Inverse relation of dimensionality and catalytic activity in CO$_2$ transformation: A systematic investigation by comparing multidimensional metal-organic frameworks

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1. Detailed Structure analysis of all the seven MOFs

The In$_2$(OH)$_3$(BDC)$_{1.5}$ MOF adopts a three-dimensional framework and crystallizes in the monoclinic system, $P2_1/c$ space group. The framework consists of two independent indium atoms, in which each In1 atom is linked to three In2 atoms and vice versa. Three oxygen atoms from the three different BDC ligands and three $\mu_2$-OH groups are coordinated with the two independent indium atoms and these are assembled into a microporous structure, denoted as In$_2$(OH)$_3$[O$_4$C$_8$H$_4$]$_{1.5}$. Bridging of each oxygen atom of OH anions with the two indium atoms results in an infinite six-membered ring containing sheets of [In$_2$(OH)$_3$]$_\infty^{3+}$. The packing diagram shows that BDC ligands act as pillars between two layers, in which each of them is linked to four different indium atoms (2 In (1) & 2 In (2) atoms). Thus the resulting 3D structure have been generated from a honeycomb (6,3) 2D structure, in which the aromatic rings are directed in the [1 0 1] and [1 0 1] directions, which is cross-linked by the tetratopic BDC linkers. A comparison with the corundum-like In$_2$O$_3$ structure revealed that in both cases the inorganic layer was formed by the vertex sharing of InO$_6$, not by edge sharing. A comparable similarity in the In-In average distance was also observed in both cases. The average In-In distance for In(BDC)$_{1.5}$(bipy) was measured to be 3.77 Å, whereas for corundum-like In$_2$O$_3$ it is found to be 3.34 Å. The In-O bond distances for both indium atoms were also measured to be in the region of 2.058 Å to 2.215 Å.

The second MOF In(BDC)$_{1.5}$(bipy) crystallizes in the orthorhombic system, $Pbca$ space group. One only type of indium metal is present in the framework which is octahedrally coordinated with six In-O bonds coming from three bidentate chelating carboxylate groups of three different fully deprotonated bridging (BDC)$^{2-}$ units and two nitrogen atoms of one bipy molecule. The crystallographic analysis shows that the BDC linkers play a crucial role in the formation of the structure. The 1D infinite zigzag chains are constructed by joining the In atoms along the b direction with one type of BDC linkers which are situated in the general position. While the other BDC, whose centroid is situated on an inversion center, keeps these chains bonded along [1 0 0] direction giving rise to the formation of hexagonal layers. Thus the resulting 3D structure has been generated from the entanglement formed by catenation of these bidimensional hexagonal layers. Also it is important to note that, while adjusting the metal:connector:chelate ratio to 1:1:1, results in a dimensionality change from 3D structure to
2D structure, where the chelate bipy ligand blocks the possibilities of connections in one direction. The average In-O carboxylic bond distance is measured to be in the region of 2.204 Å to 2.551 Å, and those of In-N bipy’s distance ranges from 2.295 Å to 2.349 Å.

The third MOF In$_2$(OH)$_2$(BDC)$_2$(phen)$_2$ crystallizes in the monoclinic system, $P2_1/n$ space group. The indium atoms are six-coordinated by two μ2-OH, two oxygen atoms from different carboxylate groups of BDC and two nitrogen atoms of phen, forming a distorted-octahedral geometry. Four indium atoms are joint together by μ2-OH groups, and forms a tetrameric $[\text{In}_2(\text{OH})_4(\text{phen})_4]^{8+}$ with an In1-In2 distance of 4.11 Å. Finally these tetramers are linked together by BDC connectors along the a and b directions, results in an infinite layers perpendicular to the (001) directions of composition $[\text{In(BDC)(OH)(Phen)}]_\infty$. The average In-O carboxylic bond distance is measured to be in the region of 2.11 Å, and those of In-N phen distance ranges from 2.326 Å to 2.33 Å. Next two compounds, In(H$_2$O)(BTC).$\times$($\times$H$_2$O)(bipy)$_{0.25}$ and In(H$_2$O)(BTC)(phen) consists of 2D structures with same stoichiometry. In(H$_2$O)(BTC).($\times$H$_2$O)(bipy)$_{0.25}$ crystallizes in the orthorhombic system with $P$bc$a$ space group whereas, In(H$_2$O)(BTC)(phen) crystallizes in the monoclinic system with $P2_1/n$ space group. In both compounds, indium ions are six-coordinated by three oxygen atoms of three carboxylate groups of three different BTC connectors, two nitrogen atoms of one bipy or phen molecule and one water molecule. The packing diagram shows that, in both compounds the BTC linker act as a connector between two layers. The three indium atoms in both compounds were monodentately linked by BTC connectors giving rise to the formation of 2D layers perpendicular to [001] and [100] directions for In(H$_2$O)(BTC).($\times$H$_2$O)(bipy)$_{0.25}$ and In(H$_2$O)(BTC)(phen) respectively. The average In-O distances were found to be almost similar for both compounds.

The sixth MOF $[\text{In}_2(\text{dpa})_3(1,10$-phen)$_2] \cdot $H$_2$O crystallizes in the triclinic system, $p\bar{1}$ space group. Like In$_2$(OH)$_3$(BDC)$_{1.5}$, $[\text{In}_2(\text{dpa})_3(1,10$-phen)$_2] \cdot $H$_2$O framework also consists of two independent indium atoms. The basic structure constructed from two independent In(111) ions, two phenantroline molecule, three types of completely deprotonated diphenic ligands and two hydration water molecule. In1 is octacoordinated, where its coordination environment being satisfied with six In-O bonds from chelating carboxylate groups of diphenic acids and two In-N bonds from phenantroline ligands, which are bounded to the In1 in a chelate mode. Generating in this way, results in a triangulated dodecahedron environment. The In2 metal center is heptacoordinated. Four In-O bonds from chelating carboxylate groups of diphenic
acids and two In-N bonds from phenantroline ligands forms the coordination environment around the in2 atoms. The resultant polyhedron is a monocapped octahedron. These arrangements together forms an one-dimensional MOF with formula \([\text{In}_2(\text{dpa})_3(1,10\text{-phen})_2]\cdot\text{H}_2\text{O}\). The In-O bond distances for both indium atoms were measured to be in the region of 2.123 Å to 2.44 Å, and those of In-N distance were measured to be in the region of 2.305 Å to 2.327 Å. Two hydration water molecules are present in which one is interact with the monodentate coordinated carboxylate group, while the other interact with the carboxylate group bonded to In2 metal. The seventh MOF \([\text{In}(\text{dpa})(\text{bpy})_2]\cdot\frac{1}{2}\text{H}_2\text{O}\) crystallizes in the orthorhombic system, \(P2_12_12_1\) chiral space group. The basic structure consists of an In(111) ions which is connected by two diphenic acid and one and 2,2'-bipyridyl molecule. The coordination of the indium metal with two ligands results in the formation of a one-dimensional and the chains packing is stabilized by several non-covalent interactions.

2. Experimental

Synthesis of all seven MOFs

1) \(\text{In(BDC)}_{1.5}(\text{bipy})\): The synthesis of \(\text{In(BDC)}_{1.5}(\text{bipy})\) was performed by a hydrothermal reaction between \(\text{InCl}_3\) (≥ 98%, Sigma-Aldrich), 1,4-benzendicarboxylic acid (\(\text{H}_2\text{BDC}\), 99%, Sigma-Aldrich), 2,2’-bipyridyl (bipy) (99%, Sigma Aldrich), in 25 ml water at 170 °C for 48 h. The pH of the solution was adjusted to 6 using triethylamine (99%, Alfa Aesar). Activation of the catalyst was performed by heating for 12 h at 100 °C under vacuum. Anal. calcd (%) for the sample \(\text{C}_{22}\text{H}_{14}\text{InN}_2\text{O}_6\): C: 51.09; H: 2.73; N: 5.42; O: 18.56; In: 22.20. Exp. found. (%); C: 51.56; H: 2.05; N: 6.02; O: 17.32 (elemental analysis), In: 23.05 (ICP-OES).

2) \(\text{In}_2(\text{OH})_2(\text{BDC})_2(\text{phen})_2\): Synthesis of \(\text{In}_2(\text{OH})_2(\text{BDC})_2(\text{phen})_2\) was similar to the synthesis of compound “1” with the change that bipy was substituted by phen. Light yellow crystals of “b” were obtained after hydrothermal treatment for 48 h at 170 °C. Anal. Calcd (%) for \(\text{C}_{40}\text{H}_{26}\text{In}_2\text{N}_4\text{O}_{10}\): C: 50.45, H: 2.75, N: 5.88, O: 16.80, In: 24.11. Exp. found. (%); C: 50.39; H: 2.81; N: 5.25; O: 16.50 (elemental analysis), In: 25.05 (ICP-OES).
3) \(\text{In(H}_2\text{O})(\text{BTC})(\text{H}_2\text{O})\text{(bipy)}_{0.25}\): Synthesis of \(\text{In(H}_2\text{O})(\text{BTC})(\text{H}_2\text{O})\text{(bipy)}_{0.25}\) was similar to the synthesis of compound “1” with the exception that \(\text{H}_2\text{BDC}\) was replaced by 1,3,5-benzenetricarboxylic acid (\(\text{H}_3\text{BTC}\), 98%, Sigma Aldrich). Hydrothermal synthesis was carried out at 170 °C for 48 h. Anal. Calcd (%) for \(\text{C}_{19}\text{H}_{14}\text{InN}_2\text{O}_{7}\): C: 45.58, H: 2.72, N: 5.60, O: 23.17, In: 22.93. Exp. found. (%); C: 46.22; H: 2.61; N: 5.10; O: 24.01 (elemental analysis), In: 23.51 (ICP-OES).

4) \(\text{In(H}_2\text{O})(\text{BTC})(\text{phen})\): Synthesis of \(\text{In(H}_2\text{O})(\text{BTC})(\text{phen})\) was similar to the synthesis of compound “2” with the exception that \(\text{H}_2\text{BDC}\) was replaced by 1,3,5-benzenetricarboxylic acid (\(\text{H}_3\text{BTC}\), 98%, Sigma Aldrich). Hydrothermal synthesis was carried out at 170 °C for 48 h. Anal. Calcd (%) for \(\text{C}_{21}\text{H}_{13}\text{InN}_2\text{O}_{7}\): C: 48.49, H: 2.52, N: 5.39, O: 21.53, In: 22.07. Exp. found. (%); C: 45.46; H: 2.85; N: 5.45; O: 22.56 (elemental analysis), In: 23.68 (ICP-OES).

5) \(\text{In}_2(\text{OH})_3(\text{BDC})_{1.5}\): The synthesis of \(\text{In}_2(\text{OH})_3(\text{BDC})_{1.5}\) was performed by a hydrothermal reaction between \(\text{InCl}_3\) (≥ 98%, Sigma-Aldrich), 1,4-benzenedicarboxylic acid (\(\text{H}_2\text{BDC}\), 99%, Sigma-Aldrich), in 25 ml water at 150 °C for 14 h. The pH of the solution was adjusted to 6 using triethylamine (99%, Alfa Aesar). Activation of the catalyst was performed by heating at 100 °C under vacuum for 12 h. Anal. Calcd (%) for \(\text{C}_{12}\text{H}_9\text{O}_9\text{In}_2\): C: 27.36, H: 1.72, O: 27.33, In: 43.59. Exp. found. (%); C: 27.15; H: 1.84; O: 28.02 (elemental analysis), In: 42.69 (ICP-OES).

6) \([\text{In}_2(\text{dpa})_3(1,10-\text{phen})_2]\cdot\text{H}_2\text{O}\): The synthesis of \([\text{In}_2(\text{dpa})_3(1,10-\text{phen})_2]\cdot\text{H}_2\text{O}\) was followed by mixing of \(\text{In(OAc)}_3\) (0.1 g, 0.3 mmol), diphenic acid (\(\text{H}_2\text{dpa}\)) (0.2 g, 0.7 mmol), and 1,10-phenanthroline monohydrate (0.07 g, 0.3 mmol) in 8 mL of distilled water. The mixture was heated for 20 h in a Teflon-lined autoclave at 170 °C. Anal. Calcd (%) for \(\text{C}_{66}\text{H}_{42}\text{In}_2\text{N}_4\text{O}_{13}\): C: 59.66, H: 3.19, N: 4.22, O: 15.65, In: 17.28. Exp. found. (%); C: 58.92; H: 3.19; N: 4.22; O: 15.65 (elemental analysis), In: 16.68 (ICP-OES).

7) \([\text{In(dpa})(\text{bpy})]\cdot\text{1/2H}_2\text{O}\): The synthesis of \([\text{In(dpa})(\text{bpy})]\cdot\text{1/2H}_2\text{O}\) was followed by mixing of \(\text{In(OAc)}_3\) (0.3 g, 1 mmol), diphenic acid (\(\text{H}_2\text{dpa}\)) (0.5 g, 2 mmol), and 2,2’-bipyridyl (0.2 g, 1 mmol) in 16 mL of distilled water. The mixture was heated in a Teflon-lined autoclave at 150 °C for 20 h. Anal. Calcd (%) for \(\text{C}_{38}\text{H}_{27}\text{InN}_2\text{O}_9\): C: 59.24, H: 3.53, N: 3.64, O: 18.69, In: 14.90. Exp. found. (%); C: 58.90; H: 3.64; N: 3.54; O: 18.70 (elemental analysis), In: 14.68 (ICP-OES).
3. Density-functional theory (DFT) Studies

DFT calculations were done with Jaguar version 8.8 using the M06 functionality and LACVP**++ basis sets, and the intermediates and transitions states illustrating the cycloaddition reaction of PO and CO$_2$ to form PC using the In$^{3+}$/TBAB catalyst is shown in the figure S1 given below. The bulky TBAB is represented simply by the Br$^-$ ion which is directly involved in the RDS (rate determining step). The RDS was found to be the ring opening of the propylene oxide that results from the nucleophilic attack of the Br$^-$ on the $\beta$-carbon of the propylene oxide ring. The activation free energy required for this Br$^-$ alone catalyzed cycloaddition is found to be 19.5 kcal/mol, which is estimated between the initial PO-Br$^-$ complex IC (-18.0 kcal/mol with respect to CO$_2$, PO, and Br$^-$ at infinite separation) and the transition state TS (1.5 kcal/mol) (Figure 1). This transition state (TS) then leads to the first intermediate Int-1, completes the ring opening as well as the formation of the $\beta$-C-Br bond and the Br-C-C-O$^-$ nucleophile to attack in the next step leading to the formation of second intermediate Int-2.

When [In(bza)$_3$(1,10-phen)] is included in addition to Br$, the initial complex (IC) is more stabilized than the IC formed by PO and Br$^-$ alone (-40.9 kcal/mol instead of -18 kcal/mol). This is most likely because the interaction of the oxygen atom of the PO with the octacoordinated In metal center and at the same time polarizes the $\beta$-C-O bond of PO so as to be vulnerable to the nucleophile attack of Br$^-$ on its $\beta$-carbon atom. This facilitates the ring opening of the PO and lowers the activation free energy to 11.5 kcal/mol. The succeeding forward process from TS to Int-2 (-47.1 kcal/mol), Int-3 (-57.1 kcal/mol) and Int-4 (-55.4 kcal/mol), that completes the ring opening and Br-C-C-O$^-$ formation, shifting the equilibrium toward the forward reaction. The final stage is the ring closure (TS2 (-44.0 kcal/mol, Int. 5 (-51.1 kcal/mol), and FC (-56.7 kcal/mol)) and the formation of the propylene carbonate.
Figure S1: The energy profile diagram of the intermediates and transition states (calculated using DFT techniques), illustrating the cycloaddition reaction of PO and CO$_2$ to form PC using the In$^{3+}$/TBAB catalyst.
Figure S2: Packing diagram of all seven MOFs, a) In$_2$(OH)$_3$(BDC)$_{1.5}$ b) In(BDC)$_{1.5}$(bipy) c) In$_2$(OH)$_2$(BDC)$_2$(phen)$_2$ d) In(H$_2$O)(BTC)$_2$.(H$_2$O)(bipy)$_{0.25}$ e) In(H$_2$O)(BTC))(phen) f) [In$_2$(dpa)$_3$(1,10-phen)$_2$]·H$_2$O g) [In(dpa)(bpy)]·1/2H$_2$O, viewed along the b and c-axis perspective view (H-atoms omitted for clarity).
Figure S3: PXRD patterns of a) In$_2$(OH)$_3$(BDC)$_{1.5}$ b) In(BDC)$_{1.5}$(bipy) c) In$_2$(OH)$_2$(BDC)$_2$(1,10-phen)$_2$ d) In(H$_2$O)(BTC)$_2$(H$_2$O)(bipy)$_{0.25}$ e) In(H$_2$O)(BTC)(1,10-phen) f) [In$_2$(dpa)$_3$(1,10-phen)$_2$]$\cdot$H$_2$O g) [In(dpa)(bipy)]$\cdot$1/2H$_2$O in comparison to the simulated single crystal pattern.
Figure S4: FT-IR spectrum of a) $\text{In}_2(\text{OH})_3(\text{BDC})_{1.5}$ b) $\text{In} (\text{BDC})_{1.5}$ (bipy) 
c) $\text{In}_2(\text{OH})_2(\text{BDC})_2(\text{phen})_2$ d) $\text{In}(\text{H}_2\text{O})(\text{BTC})(\text{H}_2\text{O})(\text{bipy})_{0.25}$ e) $\text{In}(\text{H}_2\text{O})(\text{BTC})(\text{phen})$
f) $[\text{In}_2(\text{dpa})_3(1,10\text{-phen})_2]\cdot\text{H}_2\text{O}$
Figure S5: FE-SEM images of 

- a) In$_2$(OH)$_3$(BDC)$_{1.5}$
- b) In(BDC)$_{1.5}$(bipy)
- c) In$_2$(OH)$_2$(BDC)$_2$(phen)$_2$
- d) In(H$_2$O)(BTC).$(H_2$O)(bipy)$_{0.25}$
- e) In(H$_2$O)(BTC)(phen)
- f) [In$_2$(dpa)$_3$(1,10-phen)$_2$]·H$_2$O
- g) [In(dpa)(bipy)]·1/2H$_2$O
Figure S6: CO$_2$ adsorption-desorption analysis of catalysts. 

a) In$_2$(OH)$_3$(BDC)$_{1.5}$
b) In(BDC)$_{1.5}$(bipy)
c) In$_2$(OH)$_2$(BDC)$_2$(phen)$_2$
d) In(H$_2$O)(BTC).H$_2$O(bipy)$_{0.25}$
e) In(H$_2$O)(BTC)(phen)
f) [In$_2$(dpa)$_3$(1,10-phen)$_2$].H$_2$O
Table S1: CO$_2$ adsorption amount of all indium-based MOFs.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Absolute Pressure (mmHg)</th>
<th>Quantity Adsorbed (cm$^3$/g STP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In$_2$(OH)$<em>3$(BDC)$</em>{1.5}$</td>
<td>799</td>
<td>3.64</td>
</tr>
<tr>
<td>In(BDC)$_{1.5}$(bipy)</td>
<td>800</td>
<td>0.42</td>
</tr>
<tr>
<td>In$_2$(OH)$_2$(BDC)$_2$(phen)$_2$</td>
<td>799</td>
<td>0.78</td>
</tr>
<tr>
<td>In(H$_2$O)(BTC).(H$<em>2$O)(bipy)$</em>{0.25}$</td>
<td>799</td>
<td>1.24</td>
</tr>
<tr>
<td>In(H$_2$O)(BTC)(phen)</td>
<td>800</td>
<td>1.25</td>
</tr>
<tr>
<td>[In$_2$(dpa)$_3$(1,10-phen)$_2$].H$_2$O</td>
<td>799</td>
<td>7.2</td>
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Table S2: Catalytic activity comparison of all seven MOFs for the cycloaddition reaction of PO and CO$_2$ at room temperature

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Indium CN</th>
<th>Framework dimensionality</th>
<th>$^b$Conv. (%)</th>
<th>$^b$Sel. (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>TBAB</td>
<td>-</td>
<td>-</td>
<td>&lt;3</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>In$_2$(OH)$<em>3$(BDC)$</em>{1.5}$</td>
<td>6</td>
<td>3D</td>
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<td>&gt;99</td>
</tr>
<tr>
<td>3</td>
<td>In(BDC)$_{1.5}$(bipy)</td>
<td>8</td>
<td>2D</td>
<td>15</td>
<td>&gt;99</td>
</tr>
<tr>
<td>4</td>
<td>In$_2$(OH)$_2$(BDC)$_2$(phen)$_2$</td>
<td>6</td>
<td>2D</td>
<td>46</td>
<td>&gt;99</td>
</tr>
<tr>
<td>5</td>
<td>In(H$_2$O)(BTC)$_2$.H$<em>2$O(bipy)$</em>{0.25}$</td>
<td>6</td>
<td>2D</td>
<td>38</td>
<td>&gt;99</td>
</tr>
<tr>
<td>6</td>
<td>In(H$_2$O)(BTC)(phen)</td>
<td>6</td>
<td>2D</td>
<td>42</td>
<td>&gt;99</td>
</tr>
<tr>
<td>7</td>
<td>[In$_2$(dpa)$_3$(1,10-phen)$_2$].H$_2$O</td>
<td>8,7</td>
<td>1D</td>
<td>61</td>
<td>&gt;99</td>
</tr>
<tr>
<td>8</td>
<td>[In$_2$(dpa)(Hdpa)(2,2′-bipy)].0.5H$_2$O</td>
<td>8</td>
<td>1D</td>
<td>30</td>
<td>&gt;99</td>
</tr>
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</table>

$^a$Reaction conditions: propylene oxide (PO) = 42.8 mmol (3 mL), Temperature = RT, 1.2 MPa CO$_2$, 24 h, 600 rpm, catalyst mol% = 0.5, TBAB mol% = 0.5 mol%, semi-batch.

$^b$Determined by GC.
Figure S7: Effect of reaction time on the cycloaddition of propylene oxide and CO$_2$ using 0.35 mol% [In$_2$(dpa)$_3$(1,10-phen)$_2$]·H$_2$O at 50 °C and 1.2 MPa CO$_2$. 
Figure S8: Effect of reaction temperature on the cycloaddition of propylene oxide and CO$_2$ using 0.35 mol% [In$_2$(dpa)$_3$(1,10-phen)$_2$]$\cdot$H$_2$O at different time intervals.
Figure S9: PXRD patterns of the fresh and recycled catalysts. a) $\text{In}_2(\text{OH})_3(\text{BDC})_{1.5}$ b) $\text{In} (\text{BDC})_{1.5} (\text{bipy})$ c) $\text{In}_2(\text{OH})_2(\text{BDC})_2(\text{phen})_2$ d) $\text{In}(\text{H}_2\text{O})(\text{BTC}).(\text{H}_2\text{O})(\text{bipy})_{0.25}$ e) $\text{In}(\text{H}_2\text{O})(\text{BTC})(\text{phen})$ f) $[\text{In}_2(\text{dpa})_3(1,10-\text{phen})_2]\cdot\text{H}_2\text{O}$. 


Figure S10: FT-IR patterns of the fresh and recycled catalysts. a) In$_2$(OH)$_3$(BDC)$_{1.5}$ b) In(BDC)$_{1.5}$(bipy) c) In$_2$(OH)$_2$(BDC)$_2$(phen)$_2$ d) In(H$_2$O)(BTC).H$_2$O(bipy)$_{0.25}$ e) In(H$_2$O)(BTC)(phen) f) [In$_2$(dpa)$_3$(1,10-phen)$_2$].H$_2$O.
3. Characterization

Following instrumentations were chosen for the catalyst characterizations: Powder X-ray diffraction (XRD) patterns (PANalyticalX’pert PRO power diffractometer using Ni-filtered Cu Kα radiation (λ = 1.5404 Å)), Fourier transform infrared (FT-IR) analysis (Avatar 370 Thermo Nicolet spectrophotometer), Thermo-gravimetric analysis (TGA) (Auto TGA 2950 apparatus under a nitrogen flow of 100 mL min\(^{-1}\) heating at a rate of 10 °C min\(^{-1}\) from room temperature to 600 °C), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) (Perkin-Elmer Optima 8300 instrument), elemental analysis (EA) (Vario ELIII system).

4. Cycloaddition of CO\(_2\) and epoxide

Cycloaddition reactions were performed in a 25 mL stainless-steel reactor equipped with a magnetic stirrer. For a typical semi-batch reaction process, certain amount of the catalyst and co-catalyst were introduced into the reactor followed by 42.8 mmol of the epoxide. The reactor was connected with a CO\(_2\) source during the reaction via a one-way check valve to keep the desired level of pressure. The reactions were performed under various reaction conditions of temperatures and pressures with various reaction times. After completion of reaction, the reactor was allowed to cool externally to 0 °C and excess CO\(_2\) was vented off. Toluene was added as internal standard to the final mixture and filtered by using centrifugation. The product analyzed by using gas chromatography (GC, HP 6890, Agilent Technologies) to determine conversion, selectivity, and yield.

GCMS Details:
- Column: HP-5MS (30m x 0.25mm x 0.25um).
- Oven temperature: 50 to 300 °C with 12 °C/min ratio.
- Inlet temp.: 270 °C.
- Detector: FID.
GCMS data of Propylene carbonate
NMR: Propylene Carbonate (4-Methyl-1,3-dioxolan-2-one). $^1$H NMR (300 MHz, CDCl$_3$)  δ 4.77–4.72 (m, 1H, OCH), 4.48–4.42 (m, 1H, CH$_2$), 3.94–3.89 (m, 1H,CH$_2$), 1.35 (d, J = 6.3 Hz, 3H, CH$_3$).