Supporting Information
for DOI: 10.1055/s-0030-1258484
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Supporting Information

Novel Periodic Mesoporous Silica Chlorides (PMSCl) with 2D $P_{6}$mm Hexagonal Structures: Efficient Catalysts for the Beckmann Rearrangement

Babak Karimi*, Hesam Behzadnia

Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), P.O.Box 45195-1159, Gava Zang, Zanjan, Iran

Karimi@iasbs.ac.ir

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1. **Experimental Procedure**

1.1. **General experimental details.** Tetraethyl orthosilicate (TEOS), Hydrochloric acid (37%) and solvents were obtained commercially (Merck) and used without purification. Thionyl chloride was purchased from Fluka. pluronic P123 (EO$_{20}$PO$_{70}$EO$_{20}$ (EO= ethylene Oxide, PO= Propylene Oxide), $M_{av}= 5800$) was purchased from Aldrich.

The oximes were prepared according to standard methods and their purities were established before utilization by melting point and/or $^1$H NMR.

The pore structures of the prepared materials were observed by transmission electron microscopy (Philips CM 200FEG microscope, TEM) and were verified further by the nitrogen sorption isotherm ([5.0.0.3] Belsorp, BEL Japan, Inc.). The pore size distribution was determined from the adsorption branch of the isotherms using Barrett-Joyner-Halenda (BJH) method, and surface areas were estimated from the nitrogen sorption data using Brunauer-Emmett-Teller (BET) analysis. The percentage of Si-Cl bonds in the samples surfaces were determined by suspending the calcined SBA-Cls in deionized water and acid-base titration and elemental analysis. NMR spectra were recorded using Bruker (1H frequency: 250 MHz, 13C frequency: 62.9 MHz).

Typically, 1 mol TEOS was added to an aqueous hydrochloric acid solution (5.9 mol HCl and 193 mol H₂O) containing 0.017 mol of Pluronic P123 block copolymer. The mixture was stirred at 40 °C for 20 h and aged at 80 °C a day without stirring. SBA-15 was obtained by subsequent removal of the surfactant by extraction with ethanol.

1.3. **Characterization of the SBA-15.** TEM images, adsorption-desorption isotherms and the corresponding curves are shown in underneath Figures.

![Figure 1. TEM image of SBA-15](image-url)
Figure 2. Nitrogen Adsorption-Desorption isotherm for SBA-15

Figure 3. BJH average pore diameter diagram for SBA-15
1.4. **Preparation of SBA-Cl-1.** The synthesis of SBA-Cl was carried out by chlorination of the high-quality dried SBA-15 surface. 40 ml of Thionyl chloride was added to 5 g of SBA-15 in a round bottomed flask equipped with a condenser and a drying tube, and the reaction mixture refluxed for 24h. The remainder thionyl chloride was distilled off and the resulting product was flame-dried and stored in a sealed vessel, under argon atmosphere.

1.5. **Characterization of the SBA-Cl-1.** TEM images, adsorption-desorption isotherms and the corresponding curves are shown in underneath Figures.

![Figure 4. TEM image of SBA-Cl-1](image-url)
Figure 5. Nitrogen Adsorption-Desorption isotherm for SBA-Cl-1

Figure 6. BJH average pore diameter diagram for SBA-Cl-1
1.6. **Preparation of SBA-Cl-2.** The synthesis of SBA-Cl was carried out by chlorination of the high-quality dried SBA-15 surface. 40 ml of Thionyl chloride was added to 5 g of SBA-15 in a round bottomed flask equipped with a condenser and a drying tube, and the reaction mixture refluxed for 48h. The remainder thionyl chloride was distilled off and the resulting product was flame-dried and stored in a sealed vessel, under argon atmosphere.

1.7. **Characterization of the SBA-Cl-2.** TEM images, adsorption-desorption isotherms and the corresponding curves are shown in underneath Figures.

![Figure 7. TEM image of SBA-Cl-2](image-url)
Figure 8. Nitrogen Adsorption-Desorption isotherm for SBA-Cl-2

Figure 9. BJH average pore diameter diagram for SBA-Cl-2
1.8. Collected Characterization data for SBA-Cls:

<table>
<thead>
<tr>
<th>Compound</th>
<th>$S_{BET}^{a}$</th>
<th>Pore Size$^{b}$</th>
<th>$V_{p}^{c}$</th>
<th>Cl-content$^{d}$</th>
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<td>870</td>
<td>6.3</td>
<td>0.87</td>
<td>-</td>
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<tr>
<td>SBA-Cl-1</td>
<td>710</td>
<td>5.1</td>
<td>0.80</td>
<td>1.7</td>
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<tr>
<td>SBA-Cl-2</td>
<td>682</td>
<td>5.3</td>
<td>0.79</td>
<td>3.4</td>
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</table>

$^{a}$ BET surface area (m$^2$.g$^{-1}$). $^{b}$ BJH average pore size (nm). $^{c}$ Total pore volume (cm$^3$.g$^{-1}$). $^{d}$ Surface Si-Cl content (mmol.g$^{-1}$) determined by back titration using (0.01 M, NaOH) after hydrolysis.

2. General procedure for the Beckmann rearrangement using SBA-Cl-2: In a 10 ml glass flask equipped with a magnetic stirrer and condenser, we placed oxime (1 mmol) and SBA-Cl (20 mol %) in 3 ml of Toluene. The mixture was refluxed in appropriate time.

The reaction was monitored by TLC, and after completion of the reaction, most of products were easily extracted with a simple filtration of catalyst and evaporation the solvent under reduced pressure and in other cases the crude products were required to purification on silica gel using a mixture of n-hexane and ethylacetate to give the isolated products in yields stated in the Table 2 and the following Table.
Beckmann rearrangement of various oximes using SBA-CI-2

![Diagram of Beckmann rearrangement](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>M.p. (Lit.)</th>
<th>Time (h)</th>
<th>Yield (%)</th>
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<td>13</td>
<td><img src="image" alt="Substrate" /></td>
<td><img src="image" alt="Product" /></td>
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<td>88</td>
</tr>
</tbody>
</table>

*a* 4-Methoxy-N-(4-methoxy-phenyl)-benzamide (Aldrich: R291935).  *b* 3',4'-Dimethoxy acetanilide (Aldrich: S568880, CAS number: 881-70-9).

### 2.1. Spectral data for Table 2:

1 (Table 2, Entry 1): IR (KBr): ν 3340, 1655, 1593, 1526, 1434, 1316, 1255, 1025, 803, 751, 686, 646, 503 cm⁻¹; ¹H-NMR (250 MHz; CDCl₃; TMS): δ_H = 7.888-7.861 (d, J = 6.75 Hz, 3H), 7.668-7.637 (d, J = 7.75 Hz, 2H), 7.585-7.459 (m, 3H), 7.410-
7.347 \text{(t, } J = 7.5 \text{ Hz, 2H), 7.189-7.131 \text{(t, } J = 7.25 \text{ Hz, 1H); }^1\text{H-NMR (62.9 MHz, CDCl}_3; \text{TMS): } \delta_c = 165.00, 157, 131.9, 129.11, 128.81, 126.98, 124.6, 120.13.}

\textbf{2 (Table 2, Entry 4): }^1\text{H-NMR (250 MHz; CDCl}_3; \text{TMS): } \delta_H = 7.520-7.489 \text{ (d, } J=7.75 \text{ Hz, 2H), 7.357 -7.294 \text{(t, } J=7.5 \text{ Hz, 2H), 7.142-7.083 \text{(t, } J=7.25 \text{ Hz, 1H), 2.187 \text{(s, 3H); }^1\text{C-NMR (62.9 MHz, CDCl}_3; \text{TMS): } \delta_c = 168.51, 137.90, 128.96, 124.29, 119.94, 24.54.}}

\textbf{3 (Table 2, Entry 7): }^1\text{H-NMR (250 MHz; CDCl}_3; \text{TMS): } \delta_H = 7.557 \text{(brs, 1H), 7.402-7.367 \text{(d, } J=8.75 \text{ Hz, 2H), 6.851-6.816 \text{(d, } J=8.75 \text{ Hz, 2H), 3.776 \text{(s, 3H), 2.129 \text{(s, 3H); }^1\text{C-NMR (62.9 MHz, CDCl}_3; \text{TMS): } \delta_c = 168.48, 156.39, 131.03, 121.99, 114.07, 55.44, 24.23.}}

\textbf{4 (Table 2, Entry 8): }^1\text{H-NMR (250 MHz; CDCl}_3; \text{TMS): } \delta_H = 7.718 \text{(brs, 1H), 7.269 -7.152 \text{(m, 2H), 6.994 -6.964 \text{(d, } J=7.5 \text{ Hz, 1H), 6.661 -6.630 \text{(d, } J=7.75 \text{ Hz, 1H), 3.762 \text{(s, 3H), 2.144 \text{(s, 3H); }^1\text{C-NMR (62.9 MHz, CDCl}_3; \text{TMS): } \delta_c = 168.72, 160.07, 139.19, 129.61, 112.09, 109.98, 105.77, 55.25, 24.56.}}

\textbf{5 (Table 2, Entry 9): }^1\text{H-NMR (250 MHz; CDCl}_3; \text{TMS): } \delta_H = 7.854-7.820 \text{(d, } J=8.5 \text{ Hz, 2H), 7.546 -7.510 \text{(d, } J=9 \text{ Hz, 2H), 6.992 -6.892 \text{(m, 4H), 3.877 \text{(s, 3H), 3.817 \text{(s, 3H); }^1\text{C-NMR (62.9 MHz, CDCl}_3; \text{TMS): } \delta_c = 157.24, 128.79, 122.04, 114.22, 113.94, 55.49.}}

\textbf{6 (Table 2, Entry 10): }^1\text{H-NMR (250 MHz; CDCl}_3; \text{TMS): } \delta_H = 8.367-8.336 \text{(d, } J=7.75 \text{ Hz, 1H), 7.782 \text{(brs, 1H), 7.062-6.849 \text{(m, 3H), 3.871 \text{(s, 3H), 2.194 \text{(s, 3H); }^1\text{C-NMR (62.9 MHz, CDCl}_3; \text{TMS): } \delta_c = 168.17, 147.65, 127.68, 123.58, 121.04, 119.76, 109.85, 55.61, 24.90.}
7 (Table 2, Entry 11): $^1$H-NMR (250 MHz; CDCl$_3$; TMS): $\delta$$_H$ = 7.392-7.360 (d, $J$=8 Hz, 2H), 7.129-7.097 (d, $J$=8 Hz, 2H), 2.311 (s, 3H), 2.155 (s, 3H); $^{13}$C-NMR (62.9 MHz, CDCl$_3$; TMS): $\delta$$_C$ = 168.32, 135.31, 133.94, 129.44, 120.05, 24.47, 20.83.

8 (Table 2, Entry 12): $^1$H-NMR (250 MHz; CDCl$_3$; TMS): $\delta$$_H$ = 7.553 (brs, 1H), 7.287 (s, 1H), 6.887-6.853 (d, $J$=8.5 Hz, 1H), 6.788-6.754 (d, $J$=8.5 Hz, 1H), 3.834 (s, 6H), 1.968 (s, 3H); $^{13}$C-NMR (62.9 MHz, CDCl$_3$; TMS): $\delta$$_C$ = 168.42, 148.97, 145.82, 131.57, 112.04, 111.28, 105.11, 56.07, 55.84, 24.37.

9 (Table 2, Entry 13): $^1$H-NMR (250 MHz; CDCl$_3$; TMS): $\delta$$_H$ = 7.536-7.505 (d, $J$=7.75 Hz, 2H), 7.346-7.268 (m, 3H), 7.127-7.070 (t, $J$=7 Hz, 1H), 2.440-2.350 (q, $J$=7.5 Hz, 2H), 1.280-1.220 (t, $J$=7.5 Hz, 3H); $^{13}$C-NMR (62.9 MHz, CDCl$_3$; TMS): $\delta$$_C$ = 172.03, 157.20, 137.95, 128.97, 124.14, 119.76, 30.73, 9.66.

10 (Table 2, Entry 14): $^1$H-NMR (250 MHz; CDCl$_3$; TMS): $\delta$$_H$ = 7.674 -7.332 (m, 10H), 2.201 (s, 3H); $^{13}$C-NMR (62.9 MHz, CDCl$_3$; TMS): $\delta$$_C$ = 168.64, 140.45, 137.14, 128.78, 127.56, 127.10, 126.82, 120.31, 24.56.
Copy of FT-IR, \(^1\)H and \(^{13}\)C-NMR spectra

Table 2 (Products 1-10)
Solvent: CDCl₃ – Frequency: 250 MHz

1 (Table 2, Entry 1)
Solvent: CDCl₃ – Frequency: 250 MHz

1 (Table 2, Entry 1)
Solvent: CDCl₃ – Frequency: 62.9 MHz

1 (Table 2, Entry 1)
Solvent: CDCl$_3$ – Frequency: 62.9 MHz

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1 (Table 2, Entry 1)
Solvent: CDCl₃ – Frequency: 250 MHz

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Solvent: CDCl₃ – Frequency: 250 MHz

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2 (Table 2, Entry 4)
Solvent: CDCl₃ – Frequency: 62.9 MHz

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Solvent: CDCl₃ – Frequency: 250 MHz

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Solvent: CDCl$_3$ – Frequency: 250 MHz

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Solvent: CDCl₃ – Frequency: 62.9 MHz

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3 (Table 2, Entry 7)
Solvent: CDCl₃ – Frequency: 250 MHz

4 (Table 2, Entry 8)
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Solvent: CDCl$_3$ – Frequency: 62.9 MHz

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Solvent: CDCl₃ – Frequency: 250 MHz

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Solvent: CDCl₃ – Frequency: 250 MHz

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Solvent: CDCl₃ – Frequency: 62.9 MHz

6 (Table 2, Entry 10)
Solvent: CDCl₃ – Frequency: 62.9 MHz

6 (Table 2, Entry 10)
Solvent: CDCl₃ – Frequency: 250 MHz

7 (Table 2, Entry 11)

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7.392
7.360
7.268
7.246
7.209
7.129
7.097

2.997
2.560
2.393
2.311
2.155
2.005
1.899
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Solvent: CDCl₃ – Frequency: 62.9 MHz

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Solvent: CDCl₃ – Frequency: 62.9 MHz

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Solvent: CDCl$_3$ – Frequency: 250 MHz

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Solvent: CDCl₃ – Frequency: 62.9 MHz

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Solvent: CDCl$_3$ – Frequency: 62.9 MHz

9 (Table 2, Entry 13)
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Solvent: CDCl₃ – Frequency: 250 MHz

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Solvent: CDCl₃ – Frequency: 250 MHz

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Solvent: CDCl₃ – Frequency: 62.9 MHz

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Solvent: CDCl₃ – Frequency: 62.9 MHz

10 (Table 2, Entry 14)