Adsorption properties of aerogels made of graphene oxide and metal-organic frameworks fabricated by a supercritical CO_2 methodology

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The main objective of this project is to develop different methodologies to fabricate hierarchical porous composites based on aerogels of mesoporous graphene oxide (GO) [1,2] and a microporous metal-organic framework (MOF) HKUST-1 [3], with the purpose of studying their properties and possible applications in gas adsorption and separation. In this work, two methods for preparing the composites are presented: the direct mixing and the *in-situ* preparation. The first approximation consists in the direct dispersion of previously-synthesized HKUST-1 nanocrystals in a solution of GO in MeOH. The dispersion is dried and gelled in supercritical CO_2 ($scCO_2$) [4] resulting in extremely light greyish aerogels (Fig 1a) with significant surface area, composed of micropores and mesopores (Fig. 1c). This bimodal pore size distribution could enhance the adsorptive capacities at high pressure in comparison with the pristine MOF by improving the kinetics of the system. Indeed, the first measurements show promising results.

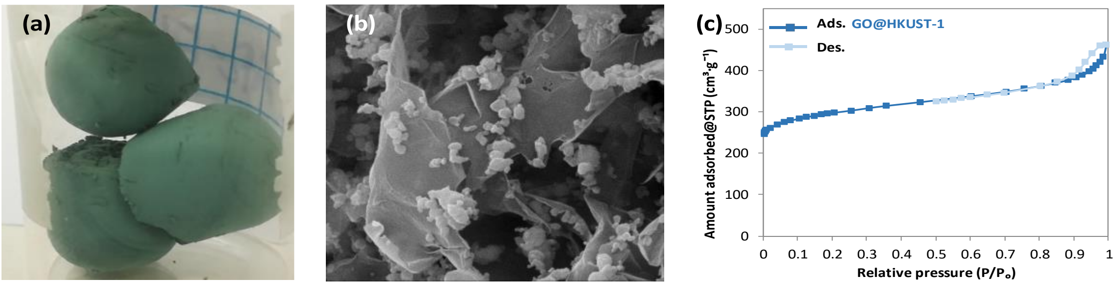

Figure 1. (a) Photograph of GO@HKUST-1 aerogels, (b) FE-SEM images of GO@HKUST-1, and (c) N_2 sorption isotherms of GO@HKUST-1.

In the *in-situ* method the HKUST-1 is synthesized in presence of GO. For that, the precursors in the synthesis of nano-HKUST-1 are introduced in a GO-MeOH dispersion. After several washing steps, the mixture is treated with $scCO_2$ and greyish aerogels are obtained. The $scCO_2$ enables fabricating aerogels in various shapes. By taking advantage of this feature we are able to produce GO@HKUST-1 aerogels inside fixed-bed stainless steel columns (Fig 2a). These filled columns are tested for gas separation by dynamic measurements showing outstanding breakthrough times in some mixture of gases such as N_2/CO_2 (Fig. 2b).

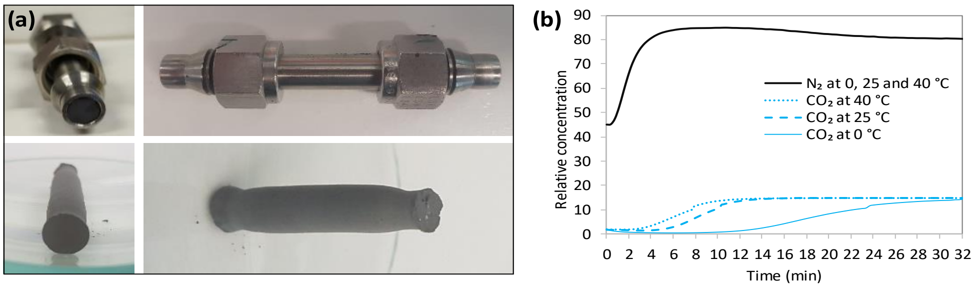

Figure 2. (a) Stainless steel column filled with GO@HKUST-1, and (b) breakthrough curves in a mixture of N_2/CO_2 (85/15) at different temperatures for GO@HKUST-1 prepared with the *in-situ* method

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