

The synthesis and characterization of copper-based metal–organic framework/graphite oxide composites

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ABSTRACT

New composites of a copper-based metal-organic framework and graphite oxide were synthesized with different ratios of HKUST-1 (also called MOF-199) and graphite oxide. These compounds, as well as the parent materials, were characterized by X-ray diffraction, sorption of nitrogen, FT-IR spectroscopy, thermal analyses, scanning electron microscopy, and sorption of hydrogen. The composites exhibit features similar to HKUST-1 as well as an increased porosity compared to the parent materials. The formation of new small pores is demonstrated by an increase in the hydrogen uptake. The results suggest that the building process of the composites occurs via the reaction/binding of the copper dimers from the HKUST-1 with/to the functional groups in graphite oxide (epoxy, carboxylic, hydroxylic, sulfonic).

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1. Introduction

Over the past decade, attention has been focused on a class of materials called metal–organic frameworks (MOFs), which can be used in gas purification [1–3]. Their high surface area (e.g. MOF-177 was reported to have a record surface area of about 4500 m² g⁻¹ of material [4]) and the diversity of their metallic centers and organic functionalities direct the potential applications of these materials towards gas adsorption and separation. The structure of MOFs is obtained by the assembly of metallic centers and organic linkers through strong covalent bonds [5]. Depending on the metal and organic ligand selected, networks with various pore shape, size, volume and chemistry can be synthesized and thus adapted to the specific needs of the adsorption process considered [5].

The porosity of MOFs, which makes them particularly attractive, is often not fully utilized. Physical adsorption forces in MOFs are not strong enough to retain small molecules such as ammonia due to the low density of atoms in MOF structures and their fully open pore space. Considering this drawback, we reported in previous studies the preparation of MOF-5/graphite oxide (GO) composites and their application in ammonia removal [6,7]. Details on the formation and structure of the composites are described elsewhere [8]. MOF-5 is a zinc-based MOF with benzene dicarboxylic as the organic bridge. GO, obtained by oxidation of graphite [9], consists of graphene layers bearing various oxygen groups (epoxy, hydroxyl, carboxylic) on the basal planes as well as the edges of the layers [10-12]. Since GO is made of dense arrays of atoms, its "incorporation" in the composites was expected to favor the dispersive forces while the MOF component would increase the porosity of the materials and enable specific interactions of ammonia with the metallic sites and functional groups on the organic linker. The presence of a synergetic effect between the two components of the composites resulting in improved ammonia uptake compared to the parent materials was evidenced [6,7]. This enhancement was linked to the increased dispersive forces

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at the interface between the MOF-5 segments and GO distorted graphene-based layers.

A few studies on the preparation of membranes formed by deposition of MOFs on a substrate have been recently reported [13-19]. Commonly used supports are alumina, silica and graphite, either virgin or modified with surface assembly monolayers (SAMs). These SAMs are usually terminated by carboxylic groups since these groups are able to bind the metal centers in MOF [17-19]. MOF-5 and HKUST-1 (HKUST stands for Hong-Kong University of Science and Technology where the material was first synthesized) are the most tested MOFs [13,15-19]. In a typical preparation, the substrates are immersed in a solution containing the precursors used to synthesize the MOF. The objective of the formation of these membranes is to extend the field of applications of MOF materials. The interactions of the substrate and MOF as well as the explanation of preferential growth orientation are still under study. The formation of hybrid materials based on MOF and carbon nanotubes (CNTs) has also been recently reported [20,21]. In their study, Yang et al. used MOF-5 as the MOF component [20]. They showed that the porosity of the composites was higher than the parent materials and that this led to an enhancement in the hydrogen uptake. The incorporation of the CNTs was also found to improve the water stability of the MOF.

Despite the encouraging results of the MOF-5/GO composites described above, the collapse of the MOF-5 structure in the presence of humidity limits the applications of the synthesized composites at ambient conditions [22]. Taking into account this weak point of MOF-5/GO composites as well as the promising concept of MOF/GO materials in general, the objective of this study is to prepare and characterize new composites with a water-stable MOF component. Therefore this paper focuses on the description of the structure of new materials and the enhancement in the porosity of MOFs caused by the presence of the GO distorted graphene-based layers. HKUST-1 (or MOF-199) was selected as the representative MOF. This material is water-stable and contains Cu²⁺ dimers as the metallic units linked to oxygen atoms from benzene tricarboxylate (BTC) [23,24].

2. Experimental section

2.1. Materials

Graphite oxide was synthesized by oxidation of graphite (Sigma–Aldrich)¹ using the Hummers' method [25]. The details are described elsewhere [6]. HKUST-1 was prepared by mixing copper nitrate hemipentahydrate (10 g) and 1,3,5 benzenetricarboxylic acid (5 g) in N,N dimethylformamide (DMF, 85 mL) followed by stirring and sonication for 5 min. Ethanol (85 mL) was then added to the mixture, which was then stirred and sonicated for 5 min. Finally, deionized water (85 mL) was added to the mixture and then stirring and sonication for 30 min were carried out. All crystals were dissolved at this point. The mixture was then transferred to a round bottom flask (500 mL) and heated at 85 °C in an oil bath. The mixture was kept in the oil bath for 21 h under shaking (intensely for the first 4 h, and then the shaking was reduced and then stopped after 20 h). After cooling, the crystals were filtered using a Büchner funnel, washed and immersed in dichloromethane. Dichloromethane was changed twice during three days. The crystals were collected after filtration and washing with dichloromethane. Drying was then performed by heating the crystals at 170 °C for 28 h inside a closed filtering flask connected to an aspirator. The aspirator was used to create a vacuum inside the flask. The resulting product was kept in a dessicator and is referred to as HKUST-1.

The preparation of the composites was done by adding GO powder to well-dissolved MOF precursors and solvent mixture obtained in the same procedure as in the preparation of HKUST-1. The resulting mixture was sonicated for 5 min, stirred for another 30 min and then the same synthesis procedure as that for HKUST-1 was carried out. The added GO consisted of 5, 9, 18, 38, and 46 wt.% of the final material weight. This corresponds to concentration of 4.3, 8.6, 17.3, 47.1 and 64.7 mg_{GO}/mL_{DMF}, respectively. The copper (from MOF) to oxygen (from GO) ratios in the composites are 2.7, 1.6, 0.71, 0.25 and 0.18, respectively [26]. The composites are referred to as MG-*n* with *n* = 1, 2, 3, 4 and 5, for the different GO contents (5, 9, 18, 38, and 46 wt.%, respectively). In the case of MG-5, unlike for the other composites, two different batches of GO were used in the synthesis.

2.2. Methods

X-ray diffraction (XRD) measurements were conducted using standard powder diffraction procedures. The materials were ground with DMF (methanol for GO) in a small agate mortar. The mixture was smear-mounted onto a glass slide and then analyzed by Cu K_{α} radiation generated in a Philips X'Pert X-ray diffractometer. A diffraction experiment was run on standard glass slide for the background correction.

Nitrogen isotherms of the samples were measured at 77 K using an ASAP 2010 (Micromeritics). Prior to each measurement, samples were outgassed at 120 °C. Approximately 0.10 g of sample was used for these analyses. The surface area, S_{BET} (BET method), the micropore volume, V_{mic} , (Dubinin-Radushkevitch method [27]), the mesopore volume, V_{mes} , the total pore volume, V_t , were calculated from the isotherms.

Hydrogen isotherms were measured on the samples at 77 K and less than 1 bar. The analysis was performed on an Autosorb 1-C instrument (Quantachrome). Approximately 0.10 g of composites and HKUST-1 was outgassed up to 150 °C before the analysis, with care taken to slowly ramp up the temperature to avoid damaging the pores. The GO was outgassed at room temperature so that the surface oxidation would not be lost. The sample cells were kept sealed and ultra-high purity hydrogen was used to prevent moisture contamination of the samples.

Thermogravimetric (TG) curves and their derivatives (DTG) were obtained using a TA Instrument thermal analyzer. The

¹ Certain commercial suppliers are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

samples were heated up to $1000 \,^{\circ}$ C with the heating rate 10 deg/min under a flow of nitrogen of 100 mL/min.

Fourier transform infrared (FT-IR) spectroscopy was carried out using a Nicolet Magna-IR 830 spectrometer using the attenuated total reflectance method (ATR). The spectrum was generated, collected 16 times and corrected for the background noise. The experiments were done on the powdered samples (initial and exhausted), without KBr addition.

High resolution transmission electron microscopy (HRTEM) was performed on a JEOL 2100F instrument with an accelerating voltage of 200 kV. The analyses were conducted on samples previously suspended in methanol.

Scanning electron microscopy (SEM) was performed on a Zeiss Supra 55 instrument. The instrument has a resolution of 5 nm at 30 kV. Scanning was performed on a sample powder previously dried and sputter coated with a thin layer of gold to avoid charging.

3. Results and discussion

The X-ray diffraction patterns of the parent materials as well as the composites are plotted in Fig. 1. It has to be mentioned that the peaks at 2Theta less than 7° are the experimental artifacts related to the slide used to run the tests and thus they should not be considered in the analysis of the material's patterns. In the case of GO, a single peak around 2Theta 9.3° is revealed. It indicates a distance between the carbon layers of 9.5 Å as determined by Bragg's law. For HKUST-1, the pattern obtained is in accordance with the one reported in the literature for this specific network [24,28]. This proves the successful synthesis procedure. The similar diffraction patterns of the composites to HKUST-1 indicate the existence of the well-defined MOF units in the synthesized materials. Thus,



Fig. 1 – X-ray diffraction patterns of the parent materials and the composites.

one can assume that GO did not prevent the formation of linkages between the copper dimers and the organic bridges. On the other hand, it is interesting to notice that the rather broad d_{002} peak observed for GO is not seen for the composites. A reason for this might be the expected exfoliation/high dispersion of GO during the preparation of the composites. Indeed, the composite's synthesis involved polar solvents (in particular DMF) that are known to disperse GO very well [29]. The intensity of the peaks in MG-3 and MG-4 is lower than the other composites.

An important parameter in gas adsorption is the porosity of the adsorbent. In our case, this feature has been evaluated using nitrogen isotherms, which are plotted in Fig. 2. The data for GO are not reported here since its porosity is negligible [30]. As seen in Fig. 2, all the materials exhibit a type I isotherm with a small hysteresis loop. This indicates the predominant microporous character of these compounds. This is expected since HKUST-1 is characterized by square channels of 9 Å by 9 Å [23]. The hysteresis loops suggest the presence of mesopores, which might be those between the small crystals of MOF or composite particles.

As seen from Fig. 3(a), HKUST-1 has a BET surface area of about 900 $m^2\,g^{-1}$ which is in the range of the values reported in the literature [23,31,32]. Details on the values of the parameters of porous structure can be found in the Supporting data (Table S1). The surface area and volume of pores of the composites with the lowest GO contents (MG-1 to MG-3) are higher than the ones of HKUST-1 while the opposite trend is observed for the composites with the highest GO contents (MG-4 and MG-5). From a theoretical point of view, it is interesting to compare the measured values of the composites' structural parameters with "the hypothetical" ones. The latter parameters correspond to the values that would be obtained if no chemical interactions were involved in the formation of the composites. In other words, they represent the parameters of porous structure of the physical mixture of GO and HKUST-1. These "hypothetical" surface areas and pore volumes reported for the composites were calculated taking into account the percentage of each component in



Fig. 2 – Nitrogen isotherms at 77 K of HKUST-1 and the composites.



Fig. 3 – Measured and "hypothetical" parameters of the porous structure for HKUST-1 and the composites with: (a) the surface area, (b) the total volume of pores and (c) the micropores volumes.

the composites and the structural parameters of GO and HKUST-1 alone. Eq. (1) provides the details of the calculation $X_n = X_{GO} \times wt.\%_{GO} + X_{HKUST-1} \times wt.\%_{HKUST-1}$ (1)

where " X_n " is the parameter of composite MG-*n* to determine (surface area or volume of pores), " X_{GO} " and " $X_{HKSUT-1}$ " are the parameters of GO and HKUST-1 separately, and "wt.%_{GO}" and "wt.%_{HKSUT-1}" are the weight percentages of GO and HKUST-1 in MG-*n*. Details on these values are presented in Table S1 (Supporting data). The measured values (surface area, micropore volume or total volume of pores) are always higher than those calculated for the physical mixture. This reveals the presence of a synergy between the two components, which leads to the formation of a compound with a higher porosity than that formed when the two phases are only a physical mixture. We can see that degree of improvement between measured and "hypothetical" values first increases with the GO content for composites MG-1, 2 and 3 and then decreases when the GO content is equal or higher than 38 wt.%. The best porous structure is found for MG-3. This trend is likely due to the presence of increased amounts of GO causing too much distortion in the structure of the materials. Another explanation could be that when a high amount of GO is present, the number of groups on GO exceeds the numbers of accessible sites on MOF with which they can react. Part of GO will thus act as if there was no other species in the system apart from the solvents. Consequently, upon drying the carbon layers of GO will be restacked together in a more or less ordered way as they usually do. This excess causes an agglomeration of GO distorted graphene-based layers and thus in a decrease in the porosity. Pore size distributions analysis commonly provides additional information about the pores. Although this data would support the formation of the new pores in our materials, the DTF method used to calculate the pore size distribution is not yet adapted to MOFs. Using existing models (carbon, silica, zeolites, etc.) could introduce additional experimental artifacts. Nevertheless, the hydrogen uptake measurements presented later in this paper support the development of new porosity in the composites.

Thermogravimetric analyses provide information about the thermal stability of the materials, which can be also linked to their chemistry. The DTG curves for the parent materials and the composites are presented in Fig. 4. Since no significant weight loss was measured above 450 °C, only the temperature range between 30 °C and 450 °C is shown here to better analyze the weight loss patterns (analyses were performed up to 1000 °C). In the case of GO, three major peaks can be observed. The first one up to 100 °C corresponds to the removal of physically adsorbed water. The second peak



Fig. 4 – Thermal analyses of the parent materials and the composites.

around 200 °C represents the decomposition of epoxy groups and the broad hump between 250 °C and 400 °C indicates the decomposition of carboxylic and sulfonic groups [33,34]. The DTG curve of HKUST-1 exhibits a small peak at about 100 °C, which corresponds to a dehydration step [32]. Additional molecules of water are released at ~300 °C [35]. The complete collapse of the HKUST-1 structure is then observed with the intense peak at ~350 °C [35]. This is accompanied by the release of CO_2 and leads to the formation of copper oxide [35]. This temperature range for the decomposition of HKUST-1 is in accordance with literature [35,36]. The DTG curves for the composites look rather similar to the one of HKUST-1 except that the peak at \sim 300 °C in the case of MG-1 has a lower intensity than that for HKUST-1 and is absent for the composites with higher graphite content. The absence of that additional step of dehydration compared to HKUST-1 suggests that some copper centers in the composites are engaged into a more hydrophobic environment. They are probably located in the vicinity of GO distorted graphene-based layers. The interesting feature here is the absence of the intense peak related to the decomposition of GO epoxy groups for the composites. An explanation for this would be the involvement of these groups in the formation of the composites and more precisely the coordination of the cupric ions to the oxygen atoms of the epoxy groups. This scenario is consistent with the observed lack of dehydration step at 300 °C. To verify that the absence of the peak at 200 °C on the composites DTG curves was not due to the reaction of the epoxy groups with compounds other than HKUST-1 during the synthesis of the composites, we subjected GO to the same synthesis process as for the composites but in the absence of copper nitrate and BTC. We then run thermal analyses on the resulting sample. The DTG curves of the latter material exhibited a peak at 200 °C. This supports our hypothesis that the absence of GO epoxy groups on the DTG curves of the composites is related to an interaction of these groups with the MOF.

Since interactions between the Cu sites and epoxy groups are proposed to explain the composites formation, it is interesting to consider the ratio between these two species in the composites. In a previous study conducted on GO material prepared by the Hummers method [26], it was found, via XPS analyses, that about two thirds of the O-containing groups were involved in a C-O configuration. The latter category includes phenolic, epoxy and carboxyl groups. Since these functionalities cannot be precisely classified, we roughly assume that two thirds of these O-containing groups corresponds to epoxy groups., which might be much overestimated. Considering this, the ratios Cu sites to epoxy groups in the composites are about 6.9, 3.5, 1.6, 0.6 and 0.4 as the GO content increases. Due to the assumption made, these values are likely an overestimation of the actual ones. Nevertheless, they tend to indicate that there were enough copper sites to react with the epoxy groups present even though the full exfoliation of GO layers is assumed. The peak on the DTG curve is related to removal of CO2. When less epoxy groups decompose (those left after reaction of the composite formation) the TA method may not be sensitive enough to show the changes.

The estimation presented above does not exclude the fact that the carboxylic, hydroxylic and sulfonic functionalities of GO have also likely reacted with the copper dimers. These interactions between the metallic species and GO, leading to the new spatial arrangement of the components, might be the source of the increased porosity of our composites as described above. It is important to note that even though the MOF units can be attached to the functional groups of GO, this should not modify the structure of the MOF. The GO distorted graphene-based layers via the oxygen groups should only act as a "termination" unit in the process of MOF formation. As seen previously and in the following, this is supported by Xray diffraction, nitrogen adsorption analysis, thermal analyses and FT-IR spectroscopy since we can recognize the pattern of HKUST-1 in each composite.

The FT-IR spectra of the parent materials and the composites are plotted in Fig. 5. Since the range above 2300 cm⁻¹ does not present features relevant to this analysis, only the range between 500 and 2300 cm⁻¹ is reported. The IR spectrum of GO has been described in detail in literature [26]. Vibration of C–O appears at 1060 cm⁻¹ and the vibration of O–H bond in water and/or oxygen surface groups is observed at 1630 cm⁻¹. C=O vibration from carboxyl and/or carbonyl groups is detected at 1735 cm⁻¹. Two other bands are observed at 990 and 1228 cm⁻¹. The first band can be assigned to epoxy/peroxide groups and the second to S=O asymmetric stretching vibration in sulfonic groups and/or vibration of C–O in epoxides [26]. The spectrum of HKUST-1 is very similar to those found in literature for the same network [35]. This



Fig. 5 – FT-IR spectra of the parent materials and the composites.

spectrum can be divided into two zones. The first zone, below 1300 cm⁻¹, shows various bands assigned to the vibrations of the BTC ligand. The zone between 1300 and 1700 cm^{-1} is related to the carboxylate ligands and is thus indicative of the coordination of BTC to the copper sites. More precisely, the bands at 1645 and 1590 $\rm cm^{-1}$ and at 1450 and 1370 $\rm cm^{-1}$ corresponds to the asymmetric and symmetric stretching vibrations of the carboxylate groups in BTC, respectively [37]. In agreement with the data of X-ray diffraction and thermal analyses, the FT-IR spectra of the composites exhibit features similar to the HKUST-1 spectrum. The variations in the ratios of the bands at $1645/1590 \text{ cm}^{-1}$ and $1450/1370 \text{ cm}^{-1}$ must be related to changes in the environment of the carboxylate ligands. A plausible explanation would be the interactions of these ligands with the functional groups from GO as well as the distortion in the structure of HKUST-1 caused by the introduction of GO. The progressive decrease in the intensity of the bands can be noticed as the content in GO increases. This decrease might be related to the lower amount of MOF in the samples.

Addition of GO to HKUST-1 causes visible changes in the materials. The composites with the highest GO content appear much darker than the ones with low GO content for which the color resembles more the one of HKUST-1 alone (Fig. S1 of Supporting data). The gradation in the color through the range of samples is more visible when the materials are immersed in DMF and then dried in air. The greenish tint of the compounds is due to the adsorption of DMF. This

color is converted to a darker green tint as the GO content increases.

HRTEM images of composites MG-1, 3 and 5 support the data obtained for other analyses. In the case of MG-1 (Fig. 6(a)), well-defined graphene-based layers with embedded HKUST-1 units are observed. On MG-3 sample (Fig. 6(b)), more graphene-based layers are present and a rather well-defined lattice image appears within the layers of GO. It is known that electron beam illumination can cause the break down of HKUST-1 and can thus prevent any visualization of its lattice structure [38]. Nevertheless, the pattern observed can be considered as representing the lattice image of HKUST-1. It is likely that GO distorted graphene-based layers present in the composite helped the MOF to retain its crystalline structure by dissipating the electrostatic charges. This phenomenon was also observed by Yang et al. with their MOF-5/CNTs composites [20]. Another explanation could be that the lattice image is a related to a crystalline structure formed by stacked GO distorted graphene-based layers and HKUST-1 units. For the MG-5 sample (Fig. 6(c) and (d)), the GO component becomes predominant. Although some HKUST-1 units can be observed within the GO distorted graphene-based layers (Fig. 6(c), separate agglomerates with only stacked distorted graphene-based layers are visualized as well (Fig. 6(d). From a general point of view, these micrographs evidence that the two composite components are well-mixed within our materials. This supports the results of thermal analyses and the hypothesis that chemical interactions are involved in the for-



Fig. 6 - HRTEM images of the composites: (a) MG-1, (b) MG-3 and (c), (d) MG-5.

mation on the composites. Moreover, we can see that the GO distorted graphene-based layers are rather well-dispersed in the materials and do not form densely packed agglomerates, which is supported by the XRD results. The alternation between graphene layers and HKUST-1 units can be explained considering that, in the synthesis medium, GO is present along with the MOF precursors. Consequently, in this system, copper ions can either react with the oxygen groups of the BTC ligands to form HKUST-1 crystals or with the oxygen groups of GO. Depending on the amount of GO, one process might be favored over another.

The SEM images presented in Fig. S2 (Supporting data) provide also details about the structure of the new composites. Crystals of different sizes are observed in the case of HKUST-1 and their surface appears relatively smooth despite the presence of some defects. Some crystals exhibit an octahedral shape characteristic of that specific MOF [28]. Dense packing of distorted graphene-based layers aggregated into flakes can be distinguished in the picture of GO. The structure of the composites show some variations compared to the ones of the parent materials. In the case of MG-2, a quite complex texture is observed with the presence of layers quite similar to the ones encountered in MOF-5/GO composites reported in a previous study [7,8]. It is possible that as for the latter materials, these layers correspond to alternation between blocks of HKUST-1 and blocks of GO distorted graphene-based layers. A few meso/macropores are also observed on the surface of MG-2. The porous character becomes more pronounced in MG-3. This is in agreement with the increase in porosity observed before. For MG-4, although some remains of the porous structure seen on MG-3 are present (Fig. S2e), these features tend to disappear (Fig. S2f). Separate agglomerates of GO are also observed for this composite (not shown here). This part of the GO which does not interact with the MOF units can be responsible for the decrease in porosity observed when high content of GO are present.

The synergy between the components of the composites is also tested by evaluation of the hydrogen adsorption capacity at 77 K. The isotherms are presented in Fig. 7(a). These isotherms show the excess adsorption as a function of the pressure. Gibb's excess or excess adsorbed mass is defined as the mass of adsorbate film minus the mass of an equal volume of adsorptive. This amount of gas is in excess of what would be in the pores if there were no adsorbent-adsorbate interaction. At the low pressures (<1 bar) used, excess adsorption can be used to approximate the absolute amount of gas adsorbed. Details on the values of the excess adsorption for the materials studied are presented in Table S1 (Supporting data). Only MG-1, MG-2 and MG-3 were chosen owing to the observed increase in the porosity noticed based on adsorption of nitrogen (see Fig. 2 and 3 and Table S1). Even though the differences in the isotherms seem to be insignificant, one has to take into account the composition of the composites. It is noticeable that GO does not adsorb any hydrogen. In spite of the small size of H_2 molecule (~ 3 Å [39]), it is not able to enter the interlayer space. This can be explained by the presence in that space of epoxy and hydroxy groups blocking the entrance of a non-polar molecule of hydrogen. The hydrogen uptakes of HKUST-1 and the composites are in the range of uptakes reported in the literature for the MOF alone [31]. The similarity



Fig. 7 – Results of hydrogen adsorption analysis with: (a) hydrogen adsorption isotherms at 77 K and (b) comparison of the measured and "hypothetical" excess adsorption for the parent materials, MG-1, MG-2 and MG-3.

in amount of hydrogen adsorbed between all the samples studied, with an increase in the GO content up to 20 wt.%, indicates the presence of a new porosity in the composites resulting from a synergy between GO and MOF. In Fig. 7(b), we compare the measured amount of hydrogen adsorbed to the "hypothetical" amount calculated assuming the physical mixture of the components. These "hypothetical" values were calculated following the same method as described in Eq. (1). Details on the "hypothetical" values of the excess adsorption are presented in Table S1. As seen in Fig. 7(b), the positive effect of the composites porosity/synergy between the two components is demonstrated in about 10% increase compared to the "hypothetical" physical mixture of GO and HKUST-1. This confirms the results obtained from nitrogen adsorption and can be linked to the measured increase in the porosity. Indeed, the total volume of micropores increased by 6% for MG-1 and MG-2 and 15% MG-3 compared to HKUST-1 alone. Even though the total volume of pores increased more (9% for MG-1, 11% for MG-2 and 18% for MG-3), they seem to not be significant for hydrogen adsorption owing to their large sizes. For hydrogen adsorption at supercritical

temperature, the volume of pores on the order of magnitude of the diameter of a hydrogen molecule should be the most important factor affecting the amount adsorbed [40]. Moreover, hydrogen can access pores much smaller than those detected by nitrogen molecules [41]. There is an agreement between an increase in the "hypothetical" surface area and an increase in the hydrogen adsorption. This implies that the composites have similar pore size distributions with narrow pores and surface areas to HKUST-1 but are superior to GO alone.

Considering the above observations, the overall structure of the composites can be envisioned. As mentioned before, the formation of the composites is hypothesized to occur via the reaction between the copper sites of HKUST-1 and the functional groups of GO and especially the epoxy, hydroxylic, sulfonic and carboxylic functionalities. The reaction of the epoxy groups with the HKUST-1 units have been identified via thermal analyses as described above. To further confirm this observation, we subjected GO to the same synthesis conditions as for the composites but in the absence of HKUST-1 precursors. Thermal analysis of the resulting material was then performed. The peak related to epoxy groups was still present on the DTG curve confirming that its absence on the DTG curves of the composites was the consequence of their reaction/interaction with the HKUST-1 units. Moreover, the reactions of the carboxylic groups with the copper sites of HKUST-1 can be expected since the BTC component already presents such functionalities. Regarding the hydroxylic groups, their interactions with the copper sites can be compared to interactions with water. Given the octahedral molecular geometry of copper complexes, the oxygen groups of GO can either act as equatorial (replacing a BTC molecule) or axial ligands (replacing a molecule of water) Detailed scenarios of the possible interactions are provided in Fig. S3 (Supporting data). These two possibilities of arrangement (axial and equatorial), along with the different types of oxygen groups from GO, leads to the formation of a composite with the relatively disordered structure proposed in Fig. 8 Although very schematic, this representation can help to visualize the texture of the materials prepared. This disordered arrangement is responsible for the creation of the new porosity detected by nitrogen and hydrogen adsorption. Nevertheless, because carboxylic groups (and sulfonic groups) of GO are located at the edges of the layers and not on the basal planes as the other functionalities, their interactions with the copper sites do not lead to the same type of arrangement as for epoxy, and hydroxylic present on the basal planes of GO. This can be seen in Fig. 8(b). Higher content of GO leads to the formation of larger pores between the GO flakes. This is the result of the interactions of more carboxylic groups (and sulfonic groups) on GO edges with copper sites. This is supported by N₂ sorption analyses which showed that the volumes of mesopores increased with the GO content (Table S1 in Supporting data). When even higher amounts of GO are present, the number of groups from GO can exceed the number of accessible MOF sites they can react with and the GO distorted graphene-based layers remains as agglomerates. This is represented in Fig. 8(c). This causes that smaller volumes of new small pores are formed. This is in agreement with the SEM pictures of the composites with high GO content for which



Fig. 8 – Schematic representation of the composites with (a) low, (b) medium and (c) high content of GO.

agglomerates of GO were observed (these SEM pictures are not shown here).

4. Conclusions

The features of HKUST-1 in the composites are dominant but their porosity is higher than the parent materials. It is hypothesized that the reaction of the HKUST-1 units with the functionalities of GO (epoxy, hydroxylic, carboxylic and sulfonic groups) leads to the creation of new pores. This enhancement in the porosity is well-seen for GO content up to 20 wt.% and then decreases. Indeed, when high amounts of GO are present, the number of groups on the distorted graphene-based layers likely exceeds the number of accessible sites in MOF with which they can react. Consequently, the GO distorted graphene-based layers remain as agglomerates resulting in a decrease in porosity. The additional porosity is responsible for the enhancement in the hydrogen uptake of the composites compared to the ones calculated for the physical mixture of HKUST-1 and GO. Owing to the water-stable character of the materials, applications in gas purification might be envisioned.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbon.2010.09.059.

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