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ABSTRACT. Paradoxically, one of the most widely and successfully tested MOF-based catalysts, i.e. the Fe-BTC material commercialized as Basolite F300, entails certain 'mystery': Its structure is unknown and only an indirect and complex preparation method has been reported. This work describes an easy preparation method of a Basolite F300-like material. Furthermore, this synthesis procedure is carried out under environmentally and economically sustainable conditions: at room temperature, in a few minutes and using water as the unique solvent. Several characterization techniques indicate that both commercial and lab-made Fe-BTC materials are very much similar in so many physicochemical properties. However, the herein reported Fe-BTC possesses better textural properties, especially regarding the external surface area. Both Fe-BTC materials catalyze the oxidation of cyclohexene with very alike selectivity. However, the sample prepared in the laboratory gives a notably higher conversion, which was attributed to its external surface area. Iron leaching, if any, was negligible and no significant structural transformation was detected. Finally, this paper also gives valuable structural information about the semiamorphous Fe-BTC: it exclusively contains the smallest mesocages of MIL-100(Fe), what provides an important input for interpreting the role of these Fe-BTC materials in any application demanding high porosity.



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KEYWORDS. Room temperature preparation, Basolite F300, Fe-BTC, cyclohexene oxidation, diffusional problem.

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INTRODUCTION

The catalytic potential of Metal-Organic Frameworks (MOFs) has already been reflected in so many investigations.¹⁻⁶ At the same time, the progress in their catalytic applications seems to be limited by certain aspects, such as their controversial stability in the reaction media, the lack of systematic studies or the subsequent scarce number of works affording some correlation between structural features of the MOF materials and their catalytic behavior. ⁷⁻¹⁰

Probably, the maximum exponent of this disparity between the possibilities and the so-far reduced development of MOFs as catalysts is found in the case of the Fe-BTC material, commercialized as Basolite F300. There are tens of publications remarking the notable catalytic performance of this material^{2, 11-22} in reactions requiring either acidic or redox centers. Moreover, this material has been used as raw material to generate highly active and stable Fischer-Tropsch catalysts.²³ It is particularly noteworthy that its catalytic behavior has been systematically compared with that of the well-known MIL-100(Fe) in a large number of reactions.^{2, 14, 20, 22, 24, 25} MIL-100(Fe) material is also formed by iron and trimesic acid, that is, it is also a Fe-BTC material, having two types of cages in the range of mesopores.²⁶ Wide and detailed comparison between both materials concluded that they are similar but essentially different from a physicochemical point of view.²⁷ Accordingly, both Fe-BTC materials catalyze the same reactions but giving different activity/selectivity, in such a way that the semi-amorphous Fe-BTC generally results more active in reactions requiring acidic centers (whereas the opposite trend was found in the redox reactions),¹⁴ despite the former possesses lower textural properties, maybe because defects also play an essential catalytic role.^{28, 29} This overcoming its homologous highly-porous MIL-101(Fe) gives an idea of the potential of this material, which of course deserves to be

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deeply investigated. In this sense, a very recent and meritorious study provides some insights into the Fe clusters in Basolite F300 material as well as into the influence of the hydratation/dehydration process on the Fe sites environment. ³⁰

Improving the performance of a catalyst is quite often based on changing the experimental conditions of its preparation, ideally taking into account the knowledge about the role and/or the environment of the active centers. However, the development of the catalytic potential of this Fe-BTC material is seriously limited by both the lack of reported synthesis methods and by the unsolved structure. Nevertheless, the preparation of a similar material was already reported albeit through an indirect method including the previous preparation and isolation of the Fe precursor, a mixed Fe^{2+}/Fe^{3+} layered double hydroxide. ²⁰ In this context, this article addresses two important advances in both synthesis procedure and structural knowledge of this semiamorphous Fe-BTC material. On one hand, it is described a direct, sustainable, cheap and almost instantaneous synthesis of a Basolite F300-like material, which opens so many possibilities of studying the influence of synthesis parameters on the final properties and adsorption/catalytic behavior of the resultant materials. As an example, the optimized lab-prepared Fe-BTC is shown to enhance the catalytic activity of its commercial homologue in the oxidation of cyclohexene. The synthesis procedure used in this work for preparing the Fe-BTC materials is based on the sustainable and widely applicable via to obtain carboxylate-based MOF materials recently described by our group, ^{31, 32} which for instance allows to achieve these materials at room temperature and in water as the unique solvent. On the other hand, a detailed and combined characterization of semiamorphous (Basolite F300-like) and crystalline (MIL-100(Fe)) Fe-BTC materials by means of N₂ adsorption/desorption isotherms, low-angle XRD and TG analyses have made clear that the former possesses just one of the two types of cages present in the latter.

The catalytic results of this work are also discussed in terms of such structural feature and the differences in physicochemical properties between the commercialized and the lab-made Fe-BTC materials. In the course of writing this article, a highly-related publication appeared addressing both a synthesis method and the structural solving of the sample A520, also commercialized by BASF and Sigma-Aldrich.³³

EXPERIMENTAL

2.1. Synthesis of the Fe-BTC materials

Fe-BTC material was prepared in water at room temperature adapting the novel concepts in the MOF synthesis^{31, 32} to the iron-trimesate system. A typical synthesis starts with the preparation of two solutions: (i) the colorless Solution 1 (pH = 10.9) was prepared by dissolving 0.263 g of trimesic acid (H₃BTC) in a NaOH aqueous solution composed by 10 g of H₂O and 0.150 g of NaOH; and (ii) the yellowish orange Solution 2 (pH = 1.8) was prepared by dissolving 0.508 g of FeCl₃·6H₂O in 10 g of H₂O. Next, Solution 2 was added dropwise over Solution 1 under magnetic stirring, generating the immediate appearance of a brownish orange solid. The resultant suspension (pH = 2.1) was maintained under stirring at room temperature (23 °C) during a period of time varying from 10 minutes to 24 hours. The molar ratio of the mixture was 1.5 Fe : 1.0 BTC : 3.0 NaOH : 880 H₂O. The solids were recovered by centrifugation, washed different times with deionized water and subsequently with ethanol, and then dried at room temperature. The samples were denoted as FeBTC-time, whereas the commercially available Fe-BTC (supplied by Aldrich) was designated as Basolite F300.

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A MIL-100(Fe) material was prepared as described elsewhere²⁶ for comparison purposes.

Powder X-ray diffraction (XRD) patterns were acquired with a Philips X'PERT diffractometer using Cu Kα radiation. Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectra were recorded using a Thermo Nicolet Nexus 670 FTIR spectrometer equipped with a SensIR Technologies DurasamplIR horizontal ATR accessory and a liquid nitrogen-cooled MCT detector. Thermogravimetric analyses (TGA) were registered in a Perkin-Elmer TGA7 instrument. TG analyses were carried out at a heating rate of 20 °C/min under air flow. Nitrogen adsorption/desorption isotherms were measured at -196 °C in a Micromeritics ASAP 2020 device. Before the measurement, the previously calcined sample was degassed at 150 °C under high vacuum for at least 18 hours. Surface areas were estimated by the BET method; microporous and external surface areas were estimated by applying t-plot method; and pore size distributions were calculated applying the BJH method corrected by Kruk-Jaroniec-Sayari method ³⁴. Scanning Electron Microscopy (SEM) studies were carried out in an Ultra-high Resolution FEI-NOVA NanoSEM 230 FESEM instrument equipped with an EDS detector for punctual elemental microanalyses.

2.3. Catalytic reactions

Catalytic tests were run as described elsewhere.^{7, 35} As a previous step, Fe-BTC samples were placed in a round flask submerged in a silicone bath at 150 °C, and kept overnight under constant N₂ flow. The oxidation of cyclohexene was carried out at 70 °C under atmospheric pressure and under stirring (400 rpm). The system was refrigerated with water at 5 °C (cyclohexene evaporation below 3 wt. % after 48 h of reaction). The substrate cyclohexene (10 times the weight of the evacuated catalyst), the solvent acetonitrile (cyclohexene/acetonitrile molar ratio of

30) and the internal GC standard toluene (the same weight than the catalyst) were added over the catalyst. Once this mixture reached 70 °C (temperature controlled with a thermometer in contact with the mixture), the oxidizing agent tert-butyl hydroperoxide (TBHP) was added, taking the moment of this addition as reaction time zero. Aliquots at different reaction times (0-25 h) were taken under stirring to follow the kinetics. These aliquots were analyzed by gas chromatography (Varian 430 GC; capillary column of 15 m length, 0.25 mm diameter, 1 μ m stationary phase thickness; FID detector) and total reflection X-ray fluorescence (TXRF) after being filtered (filter paper with pores of 0.45 μ m). Identification of the non-commercial 2-cyclohexenyl peroxide product was done as described elsewhere.³⁵ Due to the high volatility of cyclohexene, its conversion was calculated indirectly, through the sum of the detected products. Mass balance always had an error below 10 %.

RESULTS AND DISCUSSION

The PXRD patterns of the Fe-BTC samples prepared at room temperature after different synthesis times are shown in Figure 1, compared to the diffractogram of the commercial MOF Basolite F300 (supplied by Sigma-Aldrich). The low resolution of the presented XRD patterns is a consequence of the semi-amorphous nature of these materials. In any case, some relatively broad bands were detected, and they can somehow be taken as a rough finger-printed proof of the nature of the material. There is a very good agreement between the PXRD patterns of the Fe-BTC samples prepared at the laboratory and that of the commercial Basolite F300, in terms of the position, and both relative and absolute intensities of the XRD bands. Affording Fe-BTC by this method is very relevant from a sustainability viewpoint, as it can be prepared at room temperature, in a few minutes and using water as unique solvent. From a kinetics point of view,

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two aspects should be highlighted. Firstly, the material can be formed instantaneously (it is already formed after 10 minutes). Secondly, the samples as seen by XRD are maintained basically invariable during the first hours (and even days) of the synthesis. In any case, because of the low resolution of the patterns, XRD characterization is quite limited and some other characterization techniques should be used to shed light on the similarities/differences between the commercial and the lab-made Fe-BTC materials.



Figure 1. XRD patterns of the commercial Basolite F300 (black line, at the bottom) and of the Fe-BTC materials prepared in the laboratory after different synthesis times. The patterns were

not normalized but just moved along the Y-axis. The rising background is due to the fluorescence effect.

 In any case, the procurement of a material quite similar to the Basolite F300 is out of any doubt at this point. Moreover, the sustainability of the methodology deserves to be remarked. The procedure is carried out at room temperature, in a few minutes and using water as the unique solvent. Some other energetic and/or environmental advantages of the method has been discussed elsewhere.³¹ In contrast, the only reported method to prepare a similar material, which is also carried out at room temperature, implies the previous preparation (with careful control of the oxidation processes) for up to 24 hours and subsequent isolation of a mixed Fe^{2+}/Fe^{3+} layered double hydroxide, and an extra step to form the Fe-BTC material including the use of a considerable amount of ethanol.²⁰

Since the limited information about structural features of these semiamorphous materials, the IR spectroscopy region of *ca.* 650–1800 cm⁻¹ can be also taken as a fingerprint of materials nature, especially when they contain organic entities such as MOFs.^{36, 37} It was particularly useful to identify MOFs formed by crystals so small that their characterization by XRD is uncertain.³⁶ Unlike PXRD, which is sensitive to the structure of materials (long-range information), that IR region is rather sensitive to the conformational and/or local environment of organic molecules (short-range information), so both techniques are somehow complementary. Figure 2 compares the FTIR spectra of the samples Basolite F300 and FeBTC-10min. The FTIR spectra of the rest of the samples Fe-BTC prepared in the lab at different times are practically identical to that of FeBTC-10min, so they have been omitted for clarity. Both FTIR spectra are similar but not equal. Some differences are evident in the 800-1100 cm⁻¹ region, where the bands are rather weak. Nevertheless, there is a very good agreement away from that region, suggesting that both

materials are closely related to each other. Such good agreement becomes even more manifest when the FTIR spectrum of any of both materials is compared with the spectrum of the free trimesic acid (H₃BTC), which is markedly different in spite of the fact that all samples basically contain the same organic moiety. Therefore, not only the long-range information given by XRD but also the shorter-range one indicated by FTIR studies, suggests that the nature or our Fe-BTC material, although different, is near to that of the commercial Basolite F300.



Figure 2. FTIR spectra of the commercial Basolite F300 (black line, at the bottom), the sample FeBTC-10min (red, in the middle) and the free linker H₃BTC (blue, at the top).

One of the most important issues of the MOF materials is their thermal stability. At the same time, that stability as well as some other features derived from thermogravimetric (TG)

characterization could be taken as indications about the similarity between two Fe-BTC materials. The thermal stability of the commercial and our Fe-BTC materials are practically the same and 70 °C lower than the protonated linker H₃BTC (Figure S1 and Table S1).

In so many applications including heterogeneous catalysis, porosity of MOF materials becomes a key parameter. Figure 3a shows the N_2 adsorption/desorption isotherms of Basolite F300, FeBTC-10min and FeBTC-24h. The estimated BET area of the Basolite F300 (859 m²g⁻¹, Table 1) is lower than that indicated by the supplier $(1300 - 1600 \text{ m}^2\text{g}^{-1})$ but very close to that experimentally measured by others^{14, 20, 27} and substantially higher than that found very recently.³⁸ Although the lab-made Fe-BTC possesses properties guite similar to these of Basolite F300 according to XRD, FTIR and TG characterization, the porosity of the former is markedly higher, particularly in the mesoporous region. The total BET area was estimated in 1092 m²g⁻¹, more than one fourth higher than that of the commercial one. Since the main alteration between both isotherms is found in the mesoporous region, the difference is even much higher in the pore volume (1.30 and 0.38 cm³g⁻¹ for the samples FeBTC-10min and Basolite F300, respectively). That difference is more easily interpreted from the pore size distributions (PSD) (Figure 3b). Indeed, the PSD curve of the sample FeBTC-10min shows a relatively narrow peak centered at 5.3 nm, which is completely absent in the PSD profile of Basolite F300. The sample FeBTC-24h also contains certain contribution in that region, although it is quite less intense and is shifted toward smaller mesopores.



Figure 3. (a) N₂ adsorption/desorption isotherm at -196 °C of the samples FeBTC-10min, FeBTC-24h, Basolite F300 and MIL-100(Fe). (b) Pore size distribution curves of the adsorption braches of the same isotherms.

Table 1. Data estimated from the N_2 adsorption/desorption isotherms and pore size distributionsfrom Figure 3 of the indicated samples.

Sample	Total S _{BET} / m ² g ⁻¹	External S _{BET} ^a / m ² g ⁻¹	V _p ^b / cm ³ g ⁻¹	PSD peaks ^c / nm
Basolite F300	859	63	0.38	1.8
FeBTC-10min	1092	525	1.30	1.8, 2.2, 4.5

FeBTC-24h	1010	296	0.90	1.8, 2.2, 5.3
^a Data from t plat External S is the difference between the total S and the microporous S				

^a Data from *t-plot*. External S_{BET} is the difference between the total S_{BET} and the microporous S_{BET} . ^b Pore volume measured at $p/p_0 = 0.98$.

Moreover, the PSD curves of Figure 3b present a further distinctiveness that deserves to be analyzed in detail. The PSD curve of any of the semi-amorphous Fe-BTC sample indicates the existence of some cavities with narrow pore distribution with a diameter of 1.8 nm, very close to the limit between micropore and mesopore according to the IUPAC classification, i.e., near 2 nm. However, it must be taken into account that the BJH method used in the generation of PSD plots from the isotherm systematically underestimates the pore diameter.³⁹ Despite these PSD curves were corrected by Kruk-Jaroniec-Savari method,³⁴ designed for MCM-41-like materials, it is quite probable that the PSD curves from Figure 3b still underestimates the pore diameter. Indeed, the PSD curve (also obtained from the adsorption branch of an N₂ isotherm registered under the same conditions in our laboratory) of a MIL-100(Fe) material (violet curve in Figure 3b) shows two intense and narrow peaks in that region, centered at 1.8 and 2.2 nm, which were undoubtedly attributed to the two types of well-known mesoporous cages characteristic of the MIL-100(Fe) material. However, these cavities actually have diameters of 2.5 and 2.9 nm,²⁶ so the underestimation of the pore diameter in the so-generated PSD curve is still 0.7 nm for these materials. It is remarkable that, according to this interpretation, Basolite F300 is differentiated from the crystalline MIL-100(Fe) in possessing just the smallest one of the two mesoporous cages of the latter.

Figure 4 displays two extra characterization proofs supporting this interpretation. The low angle XRD patterns (Figure 4a) of both lab-made and commercial Fe-BTC materials shows a broad reflection at around 3.8 ° (d = 23.2 Å) that coincides with the 20 position of the XRD reflections

^c Maxima of the peaks found in pore size distribution by the applying BJH method to the adsorption branches. The values were corrected by the Kruk-Jaroniec-Sayari method.³⁴

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220, 311 and 222 clearly observed in the MIL-100(Fe) pattern, suggesting that some mesocages are indeed present in the semiamorphous materials. However, there is no evidence of the reflection 111 (d = 42.3 Å) in the XRD patterns of any of the two Fe-BTC materials, unlike in that of MIL-100(Fe) material. Since the reflection 111 corresponds to the largest spacing d of the structure, it is expected that it is related to the largest cages of the structure. Figure 4b plots the normalized TGA derivatives curves of the three Fe-BTC samples: Basolite F300, FeBTC-10min and MIL-100(Fe) in the region of the water loss (25-150 °C). In that temperature region, TG analysis detected two losses for the sample MIL-100(Fe) (centered at 46 and 72 °C), which were attributed to the presence of the two different cages. In good agreement with the discussion about TGA curves of Fe-BTC (Supporting Information), the TG derivative of either Basolite F300 or FeBTC-10min in the region 25-150 °C presents a unique loss centered at 66 and 71 °C, respectively (Table S1). This loss is clearly closer to the second loss of MIL-100(Fe). It seems quite logical to attribute this second weight loss to the water molecules trapped within the smallest cages, where presumably they would be more strongly retained than in the larger ones.

This result is of great importance for understanding the differences in adsorption and/or catalytic behavior of both Fe-BTC-based materials. For instance, MIL-100(Fe) but not Basolite F300 could catalytically process within its cages molecules having kinetic diameter between 4.7/5.5 Å and 8.6 Å, which are the window openings of the small and large cages, respectively.²⁶ It is also worth to underline that the lab-made Fe-BTC samples, unlike the commercial one, contain certain amount of the largest cages of MIL-100(Fe), according to their PSD (Figure 4b). Therefore, the difference in textural properties between the commercial and the herein-prepared Fe-BTC materials is not exclusively due to the presence of high external surface area. To conclude the discussion of the N₂ isotherms, it is noteworthy that the characterization of either

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 amorphous or semi-amorphous MOF material by means of adsorption/desorption isotherms is by far the most helpful, informative and revealing tool for any application that requires high porosity, even providing indirect but trustable structural information considering the limitations of XRD techniques for these scarcely-ordered materials.



Figure 4. (a) Simulated low angle XRD pattern of the simulated MIL-100(Fe) (top) and experimental low angle XRD patterns of the samples Basolite F300, FeBTC-10min and MIL-100(Fe). (b) Normalized TG derivative curves of the same samples.

Taking into account that lab-made and commercial Fe-BTC samples have different textural properties especially manifest in the external surface, it was expected that some differences could be somehow apparent in their particle morphology and/or size. Some representative SEM images

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of Basolite F300 and FeBTC-10min are shown in Figure 5. Basolite F300 is formed by two types of particles of similar sizes (around 10 μ m), as they can be seen in Figure 5a. The predominant particles are the ones appearing at the top of Figure 5a. An enlargement of one of this type of particles is shown in Figure 5b. They are formed by nanocrystals or at least these nanocrystals efficiently cover the surface of bigger particles. The less predominant particles (the particle at the bottom of Figure 5c is a good example) scarcely contain some nanocrystals on the surface. Contrasting with this morphology heterogeneity, the sample FeBTC-10min is formed by particles having uniform appearance. These particles have size in the range 10-50 μ m. The images of Figure 5d and 5e, registered at different magnifications, shows that the particles have not only homogenous appearance from a distance but also they are homogenously composed by much smaller nanoparticles of very similar shape and size. These nanoparticles are agglomerated generating some relatively-ordered 'intercrystalline' mesoporosity, in good agreement with the significant N₂ adsorption and the existence of a hysteresis loop in the mesoporous region of the isotherm (Figure 3b).

The samples were also studied by EDS elemental microanalysis, integrated into the microscope. Apart from Fe, O and C, the Fe-BTC samples prepared in our laboratory showed some traces of Cl, which is not surprising since $FeCl_3 \cdot 6H_2O$ was the iron source in the synthesis procedure. On the other hand, Basolite F300 showed some traces of S as an unexpected element, suggesting that any S-containing Fe source, probably iron sulfate, was used in the unreported synthesis procedure of this commercial material.



Figure 5. SEM images of Fe-BTC samples: (a), (b) and (c) Basolite F300; (d) and (e) FeBTC-10min. The limited resolution at high magnifications was probably due to the magnetic character of the Fe-rich samples.

To prove the benefits of lab-made Fe-BTC samples against the commercial Basolite F300, which has been pointed out by some characterization techniques, these samples were tested in the most widely used and successful application of these materials so far, i.e. as heterogeneous catalysts. In particular, the tested reaction was the oxidation of cyclohexene with peroxides in liquid Page 19 of 32

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media. This test reaction was chosen because cyclohexene can be oxidized through two different routes: epoxidation and allylic oxidation, which imply the oxidation of C atoms of the double bond and the adjacent C atoms to the double bond, respectively (Scheme 1).^{7, 35} Therefore, both mechanisms yield different oxidation products, and can provide important information about the performance of the catalysts. Thus, this reaction was recently selected to provide key insights into the redox catalytic role of the metal ion M in the isostructural series of M-MOF-74 catalysts (M = Mn, Co, Ni, Cu, Zn), concluding that the radical-route oxidation is governed by the surface area of the material as long as M is a redox metal ion, whereas the epoxidation catalytic activity was related to the reduction potential of the redox metal.⁷ Figure 6 shows the total yield (solid lines) of products resulting from the oxidation of cyclohexene with no catalysts (blank experiment) and in the presence of an activated catalyst, either FeBTC-10min or Basolite F300. Yield of products is given instead of direct cyclohexene conversion in order to avoid any error due to the evaporation of the cyclohexene throughout the reaction time despite the system was refrigerated with water at low temperature (5 °C).³⁵ Data of the catalytic results after *ca*. 24 hours are compiled in Table 2. With no catalyst, there is certain catalytic activity (18.8 % conversion), indicating that the reaction is spontaneous to some extent under the tested conditions. The presence of any Fe-BTC samples enhances the conversion of cyclohexene, certifying that they are real catalysts of this process. Moreover, the lab-made FeBTC-10min sample is significantly more active than the commercial Basolite F300. Indeed, if the spontaneous conversion is subtracted from that given by the catalysts, the activity of FeBTC-10min (39.3 %) is exactly double than that of Basolite F300 (19.5 %). Since both materials are guite similar as inferred by different characterization techniques such as XRD, FTIR and TGA, we attributed the difference in the catalytic activity to the substantial difference in external surface area.



Scheme 1. Products generated from the oxidation of cyclohexene through either the radical (top) or epoxidation (bottom) routes. 1: cyclohexene; 2: cyclohexenyl hydroperoxide or 3-hydroperoxy-1-cyclohexene; 3: , 2-cyclohexen-1-ol; 4: 2-cyclohexen-1-one; 5: cyclohexene oxide; 6: cyclohexanol; 7: cyclohexanone; 1,2-cyclohexanediol.



Figure 6. Total yield (solid lines) of cyclohexene oxidation products as a function of reaction time, resulting from the catalytic tests in the absence of any catalyst (grey) or in the presence of either the Basolite F300 sample (black) or the FeBTC-10min sample (red). The yield of the products through radical (dashed lines) or epoxidation (dot lines) routes of the reactions in the presence of catalysts are also shown.

 Table 2. Total yield and yield by different routes of the catalytic experiments with no catalyst or

 in the presence of Basolite F300 or FeBTC-10min catalysts.

Sample Total		Radical route yield / %	Epoxidation route yield / %

	yield / %	2 ^a	3 ^a	4 ^a	Total	5 ^a	8 ^a	Total
Basolite F300	38.3	29.4	1.1	3.8	34.3	0.5	3.5	4.0
FeBTC-10min	58.1	39.3	1.8	12.7	53.8	-	4.3	4.3
No catalyst	18.8	18.0	0.1	0.7	18.8	-	-	-

^a Numbers indicates the chemicals according to Scheme 1. Products 6 (cyclohexanol) and 7 (cyclohexanone) were not detected.

In principle, the difference in catalytic activity (double for the FeBTC-10min catalyst) seems to be too high for being reasonably justified by the difference in surface area (27 % higher for the same sample), especially taking into account that the oxidation by the radical mechanism, which is extensively predominant for both Fe-BTC catalysts (Figure 6 and Table 2), resulted directly proportional to the surface area (either microporous or external) and independent on the metal nature in the isostructural series of M-MOF-74⁷. However, some other aspects could influence the global activity. Since both Fe-BTC presumably contains only the smallest cages found in MIL-100(Fe), with windows entrance as small as 4.7-5.5 Å.²⁶ it is possible that reactants and products have some important diffusion problems to access the these cages. For instance, both reactants TBHP⁴⁰ and cyclohexene⁴¹ have been reported to access very limitedly to the pores of the TS-1 zeolite, one of the most typical catalysts in the oxidation of light olefins with pore diameter of precisely 5.5 Å. Although MOF structures are expected to be much more flexible than zeolite ones, it can inferred that diffusional problems would be important and therefore external surface area rather than microporous area would be the main responsible factor for the catalytic activity in the oxidation of cyclohexene with TBHP. Supporting this interpretation, the cyclohexene conversion through the epoxidation route, which requires that both TBHP and cyclohexene meet in the neighborhood of the active sites, is really low in both Fe-BTC catalysts

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compared to the conversion by the radical route, which requires that a unique TBHP molecule interacts with an Fe site to convert several cyclohexene molecules due to the propagation of radicals. Anyway, although some factors could alter the direct correlation between surface area and catalytic activity, it is clear that the cyclohexene conversion must be especially favored by the external surface area.

Finally, despite the low conversion through the epoxidation mechanism does not allow to extract important conclusions, it is worth to underline a relevant detail. Some cyclohexene epoxide remains at the end of the reaction when Basolite F300 is the catalyst but not at all when the catalyst is the sample FeBTC-10min. It is well-known that the aperture of epoxides is catalyzed by Fe acid sites.⁴² Therefore, the total transformation of the epoxide by the catalyst FeBTC-10min suggests that its catalytic activity is higher not only in oxidation reactions but also in reactions requiring acidic centers. Acidic catalytic tests with these two Fe-BTC samples are in progress.

One of the most controversial issues about the MOF catalysts is their stability under the tested reaction conditions. Figure 7 shows the conversion and the Fe leaching of three successive catalytic reactions with the same portion of the sample Fe-BTC-10min as well as the XRD patterns of the catalyst before and after the reaction. The catalytic activity is maintained or even slightly increased along the reaction cycles. At the same time, no significant metal leaching was detected, The reaction mixture of the first cycle only contained 0.3 ppm of Fe, which should be considered negligible. Reaction mixture of the second and third cycles had even lower iron content (0.015 and 0.042 ppm, respectively), whereas both the reaction mixture of the blank experiment and that of the Basolite F300, which has no leaching after similar reaction conditions,^{11, 13, 16, 22, 24} gave an Fe concentration of 0.035 ppm. That so low metal leaching

contrasts to that found in the series of isostructural M-MOF-74 materials, tested under exactly the same conditions ⁷. The XRD pattern of the as-reacted one is slightly different to that registered before reaction in terms of intensity, the presence/absence of some XRD bands/peaks, etc. These differences could be attributed to the presence of chemical species (reactants, solvent or products) within the pores, as the diffractogram after three reactions cycles of the filtered and washed catalyst recoveres the diffraction features, as the commercial Basolite F300 material does after reaction¹⁶. Therefore, Fe-BTC-10min sample is a reusable heterogeneous catalyst.





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Figure 7. (a) Yield (black columns, left Y-axis) and iron leaching (orange squares, right Y-axis) in the cyclohexene oxidation catalyzed by the Fe-BTC-10min sample. (b) XRD patterns of the Fe-BTC-10min catalysts: before reaction (red line, at the bottom), as-reacted after the first reaction cycle (green line, in the middle), and filtered and washed after the third reaction cycle.

CONCLUSIONS

This article describes a direct (one-step), easy, rapid and sustainable preparation of a semiamorphous Basolite F300-like Fe-BTC MOF material. The experimental conditions include room temperature, water as the unique solvent and synthesis time of just a few minutes. Although, according to an extensive characterization, both the long- and short-range structure features, Fe/BTC ratio, Fe and BTC environment or the BTC conformation are quite similar in both materials, the optimized Fe-BTC sample prepared in the laboratory overcomes the textural properties of the commercial Basolite F300. Such difference is due to the lab-made sample is formed by small and homogeneous nanocrystals agglomerated in ordered particles containing 'intercrystalline' mesoporosity of about 5 nm of diameter, whereas Basolite F300 lacks significant external surface area. The consequently expected advantages in, for instance, avoiding diffusion problems was made clear in the catalytic oxidation of cyclohexene, as the new Fe-BTC sample doubled the catalytic activity given by Basolite F300, maintaining the structure and with no iron leaching. In addition, this work also provides an important structural aspect about the semi-amorphous Fe-BTC materials. A careful N_2 adsorption study makes clear that these Fe-BTC materials do only contain the smallest cage of the two mesoporous ones present in the highly-related Fe-BTC MIL-100(Fe) material, which could be of substantial importance to

understand their differences/similarities in gas adsorption, in catalytic performance or in any other application in which porosity plays a key role.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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SUPPORTING INFORMATION AVAILABLE

TGA plots and data of the Fe-BTC materials. This information is available free of charge via the Internet at http://pubs.acs.org/.

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FIGURES CAPTION

Figure 1. XRD patterns of the commercial Basolite F300 (black line, at the bottom) and of the Fe-BTC materials prepared in the laboratory after different synthesis times. The patterns were not normalized but just moved along the Y-axis. The rising background is due to the fluorescence effect.

Figure 2. FTIR spectra of the commercial Basolite F300 (black line, at the bottom), the sample FeBTC-10min (red, in the middle) and the free linker H₃BTC (blue, at the top).

Figure 3. (a) N₂ adsorption/desorption isotherm at -196 °C of the samples FeBTC-10min, FeBTC-24h, Basolite F300 and MIL-100(Fe). (b) Pore size distribution curves of the adsorption braches of the same isotherms.

Figure 4. (a) Simulated low angle XRD pattern of the simulated MIL-100(Fe) (top) and experimental low angle XRD patterns of the samples Basolite F300, FeBTC-10min and MIL-100(Fe). (b) Normalized TG derivative curves of the same samples.

Figure 5. SEM images of Fe-BTC samples: (a), (b) and (c) Basolite F300; (d) and (e) FeBTC-10min. The limited resolution at high magnifications was probably due to the magnetic character of the Fe-rich samples.

Figure 6. Total yield (solid lines) of cyclohexene oxidation products as a function of reaction time, resulting from the catalytic tests in the absence of any catalyst (grey) or in the presence of either the Basolite F300 sample (black) or the FeBTC-10min sample (red). The yield of the products through radical (dashed lines) or epoxidation (dot lines) routes of the reactions in the presence of catalysts are also shown.

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Figure 7. (a) Yield (black columns, left Y-axis) and iron leaching (orange square, right Y-axis) in the cyclohexene oxidation by Fe-BTC-10min sample. (b) XRD patterns of the Fe-BTC-10min catalysts: before reaction (red line, at the bottom), as-reacted after the first reaction cycle (green line, in the middle), and filtered and washed after the third reaction cycle.

FOR TABLE OF CONTENTS ONLY

Title: Direct synthesis, structural features and enhanced catalytic activity of the Basolite F300-

like semi-amorphous Fe-BTC framework

Authors: Manuel Sanchez-Sanchez, Iñigo de Asua, Daniel Ruano and Kenya Diaz

TOC graphic:



Synopsis

This paper provides new and decisive insights into the two important limitations of the semiamorphous Fe-BTC material, one of the most successful MOF-based catalysts. Firstly, it exclusively contains the smallest cages of its counterpart MIL-100(Fe). Secondly, an instantaneous and sustainable synthesis procedure is described at last, allowing notably improving the catalytic performance of the commercialized Basolite F300 material.