Zeolite catalysed conversion of alcohols to hydrocarbons: from molecular to industrial scale

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“IPCPO’16: Innovation techniques in chemistry, petrochemistry, and oil refining”
Sint-Petersburg, 20-21 October 2016
Laboratory for Chemical Technology

from atom (nm) to full process (m)

Process
- Transport phenomena
- Reactor
- Kinetics
- Mechanism
- Materials design
- Separation units

Reaction engineering

Process level
Molecular level

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Heterogeneous Catalysis: a Multiscale process

Ultra high vacuum
0.01-1 kPa

Low-moderate pressure
5-30 kPa

Moderate –high pressure
500-30000 kPa

Reactive intermediates in reaction mechanism

Temporal Analysis of Products

Bench scale micro-reactors

Pilot plants

Industrial reactor

Reaction kinetics study for obtaining reaction rate coefficients

Sub millisecond time resolution experiments for insight into reaction mechanism

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Multi-scale modeling: la voie royale

kinetic LABORATORY data

chemical kinetics based on elementary steps

conservation laws, including transport phenomena

Ab initio CALCULATIONS

Process and product DESIGN

First-principles based kinetic modeling

- Geometry optimization
  - electronic energy (0 K)
- Vibrational analysis
  - frequencies
- Statistical thermodynamics
  - \( H(T), S(T), G(T) \)
- Thermo & Kinetics
  - \( K, k_+, k_- \)
- Reactor Model
- Conversion and Selectivity
- Reaction path analysis
- Guidelines process conditions
- Guidelines catalyst design/screening

**VASP**
- VASP 5.3
- PAW method
- GGA: PBE-D2

**Reactor Model**

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Ab Initio Molecular Dynamics

Zundel

Eigen

NVT, 300 K

Acid catalyzed ethanol conversion

**H-ZSM-5**

\[ p_{\text{EtOH},0} = 20 \text{ kPa} : W/F_{\text{EtOH},0} = 8 \text{ kg s mol}^{-1} \]
Ethanol conversion to higher HC

H-ZSM-5, $T = 573$ K, $p_{\text{EtOH,0}} = 30$ kPa

Van der Borght et al., Angew. Chem., in press
• Introduction

• Dehydration of bioalcohols on zeolites
  • First principles kinetic model development
  • Experimental validation
  • Reaction-path analysis
  • Effect of zeolite
  • Industrial reactor scale

• Conclusions
Alcohol adsorption in zeolites

Ethanol physisorption in H-ZSM-5

- van der Waals:
  - dipole-dipole
  - dipole-induced dipole
  - dispersive
- H-bonding
- electrostatic interactions
H-bonding and protonation: chemisorption

Ethanol adsorption and protonation in H-ZSM-5

Nudged Elastic Band calculation with PBE-D2 functional

ΔE (kJ/mol)
Alcohol adsorption & reaction in zeolites

\[ r = k \theta_{ads,\text{alcohol}} = k K_{ads} P_{alcohol} \]

\[ K_{ads} = \exp \left( -\frac{\Delta G_{ads}^0}{RT} \right) = \exp \left( -\frac{\Delta H_{ads}^0 - T\Delta S_{ads}^0}{RT} \right) \]

\[ k = \frac{k_bT}{h} \exp \left( \frac{\Delta S^{0,\#}}{R} \right) \exp \left( -\frac{\Delta H^{0,\#}}{RT} \right) = \frac{k_bT}{h} \exp \left( -\frac{\Delta G^{0,\#}}{RT} \right) \]
Chemisorption: effect of chain length

• Introduction

• Dehydration of bioalcohols on zeolites
  • First principles kinetic model development
    ➢ Ethanol dehydration
### Ethanol to Ethene: H-ZSM-5

#### Reaction (A):
\[ \text{EtOH}_{(g)} \rightarrow \text{C}_2\text{H}_4(g) + \text{H}_2\text{O}_{(g)} \]

- **TS1**: Transition state for the first step.
- **TS2**: Transition state for the second step.
- **TS3**: Transition state for the third step.
- **TS4**: Transition state for the fourth step.
- **TS5**: Transition state for the fifth step.
- **TS6**: Transition state for the sixth step.

**Notes:**
- Involves the conversion of ethanol (EtOH) to ethene (C$_2$H$_4$) and water (H$_2$O) using a catalyst.
- The reaction occurs in a series of steps, each involving specific transition states.

**References:**
Ethanol to Diethyl ether: H-ZSM-5

**B:** \(2\text{EtOH} \rightarrow \text{DEE} + \text{H}_2\text{O} \)

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Ethanol to Diethyl ether: H-ZSM-5

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Diethyl ether to Ethene: H-ZSM-5

C: \[ \text{DEE}_\text{(g)} \rightarrow \text{EtOH}_\text{(g)} + \text{C}_2\text{H}_4\text{(g)} \]
• Introduction

• Dehydration of bioalcohols on zeolites
  • First principles kinetic model development
    ➢ Butanol dehydration: idem
Dehydration: dominant mechanisms

Dehydration: MARI’s
### MARI's and Rate-Determining Steps

<table>
<thead>
<tr>
<th>(1) BuOH(g) + * ↔ M1</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2) M1 ↔ M2</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(3) M2 ↔ Butene* + H2O(g)</td>
<td></td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>(4) Butene* ↔ Butene(g) + *</td>
<td></td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>(5) M1 + BuOH(g) ↔ D1</td>
<td></td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>(6) D1 ↔ D2</td>
<td></td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>(7) D2 ↔ DBE* + H2O(g)</td>
<td></td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>(8) DBE* ↔ DBE(g) + *</td>
<td></td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>(9) DBE* ↔ C1</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(10) C1 ↔ Butene* + BuOH(g)</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Path A: BuOH(g) ↔ Butene(g) + H2O(g)
Path B: BuOH(g) + BuOH(g) ↔ DBE(g) + H2O(g)
Path C: DBE(g) ↔ Butene(g) + BuOH(g)

All reaction paths involving all the suggested mechanisms are included in the microkinetic model.

\[
\text{TOF}_{\text{path}} = \sum_{i=1}^{n} \text{TOF}_{\text{mech}}
\]
Effect of alkyl chain length on Arrhenius parameters

Surface species

<table>
<thead>
<tr>
<th>Surface species</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>Chemisorbed alcohol monomer</td>
</tr>
<tr>
<td>D1</td>
<td>Chemisorbed alcohol dimer</td>
</tr>
<tr>
<td>Ether*</td>
<td>Adsorbed Ether (DEE/DBE)</td>
</tr>
</tbody>
</table>

Increase in alcohol chain length has marginal influence on activation enthalpy but leads to significant increase in activation entropy.
Overview

- Introduction
- Dehydration of bioalcohols on zeolites
  - First principles kinetic model development
  - Experimental validation
  - Reaction-path analysis
  - Effect of zeolite
  - Industrial reactor scale
- Conclusions
**Experimental procedures and conditions**

### HZSM-5 Properties

<table>
<thead>
<tr>
<th></th>
<th>15</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si/Al</td>
<td>15</td>
<td>40</td>
</tr>
<tr>
<td>$c_{H^+}$ (mol kg$^{-1}$)</td>
<td>0.77</td>
<td>0.36</td>
</tr>
<tr>
<td>BET (10$^3$ m$^2$ kg$^{-1}$)</td>
<td>430</td>
<td>436</td>
</tr>
<tr>
<td>$V_{\text{micro}}$ (10$^{-5}$ m$^3$ kg$^{-1}$)</td>
<td>1.1</td>
<td>1.1</td>
</tr>
</tbody>
</table>

### Experimental conditions

<table>
<thead>
<tr>
<th></th>
<th>453 – 523</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (K)</td>
<td></td>
</tr>
<tr>
<td>$p_{\text{EtOH,in}}$ (kPa)</td>
<td>8 – 50</td>
</tr>
<tr>
<td>$W/F_{\text{EtOH,in}}$ (kg s mol$^{-1}$)</td>
<td>1.5 – 17.0</td>
</tr>
</tbody>
</table>
Reactor model equations

Reactor continuity equations for each gas-phase component $i$ with PSSA for the surface species $k$:

$$R_k = \sum_j v_{jk} r_j = 0$$

with $e.g., r_j = k_j \theta_k p_i$

$$\theta_{H^+} + \sum_k \theta_k = 1$$

$$\frac{dF_i}{dW} = C_t R_i = C_t \sum_j v_{ji} r_j$$

$F_i = F_{i,0} \text{ at } W = 0$

- $F_i$ molar flow rate of component $i$ (mol s$^{-1}$)
- $W$ catalyst mass (kg)
- $C_t$ acid site concentration (mol H$^+$ kg$^{-1}$)
- $R_i$ net production frequency of component $i$ (molecules site$^{-1}$ s$^{-1}$ = mol mol$^{-1}$ H$^+$ s$^{-1}$)
- $r_j$ turnover frequency of elementary step $j$ (molecules site$^{-1}$ s$^{-1}$ = mol mol$^{-1}$ H$^+$ s$^{-1}$)
- $k_j$ rate coefficient of elementary step $j$
- $\theta$ coverage of surface species $k$
- $p_i$ partial pressure of gas phase component $i$
- $v_{ji}$ stoichiometric coefficient of component $i$ in the elementary step $j$
Conversion and selectivities

\[
W_{\text{cat}} / F_{\text{EtOH},0} = 6.5 \text{ kg s / mol}
\]
\[
P_{\text{EtOH},0} = 24 \text{ kPa}
\]
Effect of water

\[ W_{\text{cat}}/F_{\text{EtOH},0} = 8.3 \text{ kg s / mol} \]

\[ P_{\text{EtOH},0} = 29 \text{ kPa} \]

\[ T = 503 \text{ K} \]
Overview

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  • Industrial reactor scale

• Conclusions
Reaction path analysis: effect of T

450 K

550 K

H-ZSM-5, $p_{EtOH,0} = 10kPa$, $X_{EtOH} = 10\%$

Reaction path analysis: effect of conversion

\[ C_2H_5OH \xrightarrow{\text{Path A}} C_2H_4 \]
\[ C_2H_5OH + H_2O \xrightarrow{\text{Path B}} C_2H_5OC_2H_5 \]
\[ C_2H_5OH \xrightarrow{\text{Path C}} C_2H_5OH \]

H-ZSM-5, \( p_{C_2H_5OH,0} = 10\text{kPa}, T = 500 \text{ K} \)
Reaction path analysis: Effect of water

Zeolite: H-ZSM-5
T: 450 K
$P_{\text{BuOH},0}$ : 1 kPa,
$P_{\text{H}_2\text{O},0}$ : 1 - 40 kPa,
$X_{\text{BuOH}}$ : 10%

TOF (mol/ mol H+/s)

Partial pressure of water (kPa)

TOF (mol/ mol H+/s)

Surface coverage

Partial pressure of water (kPa)
Equilibrium coefficients for adsorption @ 450K

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  • Effect of zeolite: activity
  • Industrial reactor scale

• Conclusions
Zeolite Frameworks

3D zeolites

H-FAU (Si/Al=47)

12MR: 740 x 740 pm

H-ZSM-5 (Si/Al=95)

10MR: 510 x 550 pm

10MR: 530 x 560 pm

8MR: 350 x 480 pm

H-FER (Si/Al=71)

10MR: 420 x 540 pm

10MR: 510 x 550 pm

8MR: 260 x 570 pm

H-MOR (Si/Al=95)

12MR: 650 x 700 pm

10MR: 460 x 570 pm

H-ZSM-22 (Si/Al=35)
Chemisorption

$\Delta H^0_{ads} / \text{kJ mol}^{-1}$ vs Carbon number

- $\Delta H^0_{ads}$ for H-FAU
- $\Delta H^0_{ads}$ for H-MOR
- $\Delta H^0_{ads}$ for H-ZSM-5
- $\Delta H^0_{ads}$ for H-ZSM-22
Effect of zeolite: B Ethanol to Diethyl ether

<table>
<thead>
<tr>
<th>ZeOH</th>
<th>ΔG‡ = G_{TS8} − G_{D1} (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-FAU</td>
<td>138</td>
</tr>
<tr>
<td>H-MOR</td>
<td>142</td>
</tr>
<tr>
<td>H-ZSM-5</td>
<td>129</td>
</tr>
<tr>
<td>H-ZSM-22</td>
<td>113</td>
</tr>
</tbody>
</table>

10-MR zeolites more active than 12-MR zeolites
TS stabilization: vdW & hydrogen bonds

12-MR (FAU; MOR) < 10-MR (ZSM-5; ZSM-22)
TS 8 stabilization: electrostatic interactions

Electrostatic potential / eV

H-FAU

H-MOR

H-ZSM-5

H-ZSM-22

FAU < MOR < ZSM-5 < ZSM-22
Overview

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• Dehydration of bioalcohols on zeolites
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  • Experimental validation
  • Reaction-path analysis
  • Effect of zeolite: selectivity
  • Industrial reactor scale

• Conclusions
Butanol dehydration

$P_{BuOH,0} = 10 \text{kPa}$  
Temperature = 450 K

TOF $|_{X=0}$ (mol/mol H+ /s)

Conversion (%)

Butene selectivity (%)

Site time (mol H+/s/mol)

H-FER  
H-FAU  
H-ZSM-5  
H-ZSM-22

DBE selectivity (%)

Conversion (%)
**Effect of Zeolite: reaction path analysis**

\[ P_{BuOH,0} = 10 \text{ kPa} \]

**Temperature** = 450 K

- H-FER and H-FAU: selective for butene

**H-FER**

**H-ZSM-5**

**H-ZSM-22**

**H-FER:** ether-mediated route (path B followed by path C) favored to produce 1-butene

**H-FAU:** significant contribution from path A favors formation of 1-butene
**Effect of zeolite: path B and C**

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>$\Delta G_{\text{B}}^\ddagger$ (kJ/mol)</th>
<th>$\Delta G_{\text{C}}^\ddagger$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-FAU</td>
<td>134</td>
<td>132</td>
</tr>
<tr>
<td>H-ZSM-5</td>
<td>127</td>
<td>128</td>
</tr>
<tr>
<td>H-ZSM-22</td>
<td>131</td>
<td>132</td>
</tr>
<tr>
<td>H-FER</td>
<td>137</td>
<td><strong>105</strong></td>
</tr>
</tbody>
</table>

Path B: $\Delta G_{\text{TS8}}^\ddagger - \Delta G_{\text{D1}}$ (kJ/mol)

Path C: $\Delta G_{\text{TS10}}^\ddagger - \Delta G_{\text{DBE}^*}$ (kJ/mol)

Steric constraints

DBE* (FER)

DBE* (MFI)
Caveat: effect of reaction conditions

<table>
<thead>
<tr>
<th></th>
<th>Low</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>B</td>
<td>A</td>
</tr>
<tr>
<td>$P_{ROH}$</td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>Conversion (X)</td>
<td>A / B</td>
<td>A / C</td>
</tr>
</tbody>
</table>

MARI (at X= 10 %)

dominant path (at X= 10 %)
Dehydration of 1-butanol to butene isomers

Path D

1-butanol $\xrightarrow{H_2O}$ Di-1-butyl ether $\xrightarrow{1\text{-butanol}}$ 1-butene $\xrightarrow{H_2O}$ 1-butanol $\xrightarrow{H_2O}$ Trans-2-butene $\xrightarrow{\text{Path H}}$ Cis-2-butene $\xrightarrow{\text{Path K}}$ Iso-butene

(Path D)

(Path A)

(Path B)

(Path C)

(Path E)

(Path F)

(Path G)

(Path I)

(Path J)
Dehydration of 1-butanol to 2-t-butene

Path D

Path E

[TS-12]‡

[TS-13]‡
Dehydration of 1-butanol to butene isomers

Path D

1-butene* → 2t-butene(g) → 2t-butene* → [TS-12]‡

Path E

2t-butene(g) → DBE* → [TS-13]‡ → M1

Path F

2t-butene* → [TS-14]‡ → 1-butene* → [TS-15]‡

Path G

2c-butene(g) → 2c-butene* → [TS-16]‡ → H-ZSM-5

Path I

iso-butoxy → [TS-19]‡ → iso-butene*
### Butanol dehydration: Temkin table

<table>
<thead>
<tr>
<th>Mechanism #</th>
<th>Path A</th>
<th>Path B</th>
<th>Path C</th>
</tr>
</thead>
<tbody>
<tr>
<td>m1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>m2</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>m3</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>m4</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>m5</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>m6</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>m7</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>m8</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>m9</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>m10</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

All reaction paths involving all the suggested mechanism are included in the microkinetic model.

\[
\text{TOF}_{\text{path}} = \sum_{i=1}^{n} \text{TOF}_{\text{mech}}
\]

\[
\text{TOF}_A = \text{TOF}_{m1} + \text{TOF}_{m2} + \text{TOF}_{m3} + \text{TOF}_{m4} + \text{TOF}_{m5}
\]

\[
\text{TOF}_{m1} = \text{TOF}_{R2}
\]

\[
\text{TOF}_{m2} = \text{TOF}_{R4}
\]

\[
\text{TOF}_{m3} = \text{TOF}_{R7}
\]

\[
\text{TOF}_{m4} = \text{TOF}_{R9}
\]

\[
\text{TOF}_{m5} = \text{TOF}_{R13}
\]
Reaction path analysis

Path F: 1-Butene(g) ↔ 2-t-Butene(g) {concerted mechanism}

T : 450 K  P_{BuOH,0} : 10 kPa
X=95%

Selectivity(%) vs Conversion (%)

Surface coverage vs Conversion (%)

H-ZSM-5
Butene isomer selectivity: Effect of zeolite type

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• Conclusions
Industrial dehydration reactor

bio-ethanol (aqueous ethanol solution)

Design specifications

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T^0$ (K)</td>
<td>673</td>
</tr>
<tr>
<td>$P^0$ (kPa)</td>
<td>590</td>
</tr>
<tr>
<td>Ethylene production (kT y$^{-1}$)</td>
<td>220</td>
</tr>
<tr>
<td>Ethanol content (wt.%)</td>
<td>26</td>
</tr>
<tr>
<td>Catalyst mass (ton)</td>
<td>6</td>
</tr>
</tbody>
</table>

$$
\begin{align*}
C_2H_5OH & \rightarrow C_2H_4 + H_2O & \Delta H &= 46 \text{ kJ/mol}_{EtOH} \\
2 C_2H_5OH & \rightarrow (C_2H_5)_2O + H_2O & \Delta H &= -12 \text{ kJ/mol}_{EtOH} \\
(C_2H_5)_2O & \rightarrow C_2H_4 + C_2H_5OH & \Delta H &= 70 \text{ kJ/mol}_{EtOH}
\end{align*}
$$

1 US Patent 2013/0090510 A1 assigned to IFP Energies Nouvelles and Total Research & Technology
Multiscale modeling of an industrial reactor

**NANO**
- Pore
- Active site

**“MICRO”**
- Crystallite
- Concentration of acid sites $C_t$
- Elementary reaction:
  \[ r_j = k_j \theta_k p_i \]

**MACRO**
- Reactor
- F\textsubscript{EtOH}, $T$, $p_t$
- $d_r = 10^{-1} - 10^{-m}$
- $L_{reactor} = 10^0 - 10^1 m$
- $W$

Gas phase components $i$
Surface species $k$
Concentration of acid sites $C_t$

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Microscale: possible diffusion limitations

Weisz-Prater criterion:
\[
\frac{(n + 1) d^2 \rho R_i^{obs}}{2 6D_{e,i} C_i^S} < 0.08
\]

\[
D_{e,i} = \frac{\varepsilon_p D_i}{\tau_p}
\]

Bosanquet equation:
\[
\frac{1}{D_i} = \frac{1}{D_{i,m}} + \frac{1}{D_{i,K}}
\]

Knudsen diffusion coefficient:
\[
D_{i,K} = \frac{2 d_{pore}}{3} \frac{8RT}{\pi M_i}
\]

Molecular diffusion coefficient:
\[
D_{i,j} = 1 \times 10^{-7} \frac{T^{1.75}}{P_{tot}(\Sigma v)^{1/3} + (\Sigma v)^{1/3})^2} \left( \frac{1}{M_i} + \frac{1}{M_j} \right)^{1/2}
\]
Reactor model equations

\[ R_k = \sum_j v_{jk} r_j = 0 \]

with \( e.g. r_j = k_j \theta_k p_i \)

\[ \theta_{H^+} + \sum_k \theta_k = 1 \]

\[ 0 = C_t R_i \rho_s - \frac{4}{d_p^2} \left( \frac{2}{\xi} D_{e,i} \frac{d C_i}{d \xi} + \frac{d D_{e,i}}{d \xi} \frac{d C_i}{d \xi} + D_{e,i} \frac{d^2 C_i}{d \xi^2} \right) \]

\[ C_i = C_i^{s} \quad \xi = 1 \]

\[ \frac{d C_i}{d \xi} = 0 \quad \xi = 0 \]

\[ \frac{d F_i}{d W} = C_t \bar{R}_i \]

\[ F_i = F_{i,0} \text{ at } W=0 \]

\[ \frac{dT}{d W} = \frac{1}{G c_p} \sum_{i=1}^{\Delta H_{f,i}} \bar{R}_i C_t \]

\[ T = T^0 \text{ at } W=0 \]

\[ \frac{d p_t}{d W} = -f \frac{G^2}{\rho_b \rho_f A_R^3 d_p} \]

\[ p = p^0 \text{ at } W=0 \]
Effectiveness factor

\[ \eta = \frac{\int_{0}^{R_p} R_{v,i} \pi r^2 \, dr}{R_{v,i}^S V} \]
Industrially multibed adiabatic operation

Conversion / Yield (%)

Temperature (K)

Pressure (kPa)

Catalyst mass (ton)

EtOH conversion

$C_2H_4$ yield

$x_{\text{EtOH, eq}}$
Overview

• Introduction

• Dehydration of bioalcohols on zeolites
  • First principles kinetic model development
  • Experimental validation
  • Reaction-path analysis
  • Effect of zeolite
  • Industrial reactor scale

• Conclusions
• Adsorption strength increases with alkyl chain length of alcohols

• Increase of alkyl chain length leads to an increase of $\Delta S^\ddagger_0$ and explains higher reactivity of large chain alcohols

• Dispersive interactions and H bonding plays a key role in stabilization of adsorbed species and transition states

• “Compensation effect” can be important: dispersive interaction and steric hindrance both increasing with decreasing pore size

• Stronger adsorption of alcohol and ether as compared to alkenes (limit consecutive reactions) and water (no significant inhibition effect)
• Detailed reaction network can be constructed with limited a priory assumptions

• Kinetic parameters can be calculated ab initio with chemical accuracy i.e. allowing to describe conversion and selectivity at relevant conditions

• Interaction of functional groups with catalyst can be described accurately as well as the effect of catalyst framework

• Dominant reaction path depends strongly both on conditions and catalyst framework

• Selection of optimal catalyst based on reaction path/sensitivity analysis based on microkinetics
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• **Molecular Dynamics (MD):** a technique by which one generates the atomic trajectories of a system of N particles by numerical integration of Newton’s equation of motion, for a specific interatomic potential, with certain initial and boundary conditions.

• **Radial Distribution Function (RDF):** a pair correlation function, which describes how, on average, the atoms in a system are radially packed around each other.

\[
g_{\alpha\beta}(r) = \frac{1}{N_{\alpha\beta}} \sum_{i\in\alpha,j\in\beta} \delta(r - |\mathbf{R}_j - \mathbf{R}_i|)
\]

• **Vibrational Density Of States (VDOS):** the Fourier transform of the velocity-velocity time-correlation function

\[
D(\omega) = \int_0^{\infty} e^{-i\omega t} \langle \mathbf{v}(\tau) \cdot \mathbf{v}(\tau + t) \rangle dt
\]
Glossary

- **Electrostatic potential**: evaluated from the interaction between a negative unit charge and the local charge density. This factor is critical in stabilizing positively charged adsorbed complexes and especially transition states in the zeolite.

- **Elementary step**: a reaction in which reactants are transformed into products without passing through another reaction intermediate

- **Transition state theory for reaction rate coefficients**:

  \[
  k = \frac{k_B T}{h} \exp\left( -\frac{\Delta G^\ddagger}{k_B T} \right) = \frac{k_B T}{h} \frac{q^\ddagger}{q} \exp\left( -\frac{\Delta E_0^\ddagger}{k_B T} \right)
  \]

  *where* \( q = q_{\text{vib}} \) immobile surface species

  (apart from Ethene* where a 2D translation and 1D rotation is assumed)
• **van der Waals interactions**: the attractive or repulsive interactions between molecular entities (or between groups within the same molecular entity) other than those due to bond formation or to the electrostatic interaction of ions or of ionic groups with one another or with neutral molecules. The term includes: dipole–dipole, dipole-induced dipole and dispersive (instantaneous induced induced dipole-induced dipole) interactions.

• **Dispersive interactions**: attractive interactions between any pair of molecules, including non-polar atoms, arising from instantaneous induced dipole-induced dipole forces
• **E1 reaction (elimination, unimolecular)** – In this reaction, the rate determining step involves a heterolytic cleavage of the bond between the leaving group and the carbon atom leading to formation of a carbenium ion. The second step involves deprotonation of an adjacent hydrogen by a base.
• **E2 reaction**(elimination, bimolecular) – E2 reaction is a concerted reaction involving a synchronous deprotonation and departure of the leaving group. E2-type elimination requires the atoms or groups involved in the reaction to be in the same plane with a torsional angle \( \theta = 180^\circ \), i.e. antiperiplanar orientation of the leaving group (LG) and the \( \beta \)-hydrogen (hence also called as anti-elimination).
• **Syn elimination** – This is a concerted elimination mechanism, where the leaving group (LG) and the hydrogen atom are in the same plane and have a syn coplanar orientation (torsional angle $\theta \approx 0^\circ$; eclipsed or near eclipsed conformation)
• **SN1 (substitution, unimolecular)** – In this reaction, the rate determining step involves a heterolytic cleavage of the bond between the leaving group and the carbon atom leading to formation of a carbenium ion which undergoes a substitution reaction with the nucleophile.

• **SN2 (substitution, bimolecular)** is a concerted reaction involving simultaneous bond breaking (between the carbon atom and leaving group) and bond formation (between carbon atom and the attacking nucleophile). The transition state for a SN2 type substitution involves a penta-coordinated carbon atom with a trigonal bipyramidal geometry with the incoming nucleophile and the leaving group occupying the axial positions (bond angle Nu--C--LG ≈ 180°).
Glossary: Rate-determining step

Global reaction rate:

\[ r = r_1^+ - r_1^- \]

Quasi-equilibrated:

\[ r_1^+ \approx r_1^- \Rightarrow A_1 \equiv 0 \]

Non-equilibrated:

\[ r_2^+ << r_1^- \text{ and } r_1^+ \Rightarrow A_2 \gg A_1 \]

Affinity elementary step \( j \):

\[ A_j = -\Delta G_{r,j} = -\Delta G_{r,j}^\circ + RT \ln \frac{\prod_{i} c_{i}^{n_i}_{\text{prod}}}{\prod_{i} c_{i}^{n_i}_{\text{react}}} \]

\[ \frac{r_1^+}{r_1^-} = e^{A_1/RT} \equiv 1 \]

\[ \frac{r_2^+}{r_2^-} = e^{A_2/RT} \gg 1 \]
• **Sensitivity analysis**: normalized sensitivity coefficient ($NSC_{i,j}$) of response $R_j$ to pre-exponential factor $A_i$ of reaction $i$:

$$NSC_{i,j} = \frac{d(\ln R_j)}{d(\ln A_i)} = \frac{A_i dR_j}{R_j dA_i}$$

where $R_j$ can correspond to conversion of reactants, turnover frequency, or selectivity to a product $j$.

• **Reaction-path analysis**: analyzes the reaction rates that contribute to the rate of production or disappearance of a selected species, which allows to determine actual reaction path to form intermediates and products.