for the carbons filled by KNO_3 and NH_4ClO_4, despite the lower salt loadings (Fig. 1). The heat of the decomposition peaks is much higher for the carbon/oxidizer composites (ca. 4300 for CC/$NaClO_4$ and 4600 J/g for FC/$NaClO_4$) than for the individual ingredients (ca. 1800 J/g for $NaClO_4$ and 0 J/g for the unfilled carbons). Values are in agreement with the thermal ignition temperature measured for the bulk materials (200 mg), also shown in Fig. 2. The ignition temperature and the onset of the decomposition of the carbons filled with oxidizer were lower than those of the physical mixtures of $NaClO_4$ (sieved between 25 and 50 μm) and either pristine carbon grains (500–630 μm for CC, 200–300 μm for FC) for the mm scale

Table 1
Sensitivities to impact and friction of selected energetic materials.

Material	Impact (J)	Friction (N)
Composite CC/$NaClO_4$	15	168
Composite FC/$NaClO_4$	7.5	>360
TNT	10–20	240–360
RDX	5–10	80–120
PETN	2–4	36–48



DSC onset Temperature (°C)	$NaClO_4$	NH_4ClO_4	KNO_3
Oxidizer	410	319	400
Composite CC/Oxidizer	320	250	311
Composite FC/Oxidizer	318	210	355

Temperature of ignition (°C)	Carbon CC	Carbon FC
$NaClO_4$ (bare), T 420°C	--	--
Composite CC/$NaClO_4$	332	332
physical mixture (micrometric scale)	339	359
physical mixture (millimetric scale)	393	412

Fig. 2. Differential scanning calorimetry profiles at 5 °C/min of selected samples; onset temperature of decomposition evaluated from the DSC curves, and temperatures of ignition of the bulk materials: carbon/$NaClO_4$ composites and physical mixtures. (A colour version of this figure can be viewed online.)

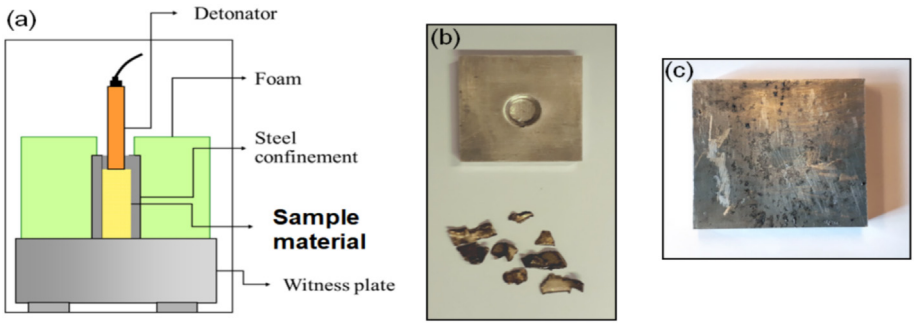


Fig. 3. (a) Scheme of a plate-dent experiment; (b) Dent and fragment of steel tube made by the detonation of composite CC/$NaClO_4$; (c) Undamaged plate when experiment is performed with composite FC/$NaClO_4$. (A colour version of this figure can be viewed online.)

mixture, or crushed carbons (sieved between 25 and 50 μm) for the μm scale mixture (Fig. 2, Fig. S7).

The thermal ignition of the bulk materials showed that they decomposed in a very short time and very violently when heated under atmospheric pressure. Comparatively, they react much more violently than commercial black powder (*aka* gunpowder) or C4 high explosive (see movie in SI). The carbon/oxidizer composites either detonated or very quickly deflagrated, generating an air blast. The violence of the reaction of these materials is remarkable, and can be compared with that of extremely reactive primary explosives like lead azide [5]. In addition, the violence of the reaction decreased significantly for the physical mixtures (see movie in SI), as a result of the limited rate of the decomposition reaction at the micrometric scale. The reactivity of the bulk composites is expected to be governed by the reactivity of the oxidizer in the small pores (<1 nm); when the decomposition in the smallest pores occurs, heat is transferred to the surroundings and initiates the decomposition in the larger pores. Indeed, the scale of fuel to oxidizer mixture is three orders of magnitude smaller in our nanoporous carbon/oxidizer composites than in the physical mixtures: namely <1 nm compared to 1–100 μm. It is this nanometric scale, comparable to that of energetic molecules, that confers them the observed reactivity and makes them have a promising potential as high performance high explosives.

Supplementary video related to this article can be found at https://doi.org/10.1016/j.carbon.2020.03.061

An important aspect of EM is related to safety during storing, handling and transportation. The safety properties of best performing carbon/oxidizer composites were investigated by measuring the amount of external stimulus (i.e. impact and friction) required to induce a reaction of the samples according to UN standard [6] (Table 1). The sensitivities of the carbon/oxidizer composites are in line with their potential use as high explosive or propellant (i.e. impact sensitivity greater than 2 J and friction sensitivity greater than 80 N); these data are comparable to that of common energetic materials (e.g., TNT, RDX, PETN) [7,8]. This indicates that the mechanical properties of the nanoporous carbon matrix are adequate to prevent the sample from being too sensitive to mechanical stimuli, notably as the result of adiabatic compression of entrapped gases in the residual porosity.

Finally, the brisance of the material (i.e. a measure of its performance as high explosive) was qualitatively studied by observing the effect on a witness plate when the materials are filled into a steel tube and initiated by a standard detonator (Fig. 3). A clear dent was observed for the composite CC/$NaClO_4$, demonstrating that this material detonated. No dent was observed for FC/$NaClO_4$, indicating that the material failed to sustain a detonation. This could be attributed to the significantly lower pore filling of carbon FC. Also, no dent was observed neither for the unfilled carbons nor for the physical mixtures of carbon CC and $NaClO_4$ in similar proportion to the composites, supporting the hypothesis that the nanoconfinement plays a key role in the detonation process.

Although the performance of the materials and the synthesis process still have to be improved before being used in real systems, these results provide a proof of concept for a novel family of EM based on nanoporous carbon as the main ingredient. The unique properties and versatility of nanoporous carbons offer promising perspectives in this field. An adequate filling of the carbon nanopores to assure stoichiometric materials with adequate oxygen balance, and the optimization of the pore structure to trigger the thermal decomposition of the oxidizer upon the nanoconfinement seem the key to obtain EMs based on porous carbons capable to sustain a detonation and in compliance with safety issues for practical applications.

Acknowledgements

COA thanks the European Research Council (European Union) for a Consolidator Grant (GA 648161 PHOROSOL).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.carbon.2020.03.061.

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15 October 2019
Available online 1 April 2020