NJC

Accepted Manuscript

Fe-MIL-101 as an efficient heterogeneous catalyst for four-component coupling synthesis of highly substituted pyrroles

ARTICLE TYPE

Heterogeneous Fe-MIL-101 catalyst for efficient one-pot four-component coupling synthesis of highly substituted pyrroles

Jia Tang, Mu Yang, Ming Yang, Jingjing Wang, Wenjun Dong* and Ge Wang

A four-component coupling reactions (4CRs) of 1,3-dicarbonyl compounds, amines, aldehydes and nitromethane has been carried out for substituted pyrroles using Iron-containing metal organic frameworks (MOFs) as heterogeneous catalysts. Due to the higher surface area and larger pore size, the Fe-MIL-101 catalyst exhibits a higher activity than that of Fe-MIL-88B and Fe-MIL-53. The reusability
10 and heterogeneity of Fe-MIL-101 catalyst was demonstrated, and over five cycles no significant reduction of its catalytic activity was observed. The structural stability of the fresh and recovered catalyst was further studied by characterization with thermogravimetric analysis, powder X-ray diffraction, and fourier transform infrared spectra. The MOFs have been demonstrated to be highly active heterogeneous catalysts for substituted pyrroles via 4CRs.

15 1. Introduction

Pyrrole and its derivatives, as a class of heterocyclic compounds in many natural products and medicinal compounds,[1] have been widely used in pharmaceutical industries due to their biological and pharmacological applications as antibacterial,
20 antitumor, antioxidant, anti-inflammatory and antifungal components.[2-4] Up to now, many synthetic methods such as hantzsch reaction,[5-6] 3-dipolar cycloaddition reaction,[7] annulations reactions,[8] and paal–knorr reaction have been developed.[9-10] Although classical reactions are very useful and
25 effective in synthesizing common pyrroles, they often suffer from some drawbacks such as multistep synthetic operation, functional group compatibility, regiospecificity, and harsh reaction conditions.

To overcome those problems, recently Multi-component
30 reactions (MCRs) have been developed in the systhesis of pyrroles.[11-18] Advantages of the MCRs include no need of isolation or purifications for intermediate products, superior atom-economy, and high variability of substrates. Meanwhile various catalysts for the synthesis of substituted pyrroles via
35 MCRs have been employed including metal chlorides,[19-21] iodine,[22] amberlyst-15,[23] nano-CoFe$_2$O$_4$ supported Mo catalyst or Sb (III) catalyst,[24-25] nano copper oxide,[26] Clay K10,[27] and Pd catalyst.[28] While these methods have their own advantages, they still suffer from several disadvantages such as use of toxic metal
40 catalyst, tedious workup and purifications with low yield, and long reaction time. In particular, the separation and reuse of catalysts still remain a challenge. Hence, the development of efficient and recoverable heterogeneous catalysts to synthesize highly substituted pyrroles becomes a very important subject.
45 In recent years, metal organic frameworks (MOFs) have

become one hot topic in heterogeneous catalysis.[29-30] The large surface area and pore size of MOFs allow the access of organic substrates to the transition metal ions inside the crystal structure of MOFs. Furthermore the highly dispersed metals ions, which
50 are involved in the coordination of MOFs, can interact with organic substrates and be used as active sites to promote catalyzed reactions such as oxidation of alcohol, alkylation of aldehyde, suzuki–miyaura coupling and reduction of nitroaromatic.[29,31] However, to the best of our knowledge, there
55 have been no reports on the synthesis of functionalized pyrroles catalyzed by MOFs via MCRs.

In the mind of the good catalytic performance of Fe^{3+} in FeCl$_3$ as a homogeneous catalyst for the MCRs,[19] we envisioned the one-pot four-component coupling reactions (4CRs) to result in
60 functionalized pyrroles by using Fe-MOFs as heterogeneous catalysts. In this paper, the highly porous Fe-MOF (Fe-MIL-101)

65

70
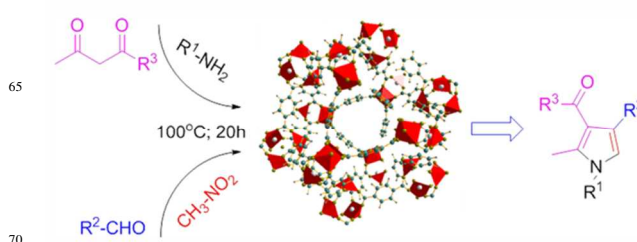
Scheme 1 Synthesis of substituted pyrroles catalyzed by Fe-MIL-101.
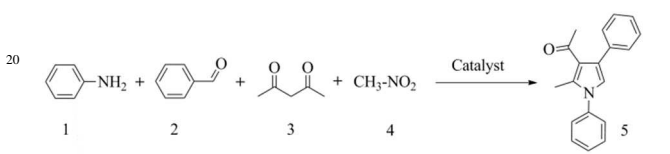
was chosen as a new heterogeneous catalyst for the one-pot four-
75 component coupling reactions (4CRs) of 1,3-dicarbonyl compounds, amines, aldehydes and nitroalkanes (Scheme 1). The mesoporous system of Fe-MIL-101 defines nano cages of about

2.9 and 3.4 nm with windows of 1.2 and 1.6 nm,[32] which allow bulky molecules to access freely. Furthermore, Fe (III) in Fe-MIL-101 has a free coordination position around the Fe (III) ion.[31] Therefore the Fe-MIL-101 can be act as a heterogeneous ₅ catalyst to promote the 4CRs for substituted pyrroles.

2. Results and discussion

As shown in Fig S1 and Table S1, the Fe-MIL-101 nanoparticles showed the octahedral structure and the octahedral length was 300-400 nm, and the Fe-MIL-101 has high surface ₁₀ areas (2670.5 m^2/g) and large pore volumes (0.75 cm^3/g). With the advantages of Fe-MIL-101 such as high dispersion of active Fe (III) ion and large pore size in the structure, the comparison of Fe-MIL-101 with Fe (III) homogeneous catalysts for the reaction of aniline **1** with benzaldehyde **2**, acetylacetone **3** and ₁₅ nitromethane **4** was explored firstly. The results are given in Table 1.

Table 1 Comparison the catalytic activity of Fe-MIL-101 with some Fe (III) homogeneous catalysts and other MOFs for 4CRs. [a]

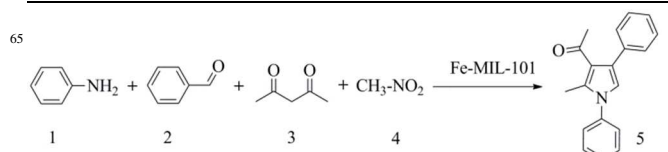| Entry	Catalyst	Conv. (%)	Sel. (%) [c]
1	None	21	87
2	FeCl₃.6H₂O	98 [b]	99
3	Fe(NO₃)₃.9H₂O	94 [b]	98
4	Fe₂(SO₄)₃	95 [b]	96
5	Fe(C₅H₅)₂	80 [b]	98
6	**Fe-MIL-101**	**90**	**99**
7	Fe-MIL-88B	85	99
8	Fe-MIL-53	67	98

[a] Reaction conditions: catalyst (50 mg), aniline (1 mmol), benzaldehyde ₂₅ (1.2 mmol), nitromethane (1 mL), and acetylacetone (1 mmol) at 100 °C for 20 h; [b] Reaction conditions: catalyst (0.2 mmol), aniline (1 mmol), benzaldehyde (1.2 mmol), nitromethane (1 mL), acetylacetone (1 mmol) at 100 °C for 20 h; [c] Determined by GC using toluene as an internal standard.

₃₀ As can be seen (Table 1, entries 1-6), Fe-MIL-101 as a heterogeneous catalyst for 4CRs exhibited high activity which was like that of the homogeneous Fe (III) catalysts. Aniline was converted to the corresponding product with 90% conversion after 20h's reaction (Table 1, entry 6). Other Fe-MOFs as ₃₅ catalysts such as Fe-MIL-88B, Fe-MIL-53 were also applied to the reaction in similar reaction condition (Table 1, entries 7-8). Both Fe-MIL-88B and Fe-MIL-53 showed lower reactivity than Fe-MIL-101. Compared to Fe-MIL-101, the pore sizes of the Fe-MIL-88B and Fe-MIL-53 structure are much smaller. The unit ₄₀ cell parameters for Fe-MIL-88B in closed states are a =9.5 Å, c =19.0 Å, V =1485 Å³,[34] and the MIL-53 structure has flexibility pore size about 8.6 Å.[32] Since reactants could not fully contact with iron ions in both MIL-88B and MIL-53 structure, the active site cannot catalyze the reaction effectively, which causes a lower ₄₅ conversion.

Exhaustive studies of the optimal reaction conditions for the synthesis of pyrrole **5** from aniline **1** with benzaldehyde **2**, acetylacetone **3** and nitromethane **4** in the presence of Fe-MIL-101 were conducted (Table 2). To identify the suitable reaction

₅₀ temperature, the 4CRs were carried out at from 60 °C to 100 °C. The results indicate that the temperature greatly affects the conversion and especially the selectivity of the reaction. When the reaction temperature was raised from 60 °C to 100 °C and the reaction time was 20h, the selectivity increases from 49.5% to ₅₅ 99.5%. It can be observed that the selectivity rises steadily as time or temperature increased. In order to get a high yield of the desired products, the reaction temperature and time were kept at 100 °C and 20h in subsequent reactions. In addition, the reaction was also carried out with different molar ratios of the reactants ₆₀ (Table 2, entries 9-12). There is no obvious change for the selectivity while the conversion slightly changes. For convenience, the molar ratio of n (**1**): n (**2**): n (**3**) =1:1:1 was chosen in following reactions.

Table 2 Effect of reaction conditions on the 4CRs. [a]

₆₅

Entry	n(1):n(2):n(3)	T (°C)	Time (h)	Conv.(%) [b]	Sel. (%)
1	1:1.2:1	60	4	91.9	0
2	1:1.2:1	60	8	89.14	7.26
3	1:1.2:1	60	20	87.08	49.52
4	1:1.2:1	80	4	83.2	17.2
5	1:1.2:1	80	8	85.9	85.4
6	1:1.2:1	80	20	81.69	92.13
7	1:1.2:1	100	4	96.1	56.8
8	1:1.2:1	100	8	84.4	98.7
9	1:1.2:1	100	20	93.14	99.5
10	1:1.2:1.2	100	20	87.9	98.6
11	1:1:1.2	100	20	82.2	99.1
12	1:1:1	100	20	90	99.4

₇₀ [a] Reaction conditions: Fe-MIL-101(50 mg), aniline, acetylacetone, and benzaldehyde were added in nitromethane (1 mL), 100 °C, 20h; [b] Determined by GC using toluene as an internal standard.

To investigate the efficient scope of Fe-MIL-101 heterogeneous catalyst for the 4CRs, various aromatic amines, ₇₅ primary aldehydes and keto esters were subjected to the protocol in the presence of Fe-MIL-101, and the results are shown in Table 3. In general, the reactions are performed well with various aromatic and aliphatic amines (Table 3, entries 1-5). Compared with m- and p-toluidine (Table 3, entries 2-3), o-toluidine (Table ₈₀ 3, entry 1) shows less reactive in the presence of Fe-MIL-101 and gives lower conversion, due to the steric hindrance of -CH₃. The weakly electron deficient aromatic aniline such as p-fluoroaniline was also applied to this reaction and the corresponding pyrrole is obtained in moderate yield (Table 3, entry 4). Compared to ₈₅ aromatic amines, aliphatic amines such as 1-butylamine exhibit slightly better reactions with a higher conversion of 99% and excellent selectivity (Table 3, entry 5). Subsequently, different kinds of aldehydes were surveyed for these 4CRs. Aromatic aldehydes bearing electron-donating groups such as -OMe and - ₉₀ Me are converted to the corresponding pyrroles with high conversions (Table 3, entries 6-7), while weak electron withdrawing aromatic aldehydes show less reactive in the 4CRs (Table 3, entries 8-9). Heteroaromatic aldehyde such as 2-formylfuran also react efficiently to obtain the corresponding ₉₅ product with good conversion and high selectivity (Table 3, entry

10). Moreover, other 1,3-dicarbonyl compounds such as methyl acetoacetate and ethyl acetoacetate were also evaluated in the 4CRs (Table 3, entries 12-13), methyl acetoacetate undergoes smooth reaction and affords 85% conversion after 20 h, however, ethyl acetoacetate is found to be less reactive in the 4CRs and only 47% conversion is observed, probably due to the steric hindrance of the pore in Fe-MIL-101 hampers the reaction. The results suggest that Fe-MIL-101 as a heterogeneous catalyst exhibits high activity in the 4CRs for broad substrates.

Table 3 Synthesis of different substituted pyrroles catalyzed by Fe-MIL-101.[a]

$$R^1\text{-}NH_2 + R^2\text{-}CHO + CH_3\text{-}NO_2 + \underset{R^3}{\overset{O\quad O}{\parallel\quad\parallel}} \xrightarrow{\text{Fe-MIL-101}} $$

Entry	R^1	R^2	R^3	Conv. (%)[b]	Sel. (%)
1	o-CH$_3$Ph	Ph	Me	63.7	97
2	m-CH$_3$Ph	Ph	Me	93.2	97.2
3	p-CH$_3$Ph	Ph	Me	92.2	96.5
4	p-FPh	Ph	Me	78.0	98.1
5	CH$_3$(CH$_2$)$_3$	Ph	Me	99	99.4
6	4-FPh	4-CH$_3$OPh	Me	89.9	96.7
7	4-FPh	4-CH$_3$Ph	Me	89.2	96.3
8	4-FPh	4-FPh	Me	69.4	95.8
9	4-FPh	2-FPh	Me	61.8	84.2
10	4-FPh	Furanyl	Me	90.1	89.2
11	Ph	Ph	Me	87.2	99.1
12	Ph	Ph	OMe	85.3	90.8
13	Ph	Ph	OEt	47	91.1

[a] Reaction conditions: Fe-MIL-101(50 mg), amine (1 mmol), aldehyde (1 mmol), nitromethane (1 mL), 1,3-dicarbonyl compound (1 mmol) and toluene (1mmol), 100 °C, 20 h; [b] Determined by GC using toluene as an internal standard.
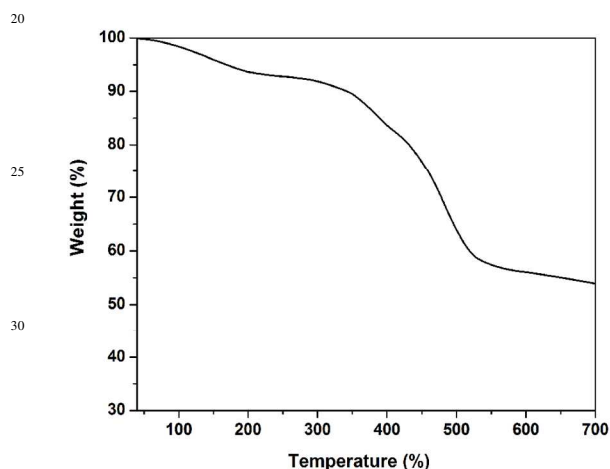

Fig 1 TGA curve of fresh Fe-MIL-101.

In order to investigate the stability of Fe-MIL-101, the thermal stability of Fe-MIL-101 was first evaluated by thermogravimetric analysis (Figure 1), The TGA curve under a N$_2$ atmosphere shows about 8% weight loss at 40-200 °C, which is due to the loss of guest solvent molecules from the pores of Fe-MIL-101. The 37% weight loss at 300-600 °C can be due to the partial decomposition of Fe-MIL-101. It implies that the catalyst shows good thermal stability in the catalytic reaction conditions (100 °C).
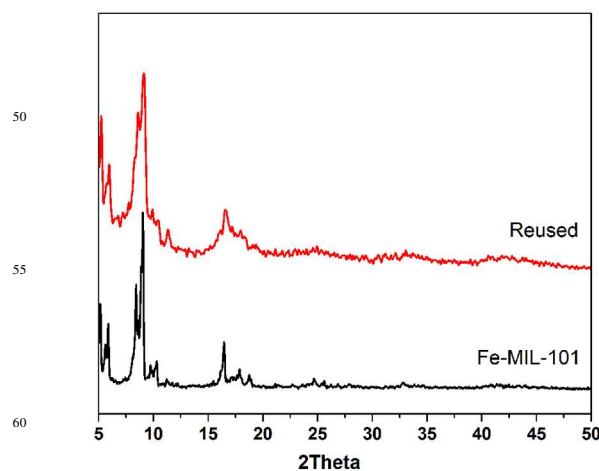

Fig 2 X-ray diffraction patterns of fresh and recovered Fe-MIL-101.

After reaction, the catalyst was recovered and analyzed by powder XRD and FT-IR. XRD results show that the recovered Fe-MIL-101 catalyst have the same peak positions as the fresh material (Figure 2), but the peaks become slightly broaden, which indicates some defect of Fe-MIL-101 structure, it's probably due to some of the coordination bonds between metal ions and organic ligands breaking,[38] which caused the surface area of the Fe-MIL-101 much less, and the total volume was also increased from 0.754 to 0.899 cm^3/g after one time used. Their FT-IR spectra have the same curves, and the sharp peak assigned to the organic linkers at 1660 cm^{-1} remains unaltered (Figure 3). The FT-IR and XRD results further confirm that the main structure of Fe-MIL-101 is stable under the reaction conditions.
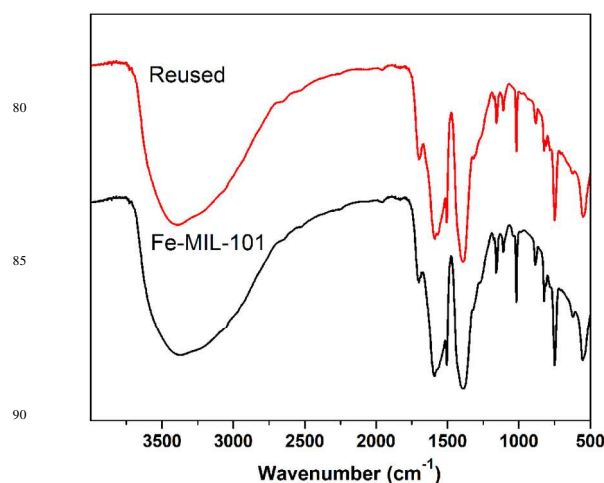

Fig 3 FT-IR spectra of fresh and recovered Fe-MIL-101.

As one key feature of heterogeneous catalysts, the recyclability of the Fe-MIL-101 catalyst was studied. After the catalytic reaction for pyrroles, the catalyst was recovered, and stirred in DMF (8 mL) at 100 °C for 24 h twice to active the pores of the catalyst efficiently, then washed with methanol three times, dried at 80°C for 24h and used in subsequent reaction. It is found that Fe-MIL-101 can be recovered and reused five times without obvious loss of catalytic activity. Indeed, the conversion of 84.8% and the selectivity of 98.5% are still achieved in the 5th run (Fig

4). XRD results indicate some defect of Fe-MIL-101 structure (Fig S2) after the 4th recycling experiment, which may be due to some of the coordination bonds breaking between metal ions and organic ligands. However, the defect of the structure doesn't cause a significant decrease of its catalytic performance or influence the Fe-MIL-101 to be a highly active heterogeneous catalyst for substituted pyrroles via the four-component coupling reactions.
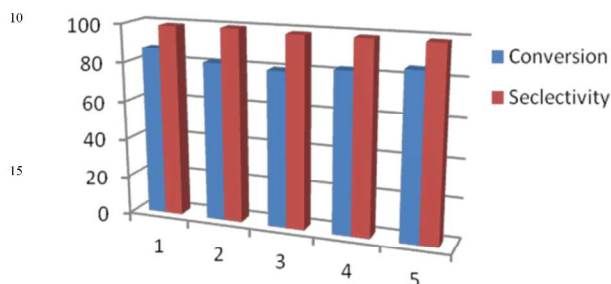

Fig 4 Reusability of Fe-MIL-101 in the 4CRs. Reaction conditions: Fe-MIL-101 (50 mg), aniline (1 mmol), benzaldehyde (1 mmol), nitromethane (1 mL), and acetylacetone (1 mmol), 100 °C, 20 h, determined by GC using toluene as an internal standard.
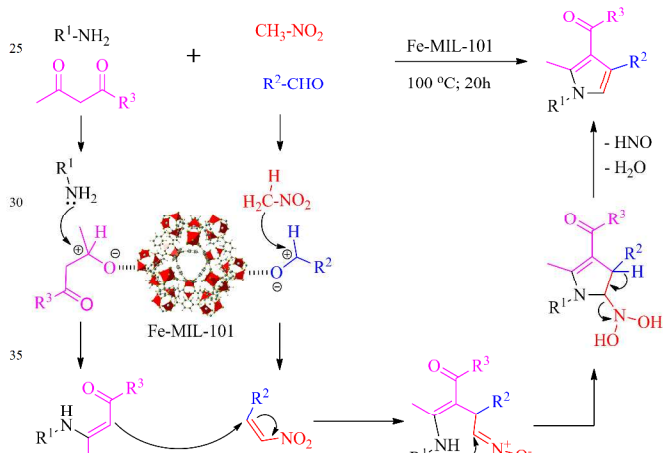

Fig 5 Proposed reaction mechanism for the formation of highly substituted pyrrole catalyzed by Fe-MIL-101.

According to the Grob and Cameisch reaction as well as the Michael reaction, pyrroles can be obtained in the presence of nitroalkenes and β-enamino ketones or esters followed by cyclization.[35] The nitroalkenes can be obtained via the reaction of aldehyde with nitroalkane, and the β-enamino ketones or esters can be generated via the reaction of 1,3-dicarbonyl compound with amines which can be catalyzed by Fe(III) ion (Fig 5).[36-37] The large surface area and pore size of Fe-MIL-101 allow the organic substrates to access the Fe (III) ions inside the crystal structure, and the highly dispersed Fe (III) in Fe-MIL-101 has a free coordination position, which makes the Fe (III) ions as high active sites to promote the 4CRs, while the coordination between ligands and Fe (III) ions could keep the physical and chemical stability of Fe (III) ions in the metal organic framework during the catalytic procedure. Therefore, the construction of the pyrrole ring via the Michael reaction of β-enamino ketones or esters and nitroalkenes followed could be completed in the presence of Fe-

MIL-101 catalyst, and these characteristics of Fe-MIL-101 guarantee the excellent catalytic activity for the 4CRs.

3. Conclusions

A porous metal organic framework (Fe-MIL-101) is used as a heterogeneous catalyst for the synthesis of highly substituted pyrroles via a one-pot four-component coupling reactions (4CRs). The highly dispersed Fe (III) ions, large surface area, and big pore size of Fe-MIL-101 ensure that the catalyst has high activity for 4CRs. The Fe-MIL-101 has high stability under the reaction conditions and the recovered catalyst can be reused over five cycles without a significant decrease in activity. Therefore, for the first time we have demonstrated that MOFs can act as good heterogeneous catalysts to catalyze the MCRs for highly functionalized pyrroles.

4. Experimental methods

4.1. General information

All the solvents and chemicals were of reagent grade and used without further purification. Powder X-ray diffraction (XRD) of Fe-MIL-101 was performed on M21X Cu Kα radiation (λ=0.154178 nm) in a scanning rang of 5-60° at 10 °/min. The surface morphology was studied on scanning electron microscopy (SEM, ZEISS SUPRA55). The specific surface areas, total pore volume and average pore size of Fe-MIL-101were measured by a Micromeritics ASAP 2420 adsorption analyzer with nitrogen sorption-desorption isotherms (N_2 adsorption). Thermogravimetric analysis (TGA) was conducted with an instrument (Netzsch STA449F) at a heating rate of 10 °C min^{-1} under a N_2 flow. Fourier transform infrared spectra (FTIR) were obtained on Nicolet 6700 using the KBr pellet technique at room temperature. The catalytic results were monitored by a gas chromatography-mass (GC-MS) spectrum on Agilent7890/ 5975C-GC/MSD.

4.2. Synthesis of Fe-MIL-101

Fe-MIL-101 was synthesized according to the literature with some modifications.[33] Typically, 0.658 g (3.96 mmol) of terephthalic acid and 1.07 g (3.96 mmol) of FeCl$_3$.6H$_2$O were dissolved into 90 mL of DMF in a 250 mL round-bottomed flask, and 3.6 mL of acetic acid was added. The reaction mixture was heated at 110 °C for 24 h, and then cooled to room temperature. The product was centrifuged and washed with DMF two times each day for two days to activate the MOF, and the brick-red solid was washed with methanol in the same way to replace DMF. Finally, the solid was dried at 80 °C for 24 h.

4.3. General procedure for the synthesis of pyrrole derivatives.

To a mixed solution of amine 1 (1 mmol), aldehyde 2 (1.2 mmol), nitromethane 3 (1 mL), 1,3-dicarbonyl compound 4 (1 mmol) and toluene (1 mmol, as an internal standard) was added Fe-MIL-101(50 mg). The mixture was stirred at 100 °C for 20 h. After the reaction, the mixture was cooled to room temperature and 5 mL ethanol was added, the pyrrole derivatives were dissolved in ethanol. Then the mixture was centrifuged to get the supernatant solution, and the solution was analyzed by Agilent

7890/5975C-GC/MSD.

Notes and references

School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, P.R. China
Tel: +86-010-62333827; E-mail: wdong@ustb.edu.cn
† Electronic Supplementary Information (ESI) available: SEM and BET of Fe-MIL-101. See DOI: 10.1039/b000000x/

1 R. A. Jones, *The Chemistry of Heterocyclic Compounds, Pyrroles;* John Wiley &Sons: Canada, 1990.

2 H. Fan, J. Peng, M. T. Hamann, J.F. Hu, *Chem. Rev.,* 2008, **108**, 264.

3 D. L. Boger, C.W. Boyce, M. A. Labroli, C. A. Sehon, Q. Jin, *J. Am. Chem. Soc.,* 1999, **121**, 54.

4 M. Protopopova, E. Bogatcheva, B. Nikonenko, S. Hundert, L. Einck, C. A. Nacy, *Med. Chem.,* 2007, **3**, 301.

5 A. Hantzsch, *Ber. Dtsch. Chem. Ges.,* 1890, **23**, 1474.

6 V. F. Ferreira, M. C. B. V. De Souza, A. C. Cunha, L. O. R. Pereira, M. L. G. Ferreira, *Org. Prep. Proced. Int.* 2001, **33**, 411.

7 F. Berree, E. Marchand, G. Morel, *Tetrahedron Lett.,* 1992, **33**, 6155.

8 C. F. Lee, I. M. Yang, T. Y. Hwu, A. S. Feng, J. C. Tseng, T. Y. Luh, *J. Am. Chem. Soc.,* 2000, **22**, 4992.

9 P. K. Chiu, M. P. Sammes, *Tetrahedron*, 1990, **46**, 3439.

10 B. Wang, Y. Gu, C. Luo, T. Yang, L. Yang, J. Suo, *Tetrahedron Lett.,* 2004, **45**, 3417.

11 H. Shiraishi, T. Nishitani, S. Sakaguchi, Y. Ishii, *J. Org. Chem.,* 1998, **63**, 6234.

12 O. A. Attanasi, G. Favi, F. Mantellini, G. Moscatelli, S. Santeusanio, *Adv. Synth. Catal.,* 2011, **353**, 1519.

13 X. Lin, Z. Mao, X. Dai, P. Lu, Y. Wang, *Chem. Commun.,* 2011, **47**, 6620.

14 Z. H. Guan, L. Li, Z. H. Ren, J. Li, M. N. Zhao, *Green Chem.,* 2011, **13**, 1664.

15. V. Estévez, M. Villacampa, J. C. Menéndez, *Chem.Soc.Rev.,* 2014, **43**, 4633.

16 S. Paul, G. Pal, A. R. Das, *RSC Adv.,* 2013, **3**, 8637.

17 L. V. Frolova, N. M. Evdokimov, K. Hayden, I. Malik, S. Rogelj, A. Kornienko, I. V. Magedov, Organic. Lett., 2011, **5**,1118.

18 X. Wang, X. P. Xu, S. Y. Wang, W. Zhou, S. J. Ji, Organic. Lett., 2013, **16**,4246.

19 S. Maiti, S. Biswas, U. Jana, *J.Org.Chem.,* 2010, **75**, 1674.

20 C.C. Silveira, S.R. Mendes, G.M. Martins, S.C. Schlosser, T.S. Kaufman, Tetrahedron, 2013, **69**, 9076.

21 A.B. Atar, Y.T. Jeong, *Tetrahedron Lett.,* 2013, **54**, 5624.

22 G. R. Reddy, T. R. Reddy, S. C. Joseph, K. S. Reddy, M. Pal, *RSC Adv.,* 2012, **2**, 3387.

23 P. R. K. Murthi, D. Rambabu , M. V. B. Rao, M. Pal, *Tetrahedron Lett.,* 2014, **55**, 507.

24 B. L. Li, M. Zhang, H. C. Hu, X. Du, Z. H. Zhang, *New J. Chem.,* 2014, **38**, 2435.

25 B. L. Li, H. C. Hu, L. P. Mo, Z. H. Zhang, *RSC Adv.,* 2014, **4**, 12929.

26 H. Saeidian, M. Abdoli, R. Salimi, C. R. Chim., 2013, **16**, 1063.

27 J. B. Bharate, R. Sharma, S. Aravinda,V. K. Gupta, B. Singh, S. B. Bharate, R. A. Vishwakarma, *RSC Adv.,* 2013, **3**, 21736.

28 G. R. Reddy, T. R. Reddy, S. C. Joseph, K. S. Reddy, C. Lakshmi, T. Meda, K.K. Priya, K.V.L. Parsa, M. Pal, *Chem. Commun.,* 2011, **47**, 7779.

29 J. Y. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen, J. T. Hupp, *Chem. Soc. Rev.,* 2009, **38**, 1450.

30 H. Furukawa, K. E. Cordova, M. O. Keeffe, O. M. Yaghi, Science, 2013, **341**, 1230444.

31 A. Dhakshinamoorthy, M. Alvaro, H, Garcia, *Adv. Synth. Catal.,* 2010, **352**, 3022.

32 P. Horcajada, T. Chalati, C. Serre, B. Gillet, C. Sebrie, T. Baati, J. F. Eubank, D. Heurtaux, R. Gref, Nat. Mater., 2010, **9**, 172.

33 S. Bauer, C. Serre, T. Devic, P. Horcajada, J Marrot, G. Ferey, N. Stock, *Inorg. Chem.,* 2008, **47**, 7568.

34 P. Horcajada, F. Salles, S. Wuttke, T. Devic, D. Heurtaux, G. Maurin, A. Vimont, M. Daturi, O. David, E. Magnier, N. Stock, Y. Filinchuk, D. Popov, C. Riekel, G. Ferey, C. Serre, *J. Am. Chem. Soc.,* 2011, **133**, 17839.

35 S. Maiti, S. Biswas, U. Jana, *J.Org.Chem.,* 2010, **75**, 1674.

36 H. Eshghi, S. M. Seyedi, E. Safaei, M. Vakili, A. Farhadipour, M. B. Mokhtari, *J. Mol. Catal. A: Chem.,* 2012, **363–364**, 430.

37 H. Hebbache, Z. Hank, S. Boutamine, M. Meklati, C. Bruneau , J. L. Renaud, *C. R. Chimie.,* 2008, **11**, 612.

38 A. Dhakshinamoorthy, M. Alvaro, H. Garcia, *Adv. Synth. Catal.,* 2010, **352**, 3022.