FULL PAPER

Terbium–organic framework as heterogeneous Lewis acid catalyst for β -aminoalcohol synthesis: Efficient, reusable and green catalytic method

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1 | INTRODUCTION

Metal-organic frameworks (MOFs) are a class of highly tunable hybrid materials composed of metal ions that are linked by organic bridges. The flexibility with which these components can be varied has led to an extensive class of MOF structures with potential applications in many areas, including gas storage, molecular sensing and catalysis.^[1] Currently, the use of MOFs as catalysts is attracting increasing attention as one of the hot topics in catalysis research owing to their design versatility, porous structure, high surface area and easy pre- and post-modification.^[2] Several strategies have been presented in the literature for the introduction of catalytically active sites to MOFs.^[3] According to the catalytically active sites, these frameworks may be categorized into four distinct groups, namely MOFs with coordinatively unsaturated metal sites (group I), MOFs with metalloligands (group II), MOFs with catalytically active centres at the organic linkers (group III) and MOFs as support materials, which are used for immobilization of an active component in the form of nanoparticles or clusters inside the pores of the material (group IV).^[4] Among these,

A terbium–organic framework (Tb-MOF) was prepared using a previously reported procedure. Tb-MOF was characterized using Fourier transform infrared spectroscopy, scanning electron microscopy, powder X-ray diffraction and surface area analysis. Tb-MOF was employed as a heterogeneous Lewis acid catalyst for the synthesis of β -aminoalcohols. Also, the effect of ultrasonic irradiation was examined in the catalytic aminolysis of styrene oxide. The reaction conditions were optimized by variation of reaction time, catalyst concentration and solvent. A variety of β -aminoalcohols were synthesized and characterized. The Tb-MOF catalyst showed excellent selectivity and high yield for these transformations.

KEYWORDS

heterogeneous catalysis, metal-organic framework

particularly potent candidates for catalysis are MOFs with coordinatively unsaturated metal sites where substrate activation in catalytic reactions takes place at coordinatively unsaturated framework metals. Such active sites are, in general, occupied by solvent molecules that can be removed by an activation process before catalytic reaction. In this case, MOFs can act as heterogeneous Lewis acid catalysts because of the Lewis acidity of the metal centres which can activate organic molecules via metal-organic interactions in catalysis. Cu-HKUST-1, Cr-MIL-101 and Mg-MOF-74 represent the most well-known examples of MOFs with open metal sites, which have demonstrated a potential for catalytic activities.^[5] Recently, lanthanide MOFs (Ln-MOFs) have received considerable attention due to their intriguing topological structures and exceptional optical and magnetic properties.^[4] Although Ln-MOFs are expected to be potential heterogeneous Lewis acid catalysts, only a few reactions including epoxidation of olefins, oxidation of organic sulfurs and acetalization of aldehydes catalysed by Ln-MOFs have been reported.^[6] In this regard, we are interested in exploring the potential of Ln-MOFs as catalysts for organic transformations.

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Recently Xu and co-workers reported a series of isostructural Ln-MOFs (Ln = Tb, Dy, Er, Yb) of the general $Ln(BTC)(H_2O)_3(DMF)_{1,1}$ (BTC = 1.3.5formula benzenetricarboxylate; DMF = N,N-dimethylformamide), which showed high thermal and chemical stability.^[6] These compounds were solvothermally obtained and their structures determined using X-ray crystallography. According to the reported procedure, reaction between terbium(III) nitrate hexahydrate and BTC in mixed solvents of DMF and water inside a Teflon-lined autoclave at 105°C for 24 h yielded $Tb(BTC)(H_2O)_3(DMF)_{1,1}$, which was characterized using powder X-ray diffraction (PXRD), Fourier transform infrared (FT-IR) spectroscopy and surface area analysis. The Tb(III) coordination environment can be considered as a distorted pentagonal bipyramidal geometry formed by six oxygen atoms from six carboxylate groups of six BTC ligands and one oxygen atom from the terminal water molecule. The open terbium sites are generated during the activation process (330°C for 4 h) as result of the removal of coordinated water and DMF molecules, trapped in pores, that remain after the MOF synthesis. The high thermal stability, accessible open metal sites and nano-sized aperture for the Tb-MOF could endow it with a very high potential in catalysis.

Epoxides are some of the most important synthetic intermediates in organic synthesis and a variety of reagents are known to nucleophilically open the epoxide ring.^[7] β -Aminoalcohols are versatile synthons for a wide range of

biologically active natural and synthetic products, non-natural amino acids and chiral auxiliaries.^[8] Therefore, there is a significant interest in the development of environmentally friendly and sustainable methods for the ring opening of epoxides. In most cases, the synthetic methods involve heating an epoxide in a protic solvent with excess amine. The non-catalytic aminolysis procedure is satisfactory in many cases. However, it suffers from many disadvantages, including the use of high temperatures or prolonged reaction times.^[9] Several modifications of the classical procedures have been reported to overcome these limitations and a variety of catalytic systems such as LiClO₄, Zn(OTf)₂,^[10] $LiBF_4$, $CaCl_2$,^[11] LiOTf,^[12] $CoCl_2$,^[13] $Ln(OTf)_3$ (Ln = Yb, Nd, Gd),^[14] ZrCl₄,^[15] VCl₃,^[16] SmCl₃,^[17] Cu(OTf)₂,^[18] Sn(OTf)₂,^[19] [(CH₃)₂CHO]₂AlOOCCF₃,^[20] CeCl₃·7H₂O-Nal,^[21] Bi(OTf)₃ and Bi(TFA)₃ under microwave irradiation,^[22] alumina,^[23] silica under high pressure,^[24] montmorillonite clay under microwave irradiation,^[25] titania-iron(III) oxide^[26] and Fe(III)-salen grafted SBA-15^[27] have been used in this regard. Although significant advances have been made in this area within the past few years, low regioselectivity, longer reaction time, use of elevated temperature, high catalyst loading, toxic solvents and lower substrate compatibility limit their applications. Thus there is a need to develop an efficient catalytic protocol for ring opening of various epoxides with aliphatic and aromatic amines under ambient conditions.

TABLE 1 Optimization of reaction of epoxy and amine, at room temperature and under ultrasonic condition

Entry	Catalyst (mg)	Condition	Time (min)	Temperature (°C)	Yield (%)
1	20	Solvent free	30	RT	<5
2	20	H ₂ O	30	RT	50
3	20	MeOH	30	RT	60
4	20	Toluene	30	RT	ND
5	20	<i>n</i> -Hexane	30	RT	ND
6	20	Acetonitrile	30	RT	ND
7	20	EtOH	30	RT	80
8	10	EtOH	30	RT	45
9	40	EtOH	30	RT	80
10	60	EtOH	30	RT	77
11	20	EtOH	60	RT	85
12	20	EtOH	60	40	84
13	20	EtOH	60	60	86
14	20	EtOH	60	Reflux temperature	85
15	20	EtOH	60	RT (ultrasonic irradiation)	85
16	20	EtOH	60	40 (ultrasonic irradiation)	86
17	20	EtOH	60	80 (ultrasonic orradiation)	85
18	20	EtOH	90	RT (ultrasonic irradiation)	95

2 | EXPERIMENTAL

2.1 | General

All materials were purchased from Merck and used without further purification. The reactions were precisely monitored using analytical TLC with ethyl acetate and *n*-hexane as eluents. Due to the need to achieve final pure and isolated target molecules, a scaled-up TLC was conducted with Merck 0.2 mm silica gel 60F-254 Al-plates. FT-IR spectral analysis was performed with a Shimadzu FT-IR-8400S spectrometer and definite characterization of all novel products was done with ¹H NMR (500 MHz) and ¹³C NMR (125 MHz) spectra recorded with а Bruker **DRX-500** Avance spectrometer using dimethylsulfoxide as solvent at ambient temperature (relative to tetramethylsilane as internal standard). All yields referred to the isolated products. Scanning electron microscopy (SEM) images were obtained with a Zeiss-Sigma VP 500. Primary results for progress of reactions were obtained using GC on an ECHROM A 90 with toluene as general solvent for injection and nitrogen as inert carrier gas.

2.2 | Preparation of Tb-MOF

TB-MOF was synthesized according to a reported procedure.^[6] A mixture of Tb(NO₃)₃·6H₂O (0.5 mmol), benzene-1,3,5-tricarboxylic acid (0.25 mmol), DMF (4 ml) and water (4 ml) was sealed in a 20 ml Teflon-lined reactor. Pure colourless needle crystals of Tb(BTC)(H₂O)(DMF)_{1,1} with a yield of 45% were obtained after 24 h of heating at 105°C. Anal. Calcd for Tb(BTC)(H₂O)(DMF)_{1.1} (%): C, 31.25; H, 2.71; N, 3.26. Found (%): C, 31.22; H, 2.62; N, 3.30. FT-IR (cm⁻¹): 1611 m, 1572 w, 1536 w, 1433 m, 1372 s, 1103 w, 939 w, 770 s, 714 m, 702 vs, 666 m, 563 s, 455 s, 434 m, 417 w. For the purpose of activation, according to the thermogravimetric analysis pattern, when Tb-MOF was heated to 330°C for 4 h, the coordinating DMF molecules began to be removed, and the compound retained its stability up to temperatures of 450°C. Anal. Calcd for Tb(BTC)(H₂O)(DMF)_{1,1}(%): C, 28.87; H, 0.81. Found (%): C, 28.78; H, 0.93. FT-IR (cm⁻¹): 1611 m, 1572 w, 1536 w, 1433 m, 1372 s, 1103 w, 939 w, 770 s, 714 m, 702 vs, 666 m, 563 s, 455 s, 434 m, 417 w.

2.3 | General procedure for preparation of β-Aminoalcohols

For optimization of the reaction conditions, a specified amount of Tb-MOF was added to a mixture of aniline and styrene oxide in an ultrasonic water bath for different periods of time (Table 1).^[5,11] The progress of the reaction was monitored using TLC. After completion of the reaction, the catalyst was separated by centrifuging and the products were purified by nonflash chromatography of the reaction mixture via silica plate. In order to understand the scope and limitations of this catalytic methodology, various amines were treated with styrene oxide under optimized conditions in the presence of Tb-MOF. The reaction was found to be fast and nearly complete conversion was obtained within 15–30 min, leading to

TABLE 2	Application of Tb-MOF for synthesis of β -aminoalcohols
under optimi	zed reaction conditions

Entry	Oxirane	Amine	Yield (%)
1		NH ₂	95
2		CH3	90
3		NH2	80
4		O ₂ N NH ₂	60
5			75
6			75
7			80
8		Ph M Ph	65
9		NH ₂	70
10	\checkmark	NH ₂	65
11		NH ₂	65
12		H ₂ N	85



FIGURE 1 Representation of the pores of terbium metal–organic framework

the quantitative yield of the corresponding 2-aminoalcohols (Table 2). FT-IR, ¹H NMR and ¹³C NMR data for selected compounds are summarized below.

2.3.1 | 1-(*N*-Phenyl)amino-3-phenoxy-2propanol (11)

FT-IR (KBr (liquid film), ν_{max} , cm⁻¹): 3395, 2924, 2858, 1595, 1496, 1397, 1242, 1098, 1040. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 7.37–7.13 (4H, m, Ph), 7.07–6.86 (3H, m, Ph), 6.81–6.67 (3H, m, Ph), 4.32–4.21 (1H, m, CH–OH),



FIGURE 3 Nitrogen adsorption and desorption isotherms for Tb-MOF at 77 K

4.05–3.95 (2H, m, OCH₂), 3.67–3.52 (2H, m, OH, NH), 3.43–3.24 (2H, m, CH₂N). ¹³C NMR (300 MHz, CDCl₃, δ , ppm): 161.2, 149.6, 131.0, 131.2, 122.1, 119.1, 117.3, 114.3, 71.8, 69.5, 48.6.

2.3.2 | 1-(*N*-4-Methoxyphenyl)amino-3phenoxy-2-propanol (12)

FT-IR (KBr, ν_{max} , cm⁻¹): 3413, 2924, 2859, 1596, 1496, 1450, 1395, 1242, 1182, 1098, 1040. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 7.38–7.26 (2H, m, Ph), 7.06–6.91 (3H, m, Ph), 6.81 (2H, d, Ph), 6.71 (2H, d, Ph), 4.28 (1H, s, CH–OH), 4.09–4.03 (2H, m, OCH₂), 3.79 (3H, s, OCH₃), 3.62 (2H, s, NH, OH), 3.43–3.35 (1H, m, CH₂N), 3.27–3.23 (1H, m, CH₂N). ¹³C NMR (300 MHz, CDCl₃, δ , ppm): 191.2, 151.5, 142.7, 131.4, 122.1, 116.8, 116.7, 116.2, 68.8, 67.4, 56.5, 48.7.



FIGURE 2 PXRD patterns of Tb-MOF: simulated, as-synthesized, after catalytic reaction and after recycling (10 times)

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3 | RESULTS AND DISCUSSION

3.1 | Characterization of Tb-MOF

Tb-MOF was synthesized and then characterized using various techniques (Figure 1). FT-IR spectroscopy, elemental analysis and PXRD confirmed the formation of $Tb(BTC)(H_2O)(DMF)_{1,1}$ (Figure 2). The MOF was activated at 330°C under vacuum for 4 h to remove any residual and coordinated solvent molecules. The activation of this framework was confirmed from FT-IR spectra, elemental analysis and PXRD analysis (Figure 2). Also, the BET surface area of the activated Tb-MOF was determined as 582 $m^2 g^{-1}$ (Figure 3). which is comparable to the reported surface area.^[8] The morphology of Tb-MOF prepared by the solvothermal method was characterized using field emission FE-SEM before and after catalytic reaction. As illustrated in Figure 4, the retention of morphology during the transformation suggests considerable stability, which is necessary for performing a reaction in the presence of a heterogeneous catalyst. The high thermal stability, accessible open metal sites and nano-sized aperture of Tb-MOF could endow it with a very high potential in catalysis.

3.2 | Application of Tb-MOF for synthesis of β-Aminoalcohols

Tb-MOF was investigated as a heterogeneous Lewis acid catalyst for the synthesis of β -aminoalcohols. To a mixture of epoxide (1 mmol) and amine (1 mmol) in water (3 ml), Tb-MOF was added (Scheme 1). The reaction mixture was



SCHEME 1 Synthesis of β -aminoalcohols catalysed by Tb-MOF

stirred at room temperature under ultrasonic irradiation and monitored by TLC.

After completion of the reaction, the catalyst was easily separated by centrifugation. To find the optimal reaction conditions, various conditions were investigated. The reaction was optimized by variation of the reaction time, temperature, reaction solvent and catalyst concentration (Table 1). Also, the PXRD pattern of Tb-MOF after the catalytic reaction indicates that the framework remains intact (Figure 2). as supported by the good agreement between the FT-IR measurements before and after the reaction. Various solvents were investigated for this reaction. Ethanol improved the yield of the conversion compared to CH₃OH, CH₃CN, H₂O and CHCl₃. Notably, the yield of the transformation increases when the reaction temperature is increased to 90 from 30°C and when the time is increased (Table 1, entries 7, 12, 13 and 14). The reaction proceeded rapidly, and it was completed after 90 min at room temperature (Table 1, entry 18). The reaction was carried out in the presence of 10, 20, 40 and 60 mg of Tb-MOF, resulting in the isolation of the product in yields of 45, 80, 80 and 77%, respectively. It should be pointed out that, in the absence of catalyst, the reaction was very slow, and even after a prolonged reaction time considerable amounts of starting materials remained unreacted (yield <10%). After finding the optimized reaction conditions we continued our investigation by reacting a series



FIGURE 4 SEM analysis of Tb-MOF particles (a) before and (b) after reaction

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of amines with styrene oxide (Table 2).^[5,6,8,11] Various amines were used as substrates in the reaction. The observed catalytic changes have been correlated to steric and electronic factors. Amines with electron-withdrawing groups and with steric hindrance were less reactive, whereas amines with electron-donating groups promote the transformation in high



FIGURE 5 FT-IR spectrum of activated Tb-MOF after adsorption of pyridine and followed by evacuation at room temperature



FIGURE 6 Loss of activity as a function of the number of recycles of Tb-MOF for the synthesis of β -aminoalcohol

yield (Table 2). The *in situ* FT-IR spectrum after adsorption of pyridine shows three bands at 1018, 1110 and 1226 cm⁻¹ (Figure 5), which are assigned to the pyridine chemisorbed on Tb³⁺ Lewis acid sites of Tb-MOF.^[28] Considering that the molar absorption coefficient of Tb-MOF at around 1110 cm⁻¹ is 1.58 cm μ mol⁻¹ determined by adsorption of calibrated doses of pyridine, the concentration of the Lewis acid sites in the currently synthesized Tb-MOF can be quantified as about 38% of the total number of Tb atoms contained in this framework.

3.3 | Catalyst reusability

From an industrial point of view, the reusability of a catalyst is important for large-scale operation. Therefore, the reusability of the catalyst was examined in the reaction of styrene oxide and amine. The catalyst can be separated from the reaction medium by centrifuging; therefore it could be recovered simply by centrifugation followed by washing with ethanol and drying at 50°C. Afterwards, the catalyst can be weighed and used directly in the next cycle of the reaction using fresh substrates. The results showed that the catalyst could be reused ten times without appreciable loss of activity (Figure 6). Further investigation of the heterogeneous character of the catalytic system as well as of the stability of the structure was carried out using a hot filtration test. After 2 h of sonication, the reaction mixture was centrifuged and the catalyst was filtered off. Then, the supernatant was sonicated at room temperature. Interestingly, within 4 h of further reaction time, no distinguishable changes were recognized in the reaction conversion. Also, the PXRD pattern of Tb-MOF indicates that the framework remains intact after the catalytic reaction, as supported by the good agreement between the FT-IR measurements before and after the reaction. In comparison with other reported catalytic systems for the aminolysis of epoxides, Tb-MOF showed good catalytic performance in terms of activity and reusability (Table 3).

TABLE 3 Performance of some reported catalytic systems for aminolysis of epoxides

Yield (%)	Ref.	Amount (mg)	Temperature (°C)	Time (min)	Solvent	Catalyst
92	[29]	20	RT	45	_	nano Fe(OH) ₃
82	[30]	10	RT	180	EtOH	Fe ₃ O ₄ @SiO ₂ -SO ₃ H
69	[23]	6000	Reflux	360	THF	Al_2O_3
88 ^a	[31]		60	480	H ₂ O	β-Cyclodextrin
98	[8]	5 mol%	RT	300	_	LiBr
96	[22]	0.05 mol%	Microwave oven	0.33	CH ₃ CN	Bi(OTf) ₃
88	[7]		RT	180	Cyclohexane	Polymer/CuSO ₄
95	This work	20	RT	30	EtOH	Tb-MOF

^aReaction between thioacids and epoxides.

4 | CONCLUSIONS

MOFs can act as heterogeneous catalysts for a variety of organic reactions, especially for liquid-phase reactions. The catalytic applications of MOFs are often limited by their chemical, hydrolytic and thermal stabilities. MOFs based on lanthanides are a very promising class of materials for addressing the challenges of heterogeneous Lewis acid catalysis. In summary, herein, Tb-MOF as a heterogeneous Lewis acid catalyst and ultrasonic irradiation as synergic factor were used for epoxy aminolysis reaction at room temperature. The framework has open metal sites at Tb(III) centres, thus providing accessible Lewis acid centres for electrophile activation. We have presented a new catalytic system which proves to be very effective not only in reducing the reaction time, but also in increasing the yield of the product. It involves a simple procedure, is environmentally friendly and also incorporates special features like reagent economy, easy workup and easy handling.

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