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Sulfonic acid-functionalized MIL-101(Cr) as a highly efficient heterogeneous catalyst for one-pot synthesis of 2-amino-4*H*-chromenes in aqueous medium

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Abstract

Sulfonic acid-functionalized MIL-101(Cr) was established to be an active heterogeneous catalyst for one-pot synthesis of 2-amino-4*H*-chromenes *via* three component condensation reaction between resorcinol, malononitrile and a diverse range of aromatic aldehydes in aqueous medium. Here, sulfonation of the parent MIL-101(Cr) has been carried out through a post synthetic modification (PSM) technique. The resulting MIL-101(Cr)-SO₃H has been characterized by employing powder X-ray diffraction, N₂ sorption, FESEM, EDS, FT-IR and TGA studies. Furthermore, the catalyst can easily be recovered and recycled without much change in catalytic activity.

Introduction

Multicomponent reaction (MCR) strategy has been gaining much attention in recent years owing to the growing concerns of the development of new synthetic routes in chemical processes using non toxic reagents, catalysts and solvents. In comparison to the conventional synthetic route, MCR type reactions have shown some advantages like facile one-pot character, high substrate scope, required less reaction time and energy, avoiding intermediate isolation etc. A variety of biologically active heterocyclic compounds like benzoxanthene, benzopyrans and benzochromene have been synthesized by employing this MCR strategy. With its unique characteristics of showing anticancer¹, antibacterial², antimicrobial³, antiviral⁴ and anti-inflammatory⁵ activities benzochromene has found to be an important class of biologically active heterocyclic compound which has also been used as the building block of several human drugs, usually employed for the treatment of neurodegenerative diseases like Parkinson's disease, Alzheimer's disease, Huntington's disease, amyotrophic lateral sclerosis, AIDS associated dementia and Down's syndrome. In addition, these compounds have made a significant contribution in the area of pigments, cosmetics and potential

biodegradable agrochemicals⁶. Therefore synthesis of these compounds has attracted an emerging interest in recent research area.

Reports are available for the synthesis of amino chromene derivative over various lewis acid and base catalyst like NaOH⁷, $K_2CO_3^{8}$, $InCl_3^{9}$, $TiCl_4^{10}$, MgO^{11} , Et_3N^{12} and heteropolyacids. Although these catalysts display a very high activity and selectivity, yet the inherent drawback associated with these catalysts is their recovery and reusability due to their homogeneous character. Therefore, development of heterogeneous catalytic system is always a demandable task for sustainable development of chemical procedures owing to their facile recovery and reusability. A few heterogeneous system have been developed for the synthesis of 2-amino-4H-chromene employing the MCR strategy like triazine functionalized mesoporous organocatalyst (TFMO-1)¹³, nano-sized magnesium oxide, Mg/Al hydrotalcite, nano-structured diphosphate (Na₂CaP₂O₇)¹⁴, tungstic acid functionalized mesoporous SBA-15¹⁵. Moreover, Fe₃O₄@CS-SO₃H NPs has been employed for the synthesis of 2-amino-4H-chromene derivatives¹⁶.

Metal-organic framework has been found to be gaining much importance owing to their potential application in the field of gas storage, separation and catalysis¹⁷⁻²⁰. In the field of heterogeneous catalysis, it plays a promising role because of its high surface area, regular and accessible pores and controllable structures. In particular, metal-organic framework like MIL-101(Cr) is observed to be a suitable candidate for catalysis perspective due to its thermal and chemical robustness²¹, possess coordinatively unsaturated metal sites (CUSs) that can act as a mild Lewis acid²², introduction of functional group through post synthetic modification (PSM) approach can be possible due to its excellent chemical stability. This chemical stability again makes this material a suitable candidate in various important applications²³⁻³⁰. However, in case of ultra-stable MOFs the lack of functional and selective sites inhibits their uses in catalysis. In order to counteract this shortcoming, functionalization of MOFs has been carried out by encapsulating or loading different active sites like heteropoly acid³¹⁻⁴², sulfonic acids into the matrix of MOFs via post-grafting, one-pot synthesis or premodification of organic linker with functionalized ligand^{36,40,43-48}. Among the different functionalized MIL-101(Cr), sulfonic acid functionalized MIL-101(Cr) is evaluated as one of the potential solid acid catalyst⁴⁹ for various important organic transformations^{46,47,49-53}. As the mentioned chemical transformation is basically an acid catalyzed reaction, therefore we adopt a protocol of synthesizing 2-amino-4H-chromene through three component condensation reaction between resorcinol, aromatic aldehyde and malononitrile in aqueous medium utilizing MIL-101(Cr)-SO₃H as solid acid catalyst. Herein we synthesized MIL-101(Cr)-SO₃H by using a

post synthetic modification approach⁵⁴ and the material has been thoroughly characterized by PXRD, FE-SEM, XPS, N_2 sorption, FT-IR and TGA studies. The catalyst shows excellent catalytic activity in short reaction time and can be recycled up to forth catalytic cycles without much change in catalytic activity.

Experimental

Synthesis of MIL-101(Cr)

MIL-101(Cr) was prepared according to the reported method by Férey et al²¹. In a typical synthesis, a mixture of 3 mmol of $Cr(NO_3)_3 \cdot 9H_2O$, 3 mmol of terephthalic acid (H₂bdc) and 0.6 ml of 5 M HF (3 mmol) is undergo hydrothermal treatment in 15 ml H₂O at 220°C for 8 h in a Teflon-lined autoclave bomb. After equilibration at ambient temperature, the resulting Cr-MIL-101 solid was filtered to remove the unreacted colourless crystals of H₂bdc and purified by double treatment with DMF at 60 °C for 3 h and then triple treatment with ethanol at 70 °C for 2.5 h. Finally the green solid was separated by centrifugation, dried in an air oven at 70 °C overnight and kept it in a vacuum desiccator.

Synthesis of MIL-101(Cr)-SO₃H

1 g of activated MIL-101(Cr) was stirred in 30 ml of dichloromethane at 0 °C for 20 minutes. Then 0.3 g of CISO₃H taken in 10 ml dichloromethane was added drop-wise to the mixture under continuous magnetic stirring. After 30 minutes, the solid product was separated through filtration, washed it with distilled water and acetone, soaked in ethanol for 24 h at 70 °C. The resultant material was then separated by centrifugation and dried under vacuum. The S content of the synthesized MIL-101(Cr)-SO₃H was found to be 0.13 mmol g⁻¹.

General procedure for the synthesis of 2-amino-4H-chromenes

A mixture of aromatic aldehyde (1 mmol), resorcinol (1 mmol) and malononitrile (1 mmol) was reflux in water for the certain period of time in presence of MIL-101(Cr)-SO₃H (0.37 mol %). The progress of the reaction was monitored through TLC. After completion of the reaction, the reaction mixture was allowed to cool to room temperature, added 10 ml ethylacetate to the mixture and stirring for 45 minutes. The catalyst was then separated through filtration, washed it with acetone by several times and then dried. The filtrate was washed with water and dried over anhydrous Na_2SO_4 and solvent was evaporated in rotavapor. The crude product was further purified by re-crystallization in ethanol to afford pure 2-amino-4H-chromenes. The products were characterized by (¹H, ¹³C) NMR spectroscopy and all give satisfactory results (ESI).

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Result and discussion

MIL-101(Cr)-SO₃H has been synthesized by employing a post synthetic modification route involving the sulfonation of the MIL-101(Cr) framework with chlorosulfonic acid in dichloromethane. No apparent modification in the crystallinity of the parent MIL-101(Cr) has been observed after sulfonation of the frameworks with chlorosulfonic acid as indicated by the PXRD pattern of MIL-101(Cr)-SO₃H (Fig. 1(black)).The pattern matches well with the patterns of the precursor MIL-101(Cr) (Fig. 1 (red)) with slight changes of the intensities, indicating the preservation of the structure of MIL-101(Cr) after inserting the sulfonic acid group onto the framework. FT-IR spectra of MIL-101(Cr)-SO₃H (Fig. S1(b), ESI) with its unfunctionalized counterpart was shown in (Fig. S1(a), ESI). The successful functionalization of MIL-101(Cr) with the acid moiety was well represented by the presence of new vibrational band at 1129 and 1287 cm⁻¹ along with a shoulder at 1426 cm⁻¹ which can be assigned to the O=S=O symmetric and asymmetric stretching mode of vibration⁵⁵. The other vibrational bands around 1400-1600 cm⁻¹ could be attributed to the framework (O-C-O)- groups, establishing the presence of dicarboxylate within MIL-101(Cr).

 N_2 physisorption analysis (Fig. 2) of both the bare (Fig. 2(a)) and acid functionalized MIL-101(Cr) (Fig. 2(b)) has been carried out at 77k. MOF-101(Cr)-SO₃H exhibits a similar typical Type-I isotherm to that of the parent MIL-101(Cr). However, an appreciable decrease in surface area and pore volume from 2787 m²g⁻¹ and 1.58 cm³g⁻¹ to 2206 m²g⁻¹ and 1.27 cm³g⁻¹ has been observed for the functionalized MOF due to the partial blockage of cavities of the parent MOF by the sulfonic acid groups.

FE-SEM images (Fig. S2, ESI) illustrate the preservation of the characteristic cubic symmetry of MIL-101(Cr) after incorporating the acid moiety into the mesocages. Energy-dispersive x-ray spectroscopy (EDS) (Fig. 3) analysis confirms the successful incorporation of $-SO_3H$ group into the framework while the elemental mapping of Cr, S, O elements of MIL-101(Cr)-SO₃H clearly demonstrate that $-SO_3H$ group is well distributed into the cages of MIL-101(Cr). XPS spectrum (Fig. 4) also shows a good agreement with this result, exhibit a typical S2p band (Fig. 4 (c)) at 168.2 eV corresponding to $-SO_3H$ group anchored with the linkers of the parent MOF. Furthermore, no change in the peak position has been observed with respect to the other elements present in the bare MIL-101(Cr) (Fig. 4(b)), establishing the conservation of the integrity of MIL-101(Cr) after the post synthetic modification.

The thermal stability of MIL-101(Cr)-SO₃H (Fig. S3(a), ESI) was analyzed through thermogravimetric analysis (TGA), operated in the temperature range from room temperature

to 800 °C with a heating rate of 10 °C min⁻¹ under N₂ atmosphere. The first weight loss of 11.56 % appeared below 150 °C is due to the loss of adsorbed water on MIL-101(Cr)-SO₃H. The second weight loss of 7.77 % appeared between 150 - 350 °C, may be attributed to the decomposition of sulfonic acid moiety anchored within the cages of MIL-101(Cr). The third weight loss step of 44.73 % is due to the decomposition of MIL-101(Cr) framework. In addition, another weight loss step of 10.1 % has been observed above 550 °C, establishing the decomposition of chromium sulphate⁵⁶.

We have estimated the loading of $-SO_3H$ group on to the framework of MIL-101(Cr) by adopting a back titration method involving the addition of a standard NaOH solution (0.01 N) to a known quantity of MIL-101(Cr)-SO₃H. After treating with NaOH, it has been assumed that all the $-SO_3H$ groups are converted into $-SO_3^-$ Na⁺ form and the excess NaOH left in the solution is allowed to titrated with a known strength of oxalic acid (0.01 N). From the titrametric experiment it may easily be estimated the exact amount of NaOH consumed during the titration or the equivalent amount of $-SO_3H$ group attached with the linkers of MIL-101(Cr). The result shows that 1 g of MIL-101(Cr)-SO₃H contains 0.15 mmol $-SO_3H$ group.

We have explored the catalytic activity of the synthesized MIL-101(Cr)-SO₃H in a three component condensation reaction between aromatic aldehydes, resorcinol and malononitrile in an aqueous medium. In presence of bare MIL-101(Cr), a low yield of desired product was formed confirming the need of strong acid moiety on the framework structure to perform the condensation reaction. The effect of different dosage of the catalyst on the mentioned condensation reaction has been monitored by taking the condensation between benzaldehyde, resorcinol and malononitrile as a model reaction. From the result (Table 1) it was observed that with increase in the mol% of the catalyst (Entry1, 2 table 1), the yield of the product increases with the maximum yield of 82 % was obtained when the reaction was carried out with 0.37 mol% catalyst (Entry 3, table 1). This may be due to the increase in the number of active sites on the catalyst with increase in catalyst dosage. No significant increase in product yield was obtained with further increase in the mol% of the catalyst (Entry 4, table1), therefore, 0.37 mol% catalyst has been considered as the optimum catalyst amount to conduct the three component condensation reaction.

The solvent effect on the condensation reaction between benzaldehyde, resorcinol and malononitrile has been studied by carry out the reaction in various types of solvents exhibit different polarities under reflux condition. From the result (Table S1, ESI) it has been concluded that the desired product formation in polar protic solvents like ethanol, methanol

and water (Entry1, 2, 4, table S1, ESI) was found to much higher than that of the polar aprotic solvent like acetonitrile, THF, DCM, (Entry 3, 5, 6, table S1, ESI) where we have observed the knoevenagel condensation adduct as the major product. This behaviour may be attributed to the more polar character of the product to that of reactant molecules. However, under solvent free condition (Entry 7, table S1, ESI) the desired product yield was found to be low that clearly demonstrate that water is the suitable solvent (Entry 4, table S1, ESI) for carrying out the three component condensation reaction that furnish the highest yield of the product under the optimized condition.

The influence of the temperature on the one pot three component condensation reaction between benzaldehyde, resorcinol and malononitrile has been invested (Table 2). The results show that at room temperature the reaction cannot proceed even running the reaction for 12 h, while with increase in temperature (Entry 2, 3 and 4, table 2) the amount of desired product increases with a maximum yield 82 % was obtained at 100 °C (Entry 5, table 2). We have also found a very low yield of the desired product in the absence of catalyst at 100 °C, owing to the thermal condensation reaction at higher temperature. Therefore, taking all these aspects we have chosen 100 °C as the optimum temperature to carry out the further studies.

The substrate scope of the catalyst has been examined by employing various aromatic aldehydes containing electron-withdrawing, electron donating substituents. The results are summarized in table 3. It has been observed that MIL-101(Cr)-SO₃H is very active to all kind of aromatic aldehydes. In fact, we do not observe any pronounced substituent effect attached to the phenyl ring over the reaction as both the electron withdrawing (Entry 8-10, table 3) and donating groups (Entry 2-7, table 3) show the condensation reaction with almost equal efficiencies. However, *ortho* substituted aldehydes display a lower yield of product as compared to its *meta* and *para* analogues, may be ascribed to the electronic effect. In addition, the heteroaromatic aldehydes like pyridine-2-carbaldehyde (Entry 11, table 3) furan-2-carbaldehyde (Entry 12, table 3) are also quite compatible with this present catalytic system. Overall MIL-101(Cr)-SO₃H has been established to be a highly flexible catalyst for the proposed one-pot three component condensation reaction.

The efficiency of the present catalytic system has been examined by taking the condensation reaction between 4-chlorobenzaldehyde, resorcinol and malononitrile as the representative case. From the results (shown in table S2, ESI) it has been observed that most of the catalysts available in the literature are homogeneous in nature that displays the basic shortcoming of their recovery and reusability. The prime advantages of our protocol are high

product yield %, facile recovery and reusability, low catalyst dosage, high TON etc. Furthermore, the high surface area of the material provides a better dispersion of catalytically active sites that actually increases the yield of the product.

A plausible reaction mechanism has been proposed based on the available literature and our experimental data. Actually, the reaction was proceed through Knoevenagel condensation reaction between aromatic aldehyde and malononitrile followed by Michael addition of resorcinol with the Knoevenagel product ((I) scheme1). The final step of the reaction is an intra-molecular cyclization ((II) scheme 1) and tautumerization to afford the desired 2-amino-4*H*-chromenes ((III) scheme 1). The catalyst MIL-101(Cr)-SO₃H containing the acid sites increases the electrophilicity of the aldehydic carbon which undergo dehydration to give the Knoevenagel product. The Cr (III) sites presented in the parent MOF may increase the electrophilicity of the –CN group of the Knoevenagel product to facilitate the Michael addition which subsequently undergoes intra-molecular cyclization and tautomerization to yield the 2-amino-4*H*-chromene derivative.

The heterogeneous nature of MIL-101(Cr)-SO₃H was examined by performing a hot filtration test involving the reaction between benzaldehyde, resorcinol and malononitrile under the optimized reaction condition. After 1h of the reaction the catalyst was removed from the reaction mixture by filtration (product yield 40 %) and allowed the reaction to proceed with the filtrate for further 2 h. No increase in the product yield beyond 40 % was observed after 2 h reaction time. This result clearly confirms the heterogeneous nature of MIL-101(Cr)-SO₃H during the course of the reaction.

The reusability of the catalyst was monitored by taking the condensation reaction between benzaldehyde, resorcinol and malononitrile as the model reaction. After completion of the reaction the catalyst was recovered from the reaction mixture through filtration, washed it with acetone for several times and then dried in an oven at 70 °C for 3 h. The activated MIL-101(Cr)-SO₃H was then subsequently employed for the next catalytic run under identical condition. The results (Fig. 5) show that the catalyst can perform effectively up to fifth catalytic cycle without any significant loss of its catalytic activity. The crystallinity of the recovered catalyst is well maintained as indicated by the PXRD analysis (Fig. 1(blue)). FT-IR analysis (Fig. S1(c)) also shows a good agreement with the PXRD results. The vibrational bands corresponding to the bare MIL-101(Cr) is well preserved in the recovered catalyst. FE-SEM image of the recovered catalyst (Fig. S2 (c)) clearly demonstrate the preservation of the integrity of the parent MOF. We have calculated the S content of the recovered catalyst and it was found to be 0.10 mmol g⁻¹. All these results strongly

recommend that a heterogeneous process was involved in the mentioned organic transformation and also establishing the chemical robustness of the catalyst.

Conclusions

In summary, sulfonic acid functionalized MIL-101(Cr) have been synthesized by adopting a post synthetic modification technique using chlorosulfonic acid as sulfonation reagent. The synthesized MIL-101(Cr)-SO₃H exhibits a high surface area and acidity and thus can be effectively employed as a heterogeneous catalyst for one-pot three component condensation reaction between aromatic aldehydes, resorcinol and malononitrile in aqueous medium to synthesize 2-amino-4*H*-chromenes. Furthermore, the catalyst can easily be recovered and reused without any significant loss of its catalytic activity. Therefore, considering all these aspects it can be concluded that MIL-101(Cr)-SO₃H acts as a potent heterogeneous catalyst for this chemical transformation and also established its potential utility as acid catalyst for various liquid phase important organic transformations.

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Captions

Fig1 PXRD patterns of MIL-101(Cr) (red), MIL-101(Cr)-SO₃H and recovered MIL-101(Cr)-SO₃H (blue)

Fig 2 N₂ adsorption isotherm of (a) MIL-101(Cr), (b) MIL-101(Cr)-SO₃H

Fig 3 a) EDS analysis of MIL-101(Cr)-SO₃H, b) mapping of different elements of MIL-101(Cr)-SO₃H

Fig 4 XPS spectra of (a) MIL-101(Cr)-SO₃H, (b) MIL-101(Cr) and (c) S2p band of -SO₃H group

Fig 5 Catalyst recycling test for MIL-101(Cr)-SO₃H

Table1 Effect of catalyst amount

 Table 2 Effect of temperature

Table 3 MIL-101(Cr)-SO₃H catalyzed one- pot three component condensation reactions with different aromatic aldehydes

Scheme1 Plausible reaction mechanism for the condensation reaction between aromatic aldehyde, resorcinol and malononitrile in the presence of $MIL-101(Cr)-SO_3H$

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Fig. 1 PXRD pattern of MIL-101(Cr) (red), MIL-101(Cr)-SO₃H (black) and recovered MIL-101(Cr)-SO₃H (blue)



Fig. 2 N₂ adsorption isotherm of (a) MIL-101(Cr), (b) MIL-101(Cr)-SO₃H



Fig. 3 a) EDS analysis of MIL-101(Cr)-SO₃H, b) mapping of different elements of MIL-101(Cr)-SO₃H



Fig. 4 XPS spectra of (a) MIL-101(Cr)-SO₃H, (b) MIL-101(Cr) and (c) S2p band of -SO₃H group



Fig. 5 Catalyst recycling test for MIL-101(Cr)-SO₃H

Table1 Effect of catalyst amount^a

| Entry | Catalyst amount (mol%) | Yield $(\%)^{b}$ |
|-------|------------------------|------------------|
| 1 | 0.15 | 48 |
| 2 | 0.23 | 62 |
| 3 | 0.37 | 82 |
| 4 | 0.45 | 83 |

^aReaction conditions: benzaldehyde (1 mmol), resorcinol (1 mmol) and malononitrile (1 mmol), water= 5 ml, temperature= 100°C, time =3h ^b Isolated yields are based on benzaldehyde

Table 2 Effect of temperature^a

| Entry | Temperature (°C) | Yield(%) ^b |
|-------------|------------------|-----------------------|
| 1 | Room temperature | No desired product |
| 2 | 40 | 20 |
| 3 | 65 | 45 |
| 4 | 85 | 68 |
| $5^{\rm c}$ | 100 | 82 |

^aRecation condition: benzaldehyde (1 mmol), resorcinol (1 mmol) and malononitrile (1 mmol), time =3h

^b Isolated yields are based on benzaldehyde, ^cWithout catalyst at 100°C yield= 6%

Table 3 MIL-101(Cr)-SO₃H catalyzed one- pot three component condensation reactions with different aromatic aldehydes a

| $R = \frac{1}{1} + \frac{NC}{NC} + \frac{NC}{HO} + \frac{MIL-101(Cr)-SO_3H}{HO} + \frac{MIL-101(Cr)-SO_3H}{HO} + \frac{CN}{HO} + \frac{CN}{2}$ | | | | | | | |
|--|------------------------|----------|---------|------------------------|--|--|--|
| Entry | Aromatic aldehydes | Time (h) | Product | Yield (%) ^b | | | |
| 1 | СНО | 3 | 2a | 82 | | | |
| 2 | СІ— | 7 | 2b | 76 | | | |
| 3 | Br-CHO | 7 | 2c | 78 | | | |
| 4 | Н ₃ С-СНО | 4 | 2d | 80 | | | |
| 5 | Н ₃ СО-СНО | 4.5 | 2e | 78 | | | |
| 6 | но-Сно | 3.5 | 2f | 80 | | | |
| 7 | НО СНО | 3.5 | 2g | 76 | | | |
| 8 | О2N-СНО | 3 | 2h | 81 | | | |
| 9 | СНО NO ₂ | 4 | 2i | 74 | | | |
| 10 | O ₂ N CHO | 3.5 | 2j | 77 | | | |
| 11 | СНО | 6 | 2k | 72 | | | |
| 12 | СНО | 7 | 21 | 70 | | | |

^aReaction conditions: aromatic aldehydes (1mmol), resorcinol (1 mmol), malononitrile(1 mmol), water=5 ml, MIL-101(Cr)-SO₃H (0.37 mol%). ^bIsolated yields are based on aromatic aldehydes. All compounds have been characterized by ¹H and ¹³C NMR (available in the ESI)



Scheme1 Plausible reaction mechanism for the condensation reaction between aromatic aldehyde, resorcinol and malononitrile in the presence of MIL-101(Cr)-SO₃H

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MIL-101(Cr)-SO₃H was found to be an active heterogeneous catalyst for one-pot synthesis of 2-amino-4H-chromenes in aqueous medium.

