Selective oxidation of tetralin over a chromium terephthalate metal organic framework, MIL-101†

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MIL-101, a mesoporous chromium terephthalate metal organic framework, was found to be an efficient heterogeneous catalyst for selective oxidation of tetralin to 1-tetralone using tert-butyl hydroperoxide or acylperoxy radicals generated in situ from trimethylacetaldehyde and O2 as an oxidant.

Metal–organic frameworks (MOFs) have generated a great deal of interest in recent years due to their potential applications in gas storage, separation, and catalysis.1 Recently, Férey et al.2 reported the synthesis of a chromium terephthalate, MIL-101, having large pores and high surface area together with huge cell volume (ca. 702 000 Å3) in a single material. The robust framework of MIL-101 was made of trimeric chromium(III) octahedral clusters interconnected by 1,4-benzenedicarboxylate anions containing removable terminal water molecules, resulting in a zeotype architecture. MIL-101 not only demonstrated very high gas storage for elementary gases,3 but proved useful as a host for supporting catalytic groups such as organic amines,4 Pd,5 and polyoxometalate.6 The iron(III) carboxylate MIL-100(Fe) also showed good catalytic activity and selectivity in Friedel–Crafts benzylation.6 However, no work making direct use of the Cr(III) in MIL-101 as catalytic oxidation sites has been reported thus far to the best of the authors’ knowledge.

For benzylic oxidation, chromium-based catalytic systems have long been known to be highly active and selective catalysts.7,8 In addition, Cr sites on mesoporous materials showed higher conversions than those on microporous supports due to more efficient mass transfer.9 In these regards, MIL-101, having abundant atomically distributed Cr(III) sites accessible to the reactants (after removal of terminal water molecules) and uniform mesopores, is a promising material for such catalytic application. In this paper, we describe the liquid phase oxidation of tetralin over MIL-101. 1-Tetralone, the major oxidation product of tetralin, is a commercially important organic intermediate and can be used as an additive to enhance the cetane number in diesel fuels.10 We conducted a rigorous set of experiments covering various aspects of the reaction including the choice of oxidant (tert-butyl hydroperoxide (t-BuOOH) vs. in situ generated acylperoxy radicals through trimethylacetaldehyde and O2), and the effect of solvent was also examined.

MIL-101 was hydrothermally synthesized2 and purification of the material was conducted through ethanol-washing followed by chemical treatment with 0.3 M ammonium fluoride solution (see ESI†). The material was characterized by XRD, SEM, TGA, N2 adsorption–desorption isotherms, and UV-Visible diffuse reflectance spectroscopy (see ESI†). Comparison of the XRD patterns of the present material with previously reported data2 confirmed the structure and crystallinity of a high quality MIL-101. N2 sorption measurement of MIL-101 shows a mean pore diameter (28 Å), pore volume (2.46 cm3 g−1), and Langmuir surface area (5300 m2 g−1) virtually identical to those previously reported.2 The UV-Visible diffuse reflectance of MIL-101 exhibits two absorption maxima, at 595 and 425 nm, assignable to distorted octahedral coordination of Cr(III).11

Initially, tetralin oxidation using t-BuOOH as an oxidant was carried out. GC analysis revealed one major product, 1-tetralone, and other products were 1-tetralol, 1-naphthol, and naphthalene. As shown in Fig. 1, tetralin conversion gradually increased from 55 to 73% as the temperature was increased from 60 to 100 °C, whilst the selectivity to 1-tetralone remained fairly constant (ca. 86%). MIL-101 exhibited excellent catalytic performance compared with that obtained for CrAPO-5 catalyst (47% conversion and 82% selectivity to 1-tetralone) at 80 °C.12

Fig. 1 Effect of temperature on the catalytic activity of MIL-101 using t-BuOOH in chlorobenzene (reaction conditions: 8 mmol tetralin, 16 mmol t-BuOOH, 5 ml chlorobenzene, and 8 h reaction).
The effects of other reaction parameters are summarized in Table 1. Tetralin conversion increased as the catalyst amount was increased from 10 to 30 mg, and then levelled off to ca. 67%. For a fixed amount of tetralin, the conversion increased with an increase in the amount of the oxidant t-BuOOH.

In situ generated acyloperoxy radicals from trimethylacetaldehyde and O₂ were considered as an alternative oxidant (Fig. 2). Whilst tetralin oxidation using t-BuOOH afforded higher conversion than the trimethylacetaldehyde and O₂ system, higher selectivity to 1-tetralone was obtained with the latter oxidant (ca. 93 vs. 86%). A group of researchers also reported similar results for the oxidation of styrene using O₂–isobutyraldehyde and t-BuOOH oxidant. Using t-BuOOH oxidant, conversion decreased in the following order: C₆H₅Cl > C₆H₆ > CH₂CN > THF. The results indicate that tetralin oxidation over MIL-101 using t-BuOOH proceeds much better in the presence of a non-coordinating solvent (Fig. 2). On the other hand, O₂ in the presence of trimethylacetaldehyde as an oxidant resulted in the following activity order: CH₃CN > C₆H₅Cl > C₆H₆ > THF. We propose that aldehyde in the oxidation of tetralin in CH₃CN using trimethylacetaldehyde and O₂ initially produces acyloperoxy radical, which may attack the nitrile to form an active oxidant, and is responsible for the higher conversion of the substrate. THF showed very poor activity in both oxidant systems due to stronger coordination of THF (C₆H₅O) through the O donor to the vacant site of the chromium centre than BuOO⁻ or the acyloperoxy radical in the intermediate stage; hence, the accessibility of the reagent molecule to the formation of [t-BuO–O–Cr] or [–CO₂–O–Cr] in the intermediate stage is diminished. A similar trend in solvent-dependent activity was observed for another MOF-based catalyst.

The tetralin conversion and selectivity to 1-tetralone in dry MIL-101 were significantly higher (68% conversion and 86% selectivity to 1-tetralone) than those with the water-entrapped sample (36% conversion and 68% selectivity to 1-tetralone). A MIL-101 sample with an excess amount of water was prepared by placing the dry sample in a large excess of water and the sample was then dried at room temperature overnight. Apparently, guest molecules of water coordinated to the active sites of MIL-101 in the solid state are sufficiently stable and are not completely replaced by available chlorobenzene or t-BuOO⁻ radical during the reaction.

It is important to verify the stability of a heterogeneous catalyst under given reaction conditions, since metals leached from a matrix can be responsible for the observed catalytic behaviour. To check the heterogeneity of MIL-101 catalyst in liquid phase oxidation of tetralin, a hot filtering experiment (separation of catalyst at the reaction temperature) and recycling runs over the spent catalysts were carried out at a fixed temperature (80 °C). In the t-BuOOH oxidant case, the catalysts were filtered off after 30 min reaction and the filtrate mixture was then stirred at 80 °C for a duration of up to 450 min (Fig. 3). Concurrently, we measured the leached Cr content in the filtrate solution by ICP-MS. A trace amount of chromium was found in the filtrate (0.12 ppm) and the reaction in the filtrate proceeded with much slower conversion of tetralin than in the presence of catalyst. We believe the reaction of the filtrate is mostly due to non-catalytic thermal oxidation, since the increase in conversion in the filtrate (15%) is rather close to the conversion (13%) by the blank reaction without MIL-101 (Fig. 3c). The slightly higher conversion (ca. 2%) after hot filtration relative to the blank test after 8 h of reaction may be due to the initially formed active radical.

### Table 1 Influence of amount of catalyst, tetralin/t-BuOOH mole ratio, and catalyst recycling in the oxidation of tetralin

<table>
<thead>
<tr>
<th>Catalyst amount/mg</th>
<th>Tetralin : t-BuOOH</th>
<th>Conv. (%)</th>
<th>Product selectivity (%)&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 : 2</td>
<td>60.0</td>
<td>Tlone</td>
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<tr>
<td>10.0</td>
<td></td>
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<td></td>
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<tr>
<td>30.0</td>
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<td>50.0</td>
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<tr>
<td>0.0&lt;sup&gt;d&lt;/sup&gt;</td>
<td></td>
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</tbody>
</table>

<sup>a</sup> Reaction conditions: 5 ml chlorobenzene, 8 mmol tetralin, 16 mmol t-BuOOH, at 80 °C for 8 h. <sup>b</sup> 2nd cycle. <sup>c</sup> 3rd cycle. <sup>d</sup> 4th cycle. <sup>e</sup> 5th cycle. <sup>f</sup> Without MIL-101 catalyst (in the presence of t-BuOOH). <sup>g</sup> 1-Tetralone, 1-tetralol, 1-naphthol, and naphthalene are denoted as Tlone, Tiol, Nthol, and Nlene, respectively.

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**Fig. 2** Conversion (light shading) and selectivity (dark shading) to 1-tetralone profiles in tetralin oxidation with tetralin–t-BuOOH or trimethylacetaldehyde (1 : 2 mole ratio), catalyst (10 mg), solvent (10 ml), at 80 °C for 8 h in different solvents: (a) THF, (b) acetonitrile, (c) benzene, and (d) chlorobenzene.
intermediates remaining in the filtrate mixture for a short duration after catalyst separation, which can convert tetralin to products via thermal autoxidation. It is also noteworthy that the selectivity to 1-tetralone was lower in the reaction product of the filtrate (73%) than that of the catalytic reaction in the presence of MIL-101 (86%). Similar experiments were also conducted using the trimethylacetaldehyde–$\text{O}_2$ system at 80 °C (see ESI†, Fig. S6). The chromium content was only 0.14 ppm in the filtrate after 60 min reaction time. The reaction profile of the filtrate also exhibited a similar trend as with $\tau$-BuOOH. Further support for the heterogeneous nature of MIL-101 in tetralin oxidation was provided by the identical catalytic activity and selectivity for up to five cycles of reaction for reuse of the catalyst (Table 1). In the recycling test, the catalyst was recovered by filtration and washed with solvent, dried at 80 °C in air for 8 h to remove the adsorbed species at the end of each reaction cycle, and reused. The conversion and product selectivity were virtually identical irrespective of the number of cycles after the first cycle. This finding is in stark contrast to other chromium-containing molecular sieve catalysts that show a significant decline in catalytic activity upon recycling. Whilst a trace amount of chromium was found in the filtrate after the first cycle of 8 h catalytic reaction (0.35 ppm by ICP-MS), the possibility of a synthesis substrate (metal ions or ligands) remaining entrapped inside the MOF structure by ICP-MS), the possibility of a synthesis substrate (metal ions or ligands) remaining entrapped inside the MOF structure cannot be ruled out completely. 

In summary, MIL-101, a chromium(III) containing MOF, showed efficient heterogeneous catalysis for tetralin oxidation using $\tau$-BuOOH or trimethylacetaldehyde–$\text{O}_2$ as an oxidant. The nature of the solvents and the sources of oxidant were found to play important roles in the activity and selectivity. The catalyst was stable and could be reused several times with retention of its high catalytic activity and selectivity.

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Notes and references

12 Chromium containing aluminophosphate, CrAPO-5 (2.0 mol% Cr) was prepared as described in ref. 7, using Al(OH)$_3$ as an aluminium source and triethylamine as a structure directing agent.

Fig. 3 Tetralin oxidation using $\tau$-BuOOH at 80 °C in chlorobenzene: (a) fresh MIL-101, (b) filtrate (MIL-101 filtered off after 30 min reaction time), and (c) without MIL-101 (in the presence of $\tau$-BuOOH).