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Control of morphology and size of microporous framework MIL-53(Al) crystals by synthesis procedure

Vera I. Isaeva,*[a] Andrey L. Tarasov,[a] Vladimir V. Chernyshev[b] and Leonid M. Kustov[a,b]

[a] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 137 2835, e-mail: sharf@ioc.ac.ru, lmk@ioc.ac.ru*
[b] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation*

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Two methods for the preparation of microporous phenylenecarboxylate framework MIL-53(Al), solvothermal high-pressure procedure and synthesis at atmospheric pressure, were compared in respect of crystal morphology and size. Lower reaction time and temperature featured microwave method providing nanocrystallites of homogeneous distribution in shape and size.

Metal-organic frameworks (MOFs) are nanoporous coordination polymers composed by ions and small metal clusters bridged by organic polydentate linkers. The outstanding texture characteristics (a large surface area and porosity) and possibility of fine tuning the composition and structure make MOFs a promising class of functional hybrid nanomaterials[1] with potential applications in many industrial processes, including the selective gas separation.[2–6]

In order to formulate MOF-based functional materials in different forms such as powder, thin layers and composite membranes,[7] novel fast preparation methods allowing a morphology control of MOFs should be developed.[8] It is well established that MOF synthesis assisted by microvawe (MW) heating is an effective route to nanocrystal formation.[9,10] The known MW syntheses of nanoMOFs are limited by a solvothermal procedure requiring an elevated pressure and a temperature above 150 °C.[11]

The known MOF family, MIL-53 frameworks,[12,13] characterized by pronounced dynamic structure transformation (a ‘breathing’ effect) possess unique adsorption properties in respect to several gases, thus allowing CO_2/CH_4 separation.[14] In the MIL-53(Al) framework usually synthesized in water, octahedral $AlO_4(OH)_2$ inorganic secondary building units (SBUs) compose diamond-shaped one-dimensional channels with a diameter of 0.85 nm, which can accommodate small gas molecules.[17,18] The ‘breathing’ effect for MIL-53(Al) framework is displayed as a transition between two stable conformations – the crystalline phase with narrow pores (np) and that with large pores (lp), these structure changes can achieve ~40% of the unit cell volume.[15,16] The prospects of MIL-53(Al) application as adsorbents behind framework dynamic flexibility are provided by its exceptional thermal stability – as high as ~550 °C.[17]

Our work was aimed at comparative study of two MIL-53(Al) materials synthesized by alternative procedures: (1) solvothermal preparation by conventional heating at elevated autogeneous pressure,[16] and (2) our original MW-assisted synthesis at atmospheric pressure. Noteworthy, the known MW-assisted preparation of F-MIL-53(Al) [with fluorobenzene-1,4-dicarboxylate linkers instead of benzene-1,4-dicarboxylate linkers in the MIL-53(Al) framework] involves the solvothermal conditions and therefore an autogeneous pressure and elevated temperatures.[18]

It is pointed out in a literature that a solvent plays a key role during the formation of MIL-53 crystalline phase MIL-53(Al).[19] MIL-53(Al) framework synthesis was carried out under solvothemal conditions with thermal heating in deionized water (220 °C). As the preliminary tests showed, the use of water in the MW-assisted synthesis at atmospheric pressure does not lead to the target framework formation (100 °C). Applying a mixed solvent (DMF–water) makes it possible to implement the MIL-53(Al) synthesis in the MW field. Noteworthy, DMF is a conventional solvent for preparation of a number of MOFs of the MIL series, such as NH_2-MIL-53(Al),[20] as well as its polymorph NH_2-MIL-101(Al).[21] Using DMF as a solvent with a higher boiling point makes it possible to perform the MIL-53(Al) synthesis at an elevated temperature (125 °C *vs.* 100 °C) and at atmospheric pressure.[†] Note also that DMF better absorbs MW irradiation. The original approach for MW-assisted synthesis allowed us to shorten the reaction time from 2.5 h [as compared to the literature MW procedure for F-MIL-53(Al)][18] to 20–30 min, and to reduce the synthesis temperature by almost 100 °C (125 °C *vs.* 220 °C).

The measured surface area (1090 $m^2 g^{-1}$) for synthesized MIL-53(Al) samples is in agreement with the literature data (1100 $m^2 g^{-1}$).[16] Morphologies of MIL-53(Al) framework samples synthesized by the procedures mentioned above are shown on the SEM micrographs (Figure 1).[‡] The SEM study revealed that the solvothermal MIL-53(Al)[17] sample is formed as crystallites with sizes changing in the range 1–10 μm. The mean microcrystallite size of 7–8 μm makes it possible to use this sample as an effective adsorbent for liquid chromatography without a narrow fraction separation.[17] The MIL-53(Al) material prepared

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[†] The solvothermal MIL-53 sample was prepared according to the described procedure.[18] The MIL-53(Al) MW-sample was synthesized according to the original method: $AlCl_3 \cdot 6H_2O$ (1.21 g), benzene-1,4-dicarboxylic acid (0.42 g) and a mixture of deionized water (3 ml) and DMF (5 ml) were transferred into a glass reactor and heated in a chamber of a Vigor MW oven (200 W, 30 min, 125 °C). The thus formed crystalline product was isolated by centrifugation, then rinsed with DMF (3×10 ml) and deionized water (3×10 ml). The crude MIL-53(Al) material was activated by calcination in air (220 °C, 72 h). The target product yield calculated in respect of started benzene-1,4-dicarboxylic acid was 60%.

[‡] Nitrogen adsorption data were obtained at 78 K by a volumetric method.[22] X-ray powder diffraction data were collected in transmission and reflection modes using two diffractometers: Huber G670 Guinier camera ($CuK\alpha_1$ radiation, λ = 1.54059 Å) equipped with an imaging-plate detector, and Panalytical EMPYREAN instrument with a linear X’celerator detector using Ni-filtered $CuK\alpha$ radiation, respectively. The microstructure of the synthesized samples was studied by field emission scanning electron microscopy (FE SEM) with a Hitachi SU8000 electron microscope. The images were recorded in the secondary electron mode at an accelerating voltage of 2 kV and a working distance of 5–6 mm. The morphology of the samples was studied with a correction applied to the surface effects of conduction layer sputtering.[23]

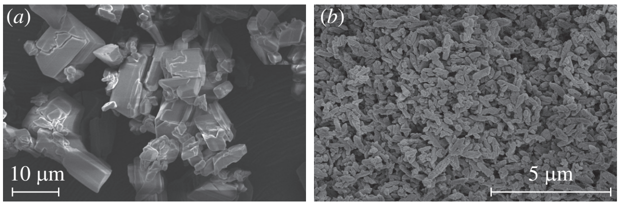

Figure 1 SEM micrographs of (*a*) ‘solvothermal’ and (*b*) MW MIL-53(Al) samples.

according to the original MW procedure features the prismatic crystallites distributed homogeneously in shape and size (~500 nm).

The crystalline structure of MIL-53(Al) synthesized samples was studied by the powder XRD method.[‡] The comparison of experimental XRD patterns [Figure 2(*a*)[17] and 2(*b*)] and calculated one[16] [Figure 2(*c*)] revealed that the crystalline phase of the solvothermal sample [Figure 2(*a*)] corresponds to the ‘low-temperature form’ of MIL-53(Al) [MIL-53(Al)$_{\mathrm{lt}}$], which features the H_2O molecule presence in the center of each framework channel.[16,17] Our tests showed that the MIL-53(Al)$_{\mathrm{lt}}$ crystalline phase is observed even after the solvothermal sample calcination for 96 h (330–450 °C). The XRD pattern of the MIL-53(Al) ‘microwave’ sample [Figure 2(*b*)] indicates the formation of the large-pore form MIL-53(Al)$_{\mathrm{ht}}$ with the open desolvated framework. This crystalline phase is characterized by the orthorhombic unit cell (Imma no. 74) and parameters $a = 6.63$, $b = 16.93$, $c = 12.62$.

Noteworthy, according to XRD results, the MIL-53(Al) sample synthesized under MW irradiation is characterized by a higher phase purity as compared to the MIL-53(Al) sample synthesized under solvothermal conditions (220 °C, 72 h) in aqueous media. Probably, this fact could be explained by the appearance of a small quantity of $\{[0.8\mathrm{Al(OH)BDC}\cdot0.2\mathrm{H_2BDC}] + 0.2\gamma\text{-}\mathrm{AlO(OH)}\}$ crystalline phase, whose formation was observed after treatment of the MIL-53(Al) material with boiling water for a few hours.[24]

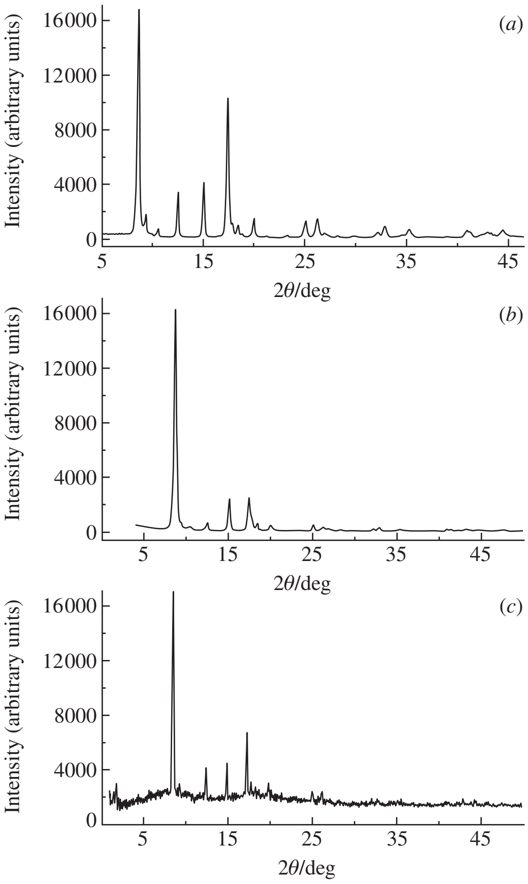

Figure 2 A comparison of powder XRD pattern of (*a*) ‘solvothermal’ and (*b*) MW MIL-53(Al) samples and (*c*) calculated for MIL-53(Al).[16,17]

Thus, a novel MW synthesis of the microporous phenylenecarboxylate framework MIL-53(Al) has been developed. The use of this method provides formation of MIL-53(Al) crystals with a uniform shape and size (up to ~500 nm) distribution. Carrying out the process in a mixed solvent (DMF–H_2O) yields the MIL-53(Al) material with a higher crystalline phase purity as compared to that formed in aqueous media.

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