Supporting information

Porous Magnesium Carboxylate Framework: Synthesis, X-ray Crystal Structure, Gas Adsorption Property and Heterogeneous Catalytic Aldol Condensation Reaction

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Table S1. Solvent Effect in Aldol Condensation of p-nitrobenzaldehyde and Ketons Catalyzed by 1 and calcined catalyst

<table>
<thead>
<tr>
<th>solvent</th>
<th>ketone</th>
<th>major product</th>
<th>isolated yield (wt %)</th>
<th>selectivity (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td>acetone</td>
<td>β-aldol product</td>
<td>a) 68  b) 90</td>
<td>a) 100  b) 100</td>
</tr>
<tr>
<td>THF</td>
<td>cyclohexanone</td>
<td>β-aldol product</td>
<td>a) 58  b) 75</td>
<td>a) 100  b) 100</td>
</tr>
<tr>
<td>THF-water (1:1)</td>
<td>acetone</td>
<td>β-aldol product</td>
<td>a) 45  b) 50</td>
<td>a) 48  b) 40</td>
</tr>
<tr>
<td>THF-water (1:1)</td>
<td>cyclohexanone</td>
<td>β-aldol product</td>
<td>a) 40  b) 44</td>
<td>a) 42  b) 36</td>
</tr>
<tr>
<td>No solvent</td>
<td>acetone</td>
<td>β-aldol product</td>
<td>a) 22  b) 38</td>
<td>a) 100  b) 100</td>
</tr>
<tr>
<td>No solvent</td>
<td>cyclohexanone</td>
<td>β-aldol product</td>
<td>a) 16  b) 26</td>
<td>a) 100  b) 100</td>
</tr>
</tbody>
</table>

(a), (b), corresponds to the catalytic performance of 1 and calcined catalyst, respectively.

¹Reaction conditions: Aldehyde (2 mmol), acetone/cyclohexanone (10 mmol), triethylamine (2 mmol), tetrahydrofuran (2 ml) and catalysts (5 mg); temperature = 5-10
°C; for dehydrated compound reaction was performed in nitrogen atmosphere. Yields were isolated after 6 h of reaction.

**Figure S1.** ORTEP diagram of compound 1 with 40% ellipsoid probability.
**Figure S2.** Comparison of IR spectra of pure and recovered catalyst for 1
**Figure S3.** X-ray powder pattern of virgin catalyst and recovered catalyst for 1
**Figure S4.** Aldol condensation of $p$-nitrobenzaldehyde and ketons catalyzed by 1 in five successive runs

**Figure S5.** Aldol condensation of $p$-nitrobenzaldehyde and ketons catalyzed by calcined complex in five successive runs
General Information

All chemicals were purchased from Aldrich and were used as received except benzaldehyde. All solvents used were analytical grade and were used as received from Merck India Pvt. Ltd. Benzaldehyde, acetone and tetrahydrofuran was distilled before use. Benzaldehyde was kept over NaA molecular sieves to trap possible traces of benzoic acid. All reactions were carried out in air, without any special precautions. Column chromatography was performed over silica gel (mesh 60-120) and hexane/ethyl acetate combination was used as the eluent. $^1$H NMR spectra were recorded at ambient temperature in CDCl$_3$ with tetramethylsilane as internal standard. The chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively on Bruker Avance 300 instrument. Elemental analysis of the products was performed by using Perkin-Elmer 240C elemental analyzer.

Characterization of Products

4-hydroxy-4-(4-nitrophenyl)-butan-2-one (Table 3, entry 1):

![Chemical Structure](image)
Yellow oil, $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ (ppm): 8.07 (d, $J = 8.8$ Hz, 2H), 7.47 (d, $J = 8.5$ Hz, 2H), 5.20 (m, 1H), 3.57 (br s, 1H), 2.81 (m, 2H), 2.15 (s, 3H); Anal. Calcd. for C$_{10}$H$_{11}$NO$_4$: C, 57.41%; H, 5.30%; N, 6.69%. Found: C, 57.6%; H, 5.4%; N, 6.6%.

4-hydroxy-4-(2-nitrophenyl)-butan-2-one (Table 3, entry 2):

![Chemical Structure 1]

Yellow oil, $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ (ppm): 7.75 (d, $J = 8.4$ Hz, 1H), 7.72 (d, $J = 10.0$ Hz, 1H), 7.50 (t, $J = 7.6$ Hz, 1H), 7.27 (t, $J = 7.9$ Hz, 1H), 5.52 (m, 1H), 3.93 (br s, 1H), 2.86 (d, $J = 17.2$ Hz, 1H), 2.63 (dd, $J = 17.2, 9.3$ Hz, 1H), 2.06 (s, 3H); Anal. Calcd. for C$_{10}$H$_{11}$NO$_4$: C, 57.41%; H, 5.30%; N, 6.69%. Found: C, 57.6%; H, 5.4%; N, 6.5%.

4-hydroxy-4-(3-nitrophenyl)-butan-2-one (Table 3, entry 3):

![Chemical Structure 2]

Yellow oil, $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ (ppm): 8.12 (s, 1H), 7.97 (d, $J = 8.1$ Hz, 1H), 7.61 (d, $J = 8.0$Hz, 1H), 7.41 (t, $J = 7.9$ Hz, 1H), 5.17 (m, 1H), 3.69 (br s, 1H), 2.81 (m,
2H), 2.13 (s, 3H); Anal. Calcd. for C₁₀H₁₁NO₄: C, 57.41%; H, 5.30%; N, 6.69%. Found: 
C, 57.7%; H, 5.4%; N, 6.5%.

4-hydroxy-4-phenylbutan-2-one (Table 3, entry 4):

![Chemical structure](image)

Yellow oil, ¹H NMR (300 MHz, CDCl₃): δ (ppm): 7.3 (m, 5H), 5.16 (m, 1H), 3.25 (br s, 1H), 2.88 (m, 2H), 2.15 (s, 3H); Anal. Calcd. for C₁₀H₁₂O₂: C, 73.15%; H, 7.27%. Found:
C, 73.3%; H, 7.1%.

4-hydroxy-4-(4-methoxyphenyl)-butan-2-one (Table 3, entry 5):

![Chemical structure](image)
Pale yellow oil, $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ (ppm): 7.2 (d, $J = 8.8$ Hz, 2H), 6.9 (d, $J = 8.8$ Hz, 2H), 4.9 (d, $J = 8.2$ Hz, 1H), 4.05 (br s, 1H), 3.8 (s, 3H), 2.75 (m, 2H), 2.15 (s, 3H); Anal. Calcd. for C$_{13}$H$_{14}$O$_3$: C, 68.02%; H, 7.27%. Found: C, 67.8%; H, 7.2%.

2-(Hydroxy-(4-nitrophenyl)-methyl)-cyclohexan-1-one (Table 3, entry 6):

![Chemical Structure](image)

Pale yellow densed oil, $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ (ppm): 8.21 (d, $J = 9$ Hz, 2H), 7.5 (d, $J = 8.7$ Hz, 2H), 4.94 (d, $J = 8.2$ Hz, 1H), 3.96 (br s, 1H), 2.75-2.8 (m, 1H), 2.36-2.49 (m, 2H), 2.07-2.14 (m, 1H), 1.59-1.88 (m, 5H); Anal. Calcd. for C$_{13}$H$_{15}$NO$_4$: C, 62.64%; H, 6.07%; N, 5.62%. Found: C, 62.8%; H, 6.2%; N, 5.7%.

2-(Hydroxy-(2-nitrophenyl)-methyl)-cyclohexan-1-one (Table 3, entry 7):

![Chemical Structure](image)

Pale yellow densed oil, $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ (ppm): 7.86 (dd, $J = 8.2$ Hz, 1 Hz, 1H), 7.78 (d, $J = 8.2$ Hz, 1 Hz, 1H), 7.65 (td, $J = 7.9$ Hz, 1.3 Hz, 1H), 7.44 (td, $J = 7.9$ Hz, 1 Hz, 1H), 5.48 (d, $J = 8.2$ Hz, 1H), 3.88 (br s, 1H), 2.74-2.8 (m, 1H), 2.36-2.48 (m,
2H), 2.07-2.15 (m,1H), 1.56-1.9 (m, 5H); Anal. Calcd. for C₁₃H₁₅NO₄: C, 62.64%; H, 6.07%; N, 5.62%. Found: C, 62.6%; H, 6%; N, 5.6%.

2-(Hydroxy-(3-nitrophenyl)-methyl)-cyclohexan-1-one (Table 3, entry 8):

![Structure of 2-(Hydroxy-(3-nitrophenyl)-methyl)-cyclohexan-1-one]

Pale yellow densed oil, ¹H NMR (300 MHz, CDCl₃): δ (ppm): 8.21 (dd, J = 8.2 Hz, 1 Hz, 1H), 7.83 (d, J = 8.2 Hz, 1 Hz, 1H), 7.65 (td, J = 7.9 Hz, 1.3 Hz, 1H), 7.43 (td, J = 7.9 Hz, 1 Hz, 1H), 4.9 (d, J = 8.2 Hz, 1H), 4.08 (br s, 1H), 2.75-2.81 (m, 1H), 2.35-2.49 (m, 2H), 2.07-2.15 (m,1H), 1.56-1.88 (m, 5H); Anal. Calcd. for C₁₃H₁₅NO₄: C, 62.64%; H, 6.07%; N, 5.62%. Found: C, 62.7%; H, 6.2%; N, 5.6%.

2-(Hydroxy (phenyl)-methyl)-cyclohexan-1-one (Table 3, entry 9):

![Structure of 2-(Hydroxy (phenyl)-methyl)-cyclohexan-1-one]

Pale yellow densed oil, ¹H NMR (300 MHz, CDCl₃): δ (ppm): 7.20-7.37 (m, 5H), 5.05 (m, 1H), 3.96 (br s, 1H), 2.73-2.8 (m, 1H), 2.33-2.47 (m, 2H), 2.05-2.13 (m,1H), 1.53-1.9 (m, 5H); Anal. Calcd. for C₁₃H₁₆O₂: C, 74.44%; H, 7.90%. Found: C, 74.6%; H, 7.9%.
2-(Hydroxy-(4-methoxy-phenyl)-methyl)-cyclohexan-1-one (Table 3, entry 10):

![Chemical structure diagram]

Pale yellow densed oil, $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ (ppm): 7.28 (d, $J = 8.8$ Hz, 2H), 6.9 (d, $J = 8.8$ Hz, 2H) 4.90 (d, $J = 8.2$ Hz, 1H), 4.05 (br s, 1H), 3.85 (s, 3H), 2.75-2.81 (m, 1H), 2.33-2.49 (m, 2H), 2.05-2.15 (m, 1H), 1.55-1.9 (m, 5H); Anal. Calcd. for C$_{16}$H$_{18}$O$_3$: C, 71.77%; H, 7.74%. Found: C, 71.6%; H, 7.6%.

2-(Hydroxy-(4-nitrophenyl)-methyl)-4-(tert-butyl)-cyclohexan-1-one (Table 3, entry 11):

![Chemical structure diagram]

Pale yellow solid, $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ (ppm): 8.20 (d, $J = 8.8$ Hz, 2H), 7.50 (d, $J = 8.9$ Hz, 2H), 5.48 (s, 1H), 3.96 (d, $J = 3.4$ Hz, 1H), 2.11-2.67 (m, 4H), 1.43-1.62 (m, 4H), 0.81 (s, 9H); Anal. Calcd. for C$_{17}$H$_{23}$NO$_4$: C, 66.86%; H, 7.59%; N, 4.59%. Found: C, 66.8%; H, 7.6%; N, 4.6%.

References

