

Seeking of COF materials for hybrid membrane preparation towards molecular separation application

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Mixed matrix membranes (MMMs) consist of a molecular sieve such as porous crystalline solids (dispersed filler) embedded in a porous polymer (continuous matrix). Among the different porous crystalline solids stand out the zeolites, MOF (metal-organic frameworks), and the recently synthesized COF (covalent organic frameworks). While MOF particles are a class of porous polymeric material consisting of metal ions linked together by organic bridging ligands (that is, a combination of inorganic and organic counterparts), COFs are only synthesized by organic materials [1]. COFs arose as a new class of 2-D and 3-D organic solids with extended structures in which building blocks are linked by strong covalent bonds. They are made entirely from light elements (H, B, C, N, and O) that are known to form strong covalent bonds in well-established and useful materials such as diamond, graphite, and boron nitride [2]. Preparation of COF materials from molecular building blocks would provide covalent frameworks that could be functionalized into lightweight materials for diverse applications ranging from gas storage to catalysis.

Giving the premise of the good performance of MOFs embedded in MMMs or hybrid membranes for gas separation, specifically in separation processes of industrial and environmental relevance such as CO₂ capture from pre- or post-combustion [3], in this work, a preliminary study of COF candidates that could be used successfully as fillers in a membrane is studied. Promising separation performance relies on a proper contact between filler and continuous polymer matrix, as interfacial defects between both phases are undesired.

The most popular COF synthesis route is a boron condensation reaction consisting in the molecular dehydration reaction between boronic acids. For instance, in COF-1 (Fig. 1a) three boronic acid molecules converge to form a planar six-membered B₃O₃ (boroxine) ring with the elimination of three water molecules. Once selected the reaction route for the preparation of several COFs, the procedure for the fabrication of MMMs comprising COF would be analogous to other nanostructured materials (in this case with MOF particles, see Fig 1b) [4]. The first step is the dispersion of the filler in the solvent in an ultrasonic bath. Polymer is then added and the whole mixture is magnetically stirred overnight. Before the casting different intervals of sonicating and stirring take place to ensure a well dispersed solution. The membranes are cast on a flat surface (petri-type dishes or film applicator) and then left overnight for natural evaporation. The last step is to place the films in a vacuum oven at a specific

temperature (depending on the polymer glass transition temperature) able to remove the remaining solvent.

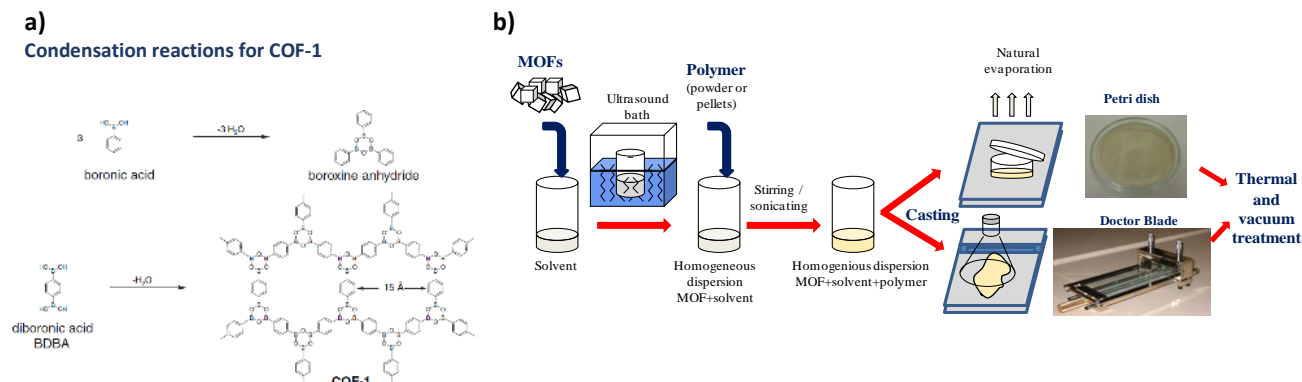


Figure 1. a) Condensation reaction of boronic acid used to produce discrete molecule and extended COF-1 [2], b) general scheme for the fabrication of MMMs containing MOFs as fillers [4].

The different COF in literature are evaluated attending to different synthesis procedures, pore structure and particle sizes. In general, harsh experimental conditions (e.g., reaction in a sealed pyrex tube, inert atmosphere, suitable solvents, longer time for crystallization, etc.) are required during COF synthesis to form well-ordered crystalline frameworks [5]. The selection of COF particles with low pore size will allow molecular sieving transport of separating molecules. Two synthesis routes such as mechanochemistry [5] or via dynamic covalent bonding, synthesizing the COF in water [6], emerge of considerable interest. This will allow the construction of bonds through a simple, economical, and environmental friendly route for MMM fabrication.

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