

# N-doped polypyrrole-based porous carbons for CO<sub>2</sub> capture\*\*

Marta Sevilla, Patricia Valle-Vigón and Antonio B. Fuertes\*

Instituto Nacional del Carbón (CSIC), P. O. Box 73, 33080-Oviedo, Spain

## Abstract

Highly porous N-doped carbons have been successfully prepared by using KOH as activating agent and polypyrrole (PPy) as carbon precursor. These materials were investigated as sorbents for CO<sub>2</sub> capture. The activation process was carried out under severe (KOH/PPy=4) or mild (KOH/PPy=2) activation conditions at different temperatures in the 600-800°C range. The mildly activated carbons have two important characteristics: a) they contain a large number of nitrogen functional groups (up to 10.1 wt % N) identified as pyridonic-N with a small proportion of pyridinic-N groups, and b) they exhibit, in relation to the carbons prepared with KOH/PPy=4, narrower micropore sizes. The combination of both of these properties explains the large CO<sub>2</sub> adsorption capacities of these mild activated carbons. In particular, a very high CO<sub>2</sub> adsorption uptake of 6.2 mmol g<sup>-1</sup> (0 °C) was achieved for a porous carbon prepared with KOH/PPy=2 and 600°C (1700 m<sup>2</sup>·g<sup>-1</sup>, pore size ~ 1 nm and 10.1 wt % N). Furthermore, we observed that this porous carbon exhibits high CO<sub>2</sub> adsorption rates, a good selectivity for CO<sub>2</sub>-N<sub>2</sub> separation and it can be easily regenerated.

**Keywords:** carbon dioxide capture, carbon, porosity, nitrogen, polypyrrole

[\*] Dr. M. Sevilla, P. Valle-Vigón, Prof. A. B. Fuertes  
Departamento de Química de Materiales  
Instituto Nacional del Carbón (CSIC)  
P.O. Box 73, 33080 Oviedo (Spain)  
Fax: (+34) 985-29-76-62  
E-mail: [abefu@incar.csic.es](mailto:abefu@incar.csic.es)

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## 1. Introduction

The mitigation of carbon dioxide emissions has attracted considerable attention due to the fact that this gas is the main anthropogenic contributor to climate change. Among the different strategies for CO<sub>2</sub> abatement, much effort has been devoted to its capture and storage [1]. CO<sub>2</sub> capture by means of chemical absorption processes based on the use of different types of amine-containing molecules is a well-established procedure [2, 3]. However, this technology suffers from several drawbacks (e. g. energy consumption, corrosion of the equipment, toxicity, etc) and, in consequence, there is great interest in developing other capture methods. One good alternative is to use sorbents to capture CO<sub>2</sub> by means of pressure, temperature or vacuum swing adsorption systems and their combinations [4-10]. Porous solids such as zeolites, metal-organic frameworks (MOFs), porous carbons or organic-inorganic hybrid sorbents have been investigated as potential candidates for CO<sub>2</sub> capture [11-17]. Hybrid sorbents require costly, multi-step fabrication procedures that involve the impregnation or grafting of porous solids (i. e. silica or carbon) using different types of amines. In addition, these materials require high regeneration temperatures and undergo a significant loss of adsorption capacity after several cycles [18].

Owing to their low-cost, wide availability, large surface area, easy-to-design pore structure, surface functionalization and low energy requirements for regeneration, carbon-based materials are considered to be one of the most promising adsorbents for capturing CO<sub>2</sub> [7, 12, 13, 19-22]. However, most of the activated carbons exhibit CO<sub>2</sub> uptakes which are well below  $\sim 3\text{-}4 \text{ mmol CO}_2\cdot\text{g}^{-1}$  sorbent (25°C, 1 atm), the value that represents the minimum working capacity necessary to compete with liquid-phase amine systems [23]. One way to improve the CO<sub>2</sub>-adsorption capacity of porous carbons is to create surface basic sites by incorporating nitrogen groups into the carbon

framework [13, 24, 25]. Two different strategies have been adopted to generate such N functionalities: i) the treatment of porous carbons with ammonia at high temperatures [24, 26, 27] and ii) the use of chemical compounds containing nitrogen as carbon precursor [28-30]. The first approach does not significantly enhance CO<sub>2</sub> uptakes (e. g. maxima adsorption amounts of  $\sim 2 \text{ mmol CO}_2\cdot\text{g}^{-1}$  sorbent at 25°C and 1 atm) and it introduces an additional complex and time-consuming synthetic step. The second strategy is more attractive in that nitrogen-doped porous carbons are directly obtained by means of a simple carbonization-activation process. However, carbons obtained in this way generally exhibit a poor porosity, which limits their capacity to adsorb CO<sub>2</sub>. Thus, Hao et al. recently reported the fabrication of N-enriched porous carbons ( $S_{\text{BET}} \sim 500 \text{ m}^2\cdot\text{g}^{-1}$ ) by the carbonization of a polymeric material in the presence of an amino acid, which show a maximum CO<sub>2</sub> adsorption uptake of 3.1 mmol CO<sub>2</sub>·g<sup>-1</sup> (25°C and 1 atm) [30].

In a recent work, Wahby et al. demonstrated that porous carbons with a high surface area are able to capture a large amount of CO<sub>2</sub> [31]. Our hypothesis is that porous carbons that combine a high density of nitrogen functionalities and a large surface area would constitute a good strategy for increasing CO<sub>2</sub> adsorption uptakes. In this paper, we report a one-step synthetic approach for synthesizing porous carbons that combine a large pore development with the presence of numerous nitrogen functional groups. For this purpose, we selected a nitrogen-rich polymer (polypyrrole) as precursor to produce N-doped porous carbons with a large surface area. Polypyrrole is an extensively studied conductive polymer that possesses a high nitrogen content and leaves a high amount of carbonaceous residue after pyrolysis (carbon yield  $\sim 60 \text{ wt } \%$ ). This polymer has been previously employed by our group and others as precursor to fabricate mesoporous carbons by means of nanocasting techniques [32-34]. However, it

has never been employed to produce highly microporous carbons in a conventional activation procedure. In order to obtain N-doped porous carbons with a well-developed porosity, polypyrrole was subjected to one-step standard chemical activation with KOH. The textural and chemical characteristics of the activated carbons were controlled by modifying the amount of activated agent (KOH/PPy ratio) and activating temperature.

## 2. Results and Discussion

### 2.1. Structural characteristics of the porous carbons

The polypyrrole used as carbon precursor exhibits a sponge-like structure formed by interconnected microparticles of around 1  $\mu\text{m}$  in diameter (see Figure 1a). This morphology offers a large interfacial area for the polymer to react with KOH and it ensures that the activation process will occur uniformly, which is essential for achieving a good pore development. The activated samples exhibit a variety of shapes depending on the degree of activation. Thus, the mildly activated samples combine sponge-like structures similar to that of polypyrrole (Figure 1b) with highly vesiculated particles (Figure 1c). In contrast, the highly activated carbons are made up exclusively of particles exhibiting an irregular shape with sharp corners (see Figure 1d). The porosity of these carbons is made up of randomly distributed uniform micropores as illustrated by the HRTEM images (Figures 1e and 1f). Furthermore, these images of samples CP-4-600 (Fig. 1e) and CP-4-850 (Fig. 1f) show the increase in micropore size on going from mildly to the highly activated materials. This observation is consistent with the pore size distributions deduced from the analysis of  $\text{N}_2$  sorption isotherms (*vide infra*).

The nitrogen sorption isotherms and corresponding pore size distributions (PSDs) of activated carbons prepared at temperatures between 600 and 800°C and with KOH/PPy=2 are displayed in Figures 2a and 2b respectively. Changes in the shape of the isotherms as the activation temperature rises from 600°C to 800°C indicate changes

in the porous structure of the activated carbons, in particular a widening of the pores. Indeed, the PSDs shown in Figure 2b indicate that the porosity of the sample obtained at 600°C (CP-2-600) is made up mostly of narrow micropores (~ 1 nm). As the activation temperature increases, there is an enlargement of the micropore size up to 800°C, at which point the activated carbon (CP-2-800) contains a large fraction of mesopores with a size of around 2.7 nm. The textural parameters of these porous carbons are listed in Table 1. It can be seen that the BET surface area and the pore volume increase significantly with the activation temperature from 1700 m<sup>2</sup>·g<sup>-1</sup> (600°C) to 3410 m<sup>2</sup>·g<sup>-1</sup> (800°C) and from 0.88 cm<sup>3</sup>·g<sup>-1</sup> (600°C) to 1.94 cm<sup>3</sup>·g<sup>-1</sup> (800°C) respectively. Most of the pore volume can be ascribed to the micropores (< 2 nm) that represent the volume of narrower micropores < 0.7 nm (V<sub>0</sub>), which is a significant fraction of the total micropore volume (see Table 1). The porous carbons obtained with KOH/PPy=4 exhibit exceptional pore development. Thus, the textural characteristics listed in Table 1 reveal that most of the activated carbons prepared with KOH/PPy=4 have ultra-high surface areas, in the 3000–3500 m<sup>2</sup> g<sup>-1</sup> range and unusually large pore volumes (up to ~2.6 cm<sup>3</sup> g<sup>-1</sup> for the samples activated at 800°C and 850°C). In the case of the samples obtained under mild activating conditions (KOH/PPy=2), the porosity of the carbons prepared with KOH/PPy=4 is mostly made up of wider pores distributed in two well-defined pore systems: one of them formed by uniform supermicropores (~ 1.2 nm) and the other by mesopores, whose size gradually increases with the activating temperature from 2.2 nm (600°C) to 3.4 nm (850°C). This is illustrated by the pore size distributions (PSDs) which are displayed in Figure S1 (Supporting Information). In a recent work, we showed that these highly activated carbons are excellent adsorbents for H<sub>2</sub> storage [35].

## 2.2. Chemical properties of N-doped activated carbons

The chemical composition of the activated carbons is presented in Table 1. As can be seen, there is a decrease in the nitrogen content with the increase in activation temperature or amount of KOH, from 10.14% for the sample activated in the mildest conditions (600°C and KOH/PPy=2) to 0.32% for the sample activated in the severest conditions (850°C and KOH/PPy=4). This is more evident in Figure S2, which shows the variation of N content and (N/C) atomic ratio with the activation temperature for (KOH/PPy)=2. This result shows that nitrogen is oxidised and more easily removed than carbon during the activation process [36-38]. This reduction is especially drastic from 600°C to 650°C. Remarkably, sample CP-2-600 contains a very large amount of N (10.1 wt %). In fact, it is one of the largest N contents ever reported for highly activated carbons.

The nature of the nitrogen functionalities was investigated by means of IR and XPS techniques. The IR spectra of the polypyrrole, polypyrrole carbonized and porous carbons prepared at temperatures between 600 and 800°C and with KOH/PPy=2 are shown in Figure 3a. The IR spectrum of polypyrrole exhibits well-defined peaks that are characteristic of this polymer (see Table S1) [39-42]. In contrast, the carbonized and activated samples exhibit broader and overlapping bands due to the strong absorption of carbon. All the spectra exhibit a peak that is characteristic of C=C stretching vibrations in aromatic rings at  $\sim 1590\text{ cm}^{-1}$  for the carbonized sample and  $1590\text{-}1620\text{ cm}^{-1}$  for the activated samples. This peak seems to have a shoulder at around  $1700\text{-}1710\text{ cm}^{-1}$ , which may be assigned to C=O stretching vibrations [40]. Additionally, bands indicating the presence of nitrogen species are present, although these are less intense. Thus, the intensity of the band corresponding to N-H and/or O-H stretching vibrations ( $3000\text{-}3700\text{ cm}^{-1}$ ) [39, 40] decreases gradually with the increase in activation temperature, indicating

that such groups are gradually disappearing. The peaks at 1355-800  $\text{cm}^{-1}$ , which are attributed to C-N stretching vibrations, in-plane C-H and N-H deformations and out-of-plane C-H and N-H deformations [39, 42], overlap and their intensity also decreases with the rise in activation temperature. These results suggest that N-H and C-N species are present in the activated samples, and that they are gradually removed with the increase of activation temperature or amount of KOH used (see Figure S3).

The nature of the nitrogen species on the surface of the activated carbons was further investigated by X-ray photoelectron spectroscopy (XPS). Thus, the N 1s core level spectra of the polypyrrole, carbonized polypyrrole and porous carbons prepared at temperatures between 600 and 700°C with KOH/PPy=2 are shown in Figure 3b. As expected, polypyrrole exhibits only one peak corresponding to pyrrolic nitrogen (399.7 eV). When the polymer is carbonized, two intense peaks at 398.1 and 400.7 eV and a small one at 403.1 eV can be distinguished, the former corresponding to pyridinic nitrogen, and the latter to N-oxides of pyridine-N [43, 44]. This pyridine-N-oxide species, which represents only ~ 2 % of all the nitrogen species in the carbonized polymer, is probably caused by the oxidation of the sample due to exposure to the ambient. On the other hand, the peak at 400.7 eV may be attributed to quaternary-N, which is the most stable N species under pyrolysis conditions [45, 46]. However, for the activated carbons, there are only two peaks, one at 398.1 eV and the other at 400 eV. The first peak corresponds to pyridinic-N and the second one may be attributed to pyrrolic-/pyridonic-N [43]. It should be noted that pyrrolic-N and pyridonic-N groups are indistinguishable by XPS. However, given the reactive conditions existing during the activation process (i. e, high temperatures and an oxidising environment), it is unlikely that this peak corresponds to pyrrolic-N and it is probably associated exclusively to pyridonic-N. Figure 3b shows that the proportion of pyridinic-N

decreases as the activation temperature increases. Thus, for the sample activated at 600°C, the percentage of pyridinic-N is ~16 %, whereas for the samples activated at 650°C and 700°C they are ~13 and ~11 % respectively. The above results show that in the porous samples obtained by chemical activation there is no quaternary-N, unlike the carbons prepared by the pyrolysis of polypyrrole, such as CP and others mentioned in the literature [34]. Therefore, the only N species observed in the activated samples are pyridonic-N and a small fraction of pyridinic-N groups. This result indicates that, whereas under pyrolytic conditions pyridinic-N and quaternary-N are the more stable N species [43], under oxidising conditions such as those present during chemical activation, pyridonic-N groups are more likely to be formed. The elemental chemical analysis data (see Table 1) together with the results deduced from XPS show that, as the activation temperature increases, both the pyridinic-N and pyridonic-N groups are gradually removed, pyridinic-N being the one that is preferentially eliminated. The high nitrogen content of the samples activated at mild conditions, combined with the fact that the nitrogen forms pyridonic-N structures, may be beneficial for CO<sub>2</sub> capture, as these basic N species can act as an anchor for CO<sub>2</sub> capture.

### **2.3. CO<sub>2</sub> capture capacity**

Table 2 summarizes the CO<sub>2</sub> capture capacities of the porous carbons at three representative temperatures (0 °C, 25 °C and 50 °C). The CO<sub>2</sub> uptakes measured for the highly activated carbons (KOH/PPy=4) are similar, irrespective of the activating temperature. Indeed, the CO<sub>2</sub> uptakes measured at 0°C and 25°C are in the 4.0-4.4 mmol CO<sub>2</sub>·g<sup>-1</sup> (175-195 mg CO<sub>2</sub>·g<sup>-1</sup>) and 2.1-2.6 mmol CO<sub>2</sub>·g<sup>-1</sup> (92-113 mg CO<sub>2</sub>·g<sup>-1</sup>) ranges respectively. Figure 5 shows the CO<sub>2</sub> adsorption isotherms of the carbon samples prepared under soft activation conditions (KOH/PPy=2). These mildly activated carbons have large CO<sub>2</sub> uptakes in the 4.3-6.2 mmol CO<sub>2</sub>·g<sup>-1</sup> (191-271 mg CO<sub>2</sub>·g<sup>-1</sup>) and 2.7-3.9



mmol CO<sub>2</sub>·g<sup>-1</sup> (117-169 mg CO<sub>2</sub>·g<sup>-1</sup>) ranges at 0 °C and 25 °C respectively. It is worth mentioning that the carbons activated with KOH/PPy=2 exhibit, in relation to the samples obtained at KOH/PPy=4, noticeably better CO<sub>2</sub> uptakes. This is because the mildly activated carbons exhibit two specific characteristics that have a positive effect on CO<sub>2</sub> adsorption: the samples obtained with KOH/PPy=2 have a narrower porosity (see Figures 2b and S1b and Table 1) and a considerably larger nitrogen content than those prepared with KOH/PPy=4. In a recent work, we showed that the CO<sub>2</sub> capture performance of porous carbons depends heavily on the presence of narrow micropores (< 1 nm) which have a high adsorption potential that enhances the adsorption of CO<sub>2</sub> molecules [47]. On the other hand, it has been observed by several authors that the presence of basic N groups leads to an improvement of the adsorption of acidic gases such as CO<sub>2</sub> [48, 49] due to the strong pole-pole interactions between the large quadrupole moment of CO<sub>2</sub> molecules ( $13.4 \times 10^{-40}$  C·m<sup>2</sup> for CO<sub>2</sub> vs.  $4.7 \times 10^{-40}$  C·m<sup>2</sup> for N<sub>2</sub>) [18] and the polar sites associated to N groups. This assumption is strongly supported by the fact that the isosteric heat of adsorption, calculated by means of the Clausius-Clapeyron equation, increases dramatically with the N content from 18.9 kJ·mol<sup>-1</sup> for 0.78 wt % N (CP-2-800) to 31.5 kJ·mol<sup>-1</sup> for 10.1 wt % N (CP-2-600) (see Figure 5). These results suggest that the large CO<sub>2</sub> uptakes by the mildly activated carbons are due to a combination of narrow microporosity and a large number of N functional groups. This is an important finding which must be taken into account when designing porous carbons for CO<sub>2</sub> capture.

#### **2.4 Kinetics of adsorption, (CO<sub>2</sub>/N<sub>2</sub>) selectivity and sorbent regeneration**

For practical applications, in addition to a high CO<sub>2</sub> adsorption capacity, carbon sorbents need to show fast adsorption kinetics, a high selectivity towards CO<sub>2</sub> and they must also be easy to regenerate. We examined the performance of polypyrrole-based

carbon sorbents in relation to these prerequisites. Thus, Figure 6a shows the adsorption kinetics of CO<sub>2</sub> and N<sub>2</sub> on the CP-2-600 sample at 25°C. It can be seen that the capture of CO<sub>2</sub> takes place at high adsorption rates, more than 95 % of the CO<sub>2</sub> being adsorbed in ~ 2 min. In contrast, N<sub>2</sub> adsorption occurs at slower rates, approximately 50 minutes being necessary to attain maximum adsorption uptake (0.77 mmol N<sub>2</sub>·g<sup>-1</sup>). This result is important because it evidences that large CO<sub>2</sub>/N<sub>2</sub> selectivities can be achieved for short adsorption times. In fact, the [CO<sub>2</sub>/N<sub>2</sub>] selectivity measured under equilibrium conditions has a value of 5.3, but the kinetic selectivity measured at an adsorption time of ~2 min (~ 95 % of CO<sub>2</sub> uptake) is considerably greater,  $\alpha[\text{CO}_2/\text{N}_2]=12$ . In conclusion, our findings show that CO<sub>2</sub> and N<sub>2</sub> can be successfully separated by mildly activated polypyrrole-based carbons, an accomplishment that would be highly beneficial for CO<sub>2</sub> capture in flue gases with swing adsorption systems that operate at short time cycles.

The regeneration of carbon sorbents was investigated by means of adsorption-desorption cycles carried out at room temperature (25°C). The results of these experiments for the CP-2-600 sample are shown in Figure 6b. It can be seen that the captured CO<sub>2</sub> is quickly desorbed after the gas carrier has been switched from CO<sub>2</sub> to He. In fact, ~ 95 % of CO<sub>2</sub> is desorbed within 3 min under these conditions. This adsorption-desorption cycle was repeated six times with no noticeable changes being observed in the kinetics of desorption or CO<sub>2</sub> uptake. Thus, the N-doped porous carbons reported here can be quickly, easily and totally regenerated over multiple cycles without any loss of adsorption performance.

### **3. Conclusions**

In summary, we have demonstrate a facile one-step synthetic strategy for the fabrication of N-doped porous carbons with high surface areas (up to 3500 m<sup>2</sup> g<sup>-1</sup>), large pore

volumes (up to  $\sim 2.6 \text{ cm}^3 \text{ g}^{-1}$ ) and a porosity inside the micropore-mesopore range. The choice of polypyrrole as carbon precursor is the key to obtaining, *via* simple one-step chemical activation with KOH, porous carbons with outstanding textural and chemical characteristics. These properties can be modulated by modifying the activation parameters (i. e. amount of activating agent KOH and temperature). Interestingly, porous carbons with a narrow microporosity and high nitrogen contents (up to 10.1 wt %) in the form of N basic sites (pyridonic-N groups) can be obtained by employing only mild activation conditions (i. e. KOH/PPy=2 and  $T < 800^\circ\text{C}$ ). These mildly activated carbons exhibit a high efficiency for  $\text{CO}_2$  capture. In particular, a high  $\text{CO}_2$  adsorption uptake of  $3.9 \text{ mmol CO}_2 \cdot \text{g}^{-1}$  at room temperature is obtained for the activated carbon CP-2-600 prepared with KOH/PPy=2 at  $600^\circ\text{C}$ . This good  $\text{CO}_2$  adsorption performance is attributed to the presence of a narrow microporosity together with a high density of N basic groups. These porous carbons also show a high  $\text{CO}_2$  adsorption rate, a good selectivity for  $\text{CO}_2\text{-N}_2$  separation and they can be easily regenerated.

#### **4. Experimental Section**

*Synthesis of porous carbons.* Polypyrrole was prepared using  $\text{FeCl}_3$  as oxidant. In a typical synthesis, 3 g of pyrrole (recently distilled under  $\text{N}_2$ ) was added to a solution of  $\text{FeCl}_3$  (0.5 M, 200 mL) and the mixture was magnetically stirred for 2 h. The polypyrrole was then separated by filtration and washed with abundant distilled water and dried. The final polypyrrole yield was around 100 %. The polypyrrole was chemically activated by heating a PPy-KOH mixture (KOH/PPy at a weight ratio of 2 or 4) under  $\text{N}_2$  (99.9992 %,  $< 2 \text{ ppm H}_2\text{O}$ ,  $< 3 \text{ ppm O}_2$ ) up to a temperature in the  $600\text{-}850^\circ\text{C}$  range (heating rate:  $3^\circ\text{C}/\text{min}$ , holding time: 1 h). The activated samples were then thoroughly washed several times with HCl (10 wt %) to remove any inorganic salts and then washed with distilled water until neutral pH. Finally, the activated carbon was

dried in an oven at 120 °C. The activated carbons thus synthesized were denoted as CP- $x$ - $y$ , where  $x$  is the KOH/PPy weight ratio and  $y$  the activation temperature (in °C).

*Characterization.* Nitrogen sorption isotherms and the textural properties of the carbons were determined by nitrogen physisorption at -196°C in a conventional volumetric apparatus (Micromeritics ASAP 2020). The surface area was calculated by the BET method based on adsorption data in the partial pressure ( $p/p_0$ ) range of 0.04 to 0.2 and the total pore volume was determined from the amount of nitrogen adsorbed at a relative pressure of 0.99. The micropore volume was obtained *via* the t-plot analysis. The pore size distributions (PSDs) were determined via a Non Local Density Functional Theory (NLDFT) method using nitrogen adsorption data and assuming a slit pore model. Scanning electron microscopy (SEM) images were obtained with a Quanta FEG650 (FEI) instrument. Transmission electron micrographs (TEM) were taken on a JEOL (JEM-2000 FX) operating at 200 kV. Diffuse reflectance infrared (IR) spectra of the powders of the materials were recorded on a Nicolet Magna-IR 560 spectrometer fitted with a diffuse reflection attachment. X-ray photoelectron spectroscopy (XPS) was carried out by means of a Specs spectrometer, using Mg K $\alpha$  (1253.6 eV) radiation from a double anode at 50 w. Binding energies for the high-resolution spectra were calibrated by setting C 1s to 284.6 eV. Elemental analysis (C, H, S and O) of the samples was carried out on a LECO CHN-932 microanalyzer.

*CO<sub>2</sub> adsorption measurements.* The adsorption of CO<sub>2</sub> was measured using a Nova 4200e (Quantachrome) static volumetric analyzer. Prior to the adsorption analysis, the sample (around 50-100 mg) was degassed at 200°C for several hours. The CO<sub>2</sub> adsorption experiments were performed at three temperatures: 0°C, 25°C and 50°C. The adsorption kinetics of the CO<sub>2</sub> and N<sub>2</sub>, and adsorption-desorption cycles were measured

in a thermogravimetric analyser (C. I. Electronics). Both sets of experiments were performed at 25 °C and the temperature was controlled by means of a circulating bath (Haake K15). For the kinetics analysis, the sample (~ 10 mg) was degassed under a He stream at 200°C for 1 hour. The gas was then switched from He to CO<sub>2</sub> or N<sub>2</sub> (100 mL·min<sup>-1</sup>) and the weight variation with time was recorded. In the case of the adsorption-desorption cycles, the sample (~ 30 mg) was degassed under a stream of He at a temperature of 200°C before the cyclic experiments. During the adsorption, the carbon sample was exposed to a stream of pure CO<sub>2</sub> (100 mL·min<sup>-1</sup>). Once the sample was saturated, the gas was switched back from CO<sub>2</sub> to He (100 mL·min<sup>-1</sup>) and the carbon dioxide was desorbed. This adsorption-desorption cycle was repeated several times.

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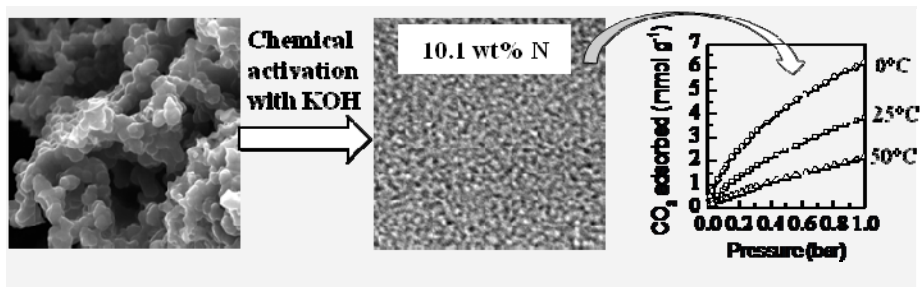




## One-step synthesis of N-doped highly porous carbons

*M. Sevilla, P. Valle-Vigón, A.B. Fuertes\**

### Synthesis and characterization of N-doped polypyrrole-based porous carbons for CO<sub>2</sub> capture



A facile one-step synthesis strategy for the fabrication of N-doped porous carbons exhibiting high surface areas, up to  $3500 \text{ m}^2 \text{ g}^{-1}$ , large pore volumes, up to  $\sim 2.6 \text{ cm}^3 \text{ g}^{-1}$ , and a porosity in the micro-mesopore range is here presented. It is based on the chemical activation of polypyrrole with KOH.

The prepared activated carbons exhibit high CO<sub>2</sub> uptakes, up to  $3.9 \text{ mmol CO}_2 \text{ g}^{-1}$ , high CO<sub>2</sub> adsorption rate, a good selectivity for CO<sub>2</sub>-N<sub>2</sub> separation and they can be easily regenerated.

## **Figure Captions**

**Figure 1.** SEM images of polypyrrole (a) and activated carbons CP-2-600 (b, c) and CP-4-850 (d). HRTEM images of CP-4-600 (e) and CP-4-850 (f).

**Figure 2.** (a) N<sub>2</sub> sorption isotherms and (b) pore size distributions (PSDs) of activated carbons prepared with KOH/PPy=2 at different activation temperatures.

**Figure 3.** a) Infrared spectra and b) N 1s core-level spectra of the activated carbons prepared with KOH/PPy=2 at different activation temperatures.

**Figure 4.** CO<sub>2</sub> adsorption isotherms at 0°C (○), 25°C (□) and 50°C (Δ) for the porous carbons obtained for KOH/PPy=2 and different activation temperatures: (a) 600°C (CP-2-600), (b) 650°C (CP-2-650), (c) 700°C (CP-2-700) and (d) 800°C (CP-2-800).

**Figure 5.** Change in the isosteric enthalpy of adsorption with nitrogen content for the samples activated with KOH/PPy=2 at different temperatures in the 600-800 °C range. Surface coverage ~ 0.6 mmol·g<sup>-1</sup>.

**Figure 6.** (a) Adsorption kinetics of CO<sub>2</sub> and N<sub>2</sub> at 25°C for the CP-2-600 sample and (b) CO<sub>2</sub> Adsorption-desorption cycles obtained for the CP-2-600 sample at 25°C (CO<sub>2</sub> concentration: 100 %).

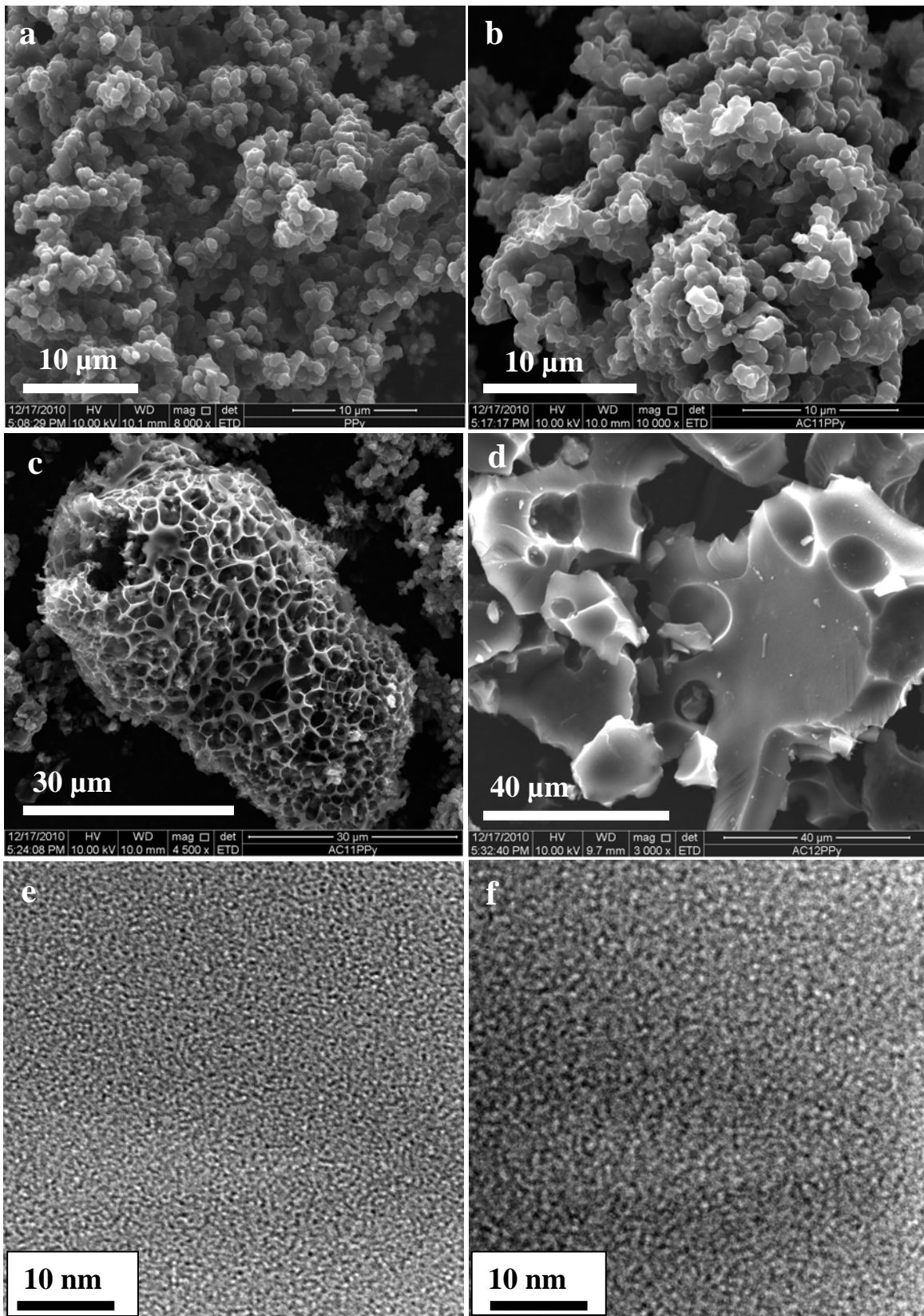


Figure 1

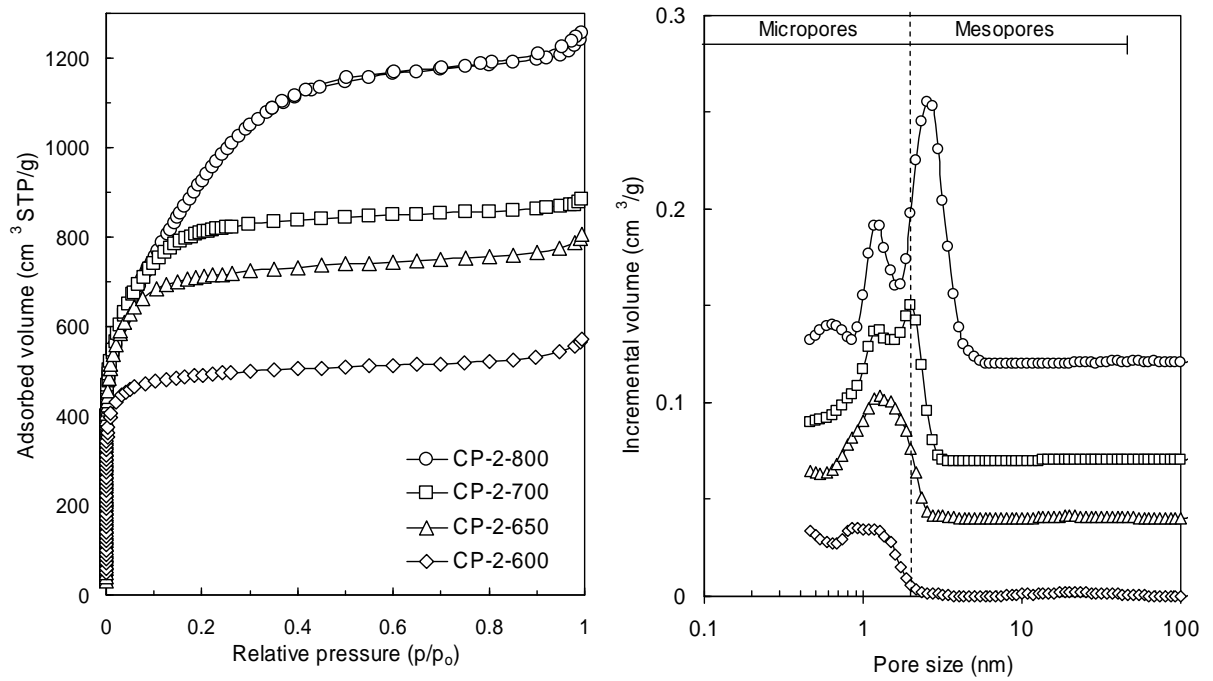


Figure 2

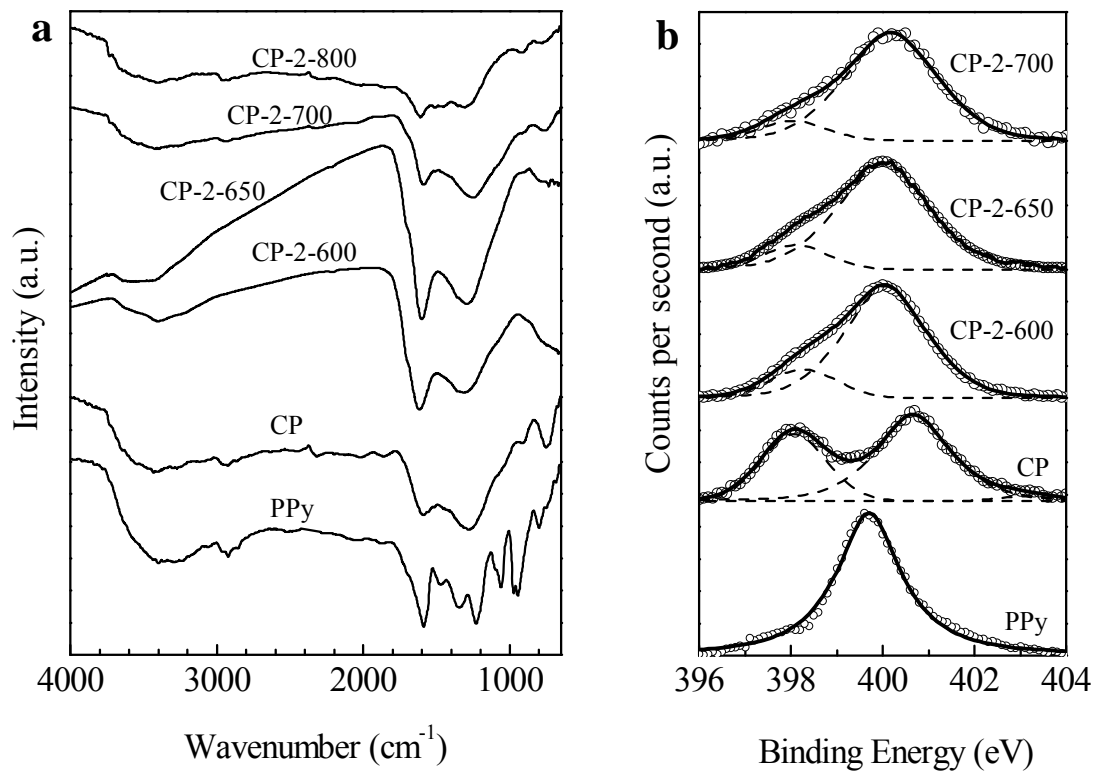


Figure 3

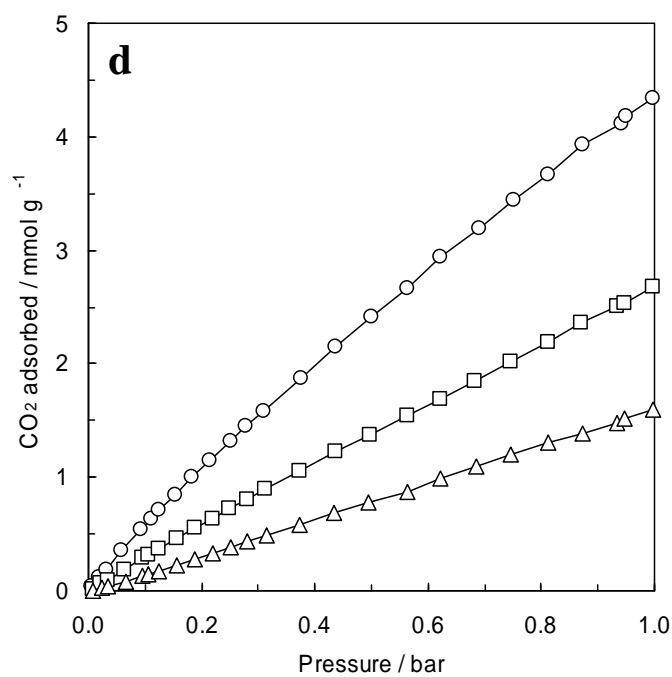
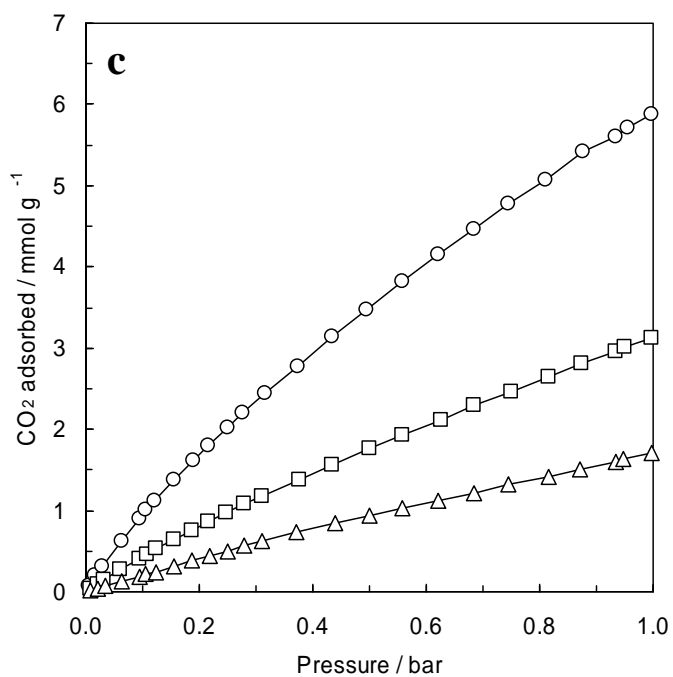
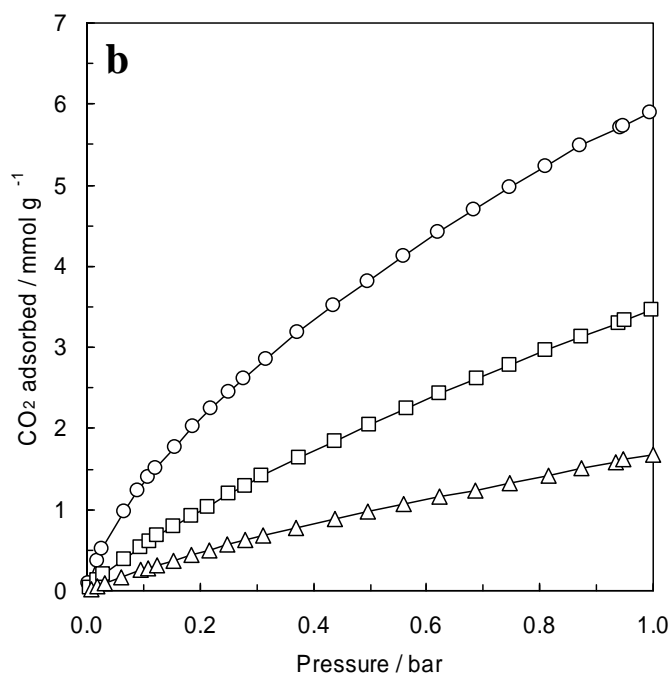
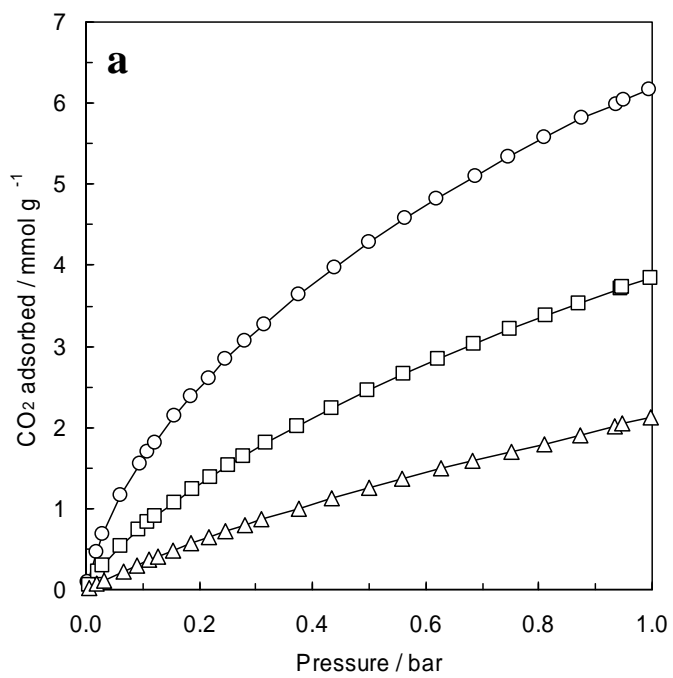


Figure 4

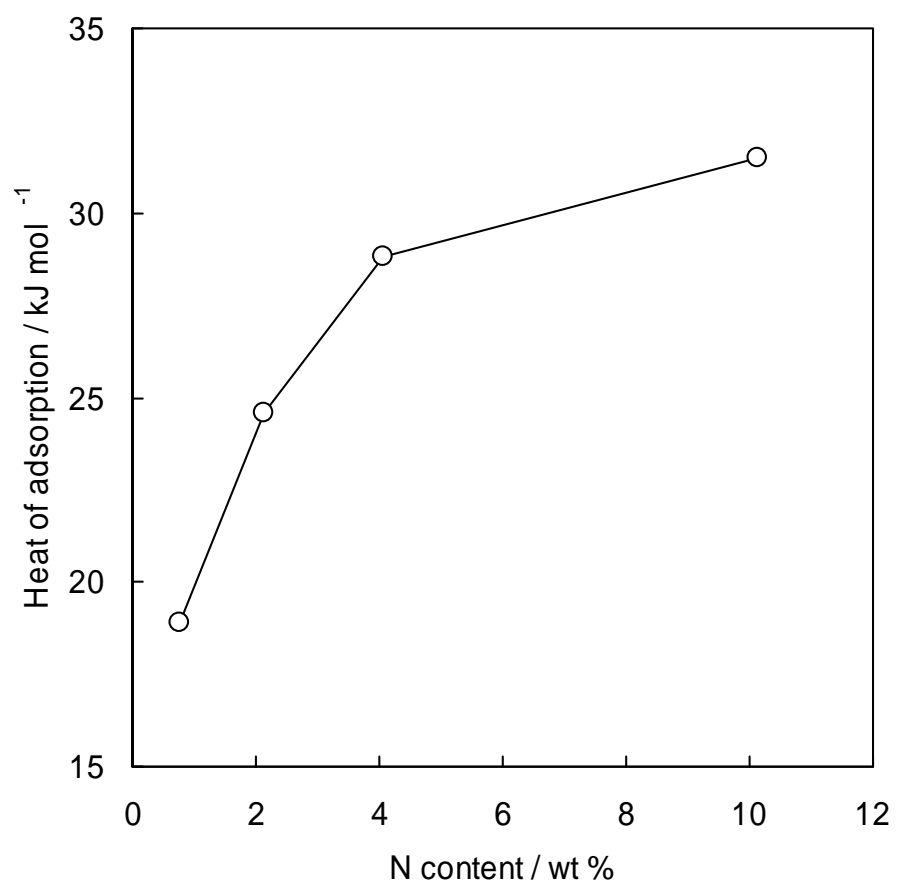


Figure 5



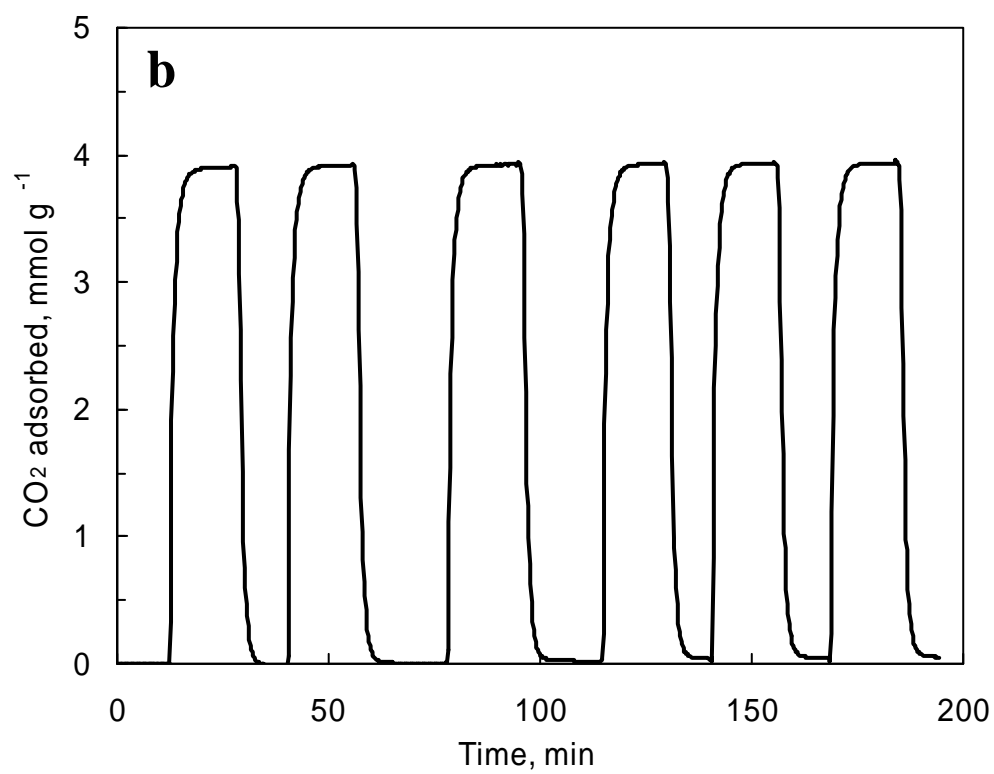
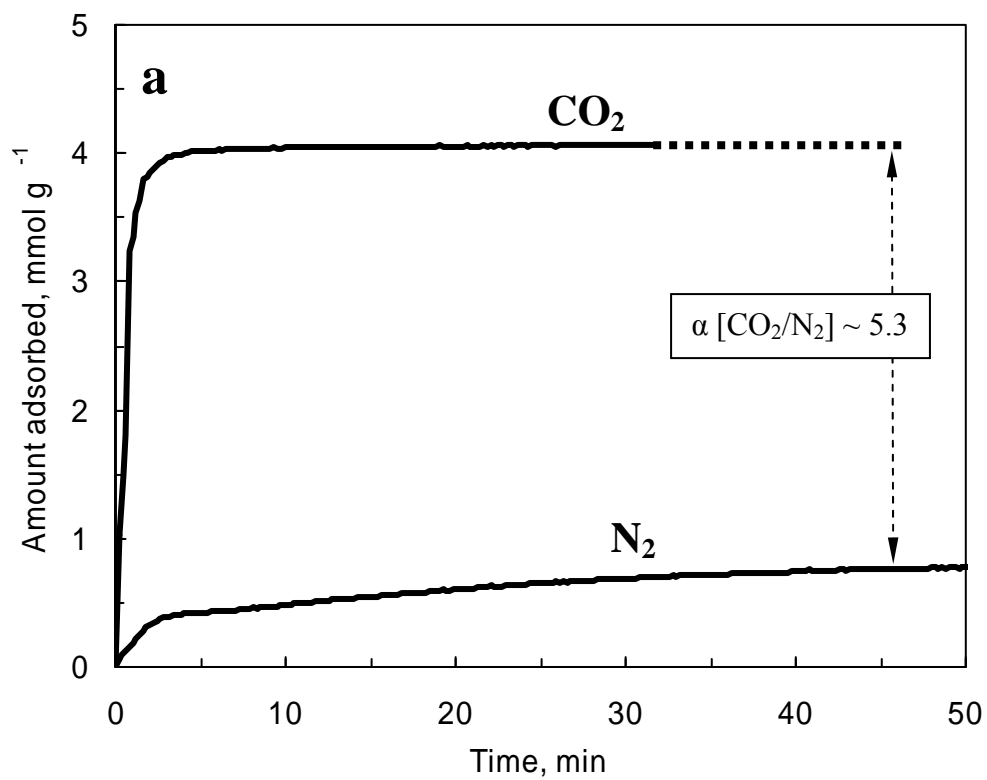


Figure 6