New crystalline complex metal oxides created by unit-synthesis and their catalysis based on porous and redox properties

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Figure S 1. Comparison of the simulated powder XRD patterns using the Rietveld method with the observed patterns, a) Na-Mo-Mn oxide and b) NH₄-Mo-Fe oxide.
Figure S 2. XPS spectra and curve fitting of a) Mo ion in Na-Mo-Mn oxide, b) Mn ion in Na-Mo-Mn oxide, c) Mo ion in NH$_4$-Mo-Fe oxide and d) Fe ion in NH$_4$-Mo-Fe oxide.
Figure S 3. TPD-MS profiles of a) Na-Mn-Mn oxide ($m/z = 18$) for water, b) NH$_4$-Mn-Fe oxide ($m/z = 18$) for water, and c) NH$_4$-Mn-Fe oxide ($m/z = 16$) for NH$_3$. 
Figure S 4. XRD patterns of the materials before and after calcination.
Figure S 5. A) XRD patterns and B) IR spectra of a) Mo-V-Bi-NC350(nano) before the methacrolein oxidation, b) Mo-V-Bi-NC350(nano) after the reaction, and c) well-crystallized Mo-V-Bi-NC350 before the reaction. Si internal standard (*)
Figure S 6. a) XRD patterns and b) FT-IR spectra of porous POMs before and after hydrolysis of cellobiose.
<table>
<thead>
<tr>
<th></th>
<th>Na-Mo-Mn oxide</th>
<th>NH₄-Mo-Fe oxide</th>
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</thead>
<tbody>
<tr>
<td><strong>Crystallographic Information</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crystal system</td>
<td>cubic</td>
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</tr>
<tr>
<td>Space group</td>
<td>F d -3 m</td>
<td>F d -3 m</td>
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<tr>
<td>a = b = c (Å)</td>
<td>19.7047</td>
<td>19.4012</td>
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<tr>
<td>V (Å³)</td>
<td>7650.82</td>
<td>7302.73</td>
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<tr>
<td><strong>Agreement Factors</strong></td>
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<tr>
<td>Rwp</td>
<td>6.14%</td>
<td>6.30%</td>
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<tr>
<td>Rwp(w/o bck)</td>
<td>11.59%</td>
<td>15.24%</td>
</tr>
<tr>
<td>Rp</td>
<td>4.43%</td>
<td>4.51%</td>
</tr>
<tr>
<td><strong>Pattern Parameter</strong></td>
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<td></td>
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<tr>
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<td>Pseudo-Voigt</td>
<td>Pseudo-Voigt</td>
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<tr>
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<td>U = 2.33109, V = -0.88222, W = 0.10675</td>
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<td>Line shift</td>
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<td>0.14627</td>
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<td>Shift#2</td>
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<td>Method</td>
<td>Berar-Baldinozzi</td>
<td>Berar-Baldinozzi</td>
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<tr>
<td>Parameter</td>
<td>P1 = 0.55455, P2 = -0.05288, P3 = -1.30706, P4 = 0.06146</td>
<td>P1 = -0.09418, P2 = -0.28598, P3 = 0.02880, P4 = 0.53677</td>
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<td>Background coefficients</td>
<td>polynomial = 100</td>
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<td>R0 (preferred orientation)</td>
<td>1.29910</td>
<td>1.62976</td>
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## Table S2: Structural information of Na-Mo-Mn oxide from structural analysis.

<table>
<thead>
<tr>
<th>atom</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>Uiso</th>
<th>Occupancy</th>
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<tbody>
<tr>
<td>O1</td>
<td>0.06803</td>
<td>0.36571</td>
<td>0.18197</td>
<td>0.06</td>
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<tr>
<td>Mo2</td>
<td>0.07721</td>
<td>0.45349</td>
<td>0.17279</td>
<td>0.018</td>
<td>1</td>
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<tr>
<td>Mn3</td>
<td>0</td>
<td>0.5</td>
<td>0</td>
<td>0.02</td>
<td>1</td>
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<tr>
<td>Mn4</td>
<td>0.125</td>
<td>0.625</td>
<td>0.125</td>
<td>0.02</td>
<td>0.6</td>
</tr>
<tr>
<td>O5</td>
<td>0.09848</td>
<td>0.22402</td>
<td>0.09848</td>
<td>0.06</td>
<td>0.55</td>
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<tr>
<td>O6</td>
<td>0.07549</td>
<td>0.46927</td>
<td>0.07549</td>
<td>0.06</td>
<td>1</td>
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<tr>
<td>O7</td>
<td>0.06657</td>
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<td>O8</td>
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<td>0.18316</td>
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<tr>
<td>O9</td>
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<td>0.02514</td>
<td>0.02514</td>
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Table S 3. Structural information of NH$_4$-Mo-Fe oxide from structural analysis.

<table>
<thead>
<tr>
<th>Atom</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>Uiso</th>
<th>Occupancy</th>
</tr>
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<tbody>
<tr>
<td>Mo1</td>
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<tr>
<td>O2</td>
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<td>0.36923</td>
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<tr>
<td>O3</td>
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<tr>
<td>O4</td>
<td>0.06545</td>
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<td>0.06545</td>
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<tr>
<td>O5</td>
<td>0.07547</td>
<td>0.46965</td>
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<td>0.06</td>
<td>1</td>
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<tr>
<td>O6</td>
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<td>0.12172</td>
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<td>O7</td>
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<td>0.03057</td>
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<tr>
<td>Fe8</td>
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<td>Fe9</td>
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<td>0.625</td>
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<td>O10</td>
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<td>0.25</td>
<td>0.06</td>
<td>0.39</td>
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Table S 4. Surface area of the POM-based microporous materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface area (m$^2$/g)</th>
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<tbody>
<tr>
<td>Mo-V-Bi-NC350</td>
<td>75</td>
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<tr>
<td>Na-Mo-Zn-NC200</td>
<td>37</td>
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<tr>
<td>NH$_4$-Mo-Zn-NC200</td>
<td>45</td>
<td>3</td>
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<tr>
<td>Na-Mo-Mn-NC200</td>
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</tr>
<tr>
<td>NH$_4$-Mo-Fe-NC200</td>
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<td>This work</td>
</tr>
</tbody>
</table>

Reference