Adsorption (2011) 17: 653–661
DOI 10.1007/s10450-011-9360-4

Assessing surface chemistry and pore structure of active carbons by a combination of physisorption (H_2O, Ar, N_2, CO_2), XPS and TPD-MS

M. Thommes · C. Morlay · R. Ahmad · J.P. Joly

Received: 7 March 2011 / Accepted: 28 March 2011 / Published online: 16 April 2011

Abstract In order to address open questions concerning the surface chemistry and pore structure characterization of nanoporous carbons, we performed extensive experiments by combining various experimental techniques on a series of commercially available activated carbons which exhibit diverse surface chemistry characteristics. Pore size analysis was performed on Ar (87 K), N_2 (77 K) and CO_2 (273 K) adsorption isotherms using state-of-the art methods based on density functional theory, including the recently developed quenched solid density functional theory (QSDFT). A detailed study of the surface chemistry was obtained by applying temperature programmed desorption coupled with mass spectrometry (TPD-MS) as well as XPS (X-Ray-Photoelectron Scattering). This information together with the pore structure information leads to a reliable interpretation of systematic water adsorption measurements obtained on these materials. Our results clearly suggest that water adsorption is indeed a sensitive tool for detecting differences in surface chemistry between chemically and physically activated active carbon materials with comparable ultramicropore structure. The occurrence of sorption hysteresis associated with the filling of micro- and narrow mesopores (in a range where nitrogen and argon isotherms are reversible) provides additional structural information, complementary to the insights from argon/nitrogen/carbon dioxide adsorption.

M. Thommes (✉) · R. Ahmad
Quantachrome Instruments, 1900 Corporate Dr., Boynton Beach, FL 33426, USA
e-mail: Matthias.Thommes@quantachrome.com

C. Morlay · J.P. Joly
Département de Chimie et Biochimie, Université de Lyon, CNRS, 43 bd du 11 Novembre 1918, 69622 Villeurbanne Cedex, France

Keywords Activated carbon · Pore size analysis · Water adsorption · Carbon dioxide adsorption · Nitrogen adsorption · Quenched solid density functional theory (QSDFT) · TPD-MS · XPS · Surface chemistry

1 Introduction

Activated carbons (ACs) are nanoporous solids which have found important industrial applications in water treatment, separation, energy storage, catalysis etc. In order to optimize these applications one needs, among other requirements, a comprehensive characterization of the adsorbent with regard to surface area, pore size distribution, and surface chemistry. The most popular method to obtain this information is gas adsorption. During recent years, major progress has been achieved in the understanding of the adsorption and phase behavior in ordered micro- and mesoporous materials with simple pore geometries (for a recent review see for instance Thommes 2010). This has led to major advances in the structural characterization by physical adsorption, also because of the development and availability of advanced theoretical approaches based on statistical mechanics (e.g. nonlocal density functional theory, molecular simulation). The application of methods based on nonlocal density functional theory (NLDFT) allows one not only to describe the adsorption and phase behavior of fluids in pores at a molecular level, but also to obtain an accurate pore size distribution over the complete micro/mesopore range (e.g., Ravikovitch et al. 2000; Lastoskie et al. 1993; Olivier et al. 1994; Seaton et al. 1989). Recently, various approaches have been suggested to account for the effect of roughness (e.g., Ravikovitch and Neimark 2006; Do and Do 2006, Neimark et al. 2009; Jagiello and Olivier 2009; Lucena et al. 2010), e.g. the so called quenched

solid density functional theory (QSDFT) quantitatively accounts for the surface geometrical inhomogeneity in terms of a roughness parameter (Ravikovitch and Neimark 2006; Neimark et al. 2009). The NLDFT and QSDFT methods have been commercialized by the producers of adsorption equipment for the interpretation of experimental data and the pore size distribution (PSD) calculation from adsorption isotherms. DFT methods are currently widely used and their application is now featured in a recent standard by the International Standard Organization ISO (ISO-15901-3 2007).

However, the effects of geometrical and chemical heterogeneities of the pore walls on the sorption, phase and wetting behaviors of fluids in porous particles are still under investigation. Within this context, the potential use of water as a probe for surface chemistry and pore structure characterization of nanoporous carbon materials has led to a lot of interest (e.g., Brennan et al. 2001; Do and Do 2000, 2006; Kaneko et al. 1999; Kimura et al. 2004; Lodewyckx and Vansant 1999; Lodewyckx et al. 2008; Liu and Monson 2005, 2006; Monson 2008; Slasli et al. 2003, 2004; Stoeckli and Lavanchy 2000; Striolo et al. 2005; Ohba et al. 2004; Sullivan et al. 2007).

The use of water adsorption is attractive because it can be performed at room temperature; water has a very small kinetic diameter (i.e. 0.28 nm) which allows it to enter pores even smaller than the ones accessible to carbon dioxide or nitrogen (e.g., Lodewyckx 1999) and is sensitive to surface chemistry. On the other hand, the interpretation of water adsorption data is not straightforward, mainly because details of the water adsorption isotherms are strongly affected by both pore structure and surface chemistry and the underlying mechanism of water adsorption in nanoporous carbon is still under investigation.

Hence, in order to shed more light into the potential of water adsorption for textural and surface characterization, we selected three commercial activated carbon samples, two physically activated carbons (F400 and TE80) and one chemically activated carbon (PBL). In order to test whether water has the potential to differentiate surface chemistry it is necessary (as indicated before) to have accurate information about the pore structure of these samples. Hence, we performed a comprehensive physical adsorption study based on nitrogen (77.4 K), argon (87.3 K), and carbon dioxide adsorption (273.15 K) coupled with QSDFT and NLDFT pore size analysis. Information about the surface chemistry of the active carbon samples (independent from water adsorption) was obtained by applying temperature programmed desorption coupled with mass spectroscopy (TPD-MS), as well XPS (X-ray photoelectron scattering). We have performed high resolution water adsorption/desorption experiments which are discussed and interpreted by taking into account the pore structure and surface chemistry of the considered active carbon adsorbents. Our data shed some light into the potential of water as a complimentary probe molecule in physical adsorption characterization.

2 Experimental

All the activated carbons (ACs) considered in this study are used for water treatment applications and are commercialized as granular ACs. Filtrasorb 400 (F400) is a Chemviron Carbon (European Operations of Calgon Carbon Corporation, USA) products, Picactif TE80 (TE80) and Picabiol (PBL) are Pica (France) products. F400 and TE80 are prepared from bituminous coal, coconut shell and peat and are physically activated (steam) whereas wood based PBL is chemically activated (H_3PO_4). The activated carbons were ground and the subsequent samples were dried under air at 130 °C overnight prior to experimental analysis.

Textural characterization was performed by argon (87.3 K), nitrogen (77.4 K) and carbon dioxide (273.15 K) adsorption by using conventional manometric sorption equipment (Quantachrome, Autosorb I MP), and water sorption experiments (within the temperature range 298–318 K) were performed with Quantachrome's Hydrosorb 1000 water sorption analyzer. Prior to adsorption experiments the already dried samples were outgassed at 573 K under vacuum for 12 hours.

The surface chemistry of the materials was also analyzed by XPS (X-ray-Photoelectron Scattering) and Temperature Programmed Desorption with attached Mass Spectrometry (TPD-MS).

TPD-MS experiments were performed using a Setaram (TGA 92 16.18 model) thermobalance equipped with a Balzers (QMG 420 model) quadrupole mass spectrometer. Experiments were carried out under an argon stream ($1.5\,l\,h^{-1}$) under 1 atm. The heating rate was $10\,°C\,min^{-1}$, from ambient temperature up to 1000 °C. H_2O, CO and CO_2 desorption rates were followed by monitoring the heights of the mass peaks $m/e = 18$, 28 and 44 amu, respectively. The mass spectrometer was calibrated by decomposing various weights of calcium oxalate.

The XPS experiments were carried out with a KRATOS AXIS Ultra DLD spectrometer using a hemispherical analyzer and working at a vacuum better than 10^{-9} mbar. All the data were acquired using monochromated AlK_α X-rays (1486.6 eV, 150 W), a pass energy of 20 eV, and a hybrid lens mode. The area analyzed was 700 µm × 300 µm. Charge neutralization was required for all samples. The peaks were referenced to the C–(C,H) components of the C1s band at 284.6 eV. The spectra were analyzed using the XPS processing program Vision 2.2.6 KRATOS with Shirley background subtraction and Gaussian-Lorentzian product peak for C1s and O1s peak fitting. For graphitized carbon, peak fitting was performed using an asymmetric peak pattern.

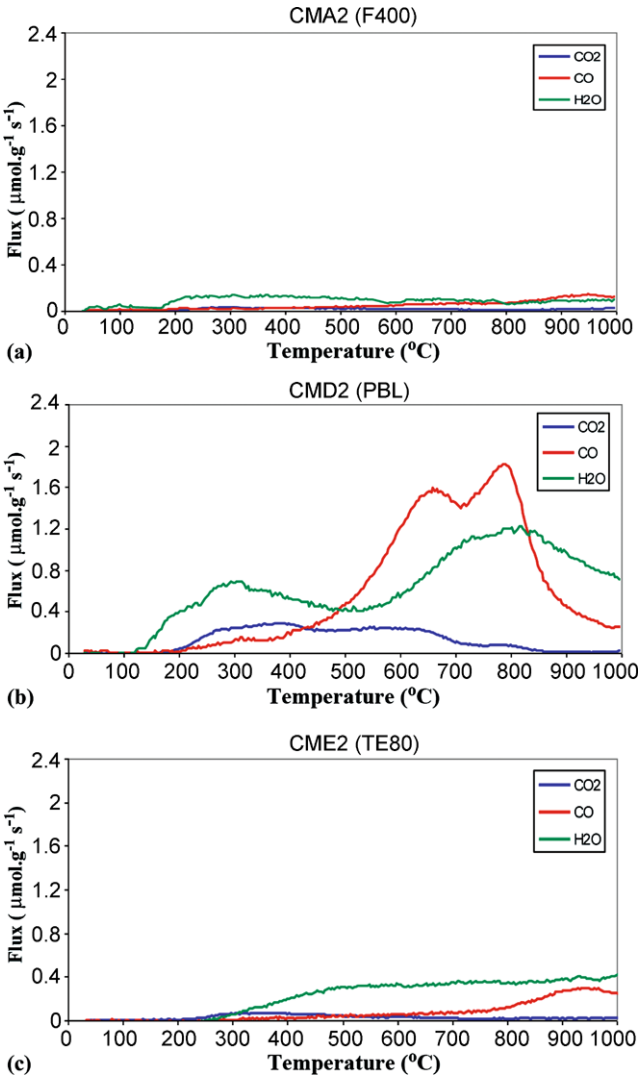

Fig. 1 Molar rates of CO, CO_2 and H_2O released during TPD-MS analysis of the activated carbons under study: (**a**) F400; (**b**) PBL; (**c**) TE80

3 Results and discussion

3.1 Surface (chemistry) characterization: TPD-MS and XPS analysis

Figure 1 shows the desorption rates of CO, CO_2 and H_2O released by the ACs when heated from 30 to 1000 °C during the TPD-MS analysis. CO and CO_2 desorption observed in a wide range of temperatures results from the thermal decomposition of a variety of oxygen groups supposed to be located at the graphene rims (Figueiredo et al. 1999; Szymanski et al. 2002; Haydar et al. 2000; De La Puente et al. 1997). Water profiles are not as reliable as CO or CO_2 profiles for several reasons, mainly because there is a time lag between water desorption from the sample and its detection by MS corresponding to about 50 °C under our experimental conditions. Further, oxygen-rich ACs, such as PBL, which contain

Table 1 Amounts of CO, CO_2 and H_2O released (µmol g^{-1}) obtained by TPD-MS

Activated carbon	CO	CO_2	H_2O
F400	280	85	510
TE80	426	150	1268
PBL	3380	710	3590

Table 2 Surface characterization by XPS

Carbon	Oxygen Content O/C
TE80	0.0472
F400	0.0621
PBL	0.1163

appreciable amounts of oxygen groups, can physisorb water from the atmosphere during their handling. Water detected at temperatures lower than 200 °C is assigned to physisorbed water. Water detected at higher temperatures results from the superficial reaction of OH containing neighboring oxygen groups. Table 1 gathers the cumulated amounts of CO, CO_2 and H_2O released during the thermal desorption of the samples. These data reveal that chemically activated carbons contain many more oxygen groups than physically activated carbons. Furthermore, the CO and CO_2 TPD profiles obtained with chemically activated carbons show strong similarities with those of the oxidized activated carbon materials (e.g. Figueiredo et al. 1999; Szymanski et al. 2002). In summary, concerning CO_2-evolving groups, the desorption temperature range is: 180–300 °C for carboxylic acid groups, 400–660 °C for carboxylic anhydride groups, 350–670 °C for lactone groups, and 550–600 °C for peroxide groups. Anhydride groups also yield CO in the same temperature range as CO_2. In addition, temperature ranges typical of CO-evolving groups are: 560–840 °C for phenolic and hydroquinone groups, 700–900 °C for carbonylic and quinonic groups, 550–830 °C for ether groups and 900–1200 °C for pyrone type groups.

In agreement with the TPD-MS results, the XPS data shown in Table 2 clearly indicate that the chemically activated carbon (PBL) has a higher oxygen content than the physically activated carbons (F400 and TE80). However, for physically activated carbons, the XPS analysis leads to systematically higher content of elemental oxygen than TPD-MS analysis. Indeed, XPS provides information corresponding to the outer surface of the studied ACs particles (a layer of about 10 to 20 nm in depth) whereas TPD-MS results reflect the oxygen content of the entire carbon surface (both outer and inner). Furthermore, TPD-MS slightly underestimates the oxygen content as part of the CO-yielding groups are not decomposed at the maximum temperature used in

TPD analysis (1000 °C). For chemically activated carbons, there is a satisfactory agreement in the results provided by the two methods, taking into account uncertainties in water estimation by MS.

3.2 Characterization by nitrogen (77.4 K), argon (87.3 K) and carbon dioxide (273.1 K) sorption

Figure 2 compares nitrogen (77.4 K) sorption and DFT pore size analysis for two carbons with different surface chemistry, i.e. with high oxygen content Picabiol (PBL), and low oxygen content Filtrasorb 400 (F400). Figure 2a shows these isotherms in linear display revealing a type H3/H4 hysteresis for PBL (according to the IUPAC classification) indicating the existence of mesoporosity, whereas the nitrogen isotherm for F400 is a classical type I isotherm. The semi-logarithmic display in Fig. 2b resolves the pressure range where micropore filling occurs. The BET *equivalent* surface areas obtained from the nitrogen adsorption experiments are 1000 m^2/g for F400 and 1540 m^2/g for PBL (linear BET range: $P/P_0 = 0.01$–0.1; for a more detailed textural analysis of these and other carbon used in water treatment applications, please refer to Morlay and Joly 2009).

An advanced pore size analysis was performed by applying appropriate QSDFT (assuming nitrogen sorption at 77.35 K in carbon slit-pores). The resulting QSDFT cumulative pore volumes and differential pore size distributions for F400 and PBL are shown in Figs. 2c and 2d (in order to highlight the micro-and narrow mesopore size range the PSD's are shown over a selected pore size range up to 50 Å). It follows from Fig. 2d that pore size distribution for PBL and F400 agree very well in the pore size range below 10 Å.

In order to evaluate the ultramicropore range (pore widths ≤ 7 Å according to IUPAC) in more detail, additional high resolution CO_2 (273 K) sorption experiments have been performed. CO_2 adsorption at 273 K had been suggested to overcome the well known problems of restricted diffusion of nitrogen and argon at cryogenic temperatures which prevents these adsorptive from entering the narrowest micropores (Garrido et al. 1987, Rodríguez-Reinoso et al. 1989). A comparison of these sorption isotherms for F400 and PBL carbon has been shown in Fig. 3a, and it appears that these sorption isotherms are essentially identical up to a relative pressure of 0.018. Correspondingly, as shown in Fig. 3b, there is almost a perfect overlap of the resulting NLDFT pore size distribution curves (obtained by applying a dedicated CO_2 (273.15 K)/carbon slit pore NLDFT kernel) for the pore size range below 10 Å.

Figure 4 compares F400 and TE80 active carbons, which have, based on the XPS and TPD_MS similar surface chemistry (i.e. low oxygen content).

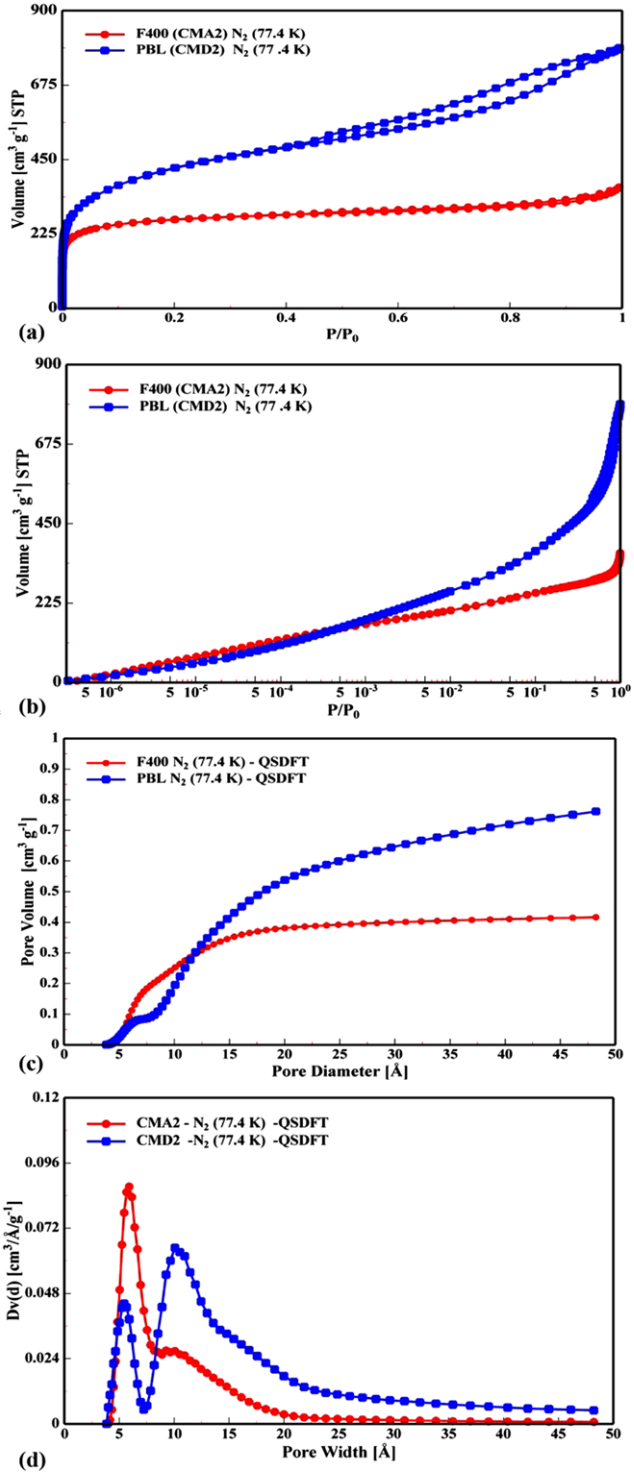

Fig. 2 Comparison of pore structure of active carbons with different surface chemistry, i.e. with high oxygen content (PBL), and low oxygen content (F400): (**a**) Linear plots of the N_2 (77.4 K) isotherms for PBL and F400; (**b**) Semi-logarithmic plot of N_2 (77.4 K) isotherm for PBL and F400; (**c**) QSDFT pore size analysis results from isotherms shown in Figs. 2a and 2b: *cumulative pore volume*; (**d**) QSDFT pore size analysis results: *differential pore size distribution*

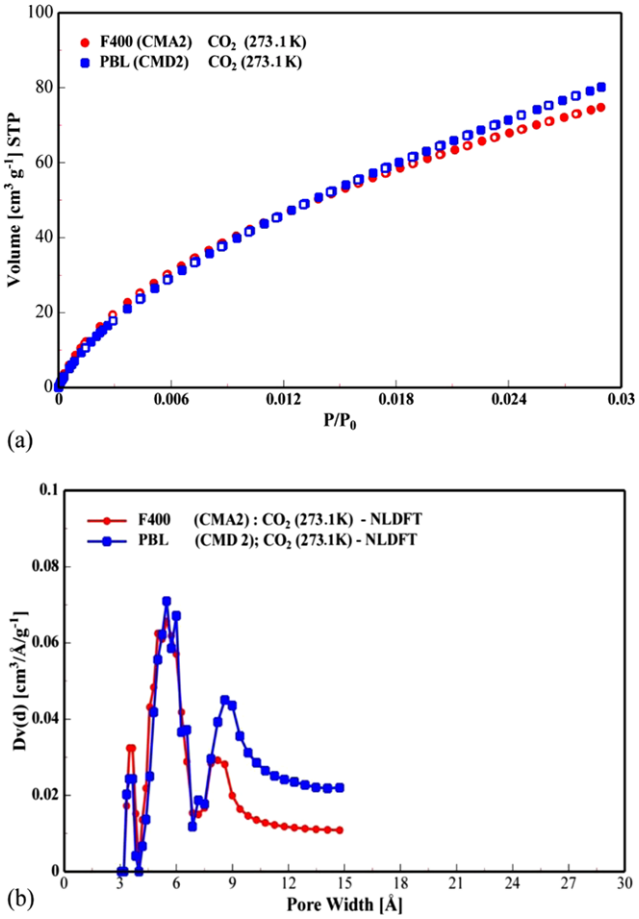

Fig. 3 Comparison of ultramicropore structure of active carbons with different surface chemistry, i.e. with high oxygen content (PBL, Picabiol), and low oxygen content (F400): (**a**) CO_2 (273.1 K) sorption isotherms for PBL and F400; (**c**) NLDFT pore size analysis from the CO_2 isotherms shown in Fig. 3a

Figure 4a shows nitrogen 77 K sorption isotherms on F400 and TE80 carbons, revealing type I isotherms (*equivalent* BET surface area of TE80 carbon is 1400 m^2/g). Figure 4b compares in particular the micropore region by comparing argon 87 K adsorption in the ultralow pressure range. The corresponding argon 87 K QSDFT pore volume/size distributions shown in Figs. 4c and 4d, respectively, reveal very good agreement between F400 and TE80 differential pore size distributions in the pore size range below 20 Å. Up to ca. 10 Å, there is even good agreement concerning pore volumes. In order to investigate the ultramicropore region in more detail, again CO_2 (273 K) has been employed. Sorption isotherms and NLDFT pores size distributions are shown in Figs. 5a and 5b. In agreement with the argon results, it follows that these two samples have essentially identical pore structure in the ultramicropore range.

Summarizing, the results from this detailed pore structure analysis reveal that based on physical adsorption experiments with various probe molecules and advanced DFT pore

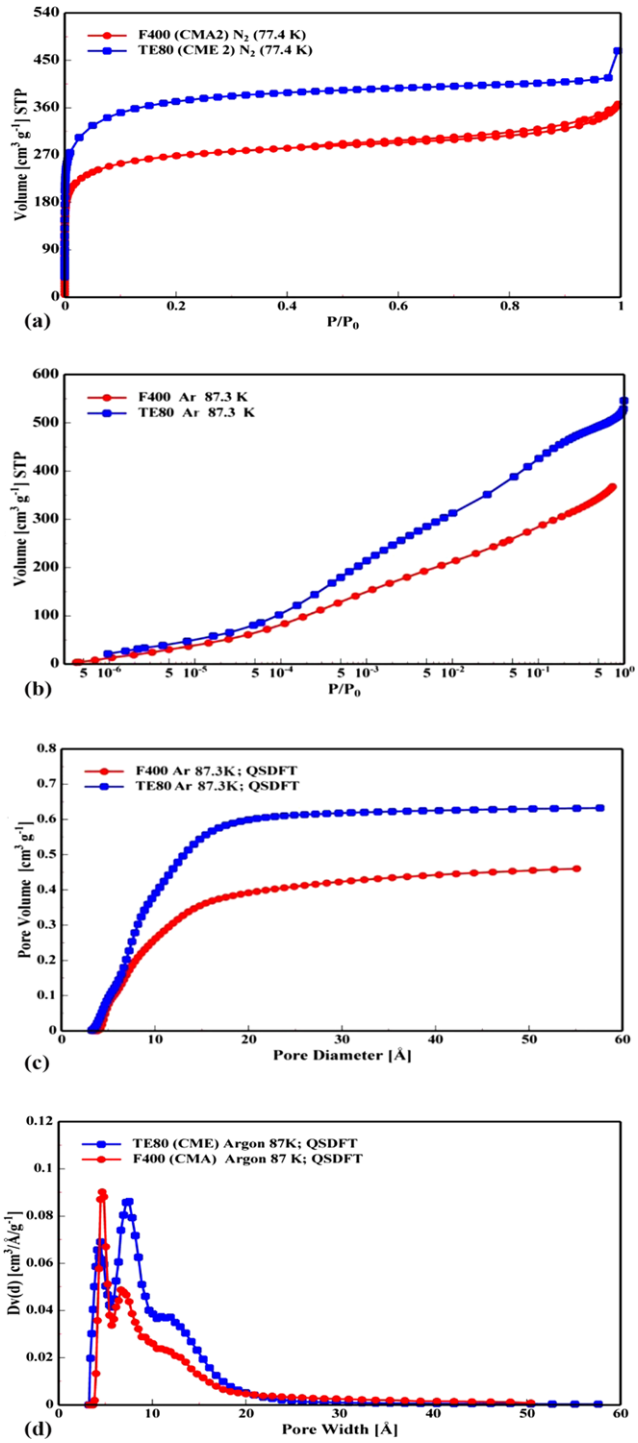

Fig. 4 Comparison of pore structure of active carbons with similar surface chemistry, i.e. low oxygen content active carbons TE80 and (F400): (**a**) N_2 (77.4 K) sorption isotherms for F400 and TE80 (linear display); (**b**) Ar (87.3 K) isotherms for F400 and TE80 (semi-logarithmic plot); (**c**) QSDFT pore size analysis results from Ar (87.3 K) sorption: *cumulative pore volume*; (**d**) QSDFT pore size analysis results from Ar (87.3 K) sorption: *differential pore size distribution*

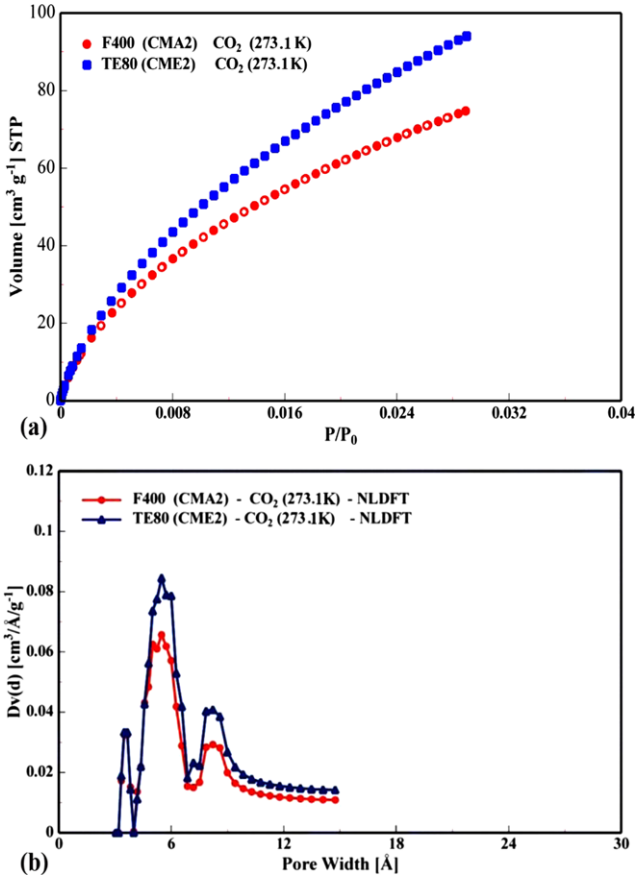

Fig. 5 Comparison of ultramicropore structure of active carbons with similar surface chemistry, i.e. low oxygen content active carbons TE80 and F400: (**a**) CO_2 (273.1 K) sorption isotherms for TE80 and F400; (**b**) NLDFT pore size distribution from CO_2 isotherms shown in Fig. 5a

size analysis all three activated carbon samples (PBL, F400 and TE80) reveal very similar ultramicropore structure.

3.3 Water sorption studies

Figure 6 depicts characteristic nitrogen and water adsorption for TE80 carbon, which is expected to be quite hydrophobic based on the XPS and TDS results.

The isotherms are of completely different shape, i.e. type I for nitrogen adsorption (based on the IUPAC classification), but a type V isotherm for water adsorption. Whereas in the case of nitrogen the micropores are already completely filled at a relative pressure < 0.1, due to the hydrophobic nature of the F400 active carbon, water starts filling the F400 micropores at relative pressures > 0.4. Up to this relative pressure almost no adsorption has been observed. Further, although TE80 contains only micropores (see QS-DFT cumulative pore volume and differential pore size distribution in Figs. 4c and 4d) the water sorption isotherm reveals a pronounced hysteresis loop, which is due to different mechanisms of adsorption/pore filling (cluster mediated water adsorption, no multilayer adsorption) and desorption

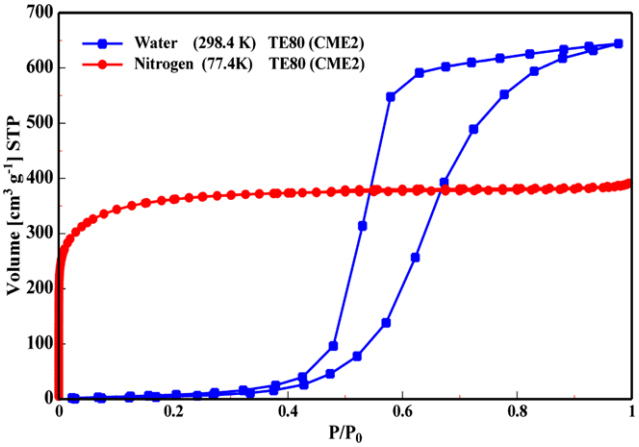

Fig. 6 Comparison of N_2 (77.4 K) and H_2O (298.4 K) sorption isotherms on TE80 active carbon

(pore emptying by molecular evaporation) as discussed for instance by Iiyama et al. (2000), who applied in-situ small angle X-ray scattering studies of water confined in carbon nanopores. Indeed, the adsorption and hysteresis observed for TE80 carbon is typical for water adsorption in hydrophobic carbons. Interestingly, the water TE80 sorption isotherm reveals a well defined plateau close to the saturation pressure indicating that all pores in TE80 have been completely filled with water. However, if one calculates from the adsorbed amount at relative pressure 0.98 the specific pore volume by applying the well-known Gurvich rule (assuming bulk liquid density of water, i.e., 0.99 g cm^{-3} at 293.15 K) the obtained pore volume is only 0.52 cm^3 g^{-1}, which is significantly below the Gurvich pore volume obtained from the nitrogen data, i.e. 0.64 cm^3 g^{-1} (it should be noted that the total pore volume by Gurvich is here in good agreement with the NLDFT pore volume). Hence, this indicates that the density of water phase confined in the hydrophobic carbons is lower than the bulk liquid, as it has been reported before for water sorption in activated carbon fibers (e.g. Iiyama et al. 2000; Alcaniz-Monge et al. 2001, 2002). Based on the results of Iiyama et al. the water density in carbon slit pores can be as low as 0.81 g cm^{-3} for carbons which consist of larger micropores (PIT-20 activated carbon fiber), but is larger in smaller pores, e.g. 0.86 g cm^{-3} in PIT-5 carbon). The position of the adsorption/desorption branches of the hysteresis loops observed here for TE80 carbon and the PIT 20 in Iiyama's work are comparable indicating similar pores size. Hence, we assume accordingly that the confined water phase in TE80 carbon has the density of 0.81 g cm^{-3} (as suggested by Iiyama et al. for PIT-20 activated carbons), and the corresponding pore volume of 0.639 cm^3 g^{-1} is now in almost perfect agreement with the pore volume obtained from the nitrogen 77 K isotherm. The observed lower density of confined liquid-like water phase (compared to bulk liquid water) had been associated with ordered/ice-like water phase in the pores (e.g., Iiyama et al. 2000;

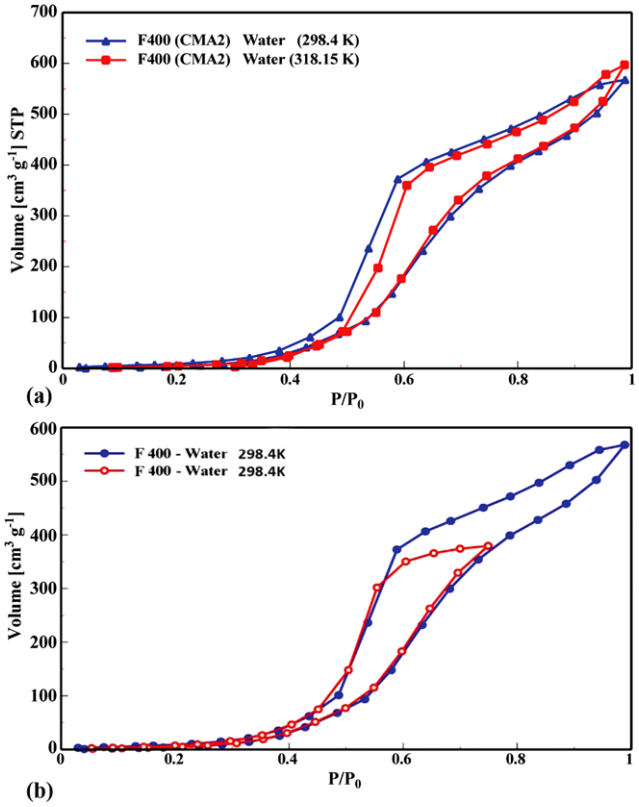

Fig. 7 (**a**) H_2O sorption on F400 at 273.1 K and 298.4 K. (**b**) Desorption scanning of F400 H_2O (298 K) sorption hysteresis loop

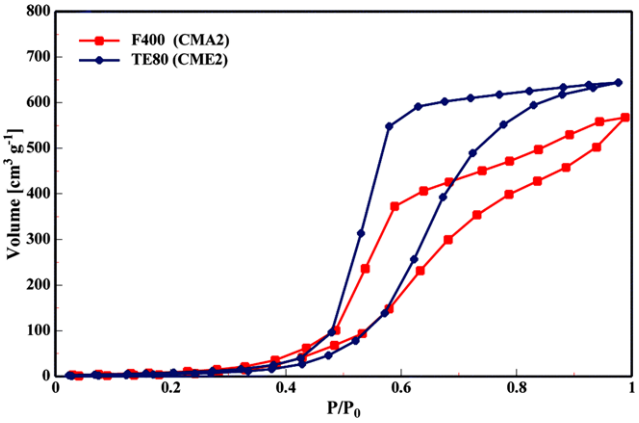

Fig. 8 Comparison of H_2O (298.4 K) adsorption in carbons with low oxygen content and very similar micropore structure (TE80 and F400)

Alcaniz-Monge et al. 2002). However, clearly more work is needed to further explore the state of water confined to essentially hydrophobic carbon pores.

Figure 7a shows the effect of temperature on the water sorption isotherms. In both cases hysteresis has been observed. However, the width of the hysteresis loop observed at the higher temperature is slightly narrower. Interestingly, the position of the adsorption branch appears not to be affected by temperature, whereas the position of the desorption branch shifts slightly to higher relative pressures with increasing temperature. This finding is in qualitative agreement with water adsorption isotherms obtained on activated carbons fibers in the temperature range from 293 K to 303 K by Ohba et al. (2004). Ohba et al. have also combined water adsorption experiments in nanoporous carbons with Grand Canonical Monte Carlo simulations (GCMC) which suggest that the desorption branch of the hysteresis water adsorption isotherms on active carbons reflect the equilibrium branch, whereas the adsorption/pore filling with water occurs delayed. In order to explore the underlying mechanism of hysteresis we performed so-called desorption scanning of the water sorption hysteresis loop. After the measurement of the initial hysteretic adsorption/desorption curve (the so-called boundary adsorption/desorption isotherms) we have measured in a subsequent second adsorption/desorption cycle the adsorption isotherm only up to a relative pressure which is smaller than the saturation pressure. Consequently only a portion of the pore system of the porous material has been filled with pore liquid before desorption data points are measured in a conventional way. As shown in Fig. 7b, we find that the primary desorption scanning curve coincides with the desorption branch of the initial desorption isotherm (i.e., the scanning hysteresis loop will have the same shape as the original hysteresis loop). Further, the capillary evaporation pressure for a given adsorbed amount does not depend on whether the pore system had been completely filled during capillary condensation or not; in other words the shape of the hysteresis loop does not depend on the degree of pore filling. This finding excludes the contribution of network effects on hysteresis, i.e. desorption and indicates that the water sorption hysteresis is caused by a delay in water pore filling; this agrees with molecular simulation results of Ohba et al. (2004) which suggest that the cluster mediated pore filling with water is associated with nucleation barriers/metastable pore fluids.

Figure 8 compares water adsorption isotherms obtained at 298 K in F400 and TE80 carbon which based on Figs. 3–5 have comparable pore structure in the pore size range below 10 Å. In addition based on the TPD and XPS results, both carbons have comparable surface chemistry, exhibiting very small oxygen content. Consequently, the obtained water sorption isotherms for F400 and TE80 are essentially identical in the lower pressure range, i.e. no appreciable adsorption is observed up to a relative pressure of 0.4. At relative pressures larger than $P/P_0 = 0.4$ hysteresis is observed and the differences in water adsorption uptake and hysteresis behavior at relative pressures > 0.5 can be correlated with the filling of pores larger than ca. 7–10 Å, i.e. based on N_2 QSDFT and CO_2 NLDFT pore size analysis (see Figs. 4c and 5b) F400 and TE80 exhibit differences in pore volume for pores larger than ca. 7 Å. Hence, it follows that water adsorption is quite sensitive to differences in pore structure. In fact, the occurrence of sorption hysteresis associated

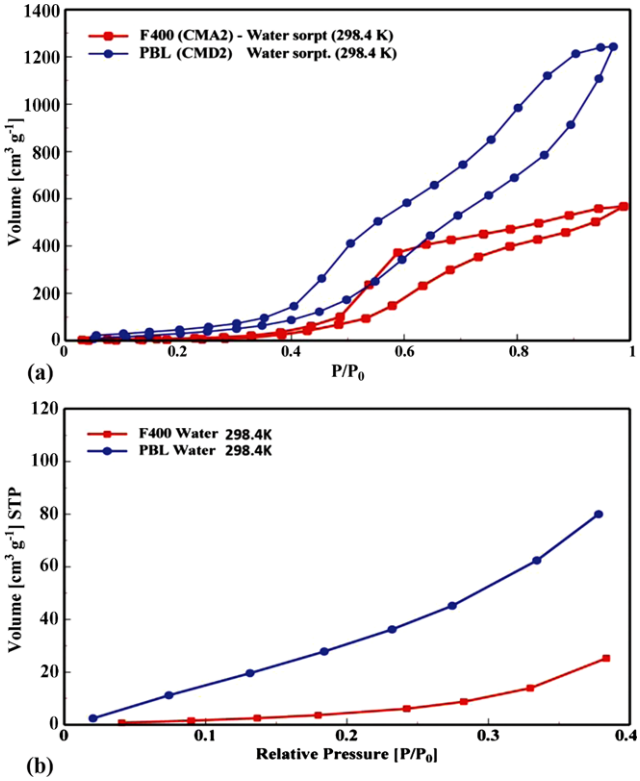

Fig. 9 Comparison of H_2O sorption in carbons with different surface chemistry, but similar ultramicropore structure, i.e. PBL carbon (high oxygen content) and F400 (low oxygen content): (**a**) H_2O sorption isotherms for PBL and F400; (**b**) Comparison of H_2O sorption on BPL and F400 carbons up to relative pressure 0.4

with the filling of micro- and narrow mesopores (in a range where nitrogen and argon isotherms are reversible) provides additional opportunities for textural characterization. Figure 4 shows that nitrogen (77.4 K) and argon (87.3 K) sorption isotherms on TE80 and F400 carbons do not show any hysteresis, however as discussed, differences in texture/pore structure between TE80 and F400 are directly visible from the differences in water sorption hysteresis. However, more experimental, theoretical and molecular simulation work is needed in order to investigate the origin of hysteresis in hydrophobic carbon materials, which would benefit the use of water sorption for textural characterization of carbon materials.

Figure 9a and in particular Fig. 9b reveals that water adsorption isotherms obtained in F400 and PBL, show significant differences in water adsorption already in the relative pressures range up to 0.4. Taking into account that the ultramicropore size distributions for F400 and PBL are essentially identical (see Figs. 2 and 3), one can indeed conclude that the significant difference in water adsorption observed in the low pressure region can be contributed to the significant differences in surface chemistry between F400 and PBL carbon. PBL adsorbs more water than F400, indicating that PBL carbon is more hydrophilic, in line with the results of the TDS and XPS experiments (see Fig. 1, and XPS results in Table 2), which show that PBL has a significantly larger amount of oxidic surface groups compared to F400 carbon.

Hence, these results clearly suggest that water adsorption is a sensitive tool for detecting differences in surface chemistry between chemically and physically active, commercial active carbon materials which exhibit comparable pore structure in the ultramicropore size range. However, more experimental and theoretical work studying water adsorption in materials with (i) well defined pore structure and (ii) well defined surface chemistry is needed in order to be able to further improve existing models describing water adsorption in nanoporous carbons. In order to be able to quantitatively correlate the water adsorption behavior with surface oxygen content (e.g. by applying the approach described by Lodewyckx et al. 2008) we are currently extending our studies to surface modified F400 carbon materials, where again texture and surface chemistry has been assessed by state-of-the art physical adsorption characterization coupled with TPD-MS and XPS analysis.

4 Conclusions

Accurate textural analysis (by analyzing gas adsorption data with state-of-the art approaches such as QSDFT) coupled with information about surface chemistry (obtained by TPD-MS and XPS analysis) allows one to interpret the results of systematic water adsorption measurements on commercial active carbon materials. Our findings on three activated carbon materials with comparable pore structure in the ultramicropore size clearly suggest that water adsorption is indeed a sensitive tool for detecting differences in surface chemistry between chemically and physically activated, (commercially available) active carbon materials. The occurrence of sorption hysteresis associated with the filling of micro- and narrow mesopores (in a range where nitrogen and argon isotherms are reversible) provides additional opportunities for textural characterization.

Acknowledgements The authors wish to thank Chemviron Carbon (European Operations of Calgon Carbon Corporation, USA), Pica (France) and Norit (The Netherlands) who kindly provided them with the activated carbon samples. Authors wish to thank Noelle Cristin and Laurence Retailleau-Mevel (IRCELYON) who performed the nitrogen physisorption and the TPD-MS experiments, respectively, and Laurence Massin and Pierre Delichère who carried out the XPS experiments.

References

Alcaniz-Monge, J.A., Linares-Solano, A., Rand, B.: Water adsorption on activated carbons: study of water adsorption in micro- and mesopores. J. Phys. Chem. B **105**, 7998 (2001)

Alcaniz-Monge, J.A., Linares-Solano, A., Rand, B.: Mechanism of adsorption in carbon micropores as revealed by a study of activated carbon fibers. J. Phys. Chem. B **106**, 3209 (2002)

Brennan, J.K., Bandosz, T.J., Thomson, K.T., Gubbins, K.E.: Water in porous carbons. Colloids Surf. **187–188**, 539 (2001)

De La Puente, G., Pis, J.J., Menendez, J.A., Grange, J.: Thermal stability of oxygenated functions in activated carbons. J. Anal. Appl. Pyrolysis **43**, 125 (1997)

Do, D.D., Do, H.D.: Modeling of adsorption on nongraphitized carbon surface: GCMC simulation studies and comparison with experimental data. J. Phys. Chem. B **110**, 17531 (2006)

Do, D.D., Do, H.D.: A model for water adsorption in activated carbon. Carbon **38**, 767 (2000)

Figueiredo, J.L., Pereira, M.F.R., Freitas, M.M.A., Orfao, J.J.M.: Modification of the surface chemistry of activated carbons. Carbon **37**, 1379 (1999)

Iiyama, T., Ruike, M., Kaneko, K.: Structural mechanism of water adsorption in hydrophobic micropores from in situ small X-ray scattering. Chem. Phys. Lett. **331**, 359 (2000)

ISO-15901-3: Pore size distribution and porosity of solid materials by mercury porosimetry and as adsorption. Part 3. Analysis of micropores by gas adsorption (2007)

Garrido, J., Linares-Solano, A., Martín-Martínez, J.M., Molina-Sabio, M., Rodríguez-Reinoso, F., Torregrosa, R.: Use of nitrogen vs. carbon dioxide in the characterization of activated carbons. Langmuir **3**, 76 (1987)

Haydar, S., Moreno-Castilla, C., Ferro-Garcia, M.A., Carrasco-Marin, F., Rivera-Utrilla, J., Perrard, A., Joly, J.P.: Carbon **38**, 1297–1308 (2000)

Jagiello, J., Olivier, J.P.: Simple two-dimensional NLDFT model of gas adsorption in finite carbon pores. Application to pore structure analysis. J. Phys. Chem. C **113**, 19382–19385 (2009)

Kaneko, K., Hanzawa, Y., Iiyama, T., Kanda, T., Suzuki, T.: Cluster mediated water adsorption on carbon nanopores. Adsorption **5**, 7 (1999)

Kimura, T., Kanoh, H., Kanda, T., Ohkubo, T., Hattori, Y., Higaonna, Y., Denoyel, R., Kaneko, K.: Cluster associated filling of water in hydrophobic carbon micropores. J. Phys. Chem. B **108**, 14043 (2004)

Lastoskie, C., Gubbins, K.E., Quirke, N.: Pore size distribution analysis of microporous carbons: a density functional theory approach. J. Chem. Phys. **97**(18), 4786–4796 (1993)

Lodewyckx, P., Raymundo-Piñero, E., Wullens, H., Vaclavikova, M., Béguin, F.: Water isotherms of structurally identical carbons with different amounts of surface oxygen groups. In: CD Proceedings of the International Carbon Conference, Nagano, Japan(2008)

Lodewyckx, P., Vansant, E.F.: Water isotherms of activated carbons with small amounts of surface oxygen. Carbon **37**, 1647–1649 (1999)

Lucena, S.M.P., Paiva, C.A.S., Silvino, P.F.G., Azevedo, D.C.S., Cavalcante, C.L.: The effect of heterogeneity in the random. Carbon **48**, 2554 (2010)

Liu, J.C., Monson, P.A.: Monte Carlo simulation of water adsorption in activated carbon. Ind. Eng. Chem. Res. **45**, 5649 (2006)

Liu, J.-C., Monson, P.A.: Does water condense in carbon pores. Langmuir **21**, 10219 (2005)

Monson, P.A.: Contact angles, pore condensation, and hysteresis: insights from a simple molecular model. Langmuir **24**, (2008)

Morlay, C., Joly, J.-P.: Contribution to the textural characterisation of Filtrasorb 400 and other commercial activated carbons commonly used for water treatment. J. Porous. Mat. **5**, 535–543 (2009)

Neimark, A.V., Ravikovitch, P.I., Lin, Y., Thommes, M.: Quenched solid density functional theory and pore size analysis of micro-mesoporous carbons. Carbon **47**, 1617 (2009)

Ohba, T., Kanoh, H., Kaneko, K.: Cluster-growth induced water adsorption in hydrophobic carbon nanopores. J. Phys. Chem. B **108**(39), 14964–14969 (2004)

Olivier, J.P., Conklin, W.B., von Szombathely, M.: Determination of pore-size distribution from density functional theory—a comparison of nitrogen and argon results. Characterization of porous solid III. Stud. Surf. Sci. Catal. **87**, 81 (1994)

Ravikovitch, P.I., Neimark, A.V.: Density functional theory model of adsorption on amorphous and microporous silica materials. Langmuir **22**, 11171 (2006)

Ravikovitch, P.I., Vishnyakov, A., Russo, R., Neimark, A.V.: Unified approach to pore size characterization of microporous carbonaceous materials from N_2, Ar, and CO_2 adsorption isotherms. Langmuir **16**, 2311–2320 (2000)

Rodríguez-Reinoso, F., Garrido, J., Martín-Martínez, J.M., Molina-Sabio, M., Torregrosa, R.: The combined use of different approaches in the characterization of microporous carbons. Carbon **27**, 23 (1989)

Seaton, N.A., Walton, J.P.R.B., Quirke, N.: A new analysis method for the determination of the pore-size distribution of porous carbons from nitrogen adsorption measurements. Carbon **27**, 853–861 (1989)

Slasli, A.M., Jorge, M., Stoeckli, F., Seaton, N.: Water adsorption by activated carbons in relation to their microporous structure. Carbon **41**, 479–486 (2003)

Slasli, A.M., Jorge, M., Stoeckli, F., Seaton, N.: Modelling of water adsorption by activated carbons: effects of microporous structure and oxygen content. Carbon **42**, 1947–1952 (2004)

Stoeckli, F., Lavanchy, A.: The adsorption of water by active carbons, in relation to their chemical and structural properties. Carbon **38**, 475–477 (2000)

Striolo, A., Gubbins, K.E., Gruszkiewicsz, M.S., Cole, D.R., Somonson, J.M., Chialvo, A.A., Cummings, P.T., Burchell, T.D., More, K.L.: Effect of temperature on the adsorption of water in porous carbons. Langmuir **21**, 9457–9467 (2005)

Sullivan, P.D., Stone, B.R., Hashisho, Z., Rood, M.J.: Water adsorption with hysteresis effect on microporous activated carbon fabrics. Adsorption **13**, 173 (2007)

Szymanski, G.S., Karpinski, Z., Biniak, S., Swiatkowski, A.: The effect of the gradual thermal decomposition of surface oxygen species on the chemical and catalytic properties of oxidized activated carbon. Carbon **40**, 2627–2639 (2002)

Thommes, M.: Physical adsorption characterization of nanoporous materials. Chem. Ing. Tech. **7**, 1059 (2010)