A new site-isolated acid–base bifunctional metal–organic framework for one-pot tandem reaction†

Yu-Ri Lee,a Young-Min Chungb and Wha-Seung Ahna*

A highly porous and stable acid–base bifunctional metal–organic framework, MIL-101–NH2–SO3H, was prepared by direct solvothermal synthesis using two mixed (–NO2, –SO3H) terephthalate linkers followed by post-synthesis reduction to the NH2 form, which showed excellent performance for a one-pot tandem decatetalization–nitroaldol reaction.

Recently, Li et al. reported the synthesis of bifunctional chromium(m) terephthalate (MIL-101) having both Brønsted acid and base sites via the three-step post-synthesis modification of MIL-101: (i) BOC (N-tert-butoxy carbonyl)-protected amino group grafting on the CUS, (ii) direct sulfonation of the phenylene backbone with chlorosulfonic acid, and (iii) BOC de-protection.8 Although the catalyst exhibited useful catalytic properties in a one pot tandem reaction, the catalyst preparation process was difficult and lengthy. An acid treatment for the direct sulfonation of the organic linkers may also give rise to undesirable deformation of the MOF structure.

This paper proposes an alternative synthetic route for the introduction of site-isolated acid and base sites in MIL-101: direct solvothermal synthesis using two common organic linkers followed by single step post-synthetic modification under mild reaction conditions. This strategy is simple and can enable easier control over the amount of Brønsted acid and base functions on its backbones.

Kitagawa and co-workers reported the preparation of MIL-101–SO3H and MIL-101–NO2 using monosodium 2-sulfoterephthalate (H2BDC–SO3Na) and 2-nitrobenzene-1,4-dicarboxylic acid (H2BDC–NO2), respectively, under similar synthesis conditions.9,10 Because H2BDC–NO2 and H2BDC–SO3H are both moderately acidic, MIL-101 bearing both SO3H and NO2 in a single structure was expected to form using a mixture of the two ligands. Subsequently, MIL-101–NH2–SO3H bearing both Brønsted acid and base functions was prepared by reducing the NO2 groups in the product to NH2 by SnCl2 as described in Scheme 1. MIL-101, MIL-101–NH2, and MIL-101–SO3H were

![Scheme 1](image-url)
prepared for comparison using the methods reported elsewhere.\textsuperscript{10,12,13}

The X-ray powder diffraction patterns of MIL-101 and its
–SO\textsubscript{3}H, –NO\textsubscript{2} and –NH\textsubscript{2} mono-functionalized structures were all
in good agreements with those reported earlier (Fig. S1, ESI\textsuperscript{†}).\textsuperscript{10–13} Both MIL-101–NO\textsubscript{2}–SO\textsubscript{3}H and MIL-101–NH\textsubscript{2}–SO\textsubscript{3}H also showed similar XRD patterns to that of simulated MIL-101
(ref. 14) suggesting that the fundamental MIL-101 structure was
also showed similar XRD patterns to that of simulated MIL-101
structure.\textsuperscript{10,12,13} This journal is © The Royal Society of Chemistry 2014

The FT-IR spectra of MIL-101\textsuperscript{10,13} and its functionalized forms; (a) MIL-101–SO\textsubscript{3}H, (b) MIL-101–NO\textsubscript{2}–SO\textsubscript{3}H, (c) MIL-101–NH\textsubscript{2}–SO\textsubscript{3}H, (d) MIL-101–NH\textsubscript{2}–NH\textsubscript{2}, and (e) MIL-101.

Table 1 Specific surface area and pore volume of MIL-101 and its functionalized structures

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area (m\textsuperscript{2} g\textsuperscript{−1})</th>
<th>Pore volume (cm\textsuperscript{3} g\textsuperscript{−1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIL-101</td>
<td>3442</td>
<td>2.06</td>
</tr>
<tr>
<td>MIL-101–SO\textsubscript{3}H</td>
<td>2090</td>
<td>1.69</td>
</tr>
<tr>
<td>MIL-101–NH\textsubscript{2}</td>
<td>1870</td>
<td>1.48</td>
</tr>
<tr>
<td>MIL-101–NO\textsubscript{2}–SO\textsubscript{3}H</td>
<td>2190</td>
<td>1.37</td>
</tr>
<tr>
<td>MIL-101–NH\textsubscript{2}–SO\textsubscript{3}H</td>
<td>2320</td>
<td>1.39</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Acid amount (mmol g\textsuperscript{−1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIL-101</td>
<td>Total\textsuperscript{a} 0.380 0.262 0.118</td>
</tr>
<tr>
<td>MIL-101–SO\textsubscript{3}H</td>
<td>Weak–medium\textsuperscript{b} 0.378 0.663</td>
</tr>
<tr>
<td>MIL-101–NH\textsubscript{2}</td>
<td>Strong\textsuperscript{c} 0.189 0.132</td>
</tr>
<tr>
<td>MIL-101–NH\textsubscript{2}–SO\textsubscript{3}H</td>
<td>0.412 0.291</td>
</tr>
</tbody>
</table>

\textsuperscript{a}373–723 K, \textsuperscript{b}373–593 K, \textsuperscript{c}593–723 K.

To measure the acid strength of the catalysts, NH\textsubscript{3}-TPD analysis was performed and the result was shown in Table 2 and
Fig. S4, ESI\textsuperscript{†}. While high population of weak–medium acidity
was detected in MIL-101, the number of strong acid sites increased further in both MIL-101–SO\textsubscript{3}H and MIL-101–NH\textsubscript{2}–SO\textsubscript{3}H, which clearly suggests that the newly introduced SO\textsubscript{3}H group in the MIL-101 structure enhanced the acid strength of
the catalyst.

The catalytic properties of MIL-101–NH\textsubscript{2}–SO\textsubscript{3}H were evaluated by examining the one-pot tandem conversion of benzaldehyde–dimethylacetal (1) to
\textit{trans}-1-nitro-2-phenylethylen (3); the acid-catalyzed deacetalization of compound 1 to benzaldehyde 2, followed by the Henry condensation of compound 2
with nitromethane to compound 3 in the presence of a base catalyst. Initially, two different kinds of ion-exchange resin catalysts with either pure Bronsted acid or base sites were tested (Table S2, ESI\textsuperscript{†}). Although the SO\textsubscript{3}H-bound catalyst converted compound 1 exclusively to 2 (entry 1), the NH\textsubscript{2}-bound catalyst did not promote the same reaction (entry 2). On the other hand, the base catalyst converted compound 2 completely to compound 3 (entry 3). These results showed that the acid and

Table 2 Acid amounts of MIL-101 and its functionalized structure based on NH\textsubscript{3}-TPD analysis

\begin{tabular}{|c|c|c|c|}
\hline
Catalyst & Acid amount (mmol g\textsuperscript{−1}) & Total\textsuperscript{a} & Weak–medium\textsuperscript{b} & Strong\textsuperscript{c} \\
\hline
MIL-101 & 0.380 & 0.262 & 0.118 \\
MIL-101–SO\textsubscript{3}H & 1.042 & 0.378 & 0.663 \\
MIL-101–NH\textsubscript{2} & 0.321 & 0.189 & 0.132 \\
MIL-101–NH\textsubscript{2}–SO\textsubscript{3}H & 0.704 & 0.412 & 0.291 \\
\hline
\end{tabular}

\textsuperscript{a}373–723 K, \textsuperscript{b}373–593 K, \textsuperscript{c}593–723 K.
The overall reaction mechanism could be proposed, as for the site isolation of antagonistic functions in a single tandem reaction consecutively. The concentration of acid and base sites at the organic linkers catalyze the one-pot reduction in CUS at the metal centres is a highly effective design for the site isolation of antagonistic functions in a single system. The overall reaction mechanism could be proposed, as shown in Scheme S1, ESI†. As summarized in Table S3, ESI†, MIL-101–NH₂–SO₃H showed high catalytic activity than the bifunctional MIL-101 prepared by the three-step post-synthesis modification,⁶ or previously reported bifunctional mesoporous silica, PMO–NH₂–SO₃H,⁴ HPAN–NH₂–SBA-15,⁵ and AB-MCM-41.²⁹

The stability of the catalyst, MIL-101–NH₂–SO₃H, was tested by performing repeated reaction cycles under the reaction conditions. At the end of each reaction cycle, the catalyst was recovered by filtration, and then washed, dried and reused. As shown in Fig. S5, ESI†, the conversion and selectivity remained almost identical after 5 recycles. The XRD pattern and FT-IR spectrum of the solid catalyst after reuse were also indistinguishable from that of the fresh catalyst.

In summary, this paper reported the synthesis of a simple site-isolated acid–base bifunctional metal–organic framework MIL-101–NH₂–SO₃H containing sulfonic acid and amine groups without any reduction of the unsaturated Lewis acid sites at the metal centres. XRD, BET surface area measurements, FT-IR spectroscopy, and elemental analysis confirmed that the –SO₃H and –NH₂ groups had been incorporated successfully without deteriorating the porous nature of the parent MIL-101 structure significantly. MIL-101–NH₂–SO₃H exhibited excellent catalytic performance for the one-pot tandem reaction of benzaldehyde-dimethylacetal to trans-1-nitro-2-phenylethylene under mild reaction conditions.

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### Notes and references


