RSC Advances

Volume 1 | Number 1 | Jan 2013 | Pages 1–100

RSC Advances

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Journal Name

Communication

Development of a Novel Brønsted acid UiO-66 Metal-Organic Framework Catalyst by Postsynthetic Modification and its Application in Catalysis

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A novel Brønsted acid derived metal-organic framework (MOF) has been developed to serve as an efficient heterogeneous catalyst for the acetalization and Morita-Baylis-Hillman reaction. Aromatic sulfonic acid groups were successfully incorporated to the framework of UiO-66 by post-synthetic modifications using commercially available anhydridic reagents. The UiO-66-RArSO$_3$H Brønsted acid catalyst was fully characterized by SEM, PXRD, FTIR, TGA and N$_2$ adsorption/desorption isotherm. Furthermore, efficient acetalization and Morita–Baylis–Hillman reaction were evaluated to demonstrate the high catalytic performance of the UiO-66-RArSO$_3$H catalyst. The UiO-66-RArSO$_3$H catalyst is compatible with a variety of substituted substrates and can be recycled five times without compromise in the yield or selectivity.

Introduction

Although mineral Brønsted acids, such as H$_2$SO$_4$ and HCl, have been commonly used for industrial chemical production for more than a century, homogeneous Brønsted acids suffer from difficulty in catalyst recycling, severe equipment corrosion, as well as environmental pollution during the catalysis application.[1] Heterogeneous Brønsted acid catalysts are desirable alternatives to traditional homogeneous ones, which are subjected to the intrinsic limitations listed above.[2] Solid support, such as organic polymers[3] and porous materials[4] have exhibited advantages as catalyst carriers, such as ease of recovery.[5] Recently, metal-organic frameworks (MOFs) are emerging as a new class of heterogeneous catalyst carriers, taking advantage of their highly tailorable nature, porous structure and large surface area.[6] Several functionalized Brønsted acid MOFs have been developed.[7] However, the number of successful Brønsted acid MOFs is limited due to the narrow range of available carboxylate ligands bearing a pre-installed sulfonic group.[8] As a result, more approaches for the formation of Brønsted acid MOF structure are necessary for the generation of low pKa MOF catalytic material.[9]

Postsynthetic modification (PSM) of porous MOFs could generate a wide variety of functionalized MOF scaffolds through stable covalent bonds.[10] In this way, Brønsted acidic moieties can be introduced easily and rapidly.[11] Yaghi[12] developed a PSM method using 1,3-propanesultone to synthesize an IRMOF-3 derived Brønsted acid MOF. Wang et al.[13] applied this PSM

strategy to the synthesis of a Brønsted acid MOF catalyst. Cohen has developed an anhydride approach for the modification of amino-functionalized MOFs and applied the modified MOFs to an organocatalytic epoxide opening reaction.[14] For the installation of a highly acidic sulfonic acid group, the choice of PSM reagent is highly important. For example, the use of chlorosulfonic acid as sulfonating agent could lead to the complete collapse of the crystalline structure.[15] It would be valuable to identify a commercially available reagent that could allow for introduction of the sulfonic acid moiety under mild conditions, to keep the MOF structure intact.[16]

In this work, we wish to report a novel Brønsted acid metal-organic framework for highly efficient, catalytic acetalization and Morita-Baylis-Hillman (MBH) reactions. This newly synthesized UiO-66-RArSO$_3$H MOF catalyst, bearing aromatic sulfonic acid groups, was obtained using commercially available o-sulfobenzoic acid anhydride, a reagent not previously utilized as a sulfonic acid MOFs precursor. A variety of aromatic aldehydes were tolerated under the optimal reaction conditions for acetalization or Morita-Baylis-Hillman reaction. Furthermore, the synthesized UiO-66-RArSO$_3$H catalyst can be readily filtered and separated from the reaction solution, allowing for recycling of the catalyst five times without compromising yield or selectivity.

Results and discussion

UiO-66-NH$_2$ was prepared from 2-aminoterephthalic acid (NH$_2$-H$_2$BDC), according to a literature procedure.[17] Subsequently, UiO-66-NH$_2$ was modified post-synthetically using o-sulfobenzoic acid anhydride in a chloroform solution to give UiO-66-RArSO$_3$H. UiO-66-RArSO$_3$H was characterized and found to be topologically identical to its precursor UiO-66-NH$_2$ (Scheme 1).

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† Footnotes relating to the title and/or authors should appear here.
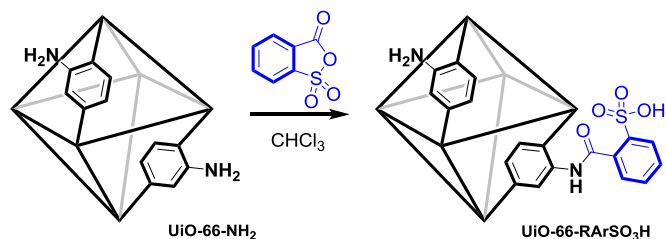
Scheme 1. Schematic illustration of the post-synthetic modification of UiO-66-NH₂.

UiO-66-NH₂ crystals appear to adopt an octahedral morphology with diameters of 160 nm as witnessed by SEM (Fig. 1a). No change in the octahedral morphology of the crystals could be observed in the Scanning Electron Microscope (SEM) images acquired after the post-synthetic modification with *o*-sulfobenzoic acid anhydride (Fig. 1b).
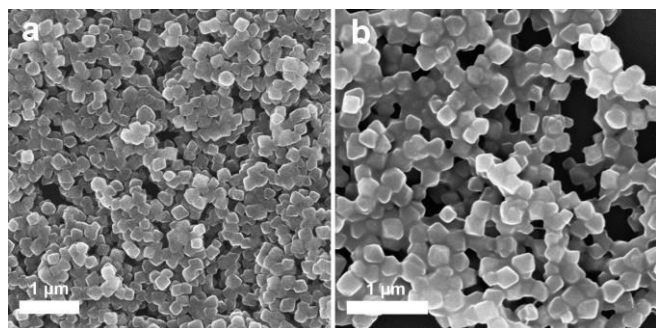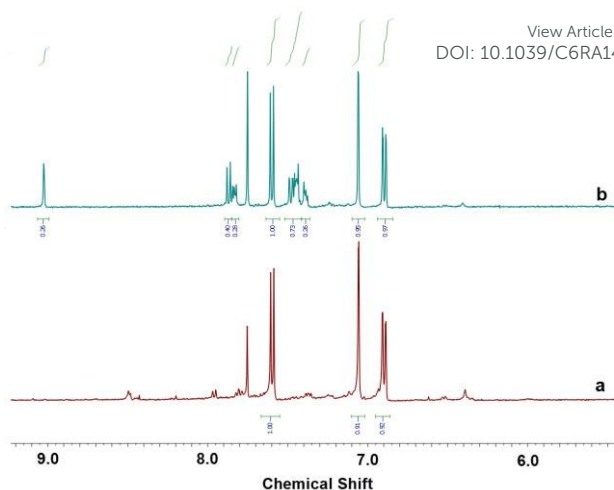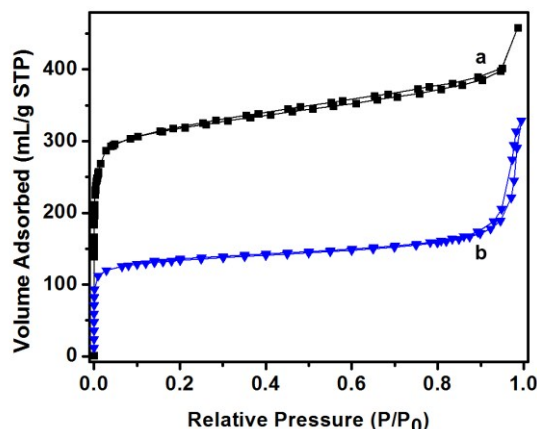

Fig. 1 SEM of (a) UiO-66-NH₂ and (b) UiO-66-RArSO₃H.
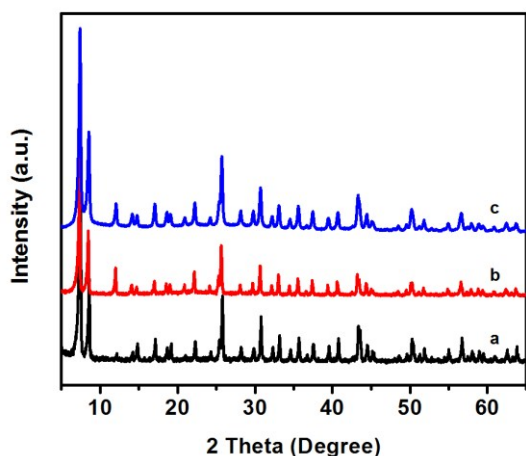
Fig. 2 PXRD of (a) UiO-66-NH₂, (b) UiO-66-RArSO₃H and (c) recycled UiO-66-RArSO₃H.

Powder X-ray diffraction (PXRD) studies were performed to confirm the successful synthesis of UiO-66-NH₂ MOFs.[17] The PSM using *o*-sulfobenzoic acid anhydride did not cause the destruction of the UiO-66-NH₂ crystalline structure, which makes the UiO-66-NH₂ derived Brønsted acid a more stable MOF acid catalyst than that of the zinc derived IRMOF-3.[18]

Fig. 3 ¹H NMR spectra of digested (a) UiO-66-NH₂ and (b) UiO-66-RArSO₃H.

The modification ratio of aromatic sulfonic moieties on UiO-66-RArSO₃H was measured by ¹H NMR integration, which was compared with ¹H NMR spectrum of UiO-66-NH₂. ¹H NMR studies of the digested sample indicated that 20 mol% of UiO-66-NH₂ amino groups were post-synthetically functionalized (Fig 3). This observation was similar to the previous literature report, which also reported a partial NH₂ group conversion.[19]

Fig. 4 Nitrogen adsorption/desorption isotherms of (a) UiO-66-NH₂ and (b) UiO-66-RArSO₃H

UiO-66-NH₂ is a highly porous MOF material with a BET surface area of 1273 m²g⁻¹, calculated by nitrogen adsorption isotherms collected for the UiO-66-NH₂ MOF. Upon post-synthetic modification, the surface area was reduced to 840 m²g⁻¹ for UiO-66-RArSO₃H, presumably due to the occupation of the pore structure caused by the aromatic sulfonic functional groups. However, UiO-66-RArSO₃H with reduced BET surface area performed exceptionally in our catalysis study, because the highly porous structure and the flexibility of the newly installed organic functional group allows for free entry and exit of the reaction substrate.

Additionally, the thermal and structural stability of UiO-66-NH₂ and UiO-66-RArSO₃H was examined by thermal gravimetric

analysis (TGA). A weight loss at 270 °C was observed according to the TGA of UiO-66-NH$_2$. The weight loss of the modified UiO-66-RArSO$_3$H sample started at slightly lower temperature, which is common for modified MOF materials (Fig. S1).[20] The TGA result proved the high thermal stability of the UiO-66-RArSO$_3$H sample, which ensures its stability in the catalytic reaction temperature range.

Table 1. Benzaldehyde acetalization with different catalysts.[a]

Entry	Catalyst	Yield[b]	TON	TOF (h^{-1})
1	-	0%	-	-
2	Cu$_3$(BTC)$_2$	8%	80	40
3	UiO-66-NH$_2$	3%	30	15
4	Cat. 1	78%	780	390
5	Cat. 2	92%	920	460
6	Cat. 3	47%	470	235
7	**UiO-66-RArSO$_3$H**	**98%**	**980**	**490**

[a] Reaction conditions: benzaldehyde (1.0 mmol), 0.1 mol% catalyst, ethanol (0.5 mL) at 23 °C for 2 h, [b] Determined by GC-MS using nitrobenzene as the internal standard.

Our investigation on the acetalization reaction of benzaldehyde **1a** was initiate d at room temperature in the absence of additional solvent (Table 1). The control experiment showed there is no formation of desired acetal product in the absence of catalyst (Table 1, entry 1). In the literature, the acetalization reaction can be promoted by certain MOF structures, such as Cu$_3$(BTC)$_2$ (BTC = 1,3,5-benzenetricarboxylate) via a Lewis acid activation mechanism using a high loading of catalyst. However, Cu$_3$(BTC)$_2$ functioned extremely poorly under 0.1 mol% catalyst loading, which suggested low acidity of the MOF metal site (Table 1, entry 2). UiO-66-NH$_2$ showed even lower reactivity at room temperature after 12 h, presumably because of the basic amino functional groups (Table 1, entry 3). Strong Brønsted acids were able to promote the acetalization of benzaldehyde (Table 1, entries 4 and 5). 2-(phenylcarbamoyl)benzenesulfonic acid (Cat. 2) showed an improved catalytic performance over *p*TsOH (Cat. 1), likely due to the electron-withdrawing effect from the carbamoyl group (Table 1, entry 5). A previously synthesized Brønsted acid MOF catalyst was also tested under the current reaction conditions (Table 1, entry 6). Unfortunately, only a moderate yield was obtained using Cat. 3 at 0.1 mol% catalyst loading. The turn-over number (TON) of Cat. 3 was calculated to be 470 and turn-over frequency (TOF) was calculated to be 235

h^{-1}. This observation indicated the relatively low acidity of alkyl sulfonic acid in comparison to aromatic sulfonic acid. Remarkably, UiO-66-RArSO$_3$H catalyst bearing an aromatic sulfonic acid group gave the desired benzaldehyde acetal product in quantitative yield after 2 h (Table 1, entry 8). The great catalytic activity of the UiO-66-RArSO$_3$H suggested a higher utilization rate of the MOF surface and pores, which efficiently reduced the diffusional limitations for movement of the catalyst and substrates in liquid phase catalysis.[21] The high activity of the UiO-66-RArSO$_3$H, which gave a TON of 980 and TOF of 490 h^{-1}, is comparable to homogeneous sulfonic acid as shown in Table 1, entries 4 and 5. The TON of UiO-66-RArSO$_3$H catalyst in the acetalization reaction is also significantly higher than existing MOF sulfonic acid catalysts reported in the literature.[22] Furthermore, we carried out the kinetic profile of the reaction between benzaldehyde and ethanol in the presence of UiO-66-RArSO$_3$H catalyst. The full conversion of benzaldehyde substrate was achieved at 2 h, and the acetalization reaction did not proceed further when the solid acid catalyst was removed from the system (Fig. S3).

Table 2. UiO-66-RArSO$_3$H catalyzed acetalization reaction.[a]

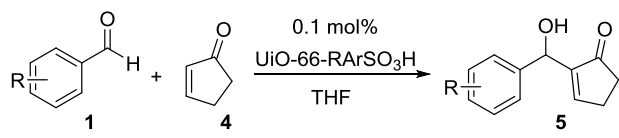| Entry	Substrate	Alcohol	Product	Yield[b]
1	**1a**	EtOH **2a**	**3a**	98%
2	R$_1$ = H, **1a**	**2b**	**3ab**	88%
3	R$_1$ = 4-F, **1b**	EtOH **2a**	**3b**	92%
4	R$_1$ = 2-F, **1c**	EtOH **2a**	**3c**	90%
5	R$_1$ = 4-MeO, **1d**	EtOH **2a**	**3d**	83%
6	**1e**	EtOH **2a**	**3e**	89%

[a] Reaction conditions: aldehyde (1.0 mmol), 0.5 mL ethanol and 0.1 mol% of UiO-66-RArSO$_3$H at 23 °C for 2 h, [b] Determined by GC-MS using nitrobenzene as the standard.
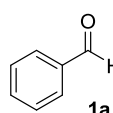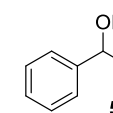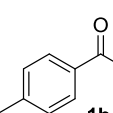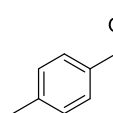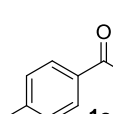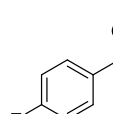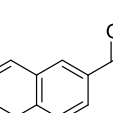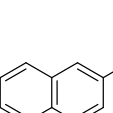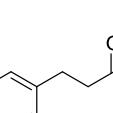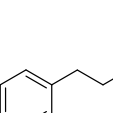
The protocol was compatible with a series of aromatic aldehydes and used to convert them into commercially important acetals in good yields. The aforementioned conditions were successfully applied to a range of acetalization reactions using 0.1 mol% of UiO-66-RArSO$_3$H solid catalyst (Table 2). Ethylene diol **2b** can also act as an acetalization reagent to form five-membered ring acetal (Table 2, entry 2). Other substituted aromatic aldehydes were evaluated to show the general application of our solid sulfonic acid catalyst.

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Fluorinated aldehydes **1b** and **1c** gave 92% and 90% yield, respectively, in the presence of 0.1 mol% catalyst (Table 2, entries 3 and 4). Para-methoxy benzaldehyde **1d**, an electron-rich substrate that is generally inert under many acetalization conditions, , provided **3d** in good yield under our UiO-66-RArSO₃H catalyzed conditions (Table 2, entry 5).[23] Heteroaromatic aldehyde, thiophene-2-carbaldehyde **1e**, also gave the desired product in good yield (Table 2, entry 6). This observation further proves the outstanding activity of the acidic UiO-66-RArSO₃H catalyst.

Table 3. Morita-Baylis-Hillman reaction promoted by UiO-66-RSO₃H.

Entry	Substrate	Product	Yield
1	1a	5a	92%
2	1b	5b	91%
3	1c	5c	90%
4	1d	5d	90%
5	1f	5f	86%

ᵃ Reaction conditions. aldehyde (1.0 mmol), 2-cyclopenten-1-one (2.0 mmol), 1,4-diazabicyclo [2.2.2]octane (0.5 mmol). UiO-66-RArSO₃H catalyst (0.1 mol%), were stirred at 23 ºC for 6 h. ᵇ The product was purified by column chromatography on silica gel and the yield was based on isolated product.

Morita-Baylis-Hillman reactions of substituted aromatic aldehydes and 2*H*-cinnamaldehyde were also evaluated with 2-cyclohexene-1-one **4** as the nucleophile and 1,4-diazabicyclo [2.2.2]octane as the Lewis basic promoter (Table 3). A control experiment demonstrated there was no reactivity in the absence of catalyst and DABCO (Table S1). DABCO was able to promote the MBH reaction of **4**, however, in a very slow reaction rate (Table S1, entry 2). Using MBH reaction of benzaldehyde as the model reaction, an excellent yield was

obtained with only 0.1 mol% catalyst loading and 0.5 eq. of DABCO (Table 2, entry 1). This amount of catalyst is significantly lower than the catalyst loading in previous reports.[24] To further extend the utility of the UiO-66-RArSO₃H catalyst, substituted benzaldehydes, such as 4-methylbenzaldehyde **1b** and 4-fluorobenzaldehyde **1c**, were tested under the optimal reaction conditions. 91% and 90% yields were obtained respectively, which indicated the great efficiency and substrate compatibility of the UiO-66-RArSO₃H catalyst (Table 2, entries 2 and 3). 2-Naphthaldehyde **1d** also reacted with 2-cyclohexene-1-one **4** nucleophile smoothly, despite its greater steric bulk (Table 2, entry 4). Furthermore, *2H*-cinnamaldehyde **1f** was also tested as a non-aromatic aldehyde and 86% yield was obtained (Table 2, entry 5).
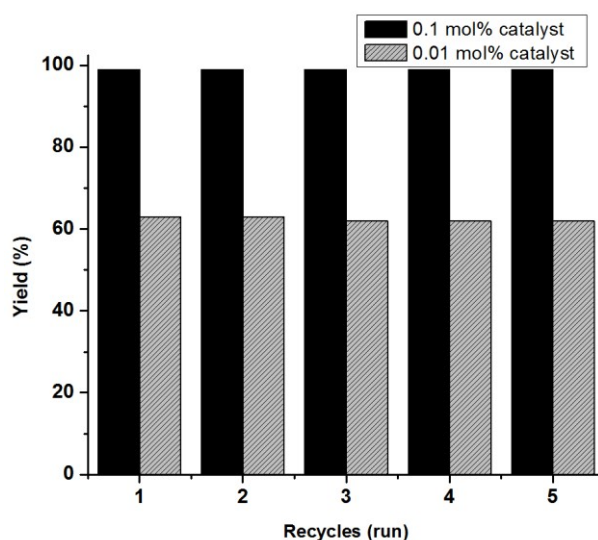
Fig 5. The catalyst recycling of UiO-66-RArSO₃H in the acetalization reaction of **1a** to **3a**.

The UiO-66-RArSO₃H was isolated and reused five times for the examination of its recyclability for the catalysis of acetalization and MBH reactions. During the acetalization reaction recycling, the catalyst was centrifuged from the reaction solution and washed with ethanol. The strong covalent bond between the aromatic sulfonic acid moiety and the amino group on UiO-66-RArSO₃H ensures the chemical stability of the active acidic sites, which demonstrated the great advantage of our strategy over other approaches using coordination bonds. The UiO-66-RArSO₃H catalyst remains intact after five reuses of the same catalyst batch, affording up to 99% yield of (diethoxymethyl)benzene **3a** (Fig. 5). Furthermore, the acetalization reaction recycle was performed at a lower catalyst loading (0.01 mol%) to reveal the good recyclability of UiO-66-RArSO₃H catalyst. Furthermore, the supernatant liquid of the ethanol suspension showed no catalytic reactivity toward the benzaldehyde, which is evidence for no leakage of acidic sites on the UiO-66-RArSO₃H catalyst. The conversion of benzaldehyde paused after the solid catalyst was filtered out of the solution, which further suggested a lack of catalyst leakage (Fig. S3). The X-ray powder diffraction pattern spectrum of the UiO-66-RArSO₃H catalyst after five uses was indistinguishable

from that of the fresh catalyst (Fig. 2c). This observation clearly demonstrates that there was no leaching or catalyst decomposition over the catalytic process or isolation. Furthermore, our UiO-66-RArSO$_3$H material behaved similarly in the MBH reaction catalyst reuse, again demonstrating good recycling capability (Fig. S4).

Conclusions

In conclusion, a novel heterogeneous UiO-66-RArSO$_3$H catalyst bearing an aromatic sulfonic acid group was synthesized in this research. The structural morphology of UiO-66-RArSO$_3$H was well retained after post-synthetic modification using commercial available *o*-sulfobenzoic acid anhydride reagent. The newly developed UiO-66-RArSO$_3$H showed high activity and selectivity in the acetalization and MBH reactions at only 0.1 mol% catalyst loadings, which provides higher TONs and TOFs than several other heterogeneous Brønsted acid catalysts. The UiO-66-RArSO$_3$H catalyst was chemically stable, due to its strong covalent bond, and did not suffer from a leaching problem during liquid catalysis. Further studies involving new applications of the UiO-66-RArSO$_3$H catalyst are in progress.

Acknowledgements

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Development of a Novel Brønsted acid UiO-66 Metal-Organic Framework Catalyst by Postsynthetic Modification and its Application in Catalysis
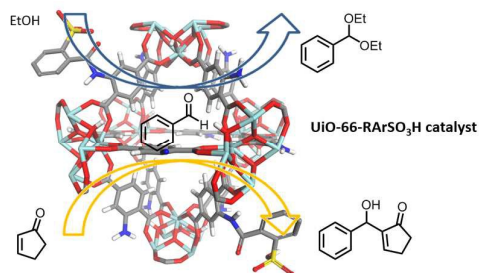
A novel Brønsted acid UiO-66 metal-organic framework catalyst has been developed and utilized for efficient acetalization and MBH reaction.