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An efficient recipe for formulation of metal-organic Frameworks

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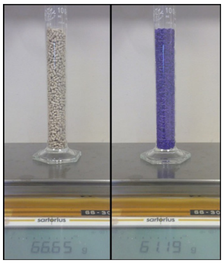
HIGHLIGHTS

- A detailed recipe for extrusion of MOFs.
- Reduction of surface area of UTSA-16 in the order of 5%.
- Hardness of the extrudates is higher than commercial zeolites.
- The density of extruded UTSA-16 pellets is comparable with zeolites.
- Increase of binder to provide hardness result in significant loss of surface area.

GRAPHICAL ABSTRACT



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ABSTRACT

A method to efficiently formulate metal-organic frameworks (MOFs) is provided. Our approach follows basic rules of extrusion where the elements of extrusion are the MOF (UTSA-16 powder), the binder (poly-vinyl alcohol, PVA) and the plasticizer (water and propanol). The extrudates produced with this method only lose a small fraction of specific surface area (SSA), in some cases only proportional to the amount of binder used for the formulation. In addition, we observe that the quality of the extrudates is strongly dependent on the activation temperature used for the MOF precursor: a higher activation temperature (393 K) gives less reduction in SSA with the content of binder. For binder contents up to 2 wt% no significant reduction in SSA is observed, while 3 wt% PVA gives only a modest 5% reduction. Moreover, the strength and particle density of the extruded material increase steadily with binder content. The density of the extruded MOF is comparable to a commercial zeolite extrudates with only 2 wt% of binder.

1. Introduction

Metal-organic frameworks (MOFs) are unique structures that combine the power of organic and inorganic chemistry to produce porous solids with extremely high surface areas and all kind of imaginable functionalities (Eddaoudi et al., 2000; Farruseng, 2011; Furukawa et al., 2013; Rowsell and Yaghi, 2004).

Since their initial discovery, a lot of different MOF structures have been generated and characterized for very diverse applications ranging from separation (Henschel et al., 2011; Krishna, 2012; Park et al., 2012; D'Alessandro et al., 2010; Llewellyn et al., 2009) gas storage (Millward and Yaghi, 2005; Wu et al., 2009; Arnold et al., 2013), catalysis (Fujita et al., 1994; Farruseng et al., 2009; Carson et al., 2012; Gascón et al., 2014; Nickerl et al., 2014), drug delivery (Horcajada et al., 2008), etc.

The total number of publications involving MOFs was higher than 1500 in 2013 and is still increasing. This large number of communications reports mostly the discovery of new structures, identification of new potential applications, fundamental understanding how they work (molecular modeling and characterization) and review papers. However, from this extensive amount of literature, much less than 1% of the manuscripts are devoted to formulation of MOFs. But to use any MOF in a given industrial application, it has to be formulated. Since their discovery, only few reports involving MOFs formulation or utilization of formulated

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MOFs (mostly tablets) have been published (Wang et al., 2002; Mueller et al., 2006; Cavenati et al., 2008; Finsy et al., 2009; Kusgens et al., 2010; Böhringer et al., 2011; Hesse et al., 2011; Schell et al., 2012; Plaza et al., 2012; Asadl et al., 2013; Cho et al., 2013). Moreover, a common feature of these publications is a sustained deterioration of the properties of the MOF (compared with the powder). In many of these publications the information about formulation is scarce or not available. In some others, the mechanical properties of the particles are not satisfactory for industrial use and thus the extension of the properties for a specific application may rely in a non-reproducible assumption.

We believe that formulation of MOFs is a key step that must be tackled in the near future to benchmark metal-organic frameworks with other existing materials like zeolites.

One structure that was recently synthesized is UTSA-16 (Xiang et al., 2005, 2012). This 3D cobalt–citric acid based MOF was claimed to have pores with the optimal dimensions to host two CO_2 molecules and thus have potential applications in CO_2 capture from flue gases aiming to mitigate climate change. A very interesting feature of this MOF is its high density which makes it comparable with zeolites in volumetric loadings.

Extrusion is the most employed technique for formulation of porous particles (Perego and Villa, 1997; Freiding et al., 2007; Mitchell et al., 2013). The extrudates are the final product of extruding a paste, which is composed by the porous material (powder), a binder material that has the ability to link together the particles and a plasticizer that reduces the viscosity of the sample to obtain a plastic mixture that can be extruded. A dispersant might also be used to avoid particle agglomeration.

The main problem in extrusion of MOFs has been to identify a proper binder and a plasticizer and finally mixing them in adequate amounts to avoid damaging the MOF properties, particularly keeping a high specific surface area.

The most commonly used plasticizer is water. However, some other organic solvent or organic–water mixtures can be used. An advantage is that after extrusion, the remaining of the plasticizer can be removed by heating (also possibly using vacuum).

The binder agents are more diverse. The most common inorganic binders used in zeolite extrusion are alumina and silica oxides, kaolin and siloxanes. These materials provide hardness to the extrudate after “firing”, which is heating to temperatures higher than 700 K. Some organic molecules are also used in the formulation of inorganic materials being cellulose, methyl cellulose and poly-vinyl alcohol the most employed ones (Chabert et al., 2008; Sapalidis et al., 2011; Romdhane et al., 2007; Voorhees et al., 1996). These materials are then removed from the material by controlled burning (few degrees per minute) generating macroporosity. No reported MOF will withstand this temperature treatment without severe structural damage so this forming strategy cannot be used and a new approach to the problem has to be used.

Our starting point was to find a binder material that can provide hardness at temperatures lower than 423 K. Since the MOF structures combine organic and inorganic ligands, we were open to a combination of organic and inorganic binders, but fundamentally focused to use an organic binder that will not be removed after extrusion. Our group has previously developed a method for using alginates as a recipe for formulation of MOFs (Blom et al., 2012).

Polyvinyl alcohol (PVA) is a biodegradable synthetic polymer with good properties for a binder material: low toxicity, anti-electrostatic properties, chemical resistance, toughness, permeable, etc. PVA is highly soluble in water, but its solubility depends on its molecular weight and on the degree of hydrolysis (Hassan and Peppas, 2000). An important property of PVA is that it has a high elastic modulus, even at low concentrations. In fact, PVA was previously used for formulation of MOFs but with considerable loss of surface area (Finsy et al., 2009). An important property of PVA is that it has a high elastic modulus, even at low concentrations and enhances the tensile strength of the formed material (Baklouti et al., 1997).

2. Materials and methods

The formulation method described here can be applied to several porous materials (not only MOFs) as long as they can withstand the presence of liquid water to a certain extent to dissolve the PVA. In general to avoid extensive structural changes in the MOF, if possible, it is recommended that the plasticizer has similar composition as the one used in the synthesis.

As mentioned before, three materials are used in this extrusion procedure:

(1) the MOF powder (UTSA-16),
(2) PVA as binder/dispersant material and
(3) a plasticizer (water–propanol mixture).

One inherent problem of the selected MOF powder, UTSA-16, is that is completely dissolved in pure water (the structure is destroyed) and thus pure water cannot be used for its extrusion. The synthesis of UTSA-16 was done in a mixture with 50% water and 50% ethanol. However, PVA is only very slightly soluble in ethanol. Several solubility tests were done and finally, a mixture of water (50%) and propanol (50%) was used as plasticizer since the desired amount of PVA could be solubilized. As will be shown, using a certain amount of this plasticizer and binder, the properties of the MOF were not drastically damaged. In order to study the influence of the binder in the final properties of the formulated MOF, the content of PVA was varied from 0 to 6.66 wt%.

The physical properties of the MOF (powder and/or extrudates) have been obtained using several characterization techniques such as thermo-gravimetric analysis, N_2 adsorption-desorption isotherm at 77 K, Hg porosimetry, scanning electron microscopy, X-ray analysis, compression tests and measurement of adsorption equilibrium of CO_2 at 298 K.

Thermo-gravimetric experiments were performed to determine a proper activation temperature to measure the surface area. According to the results obtained, activation can be performed at temperatures up to 423 K without damaging the structure of UTSA-16. This temperature is much higher than the recommended temperature of 359 K mentioned by Xiang et al. (2005, 2012).

3. Results and discussion

The loss of surface area for different amount of binder and activation temperatures is shown in Fig. 1. Using the activation

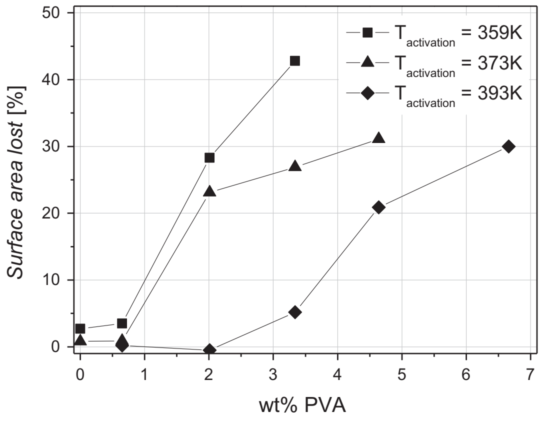

Fig. 1. Surface area lost as a function of the content of poly-vinyl alcohol (PVA) used as binder for different activation temperatures.