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Sonoelectrochemical synthesis of metal-organic frameworks

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ABSTRACT

Here we report a new synergic strategy for the synthesis of metal-organic frameworks (MOFs), the sonoelectrochemical method. The metal-organic framework HKUST-1 $[Cu_3(BTC)_2(H_2O)_3]_n$ was successfully prepared by using this approach. Structural and morphological properties of HKUST-1 were studied and results compared with those obtained for the same material synthesized via a conventional solvothermal method. The sonoelectrochemical approach allowed the preparation of powder samples with nanosized characteristics, high yields and in a short time. Furthermore, we confirmed that this route worked well for the synthesis of others MOFs, such as ZIF-8 and MIL-53. Such simple and practical strategy may allow the large-scale production of MOFs, which is of great interest for industrial applications.

1. Introduction

Metal-Organic Frameworks (MOF) have become very attractives for industrial applications in the past years due to its unique properties such as the high thermal stability, the high porosity, and absence of any dead volume just to give some examples [1]. The great interest in this kind of material has driven the search and development of new synthetic strategies allowing large-scale production with low-cost and high-yield. Thereby, several synthetic routes have been employed during the last decades, such as slow diffusion, hydro(solvo)thermal, ionothermal, free solvent, sonochemistry, mechanochemistry, and electrochemistry [2–13].

However, these techniques are more suitable for the lab scale, so the development of synthetic routes in industrial scale is still necessary. As an alternative, it seems possible to explore the synergistic effect observed when combining two different synthetic approaches, such as sonochemistry and electrochemistry. The sonoelectrochemistry route is a straightforward and easy technique with well-established foundations and widely applied in electrodeposition, organic synthesis, and preparation of nanoparticles [14–16].

The metal-organic framework HKUST-1 $[Cu_3(BTC)_2(H_2O)_3]_n$ (BTC = 1,3,5-benzenetricarboxylate) is one of the most widely studied MOFs [17–21]. This MOF presents large surface area, high pore volume, high chemical stability and also the ability to bind water, among other molecules, by coordinating to the unsaturated Cu(II) sites [17]. These properties combined with the high structural stability upon water adsorption/desorption makes HKUST-1 a very promising candidate for gas storage, catalysis and sensing applications [22–26]. In addition to direct applications of HKUST-1 can notice a significant number of investigations in the development of composite materials based on these types of MOFs with the purpose of enhancing and expand the application range [27–29]. The main structural feature of HKUST-1 is a monomeric unit containing dinuclear clusters (paddle wheel) with a square-based pyramidal geometry and copper-copper distance of about 2.63 Å. Twelve oxygen atoms, from the carboxylate groups of the four BTC ligands, bind to the four coordination sites of each of the three Cu^{2+} ions [17].

In this scenario, we present a synthetic route to prepare the HKUST-1 using a sonoelectrochemical method. Despite the need for sophisticated equipment, the increase in the yield as well as the decrease in reaction time, besides milder electrochemical conditions, certainly justify the utilization of this approach. To the best

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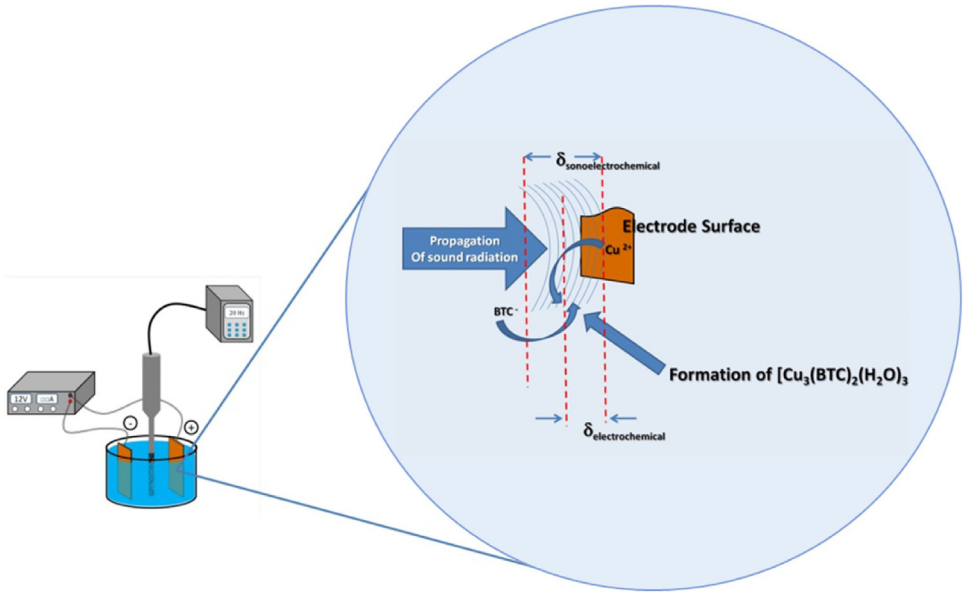

Fig. 1. Illustration of the behavior of the diffuse layer (δ) regarding the method (electrochemical or sonoelectrochemical) used in the formation of HKUST-1. Also is schematized the increase gradient of temperature (*T*) and pressure (*P*) with the distance *x* of propagation of sound radiated.

of our knowledge, this is the first time that such strategy is used to synthesize MOFs.

The use of two electrodes (without the reference electrode) enables the simple and easy application of the sonoelectrochemistry route for large-scale production of HKUST-1. As a result, this new configuration shows a synergistic effect that promotes an increase in the yields and reduction in synthesis time.

2. Materials and methods

2.1. Synthesis

2.1.1. Reactants

1,3,5-Benzenetricarboxylic acid (95.0%), NaNO3 (99.0%) and dimethylformamide (DMF) (99.8%), purchased from Aldrich (USA), were used as received and without further purification.

2.1.2. Working electrode

The working electrode (anode), a copper wire with a diameter of 0.133 cm, was previously polished using sandpaper granulometry 1200, immersed in a nitric acid solution (20% v/v) for two minutes and rinsed out with detergent.

2.1.3. Sonoelectrochemical synthesis

In a typical process, $NaNO_3$ (0.24 mol L^{-1}) and 1,3,5-Benzenetricarboxylic acid (24 and 48 mmol L^{-1}) were dissolved in a mixture of DMF/H_2O solvents (1:1, v/v). The resulting solution placed into a single-compartment electrochemical cell with two copper electrodes partially immersed. An electrical potential difference was applied between the electrodes, initiating the process of anodic dissolution ($Cu^0_{(aq)} \rightleftharpoons Cu^{2+}(aq) + 2\,e^-$), while the solution was kept under ultrasonic irradiation to ensure the expected synergic effect. This process, together with the deprotonation of trimesic acid ($H_3BTC_{(aq)} + 3\ DMF_{(aq)} \rightleftharpoons\ BTC^{3-}{}_{(aq)} + 3\ HDMF^{+}{}_{(aq)}$) allowed the formation of a blue precipitate (HKUST-1). The Table S1 displays the experimental conditions for SE(1)-(8) assays. A DC POWER SUPPLY (model FA-3005-INTRUSTHERM) was used to generated electrical potential difference (12 V). A Sonic-sVibra-CellTM apparatus generated the ultrasound frequency (20KHz, 30 and 60% of power).

All products were washed with water (2×), ethanol/acetone 1:1 (3×) and then dried at room temperature.

2.2. Characterization

Powder X-ray diffraction (XRD) analyses were performed in a SHIMADZU equipment, model XRD-7000, equipped with Cu Tube (Kα of 1.542 Å) operating at 40KV and 30 mA and using the following Slits: S = 1 deg, SS = 1 deg, e RS = 0.3 nm. The pore volume and surface area were obtained by using the BET method. All samples were previously dried at 90 °C for 16 h. About 50 mg of each sample placed into a quartz cell attached to the physisorption apparatus (Micromeritics ASAP 2010) to dry under vacuum at 100 °C for 2 h and then the nitrogen adsorption isotherms were measured at 77.4 K. The FT–IR spectra (4000–400 cm^{-1}) have been achieved with a resolution of 2 cm^{-1} at room temperature on a Bruker Tensor-27 spectrometer, fitted with a DTGS detector. The samples were previously prepared as KBr mixtures and recorded through the ATR technique. The thermogravimetric analyses were performed under N_2 atmosphere at a rate of 10 °C/min in a Shimadzu apparatus, model DTG-60. The samples were heated from room temperature up to 800 °C. The particle morphology was examined by using Scanning Electron Microscopy (SEM) in a JEOL/JSM-5900 apparatus. For Transmission Electron Microscopy (TEM) analysis was used an FEI Morgani 268D equipment, 80–100 Kv, Eindhoven, Netherlands.

3. Results and discussion

We study the effect of experimental parameters, such as the ultrasound power, the reaction time, and the ligand concentration, on the HKUST-1 synthesis. With this purpose, eight different experimental combinations were prepared (Table S1, see ESI[3]). A careful analysis of these data suggests that the ultrasound power, the reaction time, and consequently the current density are most relevant parameters when compared to ligand concentration. By

[3] Electronic Supplementary information (ESI) available: PXRD, BET, TGA, TEM and IV data.