Towards a Nano Technology “process-simulator”

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and

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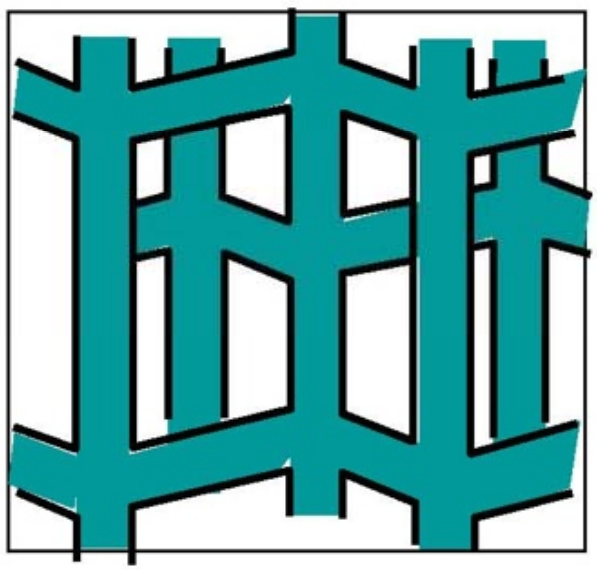
Outline

- Prehistoric nano-materials: an example of computational process design
- Scientific Case study: The Helios Simulator

materials: zeolites

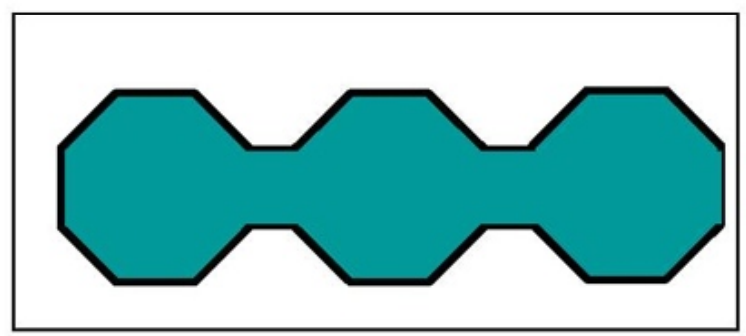
know zeolite structures

00,000 hypothetical structures

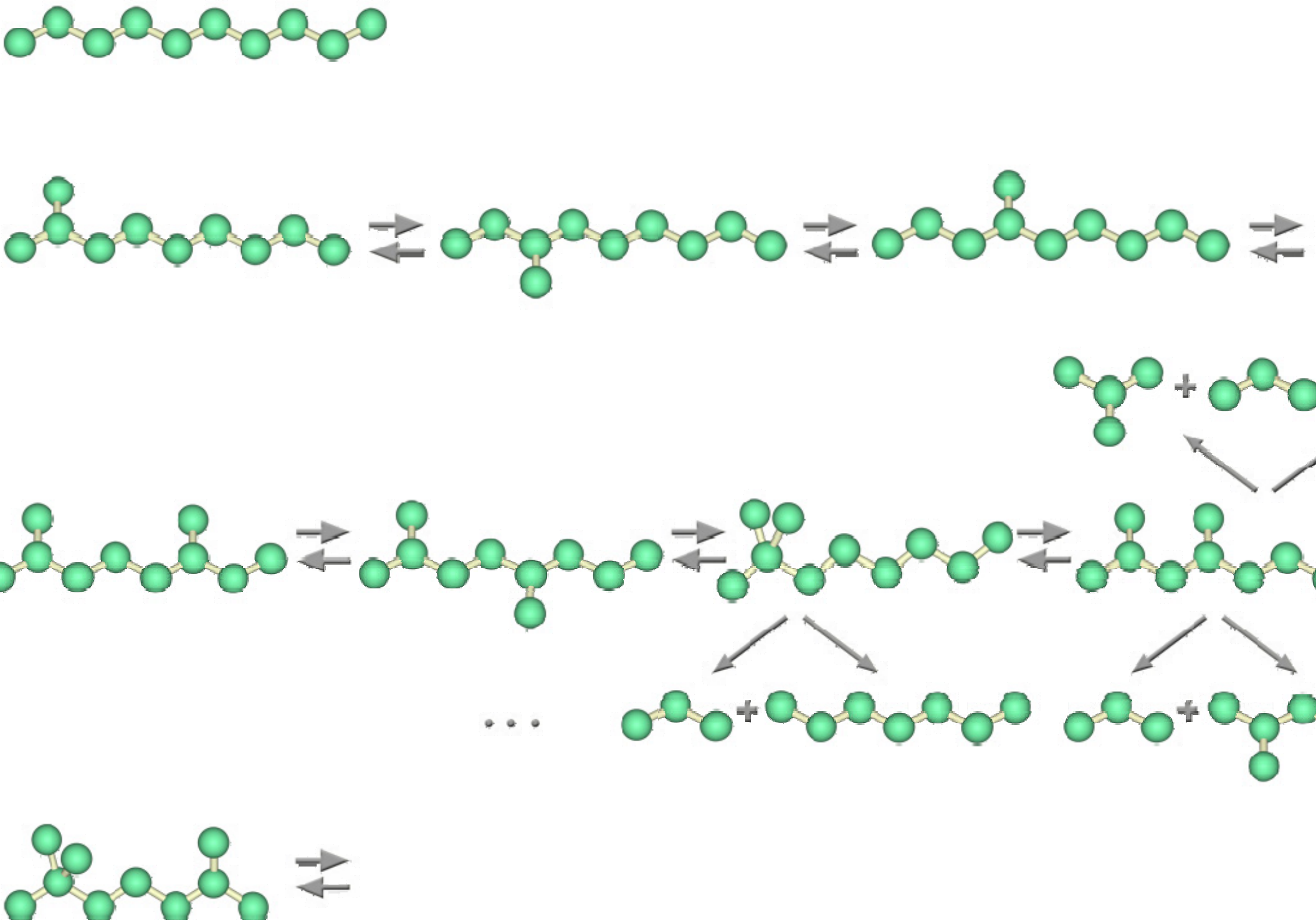


3 dimensional pore network:
MFI, MEL

1 dimensional pores:
MOR, AFI, AET, TON



Chemistry: methyl shifts and cracking



Product distribution

dsorption: reactants have to adsorb

iffusion: reactants have to diffuse to the ctive site

hemical Reaction: conversion at the activ te

iffusion: products have to diffuse away om the active site

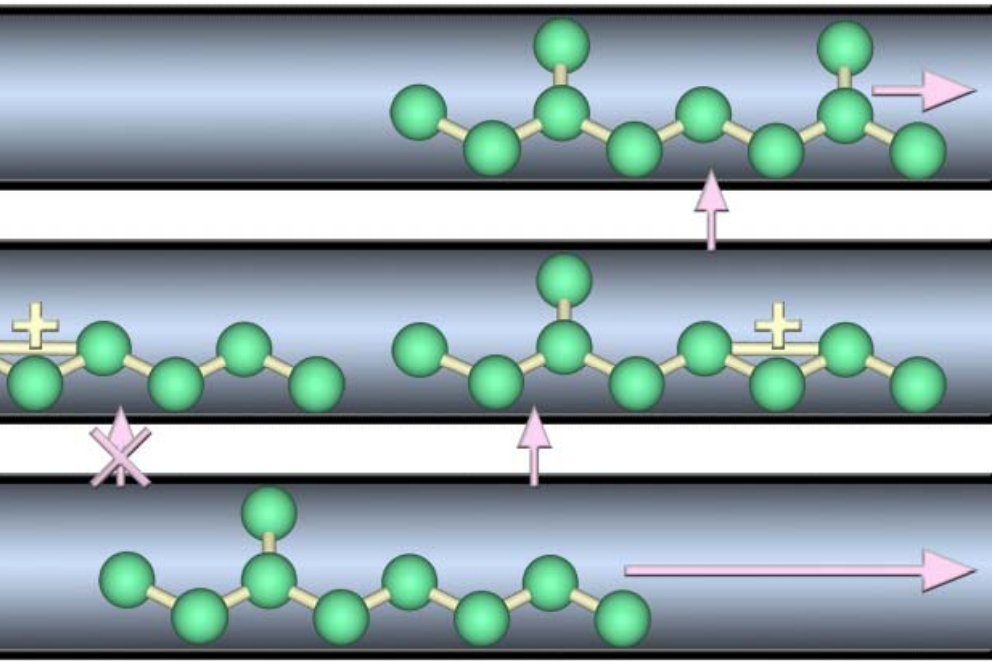
esorption: of the products

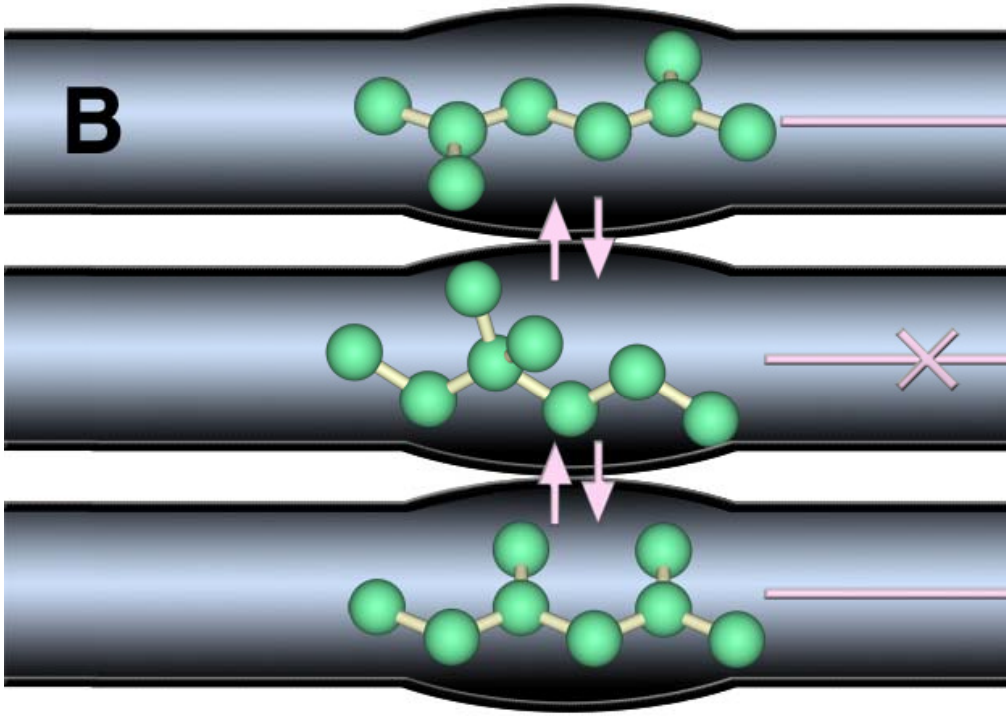
aditional: molecule too big to form in the pores w
ot be a product

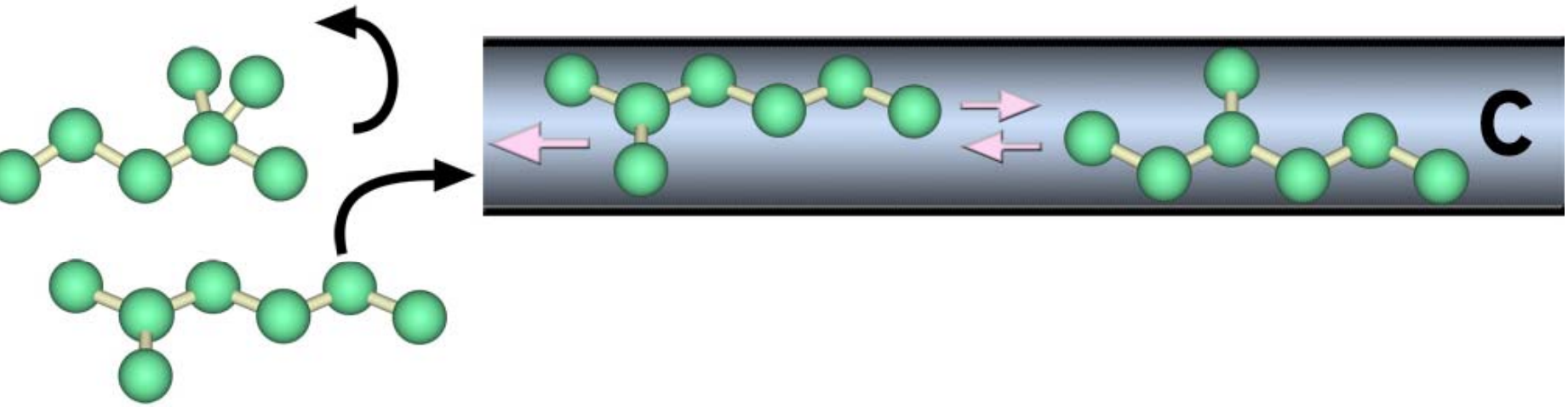
on-traditional (every zeolite its own mechanism)
Inverse shape selectivity
Diffusion selectivity (Window effect)
Reactant selectivity
Pore mouth catalysis
....

ery limited knowledge on *diffusion* and
ermodynamics in the zeolite

Forms of Shape Selectivity







Alkane-zeolite model

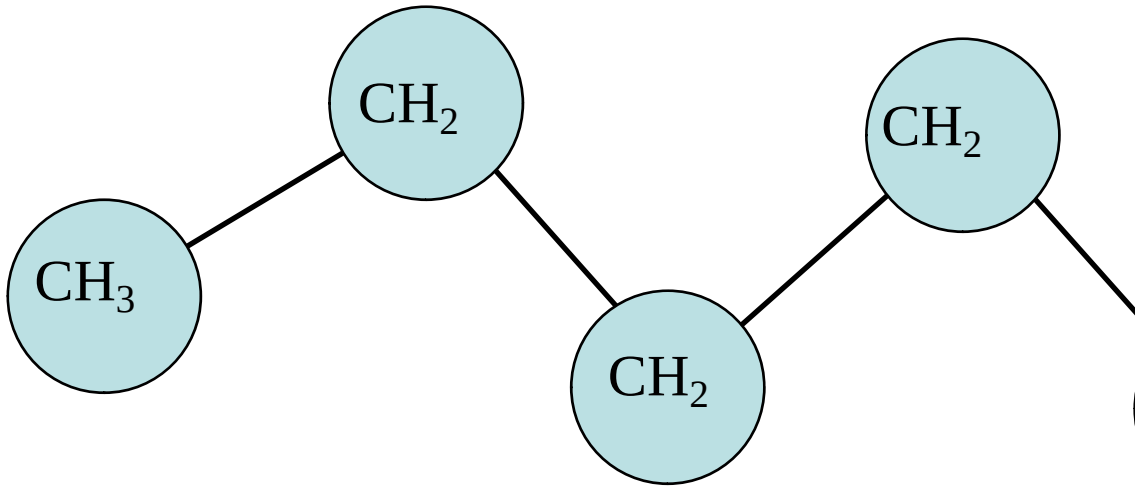
ited atom model

lkane-alkane:

- Fixed bond length
- Bond-bending
- Torsion
- Non-bonded: Lennard-Jones

lkane-zeolite

- Rigid zeolite structure
- Lennard-Jones interactions



Nature 1993, 3

arameters:

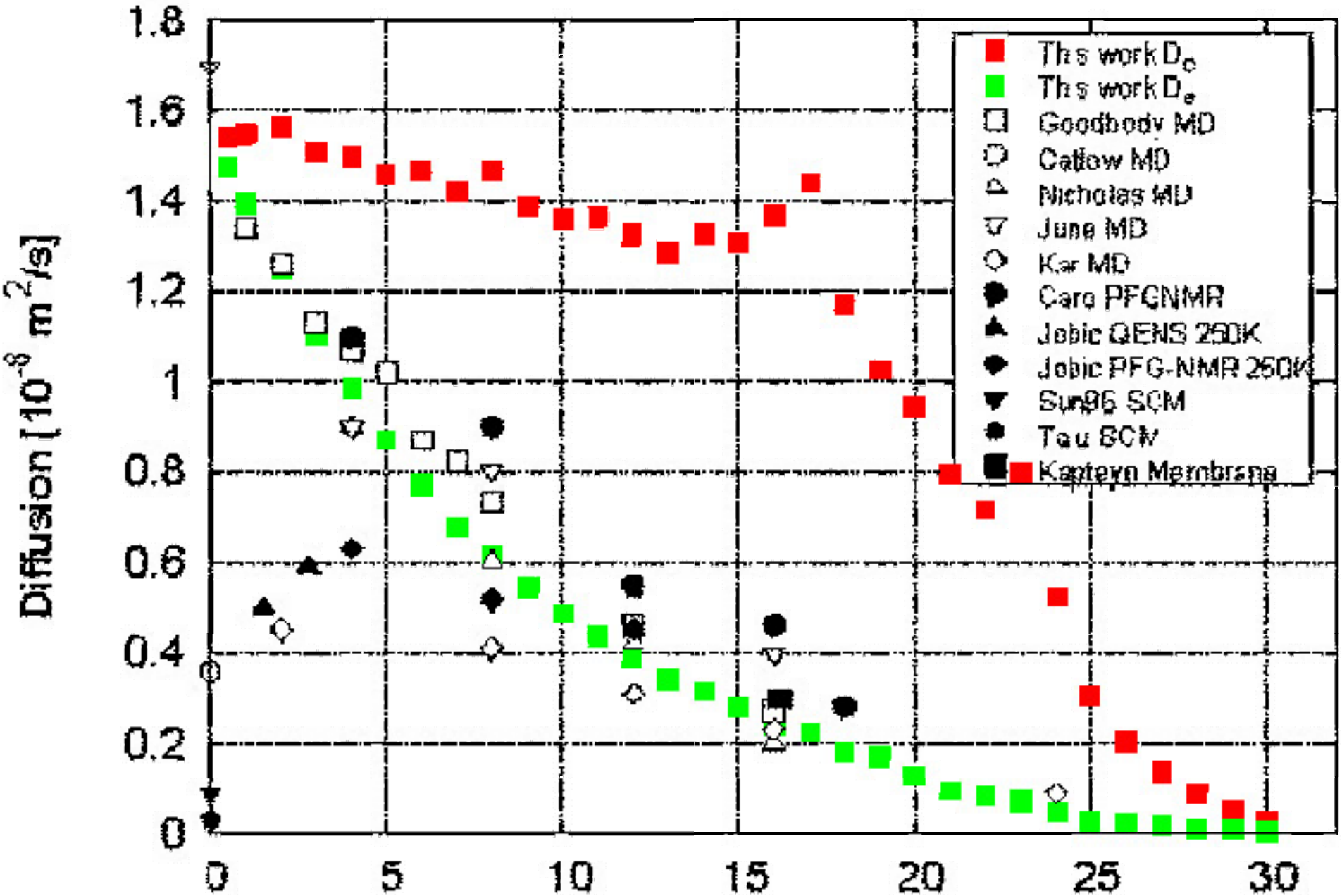
Alkane-alkane:

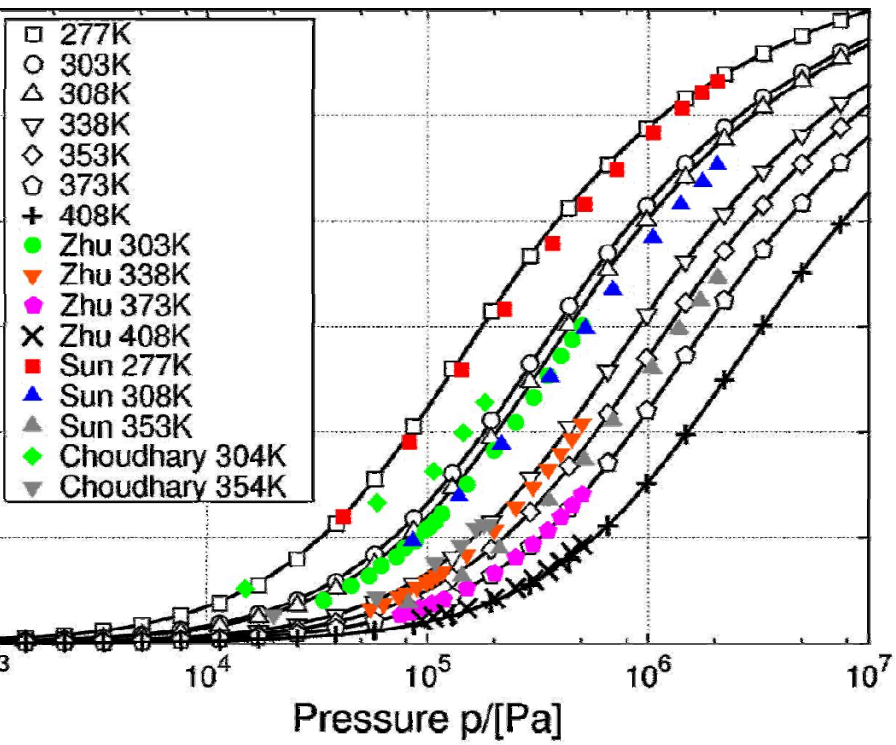
- fitted to vapor-liquid equilibria

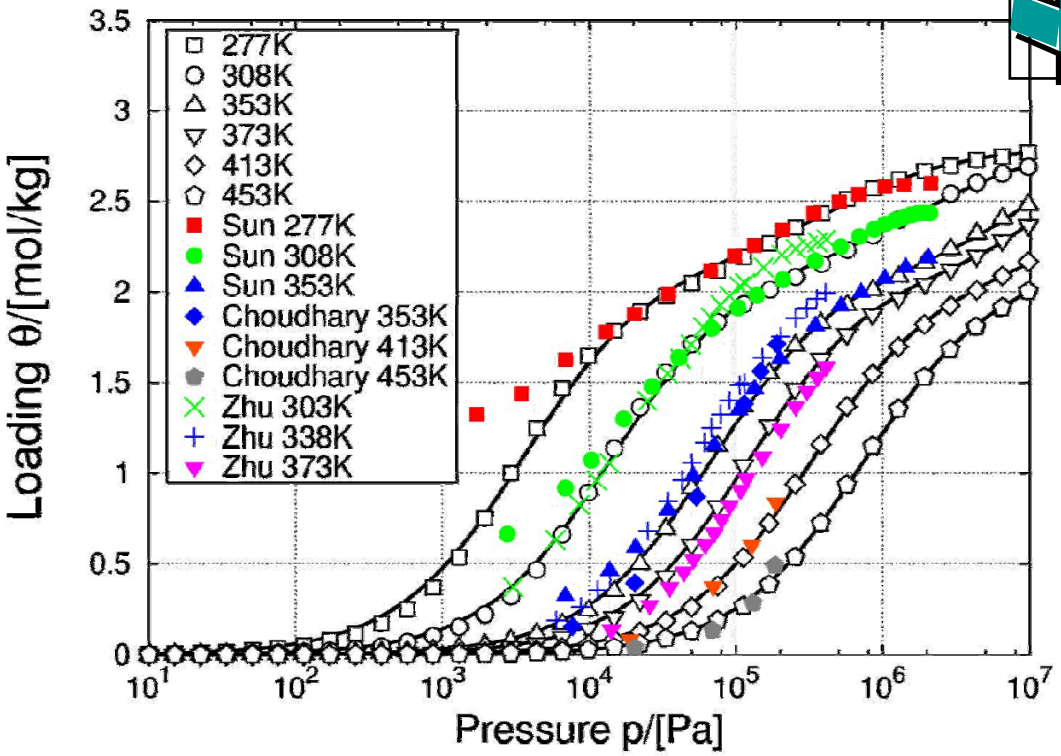
Alkane-zeolite:

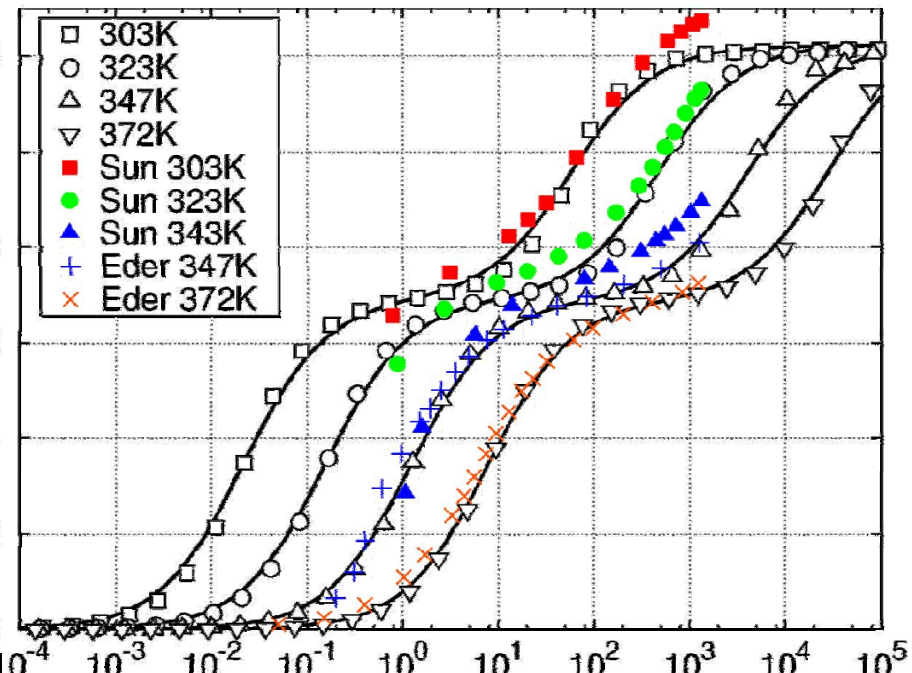
- fitted to heat of adsorption and Henry coefficients (at zero loading)

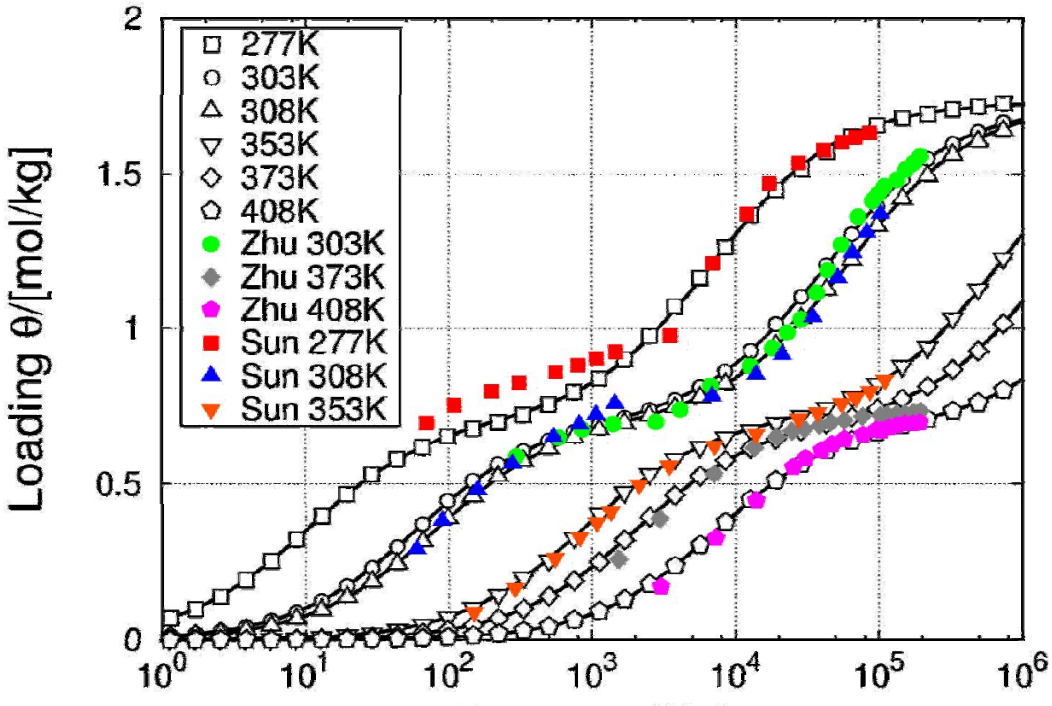
Methane in MFI (silicalite)




277K
303K
308K
338K
353K
373K
408K
Zhu 303K
Zhu 338K
Zhu 373K
Zhu 408K
Sun 277K
Sun 308K
Sun 353K
Choudhary 304K
Choudhary 354K
Pressure p/[Pa]


277K
308K
353K
373K
413K
453K
Sun 277K
Sun 308K
Sun 353K
Choudhary 353K
Choudhary 413K
Choudhary 453K
Zhu 303K
Zhu 338K
Zhu 373K
Loading θ/[mol/kg]
Pressure p/[Pa]


303K
323K
347K
372K
Sun 303K
Sun 323K
Sun 343K
Eder 347K
Eder 372K


277K
303K
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Zhu 303K
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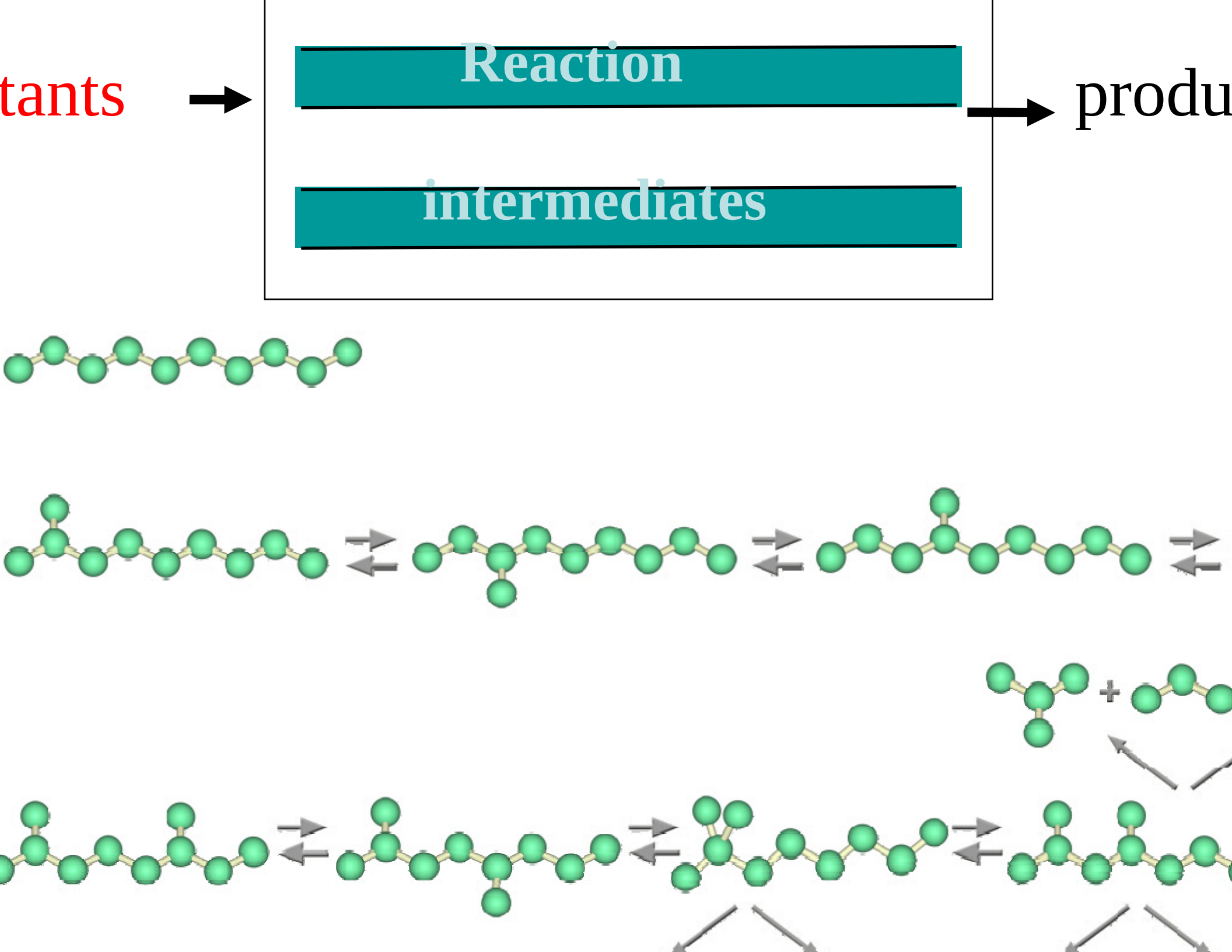
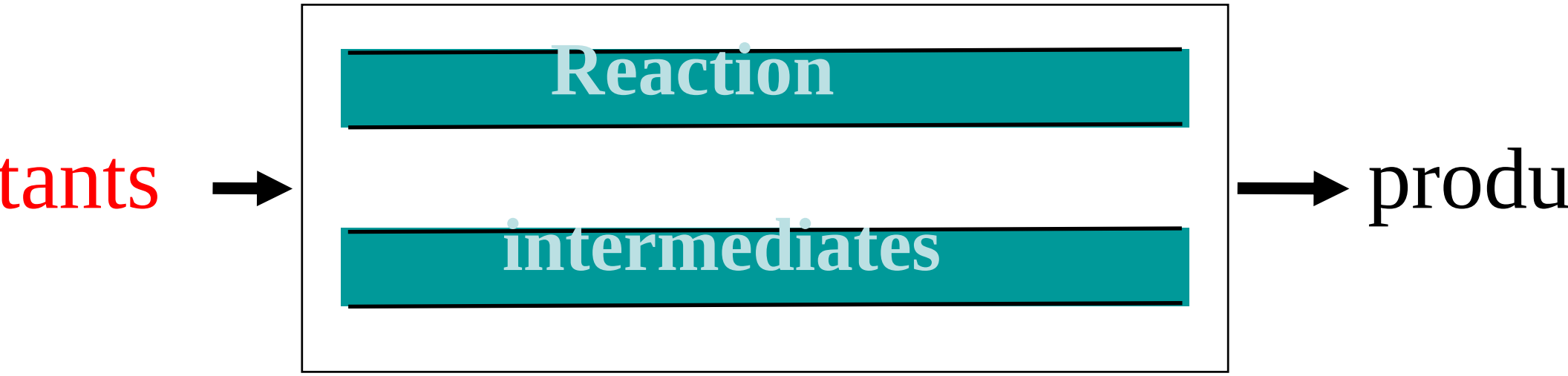
Zhu 408K
Sun 277K
Sun 308K
Sun 353K
Loading θ/[mol/kg]


tants
Reaction
intermediates
produ

(single component)



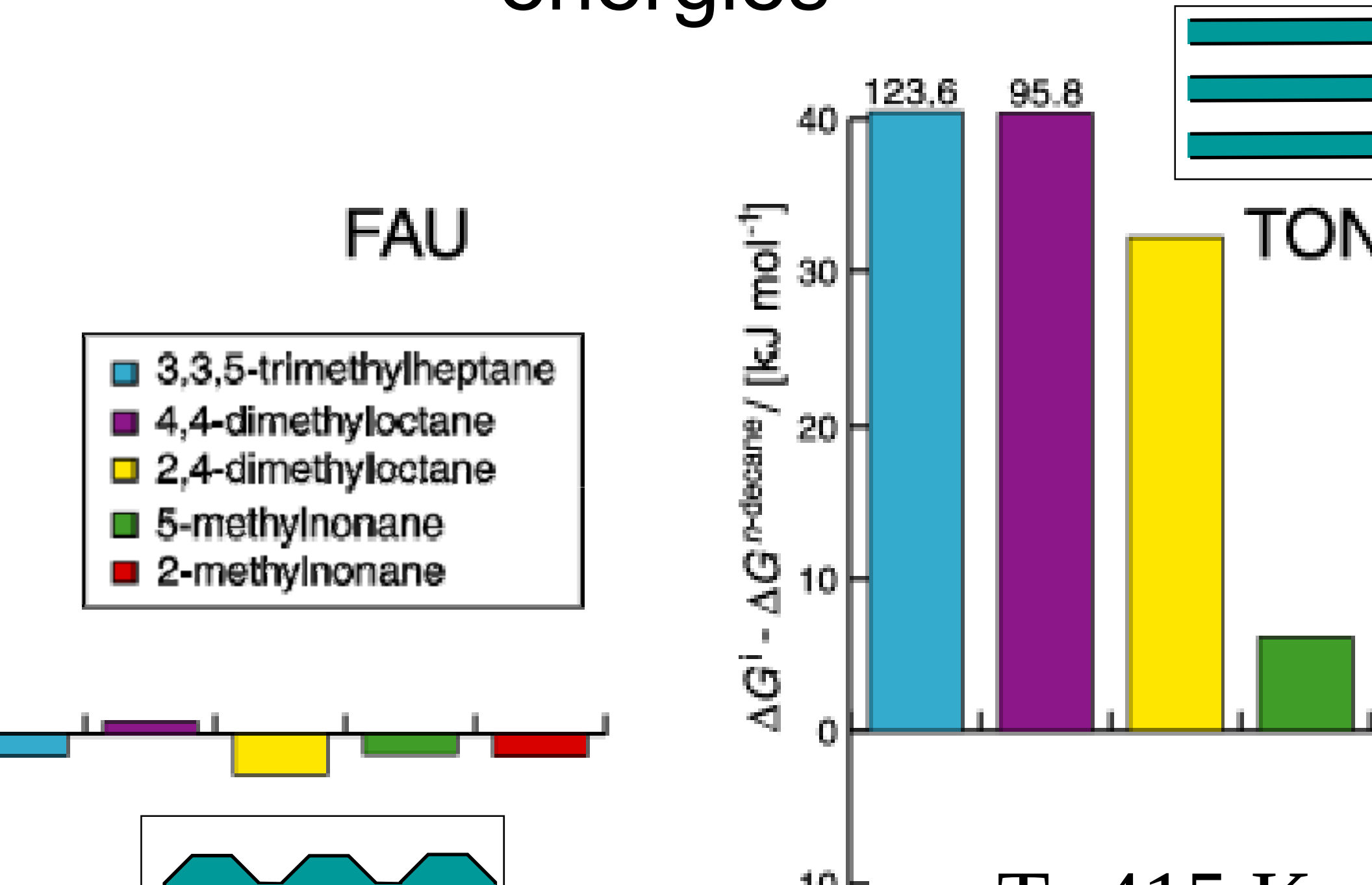
Formation of *reaction intermediates:*

- probability to find a reaction intermediate:
- *free energy of formation* ***in*** the zeolite

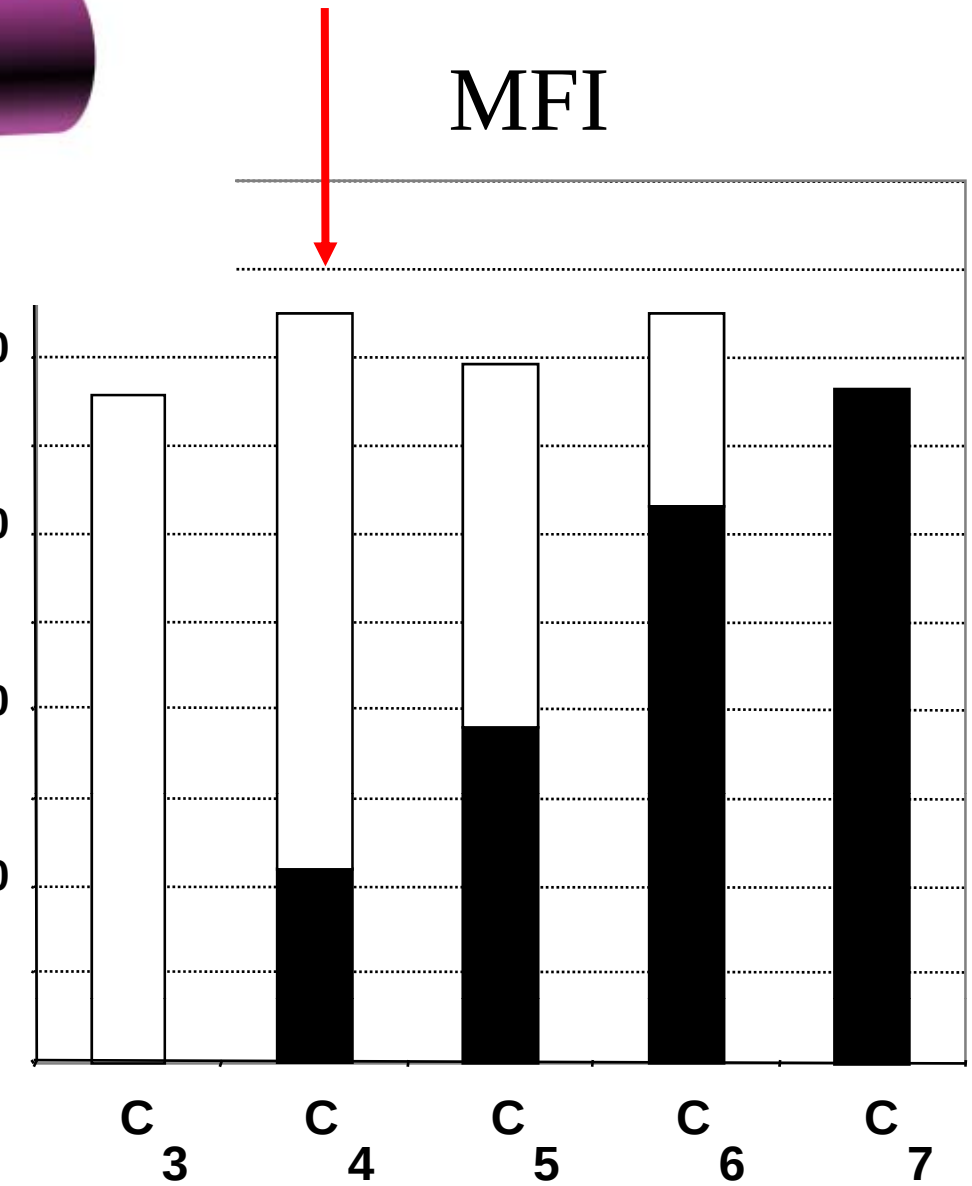
"Fate" of a reaction intermediate:

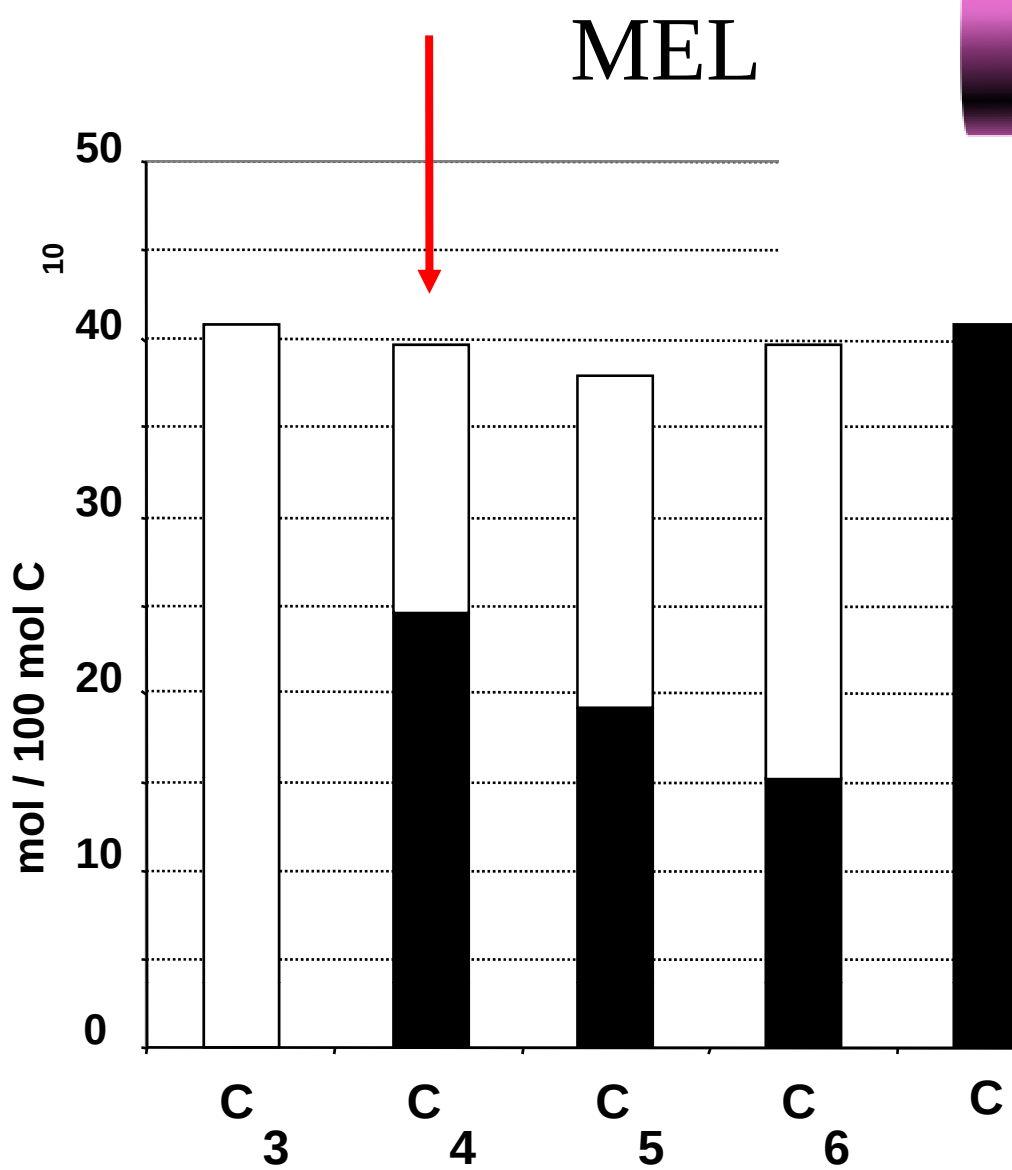
- Leave the zeolite → product
- Continue to react:
  - (hydro)cracking if cracking precursor

contribution of the zeolite to the free energies



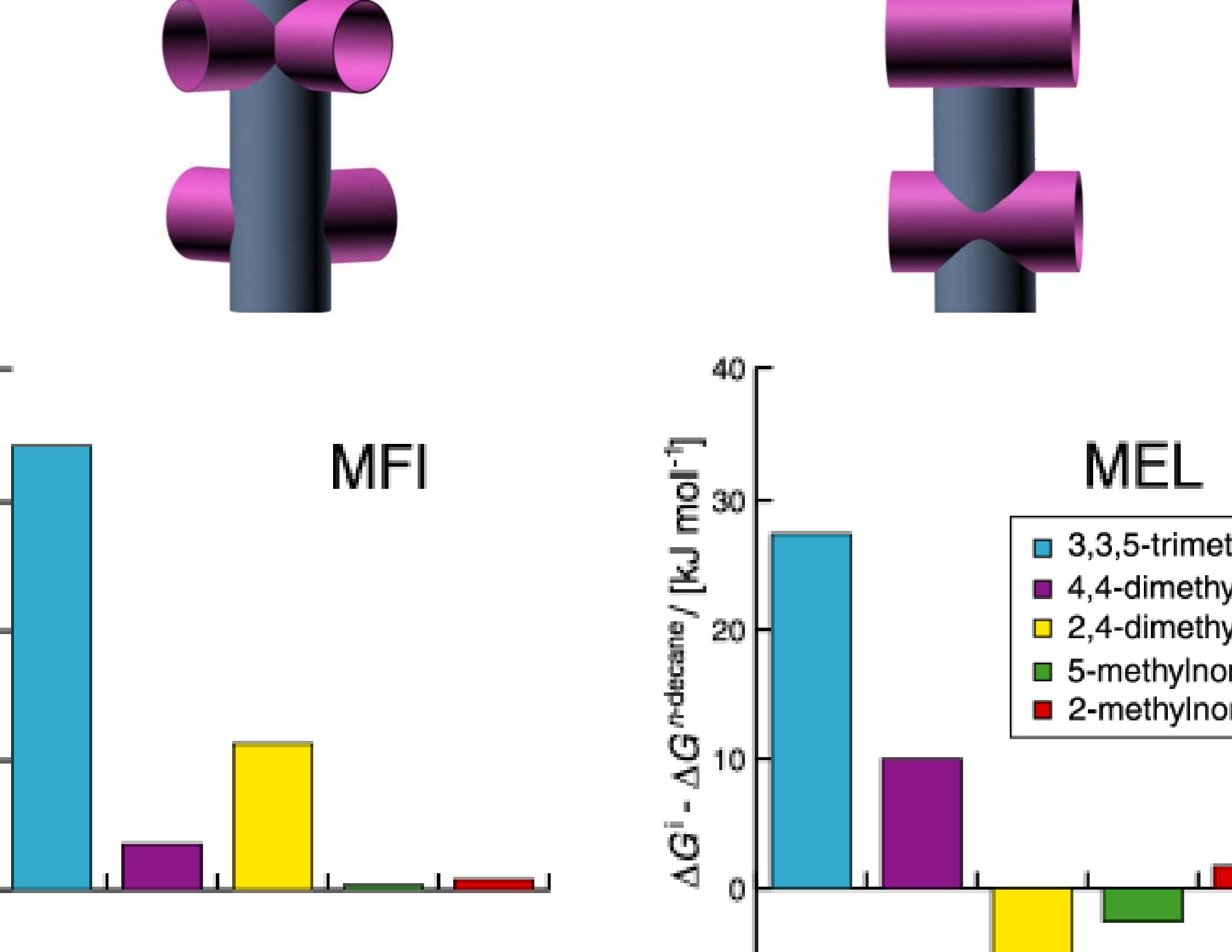
C_{10} hydroconversion, imary product slate : MFI vs. MEL





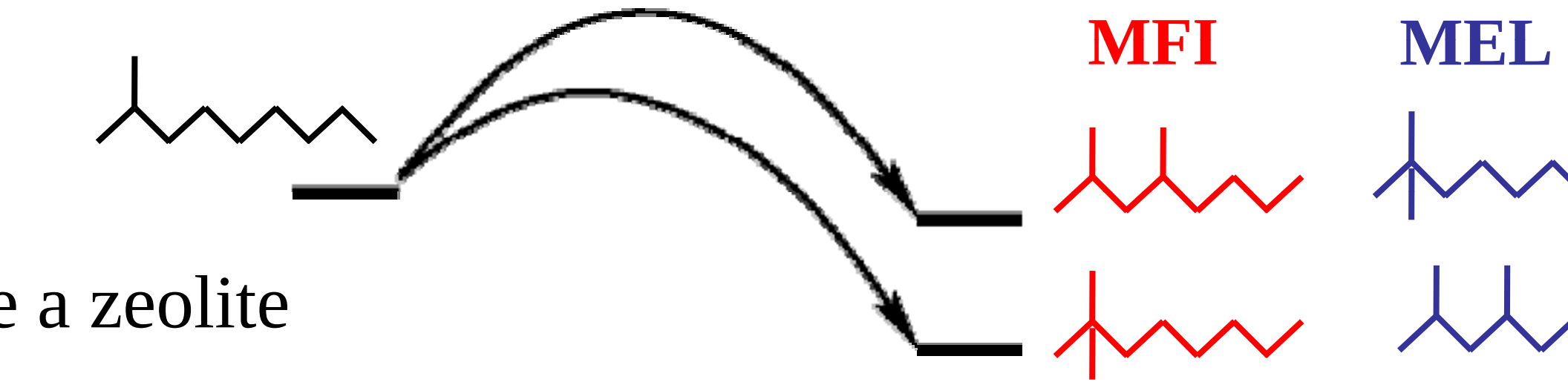
(Black = branched, white = linear)

1] Weitkamp et.al., *Appl. Catal.* **1983**, 8, p 123


MFI
MEL
40
30
20
10
0
ΔG^{i} - $\Delta G^{n\text{-decane}}$ / [kJ mol^{-1}]
3,3,5-trimet
4,4-dimethy
2,4-dimethy
5-methylnor
2-methylnor

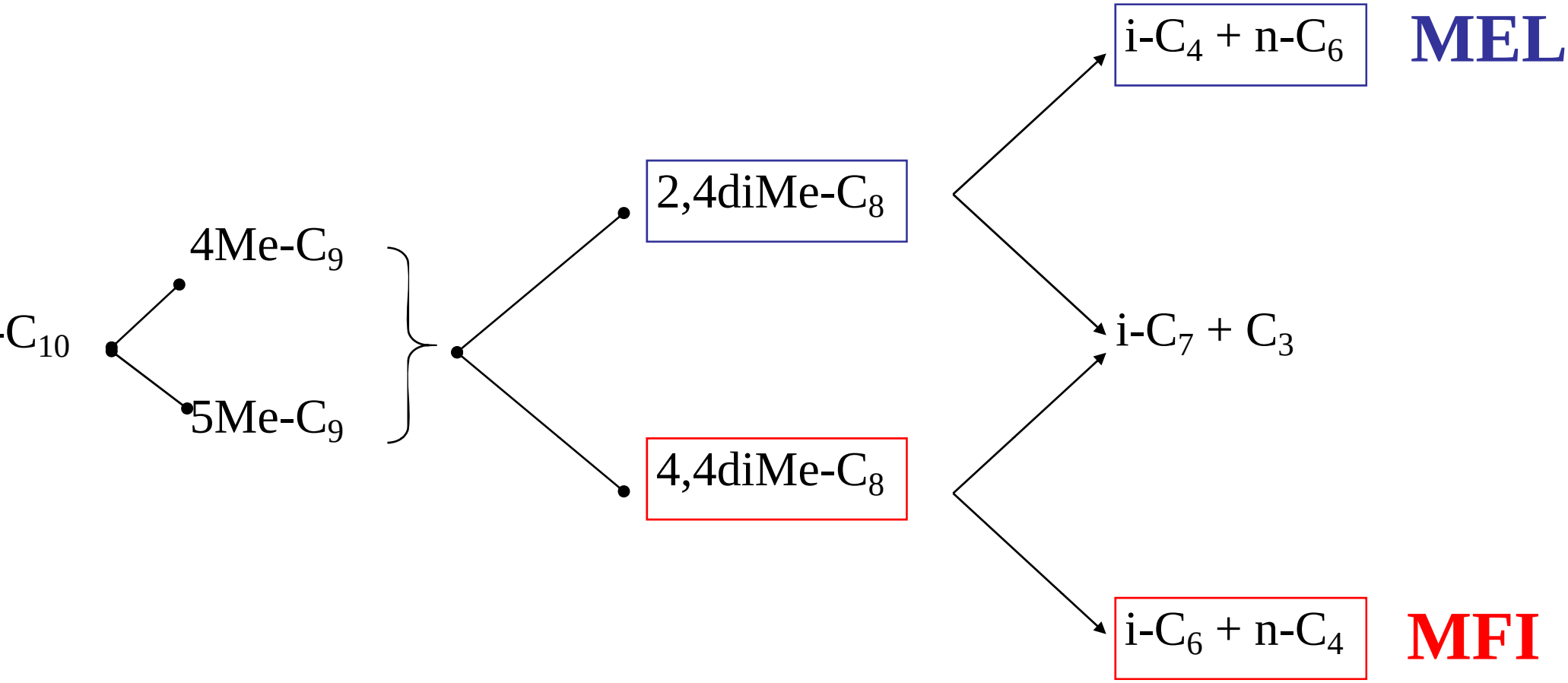
Brønsted-Evans-Polanyi- principle

phase

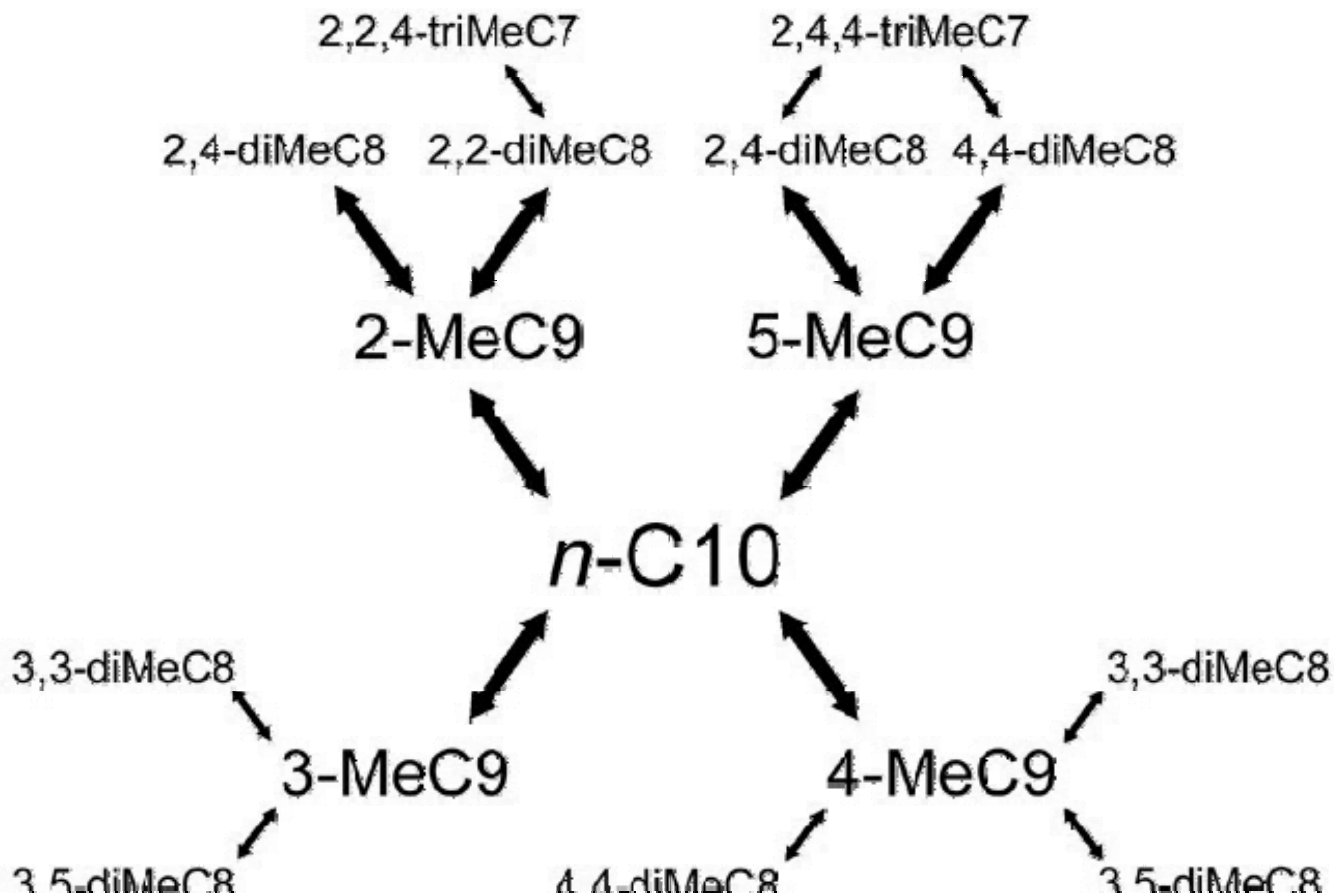


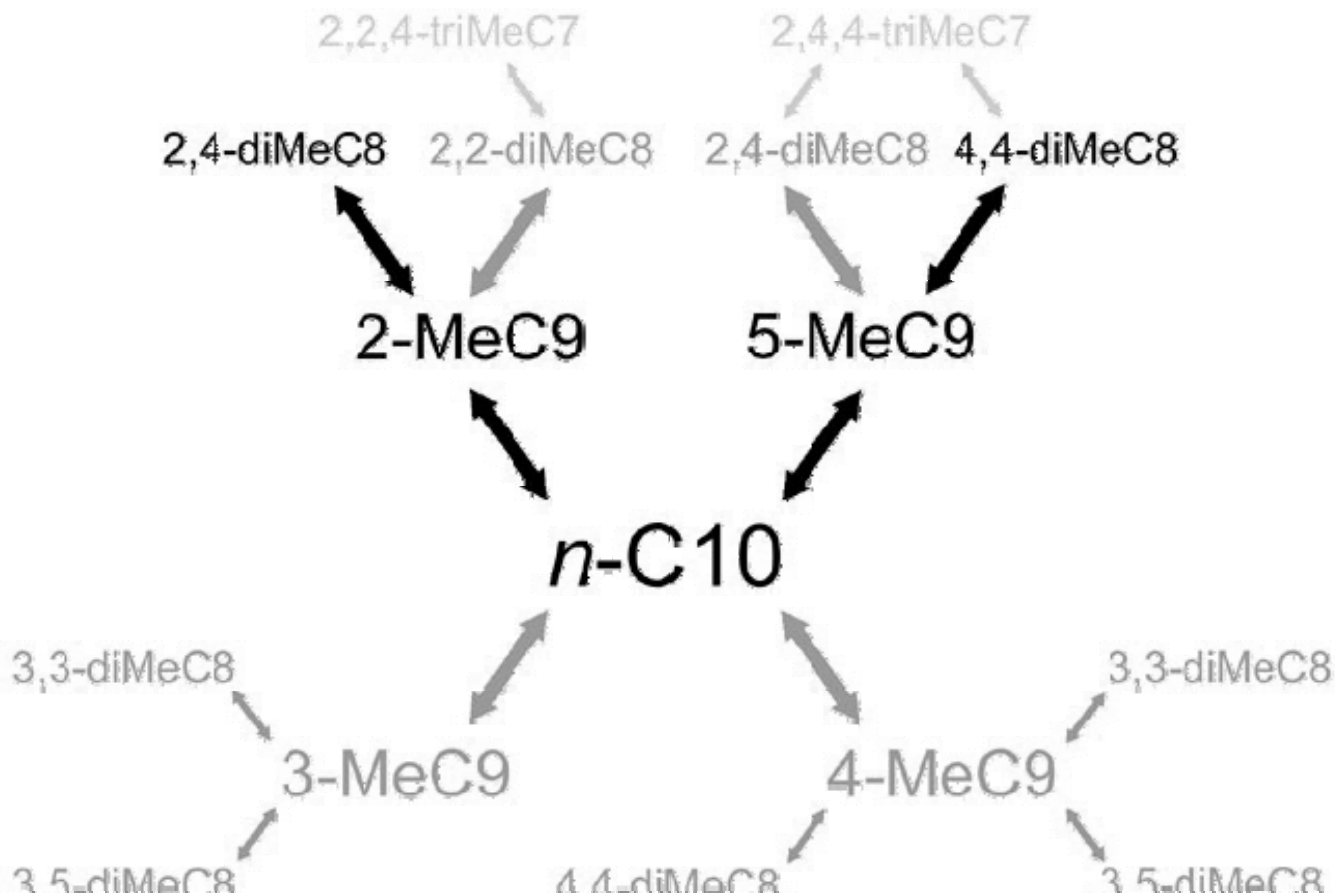
e a zeolite

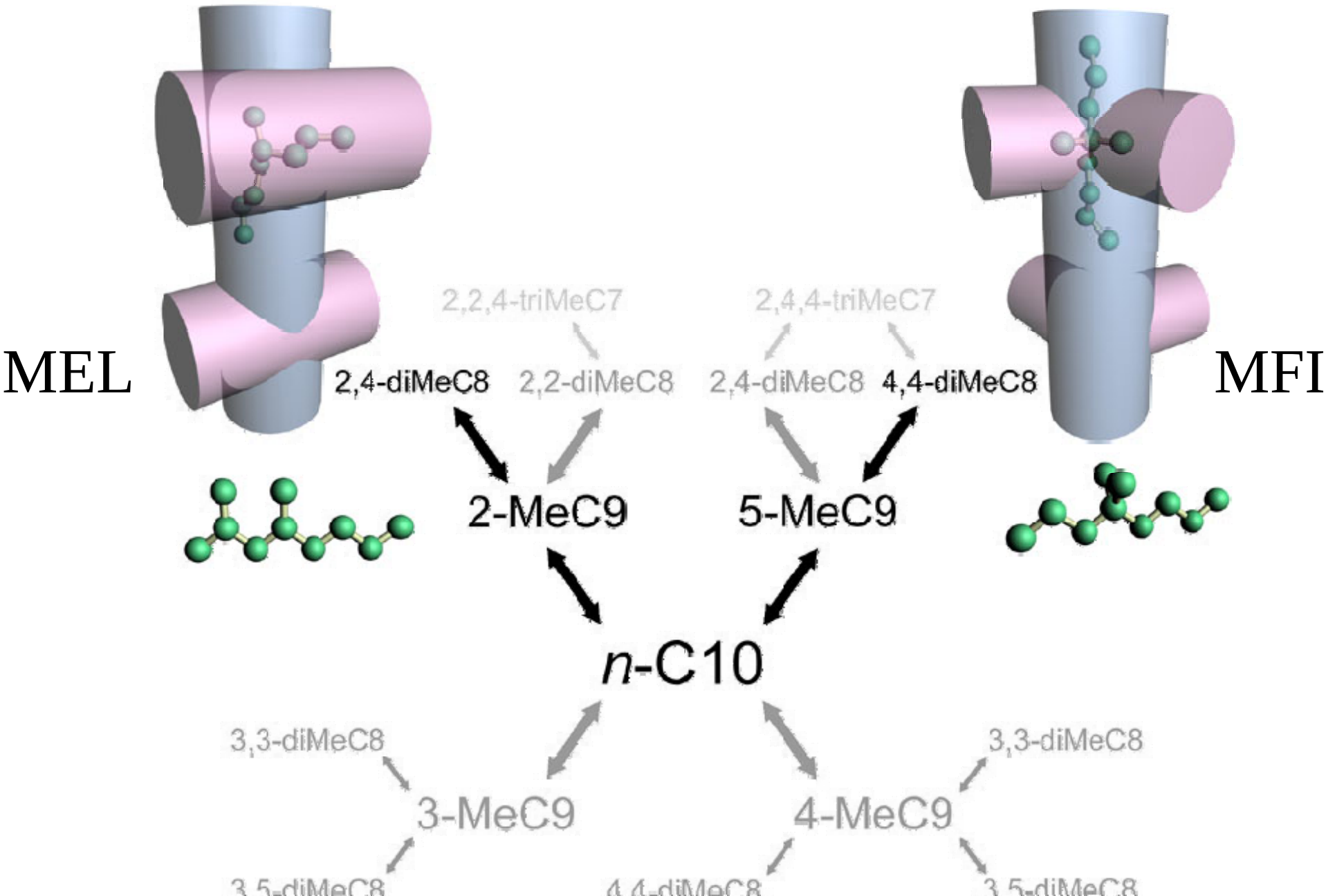
Reaction paths

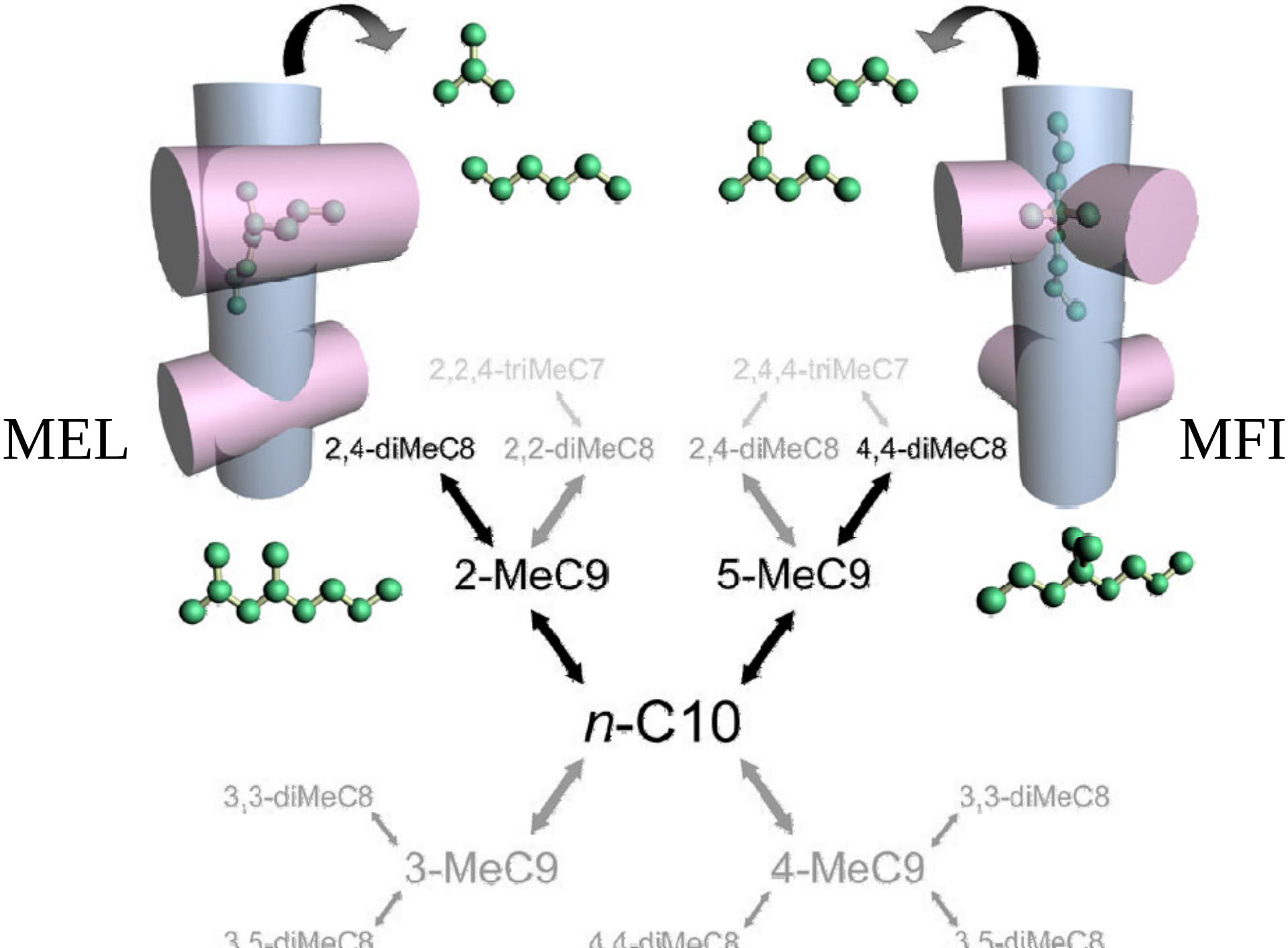


n-C10


2,2,4-triMeC7
2,4,4-triMeC7
2,4-diMeC8
2,2-diMeC8
2,4-diMeC8
4,4-diMeC8
2-MeC9
5-MeC9
n-C10
3,3-diMeC8
3,3-diMeC8
3-MeC9
4-MeC9
3,5-diMeC8
4,4-diMeC8
3,5-diMeC8


2,2,4-triMeC7
2,4,4-triMeC7
2,4-diMeC8
2,2-diMeC8
2,4-diMeC8
4,4-diMeC8
2-MeC9
5-MeC9
n-C10
3,3-diMeC8
3,3-diMeC8
3-MeC9
4-MeC9
3,5-diMeC8
4,4-diMeC8
3,5-diMeC8

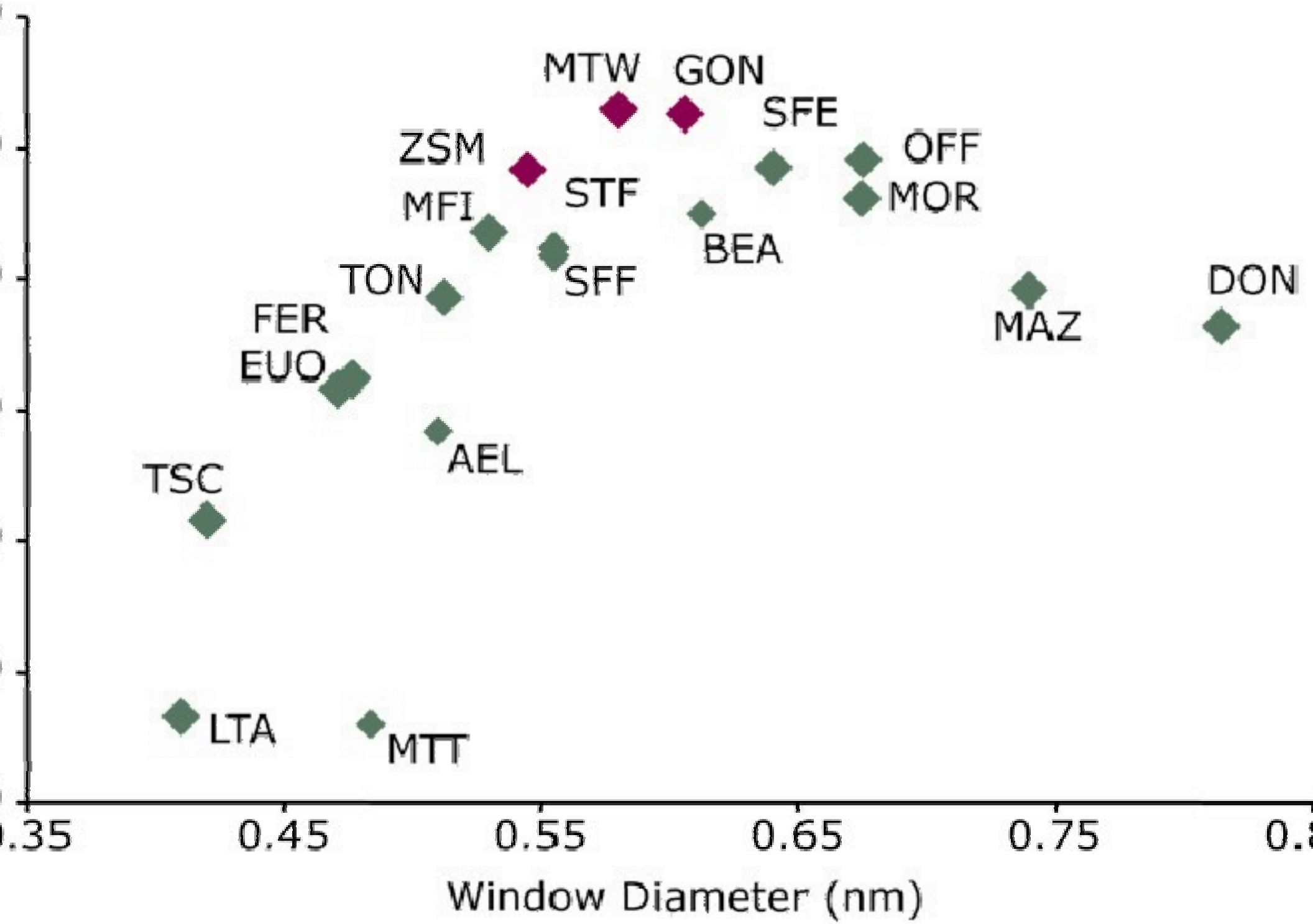

MEL
MFI
2,2,4-triMeC7
2,4,4-triMeC7
2,4-diMeC8
2,2-diMeC8
2,4-diMeC8
4,4-diMeC8
2-MeC9
5-MeC9
n-C10
3,3-diMeC8
3,3-diMeC8
3-MeC9
4-MeC9
3,5-diMeC8
4,4-diMeC8
3,5-diMeC8


MEL
MFI
2,2,4-triMeC7
2,4,4-triMeC7
2,4-diMeC8
2,2-diMeC8
2,4-diMeC8
4,4-diMeC8
2-MeC9
5-MeC9
n-C10
3,3-diMeC8
3,3-diMeC8
3-MeC9
4-MeC9
3,5-diMeC8
4,4-diMeC8
3,5-diMeC8

screening by computer

Hydrodewaxing: *removing the larger hydrocarbons but leaving the shorter unharmed*

Screen zeolites with the largest *free energ difference* between *n*-C_{25} and *n*-C_{10};

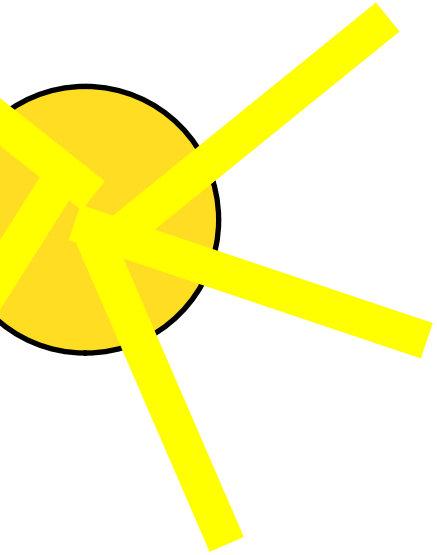

MTW
GON
SFE
ZSM
OFF
STF
MOR
MFI
BEA
SFF
TON
DON
FER
MAZ
EUO
AEL
TSC
LTA
MTT
.35
0.45
0.55
0.65
0.75
0.8
Window Diameter (nm)

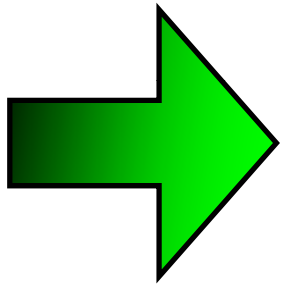
Helios

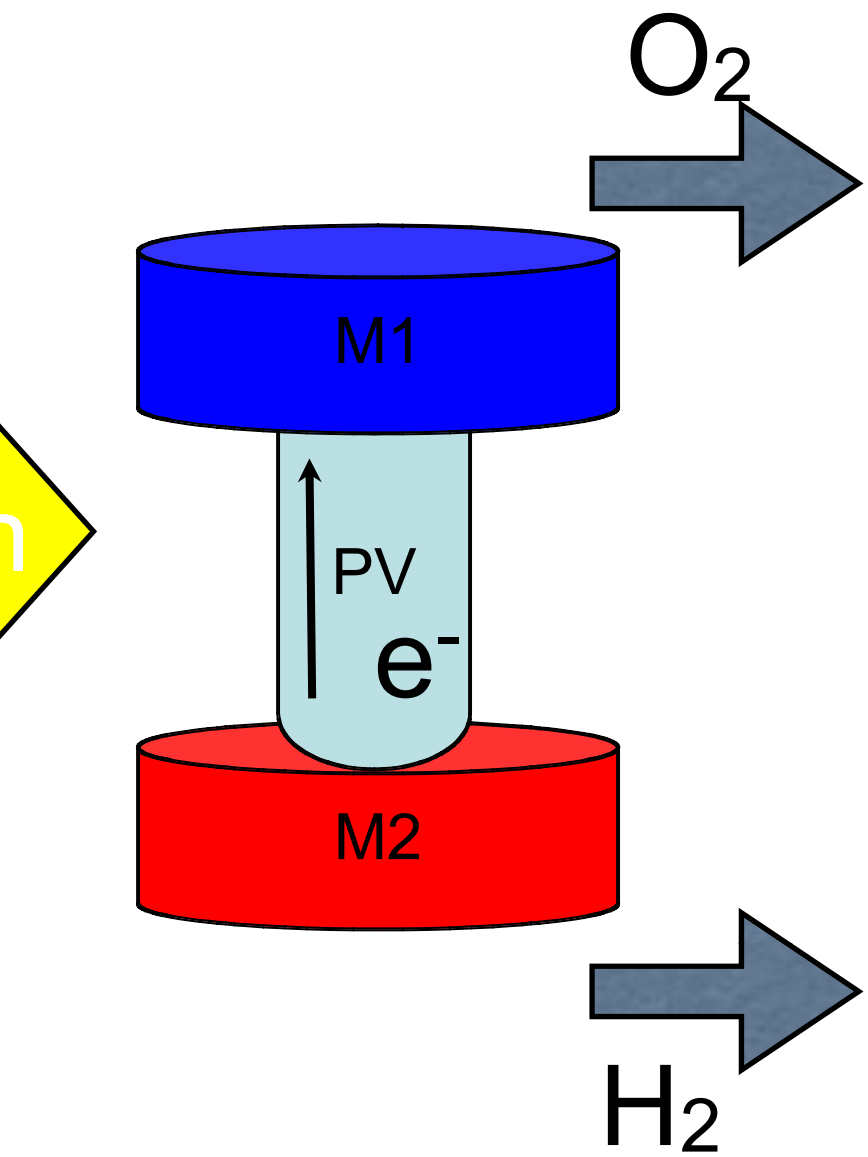
- Aim: to demonstrate that within ten years a solar fluel generator that uses *abundant* and *scalable* manufacturing processes, that has an overall power efficiency of > 1% from sunlight, and yields a chemically pure fuel having an energy density at least as large as that of methanol

Nanotechnology in Helios

- Nano-scalable photovoltaic and electrochemical system







PV (Photo voltaic system)

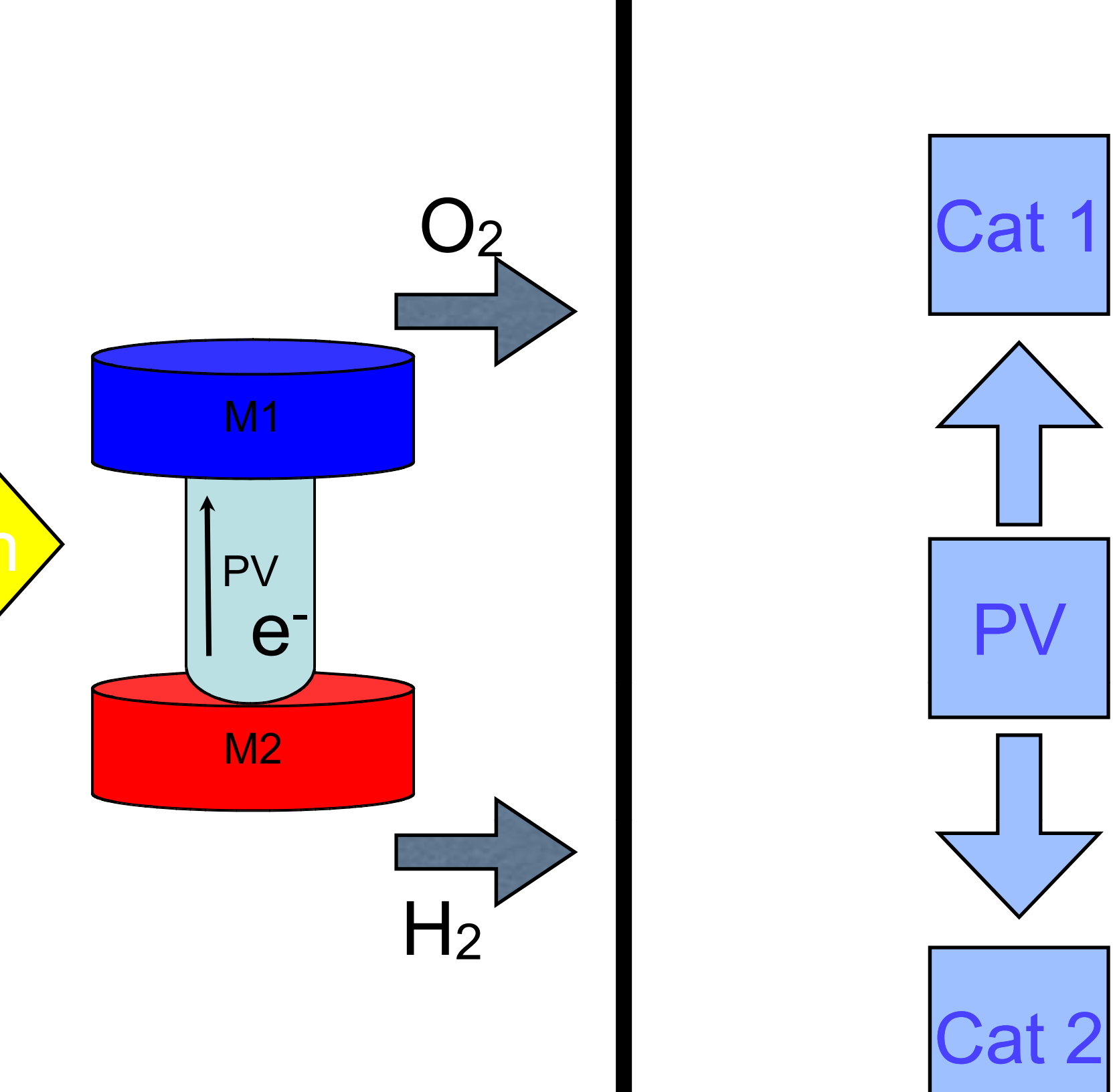
- nanorod and tube
- polymer hybrid
- nanodot/nanotube
- molecular PV

M1 2 (Catalytic centers

- proton reduction to hydro
- water oxidation
- carbon dioxide reduction

Nano-technology in Helios

- Develop nano-technology “units” that have to be integrated into a working device
- Key questions:
  - how do material choices for the units affect the overall activity?
  - how to optimize the design?
- Develop a Helios process simulator to address these questions


O2
M1
PV
e-
M2
H2
Cat 1
PV
Cat 2

Chem. Eng. process simulation

Reactor/separator

- Heat and mass balances
- Reaction kinetics, thermodynamics
- Models for the types of reactors/equipment

reactor

Models:

- Empirical models that interpolate experimental data
- Predictive models for missing experimental data; based on correlations

Design of a chemical plant

Optimization:

- changes of feedstock,
- changes of product specifications

Recent development: use molecular simulations to compute the essential materials properties “in-silica”

Helios Simulator:

Integral theoretical description

ptimize process conditions

nalyze interactions of the various components

ata base for all experimental data

onnect to economic forecasting

cientific “de-bottlenecking”

- Where should improvements be made?
- Which crucial knowledge is lacking?
- What if questions?
- Connection to molecular understanding

Towards a “Helios Simulator”

Reverse coarse graining approach:

1. Start with an “engineering model”
   a. Correlation of experimental data
   b. Empirical models
   c. Analyze the importance of the various components of the model
2. Replace these by more “science” based model
3. Introducing molecular (predictive) tools

Key factors for success

Excellent cyber-infrastructure:

- Databases; all experimental data need to be stored
- Software development; the Helios simulator require
  - electronic structure calculations
  - quantum chemistry
  - classical simulations
- computational resources

Collaboration of all groups involved

Bypassing knowledge gaps:

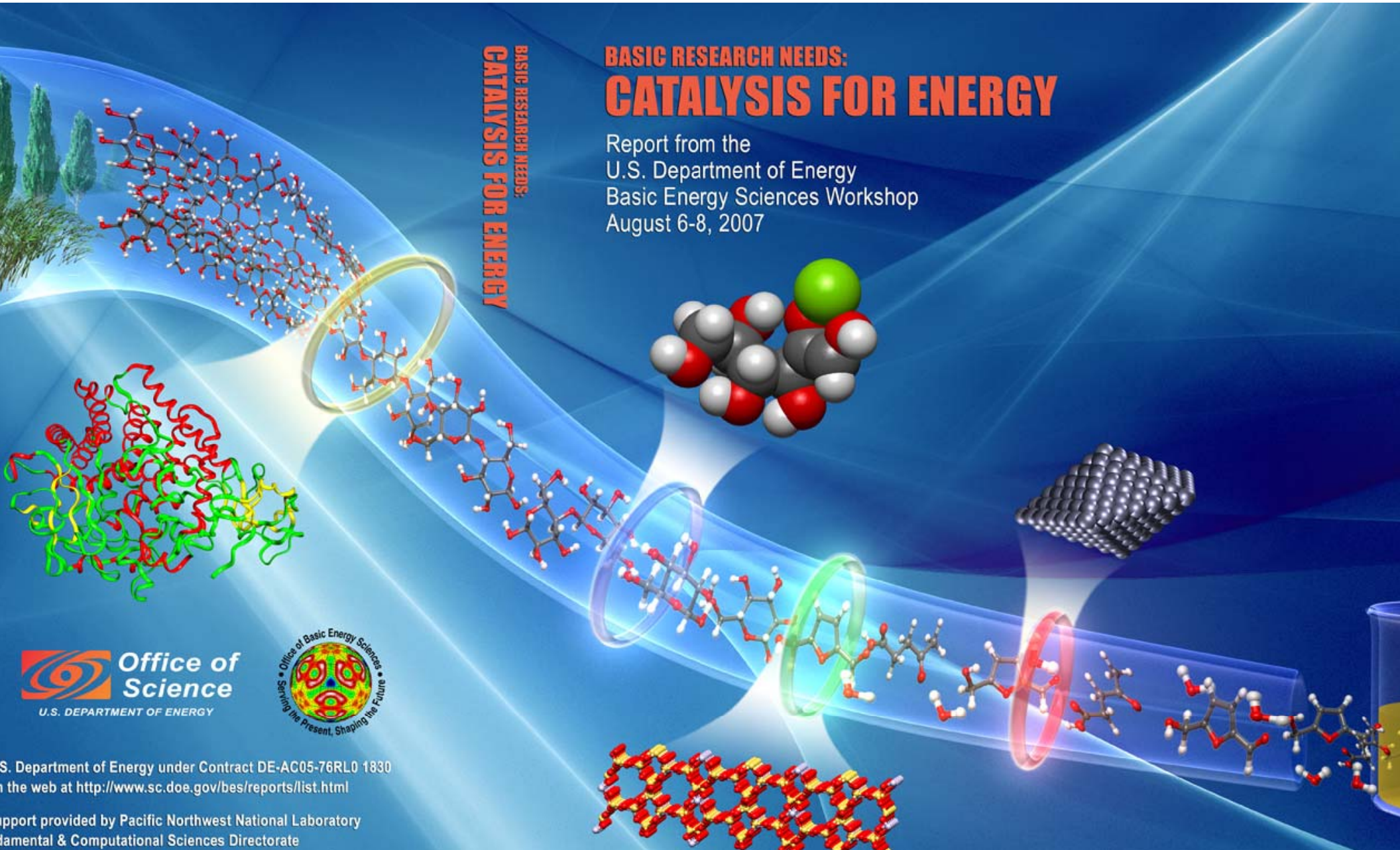
- not all computational will work at the same time at

... and if things fail...

elios is a prototype of a chemical nano-
actory; many others will follow.

It is therefore timely to have the expertise how
to build simulators of these new class of
materials.

asic Research Needs:
atalysis for Energy



Priority research directions

Advanced catalysts for the conversion of heavy fossil energy feedstocks

Understanding the chemistry of lignocellulosic biomass deconstruction and conversion to fuels

Photo- and electro-driven conversions of carbon dioxide and water

ss-cutting research: advances in theory and computat

Some observations: computational materials design

An airplane is designed by computer, but there are only a few cases in which a material is designed by computer

Experimental data on basic data of material properties will become a bottleneck in the design

Successful materials design

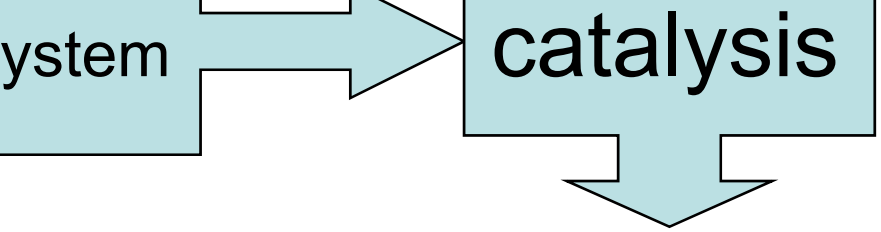
–careful analyses of the key molecular property

Goals

1. Identify expected science outcomes in key scientific domains

2. Identify expected science outcomes utilizing those systems to be deployed at the three OASCR facilities in the next 12-18 months.

3. Identify the impact of having all scientists



"reverse multi-sc

Step 1: Correlations of the experimental data

a) Data base for all experimental data
b) Empirical correlations to interpolate the data
c) Empirical models to describe the operation of the systems
® Response of a unit depending on the operational conditions

Empirical description of a device:

a) Archiving experimental data
b) Understanding of the effects of changes of the various components on overall performance

Step 2: Replacing “correlations” by “knowledge”

- Use expertise of the theory groups in Helios to replace empirical correlations by a “proper” theoretical description
- => Make reliable predictions outside the experimental window

Step 3: Replacing unknown materials properties by atomic/molecular based computations

- Use modern simulation techniques to estimate essenti materials properties.

Relation to present Helios work

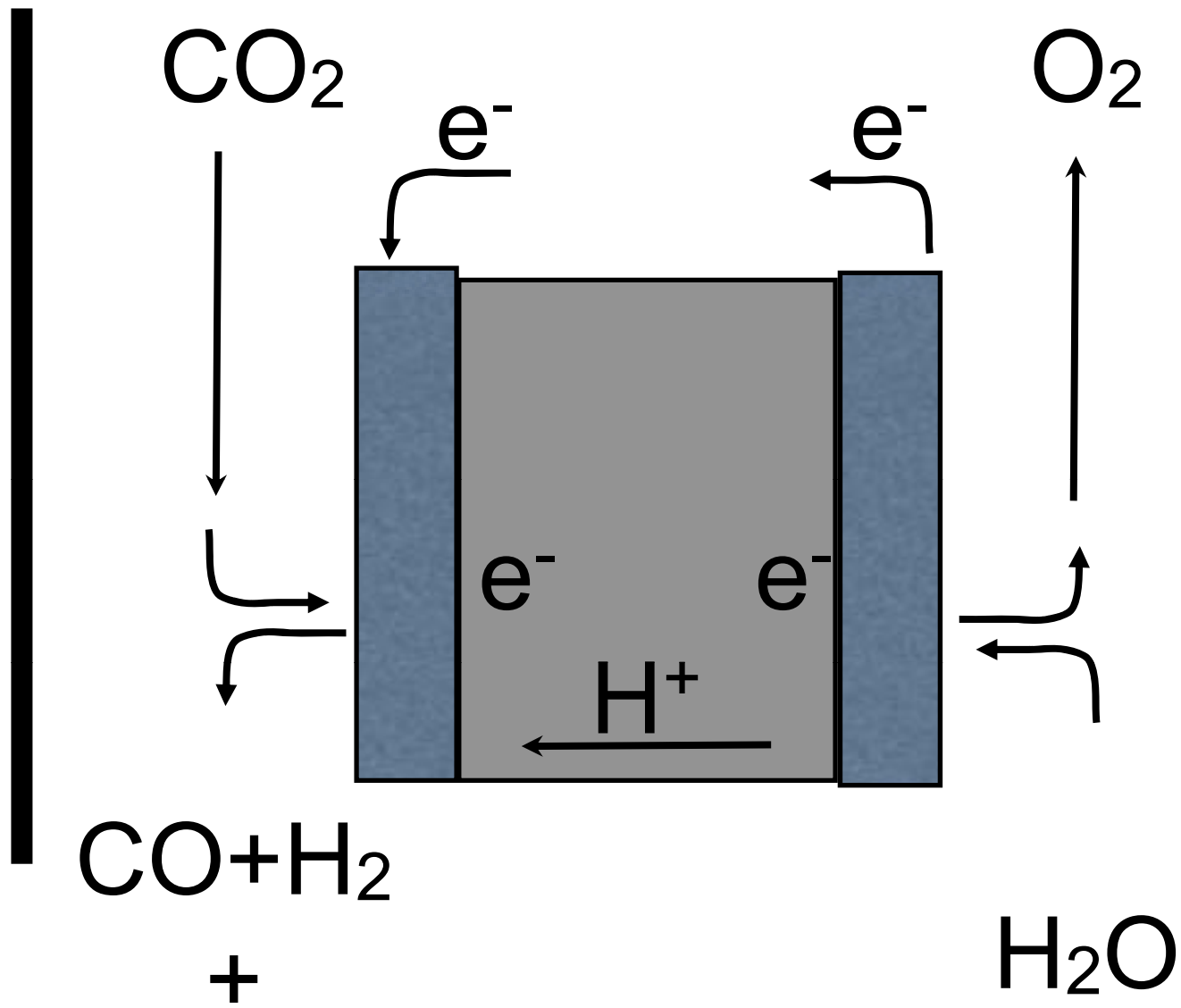
Theory in Helios is aimed to "*de-bottleneck*" specific components of Helios: the simulator is aimed to "*integrate*" the components

Synergies:

- Step 1:
  - Intelligent data base for all experimental data
  - Allows to address issues of integration of individual components that are not in the same state of development
- Step 2: state of the art theoretical insights can be used directly
- Step 3: novel materials can be screened for their efficiency

Catalysis

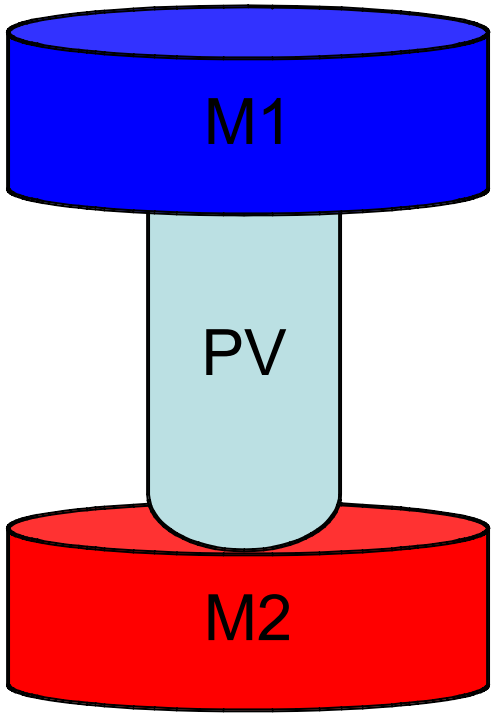
convert H_2O and
nto fuels (hydrogen,
on monoxide, formic
methanol)



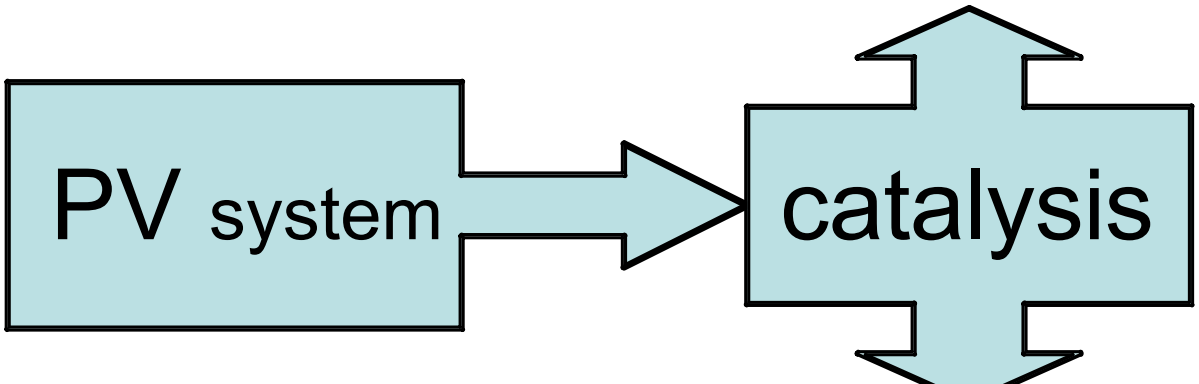
Almost black

Metal catalys

- proton reduc
- water oxidat
- CO2 reducti



Nanoscale photovoltaics:
integration with electrochemi
and catalytic aspects



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kane-zeolite

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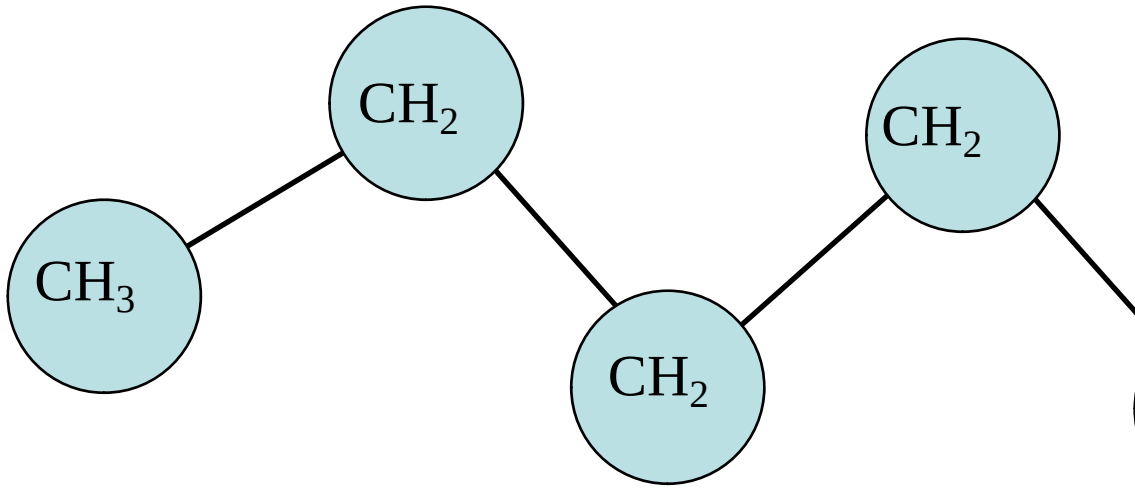

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Nature 1993, 3