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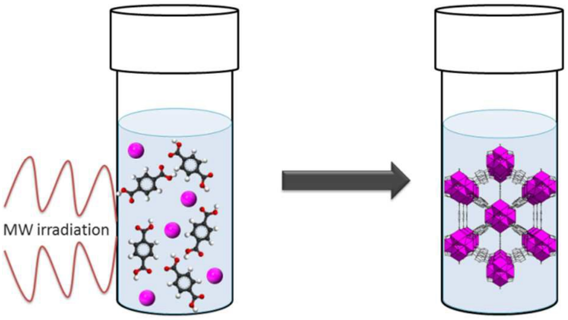
The microwave assisted synthesis of UiO-66 was optimized and scaled up to multigram production, evaluating the efficiency of the process by means of four quantitative indicators.



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Efficient Microwave Assisted Synthesis of Metal-Organic Framework UiO-66: Optimization and Scale Up

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A highly efficient and scalable microwave assisted synthesis of zirconium-based metal-organic framework UiO-66 was developed. In order to identify the best conditions for optimizing the process, a wide range of parameters was investigated. The efficiency of the process was evaluated with the aid of four quantitative indicators. The properties of the materials prepared by microwave irradiation were compared with those synthesized by conventional heating, and no significant effects on morphology, crystal size, or defects were found from the use of microwave assisted heating. Scale up was performed maintaining the high efficiency of the process.

Introduction

Zirconium-based metal-organic frameworks (MOFs) are among the most promising MOF materials for practical applications, thanks to their exceptional stability.[1] UiO-66 (Figure 1),[1a] first prepared in 2008, is based on hexanuclear $Zr_6O_4(OH)_4$ clusters and the 1,4-benzenedicarboxylic acid (H_2bdc) ligand. It displays relatively high surface area and pore volume, and its framework structure can be easily functionalized without affecting the topology, by either using modified H_2bdc ligands as starting reagents or by postsynthetic modification (PSM) or postsynthetic ligand exchange (PSE).[2] These characteristics make UiO-66 suitable for a number of potential applications, notably gas sorption/separation and catalysis.[3] The material is currently commercially available from STREM and has become a benchmark like other important MOFs such as HKUST-1, MIL-53(Al), and FeBTC, known as Basolite™ C300, Basolite™ A100, and Basolite™ F300, respectively.[4] Therefore, the development of a convenient protocol for the preparation of large amounts of UiO-66 in high yield, purity and space-time yield is very desirable.

Several approaches have been described to prepare UiO-66, demonstrating how it can be easily obtained under a rather wide range of conditions.[5] The commercially available product is prepared according to a patented procedure,[6] which requires 24 h heating at 120 °C under solvothermal conditions. The reduction of synthesis time would represent a remarkable improvement, in addition issues such as energy and mass efficiency, and the quality of the product are to be addressed for the large scale production of this material.

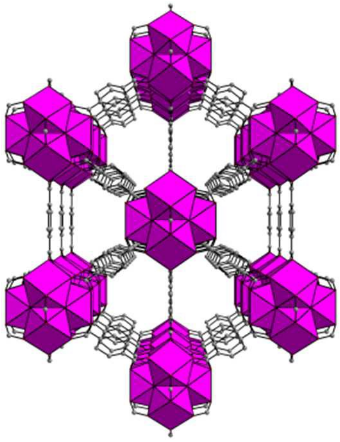

Figure 1. The crystal structure of UiO-66. Ligands (bdc) are shown as grayscale ball-and-stick and Zr(IV) ions are shown as magenta polyhedral.

Microwave (MW) heating is an established and powerful tool in synthetic organic chemistry, but it has recently been employed in the synthesis of inorganic and inorganic/organic materials as well.[7] In addition, conversion of MW radiation into heat is usually efficient and uniform throughout the sample, thus allowing to cut down the energy consumption and to minimize the need for heat transfer within the mixture.[8] These factors are crucial to allow easy scale up, as the heating process is relatively independent of reaction volume. Translation from milligram scale up to multikilogram scale was accomplished with MW for some organic chemistry processes.[9] However, it must be noted that issues related to the restricted penetration depth of the radiation into absorbing media can arise in larger batches.[10]

A relatively large number of MOFs have been prepared following MW assisted routes, generally allowing faster synthesis of smaller crystals compared to conventional heating.[11] As a matter of fact, MW heating increases the rate of both the nucleation and the crystal growth stage.[12] The MW-assisted synthesis of MOFs such as MOF-5[13] and HKUST-1[14] was deeply investigated, gaining insight into the influence of different parameters, such as irradiation power, irradiation time, concentration of the reagents, and solvent system, on the crystallization process and leading to the optimization of the synthesis.

The MW assisted preparation of UiO-66 was recently reported by Ren and coworkers[15] and by Li and coworkers,[16] showing that UiO-66 can be obtained with good crystallinity in a much shorter time than with conventional heating. The present paper reports the optimization of the MW-assisted synthesis of UiO-66 carried out using a Biotage Initiator apparatus to evaluate the effect of parameters such as concentration of the reagents, amount of modulating agent, reaction temperature, and reaction time on the efficiency of the process and on the crystallinity of the material, quantitatively assessed with the aid of four indicators. The procedure was successfully scaled up on a CEM MARS 5 synthesizer with high productivity and quality of the material, while increasing the energy efficiency.

Experimental

Chemicals.

All chemicals were purchased from Sigma-Aldrich, except for glacial acetic acid, which was purchased from Carlo Erba. The chemicals were used as received, with no further purification.

General procedure for the optimization of UiO-66 MW assisted synthesis.

$ZrCl_4$ and 1,4-benzenedicarboxylic acid (H_2bdc) were introduced in a 30 mL glass vial containing N,N-dimethylformamide (DMF). Acetic acid and water were added and the mixture was stirred for 15 min. The stir bar was recovered and the vial was capped with a septum and inserted in the heating lid of a Biotage Initiator microwave reactor. The reactor operated with variable irradiation power to keep the temperature constant. The maximum pressure was set to 10 bar, and the vial was externally cooled with the aid of a constant air flow throughout the process. Concentration of reagents, amount of modulator, volume of solvent, temperature, and irradiation time were varied according to Table S1. At the end of the process, the vial was air cooled, degassed by inserting a steel needle through the septum, and the cap was removed. The mixture was then centrifuged and the isolated solid was soaked in DMF for 12 h (2×20 mL), washed with acetone (1×20 mL), soaked in acetone for 24 h (20 mL) and washed with acetone (2×20 mL). Finally, the solid was dried in an oven at 60 °C.

Optimized MW assisted synthesis of UiO-66.

$ZrCl_4$ (291 mg, 1.25 mmol) and H_2bdc (208 mg, 1.25 mmol) were introduced in a 30 mL glass vial containing DMF (10 mL). Acetic acid (2.1 mL, 37.5 mmol) and water (0.135 mL, 7.5 mmol) were added and the mixture was stirred for 15 min. The stir bar was recovered and the vial was capped with a septum and inserted in the heating lid of a Biotage Initiator microwave reactor. The temperature was set at 120 °C, with a 15 minutes hold time. At the end of the process, the vial was air cooled, degassed by inserting a steel needle through the septum, and the cap was removed. The mixture was then centrifuged and the isolated solid was worked up as described above. 360 mg of product was recovered (Yield: 83%).

Scale up of the MW assisted synthesis of UiO-66.

A mixture composed of DMF (80 mL), $ZrCl_4$ (2.33 g, 10 mmol), H_2bdc (1.66 g, 10 mmol), acetic acid (17.1 mL, 300 mmol), and water (0.1 mL, 60 mmol) was subdivided into eight 30 mL PTFE vessels. Then, the vessels were placed inside a CEM MARS 5 oven and the synthesis was carried out in two stages: first, constant irradiation at 200 W was applied for 3 minutes, followed by 15 minutes of constant irradiation at 80 W. At the end of the synthesis, the vessels were immediately extracted from the oven and cooled down to room temperature by immersion in water. Once cooled, they were carefully opened in order to avoid abrupt pressure release, and the resulting product was worked up as described above. 2.72 g of UiO-66 was recovered (Yield: 78%).

General procedure for the synthesis of UiO-66 via conventional heating.

$ZrCl_4$ and H_2bdc were introduced in a 30 mL (Polytetrafluoroethylene) PTFE vessel containing DMF. Acetic acid and water were added and the mixture was stirred for 15 min. The stir bar was recovered, and the vessel was sealed and placed in an oven at 120 °C for 24 h. Concentration of reagents, amount of modulator, and volume of solvent were varied according to Table S1. At the end of the synthesis, the mixture was worked up as described above.

Analytical Procedures.

Powder X-Ray Diffraction (PXRD) patterns were collected in the 4-40 °2θ range and with a 15 s step^{-1} counting time with the CuKα radiation on a PANalytical X'PERT PRO diffractometer, PW3050 goniometer, equipped with an X'Celerator detector. The long fine focus ceramic tube operated at 40 kV and 40 mA. In order to ensure direct comparability among the patterns, the same sample holder loaded with the same amount of powder was used for all of the analyses. Full width at half maximum (*FWHM*) of the (004) reflection was estimated with the aid of the *PHILIPS PROFIT* software.

Thermal gravimetric Analysis (TGA) was performed using a Netzsch STA490C thermoanalyser under a 20 mL min^{-1} air flux with a heating rate of 10 °C min^{-1} from room temperature up to 700 °C.

Field Emission Scanning Electron Microscopy (FE-SEM) images were collected with a LEO 1525 ZEISS instrument, working with an acceleration voltage of 15 kV.

Gas sorption measurements were performed on samples immersed in acetone and dried prior to analysis. 40-100 mg of MOF was transferred to a pre-weighed sample tube and degassed at 120 °C on a Micromeritics ASAP 2020 Adsorption Analyzer for a minimum of 12 h or until the outgas rate was < 5 mmHg min^{-1}. The sample tube was re-weighed to obtain a consistent mass for the degassed MOF. Brunauer-Emmett-Teller (BET) measurements were collected at 77 K with N_2 on a Micromeritics ASAP 2020 (range: 0.005-0.14 P/P_0). Full N_2 sorption at 77 K of samples **23** and **24** (manually degased at 120 °C for 2 h) were measured on the same Micromeritics ASAP 2020. N_2 isotherm of sample **22su** was measured on a Micromeritics Tristar.

Results and discussion

Evaluation of process efficiency.

The optimization of a synthesis procedure demands that a number of experiments are performed, with the aim of identifying the conditions for which the efficiency of the process is maximized. To compare the results of different experiments, a method for assessing the efficiency is then needed. Nonetheless, the efficiency of a synthetic process can hardly be evaluated only by using a single parameter, as there are different aspects of the process that should be taken into account, such as mass efficiency, mass productivity in the unit of time and volume, energy efficiency, and quality of the product, intended as its purity and, in the present case, also crystallinity. In this work, the efficiency of the process was quantitatively estimated using four indicators, each describing one of the aforementioned aspects:

1. The reaction mass efficiency (*RME*), formulated as follows:[17]

$$RME = \frac{m_{UiO-66}}{m_{Zr} + m_{bdc}} \times 100$$

Where m_{UiO-66} is the mass of UiO-66 obtained (that is the absolute yield of the reaction), and m_{Zr} and m_{bdc} are the masses of zirconium chloride and H_2bdc used for the reaction, respectively. *RME* is commonly used in green chemistry and provides a measure of the yield of the reaction taking into account all of the species directly involved in the formation of the product and privileging reactions performed with stoichiometric amounts of reagents;

2. The space-time yield (*STY*), defined as the mass of product obtained per unit volume of reaction mixture per day [kg m^{-3} d^{-1}], and formulated as follows:
$STY = \frac{m_{UiO-66}}{V\times t}$3. The mass of UiO-66 produced per unit of energy supplied to the system during the reaction (μ) [mg kJ^{-1}], formulated as follows:

$$\mu = \frac{m_{UiO-66}}{E}$$

Where E is the total energy in kJ supplied by the instrument during the process, calculated as the product of the mean irradiation power and the total time of irradiation. To the best of our knowledge, such an indicator was never employed before for assessing the energy efficiency of a MW-assisted process;

4. The crystallinity, that is, the degree of structural order in the product. Crystallinity depends on a number of factors, the most relevant commonly considered are the crystallite size and lattice defects. Both of these features contribute to the broadening of the peaks in the diffraction pattern, although with a different dependence on the diffraction angle θ. However, for a series of isostructural samples, their relative crystallinity can be evaluated by means of the *FWHM* of a selected peak. The (004) reflection, located at 17.1 °2θ, was chosen because it has appreciable intensity and is not affected by overlapping with other reflections. The use of the same instrument for collecting the PXRD patterns of all the samples ensures that the instrumental contribution to the broadening is constant and therefore non influent. In this discussion the indicator

$$L^* = \frac{1}{FWHM}$$

is used for comparing relative crystallinity of the samples.

Synthesis optimization.

The microwave synthesizer Biotage Initiator was employed to investigate the effect of different parameters on the synthetic process, since it allows real-time control of temperature, pressure, and irradiation power throughout the reaction. Figure S1 shows the typical evolution of power, temperature, and pressure for a successful synthesis. Table S1 reports all the experiments carried out during this work. Figure S2 reports a graphical summary of the results shown in Table S1.

Acetic acid (AcOH) is widely used as an easy-to-remove additive for UiO-66 synthesis and was chosen as modulator.[5a] Other common modulators used in the literature are formic acid and benzoic acid: while no significant differences were observed when using either formic or acetic acid, benzoic acid was shown to be hard to remove from the pores of the freshly prepared UiO-66.[5a] Trifluoroacetic acid has also been employed as a modulator with the aim of creating open metal sites for catalysis upon its removal from the metal clusters.[3f]

The experiments performed under MW irradiation at rather low reagents concentration (Table S1, entries **1**-**5**, [Zr], [H_2bdc] = 0.016 M, T = 120 °C) failed to yield a highly crystalline product independent of the amount of AcOH used (70 equivalents) and irradiation times. The formation of a significant amount of amorphous phase was observed under these conditions (Figure S3).

By raising the concentration of reactants to 0.029 M (Table S1, entry **7**), a very crystalline product (*FWHM* (004) = 0.092 °2θ) was obtained after ~17.5 min of irradiation. The same reaction conditions without modulator did not afford a highly crystalline product (Table S1, entry **6**). The same trend was observed for n_{Zr}, n_{bdc} = 0.75-1.00 mmol, demonstrating that acetic acid is essential to yield highly crystalline products. The modulator also has a positive impact on the microwave absorption capacity of the reaction mixture, as the syntheses performed in absence of modulator required higher irradiation power to heat and maintain the mixture at the desired temperature than those containing the modulator (for example, compare entries **14** and **15** in Table S1).

A series of experiments (Table S1, entries **8-13**, n_{Zr}, n_{bdc} = 0.75 mmol, V_{DMF} = 15 mL) was performed with a gradual increase in the amount of AcOH to determine what was the optimal amount of modulator needed to obtain a highly crystalline product. The efficiency indicators for the samples in the series are plotted in Figure 2.

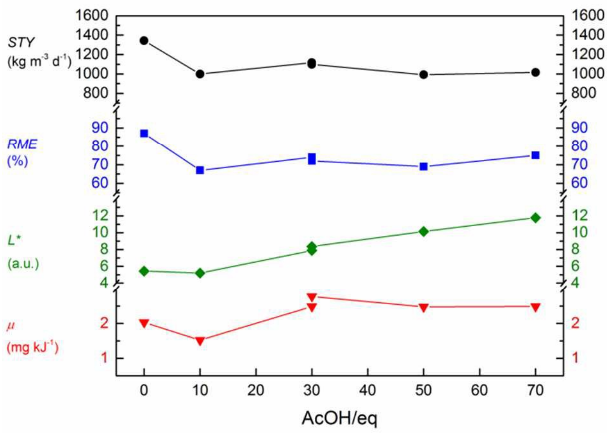

Figure 2. Effect of the amount of modulator on the efficiency of the synthesis.

Except for experiments **8** and **9** (Table S1, 0 and 10 eq AcOH, 120 °C, respectively), all the other experiments performed at 120 °C (Table S1, entries **10**, **12**, **13**) yielded products with good crystallinity (*FWHM* (004) < 0.13 °2θ). *L** improved when increasing the modulator from 30 to 70 eq while *STY*, μ and *RME* were not sensibly influenced. When 30 eq of AcOH were used, decreasing the temperature from 120 °C to 100 °C afforded very similar results (Table S1, entries **10** and **11**). This observation led to performing successive experiments with 30 eq of AcOH, with the aim of improving *STY* while maintaining the compound highly crystalline. The crystallinity of the products of experiments with n_{Zr}, n_{bdc} ranging from 1.00 to 2.00 mmol and 30 eq of AcOH was indeed excellent (*FWHM* (004) ≤ 0.11 °2θ). For n_{Zr}, n_{bdc} ≥ 1.00 mmol, syntheses were performed in either 10 or 15 mL of DMF to check if the ratio between the empty and the filled volume inside the reactor could exert any effect on the efficiency of the process (Figure 3).

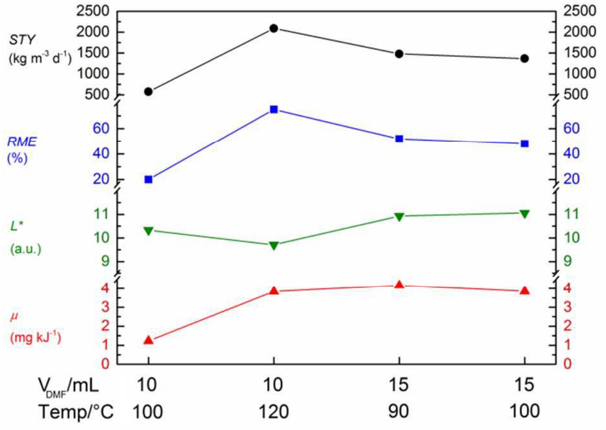

Figure 3. Effect of the head space on the efficiency of the process.

On the basis of the results in Figure 3, all conducted with [Zr], [H_2bdc] = 0.085 M and different volumes of solvent, the best values for *RME* and *STY* were observed when 10 mL of DMF were used in a 30 mL vessel and the reaction was performed at 120 °C (Table S1, entry **18**). Small amounts of product were obtained at lower temperature with the same concentration (Table S1, entry **17**). As the reaction develops pressure, a larger head space available for the gaseous byproducts formed was beneficial. It is worth noting that entries **24** and **25** were performed at 90 and 100 °C, respectively, to minimize safety concerns related to pressure build up since excessive pressure (>10 bar) was observed at higher temperatures. In terms of *L** and μ, these samples were comparable with **18**. Syntheses at [Zr], [H_2bdc] > 0.085 M were then performed only using 10 mL of solvent.

Figure 4 reports the efficiency indicators for selected experiments performed in the [Zr], [H_2bdc] range 0.016-0.149 M (Table S1, entries **3**, **7**, **11**, **16**, **18**, **21**, **22**, **25**, **26**, **28**, and **30**).

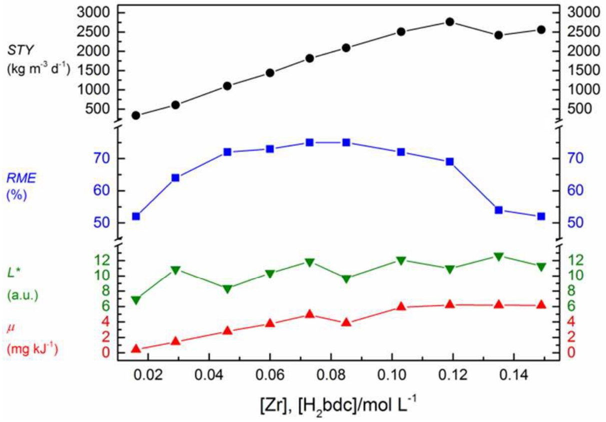

Figure 4. Effect of the concentration of Zr and H_2bdc on the efficiency of the process.

The main effects of increasing concentration of the reagents were on *STY* and μ, for which a general upward trend was observed. The values of *L** and *RME* were basically constant in all the range. At [Zr], [H_2bdc] = 0.135-0.149 M (Table S1, entries **28** and **30**), *RME* and *STY* started dropping, and higher concentrations caused even lower values, accompanied by poor reproducibility, probably because of solubility issues. The solubility limit of H_2bdc in DMF is 6.7 g/100 g solvent at 25 °C, corresponding to 0.4 M. However, the large amounts of AcOH required to modulate the reaction decreased the solubility of H_2bdc in the reaction mixture, as H_2bdc is highly insoluble in AcOH. Figure 4 suggests that the best results are obtained at [Zr], [H_2bdc] = 0.103-0.119 M (Table S1, entries **22** and **26**), which provided remarkable values for each efficiency indicator. Table 1 reports the synthesis conditions and efficiency indicators for these two experiments.

Table 1. Comparison of the efficiency between experiments **22** and **26**.

Entry	n_{Zr}, n_{bdc} (mmol)	[Zr], [H_2bdc] (mol/L)	AcOH (eq)	*T* (°C)	Irradiation Time (s)	Mean Power (W)	*E* (kJ)	Absolute Yield (mg)	*FWHM* 004 (°2*θ*)	*RME* (%)	*STY* (kg/m³d)	*μ* (mg/kJ)	*L**
22	1.25	0.103	30	120	1010	61	61.6	360	0.083	72	2504	5.90	12.11
26	1.50	0.119	30	100	1017	66	67.1	416	0.091	69	2761	6.20	10.98

UiO-66 was always obtained as the only crystalline product, despite recent reports that the polymorph MIL-140 phase could be easily accessed under MW irradiation.[7e] Stirring the mixture during the reaction was detrimental, as lower amounts of poorly crystalline product were often obtained. Attempts to use HCl as the modulator, as proposed by Hupp and co-workers,[5b] failed to yield sufficiently crystalline products under MW irradiation.

For the sake of comparison, a series of samples was prepared under conventional heating (Table S1, entries **19**, **23**, **27**, **29**, and **31**). The crystallinity of these products was comparable with the average observed for UiO-66 obtained under MW irradiation, whereas *RME* dropped when [Zr], [H_2bdc] ≥ 0.135 M. Because the reaction time was 24 h instead of about 18 min, the *STY* values for these syntheses are order of magnitudes lower than those observed for the MW assisted syntheses.

Thermal stability.

The TG curves of selected samples prepared by MW heating (Table S1, entries **18**, **22**, **24**, **26**) along with those of selected samples obtained by conventional heating (Table S1, entries **23**, **31**), are shown in Figure 5. The solvent molecules held in the pores (DMF, water, or acetone) desorb and the Zr clusters are dehydroxylated below 450 °C.[19] The various samples show different weight loss profiles, likely due to the varying amounts of solvents within the pores. The decomposition of the organic ligands is observed for all the samples between 450 and 600 °C, indicating that the framework of all samples has similar thermal stability, irrespective of synthetic conditions. It is known that UiO-66 framework can contain variable amounts of missing ligand defects, depending on the synthesis conditions.[18] The presence of such defects affects the amount of organic fraction inside the sample, and therefore its total weight loss. The calculated weight loss during this step in case of absence of defects is 148 g/mol.[19] Table 2 shows that all the samples undergo a smaller weight loss, meaning that they contain defects. The samples prepared by MW irradiation (**18**, **22**, **24**, **26**) show a slightly higher weight loss (ranging between 126 and 130 g/mol) than those prepared with the conventional method (**23** and **26**, 120 g/mol), indicating that the former might contain a smaller amount of missing ligand defects than the latter.

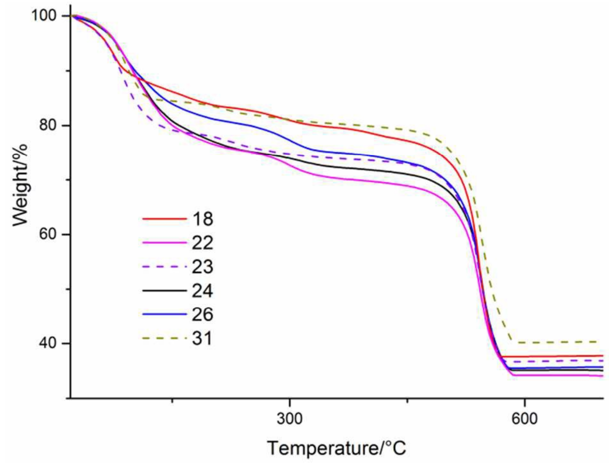

Figure 5. TG curves for samples **18**, **22**, **23**, **24**, **26**, and **31**. Sample numbers refer to Table S1.

Gas sorption properties.

BET analysis was performed on the same samples used for TGA characterization (Table 3). The BET values range between 982 and 1206 m^2/g for materials prepared under MW irradiation, and between 1089 and 1346 m^2/g for those prepared with the conventional method. These values are in agreement with TGA analysis because materials with fewer defects show lower average surface areas.[18] Full N_2 adsorption isotherms were measured for samples **23** and **24**, and displayed similar behaviour, despite the different uptake capacity (Figure S4). The measured pore volume at P/P_0 = 0.004 is 0.444 cm³ g^{-1} for **23** and 0.422 cm³ g^{-1} for **24**.

Table 2. Details of TGA data treatment for selected samples. Sample numbers refer to Table S1.

Sample	Total Weight Loss (%)	Solvent Weight Loss (%)	Organics Weight Loss (%)	Total Weight (g mol^{-1})	Solvent Weight (g mol^{-1})	Organics Weight (g mol^{-1})
18	62	23	39	324	75	126
22	66	31	35	362	112	127
24	65	29	36	351	102	126
26	65	27	38	347	94	130
23	63	27	36	332	90	120
31	60	21	39	308	65	120

Table 3. BET number for selected samples. Sample numbers refer to Table S1.

Sample	BET Number (m^2 g^{-1})
18	982
22	1171
24	1206
26	992
23	1346
31	1089

Morphological analysis.

FE-SEM images of samples **23** and **24** (Figure 5) show that the materials have the typical octahedral morphology, with homogeneous particle size. Sample **24**, prepared under MW irradiation, features crystal size, measured along the octahedra edges, of about 300 nm, whereas crystals of sample **23**, prepared under conventional heating, are smaller in size (about 150 nm). This is in agreement with the higher value of L^* observed for **24**. No other significant differences are evident from the images.

Scale up of the synthesis.

The Biotage Initiator is a so-called single-mode microwave synthesizer, in which the electromagnetic radiation is directed through a waveguide to the reaction vessel placed in a cavity at a fixed distance from the source. A standing wave is thus created, which provides high field density and consequently rapid heating of the reaction mixture. Most of the laboratory scale experiments reported in the literature employ single-mode instruments, as they provide fine control of process parameters, such as temperature, irradiation power, and pressure, and consequently a satisfactory screening aimed at defining the best synthetic conditions. Nonetheless, this instrument can only process relatively small batches, the maximum volume of solution being 20 mL in a 30 mL vial. It is also known that the energy efficiency in a single-mode system is low, because the microwave field is very dense and a significant fraction of the radiation might not be absorbed by the reaction mixture.[10,20]

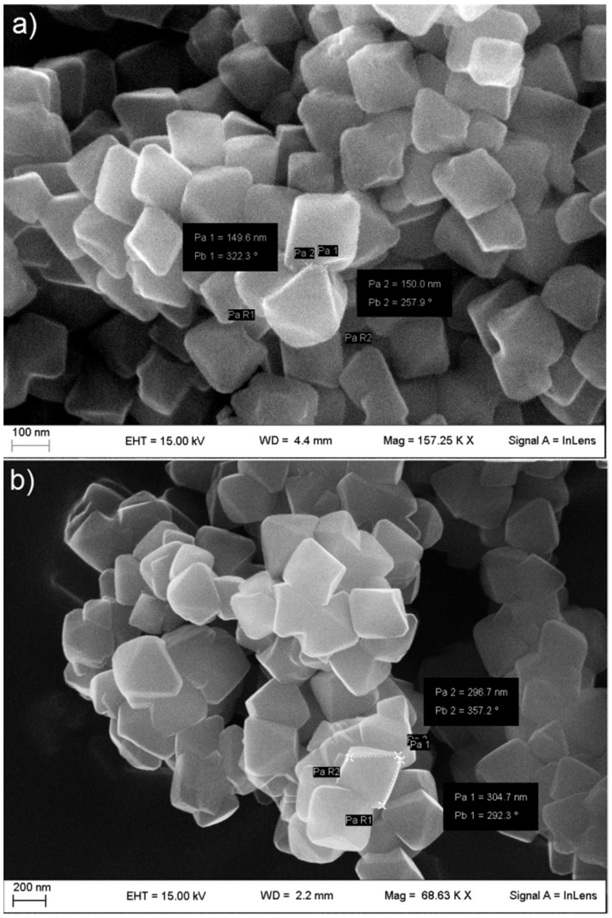

Figure 5. FE-SEM images of samples **23** (a) and **24** (b). Sample numbers refer to Table S1.

Scale up was then performed on a CEM MARS 5 multi-mode apparatus. In multi-mode instruments, the electromagnetic radiation is introduced in a cavity much larger than that of single-mode instruments, and it is randomly reflected by the walls, thus creating a less homogeneous and dense electromagnetic field if compared to single-mode instruments. Multi-mode synthesizers can process large amounts of solutions (up to liters) and are more energy efficient than single-mode ones. As a consequence, they are often used to scale up processes optimized on single-mode instruments.[10,20] However, switching from a single-mode to a multi-mode synthesizer means less control over the aforementioned relevant process parameters (temperature, pressure, irradiated power). Similarly, single-mode synthesizers produced by different companies have some relevant differences, such as geometry of the waveguide and temperature monitoring device, which can cause problems with reproducibility of results. As a consequence, transferring a protocol from different single-mode instruments or from a single-mode to a multi-mode apparatus is not a trivial task.[9]

Entry **22** in Table S1 was chosen as the experiment to be reproduced with the multi-mode apparatus, based on the excellent results obtained during the optimization. In order to avoid issues related to the limited depth penetration of MW arising when dealing with large reactors, in this work a parallel multi-vessel approach was chosen for scale up, irradiating eight 30 mL vessels at the same time. Because of the inherent differences between the Initiator and the MARS 5 instruments, a few attempts were necessary before being able to identify the optimal conditions for the scaled up synthesis. In some cases, formation of the MIL-140[1b] phase was observed, most probably due to overheating of the reaction mixture. The best procedure was performed in two stages of irradiation: the first stage at 200 W was needed to reach the reaction temperature in 3 minutes; the second stage at 80 W provided constant irradiation for the crystallization process in the following 15 min. Table 4 compares the efficiency indicators for entry **22** and for the scaled up procedure (**22su**). Figure S5 compares the PXRD patterns for **22** and **22su**. Figure S6 compares the N_2 isotherms for **22su** and **24**.

In this way we demonstrated both the flexibility of this protocol to different microwave instruments and that the synthesis can be scaled up maintaining excellent values of *RME*, *STY*, and *L**, while sensibly improving the energy efficiency. Considered that the CEM MARS 5 can accommodate up to 40 vessels at the same time, the potential amount of product obtainable in just 18 minutes of synthesis time is about 14 g, a remarkable achievement. The calculated value of *STY* for this synthesis (2241 kg/m^{3}d) is the highest reported to date for the synthesis of UiO-66, performed either in batch or continuous flow conditions under conventional heating (Table 5).

Table 4. Comparison of the efficiency between experiments **22** and **22su**.

Entry	Irradiation Time (s)	Mean Power (W)	*E* (kJ)	Absolute Yield (mg)	*FWHM* (004) (°2*θ*)	*RME* (%)	*STY* (kg/m^{3}d)	*μ* (mg/kJ)	*L**
22	1010	61	61.6	360	0.083	72	2504	5.90	12.11
22su	1080	100	108.0	2720	0.089	68	2241	25.19	11.24

Table 5. Comparison of the performances of different methods for the synthesis of UiO-66.

Synthesis Method	Reaction/Resident Time	*STY* (kg/m^{3}d)	Ref.
CH	24 h	23	This work
CH	24 h	14	5b
CH	24 h	490	5c
MW	18 min	2241	This work
CF	10 min	2016	21
CF	45 min	428	22

CH = Batch Conventional Heating; MW = Batch Microwave Assisted; CF = Continuous Flow.

Conclusions

This study shows that MW assisted heating is a valuable method for preparing high quality UiO-66 in a fast and efficient way. A quantitative approach taking into account mass efficiency, productivity, energy efficiency, and quality of the material was employed to evaluate the overall efficiency of the process and optimize the conditions. Unlike other MOFs prepared by MW heating, which usually induces formation of smaller crystals when compared to the conventional heating, UiO-66 did not display significant differences in crystal size, defects, or morphology arising from the use of MW. As previously remarked, the scale up of MW assisted processes to a certain extent is easy because of the uniform conversion of radiation into heat throughout the reactor, and this work demonstrated that this method can be easily scaled up to multigram production with high *STY*. To prevent issues related to the limited depth penetration of MW arising when dealing with large reactors, as pointed out by Kappe and coworkers,[20b] scale up was performed with a parallel multivessel approach, but the process could also be adapted for being performed in a continuous flow system.

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