Introduction

Modern Methods in Heterogeneous Catalysis

F.C. Jentoft, October 22, 2004

Outline

1. Literature & Web
2. Catalysis, definition
3. Catalysts: importance and effectiveness
4. Types of catalysis
5. Heterogeneous catalysis, examples
6. Level of understanding and motivation for research
7. Thermodynamics…
8. “Activity”

1. Literature

G.A. Somorjai: Introduction to surface chemistry and catalysis, Wiley New York [u.a.] 1994

Jens Hagen: Technische Katalyse: eine Einführung, VCh Weinheim 1996

B.C. Gates: Catalytic Chemistry, John Wiley & Sons, New York 1997

G. Ertl, H. Knözinger, J. Weitkamp, [Eds.]: Handbook of heterogeneous catalysis: VCh Weinheim 1997

J.M. Thomas, W.J. Thomas: Principles and practice of heterogeneous catalysis, Weinheim [u.a.] VCh 1997

B. Cornils, W.A. Herrmann, R. Schlögl, C.-H. Wong (Eds.): Catalysis from A to Z, Wiley-VCh Weinheim 2000

R.I. Masel: Chemical kinetics and catalysis, Wiley-Interscience New York [u.a.] 2001

J.W. Niemantsverdriet: Spectroscopy in Catalysis, Wiley-VCh Weinheim 2002

James F. Haw (Ed.): In-Situ Spectroscopy in Heterogeneous Catalysis, Wiley-VCh Weinheim 2002

I. Chorkendorff, J.W. Niemantsverdriet: Concepts of Modern Catalysis and Kinetics, Wiley-VCh Weinheim 2003

Catalysis in the Web

- University of York/Chemical Industry Education Centre
  http://www.uyseg.org/catalysis/pages/cat_frames.htm
- Organizations
  EFCATS: European Federation of Catalysis Societies
  www.efcats.org

2. Catalysis Definition – First Description

Berzelius' Ideas of "Catalytic Power" (1835)

- the ability of substances "to awaken affinities, which are asleep at a particular temperature, by their mere presence and not by their own affinity"
- used to explain conversion of starch to sugar by acid, hydrogen peroxide decomposition by metals, conversion of ethanol to acetic acid by Pt
- chose "catalysis" in analogy to "analysis"
- stated that
  catalysis was more common than believed,
  part of inorganic and organic nature,
  in living plants and animals thousands of catalytic processes may proceed

M.W. Roberts, Catalysis Lett. 67,1 (2000)
G. Ertl and T. Gloyna, Z. Phys. Chem. 217 (2003) 1207-1219

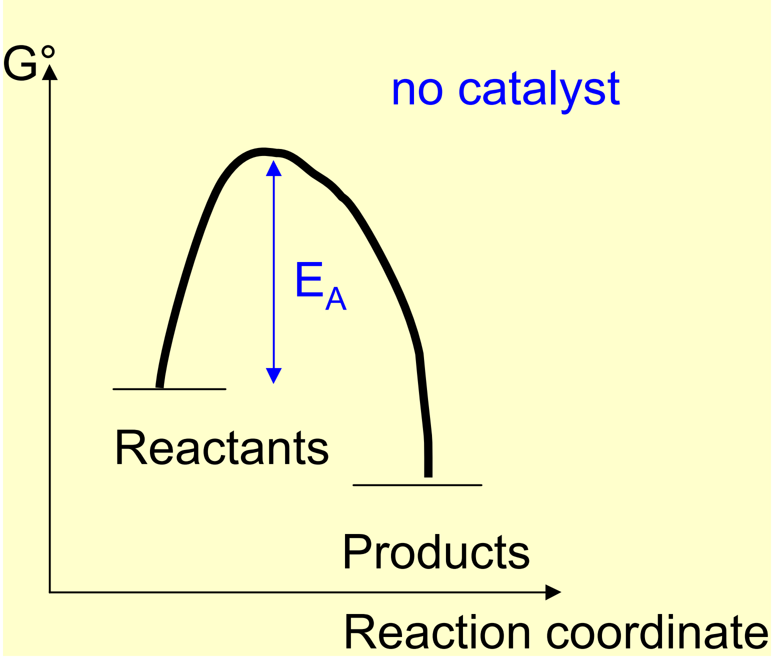
Catalysis Definition

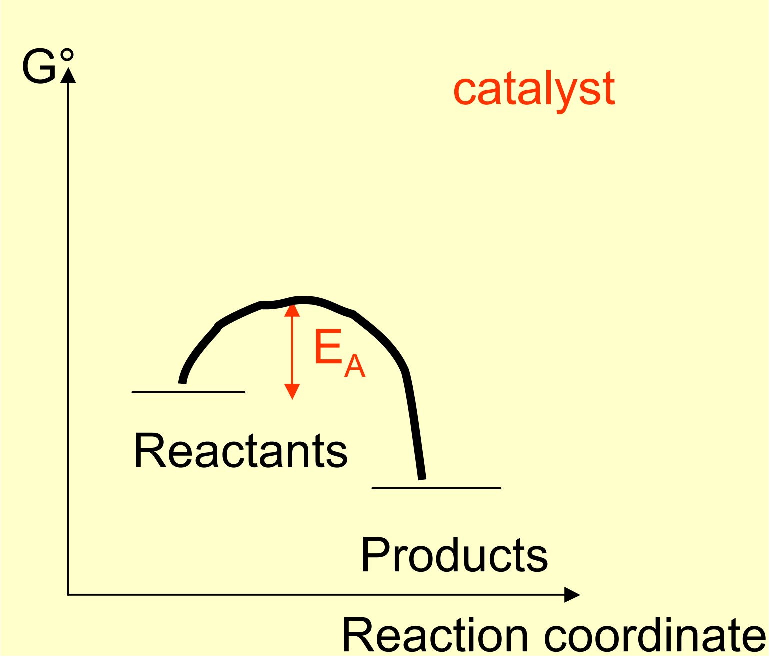
Ostwald's Definition of Catalysis (1894)

- "catalysis is the acceleration of a slowly proceeding chemical reaction through the presence of a foreign substance"
- "the acceleration occurs without a change of the energetic situation"
- "at the end of the reaction the foreign substance can be considered as removed"

Stohmann, Z. Biol. 31 (1894) 364-391
W. Ostwald, Z. Phys. Chem. 15 (1894) 705-706
G. Ertl and T. Gloyna, Z. Phys. Chem. 217 (2003) 1207-1219
N.I Rodnyj, Ju.I. Solowjew, Wilhelm Ostwald, Teubner, Leipzig 1977.

Modern Catalysis Picture

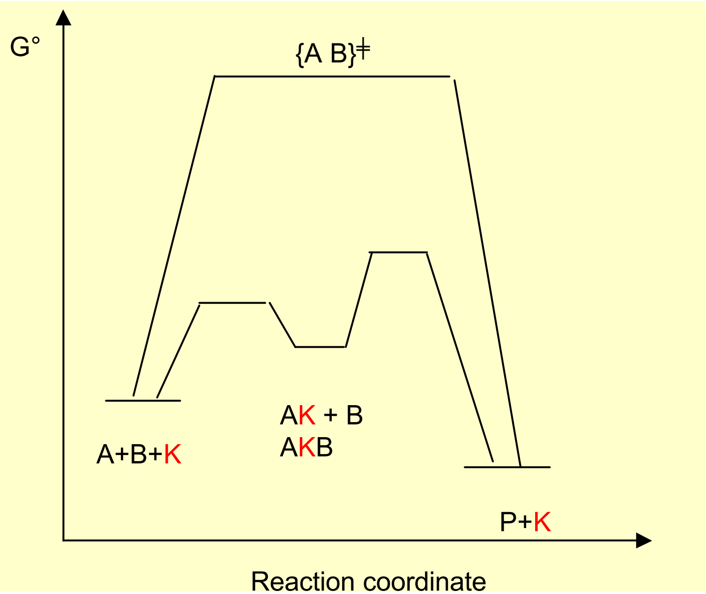




- Thermodynamics of reaction remain unchanged
- Catalyst influences reaction rate by changing the reaction coordinate and the nature of transition states or intermediates

The Sabatier principle

- Catalyst must have affinity to reactant
- Catalyst and reactants may form intermediates
- ....but not too much!



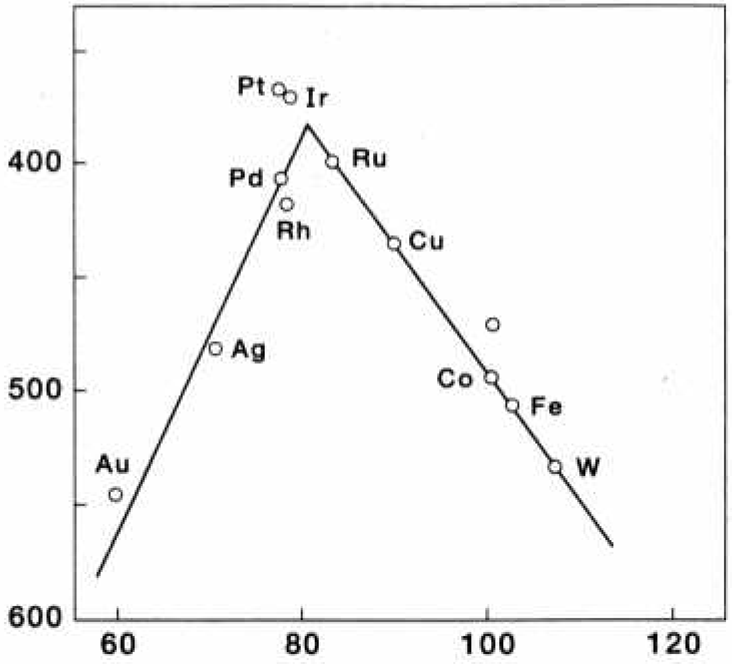


Figure 2. Sabatier's principle: volcano curves T_v/K. The temperature at which the rate of decomposition of formic acid (vertical axis) has a set value v, correlated with the heat of formation of the bulk metallic formate, in kcal per equivalent (horizontal axis) [17].

3. Importance of Catalysis

- about 85-90 % of the products of chemical industry are made in catalytic processes

Why Are Catalysts Good?

- Reactions can be conducted at lower temperature or lower pressure
- Some reactions are industrially only feasible with the help of catalysts

Example: ammonia synthesis

$N_2 + 3H_2 \quad \rightarrow \quad 2NH_3$ $\Delta_r H = -91.8$ kJ/mol

problem: equilibrium favorable at low reaction temperature

cleavage of the N≡N band requires high temperature

Großer Kontaktofen
Werk Oppau

Atom Efficiency (I)

- Molecular weight of the product divided by the total molecular weight of all products*

Example 1 (non-catalytic):

$$\underline{3C_6H_5-CHOH-CH_3}+2CrO_3+3H_2SO_4$$
$$\rightarrow\quad \underline{3C_6H_5-CO-CH_3}+\underline{Cr_2(SO_4)_3}+6\underline{H_2O}$$

atom efficiency 360/860 or 42%

Example 2 (catalytic):

$$\underline{3C_6H_5-CHOH-CH_3}+0.5O_2 \quad\rightarrow\quad \underline{3C_6H_5-CO-CH_3}+\underline{H_2O}$$

atom efficiency 120/138 or 87%

*according to Sheldon

Atom Efficiency (II)

Example 3 (catalytic hydrogenation):

$$\underline{C_6H_5-CO-CH_3}+H_2\rightarrow \underline{C_6H_5-CHOH-CH_3}$$

atom efficiency 100 %

Example 4 (catalytic carbonylation):

$$\underline{C_6H_5-CHOH-CH_3}+CO\rightarrow \underline{C_6H_5-CH(CH_3)COOH}$$

atom efficiency 100 %

E factor

- Weight of waste or undesirable byproduct divided by the weight of the desired product

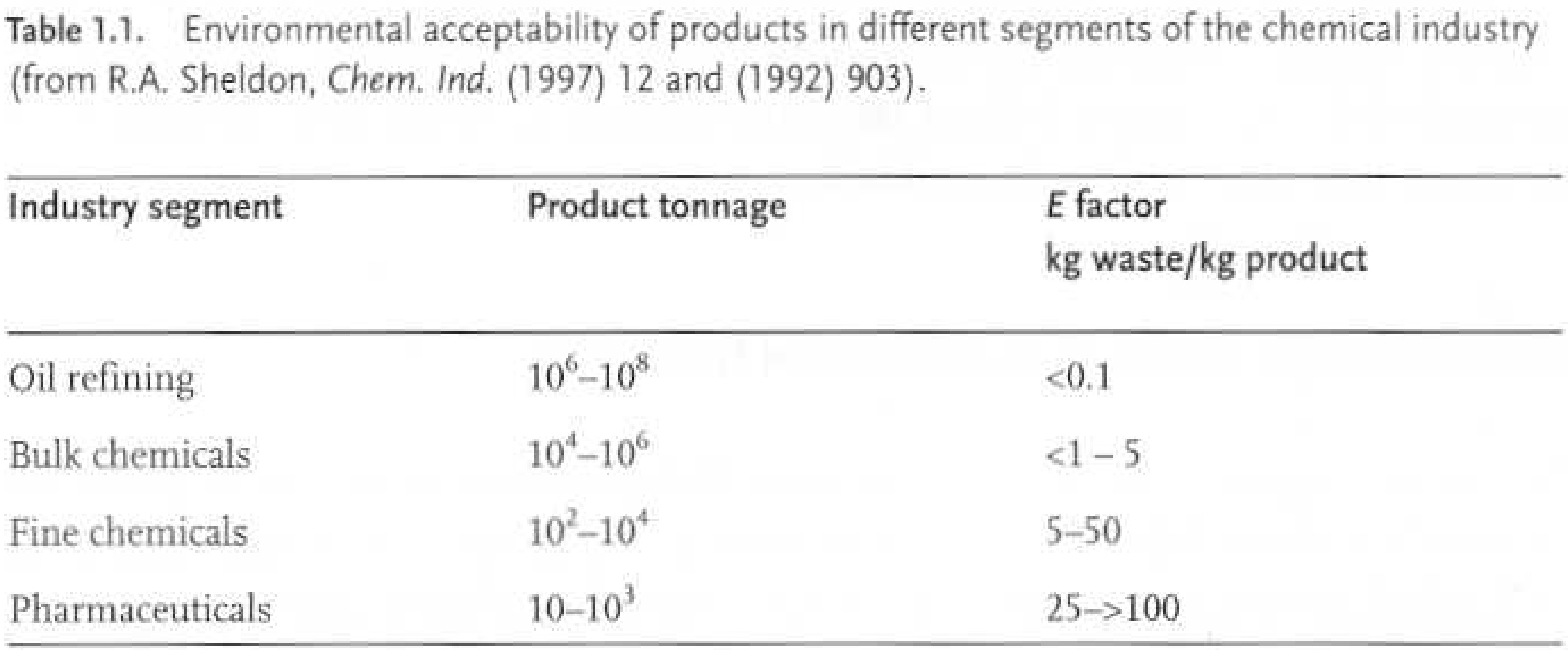


Table 1.1. Environmental acceptability of products in different segments of the chemical industry (from R.A. Sheldon, *Chem. Ind.* (1997) 12 and (1992) 903).

Industry segment	Product tonnage	*E* factor kg waste/kg product
Oil refining	10^6–10^8	<0.1
Bulk chemicals	10^4–10^6	<1 – 5
Fine chemicals	10^2–10^4	5–50
Pharmaceuticals	10–10^3	25–>100

Unfriendliness Coefficient Q & Environmental Quotient EQ

- a value assigned to indicate how undesirable a byproduct is
- Examples

  water: Q = 0

  benign salts such NaCl: Q = 1

  toxic compounds: Q = 100-1000
- EQ …..the product of E and Q

4. Types of Catalysis

- Biocatalysis

  catalyzed reactions where the catalyst is an enzyme

- Homogeneous catalysis

  catalysis with the catalyst in the same phase as the reactant

- Heterogeneous catalysis

  1) catalysis with the catalyst in a different phase than the reactants, and 2) with the catalyst on solid, porous material or impregnated in such material

Biocatalysis

- Enzymes as catalysts

  highly efficient, i.e. very fast and very selective!

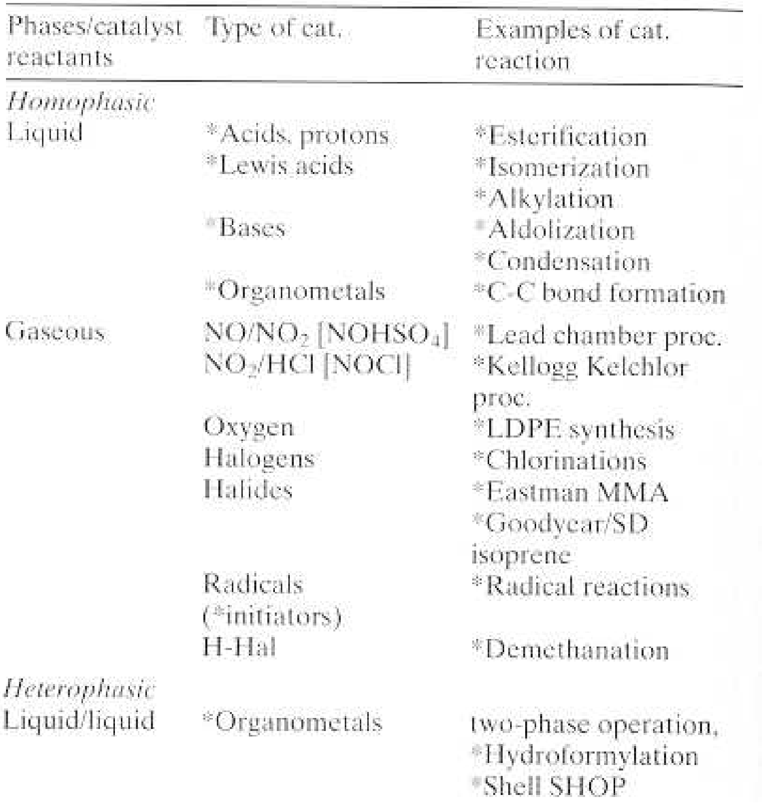
  mild conditions (T, p)… but also very sensitive (T,pH)

$$2H_2O_2 \xrightarrow{\textit{catalase}} O_2 + 2H_2O$$

Rate: 10^7 molecules/s

Catalyst	**E_a/ kJ*mol^{-1}**
None	73
iodide ion	54
Pt surface	46
iron(III)	40
Catalase	4

Homogeneous Catalysis



Phases/catalyst reactants	Type of cat.	Examples of cat. reaction
Homophasic		
Liquid	*Acids, protons *Lewis acids	*Esterification *Isomerization *Alkylation
	*Bases	*Aldolization *Condensation
	*Organometals	*C-C bond formation
Gaseous	NO/NO$_2$ [NOHSO$_4$] NO$_2$/HCl [NOCl]	*Lead chamber proc. *Kellogg Kelchlor proc.
	Oxygen Halogens Halides	*LDPE synthesis *Chlorinations *Eastman MMA *Goodyear/SD isoprene
	Radicals (*initiators)	*Radical reactions
	H-Hal	*Demethanation
Heterophasic		
Liquid/liquid	*Organometals	two-phase operation, *Hydroformylation *Shell SHOP

Homogeneous catalysis helps with understanding! Ideas can be transferred from solution chemistry to surface chemistry (e.g. in acid catalysis, 18.2.05)

Heterogeneous Catalysis

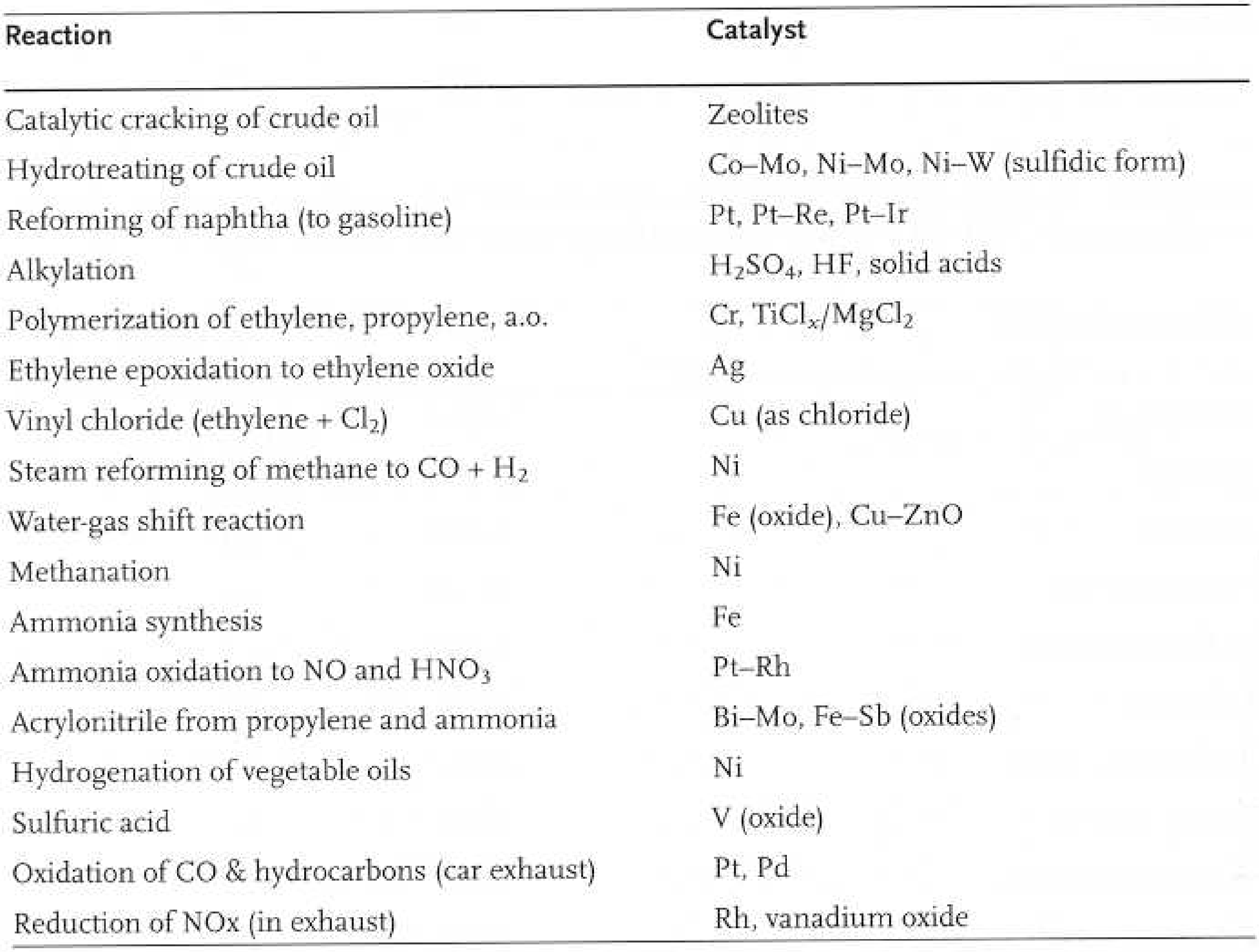
Advantages

- easy separation of product and catalysts
- high catalyst lifetimes
- particularly acid catalysis: fewer corrosion and disposal problems
- ^ca. 80 % of industrial catalytic processes are heterogeneous

Applications

- production of chemicals
- cleaning of waste and exhaust gas streams (environmental catalysis)
- energy conversion (fuel cells)

5. Largest Processes in Heterogeneous Catalysis



Reaction	Catalyst
Catalytic cracking of crude oil	Zeolites
Hydrotreating of crude oil	Co–Mo, Ni–Mo, Ni–W (sulfidic form)
Reforming of naphtha (to gasoline)	Pt, Pt–Re, Pt–Ir
Alkylation	H_2SO_4, HF, solid acids
Polymerization of ethylene, propylene, a.o.	Cr, $TiCl_x/MgCl_2$
Ethylene epoxidation to ethylene oxide	Ag
Vinyl chloride (ethylene + Cl_2)	Cu (as chloride)
Steam reforming of methane to CO + H_2	Ni
Water-gas shift reaction	Fe (oxide), Cu–ZnO
Methanation	Ni
Ammonia synthesis	Fe
Ammonia oxidation to NO and HNO_3	Pt–Rh
Acrylonitrile from propylene and ammonia	Bi–Mo, Fe–Sb (oxides)
Hydrogenation of vegetable oils	Ni
Sulfuric acid	V (oxide)
Oxidation of CO & hydrocarbons (car exhaust)	Pt, Pd
Reduction of NOx (in exhaust)	Rh, vanadium oxide

Catalysis in a Refinery (18.2.05)

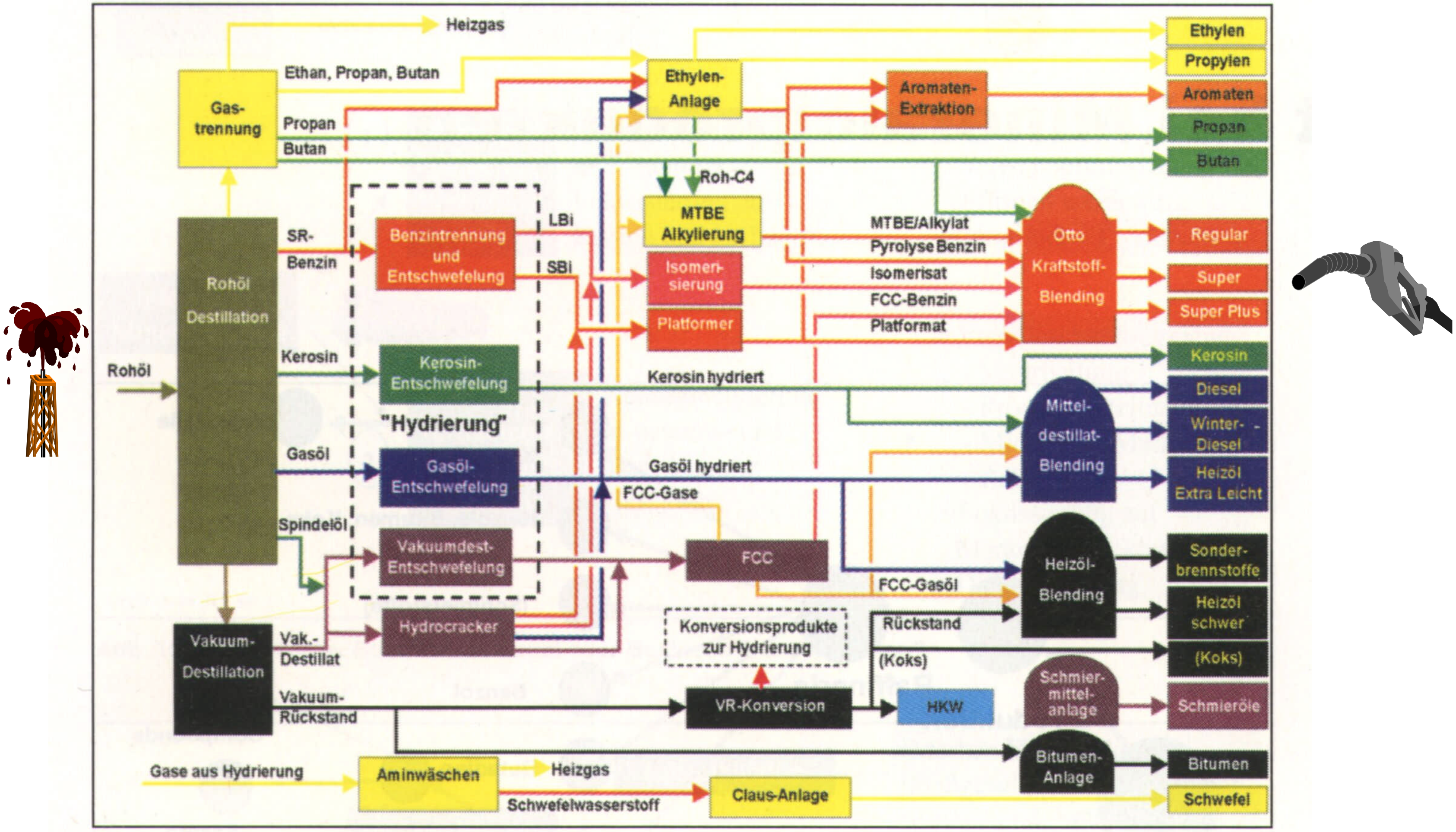
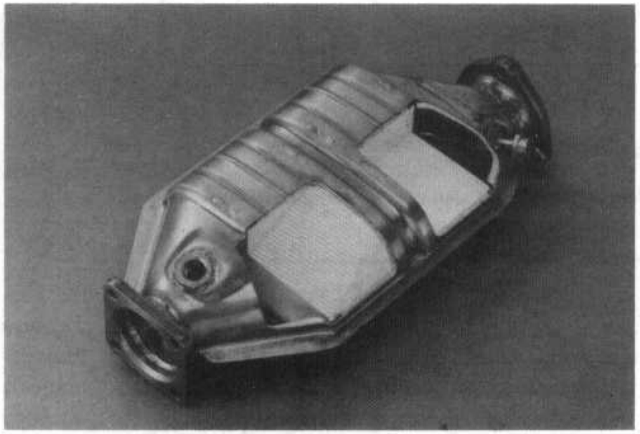


Abb. 2 Raffineriefließschema

Environmental Catalysis: Mobile Sources (I)

- Cleaning of exhaust gases from mobile sources (cars!)
- three-way-converter (TWC) for gasoline fueled spark ignition engines
- Pt/Rh on washcoated monolith



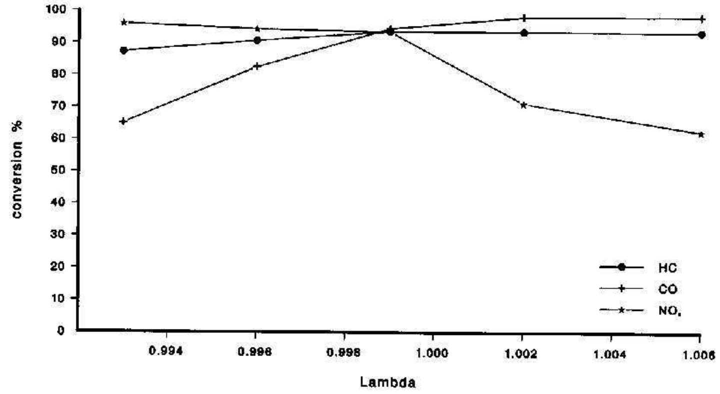
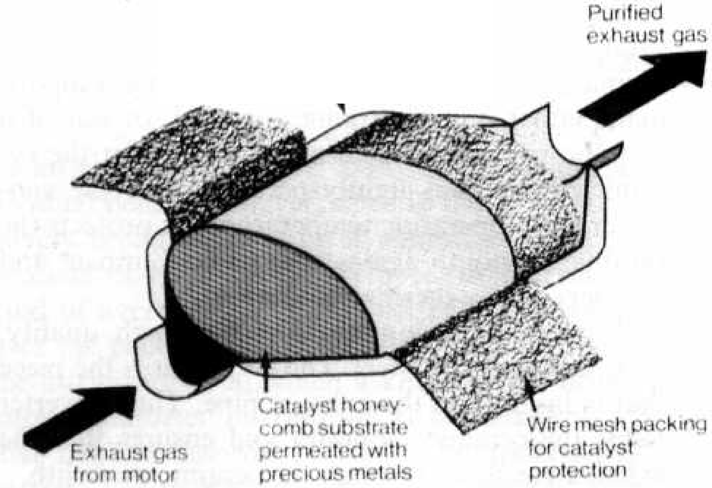
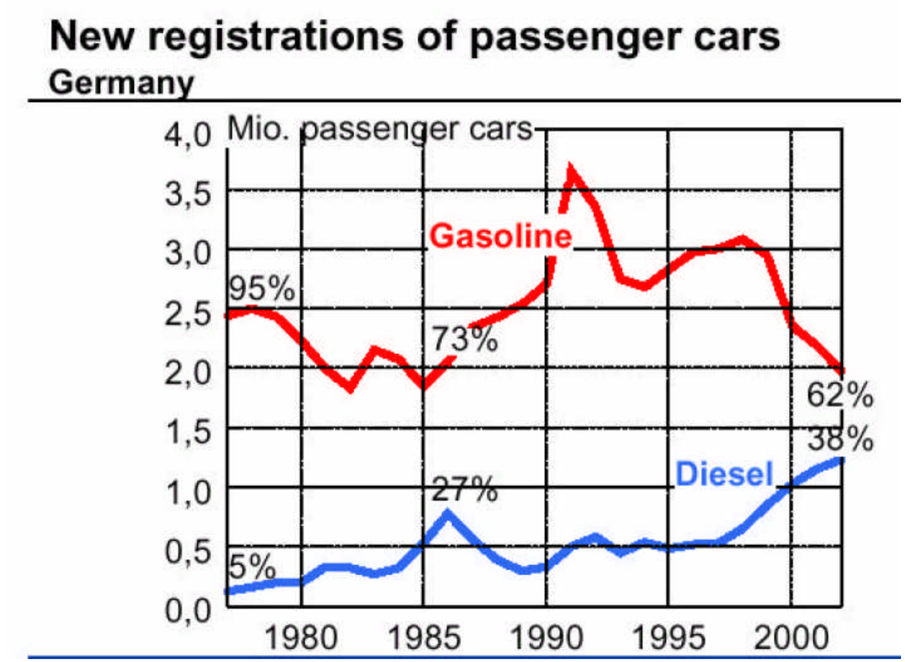


Figure 51. Conversion of CO, HC and NO_x over a three way catalyst as a function of the exhaust gas lambda value (monolith catalyst with 62 cells cm^{-2}, three-way formulation with Pt: 1.42 $g\,l^{-1}$, Rh: 0.28 $g\,l^{-1}$), fresh; engine bench test A/F scan at 623 K exhaust gas temperature; space velocity 60 000 $Nl\,l^{-1}\,h^{-1}$; dynamic conditions frequency 1 Hz; amplitude 0.5 A/F).



Environmental Catalysis: Mobile Sources (II)

- oxidation and NO_x-reduction catalysts for diesel fueled compression ignition engines
- becomes more important with “dieselization of fuels”



Environmental Catalysis: Stationary Sources

- Cleaning of exhaust gases from stationary sources (power plants, nitric acid plants, waste incineration)

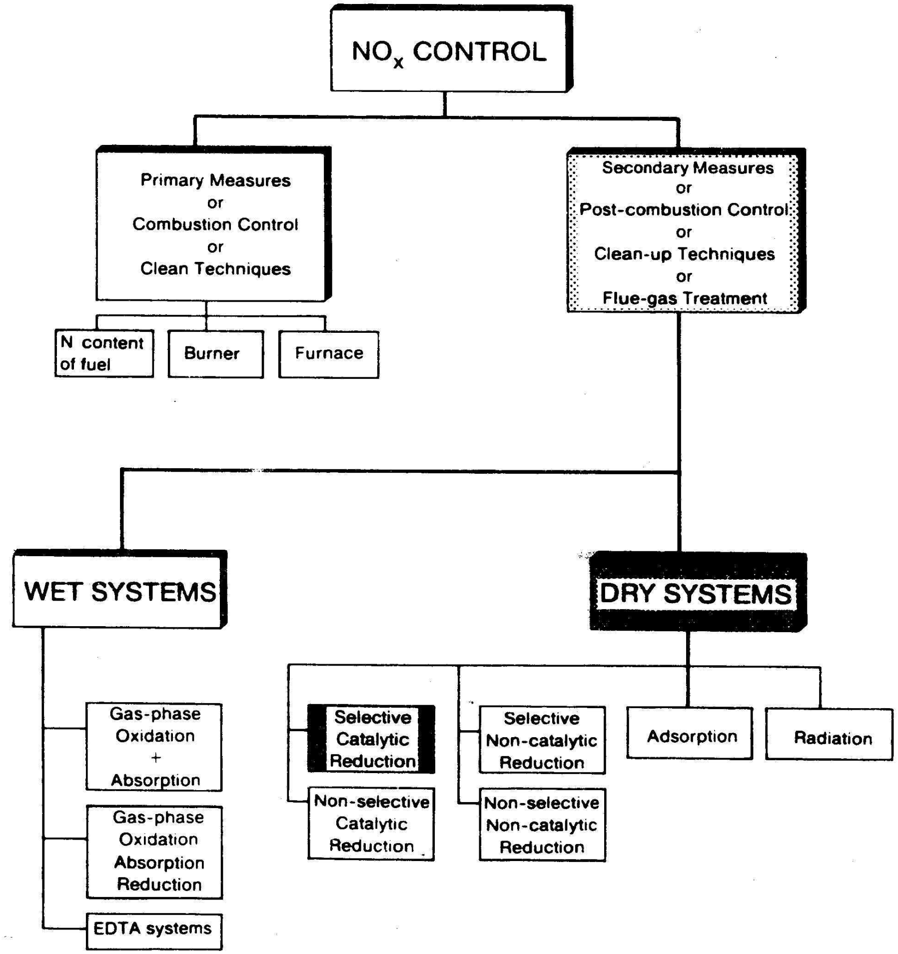


Fig. 3
Available techniques to decrease the emission of NO_x.

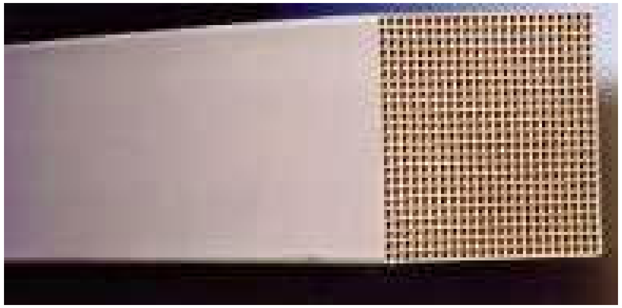
Environmental Catalysis: SCR

- Reduction of NO_x with NH_3

$$4NO + 4NH_3 + O_2 \quad \rightarrow \quad 4N_2 + 6H_2O$$

$$6NO_2 + 8NH_3 \quad \rightarrow \quad 7N_2 + 12H_2O$$

- V_2O_5 (MoO_3/WO_3) supported on TiO_2 catalysts



honeycomb or plate catalysts

Environmental Catalysis: Combustion

Catalytic Combustion

as primary (emissions prevention) control

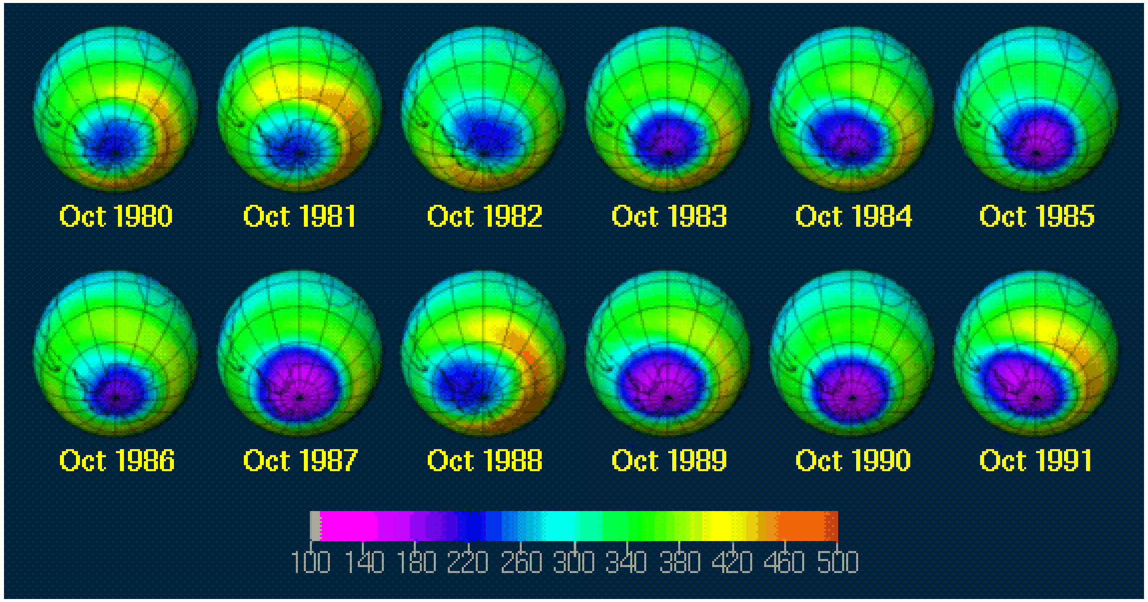
or secondary emission (emissions clean-up) control

- catalytic combustion takes place without a flame and at lower temperatures than conventional flame combustion; lower temperature means less NO_x
- removal of volatile organic compounds (VOCs) from industrial exhausts gases

Environmental Catalysis: CFCs

Chlorofluorohydrocarbon (CFC) destruction

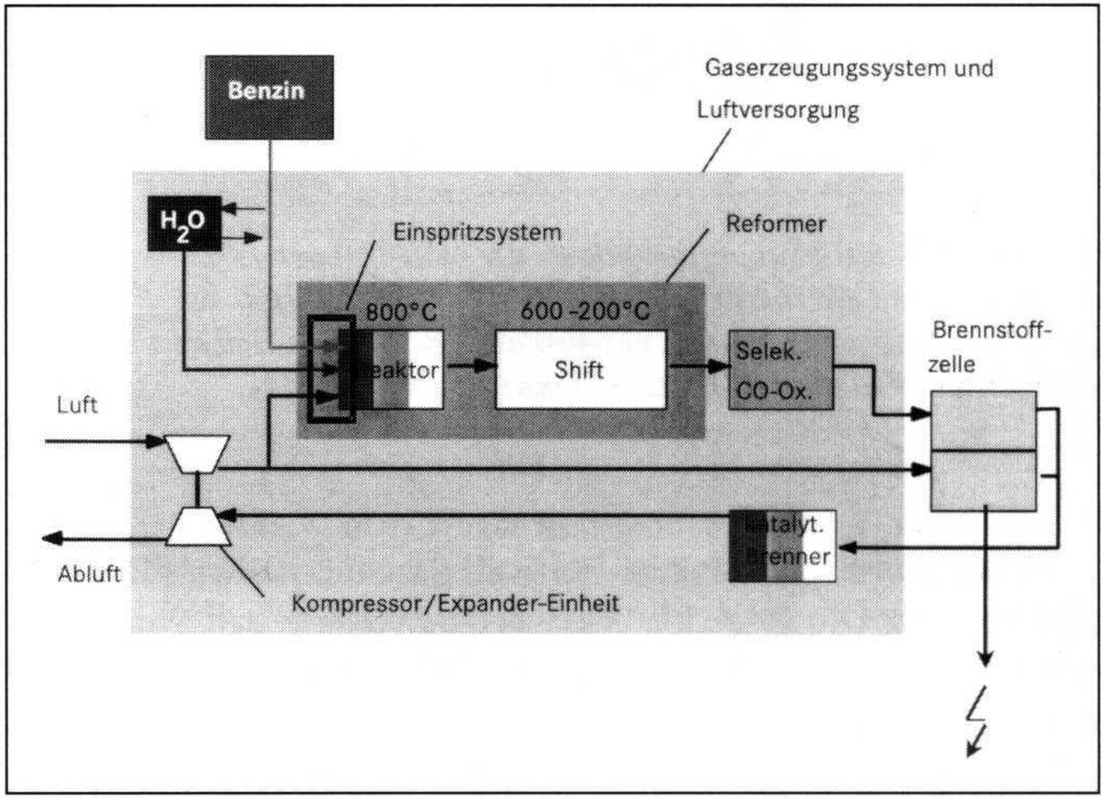
- CFCs were used for refrigeration, air conditioning, cleaning, firefighting etc.
- but: ozone layer depletion



Catalysis in Fuel Cells (28.01.05)

in fuel cell applications, catalysts may be used to

- catalyze the reaction of the fuels at the electrodes (mostly H_2 and O_2)
- reform different fuels (methanol, gasoline) to H_2
- clean the obtained H_2 (mostly from CO)
- catalytic combustion



Where catalysts are at work…(I)

Satellite maneuvering for path correction

- ❖ Catalytic decomposition of hydrazine
- ❖ Catalyst: Iridium supported on stabilized gamma-Al_2O_3 (Shell 405)

$$3N_2H_4 \rightarrow 4NH_3 + N_2$$

$$3N_2H_4 \rightarrow 6H_2 + 3N_2$$

$$N_2H_4 + 4NH_3 \rightarrow 8H_2 + 3N_2$$

- ❖ propulsion of satellite through pressure release , hot gases (exothermic reaction)

Where catalysts are at work…(II)

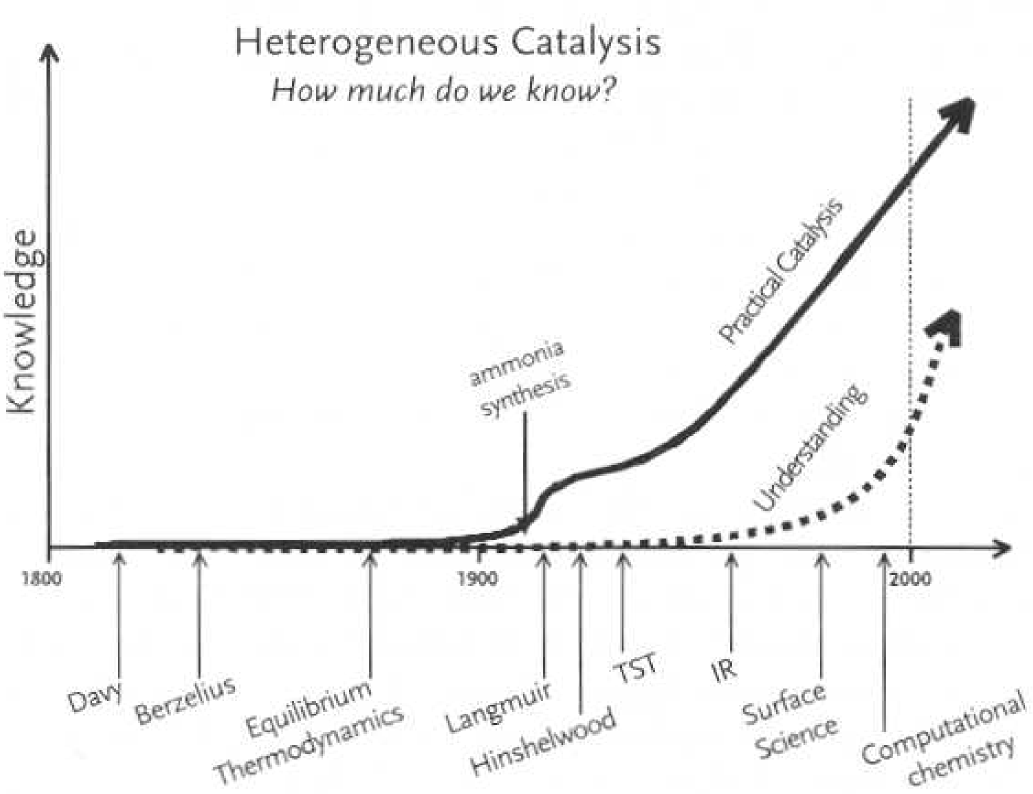
- self-cleaning oven

  oven walls contain oxidation catalyst (Ce_2O_3)

→ there are multiple applications!

How Well Do We Understand Catalysis?

- catalytic applications are much more advanced than understanding



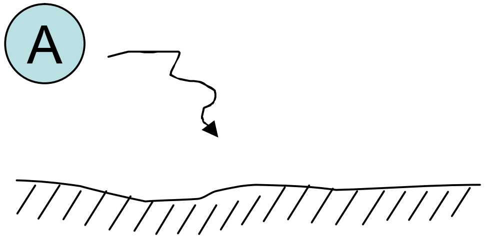
Chorkendorff, Niemantsverdriet 2003

Empirical Knowledge

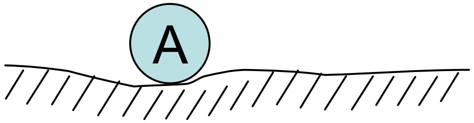
Catalyst	Transformation	Examples
Metals	hydrogenation, dehydrogenation	Fe, Ni, Pt, Ag, Ru
Semiconducting oxides	oxidation	NiO, ZnO mixed oxides
Insulating oxides	dehydration	Al_2O_3, SiO_2, MgO
Acids	polymerization, isomerization cracking, alkylation	HF, H_3PO_4, H_2SO_4, SiO_2/ Al_2O_3, zeolites

catalysts are developed empirically (trial and error) with input from experience

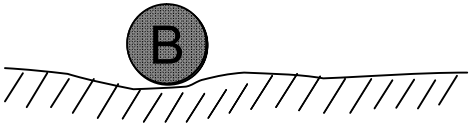
Reaction Steps in Heterogeneous Catalysis



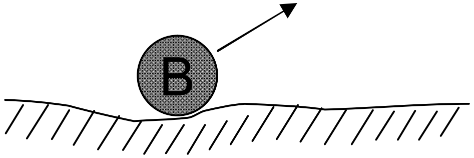
1. Diffusion of reactant to catalyst



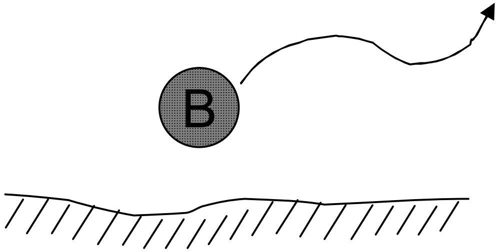
2. Adsorption of reactant on catalyst surface



3. Reaction

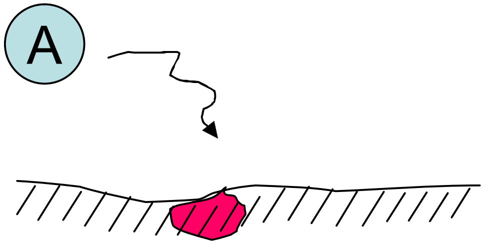


4. Desorption of products from catalyst surface



5. Diffusion of products away from catalyst

Heterogeneous Catalysis



- this picture is vague and very schematic
- what is the reaction mechanism?
- is the entire catalyst surface catalytically active?

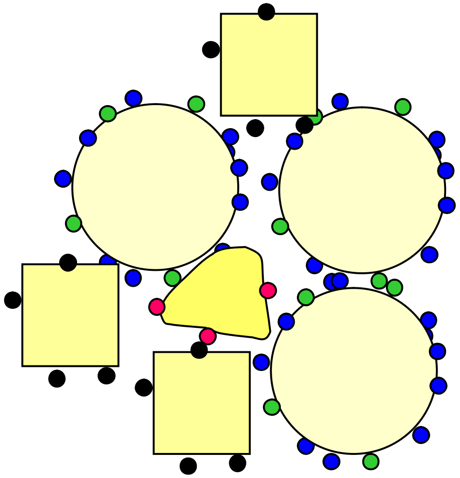
Concept of Active Sites

Hugh Stott Taylor 1925

- “only a small fraction of the surface is active”
- “the amount of surface which is catalytically active is determined by the reaction catalyzed”

H.S. Taylor, Proc. Roy. Soc. A108 (1925) 105-111

A “Real” Solid Catalyst



● Active site (for a particular reaction) one or more atoms in a particular configuration

- ❖ Catalyst materials and surface are not homogeneous
- ❖ Active sites may be few and very difficult to identify

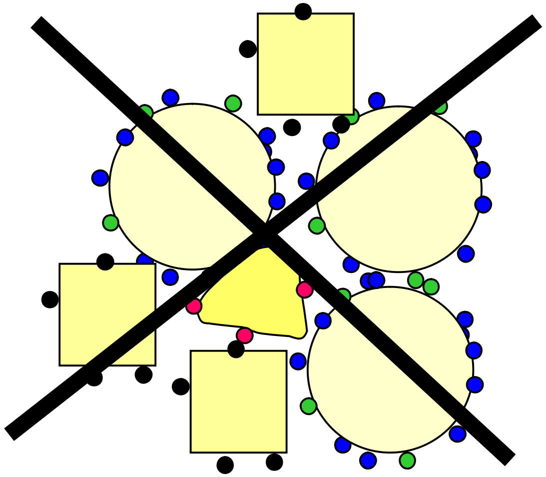
Catalysis Research: Motivation

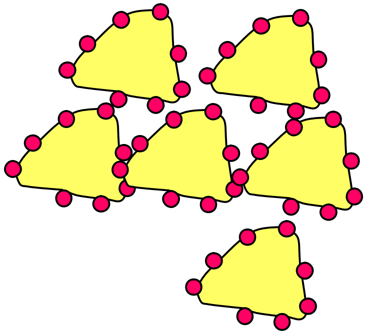
Fundamental understanding

- ❖ active site
- ❖ reaction mechanism

Targeted synthesis

- ❖ Goal: once active structure is known synthesis can be targeted





knowledge-derived catalyst synthesis

Catalysis Research: Motivation

Structure-activity relationships

- correlate catalyst properties and activity

Further goal (or a side effect)

- identify a quantity that is correlated to the catalytic activity but can be measured in a much simpler and faster way

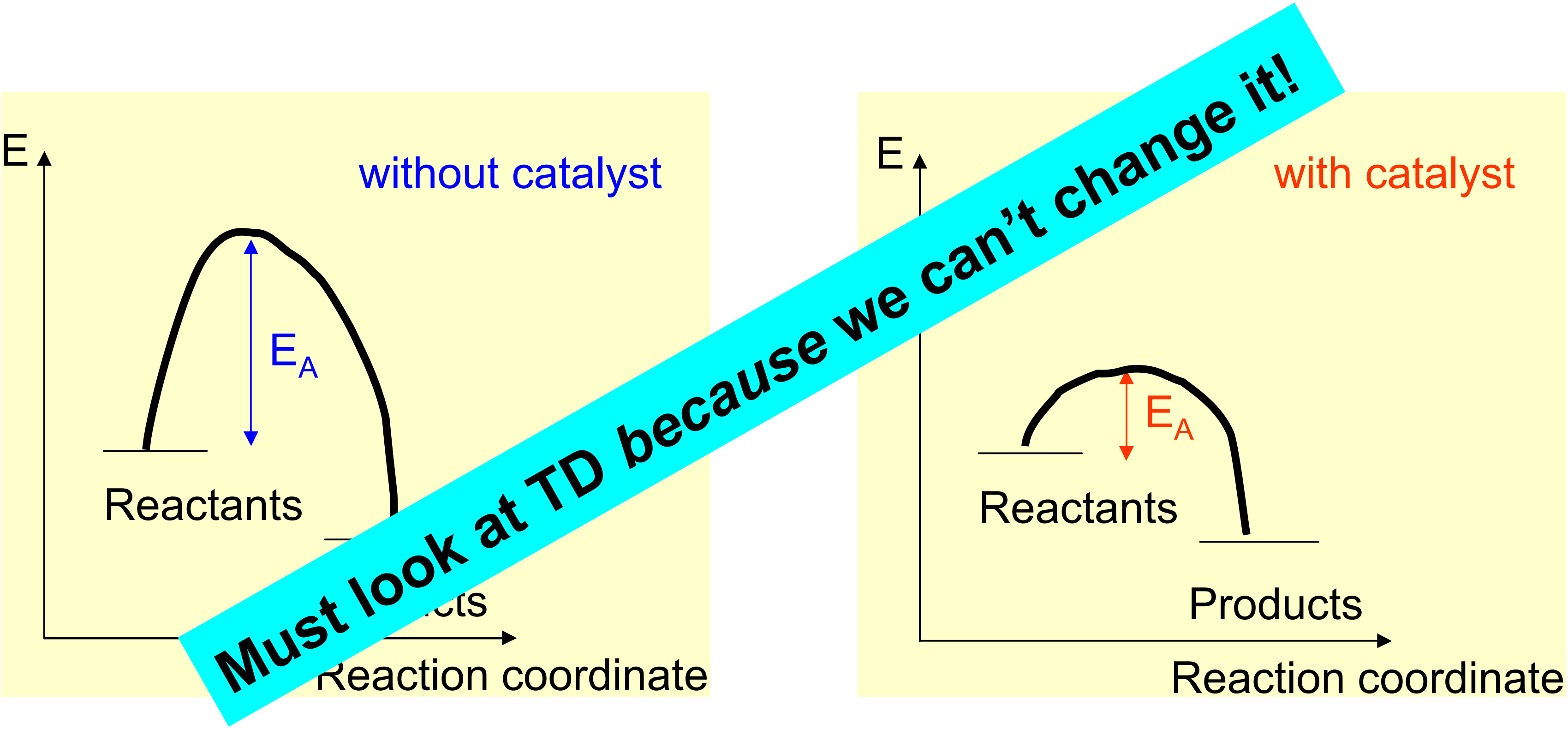
Catalysis Research: Strategy

- ….before any experiment:
  consider reaction thermodynamics
- selection of materials, model systems
- preparation of catalysts and models
- catalytic tests, kinetic experiments and modeling
- various characterization methods suitable
  for real catalysts and models
- in situ methods
- theory and catalysis

topics of this class

Thermodynamics - Motivation

- Why look at TD? …can’t change it anyway by catalysis



Must look at TD because we can’t change it!

Target Reaction – Quantities to Look at

- Enthalpy of reaction $\Delta_r H$
  exothermic / endothermic
  $\Delta_r H$ of side reactions
- Free Enthalpy (Gibbs Energy) $\Delta_r G$
  exergonic / endergonic
- Equilibrium Constant K: Equilibrium Limitations
- Change of Temperature and Pressure (variables)

Enthalpy of Reaction

- Determines reactor setup
- Determines catalyst formulation / dilution
  “hot spots” / heating power
  isothermal operation in the lab
- Enthalpy of side reactions
  parallel / secondary reactions

Enthalpy of Reaction, $\Delta_r H$

- Reaction enthalpy needs a reaction equation!!!

$$\nu_A A + \nu_B B \rightarrow \nu_C C + \nu_D D$$

- Calculate from enthalpies of formation of products and reactants

$$\Delta_r H° = \sum_{i=1}^{L} \nu_i \Delta_f H_i°$$

$\Delta_r H°$: standard enthalpy of reaction
$\Delta_f H°$: standard enthalpies of formation
v_i: stoichiometric factors, positive for products, negative for reactants

Things to Watch in Calculations…..

- Stoichiometric factors
- Standard conditions
- State of the matter (solid, liquid, gaseous)
- Which data are available (sometimes only enthalpy of combustion, $\Delta_c H°$)

1. CRC Handbook of Thermophysical and Thermochemical Data
   Eds. David R. Lide, Henry V. Kehiaian, CRC Press Boca Raton New York 1994
   FHI library 50 E 55
2. D'Ans Lax
   Taschenbuch für Chemiker und Physiker
   Ed. C. Synowietz , Springer Verlag 1983
   FHI library 50 E 54

State of the Matter

- Formation of benzene at 298.15 K

$$6\,C(s) + 3\,H_2(g) \rightarrow C_6H_6(g)$$

$$6\,C(s) + 3\,H_2(g) \rightarrow C_6H_6(l)$$

$\Delta_f H° = 82.93$ kJ mol^{-1}

$\Delta_f H° = 49.0$ kJ mol^{-1}

- Enthalpy of evaporation of benzene?

  $\Delta_{vap} H° = 30.8$ kJ mol^{-1} at 80°C

Partial Oxidation of Propene

- Oxidation of propene to acrolein

$$C_3H_6 + \frac{1}{2}O_2 \rightarrow C_3H_4O + H_2O$$

$\Delta_r H°$ = ??? kJ mol^{-1}

- Only enthalpy of combustion, $\Delta_c H°$, of acrolein is given

$$C_3H_4O(g) + 3.5O_2(g) \rightarrow 3CO_2(g) + 2H_2O(g)$$

$\Delta_c H°$ = -1633 kJ mol^{-1}

Enthalpies of combustion are easily determined quantities (e.g. from quantitative combustion in a bomb calorimeter)

Use Hess's Law

$$3C(s) + 2H_2(g) + 4O_2(g) \rightarrow 3CO_2(g) + 2H_2O(g)$$ $\Delta_cH°$ = -1754 kJ mol^{-1}

$$- \quad C_3H_4O(l) + 3.5O_2(g) \rightarrow 3CO_2(g) + 2H_2O(g)$$ $\Delta_cH°$ = -1633 kJ mol^{-1}

$$3C(s) + 2H_2(g) + 0.5O_2(g) \rightarrow C_3H_4O(l)$$ $\Delta_fH°$ = -121 kJ mol^{-1}

Enthalpy is a State Function

Partial vs. Total Oxidation

- Oxidation of propene to acrolein

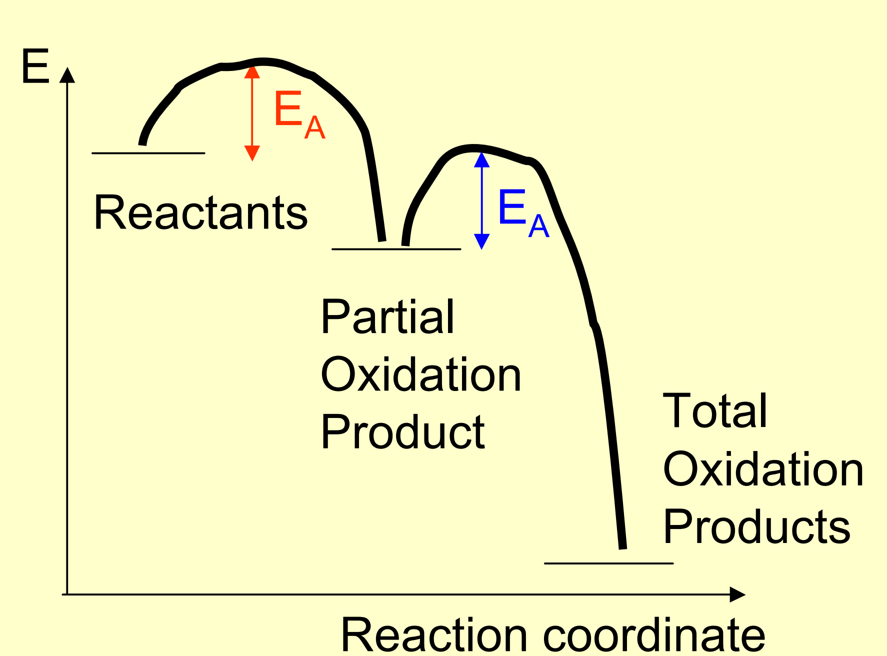
$$C_3H_6 + \frac{1}{2}O_2 \rightarrow C_3H_4O + H_2O$$

$\Delta_r H° = -427\ \text{kJ mol}^{-1}$

- Oxidation of acrolein to CO_2

$$C_3H_4O(g) + 3.5O_2(g) \rightarrow 3CO_2(g) + 2H_2O(g)$$

$\Delta_c H° = -1633\ \text{kJ mol}^{-1}$



Dehydrogenation vs. Oxidative Dehydrogenation

- Dehydrogenation of isobutane to isobutene

$$i-C_4H_{10}(g) \rightarrow i-C_4H_8(g) + H_2(g)$$

$\Delta_r H^\circ$ = 117 kJ mol^{-1}

- Oxidative dehydrogenation of isobutane to isobutene

$$i-C_4H_{10}(g) + 0.5O_2(g) \rightarrow i-C_4H_8(g) + H_2O(g)$$

$\Delta_r H^\circ$ = -124 kJ mol^{-1}

Oxidative Dehydrogenation: Thermodynamic Traps

- Combustion of isobutene

$$i - C_4H_8(g) + 6O_2(g) \rightarrow 4CO_2(g) + 4H_2O(g)$$

$\Delta_c H° = - 2525 \text{ kJ mol}^{-1}$

Nevertheless, the oxidative dehydrogenation of isobutene is in commercial operation (CrO_3/Al_2O_3 or supported Pt catalyst)

HCN Synthesis

- BMA or Degussa process:

$$CH_4(g) + NH_3(g) \rightarrow HCN(g) + 3H_2(g)$$

$\Delta_r H°$ = + 256 kJ mol^{-1}

runs at 1300°C, process needs large amount of energy

- Andrussow process

$$CH_4(g) + NH_3(g) + 1.5O_2(g) \rightarrow HCN(g) + 3H_2O(g)$$

$\Delta_r H°$ = - 474 kJ mol^{-1}

→ Both possibilities (oxidative/non-ox.) may be feasible

Isomerization

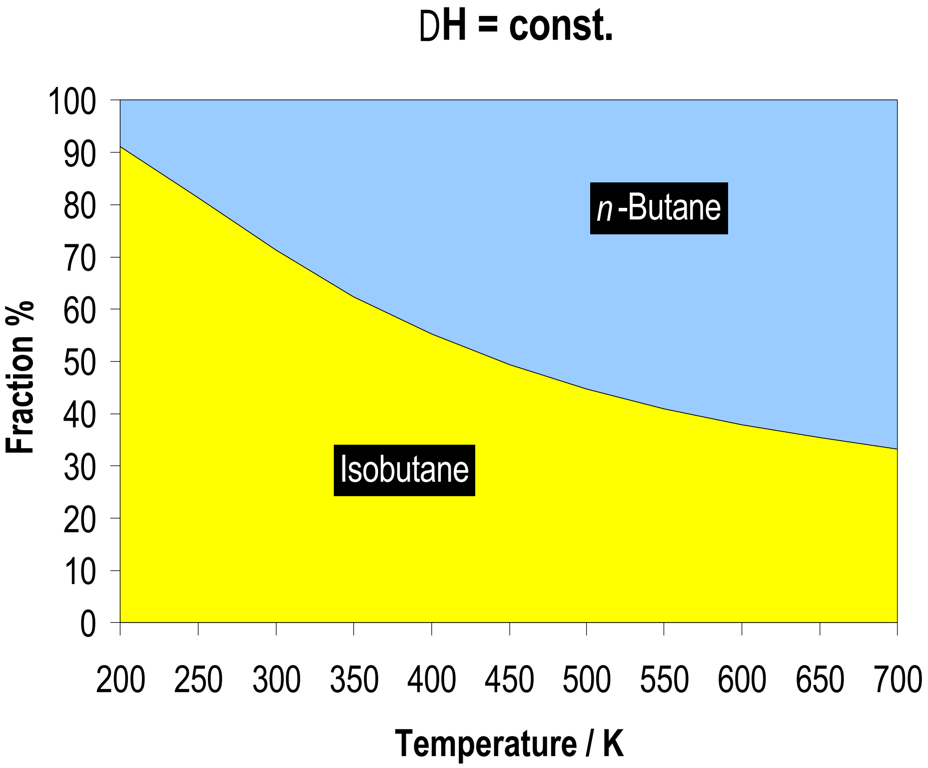
- Isomerization of butane

$$n-C_4H_{10}(g) \leftrightarrow i-C_4H_{10}(g)$$

$\Delta_r H° = - 7 \text{ kJ mol}^{-1}$

$\Delta_r S° = -15 \text{ J mol}^{-1}$

$\Delta_r G° = - 2.3 \text{ kJ mol}^{-1}$



Start your research by calculating the thermodynamics of your reaction!

The Catalytic „Activity“

“Activity”

- …is a vague term….

Conversion X (in %)

- the fraction of the reactant(s) that has been converted
- there can be conversion with respect to different reactants, e.g. oxidation reactions

Selectivity

Selectivity S (in%)

- relation between desired and undesired products
- e.g. moles of desired product/moles of all products

EXTREMELY IMPORTANT!

unconverted reactant can be recycled – a valuable reactant converted to unwanted side products is lost!

G.A. Somorjaia and Minchul Yang, Topics in Catalysis Vol. 24, Nos. 1–4, October 2003

Yield

Yield Y (in%)

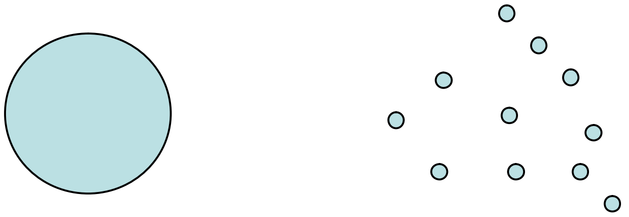
- the product of X and S

Space Time Yield (STY)

- differently defined for continuous and discontinuous operation
- continuous process:
  (feed x conversion x selectivity)/(reactor volume x time)
- discontinuous process:
  (input x conversion x selectivity)/(reactor volume x time of reaction)

Rates in Heterogeneous Catalysis

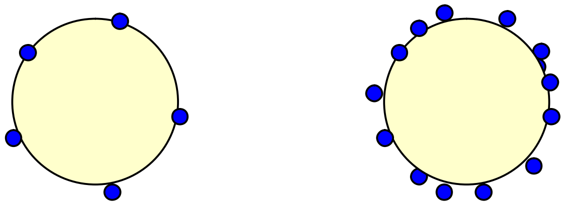
- Rate with respect to mass or surface area



$$\left[\frac{mol}{\min g_{catalyst}}\right]$$

$$\left[\frac{mol}{\min {m^2}_{catalyst\,surface}}\right]$$

Turn Over Frequency (1966)



low site density high site density

- Rate with respect to number of active sites

- Turnover frequency (TOF) is the number of molecules formed per active site per second (in a stage of saturation with reactant, i.e. a zero order reaction with respect to the reactant)

$$\left[\frac{molecules}{site\ s}\right]=\left[s^{-1}\right]$$

M. Boudart et al., J. Catal. 6 (1966) 92

TOF, TON, Catalysis

- TON

  Total number of product formed molecules per active site

  TON= TOF*catalyst life time

TON = 1	stoichiometric reaction
TON $\geq 10^2$	catalytic reaction
TON = 10^6-10^7	industrial application

- TON origins from enzyme kinetics, definitions vary

Examples for TOFs

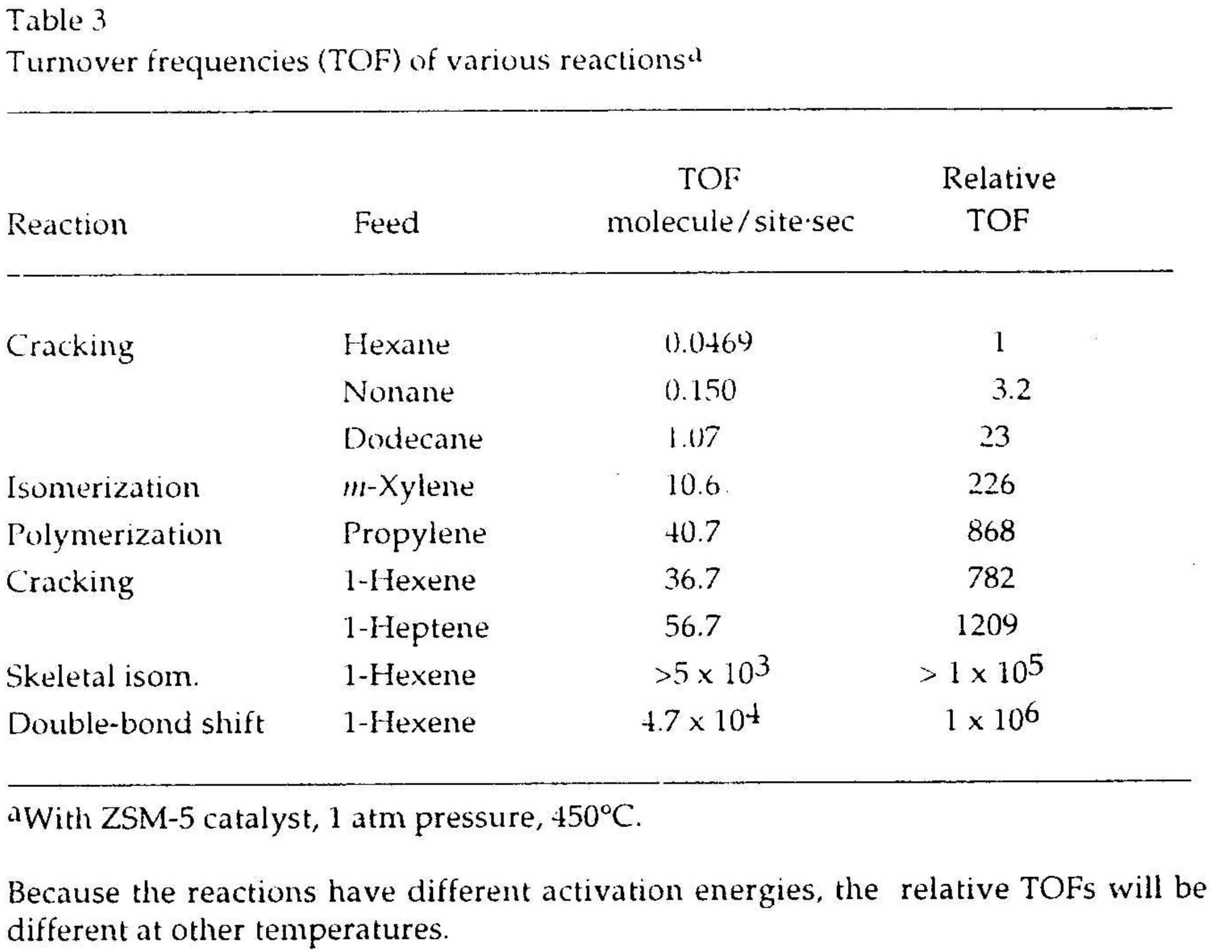


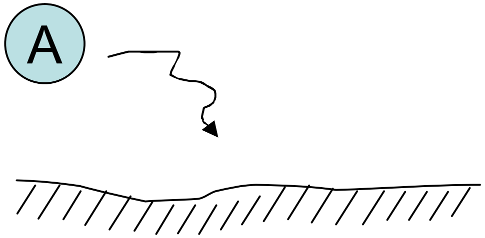
Table 3
Turnover frequencies (TOF) of various reactions[a]

Reaction	Feed	TOF molecule/site·sec	Relative TOF
Cracking	Hexane	0.0469	1
	Nonane	0.150	3.2
	Dodecane	1.07	23
Isomerization	*m*-Xylene	10.6	226
Polymerization	Propylene	40.7	868
Cracking	1-Hexene	36.7	782
	1-Heptene	56.7	1209
Skeletal isom.	1-Hexene	$>5 \times 10^3$	$> 1 \times 10^5$
Double-bond shift	1-Hexene	4.7×10^4	1×10^6

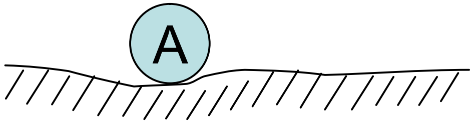
[a] With ZSM-5 catalyst, 1 atm pressure, 450°C.

Because the reactions have different activation energies, the relative TOFs will be different at other temperatures.

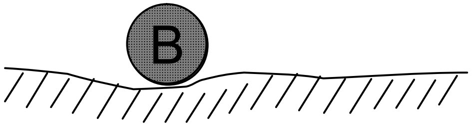
Reaction Steps in Heterogeneous Catalysis



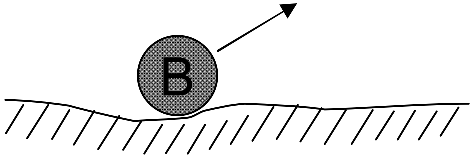
1. Diffusion of reactant to catalyst



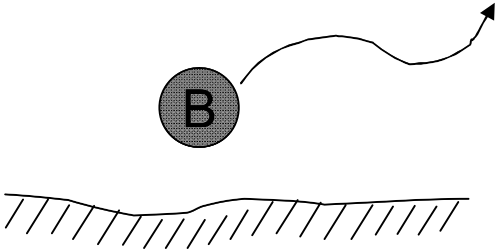
2. Adsorption of reactant on catalyst surface



3. Reaction

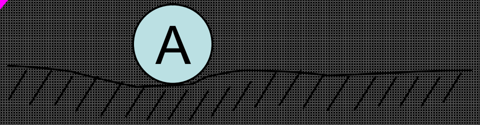


4. Desorption of products from catalyst surface



5. Diffusion of products away from catalyst

Reaction Steps in Heterogeneous Catalysis



2. Adsorption of reactant on catalyst surface