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Email: tapchikhoahoc@hcmue.edu.vn; Website: http://tckh.hcmue.edu.vn

SYNTHESIS AND EXPLORATION OF CATALYTIC ACTIVITY OF Fe-MIL-101 MATERIAL IN FRIEDEL-CRAFTS BENZOYLATION REACTION

Nguyen Duy Khoi, Nguyen Thanh Binh, Phan Thi Hoang Oanh*

Faculty of Chemistry, Hochiminh City University of Education

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ABSTRACT

The synthesis of Fe-MIL-101 material with the presence of H_2BDC linker and iron (III) chloride achieving remarkable success is a result of solvothermal method. Catalytic activity works on the Friedel-Crafts benzoylation reaction of aromatic compounds and benzoyl chloride. In addition, Fe-MIL-101 is a heterogeneous catalyst which succeeds in not only shortening duration in a significant amount, but also increasing conversion with the assistance of the microwave irradiation compared with the conventional heating. Fe-MIL-101 would be a very potential alternative in place of unfavourable and dated iron (III) chloride homogeneous catalyst, due to its thermal stability, moreover, it can be recovered and reused after aqueous work-up.

Keywords: Fe-MIL-101, Friedel-Crafts benzoylation reaction, microwave irradiation.

TÓM TẮT

Tổng hợp và thăm dò hoạt tính xúc tác của vật liệu Fe-MIL-101 cho phản ứng benzyl hóa Friedel-Crafts

Vật liệu Fe-MIL-101 được tổng hợp thành công từ $FeCl_3$ và H_2BDC theo quy trình mới bằng phương pháp nhiệt dung môi. Vật liệu thể hiện hoạt tính xúc tác cho phản ứng benzyl hóa Friedel-Crafts giữa benzoyl chloride và các hợp chất thơm. Khi kết hợp với bức xạ vi sóng, Fe-MIL-101 là xúc tác dị thể hiệu quả, thông qua việc không chỉ rút ngắn thời gian mà còn làm tăng độ chuyển hóa của phản ứng so với phương pháp gia nhiệt truyền thống. Fe-MIL-101 hứa hẹn sẽ là vật liệu tiềm năng thay thế cho xúc tác đồng thể $FeCl_3$ nhờ vào độ bền nhiệt, dễ thu hồi để tái sử dụng sau phản ứng.

Từ khóa: Fe-MIL-101, phản ứng benzyl hóa Friedel-Crafts, bức xạ vi sóng.

1. Introduction

Metal-organic frameworks (MOFs) are known as a highly ordered and porous material, in which the inorganic and organic units are linked by strong bonds [1]. MOFs have several noticeable features, such as high surface area (which ranges from 1.000 to 10.000 m^2/g), large pore volume and modified framework [2] in compare with other traditional porous materials (e.g. zeolites, activated carbon, etc.). Therefore, MOFs are

* Email: *oanhpth@hcmup.edu.vn*

ideal candidates for adsorption [2], gas storage and separation [3], heterogeneous catalysis [4] and biotechnology applications [5].

M-MIL-101 material (MIL: Material Institut Lavoisier) possesses large surface area, ultrahigh porosity, high thermal and chemistry stability, exceptionally large pore volume [6]. Open metal sites can act as Lewis acid in some organic reactions. Furthermore, Fe-MIL-101 with eco-friendly iron-sites is less toxic than Ni, Co, Cr, etc. Hence, this material is used as a catalyst in some organic reactions [7-8].

Friedel-Crafts acylation is the most important method for functionalizing aromatic compounds, which are useful precursors in the pharmaceutical and agrochemical industries [9]. In relation to the catalytic activity of some tradition catalysts, for example, $AlCl_3$, BF_3, or $FeCl_3$ is not believed to be propitious, conversely, they mostly could not be reclaimed, then recycled, or probably generate products which are likely to exert corrosive effects on material, etc. [10-11]. Moreover, the drawbacks of the honogeneous or heterogeneous catalysts (e.g. zeolite [12], montmorillonite [13], oxide of metals [14]) are that they were mainly used in acid condition, reaction time were rather long, etc. Consequently, the search to find efficient and green catalysts for Friedel-Crafts acylation is still in progress. Microwave-assisted organic synthesis has attracted much attention because they offer the shortest and most efficient routes for many reactions. Microwave irradiation applying on Friedel-Crafts acylation also achieves great success. It has been demonstrated that the short reaction time associated with microwave irradiation restricts the decomposition of the reagents or products and prevents the diacylation or dimethylation [15].

This paper will demonstrate the synthesis and analysis of Fe-MIL-101 to examine its catalytic activity in Friedel-Crafts benzoylation. This reaction takes place with the assistance of microwave irradiation to reduce reaction time, raise the efficiency of the reaction comparing to conventional method of heating. The results indicate that the material is supposed to have the probable outcome to have the way for the reaction between aromatic compounds and benzoyl chloride. In such mentioned above condition, Fe-MIL-101 is expected, therefore, to be possible material to substitute for the traditional Lewis acid catalyst.

2. Experiments

2.1. Materials

Terephthalic acid (Aldrich, 98%), $FeCl_3$ (Fisher, 97%), *N*,*N*-dimethylformamide (Acros, ≥99%), anhydrous methanol (Merck, 99,8%), ethyl acetate EMSURE grade (Merck), nitrobenzene (Nanjing Reagent, 99%), benzoyl chloride (Aldrich, 99%), anisol (Aldrich, 99,7%), phenanthrene (Aldrich, 98%), anthracene (Aldrich, 97%), flourene (Aldrich, 98%), 1,4-dimethoxybenzene (Aldrich, 99%), m-xylene (Aldrich, ≥99 %), *p*-flouroanisol (Aldrich, 99%), 1,2,4-trimethoxybenzene (Aldrich, 97%).

2.2. Synthesis of Fe-MIL-101

The synthesis of Fe-MIL-101 is an experimentally inspected process based on a sequence of particularly referable procedures [7, 16]. Accordingly, the mixture of H_2BDC (33,226 mg; 0,2 mmol) and $FeCl_3$ (72,99 mg; 0,45 mmol) are dissolved in the mixture of DMF solvent and de-ionised water in the volume ratio of 50 to 1 and then added to a twelve-milliliter-typed vial. Next, the mix is stored in the oven at the temperature of 85°C for one day. The obtained product is orange and in powder form. Then, it is washed carefully with DMF to remove H_2BDC and excessive $FeCl_3$ and exchanged with MeOH many times to dispose of DMF. Lastly, the product will be dried and activated in vacuum at 0.02 Torr, 70°C.

2.3. Fe-MIL-101 as a catalyst forFriedel-Crafts benzoylation of aromatic compounds

A mixture of Fe-MIL-101 (8,53 μmol), arene (0,5 mmol), benzoyl chloride (58 μl; 0,5 mmol) and nitrobenzene (1 ml) was heated under microwave in a CEM Discover BenchMate apparatus. After being cooled, the catalyst was filtered from the reaction mixture. The filtrate was diluted with ethyl acetate (15 – 20 ml), washed with H_2O (3 x 20 ml), aqueous $NaHCO_3$ (2 x 20 ml) and brine (20 ml) and dried over Na_2SO_4. The identity of products and the conversion of reactions were confirmed by GC-MS and GC-FID spectra, which were compared with the spectra in the NIST library [6].

In order to examine the efficiency of the mentioned reaction, a series of reactions were set out: heat a round bottom flask which contains a mixture of Fe-MIL-101 (8.53 μmol), reagent (0.5 mmol), benzoyl chloride (58 μl; 0,5 mmol) and nitrobenzene (3 ml) at the appropriate temperature and time span with the help of the magnetic stirrer. Other reactions were made with iron (III) chloride as a homogeneous catalyst to compare the catalytic activity of $FeCl_3$ with Fe-MIL-101(*). Experimental conditions are shown in Table 1.

Table 1. *Experiments survey the efficiency of microwave irradiation applied to Fe-MIL-101*

Substrate	**Condition**	
	Microwave irradiation	**Conventional heating(*)**
Anisol	120°C, 5 min	120°C, 60 min
Phenanthrene	120°C, 5 min	120°C, 60 min
Anthracene	120°C, 5 min	120°C, 60 min
Flourene	140°C, 30 min	140°C, 60 min
1,4-dimethoxybenzene	140°C, 10 min	140°C, 60 min
m-xylene	120°C, 5 min	120°C, 60 min
1,2,4-trimethoxybenzene	120°C, 10 min	120°C, 60 min
p-fluoroanisol	120°C, 20 min	120°C, 60 min

2.4. Characterization analysis methods

Powder X-ray diffraction (PXRD) patterns were recorded using a Bruker D8 Advance (Germany) operated at 40 kV and 40 mA with a Ni filtered Cu Kα radiation (λ = 1,54178 Å) source. Thermal gravimetric analysis (TGA) were performed on a TA Q500 Thermal Analysis System under an airflow. Nitrogen adsorption isotherms at 77 K were collected on a 3Flex-Micromeritics (USA). Microwave irradiation was performed on a CEM Discover BenchMate apparatus, which offered microwave synthesis with safe pressure regulation using a 10 ml pressurized glass tube with a Teflon-coated septum and vertically focoused IR temperature sensor to control reaction temperature. GC-MS analyses were performed on an Agilent GC Symtem 7890 equipped with a mass selective detector Agilent 5973N and a capillary DB-5MS column (30 m x 250 μm x 0.25 μm). Fourier Transform Infrared (FT-IR) spectra were analyzed by a Bruker Vertex 70.

3. Results and discussion

3.1. Fe-MIL-101 material

PXRD patterns indicate the successful synthesis of Fe-MIL-101 (Figure 1). The activated material displays diffraction peaks similiar to the simulated pattern. Additionally, the 2θ angle shows a slight increase compared to as-synthesised material. It is believed that the solvent has been decontaminated with activation. The activated material's intensity of diffraction peaks was highly significant in comparison with that of as-synthesis material. Thus, resulted material was crystallised well.

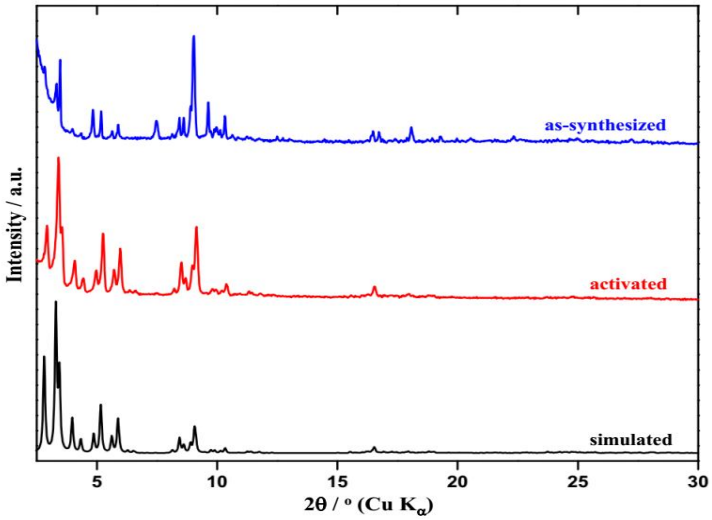


Figure 1. *PXRD patterns of as-synthesized and activated Fe-MIL-101. The simulated pattern generated from the structural model is provided as a reference*

The thermal gravimetric analysis (TGA) pattern of Fe-MIL-101 was shown in Figure 2. TGA curve of Fe-MIL-101 shows that Fe-MIL-101 is thermally stable until 300°C. Thirty-five percent of the material left in the post-reaction probably includes metal oxides or carbon.

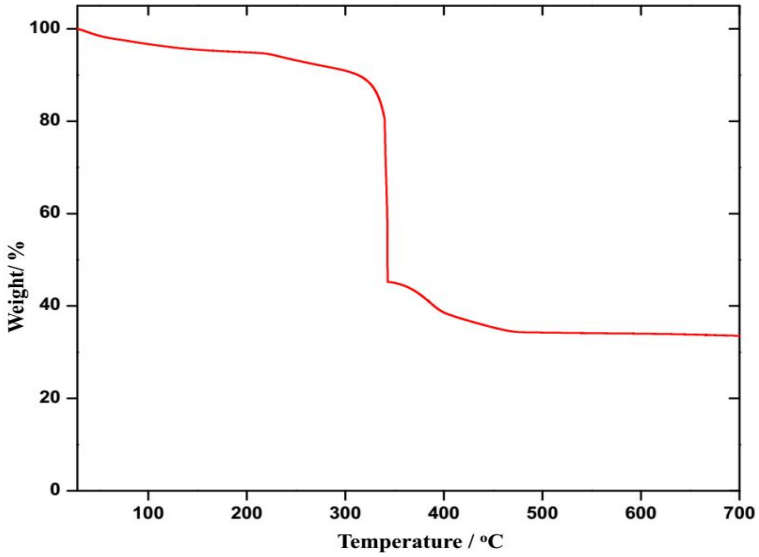


Figure 2. *TGA pattern of activated Fe-MIL-101*

FT-IR spectra of activated Fe-MIL-101 and H_2BDC linker were shown in Figure 3.

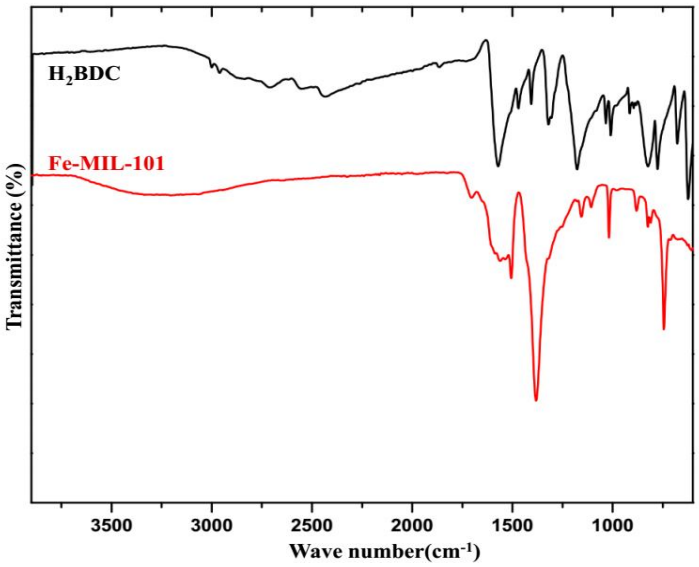


Figure 3. *FT-IR spectra of activated Fe-MIL-101 and H_2BDC linker*

FT-IR spectrum of Fe-MIL-101 (red line) shows an absorption band at 1600 cm^{-1} (strong), which is typical for $\nu_{C=O}$ in a carboxylate group. For H_2BDC (black line), $\nu_{C=O}$ has the value of 1680 cm^{-1}. The decrease in frequency of $\nu_{C=O}$ bond proved the connection between iron sites and functional groups of carboxylate. The absorption band typical for ν_{OH} group in COOH group (2500 to 3400 cm^{-1}) was not presented in the spectrum of Fe-MIL-101. This could be explained by the replacement of BDC^{2-} for H_2BDC in material on account of the separation from OH group of H^+. There is a wide absorption band in the spectrum of material in the range of 3000 cm^{-1} to 3600 cm^{-1}, which is typical for ν_{OH} group because of the increase in humidity of the material during the experiment.

Specific surface area and pore volume of Fe-MIL-101 was determined by the adsorption of nitrogen. Surface area measured in BET to Fe-MIL-101 is 2582 m^2/g. This value is higher than the one led by the Rahmanies in 2017 (1800 m^2/g) [16], and approximate to Tang's group's in 2015 (2675 m^2/g) [7]. The N_2 adsorption and desorption branches at 77 K are shown in Figure 4.

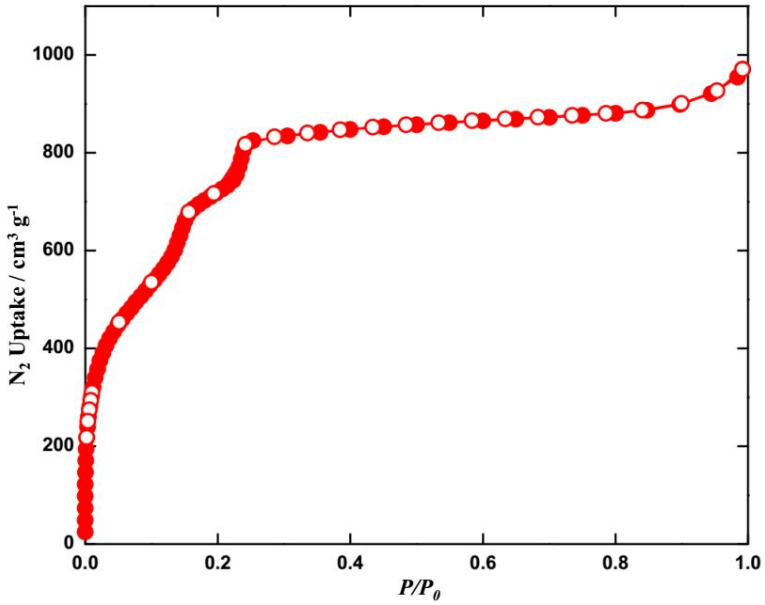


Figure 4. *N_2 isotherm of Fe-MIL-101. Curves with filled and opened symbols represent the adsorption and desorption branches, respectively*

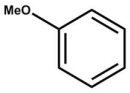
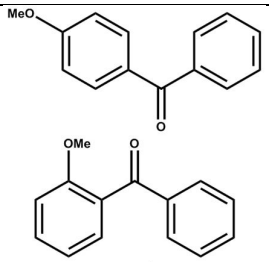
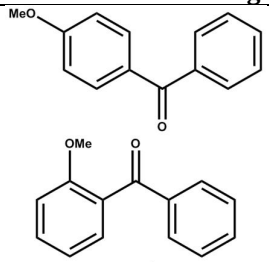
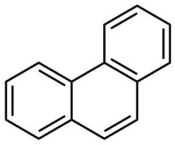
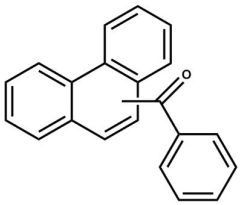
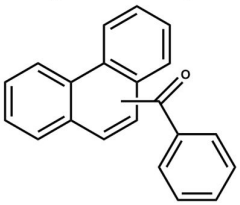
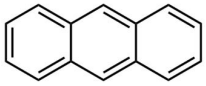
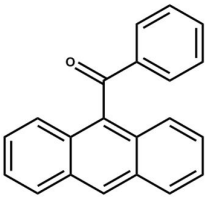
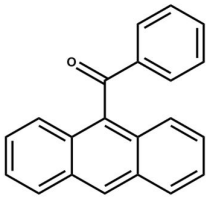
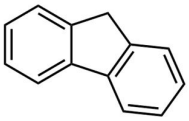
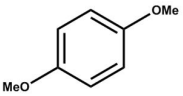
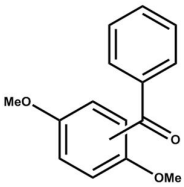
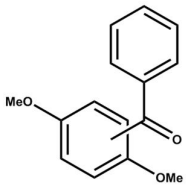
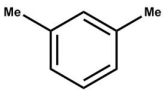
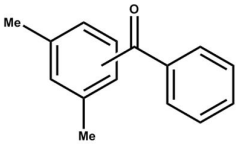
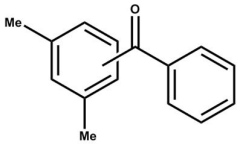
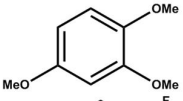
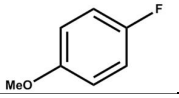
To sum up, Fe-MIL-101 is successfully synthesized. The material has a crystal structure with the high level of crystallisation and thermal stability until 300°C.

3.2. Catalytic activity of Fe-MIL-101 material on Friedel-Crafts benzoylation reaction

The GC-MS analysis result indicates that Fe-MIL-101 material can be used as the catalyst for the Friedel-Crafts benzoylation reaction with benzoyl chloride as benzoylation

agent. There are five out of eight reagents that successfully obtain desired results show as Table 2.

Table 2. *The analysis results of the catalytic activity of Fe-MIL-101 material applied in Friedel-Crafts benzoylation by microwave method and by conventional heating method*

Entry	Substrate	Product	
		Microwave irradiation	Conventional heating
1			
2			
3			
4		No product	No product
5			
6			
7		No product	No product
8		No product	No product

Conversion of reactions are determined by peak area of reagents and products on GC-FID diagram. Results are shown in Table 3.

Table 3. *Conversion of Friedel-Crafts benzoylation reactions of Fe-MIL-101*

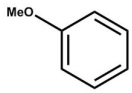
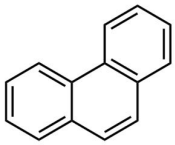
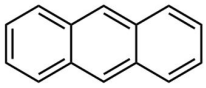
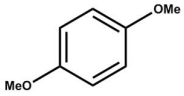
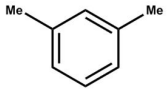
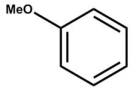
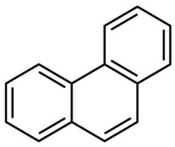
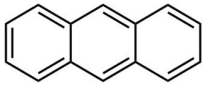
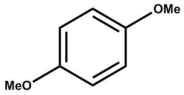
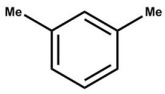
Entry	Substrate	Conversion (%)	
		Microwave irradiation	Conventional heating
1		76.0	47.2
2		53.2	8.2
3		55.4	20.9
4		67.6	47.8
5		74.5	68.9

Table 1 and Table 3 indicate that the yield of Friedel-Crafts benzoylation reactions by microwave irradiation gained considerable results. The conversion reached more than 50 percent, especially m-xylene and anisol reached the maximum conversion of 75 to 76 percent, compared to results gained with conventional heating. For example, the conversion of phenanthrene merely reached about 8 percent, hence, it means that there is a great deal of phenanthrene left at the end of the reactions. Furthermore, not only does microwave irradiation increase the yield, but it also significantly reduces the reaction time as well as the consumed energy. For instance, the conversion of the reaction with anisol as the reagent with the help of magnetic sitrrer reached inconsequentially 47 percent in an hour in relation to significantly 76 percent in just only 5 minutes with the aid of microwave irradiation (Table 3, entry 1).

The experiments show that the reactions with iron (III) chloride give similar results to the ones with Fe-MIL-101, as shown in Table 4.

Table 4. *Conversion of Friedel-Crafts benzoylation was catalysed by Fe-MIL-101 and iron (III) chloride*

Substrates	Conversion (%)		
	Fe-MIL-101 (Microwave irradiation)	**Fe-MIL-101 (Conventional heating)**	**$FeCl_3$ (Conventional heating)**
	76.0	47.2	73.1
	53.2	8.2	58.5
	55.4	20.9	77.2
	67.6	47.8	64.1
	74.5	68.9	63.4

As can be seen from these results, despite the fact that $FeCl_3$ catalyst has become less attractive because of a few disadvantages such as being easily soluble in products so it is impossible to retrieve for recycling and refining, the catalytic activity of iron (III) chloride is moderately suitable for Friedel-Crafts benzoylation as a common homogeneous catalyst used mainly in factories. Another revealing insight is the colour change of Fe-MIL-101 during the reaction. Figure 5 shows that the color of the material changes from light orange to dark gray. The reason is that the reaction results in an acid medium (pH = 1-2) which causes the collapse of the initial framework. Consequently, in order to efficiently employing time and expense, powder X-rays diffraction will not be used in this paper.

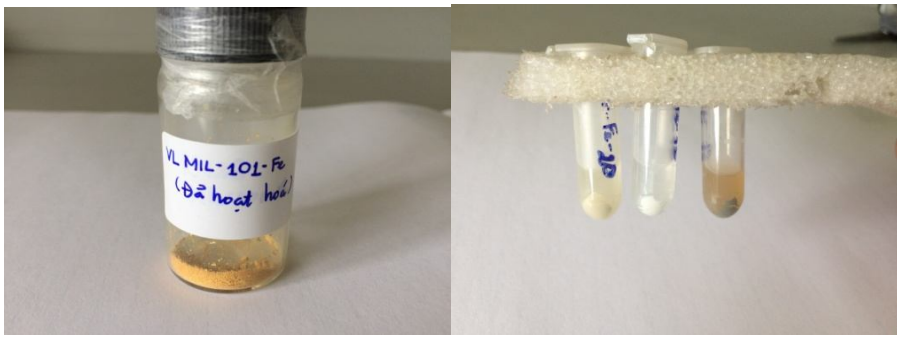


Figure 5. *The colour change of Fe-MIL-101 during the reaction*

4. Conclusion

Fe-MIL-101 is successfully synthesised from H_2BDC and iron (III) chloride. This catalyst is effective in the Friedel-Crafts benzoylation between aromatic compounds and benzoyl chloride. The simultaneity of Fe-MIL-101 material and microwave irradiation causes increased yield and reduction in time span, compared to the conventional heating.

- ***Conflict of Interest:*** *Authors have no conflict of interest to declare.*

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