Research paper

The impact of surface chemistry and texture on the CO₂ uptake capacity of graphene oxideAmira Alazmi^a, Omar El Tall^b, Mohamed N. Hedhili^b, Pedro M.F.J. Costa^{a,*}^a King Abdullah University of Science and Technology (KAUST), Physical Science and Engineering Division, Thuwal 23955-6900, Saudi Arabia^b King Abdullah University of Science and Technology (KAUST), Core Labs, Thuwal 23955-6900, Saudi Arabia

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ABSTRACT

The influence of the synthesis route on the surface characteristics and CO₂ uptake of graphene oxide was studied. Powders derived from the classical Hummer's method approach and the so-called improved Hummer's method were benchmarked against zeolite 13X and certified carbon nanotubes. With a specific surface area of 283 m² g⁻¹ and a CO₂ adsorption capacity of 2.1 mmol g⁻¹ (at 273 K), the improved Hummer's product was superior to the other two nanocarbons tested.

1. Introduction

The process of carbon dioxide capture and storage (CCS) is seen as a critical strategy to mitigate the so-called greenhouse effect and the planetary climate changes associated with it. To prevent further increases in the concentration of atmospheric carbon dioxide (CO₂), [1] it has been suggested that CCS technology should be implemented in all fossil-fuel power plants, the primary source of CO₂ emissions [2]. CCS approaches can be divided in three categories: 1) pre-combustion technology, where the CO₂ extraction from fossil fuels occurs before their combustion; 2) oxy-fuel technology, where the combustion process is performed under oxygen instead of air; 3) post-combustion technology, where the CO₂ extraction is carried out after the fossil fuel combustion [1,3,4]. Among these, the latter is possibly the most widespread since it can be retrofitted to existing power plants without major infrastructure modifications [5]. In these circumstances, the development of physical and chemical post-combustion methods has been considerable over the last few years and, today, CO₂ capture by physical adsorption is regarded to be both energetically efficient and technically feasible.

Materials such as zeolites [6,7], metal-organic frameworks (MOFs) [8,9] and some carbon allotropes [10–12] are characterized by their high surface area and regular pore structure [13], two properties that favor gas uptake. In Industry, microporous carbons, most commonly in the activated form, are one of the workhorse materials for physical gas

adsorption. Besides having minimal production costs, they are structurally stable in a wide range of temperatures and can be functionalized with diverse types of chemical groups. This allows one to tailor their selectivity towards specific gases such as CO₂ [14,15]. Analogously, for nanostructured carbon materials, it has been found that the presence of functional groups containing oxygen favors CO₂ uptake [16]. In graphene, polar groups can enhance the gas adsorption capacity by activating exposed edges and terraces, thereby introducing additional binding sites [17]. Interestingly, a high density of functional and polar groups in basal planes and edges is an inherent characteristic of graphene oxide (GO). Common moieties grafted to GO include carbonyl and epoxy groups. These are slightly basic thus a beneficial acid-base interaction between CO₂ and this material would be expected [18]. For these reasons, the porous and functionalized layered structure of GO constitutes a logical candidate for next-generation CO₂ adsorbents [19]. Whilst the work on this topic is still limited [20,21], there is a prevalence in the literature of GO powders prepared using the classical Hummer's method. Overall, claims of their CO₂ uptake capacity have been markedly disappointing (<1 mmol g⁻¹) [16,22–24]. Possible explanations are the limited accessible surface area (commonly <100 m² g⁻¹, cf. Table SI 1 in Supporting Information) and reduced porosity (due to restacking of graphene sheets after exfoliation) [19].

Previously, we demonstrated that the structure and surface chemistry of GO (and, ultimately, its reduced counterpart) are highly dependent on the oxidation conditions the initial graphite is subjected to [25,26]. In this follow-up study, we describe how the synthesis and

* Corresponding author.

Email address: pedro.dacosta@kaust.edu.sa (P.M.F.J. Costa)

drying strategy of GO materials also affects their CO₂ adsorption capacity and selectivity. For reference, the GO results are compared with those of two benchmark materials, the commercial zeolite 13X and a certified reference of single-walled carbon nanotubes (SWCNT).

2. Experimental

2.1. Materials

The zeolite 13X was purchased from STREM chemicals (CAS Number: 63231-69-6) while the certified SWCNT (SRM2483) was procured from the National Institute of Standards and Technology (NIST), US. The GO materials were synthesized from natural graphite powder using either the classical Hummer's method [14] (hereafter, HGO) or an improved Hummer's method [27] (hereafter, IGO). The detailed GO synthesis procedures are presented in reference [25] and in the Supporting Information. Several drying approaches were tested namely vacuum, freeze and supercritical [28]. The results hereafter refer to the vacuum-dried GO powders as these yielded the best uptake capacities (refer to Supporting Information).

2.2. Characterization

The structure and surface morphology of the GO materials was investigated by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and powder X-ray diffraction (XRD). The surface chemistry was analyzed using X-ray photoelectron spectroscopy (XPS). More details on the instrumentation and acquisition conditions can be found in the Supporting Information.

Nitrogen (N₂) and carbon dioxide adsorption isotherms were recorded at 273K and 298K, in up to 1 bar of absolute pressure, with a Micromeritics TriStar II 3020 surface area and porosity analyzer (Micromeritics Instrument Corporation, US). Each isotherm was recorded at least twice and the average used for analysis. Immediately previous to the data acquisition, the as-prepared HGO and IGO were degassed under vacuum at 80 °C for 12h. As for the zeolite 13X and the SWCNT, these were degassed under vacuum for 12h at 100 °C and 250 °C, respectively. The textural analysis data for all samples was obtained from N₂ adsorption-desorption isotherms recorded at 77K and using an ASAP2420 volumetric adsorption analyzer (Micromeritics Instrument Corporation, US). The specific surface area was calculated by means of the Brunauer-Emmett-Teller (BET) approach, typically in the 0.05–0.3 relative pressure range, and adjusted to lower relative pressure range for microporous samples ($P/P_0 < 0.1$) until the best correlation coefficient with positive C constant values was obtained. The pore size distribution (PSD) was assessed by means of the Barrett-Joyner-Halenda (BJH) model (adsorption isotherm) and non-local density functional theory (NLDFT), here assuming slit-pore shapes. The micropores volume was calculated using the *t*-plot method and considering a carbon black statistical thickness model. Finally, the adsorption selectivity (*S*) of CO₂ over N₂ for the zeolite 13X, the SWCNT and the IGO was obtained according to the simplified ideal adsorbed solution theory (IAST) [29]. Diffusive reflectance infrared Fourier transform spectroscopy (DRIFTS) was performed to confirm the nature of the adsorbate-adsorbent interaction. Further details can be found in the Supporting Information.

3. Results and discussions

3.1. Characterization of the benchmark and GO materials

The literature of carbon materials is very rich in studies dealing with gas uptake [30]. However, the diversity of experimental protocols and data interpretation models proposed is such that it is often chal-

lenging to reliably compare the results of different reports. One way to lessen this issue is to use commercially available materials that, due to their structural and chemical constancy, may act as standards or benchmarks. For this reason, we initiated the present study by evaluating two materials that are accessible to the community and of relevance to the analysis of CO₂ uptake by nanostructured carbon materials. The first, zeolite 13X, is a well-known molecular sieve with outstanding capability to adsorb CO₂ [31,32]. The second, is a metrology-grade, certified reference material (for chemical analysis) of single-walled carbon nanotubes [33]. In fact, the latter is one of the few standards available for nanocarbons [34]. The surface textural characteristics of these benchmark materials were analyzed, with the respective isotherms (in N₂ at 77K) and calculated pore size distributions shown in Fig. 1. Further details such as the specific surface area and micropore volume are given in Table 1.

Based on the classification of porous materials issued by the International Union of Pure and Applied Chemistry (IUPAC), the zeolite 13X exhibits a typical type I isotherm (Fig. 1a). Its surface area is 790 m² g⁻¹; of these, 96% are estimated to originate from micropores. As concerns the pore sizes, the NLDFT model points to a very narrow distribution centered at 0.7 nm (Fig. 1c). These observations match the product technical specifications provided by the vendor, thereby validating our measurements [35]. In regards to the standard SRM2483, the certificate of analysis provided by the NIST does not include surface textural data. Our analysis showed that the SWCNT soot displays a type IV isotherm with a H4 hysteresis loop at $P/P_0 > 0.5$ (Fig. 1b). From Table 1, the surface area (790 m² g⁻¹) is equal to that of the zeolite 13X but only 10% of it corresponds to micropores. The modelled PSD (Fig. 1d) follows an asymmetric bimodal distribution wherein the first region, centered at 2 nm, is a well-defined peak and the second region, from 3 nm onwards, is composed by a multitude of peaks up to 50 nm. These observations are in line with what is expected for SWCNT samples [36], making the SRM2483 a good candidate for future validation of CO₂ capture by nanocarbons.

Following the study of the two benchmark materials, the surface textural characteristics of the vacuum-dried GOs were analyzed. Fig. 2a shows that both HGO and IGO originated a combination of type I and IV isotherms with a H3 hysteresis loop at $P/P_0 > 0.5$. This is indicative of the presence of slit-shaped mesopores [37,38]. Additionally, some differences are straightforward when observing the low and high relative pressure regimes. At low pressure, the amount of N₂ adsorbed increases rapidly, hence suggesting the existence of micropores in these materials [39]. This is particularly noticeable for IGO, maybe due to a higher density of pores with <2 nm width. At high pressure, the increase in N₂ uptake is more prominent for HGO, so macropores are likely to dominate in this sample. Remarkably, the PSD of the IGO (Fig. 2b) indicates a considerable presence of ultra-micropores (<1 nm) together with micropores in the range of 1–2 nm and a smaller portion of 3–5 nm mesopores. The predominance of (ultra-)micropores in the IGO sample is confirmed by the *t*-plot data (Table 1) as these account for ~80% of the total pore volume and 93% of the total surface area. By contrast, the HGO plot in Fig. 2b shows a wider range of pore size distribution. While micropores are present, the dominant sizes are >25 nm (macropores). These observations corroborate our previous XRD and SEM results which showed smaller d-spacing and denser graphene (re) stacking in the HGO sample (cf. ref [25] or, for quick guidance, Figs. SI 1 and SI 2). Besides the contrasting PSD in the two GO samples, the differences in surface area and pore volumes were also remarkable (Table 1). At instances, the values were one order of magnitude apart (e.g., $V_{\text{micro}} = 0.01 \text{ cm}^3 \text{ g}^{-1}$ for HGO versus $V_{\text{micro}} = 0.11 \text{ cm}^3 \text{ g}^{-1}$ for IGO). On the other hand, when compared to the benchmark materials, the specific surface area of the GOs was relatively small, particularly for the HGO case. Yet, the IGO has a much

Fig. 1. (a) and (b) N_2 adsorption-desorption isotherms for the zeolite 13X and the certified SWCNT, respectively; (c) and (d) Pore-size distributions (using N_2 and calculated by NLDFT with a cylindrical pores geometry model) for the zeolite 13X and the certified SWCNT, respectively.

Table 1
Specific surface area and pore structure of the zeolite 13X, SWCNT and GO materials studied.

Material	BET Surface area (m^2/g)	pore Volume (cm^3/g)	t-Plot		
			Micropore Area (m^2/g)	External Surface Area (m^2/g)	t-Plot Micropore Volume (cm^3/g)
Zeolite 13X	$790 \pm 0.06\%$	$0.33 \pm 0.1\%$	$771 \pm 0.9\%$	$19 \pm 2\%$	$0.29 \pm 0.1\%$
SWCNT	$790 \pm 0.1\%$	$0.94 \pm 0.9\%$	$116 \pm 1\%$	$674 \pm 0.1\%$	$0.03 \pm 0.8\%$
HGO	$36 \pm 0.5\%$	$0.05 \pm 0.4\%$	$28 \pm 0.3\%$	$8 \pm 0.9\%$	$0.01 \pm 0.5\%$
IGO	$283 \pm 0.2\%$	$0.14 \pm 0.5\%$	$264 \pm 0.4\%$	$19 \pm 3\%$	$0.11 \pm 0.4\%$

more pronounced micropore area than the standard SWCNT sample (Table 1).

Given the importance of surface chemistry in assisting the sorption of CO_2 by carbonaceous materials, further analysis on the nature of the functional groups present in HGO and IGO was performed. This adds to our previous structural and (electro) chemical analyses performed in different sample batches of these materials [25,26,28]. In regards to the types of oxygen-containing functional groups, the FTIR spectra of the GOs (Fig. SI 3) show the presence of vibrational bands assigned to carboxy (C=O, 1406 cm^{-1}), epoxy (C-O, 1220 cm^{-1}), and alkoxy (C-O, 1058 cm^{-1}) groups, possibly situated at the edges of the graphene sheets [25,40]. At 1725 cm^{-1} , the peak can be interpreted as the C=O stretching in —COOH groups. The broad —OH stretching vibrational band ($3200\text{--}3700\text{ cm}^{-1}$) is common to both GOs but its predominance in the IGO spectrum (along with the more intense characteristic band

of the vibrations of residual water at 1622 cm^{-1}) [41] is an indication of higher content of intercalated water and more extensive oxidation. A more detailed look at the surface chemistry was provided by the XPS analysis. The high resolution C1s spectra are shown in Fig. 3. The peak area of each component, calculated after deconvolution, is shown in Table SI 2. Noticeable from the peak deconvolutions is the different sp^2/sp^3 ratios obtained for the HGO (0.54) and IGO (0.27). Also, the relative intensity of the C-O peak (epoxy and hydroxyl, 286.8 eV) to the sp^2 hybridized C ($\sim 284.3\text{ eV}$) peak increases from HGO to IGO. This is further reflected in the C/O atomic ratios (as estimated from the survey spectra in Fig. SI 4) which decrease from 2.9 (for HGO) to 2.4 (for IGO). Overall, these observations corroborate a higher oxidation degree for the IGO [26].

In previous studies, we demonstrated that a rational approach to the synthesis strategy of reduced GOs could lead to a manifold increase

Fig. 2. (a) N_2 adsorption-desorption isotherms of HGO and IGO, at 77 K; (b) Pore size distributions for the HGO and IGO (in N_2 and calculated using NLDFT).

Fig. 3. High resolution XPS C1s spectra of (a) HGO and (b) IGO.

in their electrochemical capacitance [25,26,28]. The above characterization confirms this line of thought for surface texture and chemistry of GOs. Importantly, it highlights how critical it is to select the correct synthesis and drying paths to optimize properties such as the microporosity of these materials.

3.2. CO_2 capture studies

Generally, it is believed that porous materials with a large population of ~ 1 nm pores show higher CO_2 adsorption capacity than those with a predominantly mesoporous network [42]. Also of note, porous carbons with ultra-micropores (< 1 nm) are able to capture large amounts of CO_2 gas at 1 bar [16,43,44]. In this section, we show how this applies to GO materials.

First, the CO_2 adsorption capacities of the two benchmark materials were measured from the adsorption isotherms at 298 K (Fig. 4a and b). When compared to the predominantly mesoporous SWCNT, a steeper profile at low pressures for the zeolite 13X is expected given its uniform microporosity. Consequently, this material is highly performant as a physical adsorbent, attaining 5.8 mmol g^{-1} at 1 bar. In identical conditions, the standard nanotubes sample took up a maximum of 1.1 mmol g^{-1} of CO_2 . For guidance, activated carbon and pyrolytic carbon materials can achieve, respectively, 1.8 mmol g^{-1} and 1.2 mmol g^{-1} (at 1 bar and 298 K) [45,46].

Following the above, the CO_2 adsorption-desorption isotherms for the GO materials were acquired at room temperature (Fig. 4c). At atmospheric pressure, the IGO (1.40 mmol g^{-1}) exhibits almost double of

the uptake capacity of HGO (0.81 mmol g^{-1}). Further to this, the two isotherms display minor hysteresis meaning that the gas adsorption is reversible.

The adsorption capacity of the GOs was further evaluated at low temperature (273 K), as illustrated in Fig. 4d. The uptake values at 1 bar were, as expected, higher but entirely consistent with those at 298 K. Again, the IGO showed much larger sorption capacity than HGO (2.10 mmol g^{-1} against 0.97 mmol g^{-1} , respectively) and, for both cases, the process was reversible. Interestingly, the increase in CO_2 adsorption with decreasing temperature was more pronounced for the IGO (33% increase) than for the HGO (15%) powder. These results suggest that, in addition to the specific surface area, other key factors are responsible for the CO_2 adsorption performance (discussed further on).

Considering the reversibility observed at room and low temperatures, it is plausible to infer that the uptake of CO_2 by the GOs takes place via physisorption. To confirm this, the IGO was subjected to a flow of CO_2 and DRIFT spectroscopy was performed (Fig. 5). The in situ IR spectrum obtained (in red, Fig. 5) overlapped almost entirely with that of the non-exposed IGO (in black). The additional bands observed, marked in Fig. 5 with a star, originate from the gaseous CO_2 flowing through the chamber: the ν_3 (asymmetric stretching) band at 2346 cm^{-1} , the combination bands ($\nu_3 + \nu_1$, $\nu_3 + 2\nu_2$) at 3714 and 3598 cm^{-1} , the ν_1 (symmetric stretching) band at 1381 cm^{-1} and the (ν_2) bend $O=C=O$ band at 665 cm^{-1} [47–49]. After interrupting the gas flow, the IR spectrum obtained (in blue) was similar to that of the non-exposed IGO (in black). Taken together, there were no new chemi-

Fig. 4. Pure component CO_2 adsorption isotherms: (a) and (b) zeolite 13X and SWCNT, respectively, measured at 298 K and 1 bar; HGO and the IGO materials measured at 1 bar: (c) at 298 K; (d) at 273 K.

Fig. 5. DRIFT spectra of IGO: in its initial non-exposed state (black curve), under a CO_2 flow (red curve) and after the CO_2 exposure (blue curve). The * identifies bands from the gaseous CO_2 .

cal bonds or formation of carbonate on the IGO surface, establishing the adsorption process as a purely physical phenomenon.

Typically, the flue gas emitted by coal-fired power plants contains approximately 15% of CO_2 which is balanced with N_2 , at a total pres-

sure of ~ 1 bar. Hence, it is critical that the adsorbent material exhibits high selectivity for CO_2 over N_2 , at room temperature and atmospheric pressure [50]. Given the diversity of experimental methods and models used to calculate the selectivity of CO_2 uptake, it is not strictly correct to refer to literature values in a comparative study. In view of this, we started by evaluating the CO_2/N_2 selectivity of the two benchmark materials, zeolite 13X and the standard SWCNT. In our process, experimental single-component isotherms and the ideal adsorption solution theory (IAST) were used (more details in the Supporting Information). Given that the CO_2 isotherms (at 298 K) for the benchmark materials had been acquired (Fig. 4), it was necessary to analyze the analogous N_2 adsorption isotherms (shown in Fig. SI 5). Subsequently, their CO_2/N_2 selectivity was calculated for the range of pressures up to 1 bar. Expectedly, the molecular sieve presented an outstanding value of 365, at atmospheric pressure (Fig. 6a). In sharp contrast, and under the same conditions, the SWCNT had a significantly lower value of 13 (Fig. 6b).

The same procedure was applied to the IGO powder (Fig. 6c) which attained the respectable mark of 70. Further to the room temperature analysis, we also investigated the selectivity for the GO materials at lower temperature (Fig. 7). The N_2 adsorption isotherms of HGO and IGO, measured at 273 K, can be seen in Fig. SI 6. Both powders showed a measurable increment in CO_2/N_2 selectivity with figures (at 1 bar) of 56 (for HGO) and 85 (for IGO). Overall, the IGO stands out as the most selective CO_2 adsorbent of the three carbonaceous materials tested. While not as performant as the benchmark zeolite 13X, it exhibits more than five times the selectivity of the standard SWCNT (despite having the same surface area of the nanotubes sample). Remarkably, even con-

Fig. 6. CO₂/N₂ selectivity calculated by IAST method for CO₂/N₂ gas mixture of 0.15:0.85 for: (a) Zeolite 13X; (b) SWCNT; (c) IGO) at 298 K.

Fig. 7. CO₂/N₂ selectivity calculated by IAST method for CO₂/N₂ gas mixture of 0.15:0.85 for: (a) HGO, (b) IGO) at 273 K.

sidering deviations originated from the application of different methods and models to estimate selectivity, the values attained with the present IGO surpass significantly many other traditional and emerging CO₂ adsorbents (see Table SI 3).

Taking advantage of the above sets of isotherms and the Clausius-Clapeyron equation [51], the isosteric heat of adsorption (Q_{st}) was calculated for the two GOs (Fig. 8). For IGO, the initial Q_{st,CO_2} value is

Fig. 8. Isosteric heat of adsorption of pure CO₂ onto HGO and IGO as a function of CO₂ uptake.

relatively high, at 35.3 kJ mol⁻¹. We attributed this to the strong adsorbent-adsorbate interaction between the (predominantly) microporous IGO and the CO₂ molecules. Still, this figure is well within the range of ordinary physisorption (i.e. < 40 kJ mol⁻¹) [50]. With increasing adsorption coverage, the favorable active sites were consecutively occupied by CO₂ and the Q_{st,CO_2} decreased to a constant 33.0 kJ mol⁻¹ (from ~0.9 mmol g⁻¹ onwards). This value is similar to the Q_{st,CO_2} of hybrid materials such as GO/ZIF (31.9 kJ mol⁻¹) [52] but lower than those obtained for other porous materials based on graphene (56 kJ mol⁻¹) [53]. [18,54–56] As concerns the HGO, the average value was 28.2 kJ mol⁻¹. The smaller Q_{st,CO_2} of HGO could be a reflection of the lower density of oxygen-containing functional groups in its structure.

For completeness, the isosteric heat of N₂ adsorption (Q_{st,N_2}) was also calculated for the IGO powder (Fig. SI 7). Again, the average value obtained (21.9 kJ mol⁻¹) was well within the physisorption range but considerably lower than the corresponding Q_{st,CO_2} . This further corroborates the preferred adsorption of CO₂ by IGO. In any case, these findings suggest that both gases (CO₂ and N₂) interact with IGO through equivalent sorption mechanisms such as electrostatic and/or van der Waals forces (i.e. weak interaction forces).

A key factor on the practical utility and reliability of a physical adsorbent material for post-combustion CO₂ capture applications is whether it can be re-used without loss of function. To address this matter, cyclic CO₂ adsorption/regeneration experiments were carried out for the IGO by swinging the pressure between vacuum (< 0.01 bar) and 1 bar at 273 K. As shown in Fig. 9, the amount of CO₂ adsorbed remained almost constant after ten adsorption/regeneration cycles.

Fig. 9. Cyclic CO₂ adsorption performance of IGO at 273 K.

4. Discussion

The two benchmark materials were critical to correctly situate the uptake capacity and selectivity of the GO materials. The results above confirm that the zeolite 13X is a perfectly defined and homogenous microporous material with a high specific surface area. As expected, it shows outstanding uptake capacity and selectivity for carbon dioxide. By contrast, the standard SWCNT (SRM2483), whilst having similar surface area to the molecular sieve, is a predominantly mesoporous material with a large PSD. Its CO₂ uptake is unremarkable and the affinity for this gas in the presence of nitrogen was the lowest of all materials tested. To our knowledge, there are no previous studies addressing the surface textural and gas adsorption characteristics of this standard [33]. As a metrology tool, the SRM2483 was not developed for the purpose used here. However, it remains the closest to a structural and chemically homogenous material that is commercially available for the perusal of the nanocarbons community (along with two other standards, SWCNT-1 [57] and RM8281 [58]).

Concerning the two GOs analyzed, it is clear that the IGO is superior in all aspects related to CO₂ adsorption. Besides having a sizeable surface area and a dual character of micro- and meso-porosity, it also incorporates a large number and diversity of oxygen-containing functional groups. Importantly, the IGO showed the best uptake capacity and selectivity of all three nanocarbons tested, whether at room or low temperature. The calculated isosteric heats of adsorption support the view of a material that has stronger affinity for CO₂ than N₂ at atmospheric pressure but maintains this interaction within the physisorption regime ($< 40 \text{ kJ mol}^{-1}$).

Taking into account the specific surface area of the standard SWCNT and IGO materials, our results confirm that the total adsorption capacity in nanocarbons is not just a function of the specific surface area. A large micropore volume is mandatory for an optimum packing of the CO₂ molecules at room temperature. To evaluate this hypothesis, we performed additional experiments with an IGO having a more pronounced mesoporous character. As previously reported [28], it is possible to tailor the porosity of these powders by carefully selecting the drying method. Effectively, when critical point drying (CPD) is employed instead of the vacuum approach used above, the PSD of the IGO shifts from predominantly micro- to meso-porous (Fig. SI 8 and Table SI 4). In these circumstances, the maximum CO₂ adsorption capacity for the CPD-dried IGO was 1.9 mmol g^{-1} (at 273 K). In addition to sur-

face area and porosity, it is feasible to state that the relatively high density of oxygen-containing functional groups also contributed to enlarge the CO₂ uptake capacity and selectivity in IGO. In fact, Liu et al. demonstrated that oxygen-containing functional groups can enhance CO₂ adsorption density in microporous carbons [59]. Therefore, we suggest that the surface chemistry of IGO provides various weakly binding mechanisms for gas molecules [18,60] – including polar charges, hydrogen bonding and acid-base interactions – which contributed to the observed CO₂ capacity improvement.

5. Conclusions

The surface textural characteristics and CO₂ adsorption capacity of two benchmark materials and two GO powders were analyzed. The use of the zeolite 13X and the standard SWCNT provided a validation tool for the surface area, porosity and gas uptake measured for the Hummer's and Improve Hummer's GOs. The results obtained for the IGO are remarkable since along with the highest specific area, microporous volume and CO₂ adsorption capacity of the three nanocarbons tested, it also shows very good CO₂ selectivity within the physisorption regime. These observations strengthens our view that it is critical to select the synthesis steps of (reduced) GO materials – drying step included – according to the envisaged application.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.ica.2018.06.031>.

References

- [1] V. Scott, S. Gilfillan, N. Markussun, H. Chalmers, R.S. Haszeldine, Last chance for carbon capture and storage, *Nature Clim. Change* 3 (2) (2013) 105–111.
- [2] P. Nugent, Y. Belmabkhout, S.D. Burd, A.J. Cairns, R. Luebke, K. Forrest, T. Pham, S. Ma, B. Space, L. Wojtas, M. Eddaoudi, M.J. Zaworotko, Porous materials with optimal adsorption thermodynamics and kinetics for CO₂ separation, *Nature* 495 (7439) (2013) 80–84.
- [3] D.Y.C. Leung, G. Caramanna, M.M. Maroto-Valer, An overview of current status of carbon dioxide capture and storage technologies, *Renew. Sustain. Energy Rev.* 39 (2014) 426–443.
- [4] D. Iribarren, F. Petrakopoulou, J. Dufour, Environmental and thermodynamic evaluation of CO₂ capture, transport and storage with and without enhanced resource recovery, *Energy* 50 (2013) 477–485.
- [5] Z.H. Lee, K.T. Lee, S. Bhatia, A.R. Mohamed, Post-combustion carbon dioxide capture: Evolution towards utilization of nanomaterials, *Renew. Sustain. Energy Rev.* 16 (5) (2012) 2599–2609.
- [6] L.J. Dunne, A. Furgani, S. Jalili, G. Manos, Monte-Carlo simulations of methane/carbon dioxide and ethane/carbon dioxide mixture adsorption in zeolites and comparison with matrix treatment of statistical mechanical lattice model, *Chem. Phys.* 359 (1–3) (2009) 27–30.
- [7] A. Martin-Calvo, J.B. Parra, C.O. Ania, S. Calero, Insights on the anomalous adsorption of carbon dioxide in LTA zeolites, *J. Phys. Chem. C* 118 (44) (2014) 25460–25467.
- [8] D.J. Tranchemontagne, Z. Ni, M. O'Keeffe, O.M. Yaghi, Reticular chemistry of metal-organic polyhedra, *Angew. Chem. Int. Ed.* 47 (28) (2008) 5136–5147.
- [9] B. Liu, W.-P. Wu, L. Hou, Y.-Y. Wang, Four uncommon nanocage-based Ln-MOFs: highly selective luminescent sensing for Cu²⁺ ions and selective CO₂ capture, *Chem. Commun.* 50 (63) (2014) 8731–8734.
- [10] N.P. Wickramaratne, M. Jaroniec, Activated carbon spheres for CO₂ adsorption, *ACS Appl. Mater. Interfaces* 5 (5) (2013) 1849–1855.
- [11] Q. Liu, J. Shi, S. Zheng, M. Tao, Y. He, Y. Shi, Kinetics studies of CO₂ adsorption/desorption on amine-functionalized multiwalled carbon nanotubes, *Ind. Eng. Chem. Res.* 53 (29) (2014) 11677–11683.
- [12] S.C. Xu, S. Irlé, D.G. Musaev, M.C. Lin, Quantum chemical prediction of reaction pathways and rate constants for dissociative adsorption of COx and NOx on the graphite (0001) surface, *J. Phys. Chem. B* 110 (42) (2006) 21135–21144.
- [13] Z. Xiang, D. Cao, J. Lan, W. Wang, D.P. Broom, Multiscale simulation and modeling of adsorptive processes for energy gas storage and carbon dioxide capture in porous coordination frameworks, *Energy Environ. Sci.* 3 (10) (2010) 1469–1487.
- [14] Y. Zhao, L. Zhao, K.X. Yao, Y. Yang, Q. Zhang, Y. Han, Novel porous carbon materials with ultrahigh nitrogen contents for selective CO₂ capture, *J. Mater. Chem.* 22 (37) (2012) 19726–19731.
- [15] S.J. Park, S.Y. Jin, Effect of ozone treatment on ammonia removal of activated carbons, *J. Colloid Interface Sci.* 286 (1) (2005) 417–419.

- [16] L.-Y. Meng, S.-J. Park, Effect of exfoliation temperature on carbon dioxide capture of graphene nanoplates, *J. Colloid Interface Sci.* 386 (1) (2012) 285–290.
- [17] B.C. Wood, S.Y. Bhide, D. Dutta, V.S. Kandagal, A.D. Pathak, S.N. Punathanam, K.G. Ayappa, S. Narasimhan, Methane and carbon dioxide adsorption on edge-functionalized graphene: a comparative DFT study, *J. Chem. Phys.* 137 (5) (2012) 054702.
- [18] Z.-Y. Sui, B.-H. Han, Effect of surface chemistry and textural properties on carbon dioxide uptake in hydrothermally reduced graphene oxide, *Carbon* 82 (2015) 590–598.
- [19] G. Srinivas, J. Burrell, T. Yildirim, Graphene oxide derived carbons (GODCs): synthesis and gas adsorption properties, *Energy Environ. Sci.* 5 (4) (2012) 6453–6459.
- [20] J.W. Burrell, S. Gadipelli, J. Ford, J.M. Simmons, W. Zhou, T. Yildirim, Graphene oxide framework materials: theoretical predictions and experimental results, *Angew. Chem. Int. Ed.* 49 (47) (2010) 8902–8904.
- [21] Z.Y. Sui, Y. Cui, J.H. Zhu, B.H. Han, Preparation of Three-dimensional graphene oxide-polyethylenimine porous materials as dye and gas adsorbents, *ACS Appl. Mater. Interfaces* 5 (18) (2013) 9172–9179.
- [22] K. Xia, X. Tian, S. Fei, K. You, Hierarchical porous graphene-based carbons prepared by carbon dioxide activation and their gas adsorption properties, *Int. J. Hydrogen Energy* 39 (21) (2014) 11047–11054.
- [23] J. Xu, W. Xing, L. Zhao, F. Guo, X. Wu, W. Xu, Z. Yan, The CO₂ storage capacity of the intercalated diaminoalkane graphene oxides: a combination of experimental and simulation studies, *Nanoscale Res. Lett.* 10 (2015) 318.
- [24] G.-J. Shin, K. Rhee, S.-J. Park, Improvement of CO₂ capture by graphite oxide in presence of polyethylenimine, *Int. J. Hydrogen Energy* 41 (32) (2016) 14351–14359.
- [25] A. Alazmi, S. Rasul, S.P. Patole, P.M.F.J. Costa, Comparative study of synthesis and reduction methods for graphene oxide, *Polyhedron* 116 (2016) 153–161.
- [26] S. Rasul, A. Alazmi, K. Jaouen, M. Hedhili, P. Costa, Rational design of reduced graphene oxide for superior performance of supercapacitor electrodes, *Carbon* 111 (2017) 774–781.
- [27] D.C. Marcano, D.V. Kosynkin, J.M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L.B. Alemany, W. Lu, J.M. Tour, Improved synthesis of graphene oxide, *ACS Nano* 4 (8) (2010) 4806–4814.
- [28] A. Alazmi, O. El Tall, S. Rasul, M.N. Hedhili, S.P. Patole, P.M.F.J. Costa, A process to enhance the specific surface area and capacitance of hydrothermally reduced graphene oxide, *Nanoscale* 8 (41) (2016) 17782–17787.
- [29] A. Myers, J.M. Prausnitz, Thermodynamics of mixed-gas adsorption, *AIChE J.* 11 (1) (1965) 121–127.
- [30] J.R. Morris, C.I. Contescu, M.F. Chisholm, V.R. Cooper, J. Guo, L. He, Y. Ihm, E. Mamontov, Y.B. Melnichenko, R.J. Olsen, S.J. Pennycook, M.B. Stone, H. Zhang, N.C. Gallego, Modern approaches to studying gas adsorption in nanoporous carbons, *J. Mater. Chem. A* 1 (33) (2013) 9341–9350.
- [31] T. Remy, S.A. Peter, L. Van Tendeloo, S. Van der Perre, Y. Lorgouilloux, C.E.A. Kirschhock, G.V. Baron, J.F.M. Denayer, Adsorption and separation of CO₂ on KFI zeolites: effect of cation type and Si/Al ratio on equilibrium and kinetic properties, *Langmuir* 29 (16) (2013) 4998–5012.
- [32] Z. Liang, M. Marshall, A.L. Chaffee, Comparison of Cu-BTC and zeolite 13X for adsorbent based CO₂ separation, *Energy Procedia* 1 (1) (2009) 1265–1271.
- [33] E.K. Lin, R.L. Watters Jr, Certificate of Analysis, SRM 2483 Standard Reference Material, Single-Wall Carbon Nanotubes (Raw Soot), National Institute of Standards & Technology (NIST), USA, 2011.
- [34] F.R.F. Simoes, N.M. Batra, B.H. Warsama, C.G. Canlas, S. Patole, T.F. Yapici, P.M.F.J. Costa, Elemental quantification and residues characterization of wet digested certified and commercial carbon materials, *Anal. Chem.* 88 (23) (2016) 11783–11790.
- [35] INC., S.C., Certificate of Analysis. STREM CHEMICALS INC. 2015, (CAS Number: 63231-69-6).
- [36] Y.H. Hu, E. Ruckenstein, Pore size distribution of single-walled carbon nanotubes, *Ind. Eng. Chem. Res.* 43 (3) (2004) 708–711.
- [37] K.S. Sing, Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (Recommendations 1984), *Pure Appl. Chem.* 57 (4) (1985) 603–619.
- [38] W. Lv, D.-M. Tang, Y.-B. He, C.-H. You, Z.-Q. Shi, X.-C. Chen, C.-M. Chen, P.-X. Hou, C. Liu, Q.-H. Yang, Low-temperature exfoliated graphenes: vacuum-promoted exfoliation and electrochemical energy storage, *ACS Nano* 3 (11) (2009) 3730–3736.
- [39] J. Xu, W. Xing, L. Zhao, F. Guo, X. Wu, W. Xu, Z. Yan, The CO₂ storage capacity of the intercalated diaminoalkane graphene oxides: a combination of experimental and simulation studies, *Nanoscale Res. Lett.* 10 (1) (2015) 318.
- [40] H. Wu, W. Zhao, H. Hu, G. Chen, One-step in situ ball milling synthesis of polymer-functionalized graphene nanocomposites, *J. Mater. Chem.* 21 (24) (2011) 8626–8632.
- [41] N.A. Kumar, H.-J. Choi, Y.R. Shin, D.W. Chang, L. Dai, J.-B. Baek, Polyani-line-grafted reduced graphene oxide for efficient electrochemical supercapacitors, *ACS Nano* 6 (2) (2012) 1715–1723.
- [42] A.M. Ribeiro, J.C. Santos, A.E. Rodrigues, S. Riffart, Pressure swing adsorption process in coal to fischer-tropsch fuels with CO₂ capture, *Energy Fuels* 26 (2) (2012) 1246–1253.
- [43] M. Songolzadeh, M. Soleimani, M. Takht Ravanchi, R. Songolzadeh, Carbon dioxide separation from flue gases: a technological review emphasizing reduction in greenhouse gas emissions, *Sci. World J.* 2014 (2014) 34.
- [44] L.-Y. Meng, S.-J. Park, Effect of heat treatment on CO₂ adsorption of KOH-activated graphite nanofibers, *J. Colloid Interface Sci.* 352 (2) (2010) 498–503.
- [45] D.P. Bezerra, R.S. Oliveira, R.S. Vieira, C.L. Cavalcante, D.C. Azevedo, Adsorption of CO₂ on nitrogen-enriched activated carbon and zeolite 13X, *Adsorption* 17 (1) (2011) 235–246.
- [46] Z. Zhou, J. Yang, Y. Zhang, L. Chang, W. Sun, J. Wang, NaA zeolite/carbon nanocomposite thin films with high permeance for CO₂/N₂ separation, *Sep. Purif. Technol.* 55 (3) (2007) 392–395.
- [47] Z. Mouline, K. Asai, Y. Daiko, S. Honda, S. Bernard, Y. Iwamoto, Polymer-derived organoamine-functionalized amorphous silica materials for CO₂ capture, *J. Ceram. Soc. Jpn.* 124 (10) (2016) 989–995.
- [48] Q. Liu, A. Mace, Z. Bacsik, J. Sun, A. Laaksonen, N. Hedin, NaKA sorbents with high CO₂-over-N₂ selectivity and high capacity to adsorb CO₂, *Chem. Commun.* 46 (25) (2010) 4502–4504.
- [49] P.A. Gerakines, W. Schutte, J. Greenberg, E.F. van Dishoeck, The infrared band strengths of H₂O, CO and CO₂ in laboratory simulations of astrophysical ice mixtures, *arXiv preprint astro-ph/9409076* (1994).
- [50] S. Zulfiqar, D. Mantione, O. El Tall, M.I. Sarwar, F. Ruiperez, A. Rothenberger, D. Mecerreyes, Nanoporous amide networks based on tetraphenyladamantane for selective CO₂ capture, *J. Mater. Chem. A* 4 (21) (2016) 8190–8197.
- [51] J.A. Dunne, R. Mariwala, M. Rao, S. Sircar, R.J. Gorte, A.L. Myers, Calorimetric Heats of Adsorption and Adsorption Isotherms. 1. O₂, N₂, Ar, CO₂, CH₄, C₂H₆, and SF₆ on Silicalite, *Langmuir* 12 (24) (1996) 5888–5895.
- [52] R. Kumar, K. Jayaramulu, T.K. Maji, C.N.R. Rao, Hybrid nanocomposites of ZIF-8 with graphene oxide exhibiting tunable morphology, significant CO₂ uptake and other novel properties, *Chem. Commun.* 49 (43) (2013) 4947–4949.
- [53] K.C. Kemp, V. Chandra, M. Saleh, K.S. Kim, Reversible CO₂ adsorption by an activated nitrogen doped graphene/polyaniline material, *Nanotechnology* 24 (23) (2013) 235703.
- [54] T.M. McDonald, D.M. D'Alessandro, R. Krishna, J.R. Long, Enhanced carbon dioxide capture upon incorporation of N, N[prime or minute]-dimethylethylenediamine in the metal-organic framework CuBTTri, *Chem. Sci.* 2 (10) (2011) 2022–2028.
- [55] K.C. Kemp, C. Vimlesh, S. Muhammad, S.K. Kwang, Reversible CO₂ adsorption by an activated nitrogen doped graphene/polyaniline material, *Nanotechnology* 24 (23) (2013) 235703.
- [56] Y. Xia, Y. Zhu, Y. Tang, Preparation of sulfur-doped microporous carbons for the storage of hydrogen and carbon dioxide, *Carbon* 50 (15) (2012) 5543–5553.
- [57] J. Kučera, J.W. Bennett, R. Oflaz, R.L. Paul, E.A. De Nadai Fernandes, M. Kubešová, M.A. Bacchi, A.J. Stopic, R.E. Sturgeon, P. Grinberg, Elemental characterization of single-wall carbon nanotube certified reference material by neutron and prompt γ activation analysis, *Anal. Chem.* 87 (7) (2015) 3699–3705.
- [58] E.K. Lin, L.R. Watters Jr, Certificate of Analysis, RM 8281 – Single-Wall Carbon Nanotubes (Dispersed, Three Length-Resolved Populations), National Institute of Standards & Technology (NIST), USA, 2013.
- [59] Y. Liu, J. Wilcox, Effects of Surface Heterogeneity on the Adsorption of CO₂ in Microporous Carbons, *Environ. Sci. Technol.* 46 (3) (2012) 1940–1947.
- [60] M. Seredych, J. Jagiello, T.J. Bandosz, Complexity of CO₂ adsorption on nanoporous sulfur-doped carbons – Is surface chemistry an important factor?, *Carbon* 74 (2014) 207–217.