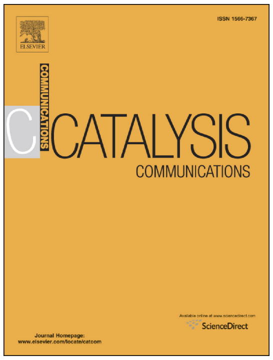

Thiourea-functionalized MIL-101(Cr) metal-organic framework as a hydrogen-bond-donating heterogeneous organocatalyst for the Friedel-Crafts alkylation and Biginelli reactions

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PII: S1566-7367(19)30366-8

DOI: https://doi.org/10.1016/j.catcom.2019.105905

Reference: CATCOM 105905

To appear in: *Catalysis Communications*

Received date: 18 September 2019

Revised date: 10 December 2019

Accepted date: 10 December 2019

Please cite this article as: R. Mohammadian, M.M. Amini and A. Shaabani, Thiourea-functionalized MIL-101(Cr) metal-organic framework as a hydrogen-bond-donating heterogeneous organocatalyst for the Friedel-Crafts alkylation and Biginelli reactions, *Catalysis Communications* (2019), https://doi.org/10.1016/j.catcom.2019.105905

Thiourea-functionalized MIL-101(Cr) metal-organic framework as a hydrogen-bond-donating heterogeneous organocatalyst for the Friedel-Crafts alkylation and Biginelli reactions

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CRediT author statement

Reza Mohammadian: Conceptualization, Methodology, Software, Data curation, Writing- Original draft preparation, Visualization, Investigation.

Mostafa M. Amini: Supervision, Writing- Reviewing and Editing, Software, Validation.

Ahmad Shaabani: Supervision, Writing- Reviewing and Editing.

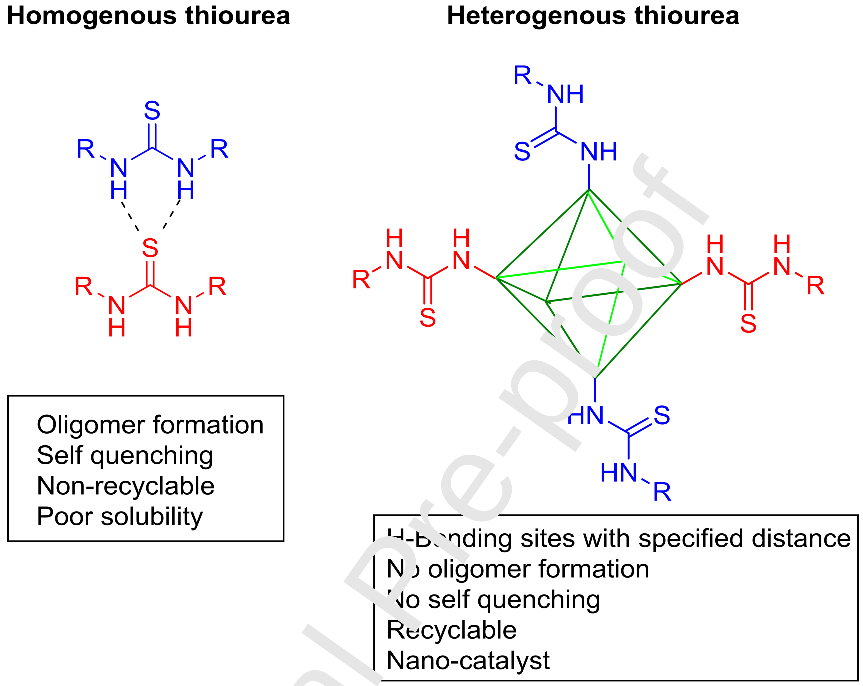
Abstract

In the present paper, a functionally diverse thiourea-grafted MOF was fabricated *via* postsynthetic modification process through complexation of MIL-101(Cr) with pyridine containing thiourea ligand. This new modified material overcomes a significant tendency of hydrogen-bond-donating (HBD) organocatalysts to undergo self-aggregation and subsequent decrease in their solubility and reactivity. A double Lewis acid-HBD catalysis activation mechanism causes the synergistic effect and to some extent has a better performance than the thiourea ligands and the parent MOF in Friedel-Crafts alkylation and Biginelli reactions.

Keywords: Hydrogen-bonding organocatalysis; Metal-organic framework; Thiourea; Postmodification; Heterogeneous catalyst

1. Introduction

Hydrogen bonding promoted catalysis has been demonstrated to be an appropriate candidate to fill a substantial gap between enzyme- and metal-catalysis, due to its great advantages such as availability, non-hazardous nature, simple handling, and low cost [1]. Of the various hydrogen-bond-donating (HBD) organocatalysts reported so far [2], those containing thiourea core are a remarkable achievement of modern synthetic strategies designation [3]. By having double hydrogen-bonding interactions with the substrates, thiourea catalysts are capable of promotion of various organic transformations such as Mannich-type reactions [4], Michael additions [5], Claisen rearrangements [6] and aldol reactions [7] in an asymmetric or racemic fashion. Although the use of thiourea organocatalysts has received much attention from organic chemists in recent years, several issues need to be addressed into consideration to take full advantage of the potential of such catalysts. The first problem is the homogeneous nature of thiourea which prevents its recyclability, and the second one is dimerization and oligomerization of thiourea organocatalyst through hydrogen bonding which leads to self-quenching phenomenon and significant reduction of its performance (Scheme 1)[8]. With these features in mind, chemical immobilization of thiourea on support [9, 10] would overcome these problems and provide a unique opportunity for the efficient utilization of organocatalyst in various reactions.

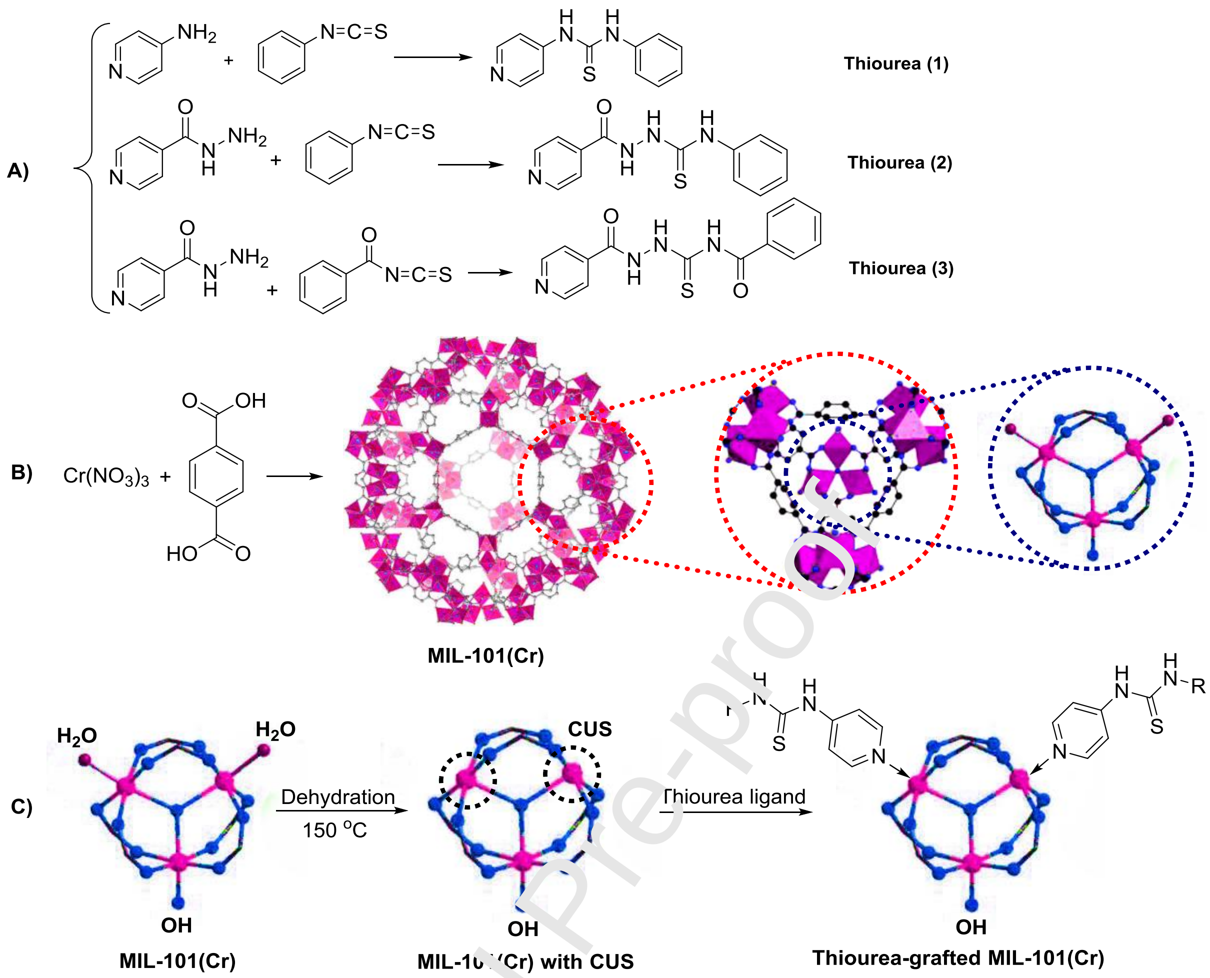


Scheme 1. Illustration of homogeneous and heterogeneous thiourea organocatalysts performances.

Metal-organic frameworks (MOFs) as novel hybrid materials are three-dimensional buildings with infinite network structure from metal ions and multipodal organic linkers [11]. These novel porous solids have attracted great attention due to their extraordinary chemical and physical properties including high surface area, well-defined pore structure, and peculiar chemical environments [12, 13]. So far, a wide variety of MOFs with different chemical properties and porous structures has been reported in which the majority of them suffer from limitations in their widespread commercial applications, due to their low framework stability and high cost [14]. One of the most stable MOFs is MIL-101(Cr), consisting of trimetric Cr(III) clusters and terephthalic acid with large Langmuir surface area, high thermal, and chemical stability [15]. One important feature of this type of MOF is its coordinatively unsaturated metal sites (CUS) formed by the removal of water coordinated with chromium atoms, providing Lewis acid centers and postsynthetic functionalization *via* chelating of active species [16]. This unique property allows the introduction of various functionalities into MOF and could be the right solution to heterogenization of homogeneous catalysts, prevention of self-quenching and self-assembly behavior of organocatalyst and creating synergistic effects in catalyst performance. In this context and concerning the advantages and drawbacks mentioned for the thiourea organocatalysis reactions and also in the continuation of our interest in developing catalytic systems based on MOFs for synthetic methodologies [17, 18], herein, we report a novel strategy to decoration of thiourea ligands onto the CUS of MIL-101(Cr). The resulting complexes showed remarkable activities in Friedel-Crafts alkylation and Biginelli reactions by overcoming recycling, self-quenching and solvation issues that homogeneous thiourea catalysts are faced with them.

2. Result and discussion

Considering that adsorption of pyridine with an unshared electron pair on the CUS of MIL-101(Cr) could be accomplished due to the strong interaction between electron donors and acceptors [15, 19, 20], an attempt has been made to synthesize various thiourea organocatalyst containing pyridine moieties. Next, several organocatalysts were coordinated onto the CUS of MIL-101(Cr), and a series of functionalized MOF materials by coordinatively attaching different thiourea ligands were achieved (Scheme 2).



Scheme 2. Schematic illustration of heterogeneous thiourea-grafted MIL-101(Cr) catalyst preparation.

2.1. Characterization of MIL-101(Cr)@thiourea catalysts

The FT-IR and XRD analyses were employed to characterize the prepared MIL-101(Cr) and three different thiourea-grafted MIL-101(Cr) materials. The introduction of thiourea moieties on MIL-101(Cr) in all three catalysts was supported by FT-IR spectroscopy based on the appearance of three stretching bands at ~1110, 1500 and 1510 cm^{-1}, related to CN symmetric and asymmetric stretching modes. Moreover, grafting of the thiourea on the scaffolds was also confirmed by the emergence of stretching bands at ~650 cm^{-1}, which is associated with the C=S bands in all three catalyst spectra (Figure 1). In addition, to show the interaction of Cr-N bond in the catalyst, FT-IR spectra of MIL-101(Cr) and MIL-101(Cr)@thiourea (3) were measured in the 4000-100 cm^{-1} region using CsCl pellet (Figure S1, ESI†). As can be seen in Figure S1, the coordination of nitrogen atom of pyridine to the Cr(III) site in MIL-101(Cr)@thiourea (3) is disclosed by the appearance of two stretching bands at ~310 and 389 cm-1 which is in accordance with the previous reports on the coordination of nitrogen atoms with Cr(III) centers [21, 22].

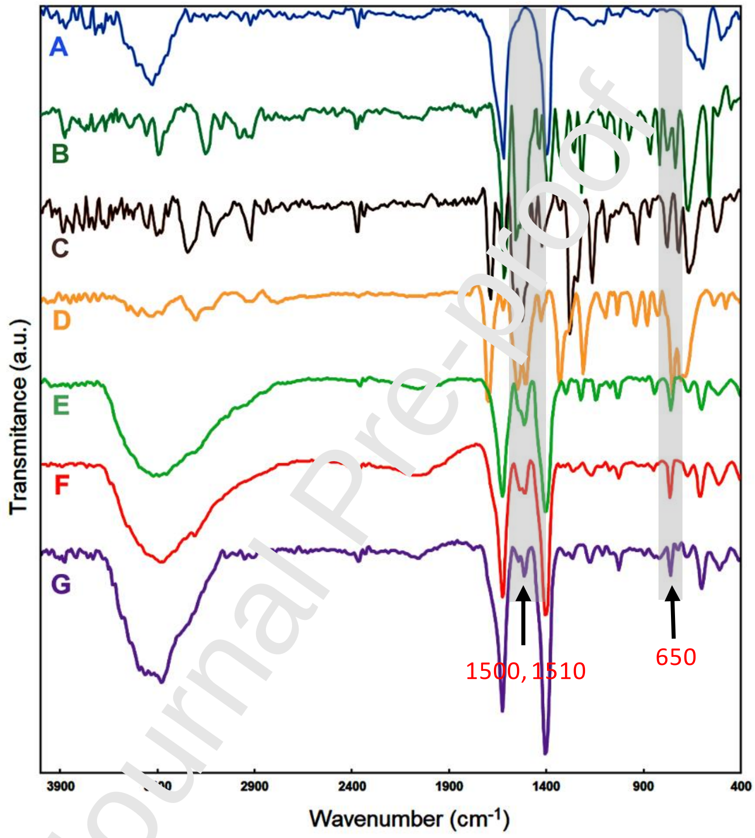


Figure 1. FT-IR spectra of MIL-101(Cr) (A), Thiourea (1) (B), Thiourea (2) (C), Thiourea (3) (D), MIL-101(Cr)@thiourea (1) (E), MIL-101(Cr)@thiourea (2) (F), and MIL-101(Cr)@thiourea (3) (G).

Powder X-ray diffraction (PXRD) analysis was performed on synthesized MIL-101(Cr), and three thiourea-grafted MIL-101(Cr) catalysts and the results illustrated that all four materials were in good agreement with the simulated one [23]. These results demonstrated the successful preparation of MIL-101(Cr) and retention of the basic structure of parent MOF in the final catalysts after postsynthetic pyridine modification (Figure 2).

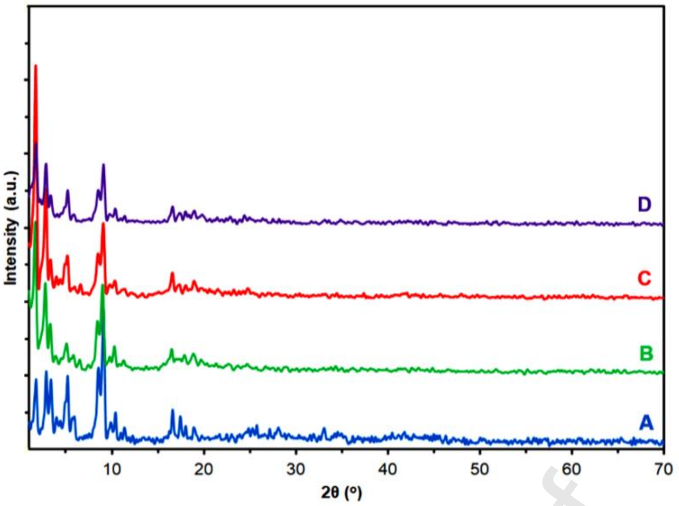


Figure 2. XRD patterns of MIL-101(Cr) (A), MIL-101(Cr)@thiourea (1) (B), MIL-101(Cr)@thiourea (2) (C), and MIL-101(Cr)@thiourea (3) (D).

At this stage, with the assurance of catalysts formation as confirmed by the FT-IR and PXRD experiments, the synthesized materials were initially tested in the Friedel-Crafts alkylation reaction between indole and *β*-nitrostyrene to choose the most appropriate catalyst with the highest performance for more characterization. The results of the comparisons in Table 1 showed that MIL-101(Cr)@thiourea (3) has the best performance in the reaction, which maybe is due to the presence of more acidic hydrogens (δ = 11.5-12.5 ppm in ^{1}H NMR, ESI†) as a result of the electron-withdrawing groups presence in its structure.

Table 1. Comparison of synthesized thiourea-grafted MIL-101(Cr) materials in the Friedel-Crafts alkylation reaction between indole and *β*-nitrostyrene[a]

Entry	Catalyst	Yield[b] (%)
1	MIL-101(Cr)	17
2	MIL-101(Cr)@thiourea (1)	65
3	MIL-101(Cr)@thiourea (2)	53
4	MIL-101(Cr)@thiourea (3)	81

[a] Reaction conditions: indole (1 mmol), *β*-nitrostyrene (1 mmol), CH_3CN (7 mL), and catalyst under reflux conditions for 48 h.

[b] Isolated yield.

After finding the most efficient catalyst (MIL-101(Cr)@thiourea (3)), TGA, BET, SEM, and EDS analyses were performed to complete characterization. The thermal stability of parent MOF (MIL-101(Cr)) and MIL-101(Cr)@thiourea (3) was assessed by thermogravimetric analysis (TGA) in air. As Figure S2 (ESI†) shows, the TGA curve of MIL-101(Cr) indicates an initial mass loss at the temperature ranges of ~25-350 ^{o}C due to the loss of the coordinated water and solvent molecules in its structure. In the case of MIL-101(Cr)@thiourea (3), a lower mass loss has occurred in the temperature ranges of ~25-350 °C, which indicates that water in parent MOF could have been replaced by the thiourea molecules. Both MIL-101(Cr) and MIL-101(Cr)@thiourea (3) represent the second weight loss between ~350-500 ^{o}C due to the collapse of the MIL-101(Cr) framework and decomposition of the dicarboxylate linkers. A higher overall mass loss (~4%) in MIL-101(Cr)@thiourea (3) diagram reflects the presence of additional organic (thiourea) moieties.

Nitrogen porosimetry experiments of the samples revealed that BET surface areas and total pore volumes of MIL-101(Cr)@thiourea (3) are substantially decreased in comparison with parent MOF, due to the thiourea ligands occupying the cavities of the MIL-101(Cr) (Table S1, ESI†). However, the surface areas of the thiourea functionalized MOF are still larger than those reported for silicas or zeolites (generally less than 1000 m^2/g) [24].

The morphology and nanostructure of the parent MOF and prepared catalyst were visualized by scanning electron microscopy (SEM) analyses (Figure S3, ESI†). The regular shapes and monodispersity of the MIL-101(Cr) are visible from Figure S3A. Similar octahedral-shaped crystals and morphology are also observed from SEM images of MIL-101(Cr)@thiourea (3) (Figure S3B, C), demonstrating that postsynthetic modification of MIL-101(Cr) by thiourea did not affect the structural integrity of parent MOF.

The energy dispersive X-ray spectroscopy (EDS) analysis disclosed the chemical composition of the final catalyst, and result showed the simultaneous presence of chromium, sulfur, and nitrogen elements (Figure S4A, ESI†). Furthermore, EDS elemental mapping demonstrated a homogeneous distribution of the chromium and sulfur in the structure MIL-101(Cr)@thiourea (3) material (Figures S4B, ESI†). Finally, CHNS analysis of MIL-101(Cr)@thiourea (3) showed 0.96 mmol.g^{-1} thiourea loading in the prepared catalyst.

2.2.Catalytic performance of thiourea-functionalized MOF

Due to the importance of tryptamine derivatives, the Friedel-Crafts alkylation of indole *via* β-nitrostyrene has received considerable attention [25]. Unfortunately, lower nucleophilicity of indole causes the Friedel-Crafts reaction became relatively slow. Developing heterogeneous catalysts, which activates the electrophilic nature of β-nitrostyrene through hydrogen bonding, is one of the possible solutions to overcome this issue. The catalytic activity of MIL-101(Cr)@thiourea (3) in the Friedel-Crafts reaction between β-nitrostyrene and indole as model substrates was evaluated and various parameters such as catalyst loading, reaction temperature, and reaction medium were optimized (Table 2). At the outset, acetonitrile was used as a reaction medium, and various amounts of catalyst were explored in the model reaction. In the absence of the catalyst, no desired product was obtained under reflux conditions for 24 h (Table 2, entry 1). When the reaction was run in the presence of MIL-101(Cr)@thiourea (3) (10 mg) at room temperature, only 16% yield was achieved, but by raising the temperature to 80 ^{o}C, 44% yield was obtained within 48 h (Table 2, entries 2, 3). The amount of catalyst was optimized to be 30 mg due to a higher yield than the other catalyst loading (Table 2, entry 5). The model reaction was also tested in the presence of other catalysts such as thiourea (3) and MIL-101(Cr) to confirm the catalytic efficiency of MIL-101(Cr)@thiourea (3). The results of the comparisons demonstrated that both catalysts could partially promote the reaction which maybe is due to the non-solubility of thiourea (3) in the reaction medium and the absence of effective active sites in parent MOF (Table 2, entries 7, 8). Moreover, the physical mixture of MIL-101(Cr) and thiourea (3) with similar loading of each component (1.00 g of MIL-101(Cr) and 0.50 g of thiourea (3)) under solvent-free conditions was also tested in the model reaction. The result demonstrated that this catalyst could not promote the reaction significantly (Table 2, entry 9). This phenomenon can be attributed to the self-aggregation of thiourea molecules since the physical mixing of MIL-101(Cr) and thiourea under solvent-free conditions is not able to separate thiourea oligomers from each other. Finally, screening different solvents revealed that the most suitable reaction medium is toluene due to a much shorter reaction time (Table 2, entry 12).

Table 2. Optimization of reaction conditions for the Friedel-Crafts alkylation reaction[a]

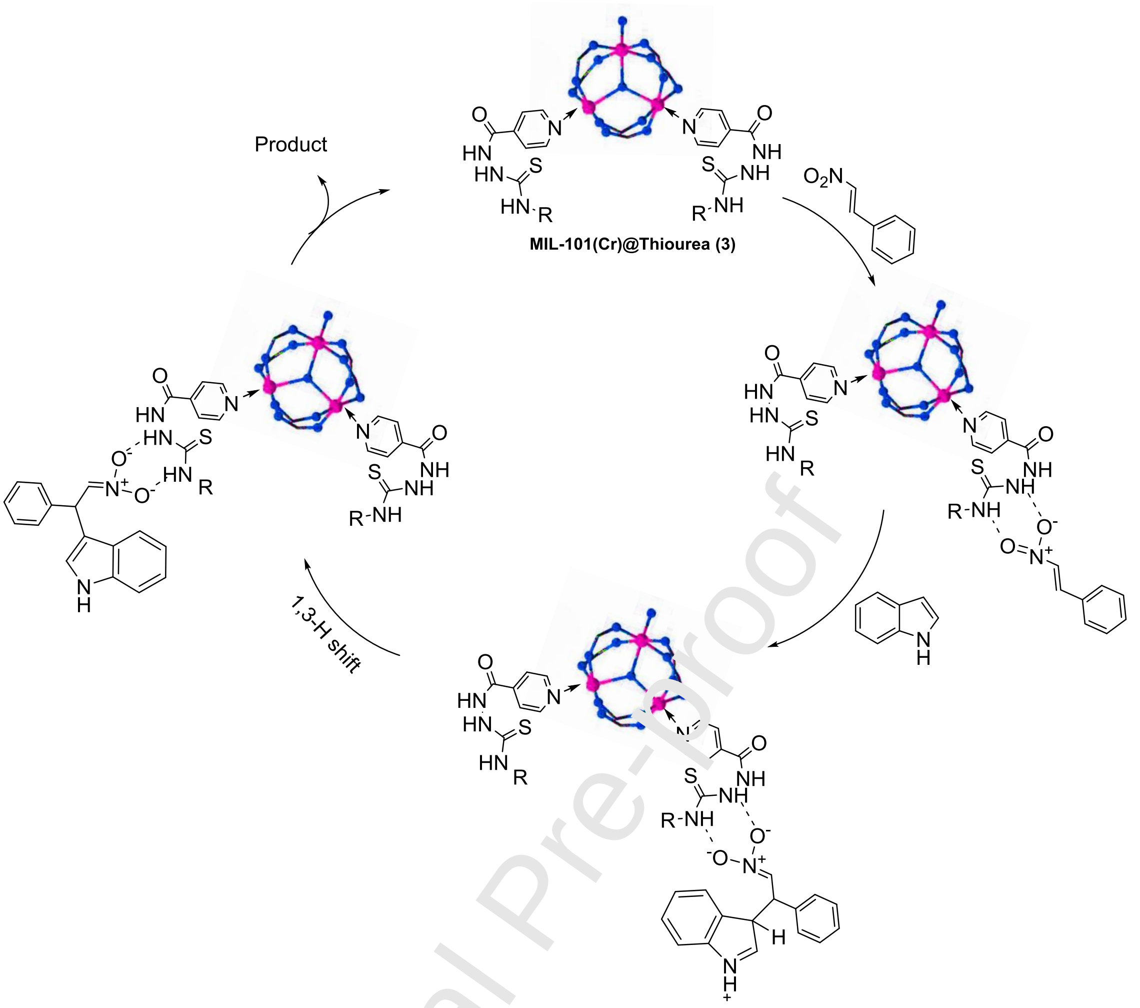
Entry	Catalyst (mg)	Solvent	Temperature (°C)	Time (h)	Yield[b] (%)
1	-	CH_3CN	reflux	24	Trace
2	MIL-101(Cr)@thiourea (3) (10)	CH_3CN	r.t.	48	16
3	MIL-101(Cr)@thiourea (3) (10)	CH_3CN	reflux	48	44
4	MIL-101(Cr)@thiourea (3) (20)	CH_3CN	reflux	48	69
5	MIL-101(Cr)@thiourea (3) (30)	CH_3CN	reflux	48	81
6	MIL-101(Cr)@thiourea (3) (40)	CH_3CN	reflux	48	83
7	MIL-101(Cr) (30)	CH_3CN	reflux	48	17
8	Thiourea (3) (30)	CH_3CN	reflux	48	29
9	Physically mixed MIL-101(Cr) and thiourea (3) (30)	CH_3CN	reflux	48	24
10	MIL-101(Cr)@thiourea (3) (30)	water	reflux	48	-
11	MIL-101(Cr)@thiourea (3) (30)	toluene	70	24	76
12	**MIL-101(Cr)@thiourea (3) (30)**	**toluene**	**80**	**18**	**84**
13	MIL-101(Cr)@thiourea (3) (30)	toluene	reflux	18	85
14	MIL-101(Cr)@thiourea (3) (30)	neat	80	48	Trace
15	MIL-101(Cr)@thiourea (3) (30)	CH_2Cl_2	25	48	53

[a]Reaction conditions: indole (1 mmol), β-nitrostyrene (1 mmol), solvent (7 mL), and catalyst.

[b]Isolated yield.

After optimizing the reaction conditions, the scope of the Friedel-Crafts alkylation reaction was explored using various nucleophiles and β-nitrostyrene with electron-donating and withdrawing substitutes (Table S2, ESI†). As shown in Table S2, β-nitrostyrene with electron-donating groups such as Me and OMe are more reactive in this reaction, and electron-withdrawing substitute (NO_2) did not produce any product. This phenomenon can be due to the greater ability of the electron donor groups to form hydrogen bonds with the catalyst in the reaction mechanism. Other nucleophiles such as pyrrole and *N*,*N*-dimethylaniline gave products in moderate to good yields, while acetylacetone and *N*-methyl-*N*-phenylformamide did not proceed the reaction.

Based on published reports on the formation of hydrogen bonding between thiourea and nitro groups [26], a plausible mechanism for the Friedel-Crafts alkylation of indole with β-nitrostyrene in the presence of MIL-101(Cr)@thiourea (3) is illustrated in Scheme 3. Initially, the interaction between β-nitrostyrene and catalyst through the formation of hydrogen bonding is led to electron deficiency in the C=C double bond of β-nitrostyrene. Next, the nucleophilic attack of indole to β-nitrostyrene from C3 carbon atom and subsequent 1,3-H shift are led to the final product.



Scheme 3. Plausible mechanism for the Friedel-Crafts alkylation of indole with *β*-nitrostyrene in the presence of catalyst.

Inspired by the success of reaction mentioned above, and literature reports of catalytic applications of HBD organocatalysts in the biginelli reaction [27, 28], we decided to extend the study to examine the efficiency of using of thiourea-grafted MOF catalyst for the Biginelli reaction (Table S3, ESI†). The best reaction conditions were 30 mg catalyst in ethanol under reflux condition.

With the optimized conditions established, the scope of the reaction was explored with different substrates (Table S4, ESI†). As can be seen, also, in this case, the aromatic aldehyde with electron donor substituent is more reactive than the one with electron-withdrawing groups.

To investigate the heterogeneity of the catalyst, hot filtration test was conducted by removing the catalyst through filtration after ~50% completion of the Friedel-Crafts alkylation of indole with *β*-nitrostyrene under specified optimized conditions. The filtrates were further stirred in the absence of catalyst under the same initial reaction conditions and sampling at different time intervals revealed no considerable progress was achieved after 24 h.

The reusability of catalyst was explored in four consecutive runs of Friedel-Crafts alkylation of indole with *β*-nitrostyrene. Figure S5 (ESI†) represents the catalytic data of reusability experiments, and as can be seen, the activity of the catalyst is retained up to next three runs with a slight decrease in the catalytic performance which can be attributed to the loss of catalyst during the recovery process and somewhat leaching of thiourea moieties from the catalyst in every catalytic run. For further clarification of the leaching phenomenon, CHNS analysis of the fresh and 3rd cycle recovered catalysts were carried out (Table S5, ESI†). Interestingly and unexpectedly, the used catalyst showed higher nitrogen content for the fresh one in contrast to sulfur, which disclosed the deposition of organic components (product or unreacted substrates) in the solid. Therefore, the leaching was obtained on the base of sulfur values in the fresh and used catalyst. On the worth scenario, the amount of leaching was below 6.5 wt.%.

The stability of the corresponding catalyst during the reactions was supported by comparison of the PXRD pattern of the recovered catalyst with the fresh one. Figure S6 (ESI†) demonstrates that no significant changes in the PXRD pattern of recovered catalyst are visible, and the crystalline nature of it is still retained.

The catalytic performance of MIL-101(Cr)@thiourea (3) has been assessed in comparison with other reported heterogeneous HBD organocatalysts in the Friedel-Crafts alkylation (Table S6, ESI†) [29-31]. The results clearly showed that the activity of MIL-101(Cr)@thiourea (3) is comparable or even better to some extent than several reported hydrogen bond donating catalysts due to shorter reaction time. Furthermore, a small amount of catalyst is sufficient enough to promote the reactions, and the catalyst can be recycled up to four runs with easy separation and work-up. To the best of our knowledge, this work is the first report of heterogeneous HBD organocatalyst in the Biginelli reaction. For this reason, the catalytic performance of MIL-101(Cr)@thiourea (3) was compared with homogeneous HBD catalysts and MOF catalytic systems [27, 28, 32-34].

3. Conclusions

In summary, a novel functionally diverse thiourea-grafted MOFs as heterogeneous catalysts were achieved *via* postsynthetic modification process. The complexation of MIL-101(Cr) and pyridine containing thiourea ligands resulted in performance superior to that of the ligand or the parent MOF acting alone in Friedel-Crafts alkylation and biginelli reactions. The synergistic effect observed in these reactions suggests a double Lewis acid-HBD catalysis activation mechanism. Future works could be on the path of chiral HBD organocatalyst grafted MOFs and their application to the asymmetric organic synthesis.

4. Materials and Methods

All reagents were purchased from Sigma-Aldrich and used without further purification. The β-nitrostyrene derivatives were synthesized according to the previously reported method [35]. The FT-IR spectra were recorded on a Bomem MB-Series FT-IR spectrometer. The X-ray powder diffraction (XRD) patterns were recorded on an STOE diffract meter with Cu-Kα radiation (λ = 1.5418 Å). Scanning electron microscopy (SEM) observations were carried out with a Philips XL-30 FESEM electron microscope equipped with an energy-dispersive spectrometer (EDS). All samples were sputtered with gold before the inspection. Thermogravimetric analysis (TGA) was carried out using STA-1500 instrument at a heating rate of 10 °C min^{-1} in the air. Adsorption/desorption isotherm measurement was performed at 77 K (BELSORP-mini II, Japanese). The specific surface areas of the samples were calculated by the Brunauer-Emmett-Teller method in the P/P_0 range of 0.05–0.1. The total pore volume was obtained at the relative pressure (p/p_0) of 0.990 in the isotherm. The ^1H NMR spectra were recorded on a BRUKER DRX-300 AVANCE spectrometer at 300.13 MHz using $CDCl_3$ and DMSO-d_6 as solvents and tetramethylsilane (TMS) as an internal standard. Elemental analysis was performed by an Elementar Analysensysteme GmbH VarioEL.

Acknowledgements

We gratefully acknowledge financial support from Shahid Beheshti University.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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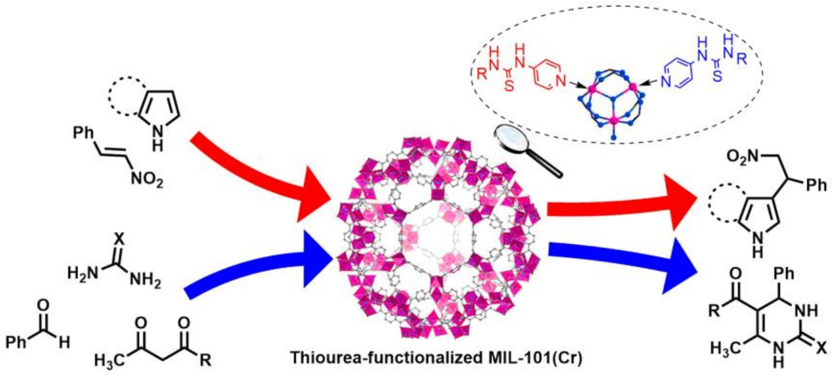

Graphical abstract

Highlights

- Thiourea moieties were homogeneously decorated on MIL-101(Cr).
- The as-decorated MOF was explored as a heterogeneous organocatalyst.
- The catalyst overcomes the essential shortcomings of homogeneous hydrogen-bond-donating catalysts.
- A double Lewis acid-HBD catalysis activation mechanism creates a synergistic effect in the reactions.