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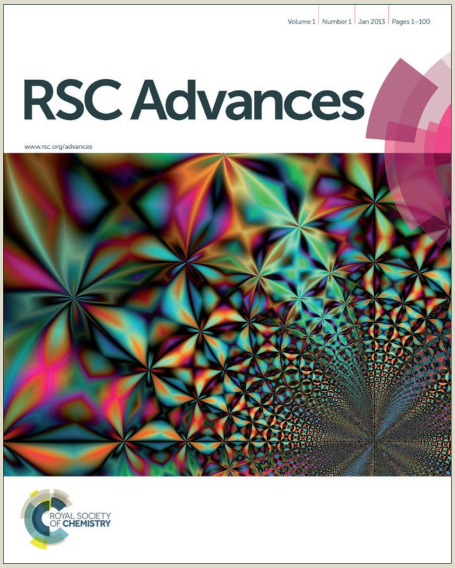

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Microwave assisted non-solvothermal synthesis of metal-organic frameworks

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Abstract

A new method for preparation of HKUST-1 using a microwave-assisted non-solvothermal synthesis is presented. The influence of reaction parameters (concentration of reactant mixtures, solvent, temperature, reaction time, microwave power) on the material textural properties and yields has been investigated and the synthetic method was optimized. By exposing the reaction mixture to microwave up to 10 minutes HKUST-1 with surface area and pore volume close to the theoretical values and yield of about 70% was obtained. In addition, yields could reach around 90% if the product formed in mother liquor is counted.

1. Introduction

In the last fifteen years metal-organic frameworks (MOFs) became the incontestable stars of the (nano)porous materials field thanks to their exceptional textural properties, structural and compositional versatilities. These extraordinary features have aroused academic and industrial interest for applications in the fields of energy storage (hydrogen,[1] methane[2]), separations,[3] catalysis,[4] drug delivery,[5] sensing[6] etc.

For industrial scale applications, MOFs with desired properties must be synthesized and processed in high yield and purity by streamlined methods. MOFs are synthesized by diverse synthetic strategies[7,8]: solvothermal, ambient pressure (non-solvothermal), slow interdiffusion of the respective building-block solutions,[9] microfluidics,[10] ionic liquids, mechano-[11,12] and electro-chemistry[13,14], etc. The most used synthethic method is under solvothermal conditions. Various solvothermal techniques were developed depending on the used source of energy: from electric heating (conventional synthesis) to microwave irradiation (microwave-assisted synthesis) and high-energy ultrasound (sonochemical synthesis).

Although novel approaches like high-throughput in continuous flow[15] or spray-drying strategy[16], were presented, HKUST-1 is produced almost exclusively by solvothermal techniques, mostly

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using electric heating, [17] except two microwave-assisted examples.[18,19] Regarding the synthesis at atmospheric pressure, the literature shows only examples using electric heating[20] and ultrasounds.[19,21]

We propose a new method for HKUST-1 preparation, a microwave assisted non-solvothermal synthesis, that combines the advantages of microwaves (power efficiency, rapid nucleation, accelerated crystal growth, phase selectivity, high yields) with those of reactions at atmospheric pressure which simplifies the synthetic requirements.[22] The influence of reaction parameters as concentration of reactant mixtures, solvent, temperature, reaction time and microwave power on the product has been investigated and optimized for HKUST-1 synthesis.

2. Experimental

All the chemicals were of analytical grade and used without further purification.

2.1 Microwave device

All syntheses were performed in a processing device in microwave field, designed, built and patented by National Institute for Research and Development of Isotopic and Molecular Technologies, Cluj-Napoca.[23] It has a 900W microwave generator (magnetron) that emits pulsed power at a rate of one pulse/second, with controllable filling factor of pulse and broad spectrum of microwave frequency for each pulse. The emission of microwave power in the reaction mixture was controlled by the treatment duration and the reaction temperature. The temperature was monitored by a sensor specific for use in microwaves field, which allows to control the temperature in the range of (-55)-125°C, with a sensitivity of 0.1°C. The treatment enclosure is a single mode type cavity with coaxial geometry designed to provide maximum volume for a single mode distribution at a frequency of 2.45 GHz. The single mode distribution of microwave power density enables a quick treatment with maximum energy transfer.

2.2 HKUST-1 synthesis

The reaction mixture, obtained from copper nitrate trihydrate (0.77 g, 3.225 mmol) dissolved in water (25 ml) and trimesic acid (0.38 g, 1.8 mmol) dissolved in dimethylformamide (25 ml) and ethanol (25 ml), was loaded in a Teflon pot, adapted to the coaxial geometry of the unimodal treatment precincts of the device for the microwave power treatment. Then, microwave irradiation (360 W, 70°C, 10 min) was started. After the completion of the process, the mixture was allowed to cool at room temperature and the solvent mixture was decanted off. For activation the as-synthesized form of HKUST-1 was suspended for 6 days in dimethylformamide (DMF). The solvent was replaced by fresh one after each 24 h. The activation was continued in the same way with ethanol. After that, the blue solid was filtered and dried in oven at 100°C. Yield: 0.27 g (50%). The yield of reaction was calculated using the mass of activated sample after subsequently degassing under vacuum at 220°C for 18 hours.

2.3 Characterization

The crystalline structures of samples were determined by powder X-ray diffraction (PXRD) on a Bruker D8 Advanced diffractometer using CuKα radiation (40 kV, 40 mA, λ of 0.15406 nm).

Scanning electron microscopy (SEM) were taken using a FEI Quanta 3D FEG SEM and a Hitachi SU 8230 SEM at an accelerating voltage of 20 and 30 kV, respectively.

Their textural properties were estimated from nitrogen adsorption/desorption isotherms obtained at (-196)°C K using a Sorptomatic 1990 (Thermo Electron Corporation) apparatus. The Brunauer-Emmett-Teller (BET) surface area (S_{BET}) was calculated using the multiple-point method in the relative pressure range p/p_0 of 0.02-0.15. The specific pore volume was determined according to Gurvich's rule at p/p_0 of 0.95. Before measurement, each sample was degassed at 220°C for 18 hours under dynamic vacuum.

The thermogravimetric analysis (TGA) of samples was performed on a SDT Q600 V20.9 Build 20 instrument in air atmosphere (100 ml/min) between 20 and 600°C at a constant heating rate of 10°C/min.

FT-IR spectra of the samples were recorded by KBr pellet method using a Jasco FT/IR 6100 spectrometer from 4000 to 400 cm^{-1} and a resolution down to 4 cm^{-1}.

3. Results and Discussion

We developed a microwave-assisted non-solvothermal synthesis of HKUST-1. The effect of synthetic parameters such as concentration of reactant mixture, solvent, temperature, reaction time and applied microwave power on the product quality was also investigated in order to optimize it. Various reaction conditions used for HKUST-1 syntheses and their outcomes are listed in Table 1.

Table 1 HKUST-1 samples with their reaction conditions and textural characteristics

Sample	Concentration	Solvent	T (^{0}C)	t (min)	P (W)/ FF (%)[a]	S_{BET} (m^2/g)	V_{pores} (cm^3/g)	Yield[b] (%)
1	c	DMF/EtOH/H_2O	70	10	360 / 40	1185	0.52	50
2	2c	DMF/EtOH/H_2O	70	10	360 / 40	1134	0.51	30
3	4c	DMF/EtOH/H_2O	70	10	360 / 40	1725	0.75	33
4	5c	DMF/EtOH/H_2O	70	10	360 / 40	1777	0.78	30
5	2c	EtOH/H_2O	70	10	360 / 40	536	0.32	9
6	2c	DMF	70	10	360 / 40	844	0.36	23
7	4c	DMF/EtOH/H_2O	60	10	360 / 40	1388	0.58	30
8	4c	DMF/EtOH/H_2O	80	10	360 / 40	653	0.27	30
9	4c	DMF/EtOH/H_2O	70	5	360 / 40	1036	0.44	16
10	4c	DMF/EtOH/H_2O	70	7.5	360 / 40	1674	0.78	25
11	4c	DMF/EtOH/H_2O	70	15	360 / 40	879	0.38	39
12	4c	DMF/EtOH/H_2O	70	10	450 / 50	1264	0.56	35
13	4c	DMF/EtOH/H_2O	70	10	540 / 60	1355	0.59	43
14	4c	DMF/EtOH/H_2O	70	10	630 / 70	1863	0.8	56
15	5c	DMF/EtOH/H_2O	70	10	630 / 70	1746	0.77	70
16	5c	DMF/EtOH/H_2O	70	7.5	630 / 70	1794	0.76	38

[a] FF is the acronym for filling factor of microwave pulse; [b] Partial yield.

3.1 Effect of reactant mixture concentration

We prepared four samples, noted **1**, **2**, **3** and **4,** starting from reaction mixtures with different concentrations. The synthetic procedure for sample **1** is presented in paragraph 2.2 and its concentration will be further denoted by **c** (see 2.2). For samples **2**, **3** and **4** reaction mixtures with concentrations equal to **2c**, **4c** and **5c**, respectively were used. The attempt to prepare a reaction mixture with a concentration of **6c** resulted in a supersaturated solution. All reaction mixtures were treated under microwave irradiation at a power level of 360 W corresponding to a filling factor of microwave pulse of 40%, for 10 minutes (total exposure time) at 70^{o}C.

The identity of prepared samples was confirmed by comparison of each PXRD pattern with the simulated diffraction pattern of HKUST-1 from the crystallographic data (Fig. 1).[21] The patterns are in good agreement with the simulated one and coincide well among each other. Each HKUST-1 sample was obtained pure and with a high degree of crystallinity as evidenced by the presence of the sharp peaks in their PXRD patterns.

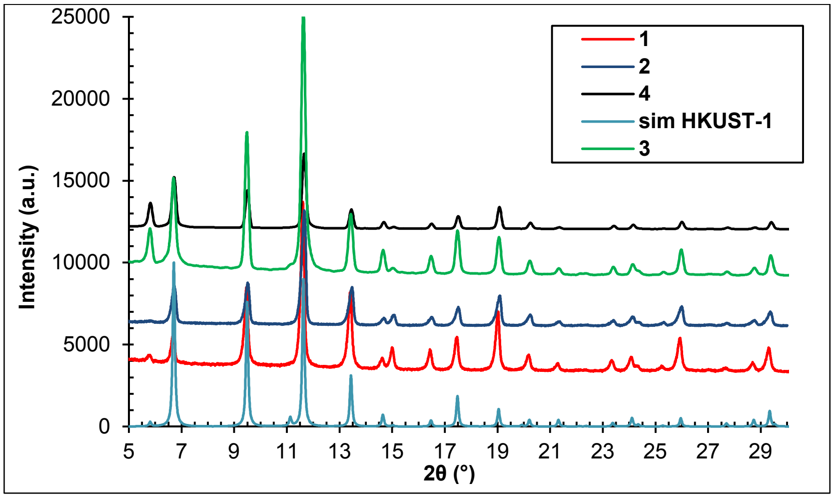

Fig. 1 The PXRD patterns of samples **1**, **2**, **3** and **4** compared with HKUST-1 simulated diffraction pattern from the crystallographic data.[24]

Further confirmation of HKUST-1 are provided by the FT-IR spectra presented in Fig. 2. The most significant feature in the FT-IR spectra of samples **1**, **2** and **3** are the asymmetric and symmetric stretching near to 1630 and 1370 cm^{-1}, respectively indicating the presence of carboxylate within the framework.[25, 26] Also can be observed the C-C stretches in the aromatic ring (~1570 and 1440 cm^{-1}), the in-plane C-H bending (~ 1100 cm^{-1}), and C-H oop (~ 725 and 735 cm^{-1}).[27] The FTIR spectra of the subsequent samples have practically similar characteristics.

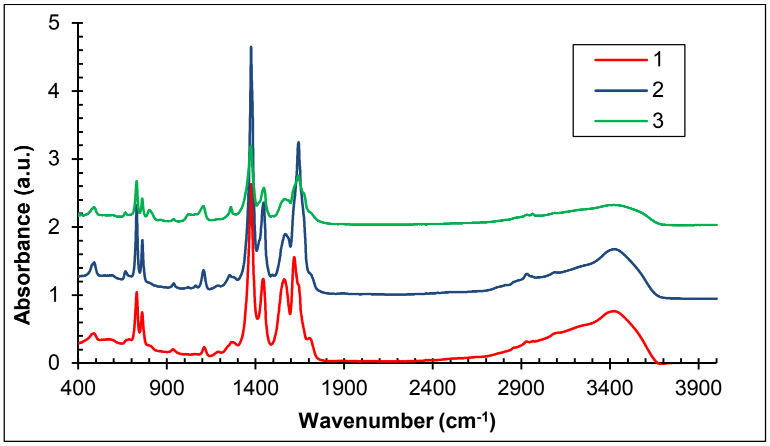

Fig. 2 FT-IR spectra of samples **1**, **2** and **3**.

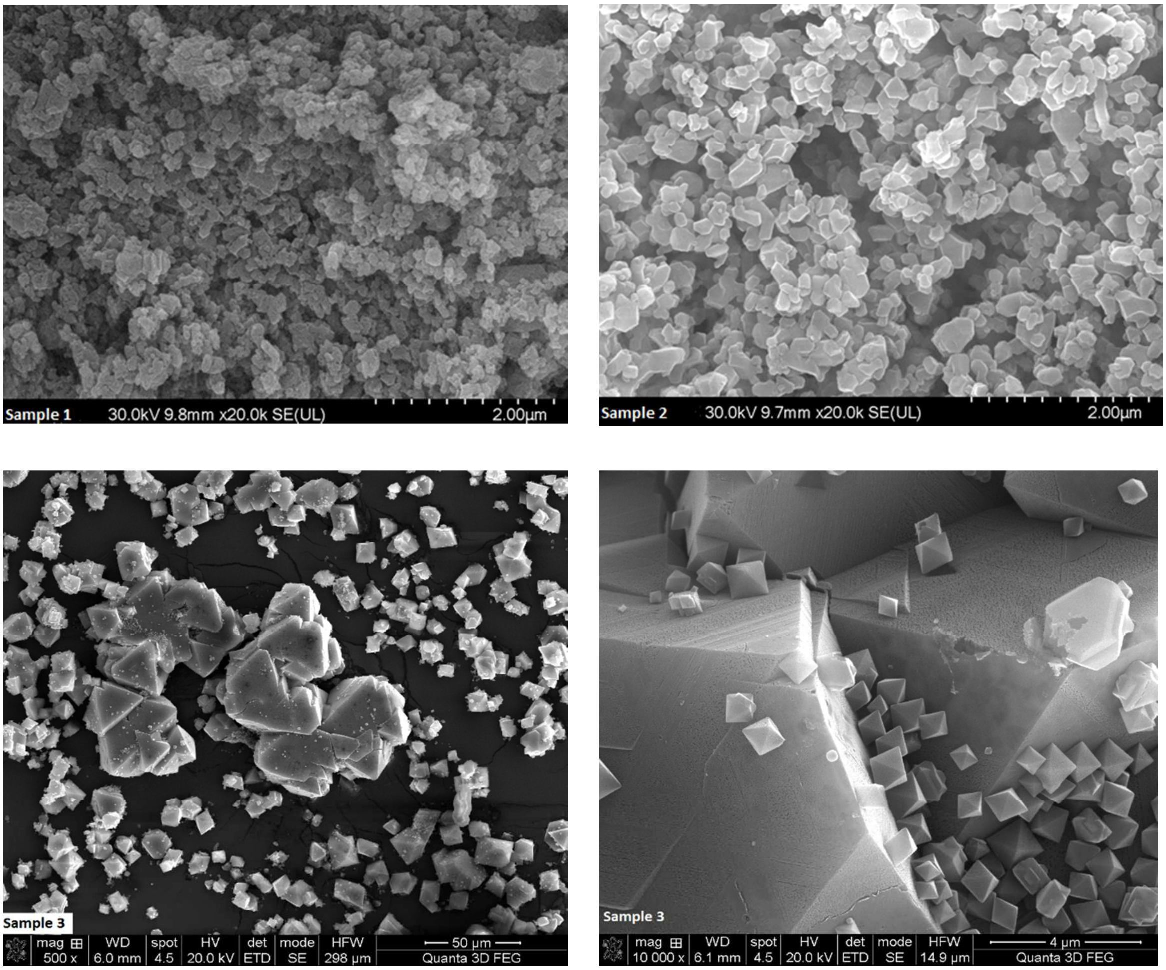

Fig. 3 SEM micrographs of samples **1**, **2** and **3**.

The crystals of HKUST-1 material usually have a typical octahedral morphology. As shown in Fig. 3, the crystal size and shape of samples are influenced by the concentration of reaction mixture. If the crystals of the first two samples had mostly a granular aspect with undefined forms, the sample **3** crystallized in large octahedra with well-defined faces and edges, together with polycrystalline agglomerates. Regarding the size, they grow with the increase of the reaction mixture concentration. The 10000x magnified image of sample **3** shows crystals of different sizes proving the continuous nucleation of them over the reaction time.

The BET surface areas and pore volumes of HKUST-1 samples, estimated from nitrogen adsorption isotherms (Fig. 4), are summarized in Table 1. Samples **1** and **2** have close surface areas but lower than 1200 m^2/g, while the surfaces of the other samples (**3** and **4**) are greater than 1700 m^2/g. This grouping highlights the relationship between the surface area of samples and the concentration of each reaction mixture: the sample surface area increases with the increase of the reaction mixture concentration. The type I isotherms recorded for samples **2**, **3** and **4** prove their microporous nature. Two steps can be observed in the adsorption isotherm of samples **3** and **4,** associated with bimodal pore size distribution of the samples.[28] The same step-like fashion of nitrogen adsorption isotherms is exhibited by MIL-101.[29] Unlike the other three samples, sample **1** shows a type IV(a) adsorption isotherm which is obtained with mesoporous adsorbents.[30] The pore size distributions of all samples calculated from nitrogen adsorption measurements using the Horvath-Kawazoe method are presented in Figure 5. Samples exhibit a narrow distribution in microporous domain with maxima at 0.5 nm (samples **1** and **2**) and 0.7 nm (samples **3** and **4**) and amplitudes that follows the observed trend of surface areas. Sample **1** has nearly 45% of pore volume in mesopores.

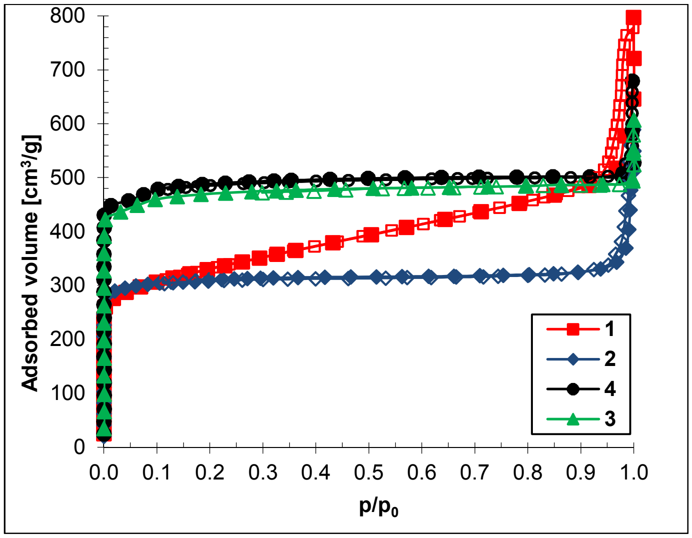

Fig. 4 Adsorption (filled symbol) and desorption (empty symbol) isotherms for nitrogen at (-196)°C of HKUST-1 samples **1**, **2**, **3** and **4**.

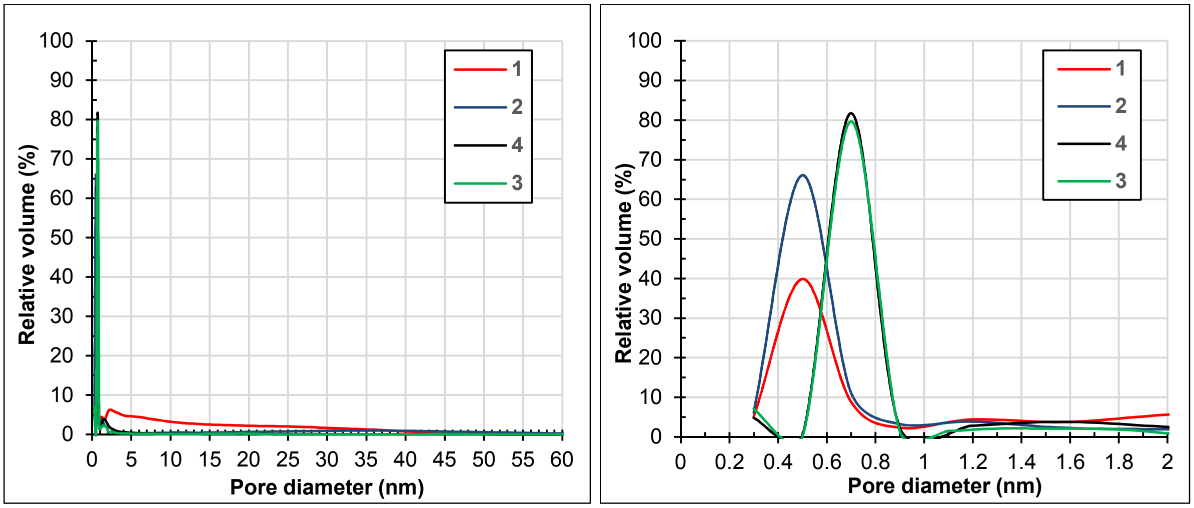

Fig. 5 Horvath-Kawazoe pore size distribution of samples **1**, **2**, **3** and **4** determined from the adsorption branches of the nitrogen isotherms depicted in Figure 3.

The thermogravimetric curves of samples **1**, **2** and **3** are depicted in Fig. 6. Each curve of the first two samples shows three distinct region: (1) weight losses of 8 and 6% until 100°C corresponding to the surface solvent loss, (2) weight losses of 26 and 28% between 100 and 290°C corresponding to the loss of solvent molecules trapped in pores and (3) weight losses of 41 and 43% between 290 and 320°C indicating the framework decomposition. Sample **3** losses weight of 9% until 50°C, 3% until 100°C, 50% until 300°C and 39% until 350°C. The weight loss corresponding to framework decomposition is most apparent at 300°C for samples **1** and **2** and 330°C for sample **3** (fig. 4 right).

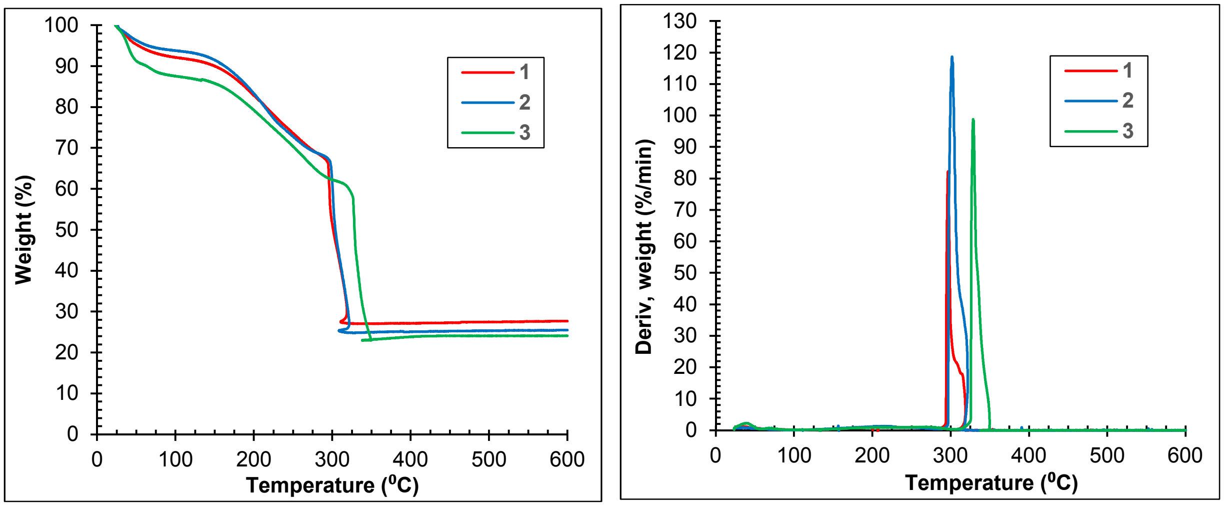

Fig. 6 TGA (left) and DTG (right) curves of samples **1**, **2** and **3** at 10°C/min.

In conclusion, reaction mixture concentrations of **4c** and **5c** are most suitable for HKUST-1 synthesis because the corresponding samples (**3** and **4**) have similar and better characteristics than the other two samples.

3.2 Effect of solvent

This parameter was studied using the following solvent mixtures: DMF/EtOH/H_2O (at 1:1:1 volume ratio) for sample **2**, EtOH/H_2O (at 1:1 volume ratio) for sample **5** and DMF for sample **6** (see Table 1). All reaction mixtures had the same concentration **2c** and were exposed at a microwave power level of 360 W (40%) for 10 minutes at 70°C. While samples **2** and **5** had blue colour, the sample **6** was greenish blue.

The PXRD patterns of samples **5** and **6** matches perfect with the calculated pattern from the HKUST-1 crystal data. Regardless of the solvent or solvent mixture used for the synthesis by microwave activation at atmospheric pressure, HKUST-1 was obtained (ESI, Fig. S1).

The surface areas of samples **5** and **6** have declined drastically compared to sample **2** at 536 and 844 m^2/g, respectively. The pore volumes followed the same trend. All samples have adsorption isotherms of type I (ESI, Fig. S3). The isotherm of sample **6** has a type H4 hysteresis, indicative of microporosity.[31] As shown in Fig. 7, sample **5** has about 70% from pore volume in micropores and the rest in mesopores.

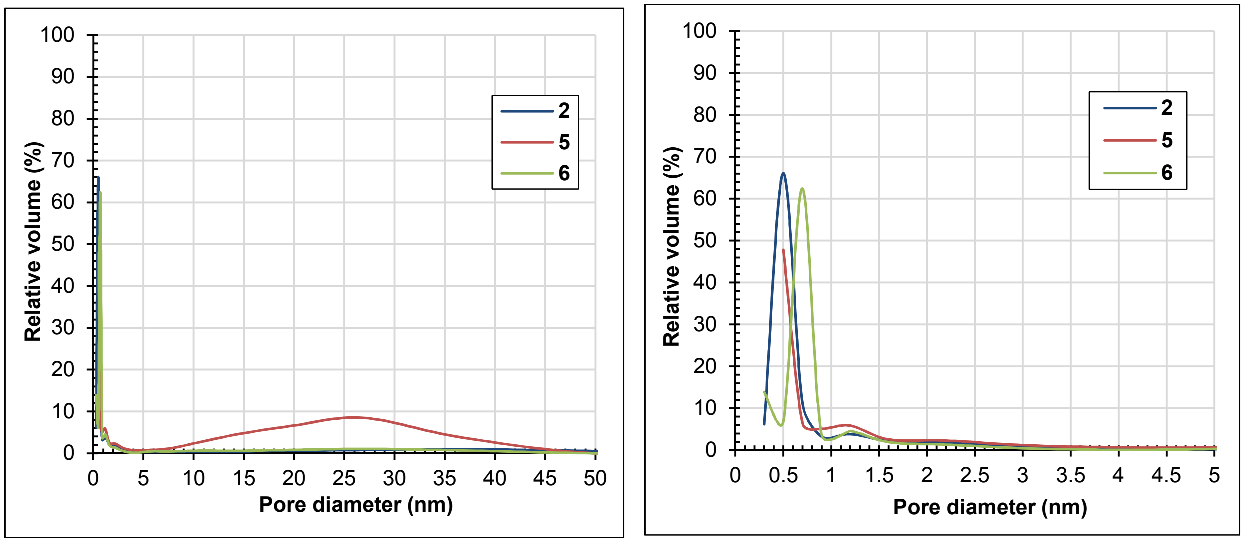

Fig. 7 Horvath-Kawazoe pore size distribution of samples **2**, **5** and **6** determined from the adsorption branches of the nitrogen isotherms depicted in Figure S3.

The TGA analysis reveals that samples **5** and **6** are stable up to 275 and 260^{o}C respectively, indicating lower thermal stabilities than sample **2** (ESI, Fig. S4).

Sample **2** exhibit the best textural characteristics, therefore the solvent mixture based on DMF/EtOH/H_2O (at 1:1:1 volume ratio) was selected for performing the following studies.

3.3 Effect of temperature

We performed syntheses at three different temperatures: 60, 70 and 80^{o}C, obtaining samples noted **7**, **3** and **8**, respectively. The reaction mixtures, with concentrations of **4c**, were treated under microwave with a power level of 360 W (40%) for 10 minutes (Table 1).

The PXRD patterns of samples **7** and **8**, compared with those of sample **3** and of the simulated one from crystallographic data, confirm that they are also highly crystalline HKUST-1 (ESI, Fig. S5).

As we expected, the octahedral crystals of sample **8** are smaller than sample **3** because lower temperature slows down crystal growth (ESI, Fig. S7; Fig. 3).[32]

Based on the estimated values of surface area and pore volume from nitrogen measurements at (-196)^{0}C (Table 1, ESI, Fig. S5), we concluded that the textural characteristics of samples improved from 60 to 70^{0}C and decreased drastically at 80^{0}C. Each sample has a type I adsorption isotherm feature of microporous compounds (ESI, Fig. S8). The isotherm of sample **8** has a type H4 hysteresis like sample **6** (ESI, Fig. S3).

Temperature of 70^{o}C leads to sample **3** which has the best textural characteristics and properties from all three samples, so the next studies of reaction parameters influence were performed at this temperature.

3.4 Effect of reaction time

The influence of microwave treatment duration over the properties of reaction products was studied by performing syntheses at different reaction time: 5, 7.5, 10 and 15 minutes obtaining samples noted with **9**, **10**, **3** and **11**, respectively (Table 1). Reaction mixtures with concentrations of **4c** were heated at a microwave power level of 360W (40%) at 70^{o}C. The sample yield is linked to the microwave treatment duration; it increases in the same direction from 16% for sample **9** to 39% for sample **11** (Table 1).

The PXRD patterns of samples **9**, **10** and **11** also matches well with that of simulated HKUST-1 confirming their identities (ESI, Fig. S10).

As you can see in Table 1, there is a relationship between the textural characteristics of samples and the duration of microwave treatment. Thus, the surface areas increased from sample **9** to **3** in parallel with the increasing of microwave treatment duration from 5 to 10 minutes. The extension of the exposure time from 10 to 15 minutes results in halving of the surface area and pore volume values. Surface areas and pore volumes of samples **10** and **3** have close values, being the highest from all four samples.

The type I nitrogen adsorption/desorption isotherms for this section samples are presented in Figure S13 (ESI). The nitrogen adsorption isotherm of sample **10** has also a two steps appearance, like sample **3**. Sample **11** has a type H4 hysteresis as sample **6** and **8** (ESI, Figs. S3 and S8).

Thermal analysis confirms the relation between duration of exposure to microwave and samples properties. Thermal stabilities of samples **9** and **10** are similar and lower than of sample **3,** but superior than of sample **11** (Fig. 8 left). The loss of weight corresponding to framework decomposition is most apparent at 299^{o}C for samples **10** and **11**, 305^{o}C for sample **9** and 330^{o}C for sample **3** (Fig. 8 right).

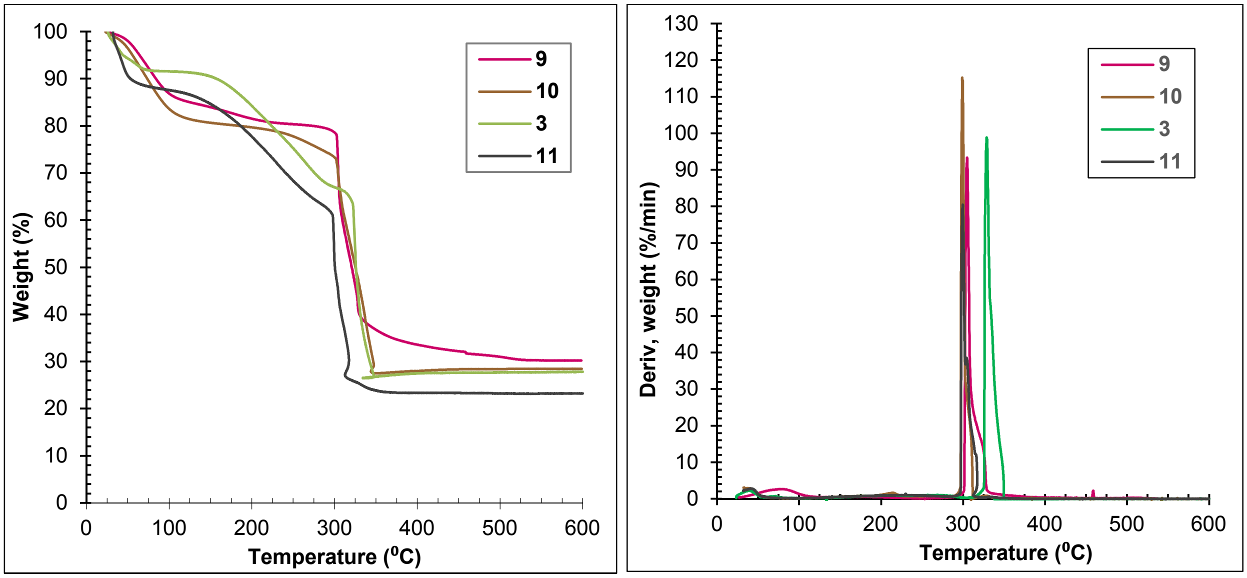

Fig. 8 TGA (left) and DTG (right) traces at 10^{o}C/min of samples **9, 10**, **3** and **11**.

In conclusion, reaction time of 7.5 and 10 minutes allow synthesizing of samples with close textural characteristics. The following syntheses will be made by microwave exposure for 10 minutes.

3.5 Effect of applied microwave power

The emission of the microwave power in the reaction mixture is controlled by the treatment duration and the reaction temperature. Four HKUST-1 samples, noted **3**, **12**, **13** and **14**, were synthesized by treating the reaction mixtures of **4c** concentration at 70°C for 10 minutes, under powers of 360, 450, 540 and 630 W corresponding to 40, 50, 60 and 70% respectively filling factors of microwave pulse (see Table 1). A microwave treatment was performed at 270 W or a pulse filling factor of 30%, but 10 minutes were not enough to reach 70°C and activate the reaction.

All synthesized sample are crystalline HKUST-1 as revealed by the unchanged PXRD pattern compared with the simulated patterns from crystallographic data (Fig. 9).

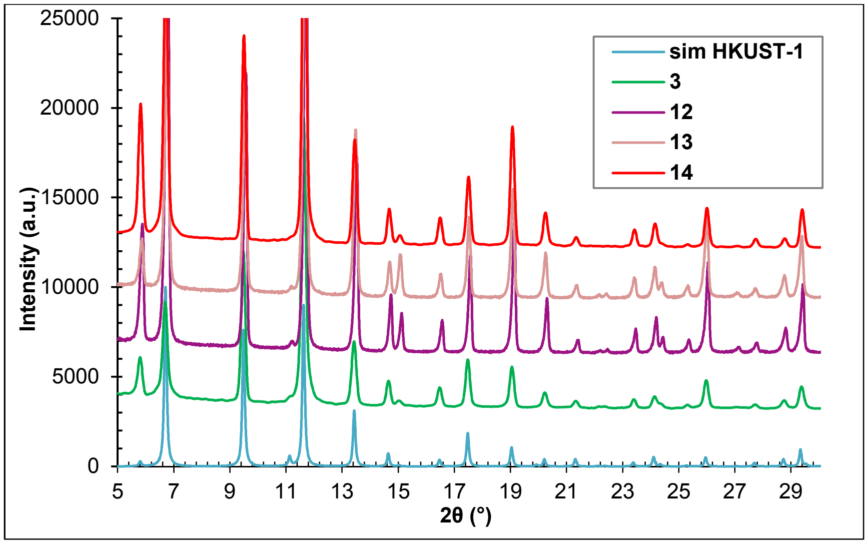

Fig. 9 The PXRD patterns of samples **3**, **12, 13** and **14** compared with simulated diffraction patterns from the crystallographic data.[24]

Figure 10 presents SEM micrographs for sample **14**. Most of the crystals of sample **14** have typical octahedron shape, but there are also some with a more irregular shape. Compare to sample **3** (Fig. 3) its crystals are more uniform as shape and with larger dimensions.

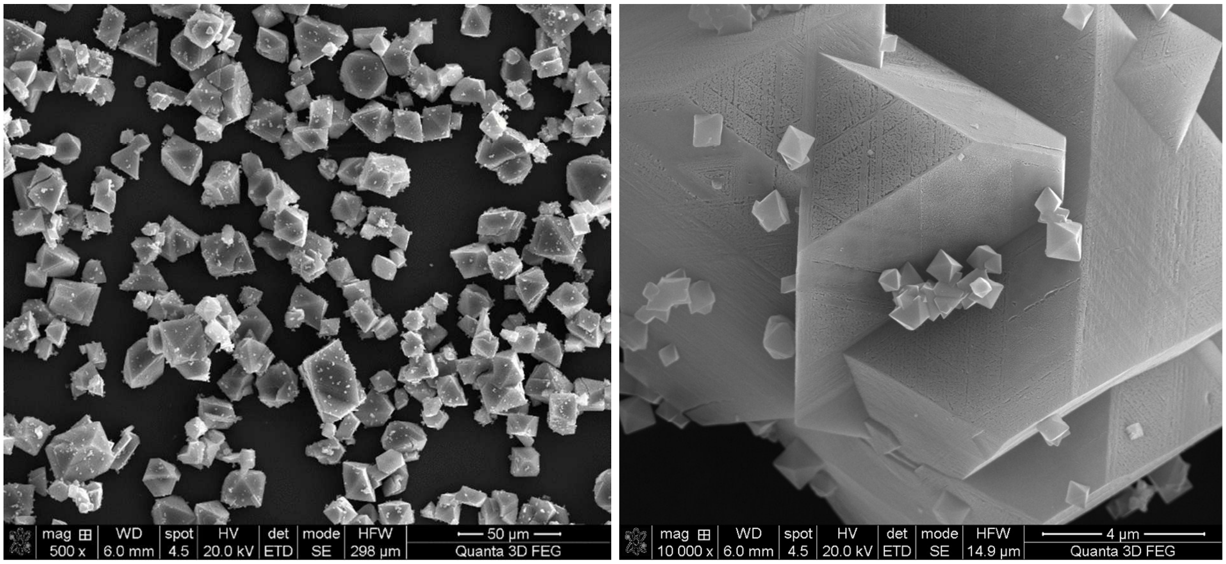

Fig. 10 SEM micrographs of samples **14**.

Samples **12**, **13** and **14** have also a type I nitrogen adsorption/desorption isotherm (ESI, Fig. S15). Their estimated surface area and pore volume presented in Table 1 show an interesting evolution with the microwave power. As the power increased from 360 to 630 W, surface areas and pore volumes decreased from sample **3** to sample **12** and then increased to samples **13** and **14**. In fact, the surface area (1863 m^2/g) and pore volume (0.8 cm^3/g) of sample **14** are the highest from all the samples presented in this work. A possible and plausible explanation for this textural properties evolution can be the specific harmonics generated by the microwave magnetron at different powers. Figure 11 present a comparison between the pore size distributions of samples. All exhibit a narrow distribution of pore size with maxima at 0.7 nm. Around 95% of pore volume from sample **14** is in micropores.

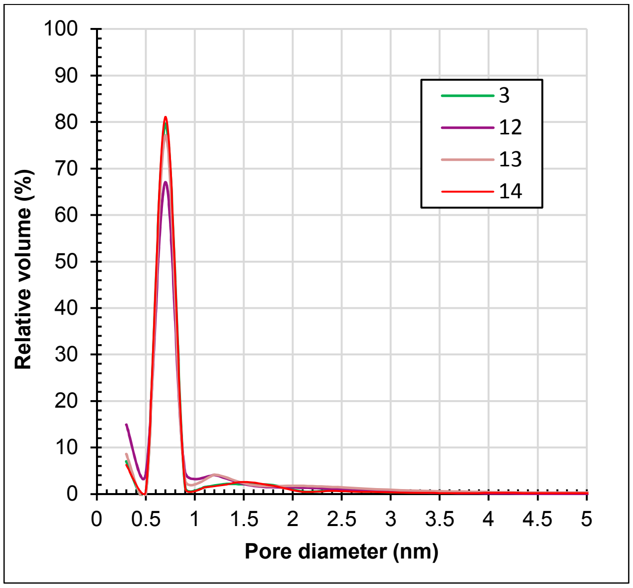

Fig. 11 Horvath-Kawazoe pore size distribution of samples **3**, **12**, **13** and **14** determined from the adsorption branches of the nitrogen isotherms depicted in Figure S15.

As we expected, the yield increases with microwave applied power to the reaction mixture (Table 1) from 33% (sample **3**) to 56% (sample **14**).

What happens with the textural properties of a sample synthesized by subjecting the reaction mixture of **5c** concentration to a microwave power of 630W at 70°C for 10 minutes? The as-prepared HKUST-1 sample, noted **15**, has surface area of 1746 m^2/g and 0.78 cm^3/g pore volume. Increasing the concentration of the reaction mixture from **4c** at **5c** pushed up the yield from 56 to 70%.

Also, we tested this reaction mixture under the same condition (630 W, 70°C) but reaction time of 7.5 minutes. Sample **16** was obtained with a yield of 38% and has a surface area of 1794 m^2/g and pore volume of 0.76 cm^3/g, close with those of sample **15**. The results are similar with those obtained for samples **3** and **10** synthesized from reaction mixtures of **4c** concentration, at 360W in 10 and 7.5 minutes, respectively, proving the reproducibility of this synthetic method.

3.6 Mother liquors

In the collected mother liquors, after a while a blue powder, identified as HKUST-1, has precipitated. Therefore, the reaction continues after completing the microwave treatment until depletion of reaction mixture. If this material exhibit the same characteristics as the product isolated after microwave treatment, then it should be used in yield calculation. This is the reason why the yield in Table 1was defined as apparent.

For this purpose, the synthesis of sample **14** was repeated 10 times. After HKUST-1 removal, the mother liquors were collected and kept for 2 months. The blue precipitate was separated by decantation and then subjected to activation as the previous samples. It was noted **14(2)**. After another two months, the blue precipitate formed in mother liquor was separated and subsequently activated. This sample was noted **14(4)**. The PXRD patterns of both samples proved they are HKUST-1 with a high degree of crystallinity (Fig. 12).

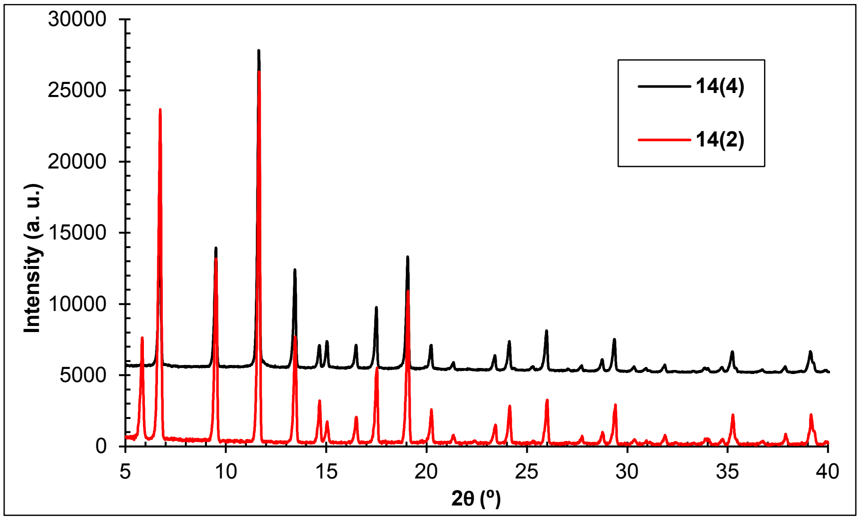

Fig. 12 The PXRD patterns of samples **14(2)** and **14(4)**.

The surface area and pore volume estimated from their nitrogen adsorption isotherms (ESI, Fig. S18) are: 1716 m^2/g and 0.76 cm^3/g for sample **14(2)** and 1775 m^2/g and 0.78 cm^3/g for sample **14(4)**.

TGA and DTG curves of samples **14**, **14(2)** and **14(4)** are presented in Fig. S19 (ESI). The weight loss corresponding to framework decomposition is most apparent at point of 307°C for samples **14,** 313°C for sample **14(2)** and 327°C for sample **14(4)**.

If we take into account samples **14(2)** and **14(4)** the total yield of sample **14** rise to 87%.

4. CONCLUSIONS

Our work opens up an alternative route for metal-organic frameworks synthesis. The microwave assisted non-solvothermal synthetic method proved to be an effective and reliable approach for pure and highly crystalline HKUST-1. The experiments were performed in an open system in significantly reduced reaction time (7.5 min). Pure phase HKUST-1 with surface area up to 1860 m^2/g could be synthesized. Since the HKUST-1 formation continues in mother liquors after the microwave treatment, excellent yields can be achieved. The success of the HKUST-1 synthesis suggests that this quick and easy method could be applicable to other metal-organic frameworks.

Acknowledgments

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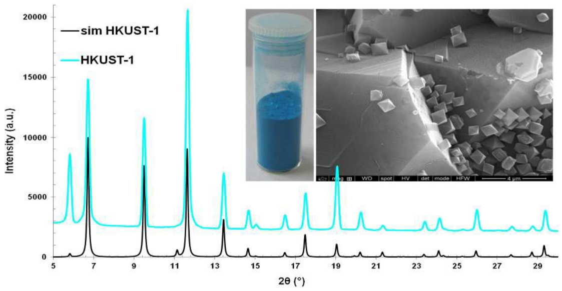

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