

PREPARATION AND TESTING OF CO₂-ADSORBENT CARBONS FROM CARBON BLACK

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Abstract

In the general framework of CO₂ capture and sequestration, the synthesis and characterization of raw and/or functionalized materials as zeolites and carbon materials for CO₂ capture are subject of a huge number of works.

In this work cheap and renewable carbon based materials with well defined chemical-physical features were prepared and tested as CO₂ sorbents. Hydrophilic carbon-based nanoparticles (HNP) were prepared starting from a commercial carbon black (CB) by using a wet oxidation route. Three different HNP, namely HNP4, HNP15 and HNP24, with an increasing oxygen loading (19,7, 21,0 and 32,0 wt.%, respectively) were produced. The oxidation treatment coupled with a moderate heating (< 450°C) in inert environment (He) was shown to increase the specific BET surface area from 150 m²/g (raw CB) to 460 m²/g (HNP24). A 15% CO₂/N₂ mixture, selected for the CO₂ adsorption tests, is representative of the average CO₂ level emitted from traditional and advanced combustion systems. Adsorption of CO₂ into meso and micro-pores of HNP was evaluated by programmed thermal desorption (TPD) of the CO₂ from the materials. The CO₂ adsorption capacities of HNP were studied at 25°C at atmospheric pressure. The HNP samples were pretreated in He at 450°C before the adsorption tests. The physical and chemical properties of the raw CB and HNP have been carefully determined before and after the thermal pretreatment by thermogravimetry and ATR-FTIR spectroscopy. The regeneration of the HNP after repeated CO₂ adsorption cycles was also studied.

Materials and methods

CB was obtained by Phillips Petroleum Co. and was classified as N110 (corresponding to 15-20 nm primary particles diameter) carbon black (furnace carbon black), according to ASTM classification. Its specific BET area is 151 m²/g. Raw CB is composed by chain-like aggregates (120±20 nm of hydrodynamic diameter as measured by dynamic light scattering DLS) of spherical primary particles (average diameter 15-20 nm). The nanoscale organization of CB primary particles is typical of a disordered carbon. Better structured areas are visible whereas the concentric organization of the stacked graphitic layers arises extending throughout each primary particle. H/C atomic ratio is 0.058 and the temperature of

the maximum combustion rate is 690 °C.

CB was oxidised according to the procedure reported by Kamegawa [1]: in a typical experiment 500 mg of CB were treated with 20 mL of nitric acid (67 wt.%) in a round bottom flask at 100 °C under stirring. After cooling at room temperature, the suspensions were centrifuged (3500 rpm, 30 min) and a solid fraction was recovered and dried. The dependence of the oxidation degree on the reaction time was studied by performing the oxidation for 4 h, 15 h and 24 h. Three different samples were obtained and labeled as HNP4, HNP15, HNP24. Following purification, the materials were carefully characterized.

H/C atomic ratio were measured by a Perkin–Elmer 2400 CHNSO elemental analyzer. The thermal stability of the samples was characterized by thermogravimetric analysis (TGA) on a Perkin–Elmer Pyris 1 Thermogravimetric Analyzer. BET specific surface area was evaluated by measuring the N₂ adsorption isotherm at -196 °C using a Quantachrome Autosorb 1-C. Fourier Transform Infrared (FTIR) spectra were recorded on a Nicolet iS10 spectrometer using the attenuated total reflectance (ATR) method. The CO₂ adsorption tests were carried out with a Micromeritics Autochem II TPD/TPR analyzer equipped with a TCD. The powder material (approximately 100 mg) was contacted 0.5h with a 15% CO₂/N₂ mixture (50 Ncm³·min⁻¹) at room temperature after a 1h in-situ pre-treatment under helium (50 Ncm³·min⁻¹) at 450°C. The evaluation of the adsorbed CO₂ was performed by heating the sample at 10°C·min⁻¹ up to 450°C. Additional adsorption/desorption cycles were carried out.

Results and Discussion

The HNP mass yields are reported in Table 1. After 4 and 15 hours of reaction time the HNP yields increase indicating that the oxidation results in a progressive oxygen addition while the carbonaceous backbone remains substantially untouched. The product yield after 24 hours of reaction time starts to decrease indicating the oxidative degradation of the carbonaceous backbone of the carbon black particles. This tendency is confirmed by the elemental analysis. The oxygen content tends to increase with increasing oxidation time as a consequence of the oxygenated functional groups (hydroxyl, carboxylic, carbonylic) introduction. The oxygen content vary from 0.5% (raw carbon black) to 30% on oxidation for 24 hours. The values of BET specific surface area are also reported in Table 1. The surface area increases from 150 to 320 m²/g on oxidation for 24 hours.

Table 1. Properties and composition of CBN110 and HNP.

	Yield (%)	BET area (m ² g ⁻¹)	C (wt. %)	H (wt. %)	O (wt. %)	O/C atomic ratio
<i>CB</i>	-	151	98.9	0.48	0.59	0.004
<i>HNP4</i>	104	164	79.4	0.55	19.7	0.187
<i>HNP15</i>	102	313	78.1	0.84	21.0	0.202
<i>HNP24</i>	95	320	67.0	0.82	31.8	0.356

The Transmission Electron Microscopy images (not shown) revealed that the 4 and 24 hours oxidative treatment leaves the carbonaceous backbone untouched with respect to the raw CB [2]. HNP microstructure and nanostructure (consisting of a concentric organization of the graphitic layers in the best structured areas) and the primary particles dimensions are not altered by the wet oxidation indicating that the progressive increase of the BET area (Table 1) is due to pores formation in the carbon black particles as previously reported by Kamegawa [1].

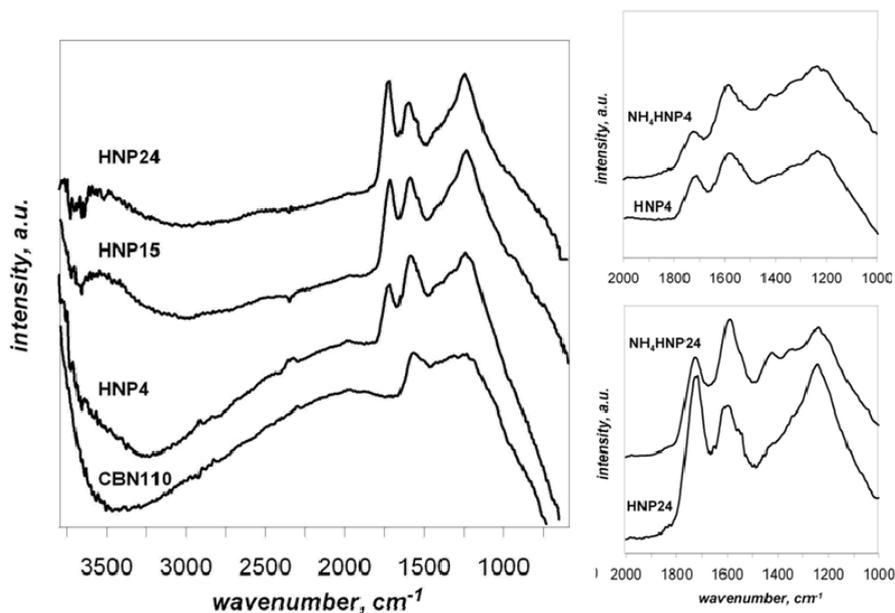


Figure 1. ATR-IR spectra ($600\text{-}3800\text{ cm}^{-1}$) of raw CB, HNP4, HNP15, HNP24 (left) and resulting ammonium-salts (right).

ATR-FTIR spectra of the HNP and CB are contrasted in Figure 1. The most characteristic features of the HNP are the progressive increase of the bands attributed to different types of oxygenated functionalities that are completely absent in the spectrum of the raw CB. Common features of the HNP spectra are a broad band in the $3000\text{-}3700\text{ cm}^{-1}$ range (O-H stretching vibrations due to carboxylic, phenolic groups and possible adsorbed H_2O), bands at $1650\text{-}1750\text{ cm}^{-1}$ (C=O stretching vibrations from carbonyl and carboxylic groups) and bands at $1500\text{-}1600\text{ cm}^{-1}$ (skeletal vibration of the sp^2 graphitic domains). In the $1300\text{-}1100\text{ cm}^{-1}$ region a broad band progressively increases and is ascribable to the overlapping of C-OH and C-O stretching vibrations (possible hydroxyls, carboxylics, oxolan-2-ones, peroxides, ethers, ketones, pyran-2,3-diones, lactols, anhydrides, benzoquinones) [3-4]. In order to get insights about the identity of the oxygenated functional groups, the HNP have been treated with excess of NH_4OH

(28% NH_3 in H_2O) for 30 min after which the excess of volatile ammonia has been easily removed under vacuum and the HNP recovered and dried. The spectra of the resulting HNP ammonium-salts (Figure 1, right) present bands characteristic for carboxylate ion (asymmetrical stretching at $1540\text{-}1615\text{ cm}^{-1}$ and symmetrical stretching at $1440\text{-}1360\text{ cm}^{-1}$) in addition to an ammonium band in the $2700\text{-}2200\text{ cm}^{-1}$ and disappearance of the O-H stretching band [5] and partially retain the band of C=O ($1650\text{-}1750\text{ cm}^{-1}$). This result indicates that functional groups other than COOH, anhydride or lactone (the latter two, via alkaline hydrolysis, would also give carboxylates) must also be present on the HNP surface which can be interpreted as single ketones or quinones [4].

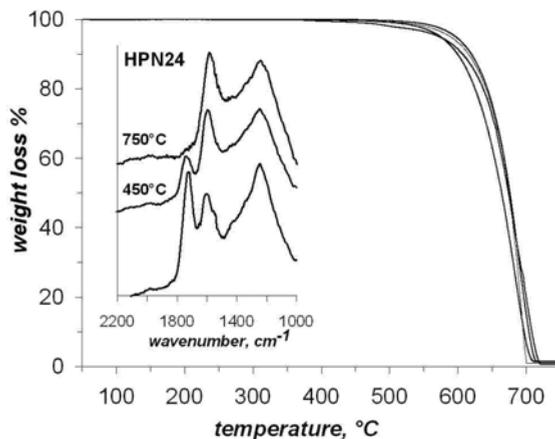


Figure 3. TG plots of HNP4, HNP15, HNP24 in oxidative environment (air) after heating in nitrogen atmosphere. The inset shows the enlarged $1000\text{-}2200\text{ cm}^{-1}$ region of HNP24 ATR-IR spectra.

Figure 3 reports the TG analyses performed in air after the heating at $750\text{ }^{\circ}\text{C}$ in inert atmosphere (nitrogen). The sample oxidation occurs nearby raw CB oxidation temperature ($670\text{-}690\text{ }^{\circ}\text{C}$) indicating the thermal stability of the HNP graphitic core. A detailed spectroscopic study of the chemical evolution of the HNP surface functional groups upon thermal treatments has been performed. The HNP has been heated in a N_2 atmosphere up to 450 , and $750\text{ }^{\circ}\text{C}$, recovered and analyzed by TG in oxidative environment and ATR-IR (Figure 3, inset). The ATR spectra (here reported only for HNP24 sample in the $1900\text{-}1500\text{ cm}^{-1}$ region) confirm a progressive loss of the oxygenated groups. The ATR spectra of the resulting HNP ammonium-salts (not shown) confirms that the carboxylic groups are completely removed after heating at $450\text{ }^{\circ}\text{C}$ leaving carbonyl groups. The removal of carboxylic groups is accompanied by an increase of the surface area ($460\text{ m}^2/\text{g}$) indicating the formation of pores in the graphitic network. It is worth nothing that the thermal treatment up to $600\text{ }^{\circ}\text{C}$ do not improve significantly the surface area.

Figure 4 shows the distribution of the pores in the HNP24 and HNP24 after heating

at 450°C. HNP24 either as fresh and after a thermal treatment at 450°C exhibit a bi-modal pore size distribution (Figure 4) with a small fraction of micro-pores ($r < 20 \text{ \AA}$) and a very large fraction of meso-pores ($r > 20 \text{ \AA}$).

Both micro- and meso-pores increase upon a thermal treatment at 450°C (inset in Figure 4) resulting in a significant increase of BET surface area as well.

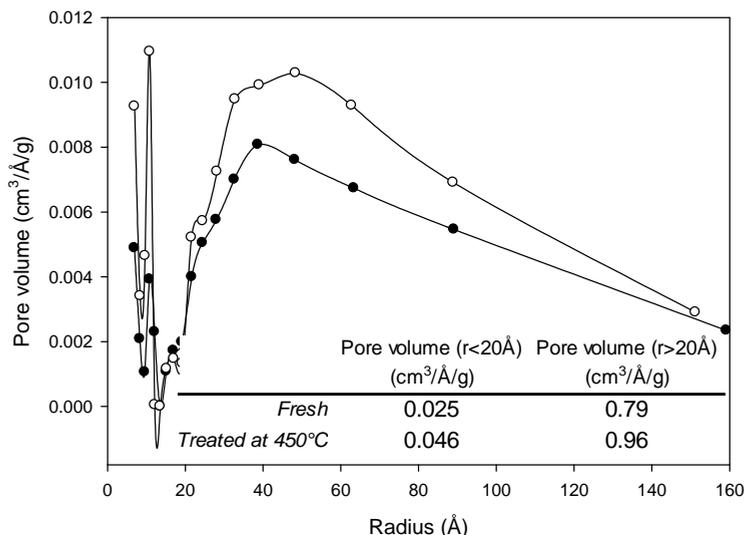


Figure 4. Pores size distribution of HNP24 (●) and after a thermal treatment at 450°C (○).

Meso-pores are likely responsible for the CO_2 desorption at low temperature in the TPD experiments due to the smaller diffusion limitations resulting in a easier physisorption of CO_2 .

The CO_2 adsorption capacities of HNP have been studied at 25 °C at atmospheric pressure by using a mixture of 15% CO_2/N_2 , which was selected to be representative of different CO_2 levels in the combustion gases from traditional and advanced combustion systems. Physical and chemical adsorption of CO_2 into meso and micro-pores has been evaluated by programmed thermal desorption (TPD) of the CO_2 . The HNP samples have been pretreated in He at 450°C in order to increase the surface area.

All the HNP samples present two main CO_2 desorption (Figure 5) at low (25-150°C, probably due to physisorbed CO_2 , LTD) and high temperature (starting from 250°C, HTD). The HTD progressively increases moving from HNP4 to HNP24 consistently with the porosity introduced after the removal of carboxylic functionalities. The total adsorbed CO_2 (LTD+HTD) is estimated to be 0.08 mmol/g, higher with respect to that observed for raw CB.

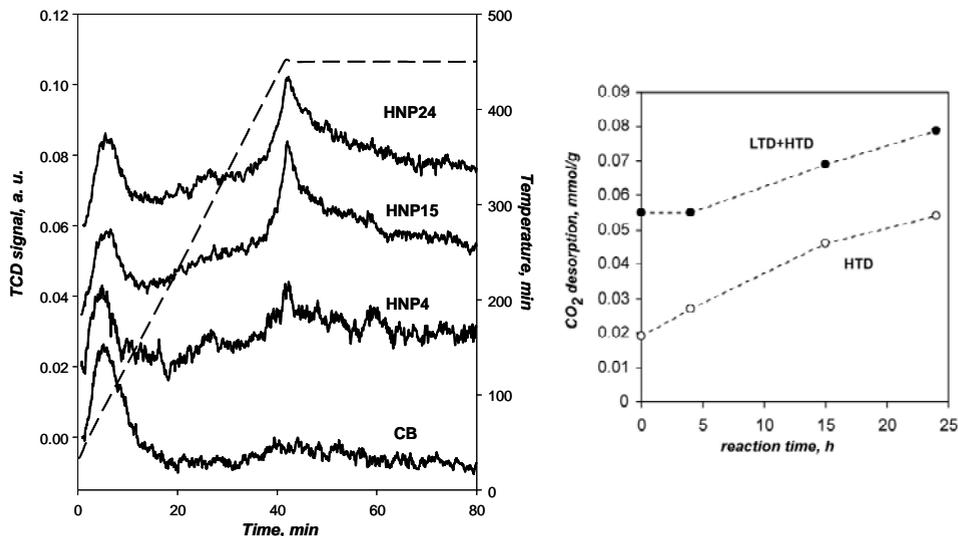


Figure 5. TPD plot of the CO₂ for each HNP (left) and total desorbed CO₂ as a function of the CB reaction time (right).

The HNP appears to be renewable after repeated CO₂ adsorption cycles. These preliminary results appear to be encouraging although the total amount of adsorbed CO₂ appears lower with respect to those adsorbed in the same experimental conditions by carbon nanotubes, granular activated carbon and zeolites (around 0.6 mmol/g [6]). Further work is ongoing aimed to improve the adsorption capacity through further treatment of HNP (oxidation strategies, oxidation followed by reduction, functionalization with amine groups, grafting of silica surfaces...).

Acknowledgments

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