Two-dimensional zeolites in catalysis

Jiří Čejka
OUTLINE

Two-dimensional zeolites
  Synthesis routes
  Properties

Catalytic applications
  Advantages – Disadvantages

Synthesis of ‘unfeasible’ zeolites from lamellas
  ADOR mechanism
Where we are – ZEOLITE CONUNDRUM

233 zeolites – IZA

Millions of possible structure

~ 15 2D zeolites

Traditional Synthesis Vector

Energies above quartz, up to +30 kJ/mol Si

Energy vs. Density

Deem MW, J Phys Chem C 2013
Where we go – 2D ZEOLITES - Outline

Synthesis

Design

Top-down

15 2D zeolites prepared by different approaches

Various Layer Architecture and Bonding

### 3-D zeolites
- FTC
- ABW
- CAS
- MWW
- FAU
- FER
- MFI
- NSI
- SOD
- ZON

### Conventional 3-D zeolite
- MCM-49 Direct, c~2.5
- MCM-22P Direct, c~2.6
- IEZ-MWW Treat, c~2.6
- EMM-10P Direct, c~2.6
- EMM-12P Treat, c~2.6
- MCM-22P/ac +acid, c~2.5

### Layered precursor
- Ordered: Unmodified, Stabilized
- Dis-ordered: Unmodified, Stabilized

### Acid-treated
- MCM-M56 Direct, c~2.5
- MCM-M56/TQ-2(T) c~2.5

### Delaminated
- Swollen/ pillared

### 1-D

### 2-D

## INTEGRATION OF 2D AND 3D ZEOLITES

*WJ Roth, Micropor Mesopor Mater (2011)*
2D ZEOLITES - MWW FAMILY – “HIT-and-MISS” SYNTHESIS

Calcined

Delaminated

Direct synthesis

Delaminated MCM-56

Post-synthesis

Delaminated ITQ-2

Standard 3-D route

3-D

MWW

Layered ordered

Pillared

Layered disordered

Swollen

‘Stabilization’

Acid treat

IEZ Stabilized

Expanded

‘Stabilization’

Roth WJ, ExxonMobil

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Department of Synthesis and Catalysis
TWO-DIMENSIONAL ZEOLITES – OPTIMIZED TEMPLATE STRUCTURE

3D to 2D - HYDROLYSIS

**Conditions** - pH neutral to acidic
- water or 0.1 M HCl
- room temperature – 100 °C

**Pailaud JL, Science (2004)**
**Corma A, Chem Commun (2004)**

**Intensity (a.u.)**
- (200) interlayer reflection

**IPC-1P**
- A = 9.0 Å
3D to 2D - SWELLING and PILLARING

Swelling - 25% $C_{16}$TMA-Cl + 40% TPA-OH (10:1 w/w)

100°C

SEM image of IPC-1SW

Pillaring – TEOS - 100°C
### 3D to 2D - TEXTURAL PROPERTIES

<table>
<thead>
<tr>
<th>Sample</th>
<th>Element mol. %</th>
<th>Si/Ge</th>
<th>Si/B</th>
<th>BET (m²/g)</th>
<th>V_{micro} (cm³/g)</th>
<th>V_{meso} (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si</td>
<td>Ge</td>
<td>B</td>
<td>Si/Ge</td>
<td>Si/B</td>
<td></td>
</tr>
<tr>
<td>B-UTL</td>
<td>85.4</td>
<td>13.6</td>
<td>1.0</td>
<td>6</td>
<td>85</td>
<td>458</td>
</tr>
<tr>
<td>IPC-1</td>
<td>95.5</td>
<td>4.3</td>
<td>0.2</td>
<td>22</td>
<td>480</td>
<td>270</td>
</tr>
<tr>
<td>IPC-1SW</td>
<td>97.3</td>
<td>2.6</td>
<td>&lt;0.01</td>
<td>37</td>
<td>&gt;100000</td>
<td>216</td>
</tr>
<tr>
<td>IPC-2</td>
<td>97.2</td>
<td>2.8</td>
<td>&lt;0.01</td>
<td>35</td>
<td>&gt;100000</td>
<td>313</td>
</tr>
<tr>
<td>IPC-1PI</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1085</td>
</tr>
</tbody>
</table>

- **IPC-1PI**, pillared
- **B-UTL**
- **IPC-2**, stabilized
- **IPC-1SW**, swollen
- **IPC-1**, hydrolysed
Catalysis on 2D zeolites
Synthesis of 2-methyl-naphthyl-4-methyl-1,3-dioxolane

orange blossom fragrance
delaminated ITQ-2

\[
\begin{align*}
\text{O} & + \text{HO} \xrightleftharpoons{}^{H^+} \text{H}_2\text{O} \\
\text{O} & + \text{HO} \xrightleftharpoons{}^{H^+} \text{H}_2\text{O}
\end{align*}
\]


Activity on External Surface

Potential for functionalization
2D ZEOLITES – IMPROVED CATALYTIC PROPERTIES

• MWW Family
  – Pillared MCM-36 as solid iso-butane/olefin (C4) alkylation
  – Delaminated MCM-56 – liquid phase short chain aromatic alkylation
  – Delaminated ITQ-2 - enhanced processing of larger molecules
  – UZM-8 – disordered – commercialized zeolite (Zones, MMM, 2011)

• MFI Single and Multilayer Nanosheets
  – MTG - delayed aging – extended time between regeneration
  – Enhanced conversions of larger molecules

• FER – Delaminated ITQ-6
  – Synthesis of diamine diphenyl methane (DADPM) - excellent activity, longer catalyst life than conventional zeolites
  – Aminopropyl modified - high adsorption efficiency in CO₂

• NSI – Delaminated ITQ-18
  – Chance of replacing HCl in synthesis of DADPM
N-HEXADECANE HYDROCARCKING

(ITQ-6)x, x = swelling time

n-Hexadecane conversion vs. T

Isomerization

Cracking

J. Heyrovský Institute of Physical Chemistry
Department of Synthesis and Catalysis

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>MCM-22</th>
<th>MCM-36</th>
<th>Faujasite, EMT</th>
<th>HF</th>
<th>H₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂/Al₂O₃</td>
<td>&lt;20</td>
<td>&gt;30</td>
<td>10-12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temp., [°C]</td>
<td>150</td>
<td>150</td>
<td>80</td>
<td>32</td>
<td>7</td>
</tr>
<tr>
<td>Yield, [wt/wt]</td>
<td>2.1</td>
<td>1.3-2.0</td>
<td>2.0</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>C₈, [wt %]</td>
<td>53</td>
<td>72-76</td>
<td>90</td>
<td>81</td>
<td></td>
</tr>
<tr>
<td>Me₃C₅/Me₂C₆</td>
<td>low or poor</td>
<td>2.4</td>
<td>4.1-4.4</td>
<td>7.6</td>
<td>6.4</td>
</tr>
<tr>
<td>RON/MON</td>
<td>91,93</td>
<td>91-97</td>
<td>94,97</td>
<td>94,96</td>
<td></td>
</tr>
<tr>
<td>Stability, [g alkyl./g cat.]</td>
<td>23</td>
<td>2.1-&gt;4.8</td>
<td>100</td>
<td>8.7</td>
<td></td>
</tr>
</tbody>
</table>


**MCM-36 – C₄ ALKYLYATION**
METHANOL to OLEFINs

Conventional MFI

Unilamellar MFI


Relative activity for Ethylbenzene

EB Selectivity
– 5% higher than beta

MCM-56 is obtained by direct hydrothermal synthesis

Reaction on the surface
TOLUENE ALKYLATION WITH ISOPROPYL ALCOHOL

1\textsuperscript{st} step

\[
\text{CH}_3\text{OH} + \text{CH}_3\text{+} \rightarrow \text{H}_3\text{C}\text{CH}_3 + \text{HO} - \text{H}_2\text{O}
\]

2\textsuperscript{nd} step

\[
\text{CH}_3\text{OH} + \text{CH}_3\text{+} \rightarrow \text{H}_3\text{C}\text{CH}_3 + \text{HO} - \text{H}_2\text{O}
\]

- Toluene conversion
- Concentration of sites
- Channel size
- Σ cymene
- Size of channels
- Product selectivity
- p-cymene selectivity
- Size of intersections
- iso-/n-propyltoluene ratio
- n-propyltoluene selectivity

\(\text{Čejka J, Wichterlová B, Catal Rev (2002)}\)
TWO-DIMENSIONAL ZEOLITES – TOLUENE ALKYLLATION WITH PROPYLENE

- Hexagonally mesostructure 10-R zeolite
- 1.4 nm MFI nanosheet, 2 pentasil layers
- Disordered mesostructure 10-R zeolite with 2.1nm thickness
- Disordered mesostructure 10-R zeolite with 2.7nm thickness

Aluminosilicate MFI nanosheets

Titanosilicate MFI Nanosheet

Activity – Selectivity – Long-term stability

R. Ryoo et al., ACS Catalysis (2011)
HYDROXYLATION of PHENOL

MTS-2 (MEL-type titanosilicate nanosheets)

\[
\begin{align*}
&\begin{array}{c}
\text{OH} \\
\end{array} \quad \xrightarrow{\text{H}_2\text{O}_2} \quad \begin{array}{c}
\text{OH} \\
\end{array} + \begin{array}{c}
\text{OH} \\
\end{array} \\
&\text{Cyclohexene} \rightarrow \text{Phenol} + \text{Phenol}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Sample</th>
<th>(d_{\text{cryst}} \ \mu m)</th>
<th>Conv, %</th>
<th>(Y_{\text{ortho}}) %</th>
<th>(Y_{\text{para}}) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTS-2</td>
<td>1-2</td>
<td>28.9</td>
<td>14.8</td>
<td>10.6</td>
</tr>
<tr>
<td>TS-1</td>
<td>0.3</td>
<td>26.0</td>
<td>13.5</td>
<td>8.7</td>
</tr>
<tr>
<td>TS-2</td>
<td>0.3</td>
<td>23.2</td>
<td>11.7</td>
<td>8.5</td>
</tr>
</tbody>
</table>

**2D ZEOLITES vs. 3D ZEOLITES vs. MESOPOROUS MOLECULAR SIEVES**

2D =

Disordered ZSM-5

3D = ZSM-5

Mesoporous = Al-MCM-41

---

### Acylation of Indole

\[
\text{Indole} + \text{Ac}_2\text{O} \rightarrow \text{AcOIndole}
\]

Catalyst, neat, 383 K

### Benzoylation of Resorcinol

\[
\text{Resorcinol} + \text{Ph-COOH} \rightarrow \text{PhCOIndole}
\]

Catalyst, neat, 363 K

### Esterification Reaction

\[
\text{OAc} + \text{Ph} + \text{OH} \rightarrow \text{PhOCOCOOAc}
\]

Catalyst, neat, 403 K

### Synthesis of Vitamin E

\[
\text{Ph} + \text{C}_6\text{H}_{13} + \text{C}_16\text{H}_{33} \rightarrow \text{Vitamin E}
\]

Catalyst, Hexane, 343 K

### Hydroamination

\[
\text{PhNH} + \text{COOME} \rightarrow \text{PhCONMe}
\]

Catalyst, neat, 363 K

---

<table>
<thead>
<tr>
<th>Reactions/Materials</th>
<th>Acylation of indole</th>
<th>Esterification of hexanoic acid</th>
<th>Benzoylation of resorcinol</th>
<th>Hydroamination of methyl acrylate</th>
<th>Synthesis of vitamin E</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conv. [a] [%] Sel. [b] [%]</td>
<td>Conv. [%] Sel. [%]</td>
<td>Conv. [%] Sel. [%]</td>
<td>Conv. [%] Sel. [%]</td>
<td>Conv. [%] Sel. [%]</td>
</tr>
<tr>
<td>Conventional ZSM-5 (50)</td>
<td>4 30</td>
<td>25 99</td>
<td>1.5 81</td>
<td>4 99</td>
<td>10 8</td>
</tr>
<tr>
<td>ZSM-5-(C₁₈-D-C₆-D-C₁₉)</td>
<td>82 72</td>
<td>76 75</td>
<td>30 80</td>
<td>48 99</td>
<td>75 74</td>
</tr>
<tr>
<td>Al-MCM-41 (50)</td>
<td>22 70</td>
<td>29 70</td>
<td>9 78</td>
<td>21 98</td>
<td>4 94</td>
</tr>
</tbody>
</table>

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*J. Heyrovský Institute of Physical Chemistry*

*Department of Synthesis and Catalysis*

*Kore et al., Chem Eur J (2014)*
Sn-Self-Pillared MFI

Glucose (GLU) into fructose (FRU)
GLU is first treated in ethanol to a mixture of FRU and ethyl fructoside (FRU ketalization product with ethanol)

Hydrolysis of the fructoside yields FRU
Synthesis of ‘unfeasible’ zeolites from lamellas
ADOR = Assembly – Disassembly – Organization – Reassembly

Assembly
UTL with Ge-rich D4R

Disassembly
Hydrolysis of D4R
→ IPC-1P  
Roth WJ et al, JACS 2011

Organization
Regular arrangement of neighboring layers

Reassembly
Layer condensation
→ PCR

Roth WJ et al, Nature Chem 2013
ADOR Extensions

Regular shift of adjacent layers

Regular alternation of inter-layer “pillars”

IEZ strategy (and more general approach)

No shift of adjacent layers

Different lamellar precursors:
- zeolites with D4R
- zeolites with D3R
- other zeolites (?)

Encouragement for experimentalists – large number of novel zeolites can be prepared from layered zeolite precursors
XRD powder pattern of novel materials are provided (useful hints)

Trachta, Nachtigall, et al 2014
3D to 2D ZEOLITES – HYDROLYSIS STUDY

Water, 0.1M-12M HCl, 95°C
STAGED STRUCTURE of IPC-6

Optimum acidity and Si/Ge ratio

Regular arrangement of IPC-4 and IPC-2 layers

Tuneable porosity

Unlimited number of combinations from 0 (IPC-4) to 100 % (IPC-2)

ADOR LANDSCAPE – Continuous Porosity


Molarity ([H+]): 012345
Micropore Volume (cm³g⁻¹): 0.00 0.05 0.10 0.15 0.20 0.25 0.30 0.35
BET area (m²g⁻¹): 0 100 200 300 400 500 600

IPC-4
IPC-6
IPC-2
IPC-7

BET area
Micropore volume

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REGULAR SHIFT OF ADJACENT LAYERS

Shift of the layers

(i)  UTL

(ii) IPC-1P

(iii) IPC-9P

(iv) IPC-9

Shift of the layers + Si addition

Effect of organics shape and charge concentration

choline

Is ADOR APPLICABLE with a SHIFT of the LAYERS?

Critical role of intercalation
Is ADOR APPLICABLE WITH a SHIFT of the LAYERS with INTERCALATION?

Critical role of intercalation and silane addition
Where we go – NEW ZEOLITES

Energy vs. Density
Energies above quartz, up to +30 kJ/mol Si

Traditional Synthesis Vector
Synthesis of zeolites via ADOR
Energetically less favored
Odd-rings
Low chance for solvothermal synthesis

Solution → Gel → Zeolite

Based on Deem MW, J Phys Chem C 2013
SUMMARY

Two-dimensional zeolites
Bottom-up approach
Accidental synthesis
Tailored structure-directing agents
Top-down approach
Hydrolysis of Ge-containing units
ADOR mechanism


Transformation to 2D zeolites (extended building units)
Intercalation chemistry
Synthesis of new zeolites even with odd rings (other materials)
Controlling the porosity of zeolites
Highly energetic zeolites (not accessible by solvothermal synthesis)

Catalysis
Activity – active sites
Selectivity – structure of the surface
Stability
Low rate of deactivation
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