Metal–Organic Frameworks of Vanadium as Catalysts for Conversion of Methane to Acetic Acid

Anh Phan, Alexander U. Czaja, Felipe Gándara, Carolyn B. Knobler, and Omar M. Yaghi

Center for Reticular Chemistry, Center for Global Mentoring, DOE-UCLA Institute for Genomics and Proteomics, and Department of Chemistry and Biochemistry, University of California—Los Angeles, 607 Charles E. Young Drive East, Los Angeles, California 90095, United States

BASF SE, Chemicals Research and Engineering, GCC/PZ, Ludwigshafen, Germany

School of EEWS, Korea Advanced Institute of Science and Technology, Daejeon, Korea

ABSTRACT: A catalytic system combining the high activity of homogeneous catalysts and the ease of use of heterogeneous catalysts for methane activation is reported. The vanadium-containing metal–organic frameworks (MOFs) MIL-47 and MOF-48 are found to have high catalytic activity and chemical stability. They convert methane selectively to acetic acid with 70% yield (490 TON) based on K2S2O8 as an oxidant. Isotopic labeling experiments showed that two methane molecules are converted to the produced acetic acid. The MOF catalysts are reusable and remain catalytically active for several recycling steps without losing their crystalline structures.

Methane is the main constituent of natural gas, which represents almost two-thirds of fossil fuels on earth. A long-standing challenge has been to find catalysts for conversion of methane to useful feedstock chemicals such as acetic acid (AA). Currently, the production of AA on an industrial scale involves multiple steps, uses expensive homogeneous metal (Rh or Ir) catalysts, and requires high temperatures (up to 250 °C).1 Thus, efforts are ongoing to identify catalysts for the direct aerobic oxidation of methane to AA and that can operate at lower temperatures. Reported heterogeneous catalysts show activity in the direct oxidation of methane to AA but give low product yields and have lower selectivity than homogeneous systems.2–5 Recently reported homogeneous catalyst systems using K2S2O8 as an oxidant are based on vanadium(IV) complexes with an oxygen-dominated coordination sphere and give improved conversions at 80 °C.6 It is desirable to develop a catalyst system that combines the high activity of homogeneous catalysts and the ease of use of heterogeneous catalysts. Metal–organic frameworks (MOFs) are promising materials for this application because of their high porosity and the flexibility with which the metal centers and the organic struts can be varied and functionalized. In this report, we show that a MOF (MIL-47), constructed from vanadium centers in an oxygen-dominated coordination sphere, can catalyze the oxidation of methane directly to AA with 70% yield using K2S2O8 as an oxidant (yields based on K2S2O8), 175 TON, and 80% selectivity at 80 °C. This performance was enhanced by functionalizing the pore with methyl groups, by which a new MOF (MOF-48) was synthesized. Also, adding CO to the reaction mixture increased the activity to 490 TON and the selectivity to 100% at 80 °C. We determined, under the same catalytic conditions, using 13C-labeled methane, that methane is entirely incorporated into the AA product (100% from the methyl carbon and 90% for the carbonyl carbon). These MOF catalysts are easily separated and reused. They remain catalytically active for several recycling steps. Their overall performance rivals that of homogeneous vanadium catalysts and exceeds that of the heterogeneous systems.

Our strategy is to use a MOF whose secondary building unit (SBU) is a vanadium center having an oxygen-dominated

Figure 1. Ball-and-stick representations of (a) an amavadin-type complex, 2,2′-(hydroxyimino)diacetic acid (HIDA; top) and vanadyl acetacetonate [V(O)(acac)2; bottom], (b) a rodlike SBU of MOF-48 (chains of corner-sharing VO6 octahedra), and (c) MOF-48 with 1D pores comprising protruding methyl groups (VO6 are shown in blue polyhedra). Color code: V, blue; O, red; N, dark blue; C, gray. Hydrogen atoms omitted for clarity.

Scheme 1. Tentative Stoichiometric Catalytic Reactions for Conversion of Methane to AA in the (a) Absence and (b) Presence of CO2

(a) 2CH4 + 2H2O + 4 K2S2O8 TFA, 80 °C, 20h MOFs CH3COOH + 8KHSO4

(b) CH4 + CO + H2O + K2S2O8 TFA, 80 °C, 20h MOFs CH3COOH + 2KHSO4

*a See the SI for the proposed source and calculation of water and the proposed stoichiometric reaction of MTFA (reaction 15 in the SI, section S9).
Table 1. Catalytic Activity of Heterogeneous MOF Catalysts in the Conversion of Methane to AA in the Absence of CO

<table>
<thead>
<tr>
<th>catalyst</th>
<th>CH3CO2H (mM)</th>
<th>CF3CO2CH3 (MFTA) (mM)</th>
<th>yield of AA (%) (^a)</th>
<th>yield of AA (%) (^c)</th>
<th>MFTA (^d) selectivity (%)</th>
<th>TON of AA (^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOF-48-as syn.</td>
<td>0.36</td>
<td>0.07</td>
<td>36</td>
<td>13</td>
<td>17</td>
<td>89</td>
</tr>
<tr>
<td>MOF-48 – 100</td>
<td>0.38</td>
<td>0.30</td>
<td>38</td>
<td>14</td>
<td>29</td>
<td>95</td>
</tr>
<tr>
<td>MOF-48 – 180</td>
<td>0.48</td>
<td>0.30</td>
<td>48</td>
<td>18</td>
<td>38</td>
<td>121</td>
</tr>
<tr>
<td>MIL-47-as syn.</td>
<td>0.38</td>
<td>0.08</td>
<td>38</td>
<td>14</td>
<td>18</td>
<td>94</td>
</tr>
<tr>
<td>MIL-47 – 350</td>
<td>0.60</td>
<td>0.08</td>
<td>60</td>
<td>22</td>
<td>11</td>
<td>150</td>
</tr>
<tr>
<td>MIL-47 – 480</td>
<td>0.70</td>
<td>0.07</td>
<td>70</td>
<td>26</td>
<td>9</td>
<td>175</td>
</tr>
</tbody>
</table>

\(^a\) Reaction conditions: \(p\)(CH4) = 10 bar (25 °C), 4 mmol of K2S2O8, 7.5 mL of TFA, 20 h at 80 °C. \(^b\) The CH3CO2H yield was calculated as \((4[CH3CO2H])/[K2S2O8]\) (Scheme 1a) because K2S2O8 is the limiting reagent (excluding gaseous products). \(^c\) Yields based on methane; the CH3CO2H yield was calculated as \((2[CH3CO2H])/[CH4]\) (Scheme 1b) (excluding gaseous products; see SI, section S9). \(^d\) The CH3CO2H to the metal content.

Table 2. Catalytic Activity of Heterogeneous MOF Catalysts in the Conversion of Methane to AA in the Presence of CO with 100% Selectivity

<table>
<thead>
<tr>
<th>catalyst</th>
<th>CH3CO2H (mM)</th>
<th>total yield (^b) (%)</th>
<th>total yield (^c) (%)</th>
<th>TON of AA (^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOF-48-as syn.</td>
<td>1.36</td>
<td>34</td>
<td>25</td>
<td>340</td>
</tr>
<tr>
<td>MOF-48 – 100</td>
<td>1.75</td>
<td>44</td>
<td>32</td>
<td>440</td>
</tr>
<tr>
<td>MOF-48 – 180</td>
<td>1.95</td>
<td>49</td>
<td>36</td>
<td>490</td>
</tr>
<tr>
<td>MIL-47-as syn.</td>
<td>0.95</td>
<td>24</td>
<td>18</td>
<td>240</td>
</tr>
<tr>
<td>MIL-47 – 350</td>
<td>1.16</td>
<td>29</td>
<td>21</td>
<td>290</td>
</tr>
<tr>
<td>MIL-47 – 480</td>
<td>1.32</td>
<td>33</td>
<td>24</td>
<td>330</td>
</tr>
<tr>
<td>VOOS</td>
<td>0.8</td>
<td>21</td>
<td>15</td>
<td>210</td>
</tr>
</tbody>
</table>

\(^a\) Reaction conditions: \(p\)(CH4) = 10 bar (25 °C), \(p\)(CO) = 10 bar (25 °C), 4 mmol of K2S2O8, 7.5 mL of TFA, 20 h at 80 °C. \(^b\) The total yield was calculated as \(([[CH3CO2H]/[K2S2O8])\) (Scheme 1b) because K2S2O8 is the limiting reagent (excluding gaseous products).

The coordination sphere. This structural motif is found in molecular complexes known as homogeneous catalysts (Figure 1a), specifically amavadin and vanadyl acetylacetonate. \(^a\) In MIL-47, \(^b\) the VO6 octahedra are sharing opposite corners to make infinite SBU’s that are linked together by terephthalate moieties to form a hexagonal arrangement of 1D channels. In the present work, we studied the conversion of methane to AA using MIL-47, VO(BDC)-H2BDC, and H2BDC. We contrast its performance with the new methyl-functionalized analogue MOF-48 and VOSO4.8 From these data, the Brunauer—Emmett—Teller (BET) surface areas were calculated and found to be 480 m2/g (MIL-47) and 180 m2/g (MOF-48). We also prepared an additional two samples for catalytic studies for which the pores were evacuated but had BET surface areas of 350 m2/g (MIL-47) and 100 m2/g (MOF-48).

MIL-47 and MOF-48 catalysts with the highest surface areas gave the best yield (70% and 48%) for AA and the best selectivity (38%) for MFTA (Table 1). The higher yields are associated with more open pores, while the higher selectivity is associated with the more hydrophobic pores of MOF-48. To reduce the amount of oxidant consumed and enhance the amount of AA, we carried out the reaction in the presence of CO. Under the same conditions, the amount of AA produced increases significantly from 0.48 to 1.95 mmol, and TON increases from 121 to 490 for MOF-48 and a similar increase of lower magnitude is observed for MIL-47 (Table 2). This suggests that CO is a carboxylating agent, which is in accordance with other reports. \(^a\) Indeed, in the presence of CO, the reaction gives 100% selectivity for AA (in the liquid phase) for both MOFs (Table 2).

To confirm the origin of the carbon atoms in the AA product, we examined the reaction both with and without CO using >99.9% 13C isotopically enriched methane under the same catalytic conditions. We found that, without CO, 90% of the AA has both carbon atoms derived from methane molecules. This was evidenced coincidence of the observed powder X-ray diffraction (PXRD) patterns with the calculated one from the single-crystal X-ray diffraction data (Figure 3S in the SI).

Both MIL-47 and MOF-48 were activated (removal of guest molecules from the pores) by calcination of the as-synthesized samples at 350 °C in air for 8 h. \(^7\) MIL-47 and MOF-48 are thermally stable up to 425 °C (Figure 4S in the SI). The adsorption isotherm measurements at 77 K showed a type I behavior consistent with the presence of a permanent porosity in these MOFs (Figure 5S in the SI). From these data, the Brunauer—Emmett—Teller (BET) surface areas were calculated and found to be 480 m2/g (MIL-47) and 180 m2/g (MOF-48). We also prepared an additional two samples for catalytic studies for which the pores were evacuated but had BET surface areas of 350 m2/g (MIL-47) and 100 m2/g (MOF-48).

The catalytic reactions (Scheme 1) were carried out using a mixture of trifluoroacetic acid (TFA; 7.5 mL), potassium peroxydisulfate (K2S2O8; 4 mmol), and MFO (4 μmol) in a 21 mL high-pressure vessel. The vessel was flushed with N2 three times, pressurized with methane (10 bar) and CO (10 bar), if required and stirred for 20 h at 80 °C. The reaction mixture was filtered, and the products were quantified by 1H NMR (see SI, section S8). The results are summarized in Tables 1 and 2 in the absence and presence of CO, respectively.

In the absence of CO, the major product is AA and the minor product is methyl trifluoroacetate (MFTA). \(^6\) The MIL-47 and MOF-48 catalysts with the highest surface areas gave the best yield (70% and 48%) for AA and the best selectivity (38%) for MFTA (Table 1). The higher yields are associated with more open pores, while the higher selectivity is associated with the more hydrophobic pores of MOF-48.

To reduce the amount of oxidant consumed and enhance the amount of AA, we carried out the reaction in the presence of CO. Under the same conditions, the amount of AA produced increases significantly from 0.48 to 1.95 mmol, and TON increases from 121 to 490 for MOF-48 and a similar increase of lower magnitude is observed for MIL-47 (Table 2). This suggests that CO is a carboxylating agent, which is in accordance with other reports. \(^6\) Indeed, in the presence of CO, the reaction gives 100% selectivity for AA (in the liquid phase) for both MOFs (Table 2).

To confirm the origin of the carbon atoms in the AA product, we examined the reaction both with and without CO using >99.9% 13C isotopically enriched methane under the same catalytic conditions. We found that, without CO, 90% of the AA has both carbon atoms derived from methane molecules. This was evidenced
This preliminary study shows promising evidence that MOFs are active heterogeneous catalysts for the conversion of methane to AA and that their performance exceeds that of other such catalysts. We anticipate further elaboration of these studies because MOFs are easily functionalized and varied.

### ASSOCIATED CONTENT

5 Supporting Information. Detailed experimental, analytical, catalytic, and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

### AUTHOR INFORMATION

Corresponding Author
E-mail: yaghj@chem.ucla.edu.

#### ACKNOWLEDGMENT

This work was supported by BASF SE (Ludwigshafen, Germany). We thank Dr. Siddhartha Das and Dr. Hiroyasu Furukawa for valuable discussions. O.M.Y. was also supported by the WCU program (R-31-2008-000-10055-0). F.G. acknowledges funding by the Spanish Ministry of Education through the “Programa de Movilidad de Recursos Humanos del Plan Nacional de I-D+i 2008-2011”.

### REFERENCES

10. Crystal data for MOF-48: space group Pmna, a = 6.7507(10) Å, b = 16.7979(13) Å, c = 12.9232(7) Å. All obtained crystals were found to be twinned. The best data were obtained with a crystal composed of three twin components. The small size of the crystals limited the maximum reached resolution. These factors account for the alerts present in the corresponding CIF file. Full crystal and refinement data and structure solution details can be found in the SI, section S4.