REVIEW

Metal–organic frameworks of the MIL-101 family as heterogeneous single-site catalysts

BY NATALIYA V. MAKSIMCHUK1, OLGA V. ZALOMAEVA1, IGOR Y. SKOBELEV1, KONSTANTIN A. KOVALENKO2,3, VLADIMIR P. FEDIN2,3 AND OXANA A. KHOLODEEVA1,∗

1 Boreskov Institute of Catalysis, pr. Lavrentieva 5, Novosibirsk 630090, Russia
2 Nikolaev Institute of Inorganic Chemistry, pr. Lavrentieva 3, Novosibirsk 630090, Russia
3 Department of Inorganic Chemistry, Novosibirsk State University, Pirogova str. 2, Novosibirsk, 630090, Russia

In this short review paper, we survey our recent findings in the catalytic applications of mesoporous metal–organic frameworks of the MIL-101 family (Fe- and Cr-MIL-101) and demonstrate their potential in two types of liquid-phase processes: (i) selective oxidation of hydrocarbons with green oxidants—O2 and tert-butyl hydroperoxide—and (ii) coupling reaction of organic oxides with CO2. A comparison with conventional single-site catalysts is made with special attention to issues of the catalyst’s resistance to metal leaching and the nature of catalysis.

Keywords: allylic oxidation; cyclohexane; carboxylation; metal–organic frameworks; MIL-101; single-site heterogeneous catalysts

1. Introduction

The concept of single-site heterogeneous catalysts (SSHCs), remarkably explored by Thomas (1988), Thomas et al. (2005) and Thomas & Raja (2006, 2010), has attracted a great deal of attention from researchers working in the field of liquid-phase catalysis. This is not surprising because SSHCs possess accessible, spatially isolated and homogeneously distributed uniform active sites on the surface and, therefore, are expected to combine the merits of both homogeneous (activity and selectivity) and heterogeneous (simplicity of recovery and recycling) catalysts. SSHCs are usually associated with transition-metal-containing molecular sieves or supported catalysts prepared by grafting or anchoring techniques (Thomas et al. 2005; Thomas & Raja 2006). Recently, transition-metal-monosubstituted polyoxometalates were considered as a specific class of single-site catalysts.

Received 30 December 2011
Accepted 14 February 2012

This journal is © 2012 The Royal Society
where active metal is isolated in and strongly bound to an inorganic metal–oxide matrix (Thomas & Raja 2006; Kholdeeva 2006; Kholdeeva et al. 2010). Considerable efforts have been made to incorporate organic moieties within inorganic metal–silica frameworks (synthesis of the so-called hybrid organic–inorganic materials) to tune the surface properties and the catalytic performance (Wight & Davis 2002; Hoffman et al. 2006). In the past decade, a new class of materials, namely metal–organic frameworks (MOFs), has appeared and immediately attracted attention from the catalytic community (Corma et al. 2010).

MOFs are functional porous coordination polymers that possess a unique combination of properties, such as extremely high surface areas, crystalline open structures, tunable pore size and functionality. All these allow them to be considered as prospective materials for applications in catalysis, gas storage, molecular recognition and liquid-phase separations (Corma et al. 2010; Dhakshinamoorthy et al. 2011; Farrusseng 2011). MOFs are composed of isolated metal atoms or clusters linked by polydentate organic ligands, resulting in a rigid porous network. Hence, the structure of MOFs meets the general requirements of single-site catalysts. An important feature of MOFs is a high content of active metal sites; all of them are uniformly spatially distributed and are accessible for reagents, provided the size of pore entrances allows penetration of the reactant molecules. In contrast to zeolites and mesoporous metal–silicates, segregation of the active metal to form extraframework metal oxide species (an undesirable process for good catalytic performance) is, in principle, impossible in the case of MOFs. Meanwhile, until recently, low thermal, chemical and solvolytic stabilities, when compared with completely inorganic zeolites and zeotypes, limited the application of MOFs in catalysis.

Férey et al. (2005) discovered the mesoporous chromium(III) terephthalate Cr-MIL-101 followed by the synthesis of an iron(III) analogue, Fe-MIL-101 (Bauer et al. 2008; Taylor-Pashow et al. 2009). This type of MOF has a rigid zeotype (MTN type) crystal structure, consisting of quasi-spherical cages of two modes (2.9 and 3.4 nm) accessible through windows of ca 1.2 and 1.6 nm (figure 1). Both materials possess huge surface areas and pore volumes (typically, 3200–3900 and 1.4–2.1 m² g⁻¹, respectively) as well as having fairly good resistance to common solvents and thermal stability (Fe-MIL-101 up to 180°C and Cr-MIL-101 up to 300°C). The MIL-101 framework consists of terephthalate linkers and M₃O-carboxylate trimers (M=Cr or Fe) with octahedrally coordinated metal ions binding terminal water molecules (figure 2). Hwang et al. (2009) have found that these H₂O molecules (according to elemental analysis and thermogravimetric data, two molecules per trimeric cluster) can be easily removed by thermal treatment under vacuum, thus providing catalytically active coordinatively unsaturated sites (CUSs). Indeed, activated CUS-containing Cr-MIL-101 was found to be active in the cyanoisilylation of benzaldehyde (Henschel et al. 2008) sulphoxidation of thioethers with H₂O₂ (Hwang et al. 2009), benzylic oxidation of tetralin (Kim et al. 2009) and allylic oxidation of alkenes with tert-butyl hydroperoxide (TBHP) (Maksimchuk et al. 2010).

In this paper, we summarize our progress in exploring the potential of Fe- and Cr-MIL-101 as SSHCs for liquid-phase transformations of organic substrates; specifically, the allylic oxidation of cyclic alkenes and oxyfunctionalization of cyclohexane with environmentally benign oxidants (O₂ and TBHP) as well as the
coupling reaction of epoxides and CO\textsubscript{2}. A comparison with conventional single-site catalysts is made, with special attention to the frequently success-limiting issues of the catalyst’s resistance to metal leaching and the nature of catalysis.

2. Catalytic properties of Fe- and Cr-MIL-101

(a) Allylic oxidation of alkenes

Allylic oxidation of cyclic alkenes is of considerable value for the production of \(\alpha,\beta\)-unsaturated alcohols and ketones, which are key intermediates in the manufacture of fine chemicals (Murphy et al. 2000; Sheldon 2001). The ketonic products are often more desirable owing to the presence of a carbonyl group.
that is very reactive towards addition reactions. Molecular sieves containing chromium(III) and iron(III) are the most frequently used solid catalysts for this reaction, while TBHP or molecular oxygen are the oxidants of choice. This prompted us to assess catalytic properties of Fe- and Cr-MIL-101 in the allylic oxidation of a range of cyclic alkenes, including natural terpenes.

Table 1 shows the results acquired over Cr-MIL-101 with non-aqueous TBHP as oxidant along with some representative literature data reported for other types of Cr single-site catalysts, such as Cr-APO-5 and ordered mesoporous chromium silicates. One can see that Cr-MIL-101 demonstrated high catalytic activity and product selectivities in the oxidation of a range of alkenes (cyclohexene, \(\alpha\)-pinene and limonene) to the corresponding \(\alpha,\beta\)-enones (2-cyclohexen-1-one, verbenone and carvone, respectively). In sharp contrast to the Cr-APO-5/TBHP system (Lempers & Sheldon 1996), where unsaturated alcohols were formed in considerable amounts along with the corresponding enones, although a higher TBHP to alkene molar ratio (5:1) was employed, very few enols were found in the presence of Cr-MIL-101 using just 1.7 equiv. of the oxidant. Thus, the main by-product in cyclohexene oxidation over Cr-MIL-101 was 2-cyclohexene-1,4-dione.

Preliminary activation of the as-prepared Cr-MIL-101 under vacuum at 150°C affected essentially the catalytic activity (turnover frequency (TOF) 1.7 versus 0.3 \(h^{-1}\) without activation) and produced some improvement of the cyclohexenone selectivity. In turn, increasing the temperature of the catalyst pre-treatment from 150°C to 180°C led to a further increase of TOF, substrate conversion and enone selectivity—by up to 93 per cent (figure 3).

Chlorobenzene and benzene were the most suitable solvents for this reaction in terms of both TOFs and selectivity (table 1, entries 1 and 2). In the absence of solvent, both the substrate conversion and selectivity decreased dramatically (just 16% cyclohexene conversion and 50% cyclohexenone selectivity were reached after 10 h). Keeping in mind that the framework of MIL-101 has a high affinity for benzene molecules (Hong et al. 2009), it is reasonable to suppose that competing sorption of solvent molecules might favour the efficiency of the allylic oxidation by timely removal of the reaction products from the catalyst surface.
### Table 1. Allylic oxidation of alkenes in chlorobenzene with TBHP over Cr-containing single-site catalysts.

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>Cr content (wt%)</th>
<th>conditions</th>
<th>substrate/oxidant (M/M)</th>
<th>substrate conversion (%)</th>
<th>TOF (^{a}) (h(^{-1}))</th>
<th>product selectivity (%)</th>
<th>Cr leaching (ppm)</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cr-MIL-101</td>
<td>23(^{b})</td>
<td>50°C, 10 h</td>
<td>0.1/0.17</td>
<td>76</td>
<td>5.4</td>
<td>95</td>
<td>&lt;1</td>
<td>Maksimchuk et al. (2010)</td>
</tr>
<tr>
<td>2</td>
<td>Cr-MIL-101</td>
<td>23(^{b})</td>
<td>50°C, 10 h</td>
<td>0.1/0.17</td>
<td>81</td>
<td>3.6</td>
<td>93</td>
<td>&lt;1</td>
<td>Maksimchuk et al. (2010)</td>
</tr>
<tr>
<td>3</td>
<td>Cr-MCM-41(^{d})</td>
<td>0.77</td>
<td>120°C, 12 h</td>
<td>1.6/3.2</td>
<td>27</td>
<td>n.d.</td>
<td>67</td>
<td>no leaching</td>
<td>Sakthivel et al. (2003)</td>
</tr>
<tr>
<td>4</td>
<td>Cr-MCM-48(^{d})</td>
<td>0.98</td>
<td>120°C, 12 h</td>
<td>1.6/3.2</td>
<td>33</td>
<td>n.d.</td>
<td>76</td>
<td>no leaching</td>
<td>Sakthivel et al. (2003)</td>
</tr>
<tr>
<td>5</td>
<td>Cr-MIL-101</td>
<td>23(^{b})</td>
<td>50°C, 10 h</td>
<td>0.1/0.17</td>
<td>87</td>
<td>5.9</td>
<td>89</td>
<td>&lt;1</td>
<td>Maksimchuk et al. (2010)</td>
</tr>
<tr>
<td>6</td>
<td>Cr-APO-5</td>
<td>0.88</td>
<td>80°C, 24 h</td>
<td>0.2/1.0</td>
<td>85</td>
<td>6.0</td>
<td>78</td>
<td>leaching</td>
<td>Lempers &amp; Sheldon (1996)</td>
</tr>
<tr>
<td>7</td>
<td>Cr-SBA-15(^{d})</td>
<td>1.7</td>
<td>85°C, 24 h</td>
<td>0.13/0.67</td>
<td>84</td>
<td>n.d.</td>
<td>79</td>
<td>no leaching</td>
<td>Selvaraj et al. (2010)</td>
</tr>
<tr>
<td>8</td>
<td>Cr-MIL-101</td>
<td>23(^{b})</td>
<td>50°C, 10 h</td>
<td>0.1/0.17</td>
<td>70</td>
<td>6.2</td>
<td>86</td>
<td>&lt;1</td>
<td>Maksimchuk et al. (2010)</td>
</tr>
<tr>
<td>9</td>
<td>Cr-APO-5</td>
<td>0.88</td>
<td>80°C, 24 h</td>
<td>0.2/1.0</td>
<td>85</td>
<td>4.0</td>
<td>22</td>
<td>leaching</td>
<td>Lempers &amp; Sheldon (1996)</td>
</tr>
</tbody>
</table>

\(^{a}\)TOF = (moles of substrate converted)/(moles of Cr \times time); determined from the initial rates of substrate consumption. TOFs for MIL-101 were calculated per CUS; the number of CUSs is equal to two-thirds of the total moles of metal (figure 2).

\(^{b}\)In activated MIL-101.

\(^{c}\)Benzene was used as the solvent.

\(^{d}\)Washed catalyst.

\(^{e}\)Not determined.
Figure 3. Effect of Cr-MIL-101 activation on its catalytic properties in cyclohexene oxidation with TBHP. Reaction conditions: 0.1 M cyclohexene, 0.17 M TBHP, 2.5 mg Cr-MIL-101, 1 ml benzene, 50°C, 10 h. Dark grey bars, cyclohexene conversion; crossed bars, cyclohexenone selectivity; striped bars, TOF.

It is noteworthy that Cr-MIL-101 revealed fairly good selectivities at reasonably high conversions in the allylic oxidation of terpenes (table 1, entries 5 and 8), the substrates being prone to various isomerization and rearrangement processes (Murphy et al. 2000). This allowed product yields superior to those reported for Cr-containing molecular sieves to be obtained. Unfortunately, TOF values were not determined for mesoporous Cr-silicates (Sakthivel et al. 2003; Selvaraj et al. 2010) and cannot be evaluated from the corresponding data reported in the literature (table 1, entries 3, 4 and 7), but when compared with Cr-APO-5 (table 1, entries 6 and 9) the activities of Cr-MIL-101 expressed in TOF values are either close to or higher than those reported for chromium aluminophosphate, though milder reaction conditions were used with the Cr-MIL-101 catalyst (Lempers & Sheldon 1996). A possible reason for this could be a better hydrophobicity of the MIL material owing to the organic linker, which favours adsorption of the organic reagents. Another reason might be better isolation and accessibility of Cr ions in the MIL-101 structure.

Both Cr- and Fe-MIL-101 mediated allylic oxidation of cyclohexene with molecular oxygen without using any organic solvent other than substrate to produce a mixture of products, namely 2-cyclohexen-1-ol, 2-cyclohexen-1-one and cyclohexenyl hydroperoxide along with a minor amount of cyclohexene epoxide. The results are given in table 2, again in comparison with other Cr single-site catalysts. Cr-MIL-101 showed a lower cyclohexene conversion after the same reaction time than Fe-MIL-101, but the selectivity towards enol/enone was much higher for Cr-MIL-101 at the expense of hydroperoxide even at the same level of conversion (compare entries 1 and 3 in table 2). Interestingly, the dependence of product distribution on cyclohexene conversion differed significantly for Fe-MIL-101 and Cr-MIL-101, indicating different reaction mechanisms. The total volume yields of the allylic oxidation products acquired over Cr-MIL-101 and Fe-MIL-101 were comparable to most of the other Cr-containing single-site catalysts (table 2). The mesoporous Cr-MCM-41 molecular sieve exhibited superior catalytic activity, but suffered from substantial Cr leaching (table 2, entry 4) (Dapurkar et al. 2012).
Table 2. Solvent-free cyclohexene oxidation with 1 atm O₂ over Fe- and Cr-containing single-site catalysts.

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>metal content (wt%)</th>
<th>conditions</th>
<th>substrate conversion (%)</th>
<th>product selectivity (mol.%)</th>
<th>enol + enone volume yield (g/l)</th>
<th>metal leaching (ppm)</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe-MIL-101</td>
<td>23&lt;sup&gt;a&lt;/sup&gt;</td>
<td>60°C, 16 h (5 h)</td>
<td>44 (16)</td>
<td>36 (20) 14 (11) 46 (65)</td>
<td>210</td>
<td>7</td>
<td>this work</td>
</tr>
<tr>
<td>2</td>
<td>Fe-MIL-101</td>
<td>23&lt;sup&gt;a&lt;/sup&gt;</td>
<td>40°C, 16 h</td>
<td>8</td>
<td>14 65 20</td>
<td>61</td>
<td>&lt;1</td>
<td>this work</td>
</tr>
<tr>
<td>3</td>
<td>Cr-MIL-101</td>
<td>23&lt;sup&gt;a&lt;/sup&gt;</td>
<td>60°C, 10 h</td>
<td>16</td>
<td>56 38 6</td>
<td>144</td>
<td>&lt;1</td>
<td>this work</td>
</tr>
<tr>
<td>4</td>
<td>Cr-MCM-41</td>
<td>2</td>
<td>70°C, 24 h</td>
<td>52</td>
<td>71 11 14</td>
<td>407</td>
<td>56</td>
<td>Dapurkar et al. (2008)</td>
</tr>
<tr>
<td>5</td>
<td>Cr-APO-5</td>
<td>1.5</td>
<td>70°C, 24 h</td>
<td>25</td>
<td>51 28 16</td>
<td>190</td>
<td>n.d.</td>
<td>Dapurkar et al. (2008)</td>
</tr>
</tbody>
</table>

<sup>a</sup>In activated MIL-101.
2008). Unfortunately, the question of chromium leaching was not addressed for Cr-APO-5 and CrY (table 2, entries 5 and 6), although the stability of catalysts towards leaching and the nature of catalysis are crucial parameters that should be taken into account while using solid catalysts in liquid-phase oxidation processes (Sheldon et al. 1998).

Following the methodology suggested by Sheldon et al. (1998), we performed fast hot catalyst filtration tests for all the elaborated catalytic systems. No further substrate conversion in the filtrate was found after removal of the catalyst in the oxidations over Cr-MIL-101 (an example is shown in figure 4a), indicating that the observed catalysis is truly heterogeneous. A trace amount of chromium (less than 1 ppm) was determined in the filtrate by ICP-AES after cyclohexene oxidation with TBHP or O2; however, such an amount of transition metal was viewed as acceptable for the production of fine chemicals (Blaser & Struder 1999). The stability of Cr-MIL-101 is higher than that of Cr-containing molecular sieves; the latter suffer from Cr leaching, at least during the first catalyst reuses, and often reveal a homogeneous nature of catalysis (Lempers & Sheldon 1996; Sakthivel et al. 2003; Selvaraj et al. 2010). In contrast to Cr-MIL-101, the solvent-free cyclohexene oxidation with O2 over Fe-MIL-101 did not stop after the catalyst was removed at ca 20 per cent conversion, and elemental analysis showed iron leaching (7 ppm), which can be reduced to 1 ppm by decreasing the reaction temperature from 60°C to 50°C. However, a contribution of homogeneous catalysis remains significant even at 50°C, but it can be avoided upon further decrease of the reaction temperature down to 40°C. Interestingly, at 40°C, the product distribution was different: the selectivity to enol increased greatly at the expense of hydroperoxide and enone (table 2, entry 2). Hence, we may conclude that Cr-MIL-101 is significantly more stable in the oxidative medium than Fe-MIL-101, which also correlates with the order of thermal stability of these materials.

Unlike zeolites and metal–silicates, MOFs cannot be reactivated by calcinations since they contain an organic moiety. For this reason, the MIL-101 materials should be thoroughly washed with methanol and dried under vacuum.
Review. MIL-101 as single-site catalysts

Figure 5. XRD patterns for Cr-MIL-101: (a) initial, (b) after treatment with 0.5 M TBHP in MeCN at 80°C for 10 h, and (c) after cyclohexene oxidation with TBHP.

Figure 6. FT-IR spectra of Fe-MIL-101: (a) initial, (b) after four runs of solvent-free cyclohexene oxidation with O₂ and (c) after five runs of solvent-free cyclohexane oxidation with TBHP.

Before reuse in order to remove adsorbed products that can block active sites and thus decrease the activity. We found that Cr-MIL-101 did not lose its activity and selectivity during, at least, five runs of cyclohexene oxidation with TBHP (figure 4b). In the solvent-free cyclohexene oxidation, the recycling behaviour of Fe-MIL-101 was not stable, but Cr-MIL-101 could be recycled at least four times without loss of the catalytic properties. The X-ray diffraction (XRD) (figure 5) and Fourier transform infrared (FT-IR) (figure 6) studies confirmed the retention of the MIL-101 structure after recycling, while the nitrogen adsorption measurements indicated stability of the porous structure.
(b) Cyclohexane oxidation

The oxidation of cyclohexane under mild conditions is a topic of great interest, because its primary products—cyclohexanone (K) and cyclohexanol (A), the so-called K-A oil—are used as a feedstock in several processes, including the production of Nylon-6 and Nylon-6,6 (Musser 2005; Cavani & Alini 2009). The conventional industrial process for cyclohexane oxidation uses cobalt salts as homogeneous catalysts to produce K-A oil with 75–80% selectivity at 150–180°C and 10–20 atm of air; the conversion is usually limited to less than 5–7% in order to reduce overoxidation processes (Cavani & Alini 2009). In the presence of anhydrous meta-boric acid, up to 90 per cent selectivity to K-A oil can be accomplished at 10–15% cyclohexane conversion (Cavani & Alini 2009). Many attempts have been made to substitute conventional homogeneous catalysts with heterogeneous ones (Chen & Sheldon 1995; Raja et al. 1999; Schuchardt et al. 2001; Anand et al. 2006; Shylesh et al. 2007; Cavani & Alini 2009). However, many of the reported solid catalysts suffered from active metal leaching and could not be used repeatedly without loss of the activity.

Both Fe- and Cr-MIL-101 were found to catalyse solvent-free oxidation of cyclohexane with TBHP (used as an anhydrous solution in decane); the product distribution depended on the nature of the active metal. The main results are presented in table 3 (entries 1 and 5). The oxidation using TBHP in the presence of Cr-MIL-101 yielded predominantly cyclohexanone (75% selectivity at 36% substrate conversion) along with cyclohexanol (8%); the main by-products were caprolactone and adipic acid (ca 10%). The selectivity to cyclohexanone can be augmented by up to 86 per cent by increasing the cyclohexane/TBHP molar ratio and decreasing the substrate conversion down to 23 per cent (figure 7). Note that TBHP efficiency (the product yield based on the oxidant consumed) was rather high (69%) even under conditions of 1.7-fold excess of the oxidant and could be improved up to 100 per cent by decreasing the oxidant amount with respect to the substrate.

In the presence of Fe-MIL-101, the main oxidation product at 24 per cent conversion was cyclohexyl hydroperoxide (CHHP; 46% selectivity) along with cyclohexanol (37%) and cyclohexanone (16%); only traces of overoxidation products were detected in the reaction mixture. As was already shown for Cr-MIL-101, preliminary activation of the as-prepared Fe-MIL-101 under vacuum at 120°C (the activation temperature should be lower for Fe-MIL-101 because of its lower thermal stability) allowed the catalytic activity to be increased (TOF 54 versus 15 h⁻¹ without activation) but had almost no effect on the product distribution. For efficient Fe-MIL-101-catalysed oxidation with TBHP, the presence of air (oxygen) is required. Under an argon atmosphere ([cyclohexane]/[TBHP] = 1.1), the substrate conversion reached only 11 per cent after 8 h, the main oxidation products were cyclohexanone and CHHP (54% and 45% selectivity, respectively). Meanwhile, cyclohexane oxidation over Fe-MIL-101 with O₂ using just small additives of TBHP as initiator ([cyclohexane]/[TBHP] = 230) produced CHHP, cyclohexanol and cyclohexanone with 45, 36 and 18 per cent selectivity, respectively, at 11 per cent conversion after 8 h. On the contrary, dioxygen did not affect the Cr-MIL-101-mediated oxidation of cyclohexane, thus indicating different reaction mechanisms in the presence of the two MIL-101 catalysts.

Table 3. Solvent-free cyclohexane oxidation over Cr- and Fe-containing single-site catalysts.

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>metal content (wt%)</th>
<th>oxidant</th>
<th>conditions</th>
<th>substrate conversion (%)</th>
<th>TOF$^a$ (h$^{-1}$)</th>
<th>product selectivity (mol.%)</th>
<th>catalyst productivity$^b$ (g/(g × h))</th>
<th>metal leaching (ppm)</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cr-MIL-101</td>
<td>23$^c$</td>
<td>TBHP</td>
<td>70°C, 8 h</td>
<td>36</td>
<td>45</td>
<td>8</td>
<td>75</td>
<td>3.4</td>
<td>0.3</td>
</tr>
<tr>
<td>2</td>
<td>Cr-PMO</td>
<td>2.3</td>
<td>TBHP$^d$</td>
<td>70°C, 5 h</td>
<td>12</td>
<td>n.d.</td>
<td>22</td>
<td>70</td>
<td>0.2</td>
<td>9</td>
</tr>
<tr>
<td>3</td>
<td>Cr-APO-5</td>
<td>1.5</td>
<td>5 atm O$_2$</td>
<td>130°C, 5.5 h</td>
<td>10.5</td>
<td>12</td>
<td>5</td>
<td>48</td>
<td>0.2</td>
<td>n.d</td>
</tr>
<tr>
<td>4</td>
<td>Cr-TUD-1</td>
<td>1.6</td>
<td>TBHP</td>
<td>70°C, 16 h</td>
<td>14</td>
<td>n.d.</td>
<td>2</td>
<td>72</td>
<td>0.1</td>
<td>34</td>
</tr>
<tr>
<td>5</td>
<td>Fe-MIL-101</td>
<td>23$^c$</td>
<td>TBHP + air</td>
<td>70°C, 8 h</td>
<td>24</td>
<td>54</td>
<td>37</td>
<td>17</td>
<td>1.5</td>
<td>0.5</td>
</tr>
<tr>
<td>6</td>
<td>Fe-ALPO-5</td>
<td>4</td>
<td>1.5 atm air</td>
<td>130°C, 24 h</td>
<td>7</td>
<td>6.5</td>
<td>36</td>
<td>16</td>
<td>0.2</td>
<td>n.d</td>
</tr>
<tr>
<td>7</td>
<td>Fe-AlPO-5</td>
<td>4</td>
<td>1.5 atm air + TBHP</td>
<td>130°C, 24 h</td>
<td>20</td>
<td>24</td>
<td>22</td>
<td>33</td>
<td>0.5</td>
<td>n.d</td>
</tr>
</tbody>
</table>

$^a$TOF = (moles of cyclohexane converted)/(moles of active metal × time); determined from the initial rates of cyclohexane consumption. TOFs for MIL-101 were calculated per CUS.

$^b$(Gram of K + A)/(gram of catalyst × time).

$^c$In activated MIL-101.

$^d$Acetone was used as solvent.
One can judge from the data shown in table 3 that the MIL-101 materials are more active and allow higher yields of cyclohexanol/-one and higher substrate conversions to be obtained when compared with the Fe- and Cr-containing silicates or aluminophosphates (Chen & Sheldon 1995; Raja et al. 1999; Anand et al. 2006; Shylesh et al. 2007). The higher selectivity to K-A oil could be due to the specific zeotype porous structure of MIL-101, which may suppress overoxidation processes. Moreover, the presence of the hydrocarbon linker in the MOF network favours adsorption of the organic reagents. Importantly, the productivities of both MIL-101 catalysts were significantly higher than productivities of the other single-site catalysts (see table 3 for comparison), which is obviously owing to the high Cr (Fe) fraction in the MIL-101 materials (ca 23 wt%).

Hot catalyst filtration tests confirmed that the observed catalysis in the presence of Cr-MIL-101 is truly heterogeneous, though a trace amount of chromium (0.3 ppm) was determined in the filtrate. On the contrary, cyclohexane oxidation did not stop completely after the removal of Fe-MIL-101 at ca 10 per cent conversion and elemental analysis showed iron leaching (2.6 ppm). The amount of Fe leached can be reduced to 0.5 ppm by increasing the Fe/TBHP or cyclohexane/TBHP molar ratio; Fe-MIL-101 behaved as a true heterogeneous catalyst in this case. Under optimal conditions, both Fe- and Cr-MIL-101 could be recycled at least five times (405 and 415 TON, respectively) without loss of the catalytic properties and with retention of the MIL-101 structure, which was confirmed by FT-IR spectroscopy (figure 5, curve C).

(c) Coupling reaction of organic oxides with CO2

Organic carbonates are valuable products that are used as raw materials in the synthesis of polycarbonates and also as electrolyte solvents for lithium batteries, fuel additives and substitutes for non-environmental organic solvents and toxic chemical reagents (Shaikh & Sivaram 1996). The common method for
cyclic carbonates production is a coupling reaction of corresponding epoxides and CO₂. Carbon dioxide is an easily available, cheap, non-toxic and renewable C₁ resource, and the development of methods for its activation at mild conditions is an attractive research goal (Sakakura et al. 2007; Aresta 2010). Currently, industry uses quaternary ammonium salts, e.g. tetraethylammonium bromide, as a catalyst for the synthesis of cyclic carbonates (Peppel 1958). The Asahi Kasei process uses an anion exchange material with (CH₃)₄NCl groups as a heterogeneous catalyst for the production of ethylene carbonate, which is used as an intermediate in the synthesis of monoethylene glycol (Fukuoka et al. 2003). Nevertheless, these methodologies require high pressure of CO₂ and/or high reaction temperature, which makes them unfavourable in terms of energy and economics. In past decades, numerous catalytic systems have been elaborated for the synthesis of cyclic carbonates. Among the catalysts are salen, porphyrin and phthalocyanine complexes of the main group and transition metals (Al, Sn, Cr, Co, Ni, Cu, Zn), onium salts, ionic liquids, polyoxometalates, metal oxides, immobilized organometallic complexes, titanosilicates and zeolites (Sakakura & Kohno 2009; North et al. 2010). There are also a few examples of the application of a hybrid material, MOF-5, for the cycloaddition of CO₂ (Kleist et al. 2009; Song et al. 2009). However, most of the known catalysts still operate at high pressure and/or temperature; therefore, the discovery of new catalysts and energy-efficient processes remains a challenge.

To estimate the scope and limitations of the MIL-101 materials in the carboxylation of organic oxides to produce cyclic carbonates, we explored their catalytic properties in a solvent-free system under mild conditions (8 atm CO₂, 25°C). In the blank experiment without any catalyst, epoxide conversion and carbonate yield were negligible. In the presence of Cr-MIL-101, the substrate conversion slightly increased but the product yield was still poor. It was mentioned above that quaternary ammonium salts are often used to promote the coupling reaction of epoxides with CO₂. In our case, the addition of tetrabutylammonium bromide (TBABr) was also crucial for the formation of cyclic carbonate with a high yield at mild conditions. It is noteworthy that TBABr itself did not catalyse the reaction at room temperature.

The main results of the catalytic study on the MIL-101/TBABr system are presented in table 4. Some representative results reported in the literature for heterogeneous systems which can operate at rather mild conditions (Srivastava et al. 2003, 2005; Song et al. 2009; Meléndez et al. 2011) are given for comparison. Both Cr- and Fe-MIL-101 were active and highly selective in the synthesis of propylene (table 4, entries 1 and 2) and styrene carbonates (entries 6 and 7). Moreover, the vacuum activation of MIL-101 is not critical for this reaction. Cyclohexene oxide is known to be a less reactive substrate than propylene and styrene oxides, which is in agreement with our results (table 4, entry 12). As one can conclude from the data shown in table 4, the MIL-101/TBABr systems show the yields of cyclic carbonates comparable to MOF-5 and even superior to conventional SSHCs.

The hot catalyst filtration tests revealed no further substrate conversion in the filtrate after removal of the catalyst, indicating the true heterogeneous nature of catalysis over both Cr- and Fe-MIL-101 (figure 8). The FT-IR spectroscopic study confirmed the retention of the MIL-101 structure after the catalyst was reused.
Table 4. Cyclic carbonate synthesis in the presence of Cr-MIL-101 in comparison with previously reported heterogeneous catalysts.

<table>
<thead>
<tr>
<th>entry</th>
<th>substrate</th>
<th>product</th>
<th>catalyst</th>
<th>co-catalyst</th>
<th>conditions</th>
<th>conversion</th>
<th>selectivity (%)</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td>Cr-MIL-101</td>
<td>TBABr</td>
<td>8bar CO₂, 25°C, 24h</td>
<td>91</td>
<td>90</td>
<td>this work</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td>Fe-MIL-101</td>
<td>TBABr</td>
<td>8bar CO₂, 25°C, 24h</td>
<td>97</td>
<td>90</td>
<td>this work</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td>MOF-5</td>
<td>TBABr</td>
<td>8bar CO₂, 50°C, 6h</td>
<td>95</td>
<td>100</td>
<td>Song et al. (2009)</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td>Ti-SBA-15-pr-Ade²</td>
<td>—</td>
<td>7bar CO₂, 120°C, 6h</td>
<td>89</td>
<td>92</td>
<td>Srivastava et al. (2005)</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td>TBA-Al(salen)/SiO₂</td>
<td>—</td>
<td>8bar CO₂, 0°C, 24h</td>
<td>73</td>
<td>100</td>
<td>Meléndez et al. (2011)</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td>Cr-MIL-101</td>
<td>TBABr</td>
<td>8bar CO₂, 25°C, 48h</td>
<td>98</td>
<td>97</td>
<td>this work</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
<td>Fe-MIL-101</td>
<td>TBABr</td>
<td>8bar CO₂, 25°C, 54h</td>
<td>88</td>
<td>93</td>
<td>this work</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td></td>
<td>MOF-5</td>
<td>TBABr</td>
<td>1bar CO₂, 50°C, 15h</td>
<td>92</td>
<td>100</td>
<td>Song et al. (2009)</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td></td>
<td>Ti-SBA-15-pr-Ade²</td>
<td>—</td>
<td>7bar CO₂, 120°C, 8h</td>
<td>94</td>
<td>95</td>
<td>Srivastava et al. (2005)</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
<td>Ti-MCM-41</td>
<td>DMAPb</td>
<td>7bar CO₂, 140°C, 10h</td>
<td>100</td>
<td>82</td>
<td>Srivastava et al. (2003)</td>
</tr>
<tr>
<td>11</td>
<td></td>
<td></td>
<td>TBA-Al(salen)/SiO₂</td>
<td>—</td>
<td>1bar CO₂, 26°C, 24h</td>
<td>86</td>
<td>100</td>
<td>Meléndez et al. (2011)</td>
</tr>
<tr>
<td>12</td>
<td></td>
<td></td>
<td>Cr-MIL-101</td>
<td>TBABr</td>
<td>8bar CO₂, 25°C, 64h</td>
<td>27</td>
<td>19</td>
<td>this work</td>
</tr>
</tbody>
</table>

²Adenine-modified Ti-SBA-15 catalysts.

bN,N-dimethylaminopyridine.
3. Conclusions

We have demonstrated that the mesoporous metal–organic frameworks Cr- and Fe-MIL-101 are efficient SSHCs for several liquid-phase reactions, including the selective allylic oxidation of alkenes and oxyfunctionalization of cyclohexane with environmentally benign oxidants (O₂ and TBHP) as well as the coupling reaction of organic oxides with CO₂. The oxidation of cyclic alkenes, including terpenes, with TBHP to α,β-unsaturated ketones with selectivity as high as 86–93% at 70–87% substrate conversions can be accomplished using Cr-MIL-101. Both Fe- and Cr-MIL-101 catalyse allylic oxidation of cyclohexene with molecular oxygen and oxidation of cyclohexane with TBHP in the absence of additional organic solvent. The nature of the active metal has a strong impact on the product distributions. In the cyclohexene oxidation with O₂, Cr-MIL-101 allows higher selectivities towards cyclohexenol/-one to be achieved. Cyclohexane oxidation over Cr-MIL-101 yields selective cyclohexanone formation (up to 86% selectivity at 23% cyclohexane conversion or 75% selectivity at 36% conversion). To the best of our knowledge, this result is superior to the results ever published in the literature. Both Fe- and Cr-MIL-101 behave as true heterogeneous catalysts and can be used repeatedly without sustaining a loss of activity and selectivity if anhydrous TBHP is employed as the oxidant, but thermal reactivation under vacuum is needed for successful catalyst reuse. Fe-MIL-101 is less stable than Cr-MIL-101, but leaching of iron can be eliminated by a proper choice of reaction conditions.

Both Fe- and Cr-MIL-101 coupled with TBABr catalyse heterogeneously the coupling reaction of organic oxides and CO₂ at mild conditions (8 bar, 25°C) and produce cyclic carbonates with a yield as high as 95 per cent at almost complete substrate conversion, which is comparable to the best results published to date in the literature (MOF-5).

Finally, we may conclude that the MIL-101 materials (especially Cr-MIL-101) are prospective catalytic materials for liquid-phase transformations of organic
compounds. These materials may show advantages over conventional SSHCs in terms of activity, productivity, yields and selectivity as well as stability towards active metal leaching.

The research was partially supported by the Russian Foundation for Basic Research (grant nos 09-03-12112 and 09-03-93109).

References


