WEBINAR

Modelling Catalyst Deactivation: Multiscale Modelling of Zeolite Catalysis

Professor Rutger A. van Santen
Eindhoven University of Technology, Netherlands

Materials Design UGM

WEBINAR

Modelling Catalyst Deactivation: Multiscale Modelling of Zeolite Catalysis

Professor Rutger A. van Santen
Eindhoven University of Technology, Netherlands

UGM Plenary Session Speakers

Professor Rutger A. van Santen

Eindhoven University of Technology

Dr. René Windiks

rwindiks@materialsdesign.com

Katherine Hollingsworth

khollingsworth@materialsdesign.com

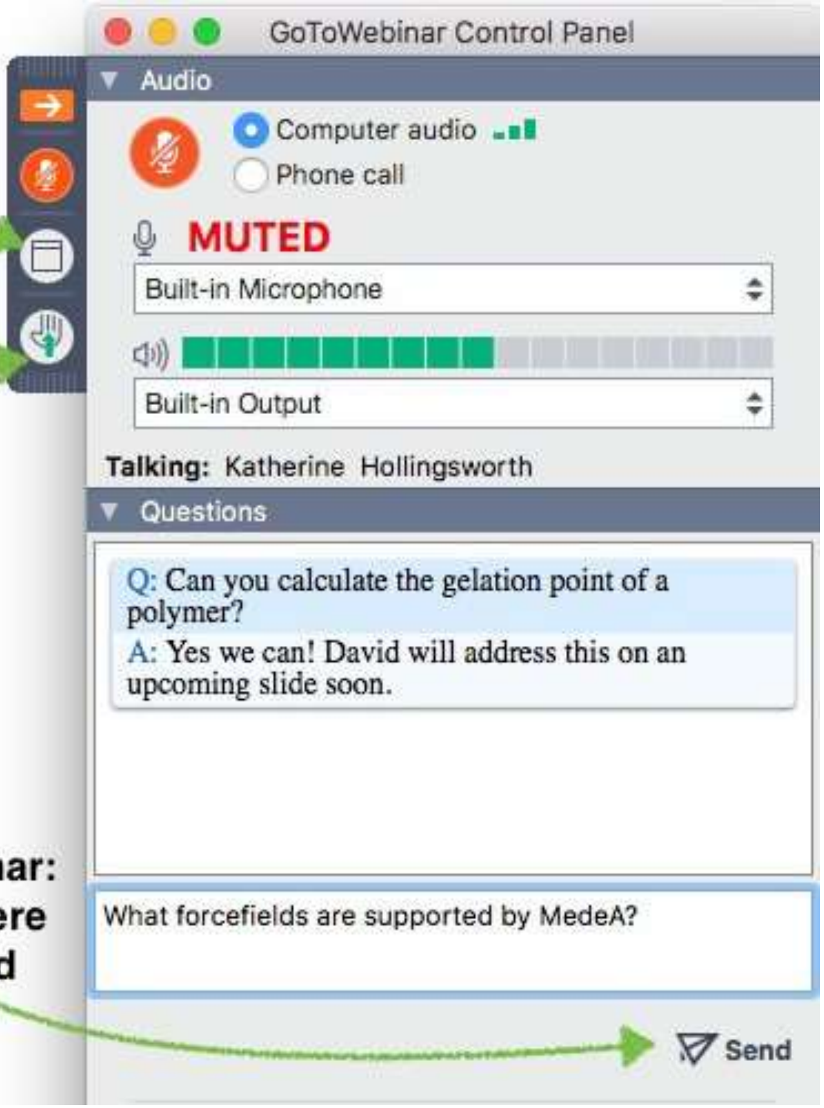
Materials Design UGM Plenary Sessions

- Share the plenary sessions with your colleagues!
  - Registration details

    https://www.ugm.materialsdesign.com
- We will be recording this session
  - Upcoming sessions are posted on the UGM site
  - Watch any of our earlier webinars anytime

    www.materialsdesign.com/webinars
- Brief survey
  - Take a 2-minute brief survey at the end of this webinar!

Please Ask Questions



Talking: Katherine Hollingsworth

Q: Can you calculate the gelation point of a polymer?

A: Yes we can! David will address this on an upcoming slide soon.

What forcefields are supported by MedeA?

full screen

during discussion:

Use the raise hand icon to bring attention to your question

any time during webinar: type your question here and then press Send

Question and Answer Session

Announcements

www.materialsdesign.com/webinars

ugm.materialsdesign.com

Dr. Kevin Gagnon

Vertex Pharmaceuticals Incorporated

Dr. René Windiks

Materials Design

Next Week's Plenary Speaker

Thursday, October 29th

Training MedeA Transition State Search

Tuesday, October 27th

Question and Answer Session

Professor Rutger van Santen

Technical University Eindhoven

Dr. René Windiks

Materials Design

Questions about the Materials Design UGM Plenary Sessions

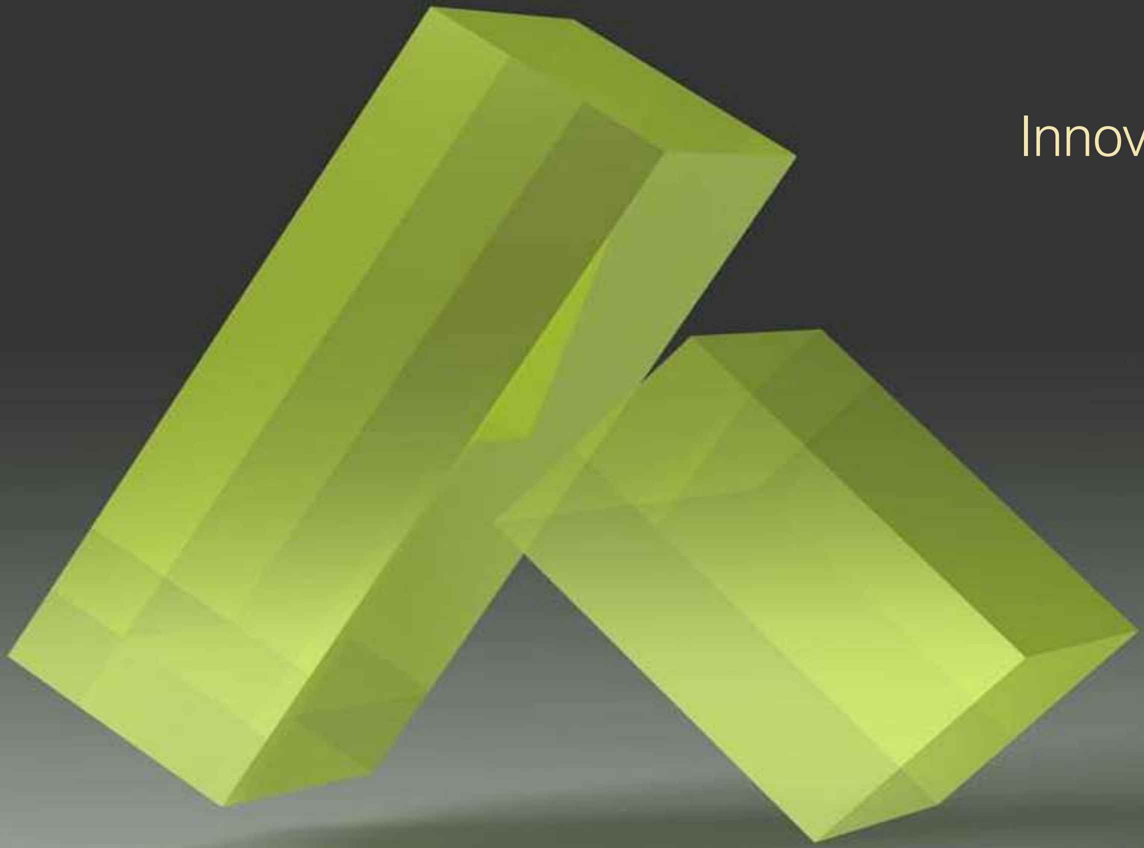
Katherine Hollingsworth

khollingsworth@materialsdesign.com

materials design

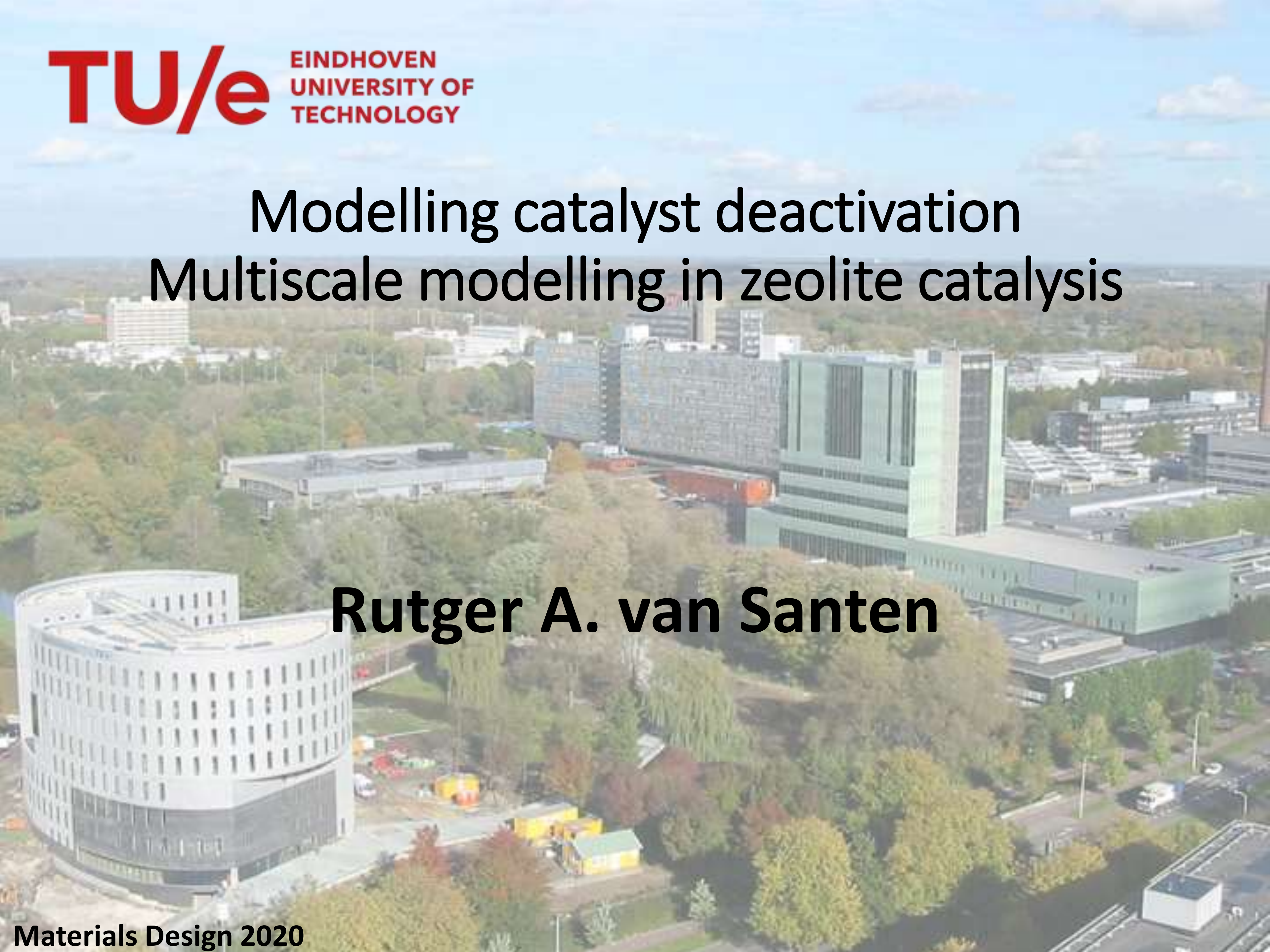
info@materialsdesign.com

www.materialsdesign.com



MedeA

Innovation by Simulation



TU/e EINDHOVEN UNIVERSITY OF TECHNOLOGY

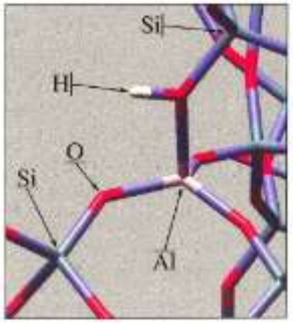
Modelling catalyst deactivation
Multiscale modelling in zeolite catalysis

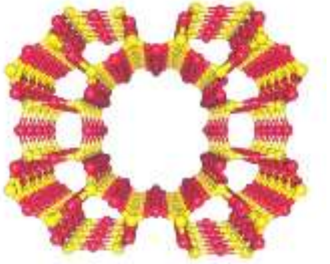
Rutger A. van Santen

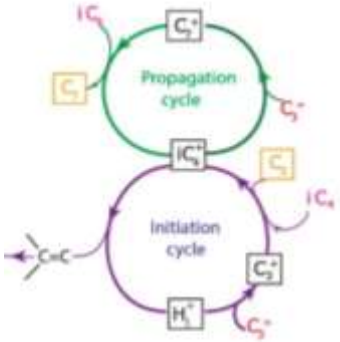
Materials Design 2020

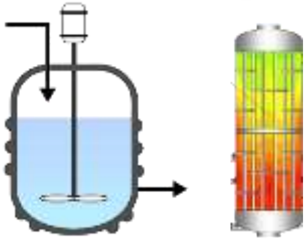
Contents

- Introduction
  - Solid acid zeolite catalysis, deactivation issue
- Alkylation reaction
  - Catalysis as a function of structure and composition
- Microkinetics simulations
- Coarse graining, catalyst deactivation time expressions
- Deactivation theory of Continuous Stirred Tank Reactor (CSTR) and Plug Flow Reactor (PFR)
- Summary and conclusions

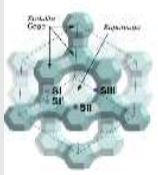
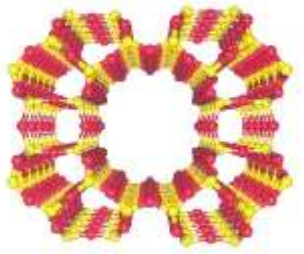
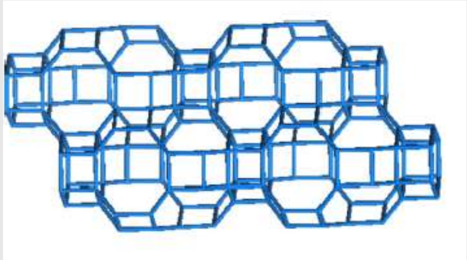
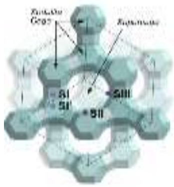








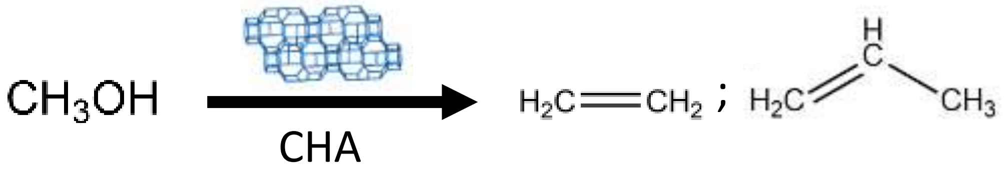
Solid acid zeolite catalyzed reactions

Temperature	Catalyst	Reaction
- 10 °C / 80 °C	HF/H_2SO_4 ; Faujasite 	Alkylation C-C bond formation
250 °C	Pd promoted H^+ / Mordenite 	n-alkane → i-alkane Hydroisomerisation (high octane gasoline)
350 °C	Chabasite 	Dehydration $CH_3OH \rightarrow C_3H_6 + 3\ H_2O$ (natural gas, biomass)
550 °C	Faujasite 	Catalytic cracking; C-C bond cleavage reactions (Crude oil → gasoline)

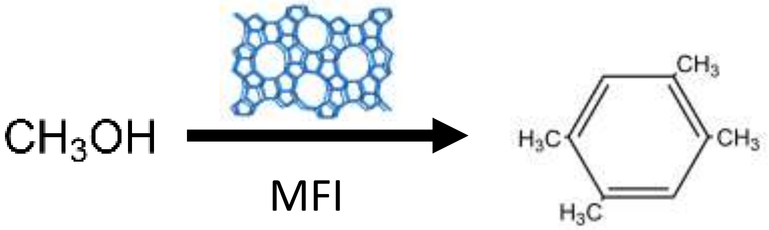
Zeolite catalysed reactions are stereoselective

Methanol dehydration

MTO:
(methanol to olefins)

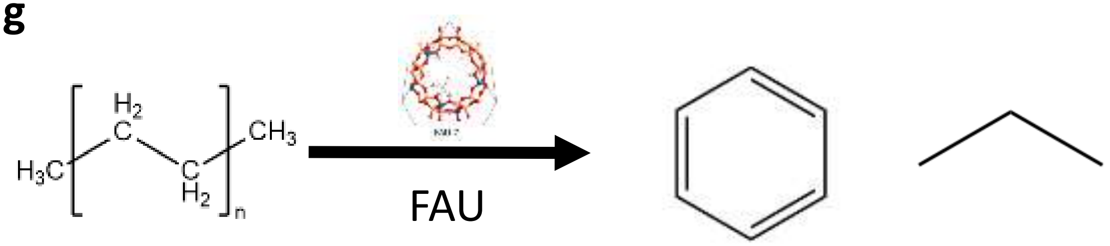


MTG:
(methanol to gasoline)

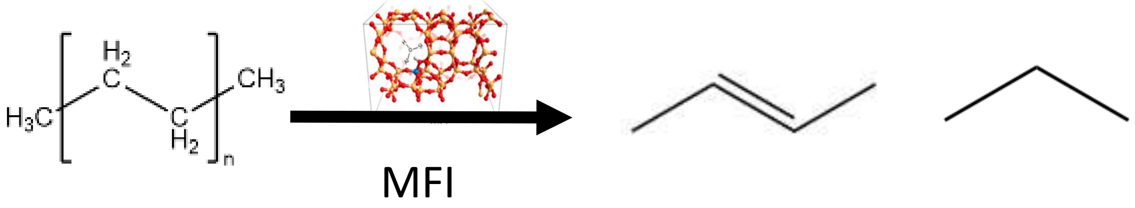


Alkane cracking

Alkane to aromatics/short alkane

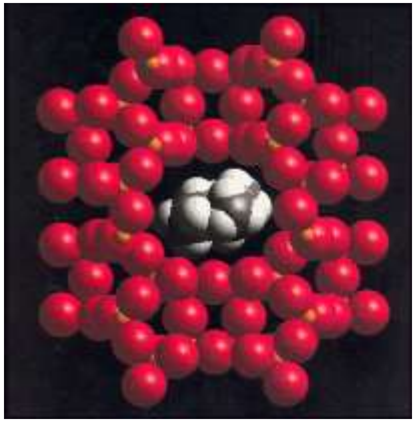


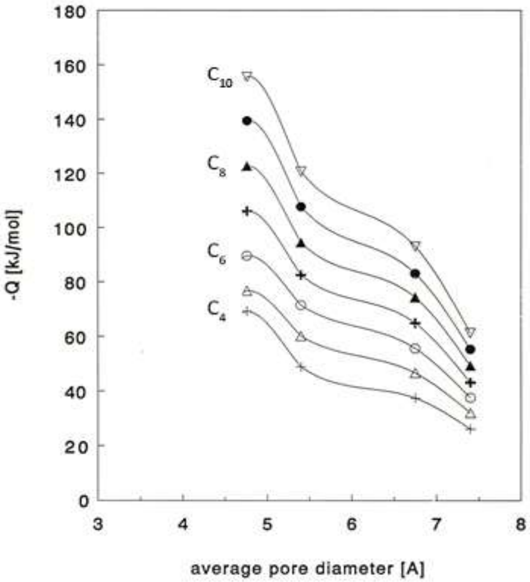
Alkane to short alkenes/alkanes



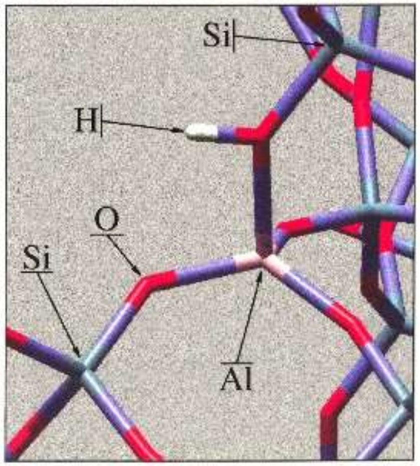
Two zeolite catalyst reactivity descriptors

1. Confinement
    - Match of adsorbate shape with cavity size and form

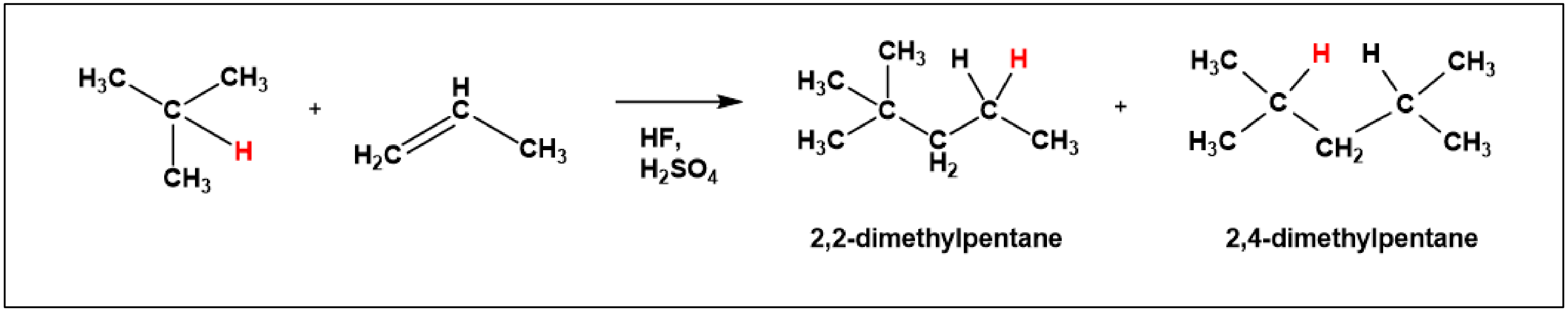




2. Proton affinity
    - Depends on zeolite lattice composition



The alkylation reaction of isobutane and propylene



Alkylate is high octane kerosene. The process is used in more than 300 refineries. Candidate process to produce biofuel.

Catalytic challenge

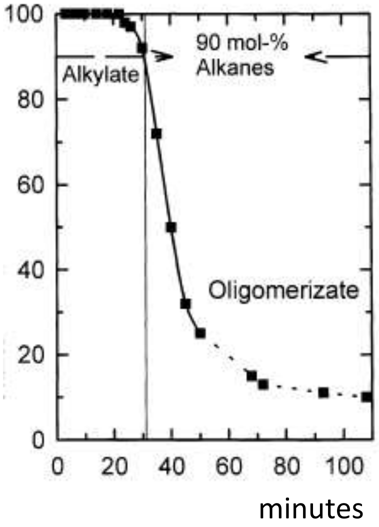
- Increase safety of process by replacing neat HF or H_2SO_4 (harmful liquids) by a solid acid catalyst.

- Problem: the solid acid catalyst deactivates too fast

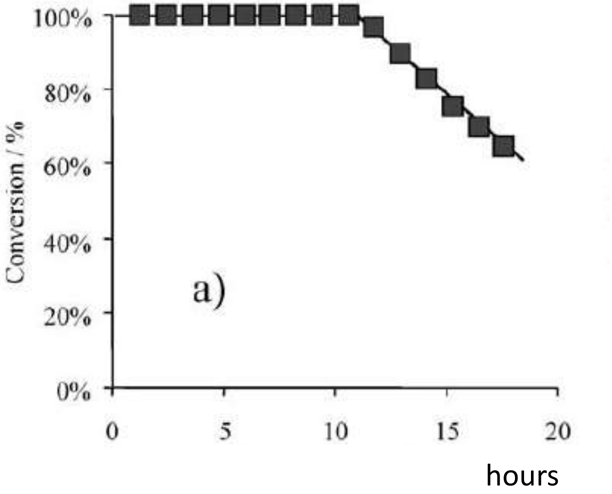
- Question: which zeolite structure (confinement) and composition (Proton affinity) is optimum?

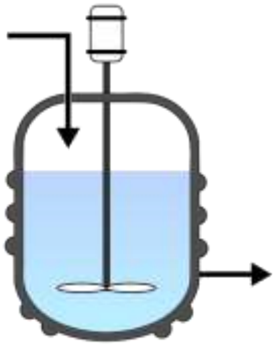
Catalyst performance depends on choice of reactor

PFR

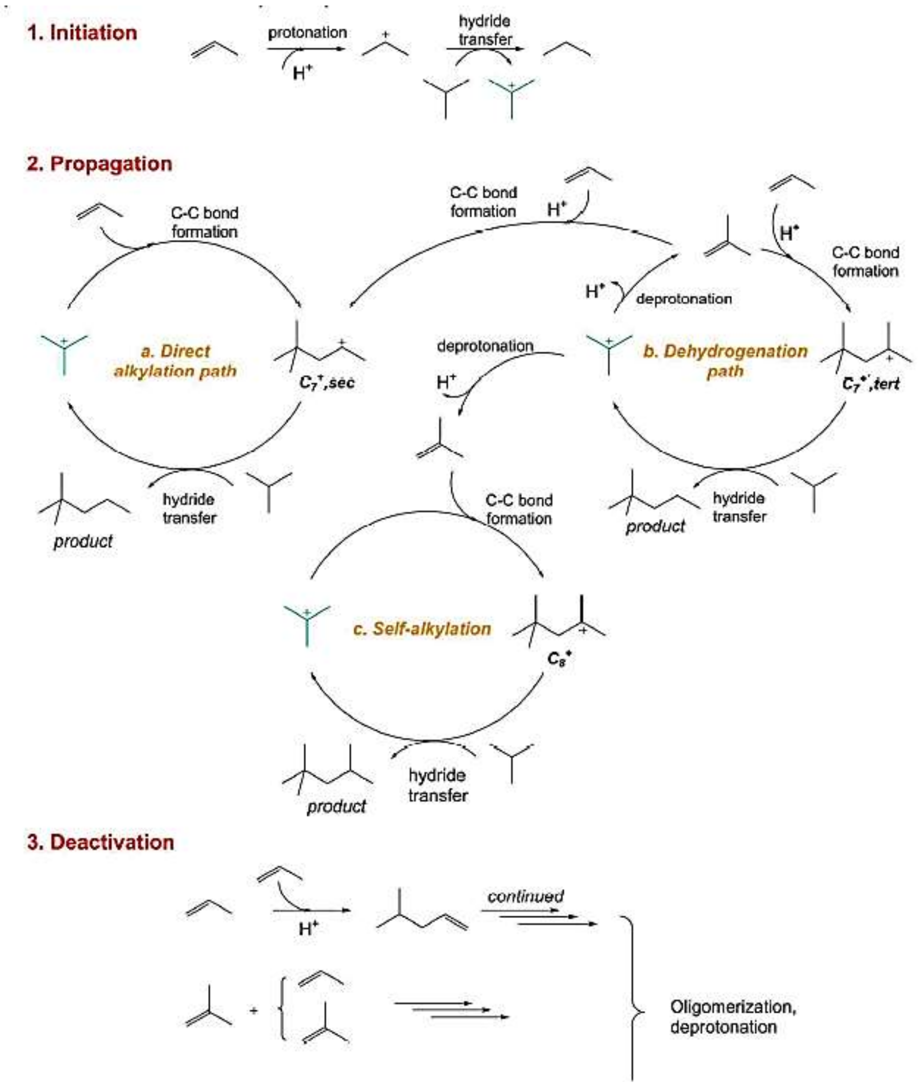


CSTR





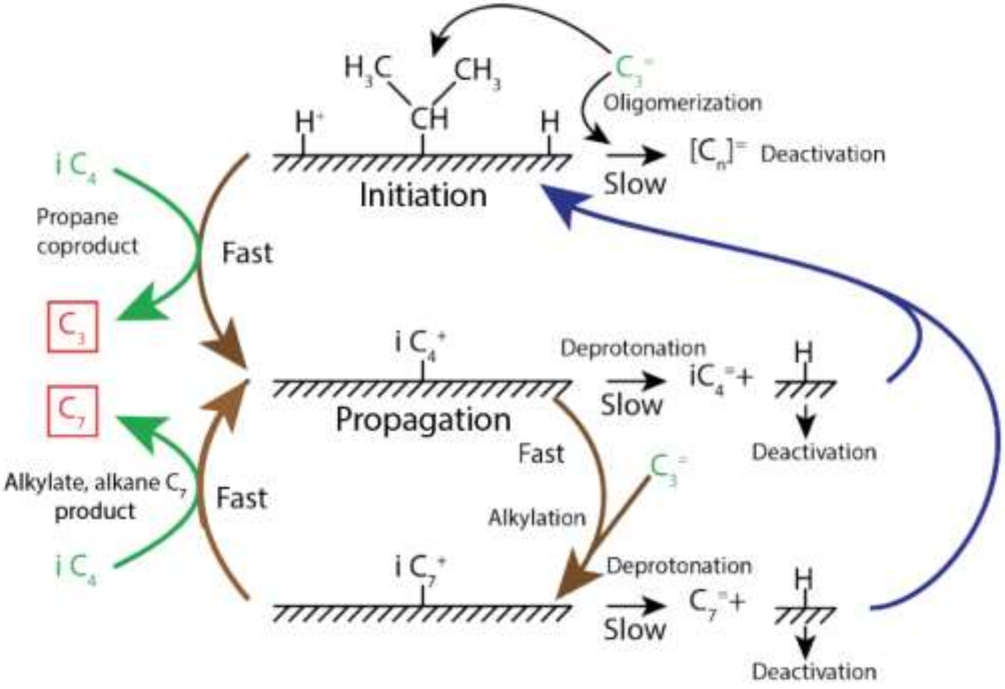
Microkinetic simulations of alkylation reaction



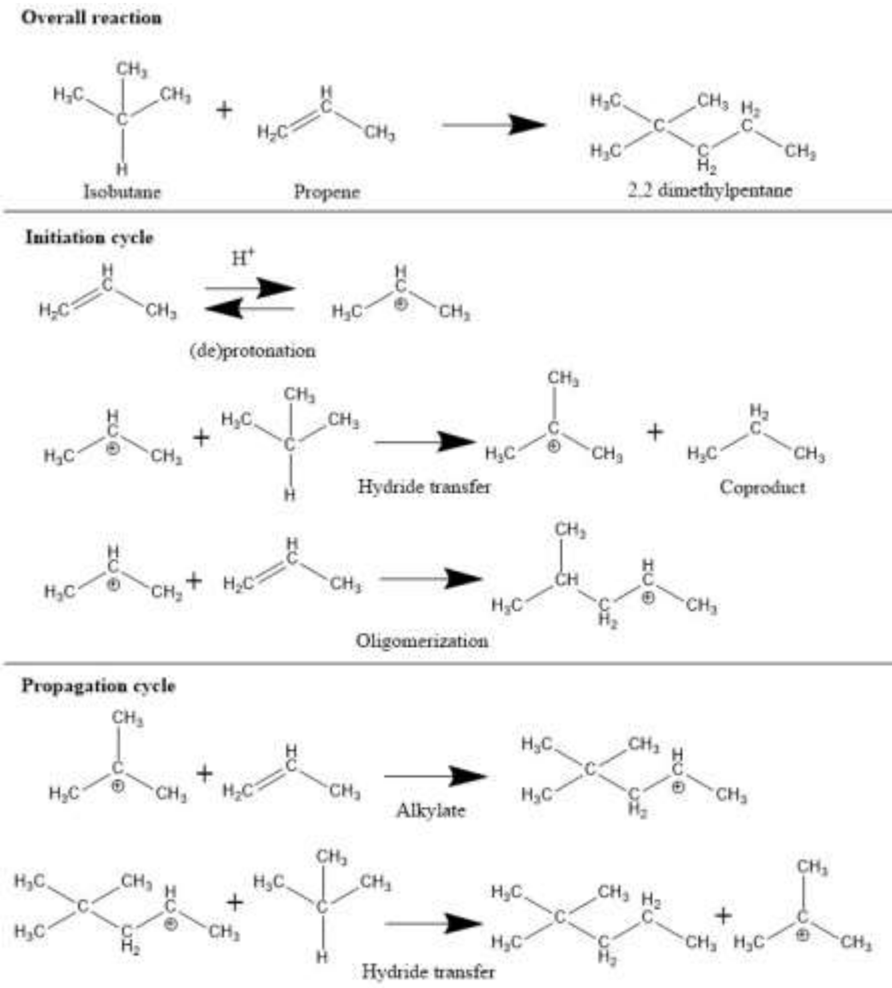
- Reaction mechanism
- Inorganic chemistry, catalytic site, PA
- Elementary reaction rate constants (QM-DFT)
- Adsorption free energies (force field Monte Carlo simulations), confinement

Mechanism of the alkylation reaction

Initiation and propagation reaction cycles



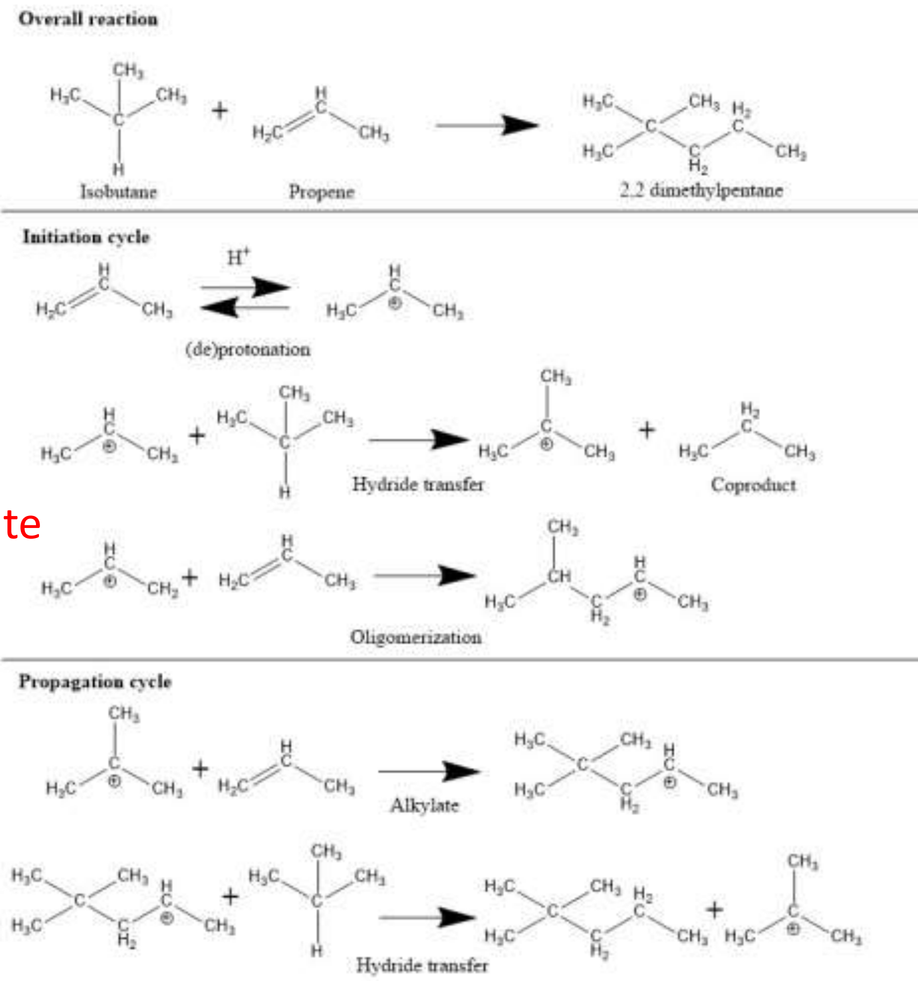
The elementary reactions



Conditions for long catalyst life

Minimize alkene concentration. Cause of rapid deactivation

Hydride transfer reaction rate has to be fast compared to carbenium ion deprotonation and propylene addition rates



Zeolite descriptor demands:

- Since hydride transfer reaction is bimolecular **wide pores** (larger than 10 ring channel) are required
- Slow deprotonation and high hydride transfer rate requires protons with **high PA**
- Long deactivation time requires **high proton concentration**

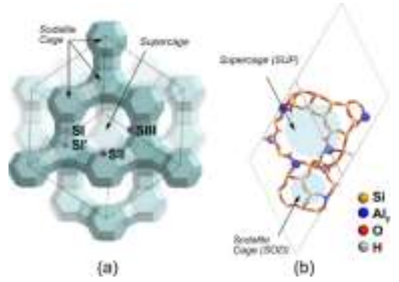
Reaction condition demands

Minimize propylene concentration.

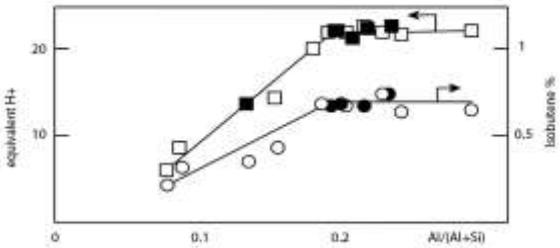
- High isobutane /propylene ratio
- Integral reaction condition: 100% propylene conversion

Inorganic chemistry: conflicting composition requirements
(high proton density versus high proton affinity)

- Good news: wide pore (12 ring diameter) zeolite FAU has high Al/Si lattice composition (high proton concentration)

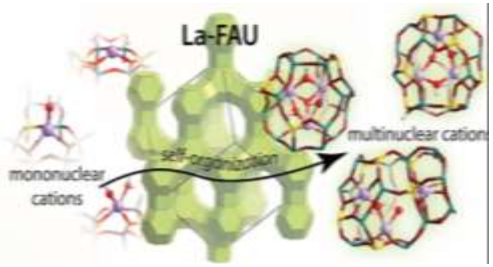


- Bad news :When Al/Si compositions exceeds 10%, PA strongly decreases. Interacting protons deactivate each other



Bartomeuf 1988

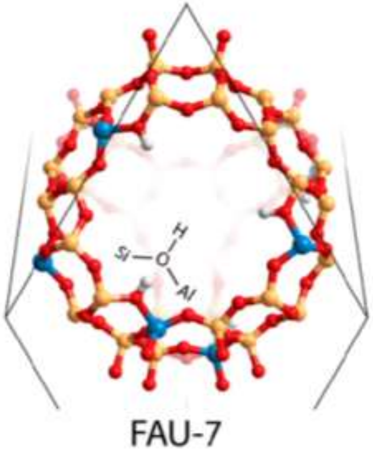
- Promotion :exchange of protons with (rare)earth alkali cations as La^{3+} promotes PA, and high proton density can be maintained



F.Schüßler 2011

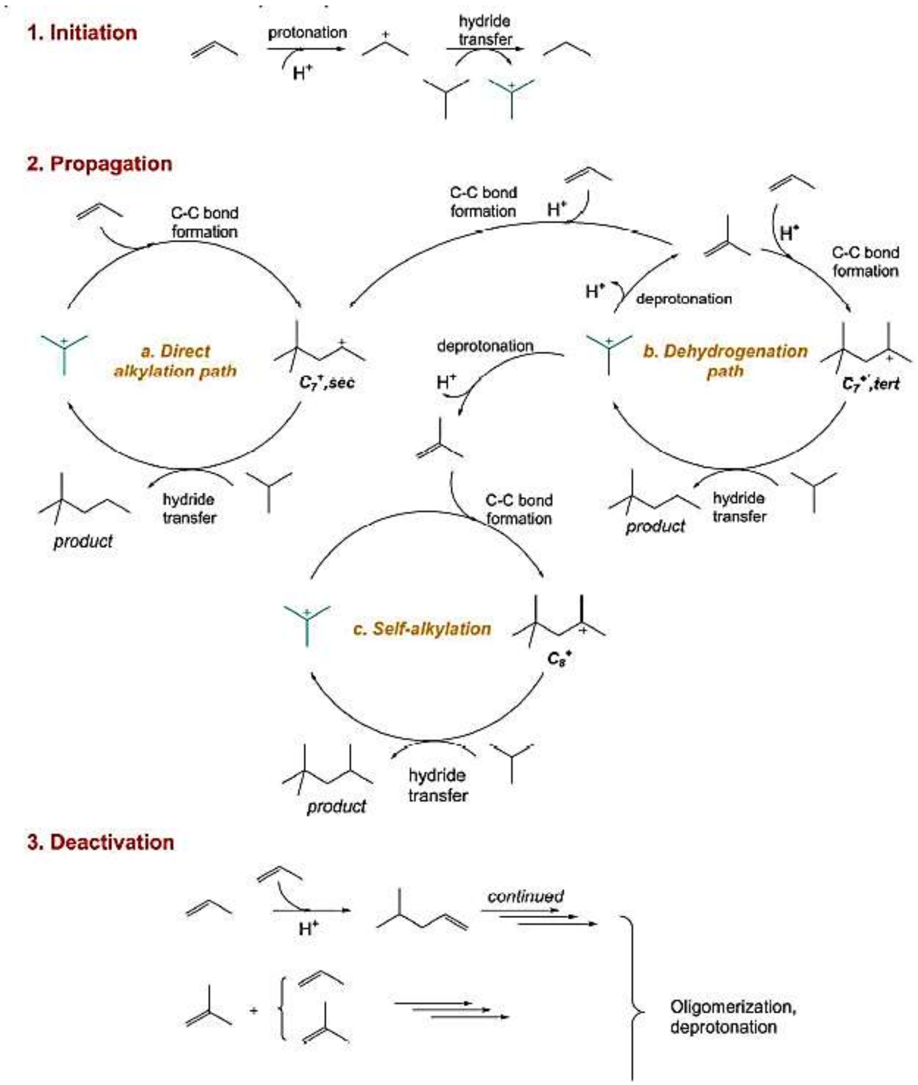
Calculated adsorption energies of NH_3 probe molecule are measure of proton affinity and can de compared with experiment

Zeolite model(Al/Si)	**NH_3 adsorption energies**
	ΔE_{ads}
Fau-0.02	-142
Fau-0.14	-125
FAU-0.4	-104
FAU-0.4, La	-156



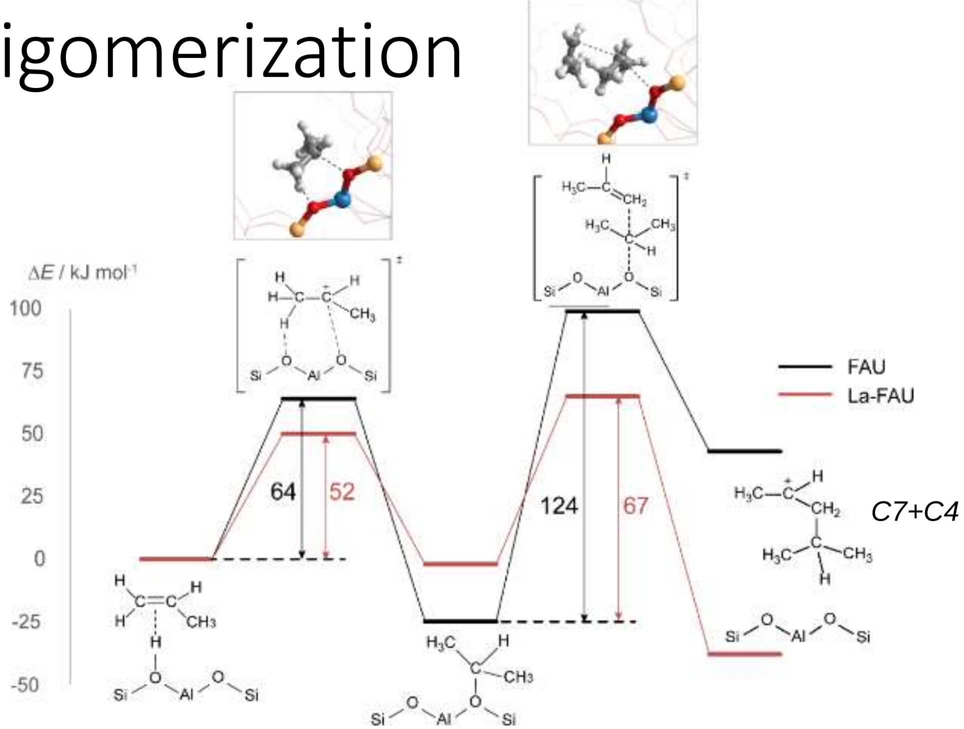
- Proton affinity(ammonia adsorption energy) decreases with increase of Al/Si framework ratio (proton concentration increases)
- Proton affinity increases with La^{3+} substitution

Microkinetic simulations of alkylation reaction

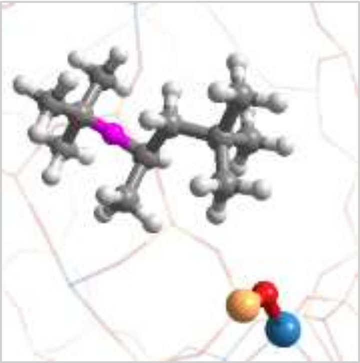


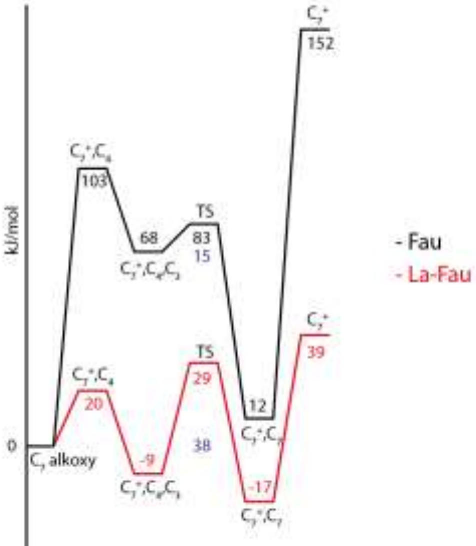
- Reaction mechanism
- Inorganic chemistry, catalytic site, PA
- Elementary reaction rate constants (QM-DFT) as a function of PA
- Adsorption free energies from force field Monte Carlo simulations
- Microkinetics simulations

High proton affinity increases rate of hydride transfer versus oligomerization



- Oligomerization
  - Tight transition state
  - Partial proton transfer
- Hydride transfer
  - Loose transition state
  - Complete proton transfer



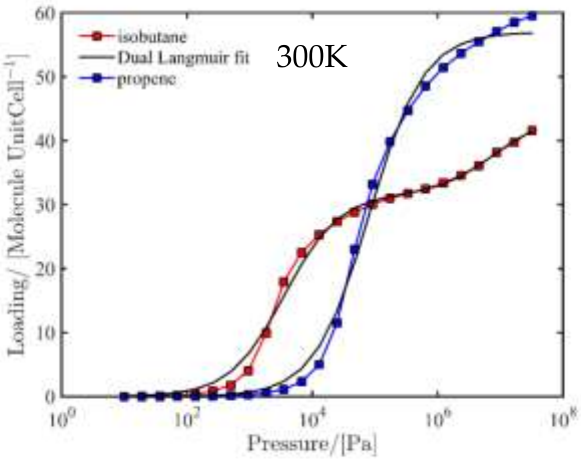


Transition State Theory

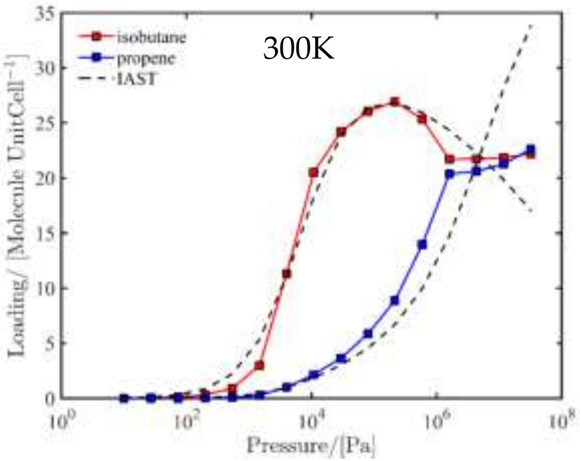
$$k_r = \frac{kT}{h}\frac{(p.f.)^{\#}}{(p.f.)_0}e^{-\frac{E_b-E_0}{kT}}$$

$$p.f. = \prod_i \frac{e^{-\frac{1}{2}\frac{h\nu_i}{kT}}}{1-e^{\frac{-h\nu_i}{kT}}}$$

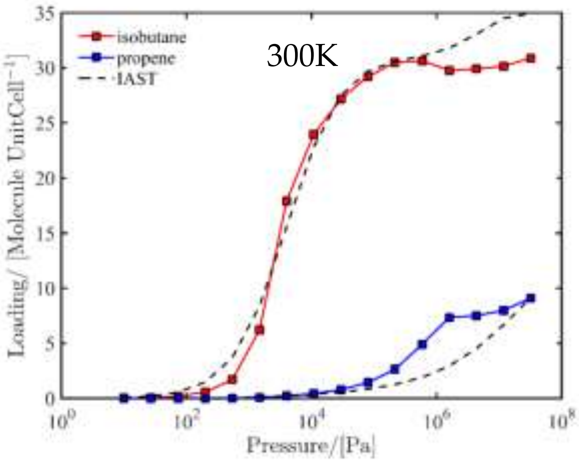
CB-Monte Carlo calculated adsorption isotherms of iso-butane and propene mixtures in FAU(force field derived from hexane in MFI)



CBMC Single component



CBMC Mixture C4/C3 =1



CBMC Mixture C4/C3=7

In zeolite: Isobutane suppresses coadsorption of propylene. This desirable effect, due to competitive adsorption, is largest in narrow pore zeolites.

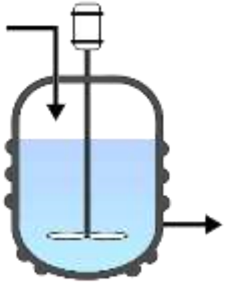
The microkinetic equations

CSTR:

$$\frac{dC_i}{dt} = \phi(-C_i + C_{inflow}) + R_i''(C_1, C_2 \dots . C_k, \dots \theta_{C7+}, \theta_{iC4+} \dots)$$

$$\frac{d\theta_i}{dt} = R_i'(C_1, C_2 \dots . C_k, \dots \theta_{C7+}, \theta_{iC4+} \dots)$$

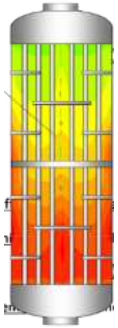
$$\frac{d[X]}{dt} = [S].[v] \qquad [S] = \begin{bmatrix} S'' & S''' \\ S' & 0 \end{bmatrix} \qquad [v] = \begin{bmatrix} v' \\ v'' \end{bmatrix}$$



PFR:

$$\frac{\partial C_i}{\partial t} + v.\frac{\partial C_i}{\partial z} = R_i''(C_1, C_2 \dots . C_k, \dots \theta_{C7+}, \theta_{iC4+} \dots)$$

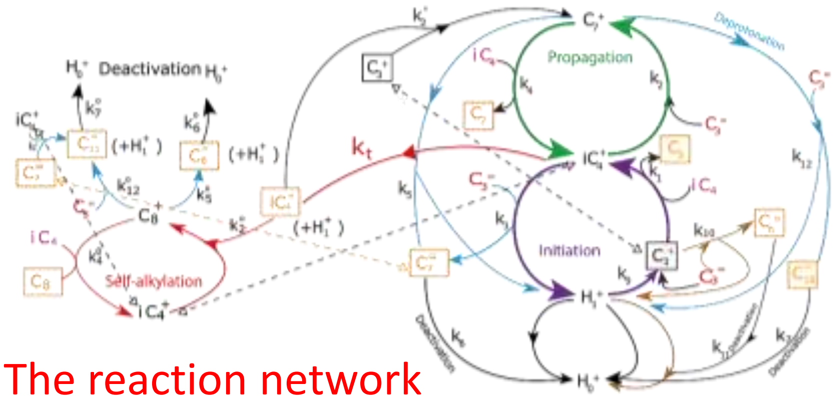
$$\frac{\partial \theta_i}{\partial t} = R_i'(C_1, C_2 \dots . C_k, \dots \theta_{C7+}, \theta_{iC4+} \dots)$$



Flow rates : $\Phi; \frac{v}{L}$

One dimensional, ideal flow (low Reynold number), no mass transfer or heat transfer limitation. Mean field solutions

The microkinetic ODE equations.



The reaction network

X contains reactant and intermediate concentration (**nodes**) They follow from with **v** mass law elementary reaction rates (**connection strengths**). **S** defines network connectivity (**topology**)

Solve matrix equation:

$$\{\dot{X}\} = [S]\{v\}$$

$$X = \begin{pmatrix} \theta_{C7+} \\ \theta_{iC4+} \\ \theta_{H1+} \\ \theta_{H0+} \\ \theta_{C3}+ \\ \theta_{C8}+ \\ [C_{10}^=] \\ [C_7^=] \\ [C_3] \\ [C_7] \\ [C_n^=] \\ [C_3^=] \\ [iC_4] \\ [iC_4^=] \\ [C_8] \\ [C_{11}^=] \\ [C_8^=] \end{pmatrix}$$

$$S = \begin{pmatrix}
0 & 1 & 0 & -1 & -1 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & -1 & -1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & -1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 1 & -1 & -1 & -1 & 1 & -1 & 1 & 1 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
-1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\
0 & -1 & -1 & 0 & 0 & 0 & 0 & -1 & -1 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & -1 & 1 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
-1 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 1 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 & -1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix}$$

v=

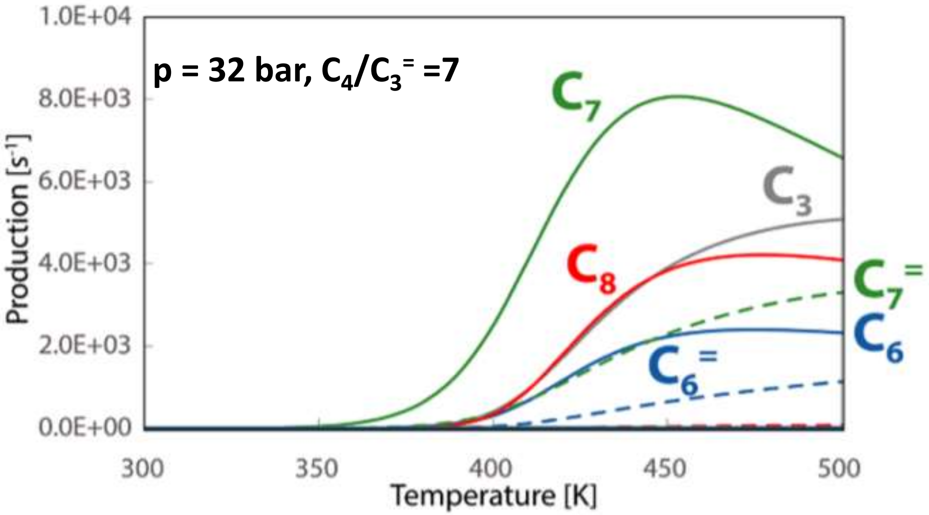
$k_1[iC_4]\theta_{C3+}$	v_1
$k_2[C_3^=]\theta_{iC4+}$	v_2
$k_3[C_3^=]\theta_{iC4+}$	v_3
$k_4[iC_4]\theta_{C7+}$	v_4
$k_5\theta_{C7+}$	v_5
$k_6[C_7^=][C_3^=]\theta_{H1+}$	v_6
$k_7[C_{10}^=][C_3^=]\theta_{H1+}$	v_7
$k_9[C_3^=]\theta_{H1+}$	v_9
$k_{10}[C_3^=]\theta_{C3+}$	v_{10}
$k_{11}[C_n^=][C_3^=]\theta_{H1+}$	v_{11}
$k_{12}[C_3^=]\theta_{C7+}$	v_{12}
$k_t\theta_{iC4+}$	v_t
$k_2^{'}[iC_4^=]\theta_{C3-}$	$v_2^{'}$
$k_2^o[iC_4^=]\theta_{iC4-}$	v_2^o
$k_4^o[C_8^+]\theta_{iC4}$	v_4^o
$k_5^o\theta_{C8+}$	v_5^o
$k_{12}^d[C_3^=]\theta_{C8+}$	v_{12}^o
$k_6^o[C_8^=]\theta_{H1-}$	v_6^o
$k_7^o[C_{11}^=]\theta_{H1+}$	v_7^o
$\phi[C_3^=]^o$	v_{13}
$\phi[iC_4]^o$	v_{14}
$\phi[C_3^=]$	v_{15}
$\phi[iC_4]$	v_{16}
$\phi[C_{10}^=]$	v_{17}
$\phi[C_7^=]$	v_{18}
$\phi[C_3]$	v_{19}
$\phi[C_7]$	v_{20}
$\phi[C_n^=]$	v_{21}
$\phi[iC_4^=]$	v_{22}
$\phi[C_8]$	v_{23}
$\phi[C_{11}^=]$	v_{24}
$\phi[C_8^=]$	v_{25}

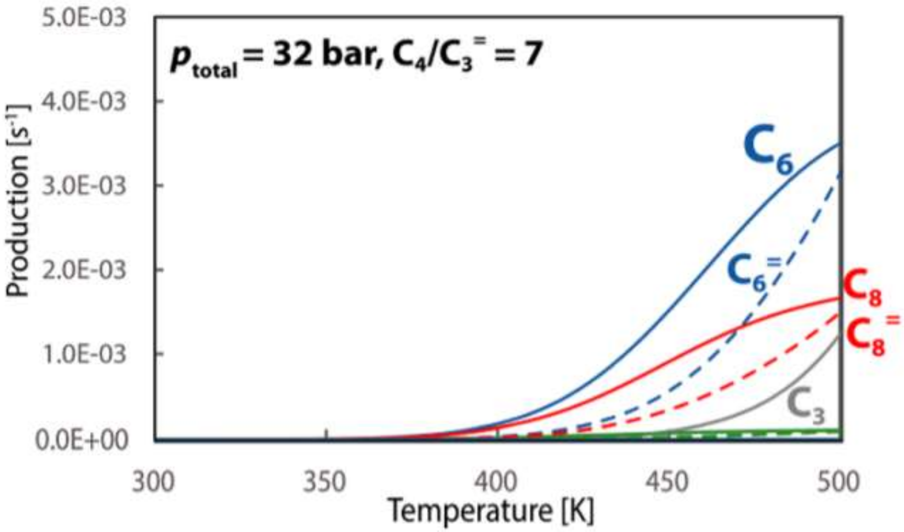
Microkinetics simulations

Steady state product distributions(k_{deact}=0) .Alkane/alkene product ratio measure of deactivation time

La-Fau, high PA

Fau , low PA

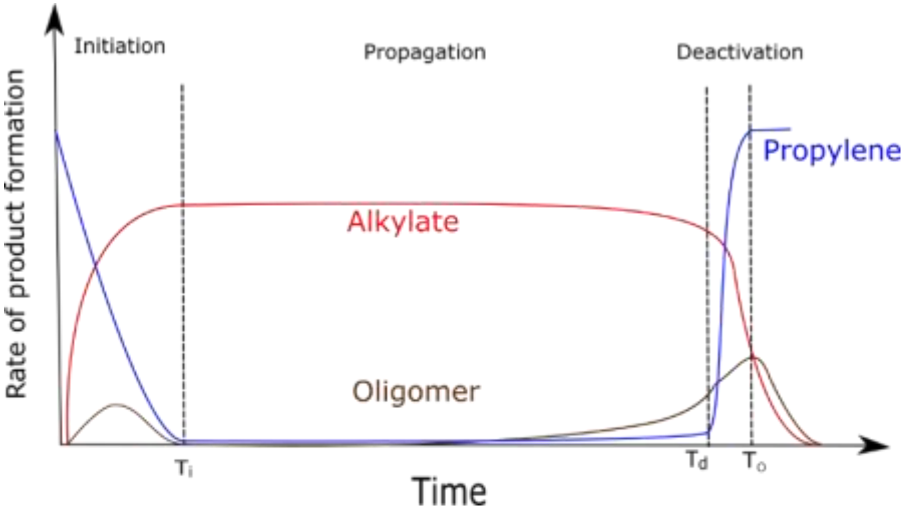


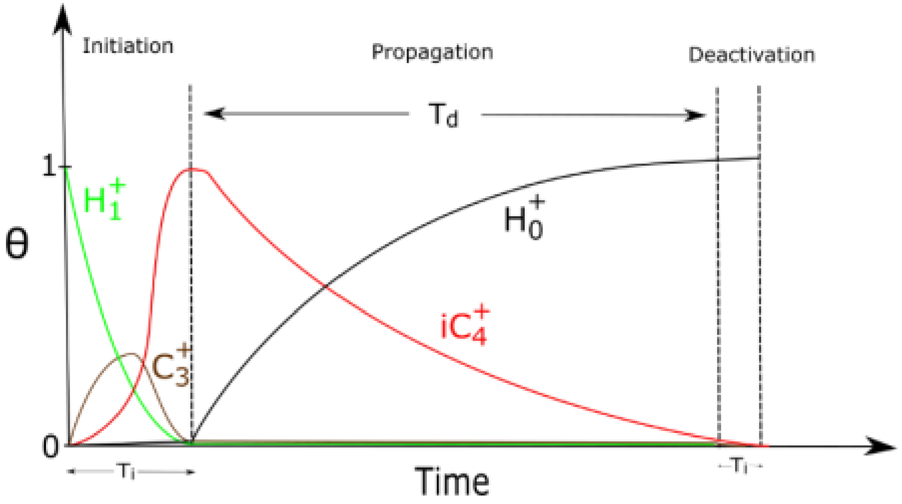


La-Fau: $r_{hydr} \approx r_{C_4^+ + C} >> r_{deprot} > r_{dimer}$

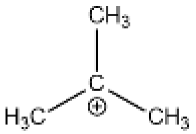
Fau: $r_{dimer} > r_{C_4^+ + C} > r_{hydr} > r_{deprot}$

Time evolution and deactivation of catalyst activity;Three reaction regimes





- High alkylate selectivity as long as 100% conversion of propylene
- In quasi steady state product formation constant but catalyst surface composition not at steady state ;
- One surface intermediate (iC_4^+) dominates in quasi-steady state regime



Question: What is time scale of deactivation?

For this we need coarse graining approach to deduce analytical expressions for deactivation time

Reversible full microkinetics is reduced to unidirectional lumped microkinetics

Transform microkinetics into powerlaw macrokinetic equations by coarse graining

$$[\dot{X}] = [S][\nu] \rightarrow -\frac{d[C_3^=]}{dt} = \phi\left(C_{3,0}^= - C_3^=\right) - \kappa_1\sigma[C_3^=][iC_4] - \kappa_1\xi_m\sigma[C_3^=]^2$$

Micro

Macro

Alkylate formation

Oligomer formation

Additional equations for reaction products

Reactant and product equations are solved using steady state approximation

Time dependence follows from slow time evolution equation of surface site $\sigma(t)$

$$-\frac{d\sigma(t)}{dt} = F([C_3^=]).\left[k_d[C_n^=] + k_d'[C_7^=] + k_d''[C_{11}^=]\right]\sigma$$

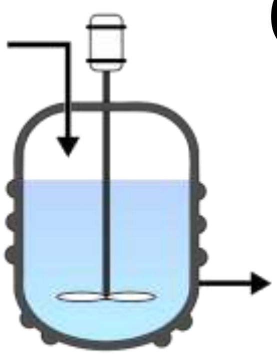
$$F = \frac{1}{k_9}\left(\frac{k_t}{[C_3^=]} + (\chi k_t + \kappa_2) + \chi\kappa_2.([C_3^=])\right)$$

Reaction site is not free site but occupied by iC4+ :$\sigma(t) = \sigma_i\theta_{iC_4^+}(t)$

Coarse graining exploits dominance of one reaction intermediate (iC_4^+)

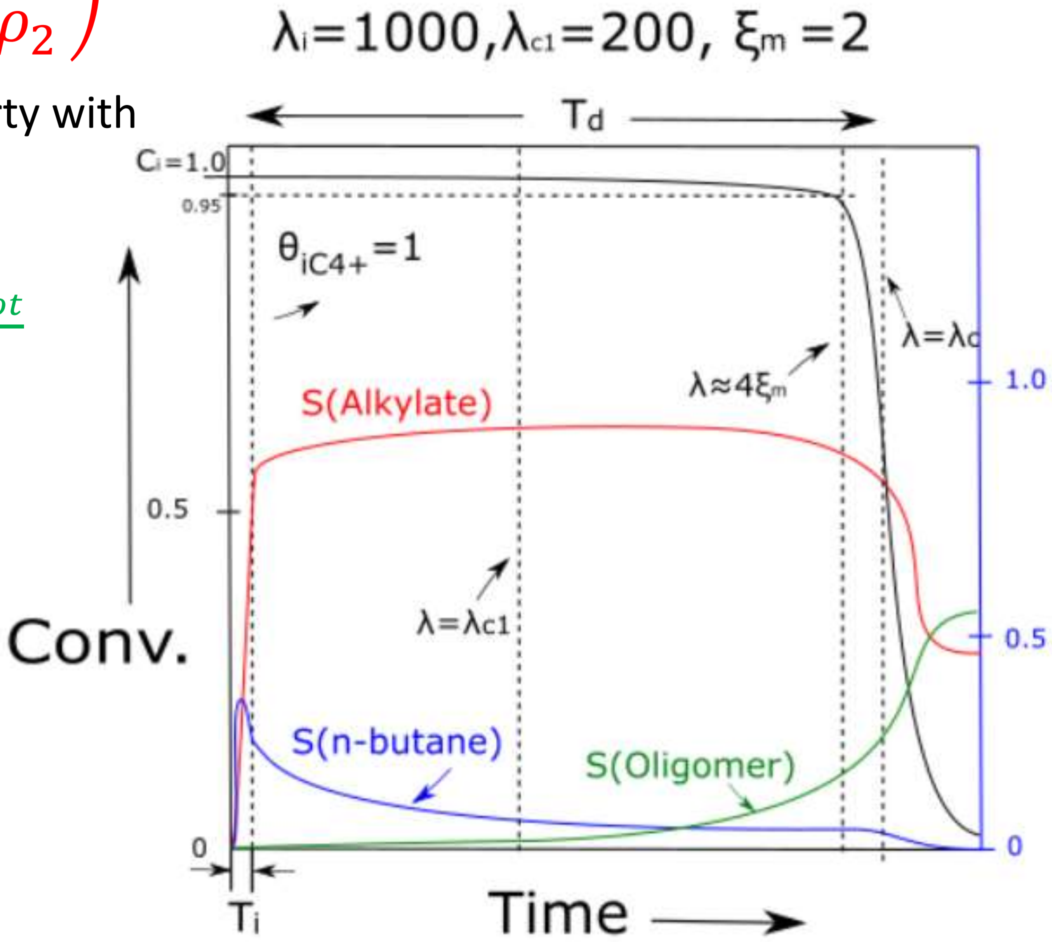
No explicit dependence on reaction intermediates.

Catalyst deactivation theory



$$T_d \approx \frac{1}{K_d}\left(1 + \ln\frac{\lambda_{in}}{\rho_2}\right)$$

Relates material property with reaction rate function



Long life:

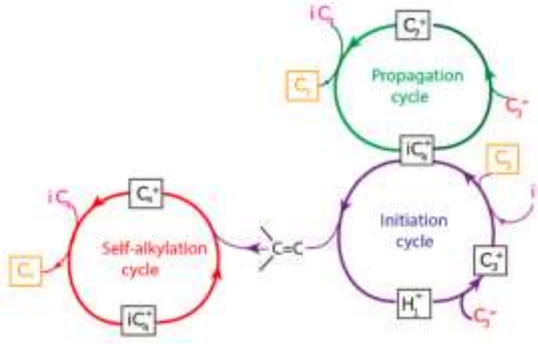
$$\textit{Proton density } \sigma_{in} \gg \frac{k_{olig}}{k_{hyd}}\frac{k_{deprot}}{k_{alk}}$$

$$\textit{Long } K_d^{-1}\text{:}\quad a\,\frac{k_{alk}}{k_{deprot}} \gg 1$$

$$b\ high\,\frac{iC_{4,0}}{C_{3,0}^{=}}$$

$$\textit{Self alkylation } (C_8)\text{ :}$$

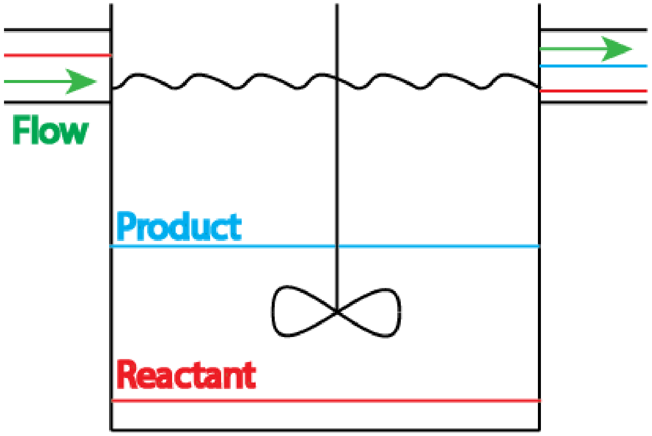
$$\textit{Proton density } \sigma_{in} > \frac{k_{deprot}}{k_{self}}$$



$$\text{Time scale } \approx \frac{1}{K_d} = \frac{k_9}{k_6}\frac{\kappa_1}{\kappa_2^2}\frac{1}{x_o V_b [iC_4]} \approx 25000\text{s; Dimensionless parameters:}$$

$$\lambda = \kappa_1\frac{\sigma}{\phi} \approx \text{reaction site density } \sigma;\ \xi_m = 2\chi x_0\frac{\kappa_2}{\kappa_1};\ \chi = \frac{k_{10}}{k_1}$$

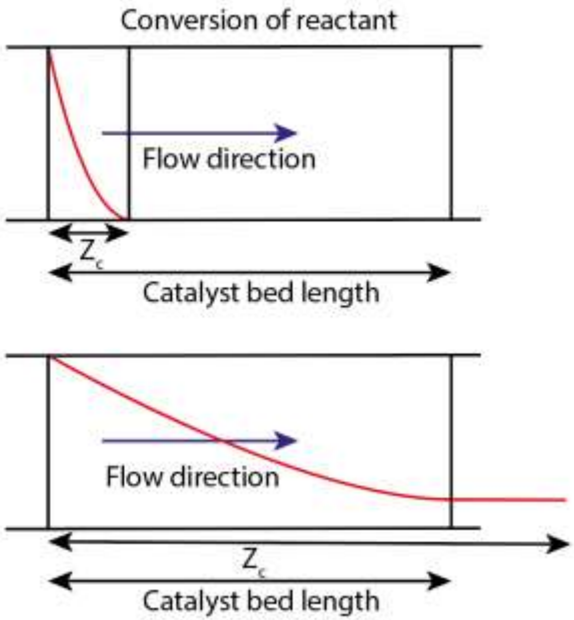
PFR versus CSTR - Essentials



Continuous stirred-tank reactor

CSTR uniform concentration profiles

- Concentration equal to outlet concentration



PFR concentration gradient

a) High conversion

-Reaction zone smaller than catalyst bed length

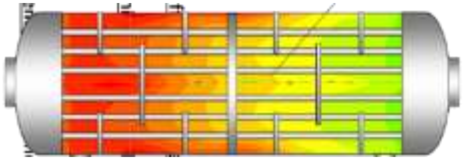
$$Z_c < L$$

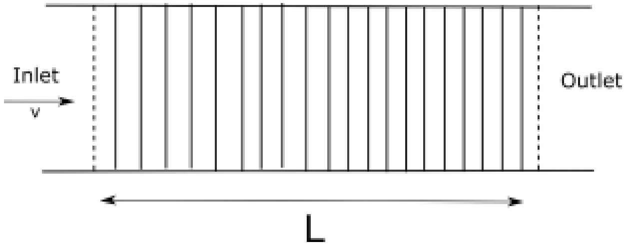
b) Low conversion

-Reaction zone larger than catalyst bed length

$$Z_c > L$$

PFR simulations





Plugflow reactor is simulated as a series of **n** continuous stirred tank reactors

The reaction zone

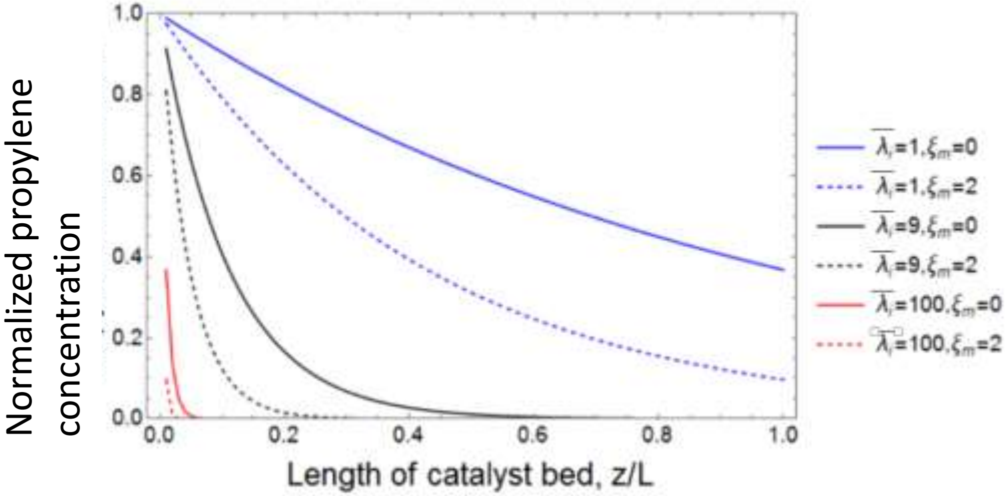
$$\frac{z_c}{L} < 1: \quad \sigma_i > L\frac{v}{k_{alk}}$$

Reaction zone less than reactor length proton concentration large compared to reactor catalyst bed length and reaction time.

Also average propylene concentration invariant

$$\left\langle \frac{C_3^{=}}{C_3^{=}(0)} \right\rangle_{avg} = \frac{1}{3}$$

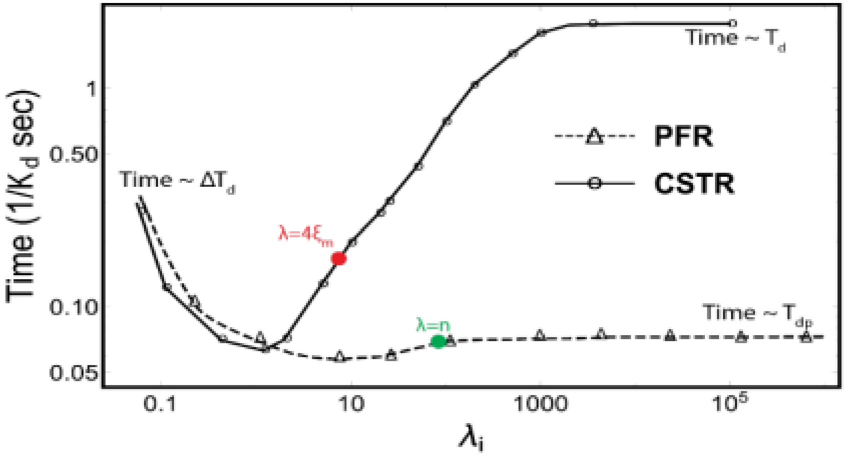
Deactivation time will not vary with site density as long as: $\bar{\lambda}_i > n$



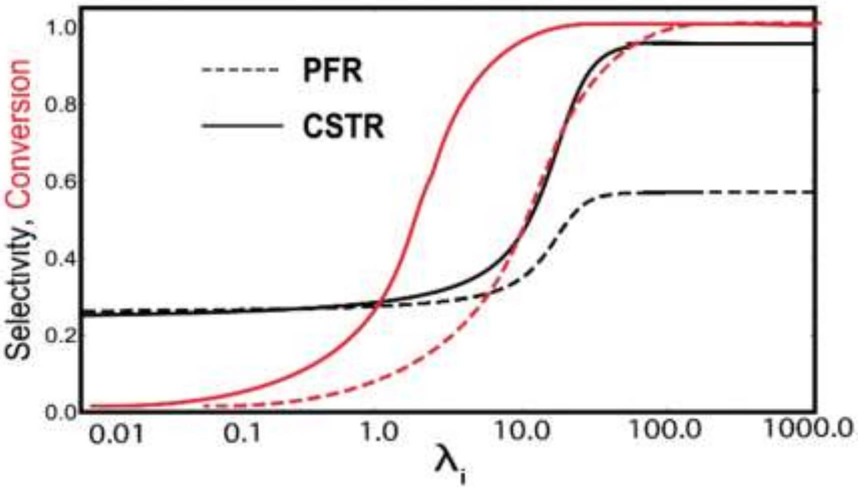
$\bar{\lambda}_i$ is the dimensionless reaction site density

Comparison CSTR and PFR

Difference PFR –CSTR increases with increase reaction sites

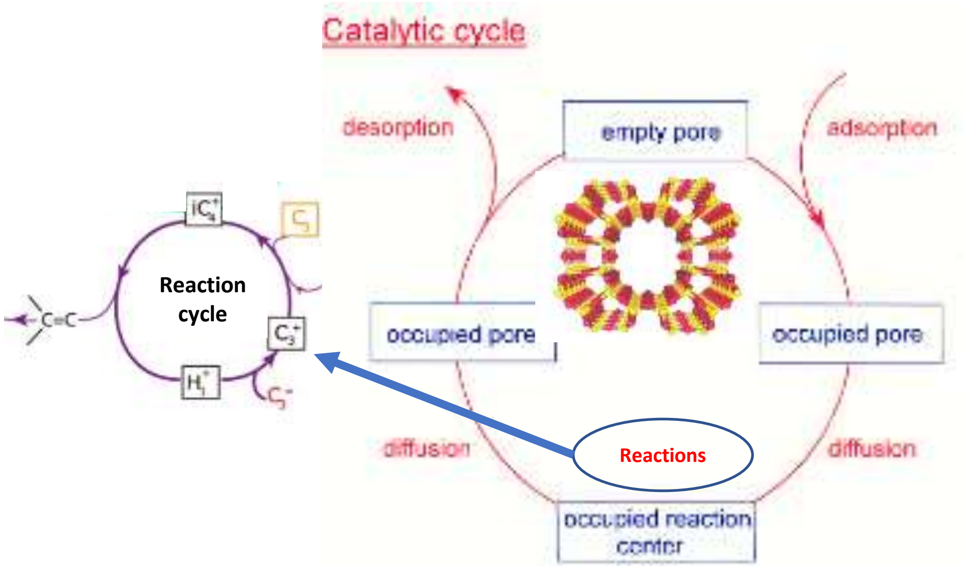


Conversion and selectivity in CSTR and PFR

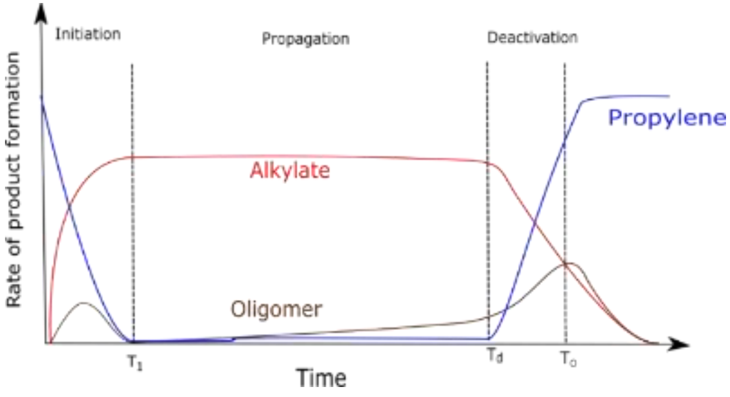


Complexity of zeolite catalysis modelling

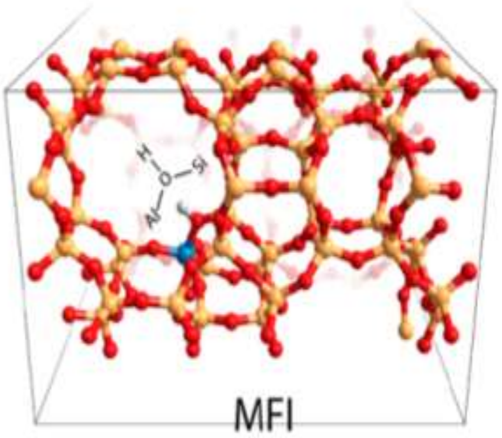
Chemistry of reactants



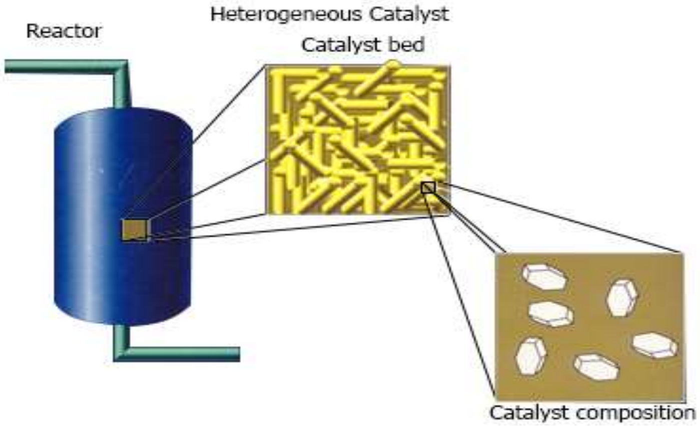
Time evolution of reaction



Chemistry of the solid



Multiscale event in time and space



The four stages of catalyst modelling

- Establish (postulate) reaction network
  - Physical organic/inorganic chemistry
  - Mechanism of reaction

- Calculate the elementary reaction rate constants
  - Adsorption free energy
  - Activation reaction free energy
  - Diffusion rate

- Formulate micro kinetics equations
  - Stochastic simulation (KMC)
    - Intermediate surface reaction intermediate, pattern formation
  - Mean field equations

- Deduce macroscopic kinetic equations
  - Eliminate the reaction intermediates
  - MARI assumption

Summary and conclusions

Major challenges and successes of computational catalytic kinetics

-Simulations provide tools to resolve conflicting material requirements with respect to optimum catalytic functionality.

-A priori prediction and generation of reaction mechanism not yet possible without experimental input (will AI help?)

-Once mechanism is established microkinetics tools and statistical mechanical techniques are available that relate proposed catalyst structure and composition with catalyst performance. There is a need for improved quantitative accuracy of free energies to make kinetics truely predictive (1kJ/mol)

-Current methods discriminate between conflicting mechanistic proposals (QM-DFT elementary reaction rate comparison)

-Issue: Catalyst surface state changes by reaction. This is a self reference problem.

This surface reconstruction problem due to self reference between surface reactivity and surface state change is intrinsically a feedback optimization problem in System Dynamics. To properly model this is still largely an unresolved problem .

Acknowledgements

C. Liu	Michigan University
A. Sengar	Imperial College London
J. Kuipers	Technical University Eindhoven
E. Hensen	Technical University Eindhoven
E. Pidko	Technical University Delft
T. Vlugt	Technical University Delft
J. Padding	Technical University Delft

-Chong Liu, Rutger A. van Santen, Ali Poursaeidesfahani, Thijs J. H. Vlugt, Evgeny A Pidko, and Emiel J. M. Hensen, ACS Catal. 2017, 7, 8613−8627.

-Chong Liu, Ionut Tranca, Rutger A. van Santen, Emiel J. M. Hensen, and Evgeny A. Pidko, J. Phys. Chem. C 2017, 121, 23520-23530

-Aditya Sengar, Rutger A. van Santen, Erik Steur, Johannes A. M. Kuipers, and Johan Padding , ACS Catal. 2018, 8, 9016−9033

-Aditya Sengar, Rutger A. van Santen, and Johannes A.M. Kuipers, ACS Catal. 2020, 10, 6988−7006