

MOF-GRAPHENE COMPOSITES: AN INSIGHT INTO THE TEXTURE AND ADSORPTION PROPERTIES OF NEW MATERIALS

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Introduction

A new class of materials called metal-organic frameworks (MOFs) introduced by Yaghi and coworkers has drawn the attention of many scientists [1] owing to their high porosity and their “cumulative” features originating from combining both inorganic and organic solids via assembly of metallic ions and organic ligands [1]. Their applications include gas separation/purification/storage and catalysis [1].

Despite their interesting properties, MOFs suffer from some limitations. One is their instability towards the solvent removal step performed during their synthesis [1]. Other drawbacks include their inability to provide strong, non-specific interactions to retain small molecules of gas and the collapse of some MOF networks in the presence of humidity [2].

To address these issues and to expand the field of applications of MOFs, the concept of MOF-based composites has been developed. Only a few composites have been reported so far such as: MOF/substrate (e.g. silica) to be used in membrane fabrication [3] and MOF/carbon nanotubes to increase hydrogen storage and water stability [4].

In this study, we propose to synthesize and test for ammonia adsorption MOF/graphite oxide (GO) composites. GO is obtained by oxidation of graphite which leads to the formation of various oxygen groups on the basal planes and the edges of the graphene layers [5]. The graphene layers from GO are expected to increase the dispersive forces in MOFs and thus to enhance the retention of small gas molecules.

Experimental

A zinc-based (MOF-5) and a copper-based (HKUST-1) MOFs were prepared following the methods detailed in Ref. [6] and [7]. GO was synthesized as described elsewhere [6]. Two series of MOF/GO composites were prepared: one based on MOF-5 and another one on HKUST-1. In both cases, various amounts of GO were dispersed in the mixture of precursors used to prepare MOF and the same procedure as for the MOF synthesis was applied to form the composites. The zinc-based and copper-based composites are referred to as ZnMG-n and CuMG-n, respectively (with n = 1, 2, 3 and 4 for ~ 5, 10, 20 and 50 wt% of GO, respectively).

The samples (parent materials and composites) were tested for ammonia adsorption in dynamic conditions, at room temperature, in dry (-ED) and moist conditions (-EM).

In order to characterize the new materials and to propose the mechanism(s) of adsorption, the samples were analyzed

before and after exposure to ammonia by X-ray diffraction (XRD), N₂ adsorption and thermogravimetric analysis (TG).

Results and Discussion

XRD patterns of the parent materials and selected composites are plotted in Figure 1. The features of each MOF are dominant in the composites suggesting that GO did not prevent the formation of the MOF networks. However, the splitting in the peak at ~9.7 ° for ZnMG-2 indicates a distortion in the symmetry of MOF-5 in that sample, likely caused by the presence of GO [2]. The peak at ~9.3 ° for GO, related to a distance between the graphene layers of ~9.5 Å, is not seen on the patterns of the composites. This is likely due to the fact that the solvent used to synthesize the composites (Dimethylformamide) is known to exfoliate GO [8].

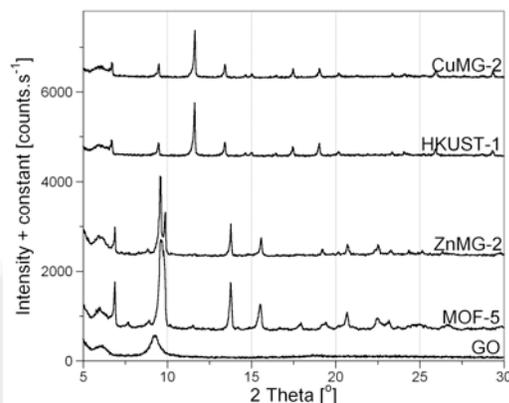


Fig. 1 XRD patterns of selected samples.

Table 1. Parameters of porous structure derived from N₂ isotherms and the hypothetical values (H) for all samples.

Sample	S _{BET} [m ² .g ⁻¹]	V _{tot} [cm ³ .g ⁻¹]	V _{mic} [cm ³ .g ⁻¹]	S _{BET} H [m ² .g ⁻¹]	V _{tot} H [cm ³ .g ⁻¹]	V _{mic} H [cm ³ .g ⁻¹]
GO	nil	nil	nil	-	-	-
MOF-5	793	0.408	0.385	-	-	-
ZnMG-1	706	0.365	0.341	753	0.388	0.366
ZnMG-2	806	0.416	0.388	714	0.367	0.347
ZnMG-3	603	0.325	0.288	634	0.327	0.308
ZnMG-4	742	0.399	0.397	335	0.180	0.179
HKUST-1	909	0.471	0.449	-	-	-
CuMG-1	989	0.515	0.478	864	0.447	0.426
CuMG-2	1002	0.527	0.478	827	0.428	0.406
CuMG-3	996	0.566	0.522	746	0.386	0.368
CuMG-4	704	0.370	0.348	656	0.292	0.278

As seen from Table 1, the porosity of the composites is enhanced compared to the hypothetical one calculated assuming the physical mixture between MOF and GO (except for ZnMG-1 and -3). This new porosity must be formed between the MOF blocks and the graphene layers.

Derivative of the TG curves (DTG) are presented in Figure 2 for the selected materials. The composite DTG curves exhibit features similar to the ones of the related MOF.

Interestingly, the well-defined peak at 200 °C corresponding to epoxy groups decomposition [6], is not observed for the composites. This suggests that these groups are involved in the composite building process. More generally, the formation of the composites likely occurs via the interaction of GO oxygen groups with the metallic centers of MOFs.

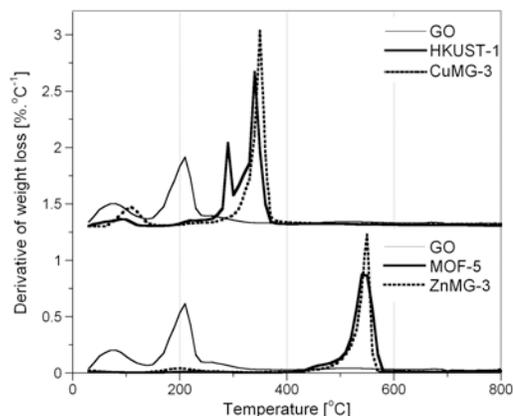


Fig. 2 DTG curves of selected samples.

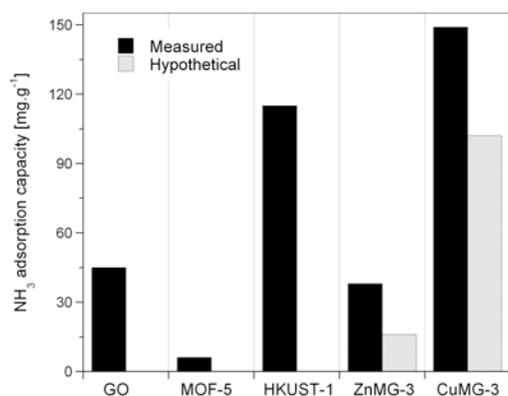


Fig. 3 Measured and hypothetical ammonia adsorption capacities for selected samples tested in dry conditions.

The composites have been tested for NH₃ removal. The selected adsorption capacities are plotted in Figure 3. The Cu-based materials are better NH₃ adsorbents than the Zn-based ones. This is likely due to the fact that, unlike in MOF-5, the metallic sites in HKUST-1 are unsaturated and are thus able to coordinate ammonia. For the composites, the adsorption capacities measured are higher than the ones calculated assuming the physical mixture of GO and MOF. This indicates a synergetic effect between the two components. We link this to the increased dispersive forces (via the graphene layers) and the new pore space created in the composites.

Results of N₂ sorption analyses of the exhausted samples are presented in Table 2. The retention of significant quantities of NH₃ causes the collapse of the MOF structure. This effect is linked to the reaction of ammonia with the MOF components. It has to be mentioned here that water is known to cause the collapse of the MOF-5 structure via H-bonding with the zinc oxide centers in MOF-5 [3]. Considering similar chemistries

of H₂O and NH₃ molecules, similar H-bonding interactions are expected between NH₃ and the metallic centers. Moreover, changes of the adsorbent bed color were observed during the breakthrough tests on the copper-based samples indicating the formation of new copper complexes.

Table 2. Parameters of porous structure derived from N₂ isotherms for selected samples after NH₃ adsorption.

Sample	S_{BET} [m ² .g ⁻¹]	V_{tot} [cm ³ .g ⁻¹]	V_{mic} [cm ³ .g ⁻¹]
MOF-5-ED	739	0.399	0.389
ZnMG-1-ED	710	0.368	0.341
ZnMG-3-ED	475	0.254	0.229
HKUST-1-ED	27	0.020	0.011
CuMG-1-ED	nil	nil	nil
CuMG-3-ED	nil	nil	nil

Conclusions

Composites of MOF and GO have been successfully prepared. Their formation likely occurs via the coordination of the oxygen groups of GO and the metallic centers of the MOF. This results in the materials with enhanced porosity compared to the one determined for the physical mixture of MOF and GO. This new pore space and the presence of graphene layers increase the dispersive forces and favor ammonia adsorption. Via complexation/reaction with the MOF components, NH₃ eventually causes the collapse of the composites (and MOF).

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