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MIL-101-SO₃H: A Highly Efficient Brønsted Acid Catalyst for Heterogeneous Alcoholysis of Epoxides under Ambient Conditions

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Abstract: For the first time, a ~100% sulfonic acid functionalized metal–organic framework (MOF), MIL-101-SO₃H, with giant pores has been prepared by a hydrothermal process followed by a facile postsynthetic HCl treatment strategy. The replete readily accessible Lewis acidic and especially Brønsted acidic sites distributed throughout the framework as well as high stability endow the resultant MOF exceptionally high efficiency and recyclability, which surpass all other MOF-based catalysts, for the ring opening of epoxides with alcohols (especially, methanol) as nucleophiles under ambient conditions.

Epoxides are highly important and versatile synthetic intermediates in organic synthesis and they undergo ring-opening reactions with different nucleophiles such as alcohols to afford β-alkoxyalcohols, which are precursors for a broad range of pharmaceuticals.[1] Alcohols have relatively poor nucleophilicity and thus strong acids or bases are required to promote such kind of alcoholysis of epoxides. Quite a few conventional acids or metal complexes were reported, while these homogeneous systems have inherent limitations in terms of the separation of the product and catalyst recycling.[2] Recently, a few heterogeneous catalysts, such as amberlyst-15, clays, aluminosilicate, silica, or polymer stabilized metal complexes, etc., have been developed for the transformation.[3] However, these reactions have still witnessed more or less drawbacks like tedious catalyst preparation or workup procedures, harsh reaction conditions, unsatisfactory selectivity, etc. Therefore, it is of great importance to develop highly efficient heterogeneous catalysts for nucleophilic ring-opening of epoxides under mild conditions.

Metal-organic frameworks (MOFs) as a relatively new class of crystalline porous materials feature versatile and tailorable structures as well as very high surface area[4] and exhibit potential applications in various fields.[5–7] In addition, MOFs usually contain coordinatively unsaturated metal centers as Lewis acids and also catalytically active sites suspended on the organic linkers, endowing MOFs powerful functionality in heterogeneous catalysis.[8] Particularly, the active sites are uniformly spatially distributed throughout the MOF and well accessible, and the pore structure greatly facilitates the transfer of substrates and products. Therefore, MOFs with high-density acid sites may outperform the supported metal complexes for heterogeneous alcoholysis of epoxides. To date, only a couple of Cu-, Zn- and Fe-based MOFs and an recent Eu-MOF have been investigated for the alcoholysis of epoxides and all of them are Lewis acid type catalysts.[9a–f] Most recently, MIL-101(HPW), a Keggin phosphotungstic acid as active nanomaterial incorporated into a MOF, has been demonstrated to be an active heterogeneous catalyst for the ring-opening reaction of styrene oxide.[9g] Herein, a sulfonic acid group functionalized MOF, MIL-101-SO₃H, featuring giant cages replete with Lewis acidic Cr^{III} and Brønsted acidic −SO₃H sites, has shown exceptionally high activity, excellent selectivity and recyclability for alcoholysis of epoxides under ambient conditions. Moreover, the catalytic activity from Lewis acid sites is negligible compared to that from Brønsted acid sites in MIL-101-SO₃H. To the best of our knowledge, this is the first work on the ring opening of epoxides over a MOF with Brønsted acid sites.

The reaction of 2-sulfoterephthalic acid monosodium salt and CrO₃ in aqueous HCl solution yielded MIL-101-SO₃Na(H),[10a] which contains 1.02% Na based on ICP and gave a pH value of 2.94 in the solution (Table 1). To eliminate the Na species and

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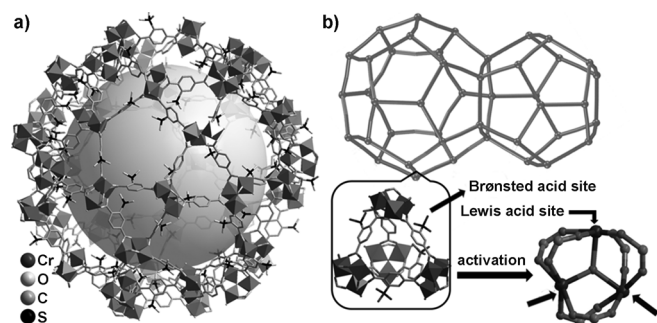🖳 Supporting information for this article is available on the WWW under
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Table 1. ICP-AES results for the contents of Na and Cr involved in MIL-101-SO₃Na(H) and MIL-101-SO₃H.

ICP-AES	Element	MIL-101-SO₃Na(H)	MIL-101-SO₃H
found [%]	Cr	14.88	14.8
	Na	1.02	0.0028

maximize the strength of Brønsted acidity, a postsynthetic HCl treatment afforded MIL-101-SO₃H with <0.003% Na and a lower pH value of 1.72 in solution, revealing a successful ion exchange of all residual Na⁺ with proton (Table 1) and such an approach is different from previous reports for the preparation of MIL-101-SO₃H.[10b–d] The MIL-101-SO₃H ideally formulated Cr₃-

Figure 1. a) The large cage involved in MIL-101-SO₃H with the readily accessible acid sites. The grey ball highlights the large void inside the cage. b) Schematic illustration for the two types of cages in MIL-101-SO₃H with Brønsted and Lewis acid sites.

$(H_2O)_3O(BDC-SO_3H)_2(BDC-SO_3)$ (BDC = 1,4-benzenedicarboxylic acid) presents a 3D MTN-type zeolitic architecture involving two types of similar mesoporous cages replete with sulfonic acid groups and exposed Cr^{III} centers upon activation (Figure 1). N_2 sorption isotherms confirm the permanent porosities and similar BET surface areas of 1508 and 1599 $m^2 g^{-1}$, respectively, for MIL-101-SO₃Na(H) and MIL-101-SO₃H (Figure 2).
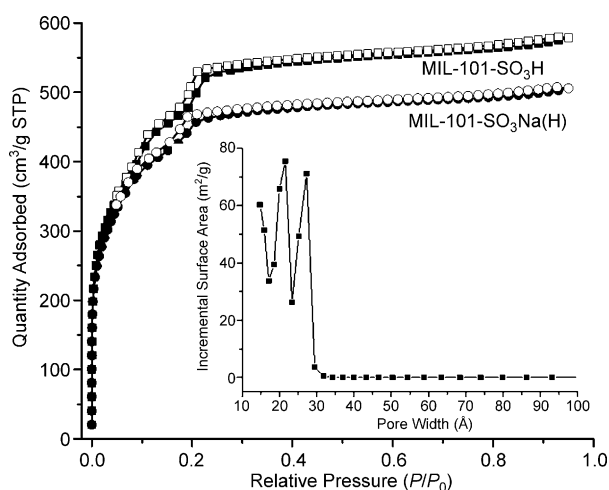

Figure 2. Nitrogen adsorption and desorption isotherms for MIL-101-SO₃Na(H) and MIL-101-SO₃H at 77 K. Inset: pore-size distribution analysis for MIL-101-SO₃H (DFT method).

The pore-size distribution showing two types of cages in MIL-101-SO₃H is in good agreement with that in the structure (Figure 2, inset). The SEM images indicate that MIL-101-SO₃H particles with sizes of 100–300 nm have some extent of aggregation (see Figure S1 in the Supporting Information).

The high-density −SO₃H groups acting as Brønsted acid sites and Lewis acidic Cr^{III} sites in MIL-101-SO₃H encourage us to explore its activity for the ring opening of styrene oxide in methanol (MeOH, Table 2, entries 1–9). In the absence of catalyst, almost no reaction occurs even after 1 h. Although the reported Lewis acid sites in different MOFs displayed considerable activities,[9] it is surprising that the activity over desolvated MIL-101 with well demonstrated Lewis acid sites[11] in both N_2

Table 2. Ring opening of styrene oxide with MeOH catalyzed by MIL-101-SO₃H or other catalysts.[a]

Entry	Catalyst	Atm.[b]	t [min]	Conv. [%][c]
1	–	N₂	60	0.2[d]
2	MIL-101	N₂	48 h	44[e]
3	MIL-101	N₂	48 h	83[f]
4	MIL-101	air	48 h	7
5	MIL-101-SO₃Na(H)	N₂	60	28
6	MIL-101-SO₃H	N₂	30	99
7	MIL-101-SO₃H	N₂	60	1.6[g]
8	MIL-101-SO₃H	air	30	99[h]
9	MIL-101-SO₃H	air	10	99
10	H₂SO₄	air	5	99
11	H₃PO₄	air	60	99
12	p-CH₃-C₆H₄-SO₃H	air	120	99
13	CH₃COOH	air	120	99
14	2-SO₃Na-BDC	air	12 h	70
15	Cr(NO₃)₃·9H₂O	air	10	99

[a] Reaction conditions: **1a** (1 mmol), MeOH (10 mL), catalyst (0.02 mmol), room temperature, unless otherwise mentioned. [b] Atmosphere, distilled MeOH used in N_2 while commercial MeOH in air. [c] Determined by GC analysis. [d] Reaction without catalyst. [e] Catalyst (0.05 mmol), 80 °C. [f] Catalyst (0.05 mmol), solvent: toluene, 80 °C. [g] With pyridine (0.1 mL). [h] Catalyst (0.04 mmol).

and air atmosphere was quite poor and its conversion in N_2 was 44% with almost simplex selectivity in MeOH for 48 h (entries 2 and 4). Under similar conditions, the conversion increased to 83% while the selectivity to 2-methoxy-2-phenylethanol decreased to 46% in toluene under a N_2 atmosphere (entry 3). Similarly, the MIL-101-SO₃Na(H) also showed poor activity toward the reaction, possibly due to the weak Brønsted acidity indicated above (entry 5). Strikingly, MIL-101-SO₃H was very active and complete conversion was achieved in 30 min (entry 6). The introduction of a little bit of pyridine greatly inhibits the transformation, revealing a poisoning of the active acid sites (entry 7).[12] To demonstrate the capability of Brønsted acidity in MIL-101-SO₃H, the catalytic reaction was carried out with commercial MeOH in air to diminish/avoid the contribution from the Lewis acid sites as far as possible. Unexpectedly, MIL-101-SO₃H was still able to complete the reaction in 30 min with ~100% selectivity and gave the only product of desired 2-methoxy-2-phenylethanol under ambient conditions (entry 8). Slightly increasing the amount (0.04 mmol) of catalyst renders the completion of the reaction in only 10 min (entry 9), which clearly indicates that the contribution from Lewis acidity is relatively negligible and the Brønsted acidity accounts for the exceptionally high activity in MIL-101-SO₃H.

For the sake of comparison, the reactants for MIL-101-SO₃Na(H) and different homogeneous acids were investigated as catalysts for the same transformation (Table 2, entries 10–15). The commercial acids, H₂SO₄, H₃PO₄, p-toluenesulfonic acid, and acetic acid and the ligand for MIL-101-SO₃Na(H) show gradually decreasing activity, in positive correlation with

their strength of Brønsted acidity. Chromium(III) nitrate nonahydrate showed remarkable conversion and revealed the intrinsic activity of Cr^{III} as a Lewis acid site to promote the reaction. It is worth emphasizing that all these catalytic systems are homogeneous with the inherent limitation of catalyst recovery regardless of the catalytic activity. To verify the nature of the MIL-101-SO$_3$H catalyst, the hot filtration test was carried out from the mixture after 5 min of reaction. As shown in Figure 3a, no further product was formed even after 1 h in the absence of catalyst under similar reaction conditions, which inferred that the catalysis cannot occur without MIL-101-SO$_3$H and the process should be truly heterogeneous. The reusability of MIL-101-SO$_3$H was approved and the activity, selectivity, and framework integrity of the catalyst were well retained after three or even five more consecutive runs (Figure 3). Therefore, MIL-101-SO$_3$H presents a superb catalytic activity and selectivity, and possesses a truly heterogeneous catalytic nature with excellent catalytic recyclability and stability for the methanolysis of styrene oxide.

It is worth stressing that the catalytic performance of titled MIL-101-SO$_3$H far exceeds all previously reported Lewis acid type MOF catalysts and also surpasses MIL-101 encapsulating guest Keggin phosphotungstic acid,[9] the latter of which has instable catalytic recyclability, possibly due to the leaching of guest active species during recycling, although it initially affords a comparable TOF value at 40 °C to ours at room temperature (Table 3). As far as we know, MIL-101-SO$_3$H in this work represents the best catalytic performance among all MOF-based catalysts for the ring opening of styrene oxide in methanol.

Upon the optimization of reaction conditions with MeOH using styrene oxide as a probe substrate, different alcohols, such as ethanol, 1-propanol, and *tert*-butanol as nucleophiles and various epoxides have been examined. As shown in Table 4, the reaction in ethanol and larger alcohols proceeded more slowly than in MeOH (Table 4, entries 2 and 3). Especially, the conversion was the lowest *tert*-butanol (entry 4), and this may be attributed to the steric hindrance caused by the crowded methyl groups and/or delayed diffusion of *tert*-butanol within the MOF pores to reach the activated epoxide interacting with the acid sites,[9c, 12] and revealed that the catalytic conversion occurred inside the MOF pores, which were further supported by similar conversions over H$_2$SO$_4$ with different-sized alcohols (see Table S2 in the Supporting Information). De-
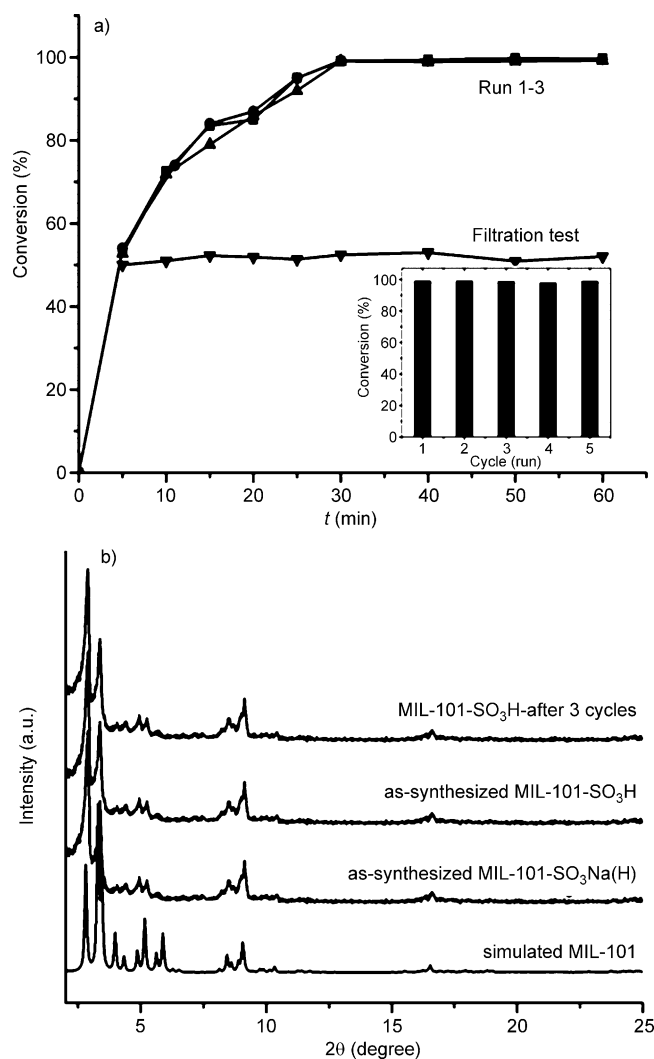

Figure 3. a) Time-conversion plot for the filtration test and five runs of the ring opening reaction of **1a** over MIL-101-SO$_3$H in MeOH. b) Powder XRD patterns for MIL-101-SO$_3$Na(H) and MIL-101-SO$_3$H before and after three runs of catalysis, showing their retained structure and excellent crystallinity.

lightedly, with MIL-101-SO$_3$H catalyst, the reaction selectivity points to an almost a single regioisomer in all alcohols. The methanolysis of 2-methyl-oxirane resulted in a conversion of 54 % in 24 h with 100 % selectivity to 2-methoxypropanol (entry 5). Epichlorohydrin produced very low (7 %) alcohols with favored secondary alcohol (entry 6), whereas glycidol had a conversion of 42 % to give the two isomers with favored primary alcohol (entry 7). The 1,2-epoxy-2-methylpropane exhibited a similar conversion of 41.6 %, whereas a relatively high selectivity of 90 % was obtained to 2-methoxy-2-methyl-1-propanol (entry 8).

Based on the above results, a possible reaction mechanism

Table 3. Comparison of catalytic performance of titled and reported MOF-based catalysts for ring opening of styrene oxide with MeOH.

Catalyst	Conv. [%]	Recyclability	TOF [h^{-1}] (temperature)	Ref.
Cu-MOF	93	4 runs	5.3 (RT)	[9a,b]
Fe-BTC	99	3 runs	10 (40 °C)	[9c]
Cu$_3$(BTC)$_2$	93	no data	9.3 (40 °C)	[9c]
Al$_3$(BTC)$_2$	67	no data	6.7 (40 °C)	[9c]
HKUST-1	90	no data	5.6 (40 °C)	[9e]
Eu-MOF	100	no data	0.2 (40 °C)	[9f]
MIL-101(HPW)	99.8	drop to ~60 % in the 3rd run	98.5 (40 °C)	[9g]
MIL-101-SO$_3$H	99	5 runs	99 (RT)	this work

Table 4. Ring opening of epoxides with various nucleophiles catalyzed by MIL-101-SO$_3$H.[a]

$R_1 = H, CH_3$; $R_2 = CH_3, ClCH_2, HOCH_2, C_6H_5$
$R_3 = CH_3, CH_3CH_2, CH_3CH_2CH_2, tBu$

Entry	Substrate	t [h]	Conv. [%][b]	Selectivity [%][b]		
				2a–e	3a–e	4a–e
1	1a	0.5	>99	>99	–	–
2	1a	5	94[c]	99	–	1
3	1a	5	74[d]	99	–	1
4	1a	5	60[e]	99	–	1
5	1b	24	54	100	–	–
6	1c	24	7	12	88	–
7	1d	24	42	78	22	–
8	1e	24	41.6	90	10	–

[a] Reaction conditions: substrate (1 mmol), methanol, ethanol [c], 1-propanol [d], or *tert*-butanol [e] used as a nucleophile (10 mL), catalyst (0.02 mmol), under ambient conditions. [b] Determined by GC analysis.
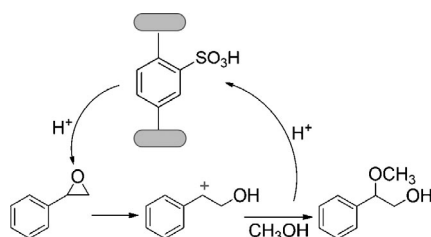
Scheme 1. Proposed mechanism for the ring opening of styrene oxide in MeOH catalyzed by the Brønsted acid sites in MIL-101-SO$_3$H.

for the methanolysis of styrene oxide over MIL-101-SO$_3$H could be proposed in Scheme 1 as a representative. It is likely that the reaction occurs through a S$_N$1 (unimolecular nucleophilic substitution) mechanism. The mechanism for the ring opening of styrene oxide in MeOH catalyzed by Lewis acid sites was well documented.[9c, 13] The origin of the catalytic activity in MIL-101-SO$_3$H should be basically ascribed to Brønsted acid sites, in which the protons are ionized and attack the oxygen atom of styrene epoxide to produce an increase in the electrophilic nature of the carbon attached to the phenyl group. Therefore, the nucleophiles (i.e., MeOH) would mainly attack the more stable benzyl carbocation, giving rise to the resultant β-alkoxyalcohols.

In conclusion, a Brønsted and Lewis acid dual-functionalized mesoporous MOF was successfully prepared based on MIL-101-SO$_3$Na(H) synthesis followed by HCl treatment. The ob-

tained MIL-101-SO$_3$H has been demonstrated to be highly efficient and selective for heterogeneous alcoholysis of epoxides under ambient conditions. Steric hindrance or impeded diffusion makes a larger alcohol unfavorable in the transformation of epoxides while it is easy for methanol to accomplish the reaction. The high region selectivity in most cases allows the product to be predictable based on an acid-catalyzed S$_N$1 ring-opening mechanism. The catalyst is readily recyclable due to its heterogeneous nature. The highly dispersed and readily accessible Brønsted acid sites throughout the MOF may account for the excellent performance of MIL-101-SO$_3$H. The facile and scalable synthesis and high stability of MIL-101-SO$_3$H as well as the exceptionally high catalytic efficiency under ambient conditions greatly facilitates the large-scale implementation for the transformation. Given the intrinsic advantages and excellent manifestation, the catalyst could be a promising candidate for many acid-catalyzed reactions in future.

Experimental Section

Catalyst preparation

Preparation of MIL-101-SO$_3$Na(H): A mixture of monosodium 2-sulfoterephthalic acid (3.35 g, 12.5 mmol), CrO$_3$ (1.25 g, 12.5 mmol), and concentrated aqueous hydrochloric acid (0.8 mL, 12 M, 25 mmol) was dissolved in water (25 mL) and then transferred to a Teflon-lined stainless steel autoclave. The solution was heated at 453 K for six days under the hydrothermal conditions. The reaction product was harvested by centrifugation and washed three times with deionized water (400 mL) and methanol (100 mL) followed by drying in air at room temperature. The green powder was purified in DMF at 120 °C for 24 h followed by in a mixed solution of methanol and H$_2$O at 120 °C for 24 h.

Preparation of MIL-101-SO$_3$H: The obtained green microcrystalline powder of MIL-101-SO$_3$Na(H) was postsynthetically treated in a mixed solution of diluted HCl (0.08 M) in methanol and water, and was further treated in methanol and water to remove additional HCl. The resultant green solid was finally dried overnight at 120 °C under vacuum prior to the further use.

Experimental procedure for the evaluation of acidity strength for MIL-101-SO$_3$Na(H) and MIL-101-SO$_3$H

In a typical procedure, 0.5 g of solid was suspended in 20 g of aqueous NaCl saturated solution. The resulting suspension was stirred at room temperature for 12 h until an equilibrium was reached. The pH value was measured for the filtrate.

A typical procedure for ring opening of epoxides with alcohols

A 25 mL round-bottomed flask was charged with the catalyst (commercial catalyst or activated MOF, 0.02 mmol otherwise mentioned) and substrate (1 mmol) in alcohol (10 mL). The reaction mixture was stirred for the required time in air (with commercial alcohol without further treatment) or N$_2$ (with distilled alcohol) atmosphere. The reaction was monitored periodically by analyzing the sample by GC analysis until the completion of reaction.

Experimental procedure for reusability test

The reusability of MIL-101-SO$_3$H was tested for the ring opening of styrene oxide with methanol. At the end of the reaction, the heterogeneous mixture was centrifuged and the recovered catalyst was activated at 393 K and then reused for a consecutive reaction with fresh styrene oxide and methanol.

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