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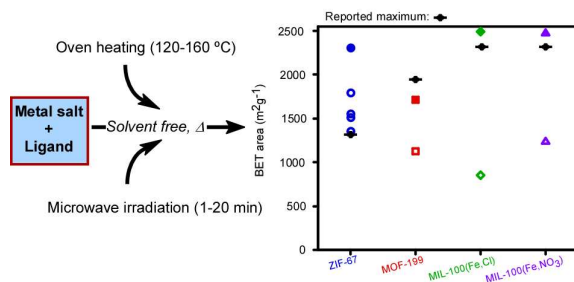
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TOC

Four types of benchmark MOFs are prepared by using solvent-free reactions under moderate oven heating (120-160 °C) or minute-scale fast microwave heating, obtaining competitive yields and high adsorption performance when compared to conventional synthesis methods.



COMMUNICATION

Two appealing alternatives for MOFs synthesis: solvent-free oven heating vs microwave heating

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Herein we present a solvent-free process to afford the synthesis of imidazolate and carboxylate based MOFs performed under moderate oven-heating or fast microwave irradiation, paying special attention to the yield and adsorption performance of the products. The measured adsorption surface area values of the resulting samples compare well, and in several cases surpassed, the maximum surface area previously reported for the same compounds prepared using a solvent based synthesis.

During the last decade published works focused on metal-organic frameworks (MOFs) have experienced an unremitting increase.[1] The cornerstones of such interest lies on the versatile geometry, size, and functionality of their constituents (secondary building units and organic linkers) which has led to a myriad of materials with broad number of applications.[2] In general, the high surface area of MOFs overtakes that of typical porous materials (zeolites, silicas and carbons) reaching record values of 7000 m²g⁻¹. [3] It must be pointed out that adsorption performance strongly depends upon the synthesis procedure. For instance, Tsao et al. assessed the influence of the heating rates, synthesis temperature and solvent on the preparation of MOF-5 to obtain specific surface areas spanning from 800 to 3100 m²g⁻¹. [4]

There are many reported synthetic routes for the synthesis of MOFs. The most common one implies the reaction between a metal salt and a ligand under solvothermal or microwave assisted solvothermal conditions.[5] In many cases, the employed solvents are expensive and/or toxic hindering the industrial scale production of MOFs. Thus, green solvents as water and alcohols have gained interest in solvothermal syntheses.[6] Another option relies on the mechano-chemical synthesis, where the reagents are subjected to a vigorous and continuous ball-mill grinding.[7] The less common

electrochemical synthesis of MOFs in which metal ions are continuously supplied from a metal anode to the reaction media containing the ligand and a protic solvent has attracted the interest of chemical companies.[8] In 2012, it was shown that the solvent-free reaction of a metal oxide or a hydroxide with a diazole or triazole ligand yields zeolitic metal-azolate frameworks when the reaction mixture is heated in an oven for 24-48 hours.[9] The lack of solvent makes this novel route more sustainable according to green chemistry principles and it allows to produce MOFs at much lower prices. Moreover, its technical simplicity and ease of scaling makes it highly appealing for the massive MOFs production.

Herein we demonstrate that this oven-heated solvent-free route is not limited to metal-azolate coordination polymers, but probably it could be applied to other MOFs. Additionally, it is shown for the first time how the dielectric heating through microwave radiation can accelerate the solvent-free synthesis of MOFs producing microporous materials at astonishing reaction times of few minutes. Four types of MOFs (ZIF-67, MOF-199, MIL-100(Fe/Cl), MIL-100(Fe/NO₃)) were prepared by oven-heating and microwave-heating with a reaction mixture consisting solely of the ligand (HmIM: 2-methylimidazole; H₃BTC: benzene-1,3,5-tricarboxylic acid) and the metal source (Co(OH)₂, Cu(OOCCH₃)₂·H₂O, FeCl₃·6H₂O, Fe(NO₃)₃·9H₂O). In a first step, stoichiometric amounts of the solid reagents are grinded together to ensure a homogeneous mixture and placed in the reaction vessel, which is oven-heated for 10-48 hours, or microwave-heated on a household microwave oven (700 W) using reaction times between 1 and 20 minutes. All the products were washed with ethanol to remove unreacted soluble reagents and remaining byproducts. A detailed description of the syntheses and characterization is provided in the ESI, while Table 1 gathers a summary of the obtained results.

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Table 1. Summary of reaction conditions and obtained MOFs indicating the reaction yields and sample codes.^a

Metal:ligand ratio	MOF / net / Formula	Oven heating				Microwave heating		
		Heating rate	Setpoint	Yield(%)	Code	Time	Yield(%)	Code
1:2	ZIF-67 (<i>sod</i>) [Co(mIm) ₂] _n	10 °C h ⁻¹	160 °C	89	ZIF67-OH1	6.0 min	90	ZIF67-MW1
		1.25 °C h ⁻¹	160 °C	92	ZIF67-OH2	7.5 min	91	ZIF67-MW2
						12 min	88	ZIF67-MW3
						20 min	90	ZIF67-MW4
3:2	MOF-199 (<i>tbo</i>) [Cu ₃ (μ ₆ -BTC) ₂ (OH) ₂] _n	4 °C h ⁻¹	120 °C	89	MOF199-OH1	6.0 min	97	MOF199-MW1
		2 °C h ⁻¹	120 °C	99	MOF199-OH2	7.5 min	89	MOF199-MW2
						12 min	97	MOF199-MW3
						20 min	97	MOF199-MW4
3:2	MIL-100(Fe/Cl) (<i>moo</i>) [Fe ₃ (μ ₃ -O)(μ ₆ -BTC) ₂ Cl(OH) ₂] _n	4 °C h ⁻¹	120 °C	40	MIL-C-OH1	0.8 min	24	MIL-C-MW1
		2 °C h ⁻¹	120 °C	34	MIL-C-OH2	1.0 min	17	MIL-C-MW2
		4 °C h ⁻¹	140 °C	48	MIL-C-OH3	1.6 min	41	MIL-C-MW3
		4 °C h ⁻¹	160 °C	79	MIL-C-OH4	2.7 min	26	MIL-C-MW4
		4 °C h ⁻¹	160 °C	62	MIL-C-OH5 ^b	3.0 min	80	MIL-C-MW5
		4 °C h ⁻¹	170 °C	66	MIL-C-OH6	4.0 min	77	MIL-C-MW6
3:2	MIL-100(Fe/NO ₃) (<i>moo</i>) [Fe ₃ (μ ₃ -O)(μ ₆ -BTC) ₂ (NO ₃)(OH) ₂] _n	4 °C h ⁻¹	120 °C	42	MIL-N-OH1	0.8 min	57	MIL-N-MW1
		2 °C h ⁻¹	120 °C	52	MIL-N-OH2	1.0 min	31	MIL-N-MW2
		4 °C h ⁻¹	140 °C	91	MIL-N-OH3	1.6 min	52	MIL-N-MW3
		4 °C h ⁻¹	160 °C	82	MIL-N-OH4	2.7 min	71	MIL-N-MW4
		4 °C h ⁻¹	160 °C	99	MIL-N-OH5 ^b	3.0 min	82	MIL-N-MW5
		4 °C h ⁻¹	170 °C	75	MIL-N-OH6	4.0 min	83	MIL-N-MW6

^a: see details of the syntheses in the ESI. ^b: a stoichiometric amount of NaOH was added to reaction mixture.

It must be pointed out that in all cases the metal/ligand synthesis ratio fits the amounts required by the formula of the MOF, and as result, the heating of the reagents mixture promote an acid-base reaction that leads to the desired MOF and to a stoichiometric minor amount of a by-product. The kind of by-product (H₂O, CH₃COOH, HCl, or HNO₃) depends upon the metal source employed, but its volatility at the synthesis temperature favours its removal from the reagents mixture, fostering the reaction progress. The reaction yields are comparable for samples prepared by oven heating and microwave irradiation, in spite of the shorter reaction times that involves the latter route. The yields of ZIF-67 and MOF-199 are in the 90-99% range. On the other hand, most of MIL-100(Fe/X) (X: Cl⁻, NO₃⁻) syntheses present yields of 20-90%. To understand such differences it must pay attention to the acid-base nature of the solvent-free reactions. The formation of ZIF-67 and MOF-199 only requires the deprotonation of the ligand, and entails water and a weak acid (acetic acid) as byproducts, respectively, being both volatile at the synthesis temperature. In MIL-100(Fe/X) samples, as the reaction progresses a strong acid (HCl or HNO₃) is released which hinders further deprotonation of H₃BTC and the formation of the μ₃-oxido bridge. Despite HCl is highly volatile, the high stability constant of Fe(III) chlorido complex [10] prevents its removal from the reaction media. Increasing the synthesis setpoint temperature to 160 °C improves the yield of MIL-C-OH samples (120/140 °C: 34-50%; 160 °C: 79%), but higher temperatures led a decrease of the reaction yield. HNO₃ is less

volatile but the lower affinity of nitrate ligand towards Fe(III) allows to vent the acid from the reagent mixture when the temperature is increased up to 140 °C, promoting the progress of the reaction of MIL-N-OH samples (120 °C: 42-52%; 140 °C: 91%). Higher synthesis temperatures again diminish the reaction yields. However, the addition of an stoichiometric amount of NaOH (see ESI) to counteract the acid byproducts led to significant increase in the yield of MIL-100(Fe/NO₃) (MIL-N-OH5: 99%), while no improvement was observed for the analogous synthesis of MIL-100(Fe/Cl) (MIL-C-OH5: 66%).

The adsorption performance of MOFs is closely related to their crystallinity. In this sense PXRD analyses were performed on all samples to assess the influence of synthesis conditions on crystallinity (see ESI). Best results are obtained for samples prepared by oven heating when slowest heating rates are used, while the sudden heating that implies the microwave assisted synthesis renders less crystalline samples. Figure 1 shows the PXRD patterns and SEM images of MOF-199 prepared by 7.5 min of MW irradiation and by two oven heating processes involving fast and slow rates, respectively. Figure 2 shows a comparison between the BET surface areas of samples prepared by oven heating and microwave irradiation with respect to the maximum values reported for each type of MOF (see ESI). In accordance with the crystallinity trend, samples prepared by oven heating show greater surface area values than those obtained by microwave irradiation. In fact, samples prepared by oven heating surpass the reported maximum in three cases

(ZIF67-OH1: 1851 m²/g, MIL-C-OH1: 2492 m²/g, MIL-N-OH2: 2486 m²/g). The MW heating provides lower area values, but in ZIF-67 samples it still exceeds the reported maximum (Figure 2), whereas in MOF-199 and MIL-100(Fe/Cl) the values are within the range reported for other synthetic approaches (see Table S6.1 of ESI). On the other hand, MIL-N-MW samples render extremely low surface area values (< 100 m²/g) due to the difficulty of fitting the reaction requirements by using a domestic microwave oven. However, this drawback is overcome when an stoichiometric amount of NaOH is added to the reaction media (see ESI) which shifts the equilibrium towards the MOF and improves its crystallinity reaching competitive surface area values (MIL-N-MW4': 1245 m²/g).

only because of the versatility of the achievable SBUs but also because of the possibility of modifying the geometric features of the linker. If the length of the linker is increased, ultraporous structures can be produced, retaining or varying the network topology.

Another possibility would be to develop MOFs containing more than one type of ligand which can be more synthetically demanding compared to the previously analyzed systems. In this sense, herein we present the preliminary results on the suitability of the oven heating and microwave assisted solvent-free synthesis for a MBOF of formula [Co(μ -propionate)(μ_3 -adeninate)]_n that it is characterized by its great selectivity towards CO₂. [11] The previously reported synthesis for this compound involves the use of pre-dried DMF as solvent under solvothermal conditions and leads to a yield of 78%. Our results show yields around 90%. Detailed data on synthetic parameters and characterization are gathered in the Supplementary Information.

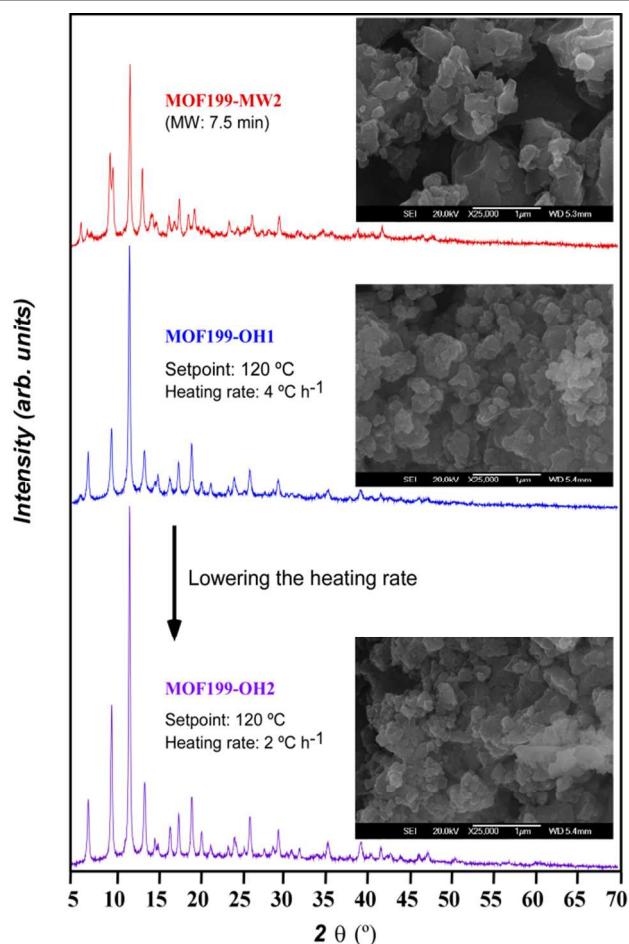


Fig.1. A comparison of the XRPD patterns and SEM images of three samples of MOF-199 prepared through microwave heating and oven heating.

A necessary condition that enables the solvent-free process relies on the melting of at least one of the reagents. The careful selection of the reagents and heating conditions to fulfil the previous condition has yielded MOFs belonging to the two paradigmatic families: metal-carboxylate and metal-azolate frameworks. Regarding the reticular design, the reaction conditions allow to achieve SBUs (secondary building units) of variable complexity: tetrahedral Zn(N₄) in ZIF-67, square planar Cu₂(CO₂)₄ in MOF-199, and trigonal prism Fe₃O(CO₂)₆ in MIL-100. At first sight, the herein reported synthetic methodology could be extrapolated to other type of MOFs, not

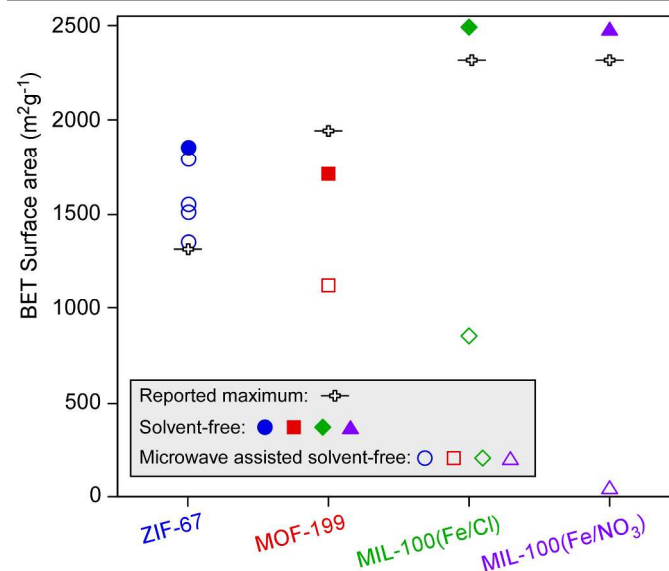


Fig.2. BET surface areas of samples prepared by oven heating and microwave irradiation with respect of the maximum values reported for each type of MOF.

Despite the economic and environmental benefits of the solvent-free processes are well known for pure organic and inorganic systems, this work validates its applicability for the synthesis of chemically and structurally versatile MOFs via conventional oven heating and minute-scale microwave heating. In general, compared to solventless oven heating, the microwave heating provides similar reaction yields but products of lower crystallinity and surface area. In this sense, instead a household microwave oven, the use of a microwave reactor equipped with temperature control can be a more suitable choice to try to rise the adsorption performance of the samples. In any case, as above stated, the surface area of samples prepared by microwave irradiation is still comparable to the ones provided by many other synthetic routes. Thus, the results herein presented for microwave solvent-free synthesis can be regarded as somewhat advantageous in terms of the

shorter reaction times (microwave heating: 1-20 minutes; oven heating: 8 – 50 h) and of energy savings.[12]

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Notes and references

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- H. Furukawa, K. E. Cordova, M. O’Keeffe, O. M. Yaghi, *Science*, 2013, **341**, 975.
- Chem. Rev.*, 2012, **112**, and references therein; M. Jacoby, *Chem. Eng. News*, 2008, **86**, 13; U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt, J. Pastré, *J. Mater. Chem.*, 2006, **16**, 626.
- O. K. Farha, I. Eryazici, N. C. Jeong, B. G. Hauser, C. E. Wilmer, A. A. Sarjeant, R. Q. Snurr, S. T. Nguyen, A. O. Yazaydin, J. T. Hupp, *J. Am. Chem. Soc.*, 2012, **134**, 15016.
- C.-S. Tsao, M.-S. Yu, T.-Y. Chung, H.-C. Wu, C.-Y. Wang, K.-S. Chang, H.-L. Chen, *J. Am. Chem. Soc.*, 2007, **129**, 15997.
- Y.-R. Lee, J. Kim, W.-S. Ahn, *Korean J. Chem. Eng.*, 2013, **30**, 1667; A. Czaja, E. Leung, N. Trukhan, U. Müller, in *Metal-Organic Frameworks - Applications from Catalysis to Gas Storage*, ed. D. Farrusseng, Wiley-VCH Verlag GmbH & Co. KGaA, 2011, ch. 14, pp. 337-352; N. Stock, S. Biswas, *Chem. Rev.*, 2012, **112**, 933.
- A. García-Márquez, A. Demessence, A. E. Platero-Prats, D. Heurtaux, P. Horcajada, C. Serre, J.-S. Chang, G. Férey, V. A. de la Peña-O’Shea, C. Boissière, D. Grosso, C. Sanchez, *Eur. J. Inorg. Chem.*, 2012, 5165. A. F. Gross, E. Sherman, J. J. Vajo, *Dalton Trans.*, 2012, **41**, 5458; F.-K. Shieh, S.-C. Wang, S.-Y. Leo, K. C.-W. Wu, *Chem. Eur. J.*, 2013, **19**, 11139; A. C. Kathalikkattil, D.-W., J. Tharun, H.-G. Soek, R. Roshan, D.-W. Park, *Green Chem.*, 2014, **16**, 1607. B. Chen, M. Eddaoudi, T. M. Reineke, J. W. Kampf, M. O’Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.*, 2000, **122**, 11559. Y. Xiao, Y. Cui, Q. Zheng, S. Xiang, G. Qian, B. Chen, *Chem. Commun.* 2010, **46**, 5503.
- H. Sakamoto, R. Matsuda and S. Kitagawa, *Dalton Trans.*, 2012, **41**, 3956; T. Friš i , and L. Fábán, *CrystEngComm.*, 2009, **11**, 743; S. T. Meek, J. A. Greathouse, M. D. Allendorf, *Adv. Mat.*, 2011, **23**, 249; M. Schlesinger, S. Schulze, M. Hietschold, M. Mehring, *Micropor. Mesopor. Mater.*, 2010, **132**, 121; A. Pichon, A. Lazuen-Garay, S. L. James, *CrystEngComm*, 2006, **8**, 211; M. Klimakow, P. Klobes, A. F. Thünemann, K. Rademann, F. Emmerling, *Chem. Mater.*, 2010, **22**, 5216.
- N. Stock, S. Biswas, *Chem. Rev.*, 2012, **112**, 933; A. M. Joaristi, J. Juan-Alcañiz, P. Serra-Crespo, F. Kapteijn, J. Gascon, *Cryst. Growth Des.*, 2012, **12**, 3489; U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt, J. Pastre, *J. Mater. Chem.*, 2006, **16**, 626; I. Richter, M. Schubert, U. Müller, *PCT Patent*, 2007, 131, 955.
- M. Lanchas, D. Vallejo-Sánchez, G. Beobide, O. Castillo, A. T. Aguayo, A. Luquea, P. Román. *Chem. Commun.*, 2012, **48**, 9930.; J.-B. Lin, R.-B. Lin, X.-N. Cheng, J.-P. Zhang, X.-M. Chen, *Chem. Commun.*, 2011, **47**, 9185.
- A. Ringbom, *Complexation in analytical chemistry*, Wiley (Interscience), New York, 1963.
- T. Li, D.-L. Chen, J. E. Sullivan, M. T. Kozlowski, J. K. Johnson, N. L. Rosi, *Chem. Sci.*, 2013, **4**, 1746.
- C. O. Kappe, *Angew. Chem. Int. Ed.*, 2004, **43**, 6250; N.E. Leadbeater, in *Comprehensive Organic Synthesis II*, ed. P. Knochel, G. A. Molander, Elsevier, 2014, vol. 9, ch. 10, pp. 234-286