CO$_2$ adsorption on crystalline graphitic nanostructures

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ABSTRACT

CO$_2$ adsorption has been measured in different types of graphitic nanostructures (MWCNTs, acid treated MWCNTs, graphene nanoribbons and pure graphene) in order to evaluate the effect of the different defective regions/conformations in the adsorption process, i.e., sp^3 hybridized carbon, curved regions, edge defects, etc. This analysis has been performed both in pure carbon and nitrogen-doped nanostructures in order to monitor the effect of surface functional groups on surface created after using different treatments (i.e., acid treatment and thermal expansion of the MWCNTs), and study their adsorption properties. Interestingly, the presence of exposed defective regions in the acid treated nanostructures (e.g., uncapped nanotubes) gives rise to an improvement in the amount of CO$_2$ adsorbed; the adsorption process being completely reversible. For N-doped nanostructures, the adsorption capacity is further enhanced when compared to the pure carbon nanotubes after the tubes were unzipped. The larger proportion of defect sites and curved regions together with the presence of stronger adsorbent–adsorbate interactions, through the nitrogen surface groups, explains their larger adsorption capacity.

1. Introduction

CO$_2$ capture using porous solids might become an advanced technology able to mitigate the large emissions of this greenhouse gas to the atmosphere [1]. Among the different porous materials studied until now, activated carbons exhibit certain advantages such as a high adsorption capacity, both at atmospheric and high pressure, an easy regeneration and, if properly designed, a high selectivity for CO$_2$ toward other molecules of similar dimensions such as CH$_4$ and/or N$_2$ [2–6]. Although the large adsorption capacity on carbon materials under atmospheric pressure conditions has been preferentially associated to the presence of a highly developed specific porous structure (pores < 1.0 nm), the role of surface defect sites on the adsorption process is still not completely understood [3,4,7]. Taking into account that the structure of activated carbons is associated with a disordered arrangement of

defective graphitic layers in the form of twisted lamellae, the knowledge of the adsorption process on the different surface sites and/or regions seems mandatory to better understand their excellent adsorption behavior. Another critical parameter in the design of a porous carbon for CO$_2$ capture concerns the control of the surface chemical functionalities. For instance, previous studies have shown that the incorporation of nitrogen functionalities within the porous structure of the carbon material give rise to an improvement in the amount of CO$_2$ adsorbed [8–11]. These nitrogen functionalities can be present either on the surface in the form of amines, imines, and so other functional groups, or embedded in the carbon framework after appropriate selection of a nitrogen rich carbon precursor. CO$_2$ adsorption improvement in these materials has been associated with the presence of stronger electrostatic interactions established between the basic nitrogen functionalities and the acidic CO$_2$ molecule due to the distortion of the electronic structure of the basal planes.

Theoretical calculations on graphitic surfaces have predicted a low binding energy for CO$_2$ physisorption (~151 meV) in non-defective graphene surfaces [12]. Using density functional theory

(DFT) calculations, physisorption of the CO_2 molecule occurs in a parallel fashion on the graphene rings, the adsorption geometry being slightly distorted in the presence of oxygen surface groups [13,14]. In addition, Bader charge analysis predicts an important distortion of the electronic structure of the basal planes in the presence of surface functionalities (oxygen atoms are highly electronegative, acting as basic adsorption sites), thus increasing the adsorption energy for CO_2 molecules, i.e., the carbon atom on the CO_2 molecule would be more attracted to the embedded oxygen functional groups [14]. A similar enhancement in the adsorption energy for CO_2 has been also predicted for defective graphene sheets, the adsorption of the CO_2 molecule taking place on top of vacancy defects, with the molecule linear axis parallel to the surface [15]. Concerning carbon nanotubes (CNTs), theoretical and experimental analysis have shown a preferential adsorption of CO_2 on the grooves and interstitial sites on bundle of single-walled nanotubes (SWCNTs); the adsorption energy being very low on the surface positions [12,16]. Jiang and Sandler used a C_{168} schwarzite to evaluate the preferential adsorption of CO_2 from other molecules, such as N_2, on different carbon configurations [17]. According to their analysis, the curved surface of the C_{168} schwarzite results in an enhancement in the CO_2–carbon interaction potential compared to planar graphite. The enhancement observed can be attributed to the presence of combined sp^3 and sp^2 hybridized carbon atoms in the curved regions when compared to planar graphite containing preferentially sp^2 hybridized carbon.

In summary, theoretical calculations together with experimental analyses predict important changes in the electronic density of the graphitic basal planes, and indirectly, in the adsorption potential for CO_2 depending on the nature of the carbon regions and surface defects (e.g. sp^2/sp^3 ratio, defective sites, surface groups, curved regions, etc.). With this in mind and in order to provide a deeper insight into the understanding of the adsorption process on carbon materials, the aim of the present paper is to evaluate the role of different surface heterogeneities (unsaturated sp^3 hybridized carbon atoms, curved regions, uncapped regions, nitrogenated sites, etc.) in the adsorption/desorption process on carbon nanostructures that could eventually be used for CO_2 capture. Selected carbon nanostructures comprise multi-walled carbon nanotubes (MWCNTs), acid treated MWCNTs and graphene nanoribbons, either pure or nitrogen-functionalized.

2. Experimental

The synthesis of pristine nitrogen-doped MWCNTs (MWCNT-CNx) and ethanol synthesized MWCNTs (MWCNT-COx) were carried out by chemical vapor deposition (CVD). The CVD process was performed in an argon atmosphere carrying an aerosol containing 5 wt.% of ferrocene ($FeCp_2$) and 95 wt.% of benzylamine

(C_7H_9N) for the MWCNT-CNx [18], and with 1 wt.% ethanol and 5 wt.% of ferrocene in toluene (C_7H_8) for the MWCNT-COx [19]. These tubes were then acid treated in order to create structural defects (e.g. uncapped tubes, pyridine-like sites, and large vacancies) to facilitate the diffusion of liquid nitrogen into tube' core and within their external concentric cylinders, thus promoting the subsequent atomically smooth unzipping. The acid treatment was performed by adding 200 mg of MWCNTs in 30 ml of a solution of H_2SO_4:HNO_3 (3:1) and sonicated for 6 h. After sonication, the resulting suspension was filtered and washed with deionized water and then dried. Subsequently, the acid treated MWCNTs (MWCNT-COx-A and MWCNT-CNx-A) materials were kept on a receptacle with liquid nitrogen during 5 min. The abrupt unzipping occurs when adding boiling water to the recipient containing the acid treated nanotubes and liquid nitrogen. Since the temperature changed from ca. −196 °C to 45 °C between 5 and 10 s, N_2 molecules inserted in previously created surface defects and in the hollow core of the concentric tubes undergoes a sudden thermal expansion giving rise to the unzipping of the nanotubes [20]. In addition, the dispersion was maintained under sonication at 80 °C for 30 min. For the sake of comparison, the CO_2 adsorption characteristics of pure graphene (1–2 layers) from Avanzare Corp. (Spain) were also obtained. As it can be observed in Fig. S1 (see Supporting Information), commercial graphene exhibits the typical structure consisting of corrugated graphene sheets.

Powder samples were characterized by scanning electron microscopy (SEM) using a FEI Helios 600 Nanolab equipment. The powders were also ultrasonically dispersed in isopropanol in order to carry out high-resolution transmission electron microscopy (HRTEM) studies using a Cs-corrector (2) equipped HR-TEM, JEM2100, JEOL, Japan.

X-ray photoelectron spectroscopy (XPS, K-ALPHA, Thermo Scientific) was used to analyze the samples surface. All spectra were collected using Al–K radiation (1486.6 eV), monochromatized by a thin crystal monochromator, yielding a focused X-ray spot with a diameter of 400 μm, at 3 mA × 12 kV. The alpha hemispherical analyzer was operated in the constant energy mode with survey scan pass energies of 200 eV to measure the wide scan and 50 eV in a narrow scan to selectively measure the particular elements. Charge compensation was achieved with the system flood gun that provides low energy electrons and low energy argon ions from a single source. The carbon sp^2/sp^3 ratio was estimated from the area of the XPS C1s signal at 284.2 eV, for C sp^2 and 285.1 eV, for C sp^3, respectively. Additionally, the C/O ratio was estimated from the C1s and O1s signals.

Gas adsorption measurements (N_2 at −196 °C and CO_2 at 0 °C) at atmospheric pressure were performed in a home-made fully automated equipment designed and constructed by the Advanced Materials Group (LMA), now commercialized as N_2-Gsorb-6 (Gas to Materials Technologies; www.g2mtech.com). Before any experiment, samples were degassed (10^{-8} MPa) at 523 K for 4 h. BET surface area was calculated from the nitrogen adsorption data after application of the Brunauer–Emmett–Teller equation. Micropore volume (V_{N_2}) was estimated after application of the Dubinin–Radushkevich equation whereas the total pore volume (V_t) was taken as the amount adsorbed at a $p/p_0 \sim 0.9$.

3. Results and discussion

Scanning electron microscopy (SEM) images show that pristine MWCNT-COx and MWCNT-CNx exhibit an average diameter of 64 nm and 74 nm, respectively (see Fig. 1a and d). The unzipping process involves an intermediate step with acid treatment used to uncap the nanotube ends and intercalate sulfuric species within the outer layers of the MWCNT [20,21]. Acid treated MWCNTs do not exhibit any apparent morphological changes besides the