Methanol to Olefins (MTO): Development of a Commercial Catalytic Process

Simon R. Bare
Advanced Characterization, UOP LLC

Modern Methods in Heterogeneous Catalysis Research

FHI Lecture November 30, 2007

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Polyethylene and Polypropylene

- Thousands of uses of polyethylene and polypropylene.
Polyethylene and Polypropylene

• Main source of the ethylene and propylene (monomer feedstock for polyethylene and polypropylene) is steam cracking of naphtha or other hydrocarbon.

Naphtha (C5-C9)

Ethane

HCBN

Steam Cracking

$C_2^+ + C_3^+ + C_3^+$

$>850^\circ C$, millisec
Methanol To Olefins (MTO) Reaction

- Methanol is an alternate source of light olefins.
- Dehydration with shape selective transformation to low molecular weight alkenes.

Other By-Products

- H₂O
- H₂, COₓ
- C₁-C₅ Paraffins
- C₅+
- Coke
UOP/Hydro MTO Process

SAPO-34 Catalyst

Courtesy to Unni Olsbye, University of Oslo
MTO Reaction

- High selectivity and yield to light olefins.

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<th>Material</th>
<th>SAPO-34</th>
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<td>T atom %</td>
<td>10% Si (gel)</td>
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- Many acid catalysts are active for the methanol dehydration – what makes SAPO-34 the preferred catalyst?

Outline

• Zeolites
• Zeolites as industrial catalysts
• Acid sites in molecular sieves
• Aluminum phosphate (AlPO₄) molecular sieves
• Characterization methods for molecular sieves
• SAPO-34
• Methanol conversion using zeolites
• Zeolites vs. SAPO’s in methanol conversion
• CHA and AEI
• MTO mechanism
• MTO reactor design
• Putting it all together: methanol & natural gas
• Discovery to commercialization
What is a Zeolite?

Zeolite

From Wikipedia, the free encyclopedia

Zeolites (Greek, zein, "to boil"; lithos, "a stone") are minerals that have a micro-porous structure. The term was originally coined in the 18th century by a Swedish mineralogist named Axel Fredrik Cronstedt who observed, upon rapidly heating a natural mineral, that the stones began to dance about as the water evaporated. Using the Greek words which mean "stone that boils," he called this material zeolite.

• Zeolites occur in nature.

Mordenite  Chabazite  Natrolite
Zeolites

- Zeolites consist of a framework built of tetrahedra.
- Each tetrahedron comprises a T-atom bound to four O atoms.
- Oxygen bridges connect the tetrahedra.
- T-atoms are Si or Al.
Zeolites

• Alumino-silicate framework
• Crystalline, microporous (pore diameter 3-14Å)
• Framework density <20 T-atoms/1000Å³

$LTA = Zeolite A$
Ways to Visualize a Zeolite: ZSM-5 (MFI)

- Medium pore size 5.1 x 5.5Å
  - Wire frame structure showing only T-atoms
  - Pore structure – critical for thinking about a molecule diffusing through the structure.
Range of Pore Sizes

- Zeolites exhibit a range of pore sizes of molecular dimensions (molecular sieves).

Small 8-ring
~ 4Å

Medium 10-ring
~ 5-6Å

Large 12-ring
~ 6-8Å

Very Large >12-ring
>8Å
Acid Sites in Zeolites

• Substitute Al\(^{3+}\) for Si\(^{4+}\): charge imbalance – need additional cation to compensate.

• No total charge.

• One extra charge per Al atom introduced into the lattice.

• Cations compensate for total charge.

• Protons as cations give Brønsted acid properties.

Courtesy to Francesca Bleken, University of Oslo
# Evolution of Molecular Sieve Compositions

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<td>Late 40's to Early 50's</td>
<td>Low Si/Al Ratio Zeolites</td>
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<td>Mid 50's to late 60's</td>
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<td>Early 70's</td>
<td>Pure SiO$_2$ Molecular Sieves</td>
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<td>Late 70's</td>
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<td>Octahedral-tetrahedral Frameworks</td>
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Framework Types

- 176 framework types recognized by the International Zeolite Association (IZA) ([http://www.iza-online.org/](http://www.iza-online.org/)).
- IZA Structure Commission assigns framework type codes to all unique and confirmed framework topologies.

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Zeolites as Industrial Catalysts

- But only ~18 framework types have seen commercial utility.
## Commercial Catalytic Uses of Zeolites (Refining & Petrochemicals)

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<td>Toluene trans-alkylation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>x</td>
<td></td>
<td>x</td>
</tr>
</tbody>
</table>

FAU = Y, USY  
LTL = Linde L, K-L  
MOR = mordenite  
BEA = beta  
MWW = MCM-22  
MFI = ZSM-5  
AEL = SAPO-11, SM-3  
FER = ferrierite  
RHO = zeolite RHO  
CHA = chabazite, SAPO-34

Alumino-phosphate (AlPO$_4$) Molecular Sieves

- Microporous solids similar to silico-aluminate zeolites – but composed of interlinked tetrahedra of AlO$_4$ and PO$_4$ vs. AlO$_4$ and SiO$_4$.
- Alternating Al-O-P bonds
- Almost never Al-O-Al, and never P-O-P (due to charge and lack of hydrothermal stability).
Idealized 2D Connectivity of tetrahedral AIPO$_4$ framework

- Al and P strictly alternating.
- Neutral framework.
Si Substitution for P in AlPO$_4$ to give SAPO

- Si substitution for P in AlPO$_4$ yields negative framework charge and Brønsted acid sites.

**Isolated Si:** $\text{Si}^{+4} \rightarrow \text{P}^{+5}$

**Negative framework charge**

**Template decomposition** $\rightarrow \text{H}^+$

**No Si-O-P**

**No P-O-P**
Si Substitution Produces Brønsted Acid Sties

Isolated Si
1 Si = 1P
1 Si = 1 H⁺

Adjacent isolated Si
2 Si = 2P
2 Si = 2 H⁺

Si island
5 Si = 4P + 1 Al
5 Si = 3 H⁺

Yes
Al-O-P
Si-O-Al
Si-O-Si

No
Al-O-Al
P-O-P
Si-O-P
Outline

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Characterization Methods for Zeolites

- NH$_3$ TPD
- Hydroxyl FTIR
- Pyridine FTIR
- Framework FTIR
- Low temperature CO FTIR
- Solid State NMR
- Electron microscopy: SEM/TEM
- XPS
- XRD
- EXAFS
- Many others
Acidic Sites: Use of Base for Characterization

- Acidic catalyst surface may expose both protic (Brønsted) and aprotic (Lewis) sites.
- Protic sites in a zeolite are surface hydroxyl groups OH.
- Aprotic sites in zeolite are typically extraframework Al surface cations.
- Basic probe molecule will interact with OH via hydrogen bonding:
  \[
  \text{OH}_s + B \leftrightarrow \text{OH}_s \cdots B
  \]
- If OH is sufficiently acidic then proton transfer:
  \[
  \text{OH}_s \cdots B \leftrightarrow \text{O}_s \cdots \text{H}^+B
  \]
- For aprotic sites the base will form a Lewis acid-base adduct:
  \[
  L + B \leftrightarrow L\leftarrow B
  \]
Ammonia Temperature Programmed Desorption

- NH$_3$ TPD is used to measure the amount and relative strength of the acid sites.
- NH$_3$ small molecule but not very specific.
Linear temperature ramp. Amount of ammonia desorbed as a function of temperature recorded and quantified.
Hydroxyl FTIR

- Use FTIR to measure the infra red spectrum of the zeolite.
- The vibrational frequency of the hydroxyl species in the sample is dependent on the type of hydroxyl species present.
- Can differentiate between framework and extraframework species.

![FTIR Spectrum Image]

**Terminal Si-OH**

**Extra-framework Al-OH**

**Bridging Si-OH-Al**

**BEA**


*H. Knözinger in Handbook of Heterogeneous Catalysis, Vol 2, p. 707*
Hydroxyl FTIR

- Transformation of IR spectrum on steaming of zeolite BEA.
- Dealumination of framework Al species.
Pyridine FTIR: Basics

- Pyridine is a weak base which coordinates with both Brønsted and Lewis acid sites.
- Distinct FTIR-active bands are observed for each type of acid site.
- The integrated intensity provides a relative measure of the number of each site.
- The desorption temperature provides a relative measure of the acid site strength.
- Most useful when comparing a series of samples.

\[
\text{Ring vibrational modes} \quad 1450 \text{ cm}^{-1} \quad 1550 \text{ cm}^{-1}
\]

**Lewis (aprotic)** \[\text{Brønsted (protic)}
\]
Pyridine FTIR: Spectrum

Hydroxyl Region Pyridine Adsorption

Pyridine adsorption attenuates bridging OH groups; bands are restored upon pyridine desorption.

Pyridine Adsorption Spectral Region

Pyridine adsorption yields distinct Brønsted and Lewis acid site absorbance bands in this region.

Key:
- Pretreated
- After 150°C
- After 300°C
- After 450°C
Pyridine FTIR: Acid Site Distribution

Weak Site: pyridine desorbed between 150°C and 300°C

Moderate site: pyridine desorbed between 300°C and 450°C

Strong site: pyridine remaining after 450 °C desorption

Integrated area of pyridine adsorbed on Brønsted acid site; ~ 1550 cm⁻¹

Integrated area of pyridine adsorbed on Lewis acid site; ~1450 cm⁻¹.
Framework FTIR

- Framework region (1400 - 400 cm\(^{-1}\)) contains information on T-O-T modes, ring modes of zeolites
- T-O-T\(_{(\text{asym})}\) frequency shifts with Si/Al\(_2\) ratio.

![FTIR Spectrum](image)

- Before calcination – 1091.4 cm\(^{-1}\)
- 325°C Steamed - 1095.6 cm\(^{-1}\)
- 550°C Steamed - 1098.9 cm\(^{-1}\)
- 610°C steamed - 1100.8 cm\(^{-1}\)

Loss of framework aluminum from higher temp steaming results in shift of T-O-T stretch.
Low Temperature CO FTIR

• CO is a small, very weak, soft base
  - Accessible to small pores
• Reversible adsorption at <150K
• Number/strength distributions without high temperature desorption
• Can detect very low levels of Brønsted acidity
• Complimentary, more detailed information
  - $\nu$(CO) 2160-2190 cm$^{-1}$(B)
  - $\nu$(CO) 2160-2240 cm$^{-1}$(L)
  - $\Delta\nu$(OH) 0-350 cm$^{-1}$(B)
• Shift in OH band gives measure of acid site strength
Low Temperature CO Adsorption

- All acid sites accessible to CO
- Interaction of CO with acid hydroxyl results in frequency shift → strength of sites
- Integrated CO band area → number of sites
- Difference spectra clarify OH band shifts
Low Temp CO Adsorption on Different Materials

- Low temp CO adsorption clearly shows strength difference in Brønsted acidity of SAPO and zeolitic materials

![BEA and SAPO spectra](image)

BEA

SAPO

Before CO Adsorption

After CO Adsorption

322 cm⁻¹

280 cm⁻¹
Solid State NMR


Si/Al ratio from $^{29}\text{Si}$ NMR

$$\frac{\text{Si}}{\text{Al}} = \frac{\sum_{n=0}^{4} I_{\text{Si}[n\text{Al}]}}{\sum_{n=0}^{4} 0.25 n I_{\text{Si}[n\text{Al}]}}$$

Si/Al = 1.75
**29Si NMR of SAPO-34: Effect of Sample Preparation Conditions**

- **Synthesis Route #1**
  - Isolated Si
  - Si islands
  - Sample A
  - Sample B
  - Sample C

- **Synthesis Route #2**
  - Isolated Si
  - Route #2 has no Si islands
  - Sample D
  - Sample E

- **Notes:**
  - Route #1 produce more silica islands than Route #2
  - Silica islands result in lower acidity
High Resolution TEM

- High resolution TEM powerful technique for “visualizing” pore structure and any non-crystalline material in zeolites.

- Can also be used for structure determination using imaging and electron diffraction, e.g. determination of structure of new UOP zeolite UZM-5.
  - UZM-5: Rietveld refinement by XRD was not definitive due to broadening of the peaks due to the morphology of the zeolite (thin plates).
High Resolution TEM

- Combination of high resolution imaging together with electron diffraction.
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The particular molecular sieve of interest to the MTO process is SAPO-34.

This material is structurally analogous to, but compositionally distinct, from the silico-aluminate zeolite mineral chabazite (CHA).

In chabazite all T sites are occupied by either Si\(^{4+}\) or Al\(^{3+}\).

In SAPO-34 Al and P atoms occupy alternately, and some Si atoms occupy sites normally occupied by P.
SAPO-34 (CHA) Structure

- Three-dimensional pore system consisting of large cavities (about 9.4 Å in diameter) separated by small windows (3.8 x 3.8 Å)
- Periodic building unit is the double 6-ring layer – connected through 4-rings.

SEM of SAPO-34 crystals
~1 μm
Structural Characteristics of CHA Framework

- The CHA cage.

4-rings inaccessible to most molecules (door closed)

Cage bounded by 36 TO$_2$
Dimensions: 7.5 x 8.2Å
Pore opening: 4.4 x 3.6Å
Every TO$_2$ shared by 3 cages
# SAPO vs. Zeolite Synthesis

<table>
<thead>
<tr>
<th></th>
<th>Zeolite</th>
<th>SAPO</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Oxide Reactants</strong></td>
<td>Alumina</td>
<td>Alumina</td>
</tr>
<tr>
<td></td>
<td>Silica</td>
<td>Silica H₃PO₄</td>
</tr>
<tr>
<td><strong>Alkali hydroxide</strong></td>
<td>Common</td>
<td>Almost never</td>
</tr>
<tr>
<td><strong>Organic structure-</strong></td>
<td>Common</td>
<td>Required</td>
</tr>
<tr>
<td><strong>directing agent</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>pH</strong></td>
<td>Usually &gt; 11</td>
<td>Usually &lt; 9</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>25 – 200°C</td>
<td>100 – 200°C</td>
</tr>
<tr>
<td><strong>Time</strong></td>
<td>Hours – weeks</td>
<td>Usually &lt; 3 days</td>
</tr>
</tbody>
</table>
Template Packing in SAPO-34

- >30 templates make SAPO CHA framework type.
  - Most not well studied
  - TEAOH is most common

N-MeButylamine  Morpholine  Cyclam
Calculating Acid Site Density of CHA Framework

- Elemental analysis of SAPO best expressed as mole fraction:
  \[ \text{Si}_x\text{Al}_y\text{P}_z\text{O}_2 \text{ where } x + y + z = 1.00 \]
- Framework charge = [Al – P] = [Si] if Si is isolated

- Each cage bounded by 36 TO$_2$
- Each TO$_2$ is shared by 3 cages
- 1 acid site per cage = 0.03 Si
• Neutron diffraction used to locate the actual position of the acid sites in CHA cage.

Protons attached to O4 (4.0% occupancy)
More acidic
3630 cm$^{-1}$

Protons attached to O2 (3.4% occupancy)
Less acidic
3601 cm$^{-1}$

Discovery of ALPO and SAPO Materials

• In late 70’s Edith Flanigen’s group at Union Carbide given the challenge:

“Discover the next generation of molecular sieve materials”

• Words of Edith Flanigen …..
Discovery of ALPO and SAPO Materials

• A commitment on part of management to support long-range innovative discovery with no guarantee for commercial success.

• Willingness to take that risk and to assign significant resources to back up that commitment.

• Patience to allow major discoveries to find their place in the commercial world.

• Creating an environment and culture that fostered innovation and that attracted the best scientists and challenged them to their limits.

• Allowing them freedom to dream, and trusting that they would succeed.

• Recognizing and rewarding them when they did succeed.
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Methanol Conversion using Zeolites

• 1975 – Mobil Oil discloses ZSM-5 catalyst for conversion of methanol to gasoline (MTG)

\[
2 \text{CH}_3\text{OH} \xleftrightarrow{-\text{H}_2\text{O}} \text{CH}_3\text{-O-CH}_3
\]

- Isoparaffins
- Aromatics
- C\(_6^+\) olefins
- C\(_2\) - C\(_5\) olefins

\[
\text{CH}_3\text{-O-CH}_3 \xrightarrow{+\text{H}_2\text{O}} \text{C}_2\text{-C}_5\text{ olefins}
\]

Chang, Silvestri, and Smith, US 3894103 and 3928483
Methanol Conversion over Zeolites

- Several zeolites with Brønsted acid sites show activity for methanol conversion.

<table>
<thead>
<tr>
<th>Pore Size</th>
<th>Examples</th>
<th>Performance (low conversion)</th>
<th>Performance (high conversion)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small</td>
<td>ERI</td>
<td>Light olefins</td>
<td>Paraffins</td>
</tr>
<tr>
<td></td>
<td>ERI/OFF</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>KFI</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Medium</td>
<td>MFI</td>
<td>Olefins</td>
<td>Paraffins</td>
</tr>
<tr>
<td></td>
<td>FER</td>
<td></td>
<td>Aromatics</td>
</tr>
<tr>
<td></td>
<td>MTT</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Large</td>
<td>MOR</td>
<td></td>
<td>Olefins</td>
</tr>
<tr>
<td></td>
<td>FAU</td>
<td></td>
<td>Aromatics</td>
</tr>
<tr>
<td></td>
<td>FAU</td>
<td></td>
<td>Paraffins</td>
</tr>
</tbody>
</table>

G.F. Froment et al, Catalysis (London), 9, 1 (1992)
Methanol to Hydrocarbons

CHA, SAPO-34
8-ring window, only linear hydrocarbons can enter.

MTO

MTG

ZSM-5, MFI-topology
Cages = Windows

10-ring window, aromatic hydrocarbons can enter.
MTO Catalysts

- **Medium-pore zeolites (ZSM-5)**
  - Major olefin product is Propylene
  - Significant C_{5+}/aromatics by-products
  - Slow deactivation

- **Small-pore molecular sieves (SAPO-34)**
  - Major olefin products are Ethylene and Propylene
  - Fast deactivation by aromatic coke
  - SAPO molecular sieves more stable than corresponding zeolite structure

Shape Selectivity
Structural Comparison

SAP0-34

3.8 Å

H

(Al-O)₃Si

O

H

Al(O-P)₃

Ethylene

Propylene

Isobutylene

Benzene

ZSM-5

5.5 Å

H

(Si/Al-O)₃Si

O

H

Al(O-Si)₃

Small Pore
Weak Acid Sites

Medium Pore
Strong Acid Sites
Small, Medium & Large Pore

- Small, medium and large pore SAPO’s show MTO activity – but distinct selectivity differences.

350°C, WHSV = 0.3 h⁻¹, MeOH = 0.02 bar, N₂ = 0.98 bar

SAPO-34 vs. SSZ-13

- SSZ-13 has same structure (CHA) as SAPO-34 but is an aluminosilicate zeolite.
- Selectivity to olefins substantially less in SSZ-13.

<table>
<thead>
<tr>
<th>Material</th>
<th>SAPO-34 10% Si (gel)</th>
<th>SSZ-13 (Chabazite) 18% Al</th>
<th>SSZ-13 (Chabazite) 10% Al</th>
<th>SSZ-13 (Chabazite) 3.3% Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selectivities (2 hr)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂-C₄ olefins</td>
<td>96</td>
<td>69</td>
<td>75</td>
<td>87</td>
</tr>
<tr>
<td>CH₄</td>
<td>1.4</td>
<td>3.9</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>0.3</td>
<td>5.4</td>
<td>19.3</td>
<td>15.0</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>0.9</td>
<td>18.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stability</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hr at &gt;50% conversion</td>
<td>&gt;40</td>
<td>6</td>
<td>13</td>
<td>7</td>
</tr>
<tr>
<td>Coking</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>carbon on used catalyst</td>
<td>19% after 54 HOS</td>
<td>16.6% after 18 HOS</td>
<td>19.3% after 18 HOS</td>
<td>15.0% after 18 HOS</td>
</tr>
</tbody>
</table>

Another Twist in the Story......

- SAPO-34 has CHA topology. Related framework type is AEI.

Structures depicted as layers of D6R

CHA

Layers of a, a, a

AEI

Alternating layers of b, a, b, a
AEI and CHA

- Exxon and Hydro patents teach that intergrowth of AEI and CHA topology are readily formed and are also active in MTO.

# Table 3 - Methanol to olefin catalytic performances

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO₂/Al₂O₃</th>
<th>AEI/CHA*</th>
<th>Ethylene selectivity (%)</th>
<th>Propylene selectivity (%)</th>
<th>Ethylene + propylene selectivity (%)</th>
<th>Propane selectivity (%)</th>
<th>C₄+ selectivity** (%)</th>
<th>Ethylene to propylene ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (ex. 1)</td>
<td>0.15</td>
<td>0.18</td>
<td>85</td>
<td>34.9</td>
<td>40.8</td>
<td>75.7</td>
<td>1.0</td>
<td>21.4</td>
</tr>
<tr>
<td>B (ex. 2)</td>
<td>0.06</td>
<td>0.33</td>
<td>75</td>
<td>33.6</td>
<td>42.6</td>
<td>76.3</td>
<td>0.4</td>
<td>21.8</td>
</tr>
<tr>
<td>C (ex. 3)</td>
<td>0.09</td>
<td>0.43</td>
<td>70</td>
<td>33.9</td>
<td>42.3</td>
<td>76.2</td>
<td>0.6</td>
<td>21.8</td>
</tr>
<tr>
<td>D (ex. 4)</td>
<td>0.14</td>
<td>0.43</td>
<td>70</td>
<td>34.4</td>
<td>41.1</td>
<td>75.5</td>
<td>0.7</td>
<td>21.9</td>
</tr>
<tr>
<td>E (ex. 5)</td>
<td>0.12</td>
<td>0.43</td>
<td>70</td>
<td>35.1</td>
<td>40.8</td>
<td>75.9</td>
<td>0.9</td>
<td>21.4</td>
</tr>
<tr>
<td>F (ex. 6)</td>
<td>0.16</td>
<td>0.25</td>
<td>80</td>
<td>35.9</td>
<td>40.0</td>
<td>75.9</td>
<td>1.0</td>
<td>21.1</td>
</tr>
<tr>
<td>G (ex. 7)</td>
<td>0.13</td>
<td>0.67</td>
<td>60</td>
<td>34.2</td>
<td>41.4</td>
<td>75.6</td>
<td>0.6</td>
<td>21.1</td>
</tr>
<tr>
<td>Comparative 1 (ex. 2)</td>
<td>9.0</td>
<td>10</td>
<td>29.6</td>
<td>42.5</td>
<td>72.1</td>
<td>0.7</td>
<td>25.0</td>
<td>0.69</td>
</tr>
<tr>
<td>Comparative 2 (ex. 8)</td>
<td>0.10</td>
<td>4.0</td>
<td>20</td>
<td>30.0</td>
<td>43.3</td>
<td>73.3</td>
<td>0.9</td>
<td>24.3</td>
</tr>
</tbody>
</table>

* Determined by DIFFaX
** Selectivity for hydrocarbons having 4 or more carbon atoms
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MTO Mechanism

- More than 20 proposed mechanisms during the past 30 years (Involving intermediates such as radicals, carbenes, oxonium ions, carbocations)

- How can two or more C_1-entities react so that C-C bonds are formed?

- No simple $\beta$-hydride elimination so no straightforward mechanism to olefins from methanol.

- Don’t have time to go into great detail on some of the elegant mechanistic work performed.
Hydrocarbon Pool Mechanism

• What is the identity of the hydrocarbon pool?
• How does it operate?

Zeolite Beta as a Model System

- The beta zeolite is a wide pore zeolite allowing direct introduction of rather large molecules.
- It is not interesting as a commercial catalyst for MTO/MTH chemistry.

**Model:** Beta, BEA-topology

Cages = Windows

12-ring window, substituted aromatic hydrocarbons can enter.

7.7 x 6.6 Å
Hexamethylbenzene is a dominant gas phase product

The olefin production goes on for several minutes after the methanol feeding has been terminated.

What is the active pool contained inside the zeolite?

*Courtesy Unni Olsbye, Univ. Oslo*
Hydrocarbons Retained in Zeolite Pores

- Analyzed ex-situ by:
  - Quenching the reaction (after a set time, few mins)
  - Dissolving the zeolite (15% HF)
  - Extracting the organic material from the water phase
- Trapped organic species are liberated and can be analyzed

Analysis (GC-MS, HRMS, NMR)

Courtesy Unni Olsbye, Univ. Oslo
Trapped Hydrocarbons

- Methanol reacted over the H-beta zeolite (GC-MS)

The trapped material is nearly exclusively composed of polymethylated aromatics.

Hexamethylbenzene is a dominant retained species. Among the trapped hydrocarbons, hexaMB shows the fastest decomposition.

Stability of the retained hydrocarbons was probed by stopping the feed and flushing the catalyst with carrier gas for 1 minute.

Retention time (minutes)

Hexamethylnaphthalene

Hexamethylbenzene

Pentamethylbenzene

Tetramethylbenzene

Courtesy Unni Olsbye, Univ. Oslo
Hexamethylbenzene over H-Beta

- The same gas phase products as observed when methanol was reacted
- The retained compounds were the same as those obtained from methanol


*Courtesy Unni Olsbye, Univ. Oslo*
Hexamethylbenzene in zeolite pore can take up another CH$_3$ to form heptamethylbenzenium ion

Exocyclic Mechanism

- Deprotonation of heptaMB⁺
- Exocyclic double bond reacts with incoming CH₃OH resulting in ethyl group on benzene ring
- Subsequent dealkylation to ethylene

- Essential intermediate in cycle is formation of two gem-methyl groups attached to benzene ring.
Paring Mechanism

Alkyl side chain growth by ring contraction/expansion
Leads predominantly to propylene and isobutene

Leads to carbon atom interchange between ring and substituents

MTO Site – Organic-Inorganic Hybrid

Courtesy Unni Olsbye, Univ. Oslo
SAPO-34

- SAPO-34 (CHA) has large cages connected with small windows.
- Large aromatics are accumulated in these cages during the reaction.
- An array of nanoreactors!

(001) projection

Courtesy Unni Olsbye, Univ. Oslo
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Fixed Bed MTO Performance

- SAPO-34 catalyst highly active with good selectivity then conversion drops rapidly.

![Graph showing conversion and selectivity over time for different olefins and propane.]

- Conversion and selectivity over time for different olefins and propane.

- Total Olefins, Ethylene, Propylene, and Propane.
Molecular View of Initial Deactivation

- Hexamethylbenzene in CHA cage
- With increasing TOS some methylbenzenes age into methylnaphthalenes.
- Further aging to phenanthrene causes loss of activity
- Largest ring system to form in SAPO-34 is pyrene.

MTO Reactor Design

• **Fixed Bed Reactor**
  - rapid deactivation due to coke formation
  - reactor would have to swing between process & regeneration
  - product composition varies with time
  - expensive high-temperature valves required

• **Fluidized-Bed Reactor**
  - transport reactor, internal catalyst circulation
  - continuous movement of portion of used catalyst to separate regenerator
  - reduced catalyst inventory, increased capacity
  - uniform product distribution with time
Fluidized Bed Reactor

Fast Fluidized-Bed

Product

MeOH

Regenerator

Offgas

Air

MeOH
Fluidized Bed Reactor Results

- Conversion and selectivity remain high over months of operation.

Often in catalysis some clever chemical engineering required to make the catalytic process commercially viable.
The catalytic reactor is only one small part of the overall process!
Olefin Cracking Technology

- Another piece of the process.....
- Production of propylene and ethylene from \( \text{C}_4 \) to \( \text{C}_8 \) olefins.

\[ \begin{align*}
\text{C}_4 \text{ to } \text{C}_8 \\
\text{Olefins} \\
\text{C}_4\text{H}_8 \text{ to } \text{C}_8\text{H}_{16}
\end{align*} \]

Catalyst

Olefin Cracking

\(-\Delta T\)

Propylene \\
& Ethylene

\[ \begin{align*}
\text{C}_3\text{H}_6 & \text{ & } \text{C}_2\text{H}_4
\end{align*} \]
Olefin Cracking integration with MTO

- Upgrade C4+ MTO product to C2= and C3=.

- 20% increase in light olefin yields

- Nearly 80% reduction in C4+ by-products

- Can achieve 2:1 propylene/ethylene product ratio
MTO Reaction with Olefin Cracking

SAPO-34 Catalyst

Methanol $\Delta$ Other By-Products

Ethylene

Propylene

Butenes

Other By-Products

$\text{H}_2\text{O}$

$\text{H}_2$, $\text{CO}_x$

$\text{C}_1$-$\text{C}_5$ Paraffins

$\text{C}_5^+$

Coke
Outline

• Zeolites
• Zeolites as industrial catalysts
• Acid sites in molecular sieves
• Aluminum phosphate (AlPO₄) molecular sieves
• Characterization methods for molecular sieves
• SAPO-34
• Methanol conversion using zeolites
• Zeolites vs. SAPO’s in methanol conversion
• CHA and AEI
• MTO mechanism
• MTO reactor design
• Putting it all together: methanol & natural gas
• Discovery to commercialization
Why Natural Gas Conversion?

• Large reserves of remote natural gas.
• Environmental need to minimize venting or flaring of associated gas from oil fields.
• Existing technologies for methane conversion limited by market size or marginal economics.
Natural gas utilization is desired by many companies and nations

- Monetization of stranded gas reserves
- Reduced gas flaring
- Less dependence on crude oil

World Total = 179 x 10^{12} Cubic Meters

Source: Oil & Gas Journal 2003
Ethylene Supply & Demand

- Demand for ethylene predicted to increase: source will have to come from new capacity.

2004 Supply (PG)
103 MM MTA

- Naphtha 54%
- Ethane 27%
- Propane 7%
- Butane 4%
- Gas Oil 6%
- Others 2%

“PG” = polymer-grade

Demand
Non-Ethane?
Ethane?

Current Capacity

Data Source: CMAI 2005
Propylene Supply & Demand

- Propylene demand also predicted to rise.

2004 Supply
61 mm MTA

Data Source: CMAI 2005
Stranded Gas Monetization Processes

Production → Liquefaction → Shipping → Revaporation → Natural gas

Synthesis gas production → Hydrocarbon synthesis → Upgrading → Liquid fuels

CO + H₂ → Methanol synthesis → MTO → Ethylene, Propylene

MTO → Polymers

Polymers → Polyethylene, Polypropylene

GTL → GTO → GTP
Value of Products Produced from 1 MM BTU of Natural Gas

Polymers are highest value product
Large Gas Fields by Size

- Substantially more fields economically viable for GTP technology than other technologies.

<table>
<thead>
<tr>
<th>Size of Fields</th>
<th>Number of Fields</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 - 1 Tcf</td>
<td>269</td>
</tr>
<tr>
<td>1 - 5 Tcf</td>
<td>234</td>
</tr>
<tr>
<td>5 - 50 Tcf</td>
<td>71</td>
</tr>
<tr>
<td>50 - 500 Tcf</td>
<td>15</td>
</tr>
</tbody>
</table>

86 Suitable for LNG & GTL
320 Suitable for GTP

Total = 589 Large Fields

1 Trillion cf = 28.2 BCM

Source: Oil & Gas Journal
Methanol to Olefins Process

• MTO process is new viable route to polymer grade ethylene and propylene.
MTO Commercial Status

• MTO Demo Unit
  - Started-up in 1995 at Norsk Hydro facilities in Norway
  - Used commercial methanol feedstock

• UOP and Total Petrochemicals announced in Dec 2005 an integrated demonstration unit consisting of both a UOP/HYDRO Methanol-to-Olefins unit and a Total Petrochemicals/UOP Olefin Cracking unit.

• Construction started at Total’s petrochemical complex in Feluy, Belgium. Start-up in 2008.
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SAPO-34 vs UZM’s

• For SAPO-34 it took 20+ years from discovery of the material to its use in a commercial process.

• In 1998 New Materials Group formed at UOP to discover new zeolites.


• Identified as a candidate for ethylbenzene production.

\[
\text{C}_6\text{H}_6 + \text{C}_2\text{H}_4 \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3
\]

benzene  ethylene  ethylbenzene

• Performance of UZM-8 allowed for the design of a more economical process.

• New process with new catalyst for EB production offered for sale in late 2006.

6 years to commercialization!
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