



Liquid-assisted mechanochemical synthesis of an iron carboxylate Metal Organic Framework and its evaluation in diesel fuel desulfurization



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ARTICLE INFO

Article history:

Received 3 February 2015

Received in revised form

4 April 2015

Accepted 6 April 2015

Available online 14 April 2015

Keywords:

Liquid-assisted grinding

Metal-organic framework

Desulfurization

4,6-Dimethyldibenzothiophene

ABSTRACT

An iron (III) carboxylate Metal Organic Framework isostructural with MIL-100(Fe) was synthesized through a mechanochemical route. The material, rapidly obtained by liquid-assisted grinding at room temperature, was characterized by X-ray powder diffraction, infrared spectroscopy, scanning electron microscopy, thermal gravimetry, nitrogen physisorption and adsorption microcalorimetry of ammonia. For comparison, the features of a commercial iron trimesate produced via electrochemical route were investigated as well. The ball-milled sample showed better crystallinity, associated with good thermal stability, higher surface area and pore volume. The adsorption performance of both the ball-milled and commercial samples for the ambient-temperature removal of 4,6-dimethyldibenzothiophene (4,6-DMDBT) from 4,6-DMDBT/n-heptane solutions simulating a diesel fuel was also investigated. The maximum adsorption capacity for the ball-milled sample resulted twice as big as that for the commercial one. An interpretation of the different adsorption behavior is proposed.

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1. Introduction

Metal Organic Frameworks (MOFs) are hybrid organic/inorganic crystalline materials with unique characteristics, such as very large surface area and fully accessible internal volume. The cavities within their stable network can be tailored to accommodate different guest molecules. The huge interest for these hybrid materials has originated in the past decade a large number of papers in different research areas [1–13]. Among the different MOFs, MIL-100(Fe) (MIL: Materials of Institut Lavoisier) is one of the most interesting structures and in the past decade it has been used in many applications as an adsorbent and a catalyst. This crystalline 3D iron (III) carboxylate (also named trimesate) MOF was

synthesized for the first time in 2007 by Horcajada et al. [14] by solvothermal synthesis with HF. A non-fluorinated structure was later synthesized by Canioni et al. [15] in absence of HF. The polar framework of MIL-100(Fe) is built up by trimers of carboxylate oxygen octahedra sharing μ_3 -O corners, with the Fe (III) ions located in the center of octahedra. Linking of the trimers by benzene-1,3,5-tricarboxylate leads to the formation of a hybrid supertetrahedral structure that displays two types of cages of ca. 25 and 29 Å, accessible through pentagonal and hexagonal windows, respectively (ca. 5.5 and 8.6 Å). Two of the three octahedra of the trimers in terminal position are bonded with a water molecule and the other with a fluoride or hydroxyl group [14,15]. The water molecules can be removed, leaving Fe(III) coordinatively unsaturated metal sites (CUS), which can act as electron acceptors (Lewis acid sites) to form π bonds. It is possible to reduce Fe(III) sites to Fe(II) under controlled conditions, thus changing the preferential sorption properties of this material, and so offering new opportunities in particular for separation processes. For instance,

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remarkable results were obtained in the CO removal from CO₂ [16] and in the separation of propane, propylene and isobutene mixtures [17]. The MIL-100(Fe) is stable to moisture and to hydrothermal conditions, and is an useful adsorbent material in water sorption technologies [18,19], contrary to other MOFs, which suffer of hydrothermal instability. In catalysis, this MOF has been used both as a solid catalyst, taking advantage of redox property of trivalent iron species [14], and as a 3D mesoporous system for the encapsulation of other catalytic species [15]. MIL-100(Fe) seems also interesting as a carrier in drug delivery [20] by virtue of its low acute toxicity in vivo [21]. Promising capacities in removing contaminants from fuel at mild conditions have been reported as well [22,23].

The usually reported method for MOFs synthesis, including MIL-100(Fe), is the solvothermal one. Unfortunately, the solvothermal method imposes, already at the laboratory scale, hard reaction conditions, i.e. high temperature and pressure, use of large solvent amounts, and long synthesis times. Such reaction conditions would represent a serious drawback in the scale-up of the synthesis.

In recent years, large-scale synthesis methods of well-known MOFs, such as MOF-5, MIL-53 (Al), HKUST-1, ZIF-8, and MIL-100(Fe), have been developed using both solvothermal and non-conventional procedures, including electrochemical and microwave methods. Only in few cases commercial products have been obtained as a result of such efforts. Furthermore, the scale-up procedures so far proposed do not completely match the criteria for industrial-scale syntheses [24]. In according to [25], a promising alternative for the large-scale production of MOFs could be based on a mechanochemical approach. Through this technique high yields can be obtained in short reaction times working under mild conditions (room temperature, ambient pressure) using small solvent amounts or even without solvent. Moreover, low-cost starting materials can be used with this technique. Two different ball-milling synthetic methods, called Neat Grinding (NG) and Liquid-Assisted Grinding (LAG) [26], have been already reported for MOFs synthesis [27–29]. NG is a solvent-free method while in the LAG method small amounts of solvent are added to the solid reaction mixture. The reaction kinetics of the MOFs synthesis is favored by the presence of a liquid phase [28,29] as already seen for other systems [30]. Several structures can be obtained from the same precursors by using different solvents. A careful solvent selection, as well as its accurate dosing, is required in order to obtain 3D structures [31] with the desired final properties [32].

In this paper we propose a mechanochemical approach as an alternative synthetic route for MOFs preparation, in view of a possible large scale production. The LAG method was used to synthesize a non-fluorinated MIL-100(Fe) structure under mild conditions. Several papers dealing with the synthesis of carboxylate MOFs using the LAG method have been recently published [28,29,31–34]. However, to the best of our knowledge, the applicability of such method for preparing a non-fluorinated MIL-100(Fe) structure has not so far been reported in the open literature. Furthermore, while catalytic amounts of solvent are usually added to the reaction mixture in the LAG method, in this work an alkali solution has been used to increase the yield and to avoid the presence of unreacted 1,3,5-benzenetricarboxylic acid in the final product. Tetramethylammonium hydroxide (TMAOH) has been selected as a base [35].

An iron (III) carboxylate framework isostructural with MIL-100(Fe) was obtained and characterized as to its structure (by X-ray powder diffraction, XRPD, and Fourier transform infrared spectroscopy, FTIR) and morphology (by scanning electron microscopy, SEM). The thermal stability was evaluated by thermal gravimetry (TG) and the textural features were assessed by nitrogen physisorption. Adsorption microcalorimetry of ammonia was

used as a direct and reliable method for determining both the concentration and the strength of the acid sites present on the sample. For comparison, a commercial iron trimesate (Basolite F300, one of the several MOFs produced in large scale by BASF using electrochemical methods [24,36]) was characterized as well.

The adsorption performance of the ball-milled sample for the removal of 4,6-dimethyldibenzothiophene (4,6-DMDBT) from 4,6DMDBT/*n*-heptane solutions simulating a diesel fuel was also investigated. The stringent regulations on the sulfur content of fuels make adsorption technology an interesting, environmentally-friendly alternative to the conventional catalytic hydrodesulfurization processes [37]. Being energy- and hydrogen-consuming, the latter seems hardly sustainable for the removal of refractory dibenzothiophenes with one or two methyl groups at 4-or/and 6-position from gasoil streams, where such compounds are particularly abundant. Though a MIL-100(Fe) MOF has already been used as a component of copper-based adsorbents for the separation of benzothiophene from *n*-octane solutions [23], investigations of the adsorption behavior of unmodified non-fluorinated MIL-100(Fe) structures are rare [38] and no papers on the use of such adsorbents prepared by ball-milling have so far reported. The present liquid-phase 4,6-DMDBT adsorption experiments were carried out on the as-synthesized MOF sample at room temperature and atmospheric pressure. *n*-Heptane was selected as a single-component surrogate diesel fuel because its cetane number is comparable to that for current European diesel fuel [39]. 4,6-DMDBT was regarded as a model compound for the refractory organosulfur fraction in a diesel fuel. For comparison, 4,6-DMDBT adsorption experiments were also carried out on the commercial iron trimesate sample (Basolite F300).

2. Experimental

2.1. Materials

For synthesis, 1,3,5 benzenetricarboxylic acid (H₃BTC, 95% Sigma Aldrich), iron (III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O, 98% Sigma), tetramethyl ammonium hydroxide (TMAOH, 97% Sigma Aldrich), were used as received without further purification. Basolite F300 was purchased from Sigma Aldrich.

For batch adsorption experiments, 4-6-dimethyldibenzothiophene (purum > 98%, Aldrich) and *n*-heptane (HPLC grade, Suprasolv Merck KGaA) were used as received.

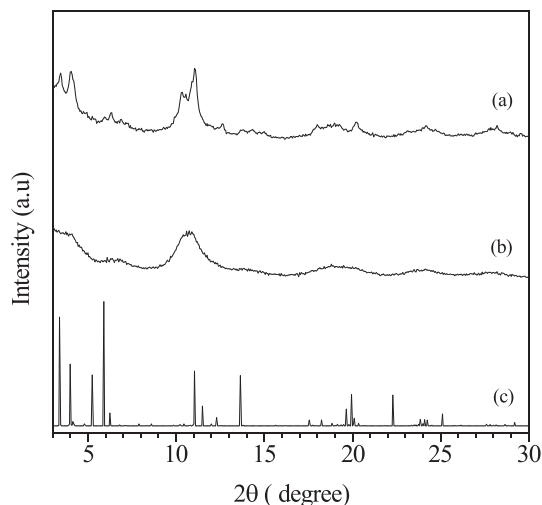


Fig. 1. Experimental X-ray powder diffraction patterns for (a) MFeLAG and (b) Basolite F300. Curve (c): Simulated XRPD pattern of MIL-100(Fe) phase [14].

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