Introduction:
A Historical Approach to Catalysis

Modern Methods in Heterogeneous Catalysis

F.C. Jentoft, October 24, 2003

Outline - Part I

The phenomenon	Early catalytic processes The Döbereiner lighter (1823) Definition of “Catalysis” (1835)
Fundamental understanding of catalysis	Temperature dependence & activation energy Reaction rate & catalysis
Industrial catalysis	Fat hydrogenation Ammonia Synthesis

Outline - Part II

Heterogeneous / surface catalysis

- Adsorption (1916)
  - Adsorption isotherms and surface area
- Active Sites (1925)

Industrial catalysis

- New processes

The Schwab Handbook

Outline - Part III

Reaction mechanisms, rates & rate laws

Langmuir Hinshelwood / Eley Rideal mechanism
Turnover frequency
Structure sensitivity / insensitivity

Industrial & Environmental Catalysis

More processes (1950 - 1979)
Three-way converter

The Handbook of Heterogeneous Catalysis

Industrial & Environmental Catalysis

Recent processes (1980 – 199x)

?

Early Catalytic Processes

-6000	Beer brewing by malting procedure	Malt enzymes
-3000	Wine making by fermentative conversion of grape juice sugars	Yeast a.o.
-2000	Alcohol(ic drinks) by fermentation of various carbohydrate sources	Yeast a.o.
	Bread and other leavened bakery products by carbon dioxide and alcohol	Baker's yeast
	Vinegar (acetic acid) by aerobic fermentation of ethanol	Acetobacter
-800	Cheese making (coagulation) by casein hydrolysis with calf stomach extract	Calf rennet (chymosin)
1850	Yogurt formation from milk by lactose to lactic acid conversion	Lactobacillus

Kieboom, Moulijn, van Leeuwen, van Santen, Stud. Surf. Sci. Catal. 123 (1999)3-28

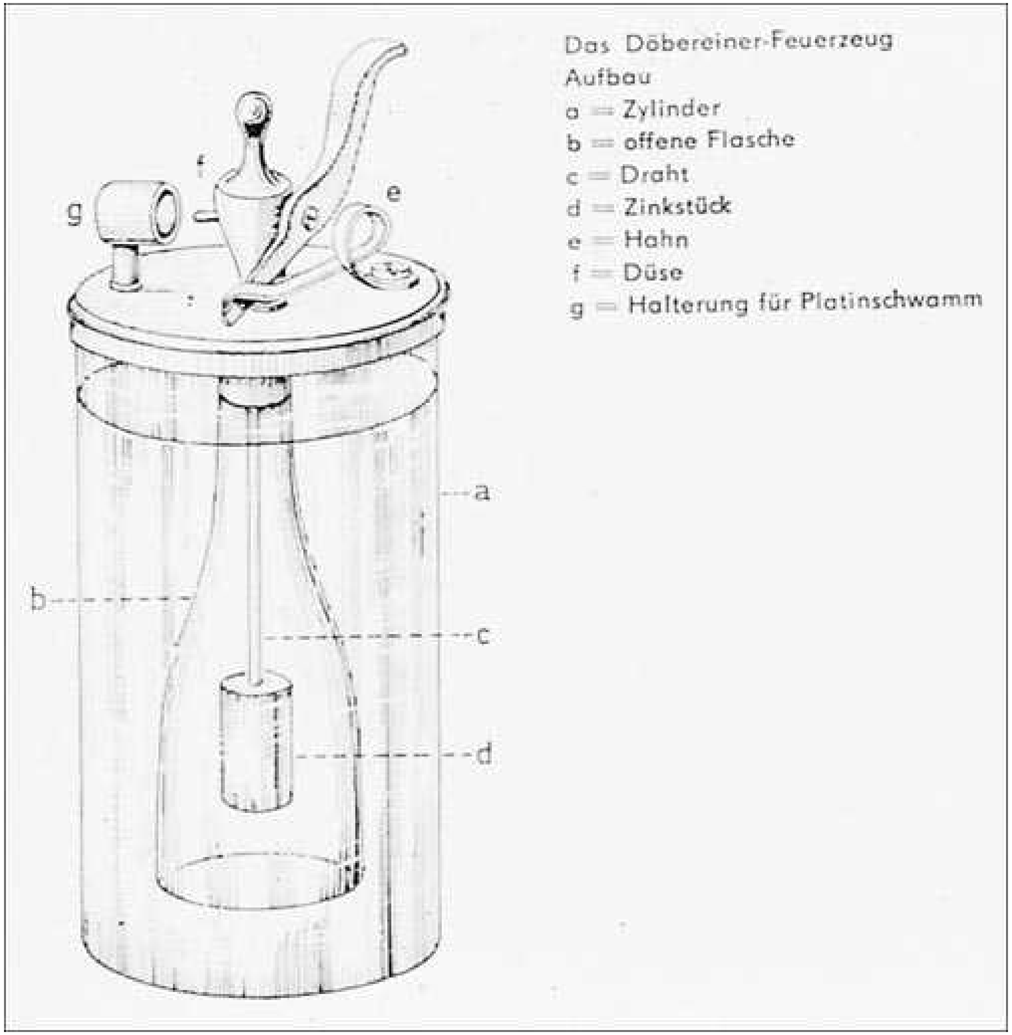
Johann Wolfgang Döbereiner (1780-1849)

- apothecarian, studied chemistry later
- 1810 Chair for Chemistry and Pharmacy in Jena
- exchanged letters with Goethe (and gave him one of his lighters as a gift)

Döbereiner's Experiments

- obtained several kg platinum from Duke Karl August in Weimar
- 1816 conversion of alcohol to acetic acid / Pt wire
- 1832 conversion of alcohol to acetic aldehyde / Pt wire

The Döbereiner Lighter



Das Döbereiner-Feuerzeug
Aufbau
a = Zylinder
b = offene Flasche
c = Draht
d = Zinkstück
e = Hahn
f = Düse
g = Halterung für Platinschwamm

- ❖ Production of H_2 from Zn and sulfuric acid (25%)
- ❖ ignited at Pt sponge on top

The Döbereiner Lighter

- 20,000 lamps in use in Germany and England within 5 years
- In 1829 a Berlin manufacturer offered "… as a pleasant and useful Christmas present a lighting machine, outfitted with platinum, elegant, clean, and sturdily constructed, with Chinese and other decoration, insensitive to wetness and cold…."
- replaced by safety match

Humphry Davy (1778-1829)

- 1817 reactions of coal-gas and oxygen on Pt, Pd (active) and Co, Ag, Au, Fe (ineffective) wires
- developed safety lamp for miners
- detected anesthetic effect of N_2O (breathing it became the highlight of social events)

Michael Faraday (1791-1867)

- studied reactions of hydrogen and oxygen at the surface of platina plates
- these phenomena are "dependent upon natural conditions of gaseous elasticity *combined with the attractive forces possessed by many bodies, especially those which are solid*"

Eilhard Mitscherlich (1794-1863)

- studied oriental languages, PhD on Persian texts
- discovered isomorphism “an equal number of atoms, combined in the same way, produce the same crystal forms: the crystal form does not depend on the nature of the atoms, but only on their number and mode of combination”
- synthesized benzene

Mitscherlich’s Experiments

- showed (1834) that a mixture of ether and water distills out of a mixture of alcohol and dilute sulfuric acid, the latter acting as a dehydrating agent
- enunciated the ”Contact Theory", whereby certain chemical reactions can take place only in the presence of certain other substances
- applied the theory to explain fermentation, the contact in this process being yeast which is necessary for the conversion of sugar into alcohol.

E. Mitscherlich, Ann. Phys. Chem. 31 (1834) 273-282

Jöns Jakob Berzelius (1779–1848)

- studied medicine and chemistry in Uppsala, Sweden
- worked as medical doctor, became Professor of Medicine and Pharmacy, 1810 Professor of Chemistry and Pharmacy
- stopped teaching in 1829 to devote himself to research

Berzelius' Experiments

- developed system of chemical symbols
- measured atomic weights
- wrote chemistry textbook

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

Justus von Liebig (1803-1873)

- German apothecarian, studied in Bonn, Erlangen, Paris
- 1824 Professor of Philosophy in Gießen
- 1825 Professor of Chemistry in Munich
- wrote letters to Wöhler and Berzelius (and others)

Reactions on Berzelius’ “Catalytic Power”

Liebig to Wöhler, June 2, 1837:

Weisst Du denn nicht, dass die Esel, welche in Deutschland Bücher schreiben, seine [Berzelius] katalytische Kraft ohne zu prüfen, annehmen und unsern Kindern in den Kopf setzen werden, weil sie bequem und die Faulheit begünstigend ist?

Don’t you know that the idiots who write books in Germany will adopt his [Berzelius’] catalytic power without scrutinization, and will teach it to our children because it [the catalytic power] is convenient and favors the laziness?

Berzelius und Liebig, Ihre Briefe von 1831-1845, Hrsg. T. Reschke, WiSoMed 1978, Göttingen

Svante August Arrhenius (1859-1927)

- Swedish chemist and physicist
- Nobel Prize in Chemistry 1903 "in recognition of the extraordinary services he has rendered to the advancement of chemistry by his electrolytic theory of dissociation"

Arrhenius’ Experiments

- reaction rate of inversion of cane sugar (saccharose) through acids
- discussed the temperature dependence of rate
- only a fraction of the molecules reacts, namely the "active" molecules
- energy is needed to obtain these active molecules

S. Arrhenius, Z. Phys. Chem. 4 (1889) 226-248
K.J. Laidler, J. Chem. Ed. 61 (1984) 494-498

Arrhenius Theory (1889)

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

$$K = \frac{k_1}{k_{-1}}$$

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta H}{RT^2}$$

van’t Hoff’s Equation

$$\left(\frac{\partial \ln k_1}{\partial T}\right) - \left(\frac{\partial \ln k_{-1}}{\partial T}\right) = \frac{\Delta H}{RT^2}$$

$$\left(\frac{\partial \ln k_1}{\partial T}\right) = \frac{E_1}{RT^2} \qquad \left(\frac{\partial \ln k_{-1}}{\partial T}\right) = \frac{E_{-1}}{RT^2} \qquad E_1 - E_{-1} = \Delta H$$

Arrhenius Theory

$$\ln k = \ln A - \frac{E_A}{RT}$$

- With E the activation energy in kJ mol^{-1}
  A the frequency factor
- Plot of ln k vs. 1/T gives a slope of $-E_A/R$
  which allows the calculation of the activation energy
- A rule of thumb: the rate doubles for 10 K rise in temperature

Example for Arrhenius Plot

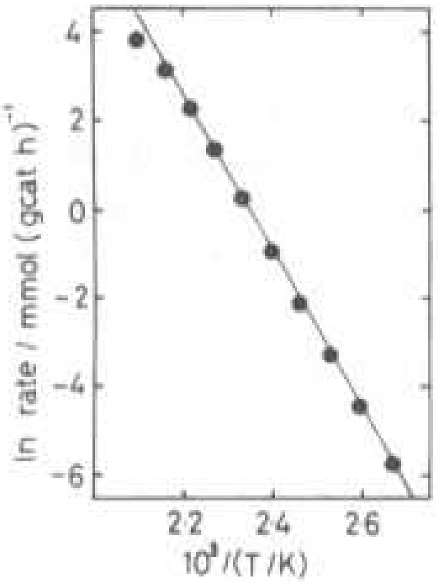


Fig. 2. Arrhenius plot for hydrogenolysis of n-butane over 1% Ru/Al_2O_3 (H_2:n-butane = 10:1) [1].

2 different slopes may indicate change in mechanism or change from reaction to diffusion control

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Temperature-Dependence of Rate Constant

- Berthelot, 1862

$$k = Ae^{DT} \qquad \ln k = A' + DT$$

- Arrhenius 1889, van’t Hoff 1884, Kooij 1893

$$k = Ae^{-\frac{B}{T}} \qquad \ln k = A' - \frac{B}{T}$$

- Harcourt & Esson, 1895

$$k = AT^{c} \qquad \ln k = A' + C \ln T$$

Wilhelm Ostwald (1853-1932)

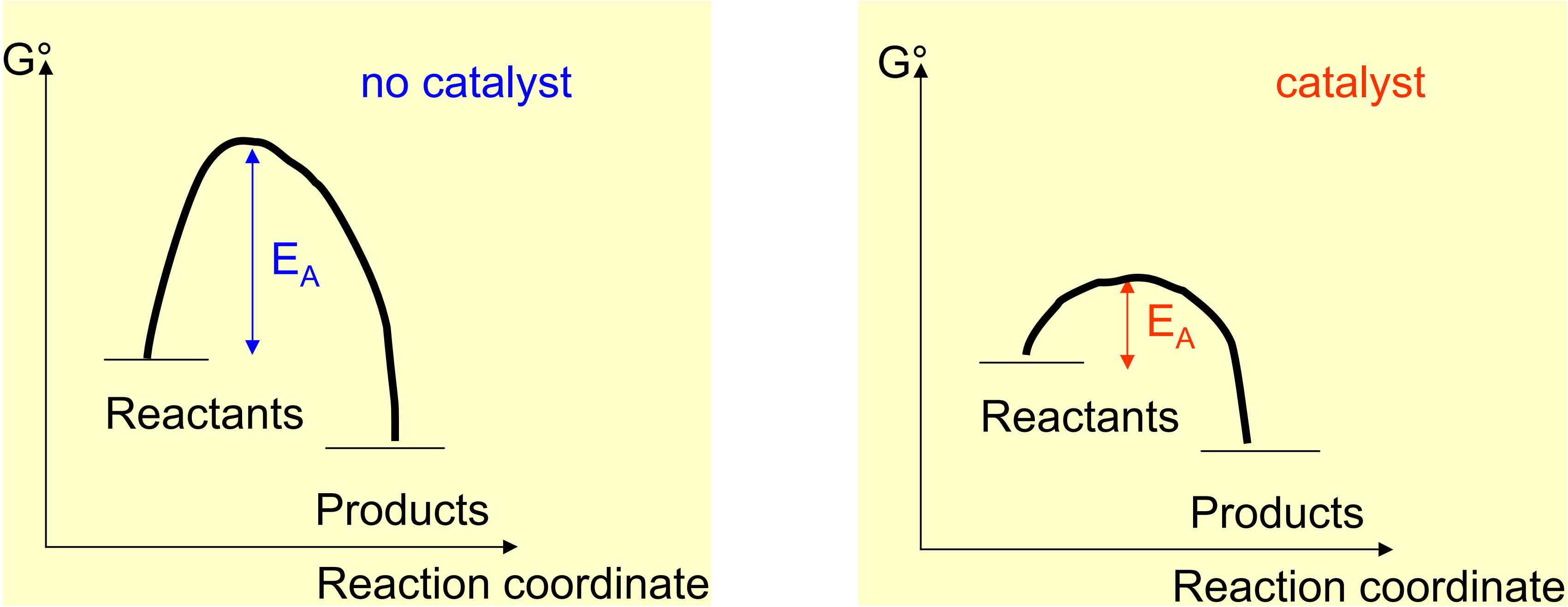
- Studied chemistry, 1881 Professor of Chemistry in Riga, 1887 Professor of Physical Chemistry in Leipzig
- Nobel Prize in Chemistry 1909 "in recognition of his work on catalysis and for his investigations into the fundamental principles governing chemical equilibria and rates of reaction"

Ostwald’s Definition of Catalysis (1894)

- in reply to a definition given by Stohmann (Z. Biol. 31 (1894) 364-391)
- "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"

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

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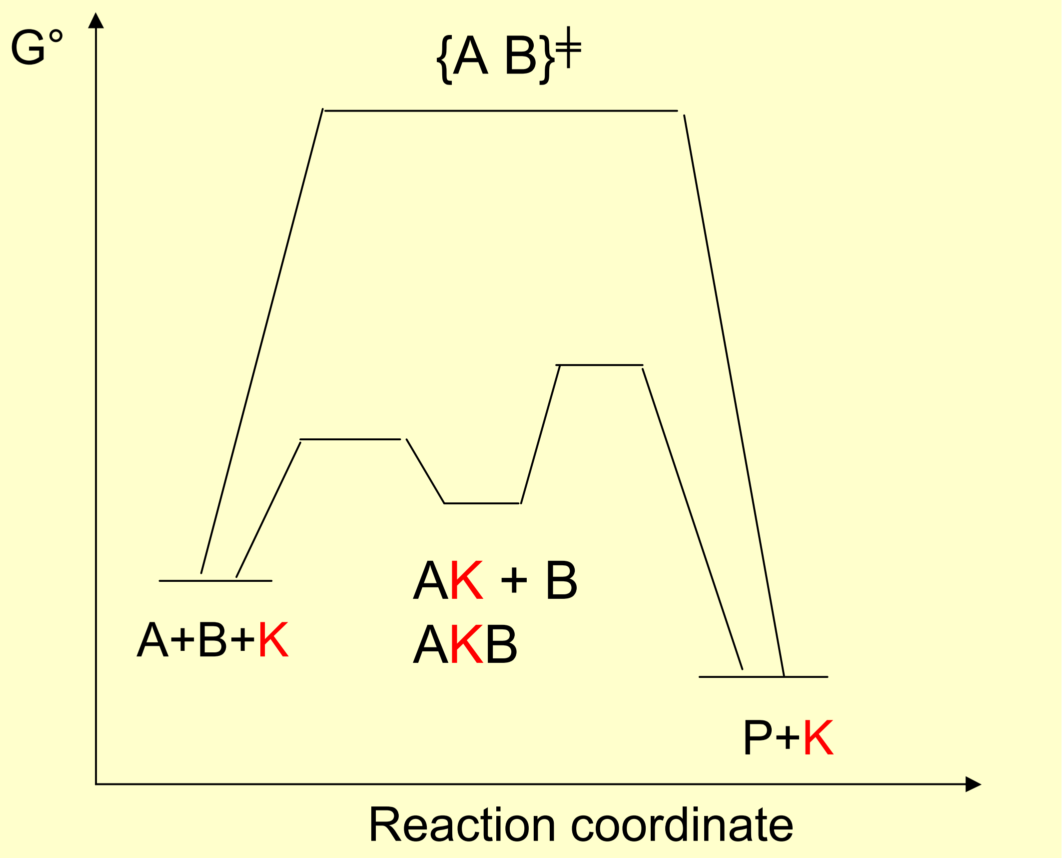
Catalysis



- Catalyst and reactants may form intermediates

Early Industrial Catalysis

1750	H_2SO_4 lead chamber process (homogeneous process)	NO, NO_2
1870	SO_2 oxidation	Pt
1880	Deacon process (Cl_2 from HCl)	$ZnCl_2/CuCl_2$
1885	Claus process (H_2S and SO_2 to S)	Bauxite
1900	Fat hydrogenation	Ni
	Methane from syngas	Ni
1910	Coal liquefaction	Fe
	Upgrading coal liquids	WS_2
	Ammonia synthesis (Haber-Bosch)	Fe/K
	NH_3 oxidation to nitric acid	Pt

Paul Sabatier (1854 - 1941)

- Nobel Prize in Chemistry 1912 together with V. Grignard "for his method of hydrogenating organic compounds in the presence of finely disintegrated metals whereby the progress of organic chemistry has been greatly advanced in recent years"
- Margarine!

Ammonia Synthesis

$$3\ H_2 + N_2 \rightleftharpoons 2\ NH_3$$

- measurements of the equilibrium (Haber, 1904/05)
- experiments with high pressure by Le Chatelier
- Nernst suggests to use high pressure to Haber
- osmium as a first catalyst (1909)
- by 1912: 6500 tests with 2500 catalysts
- by 1919: 10000 tests 4000 catalysts

A. Mittasch, Die Geschichte der Ammoniaksynthese, VCh Weinheim, 1951
M.W. Roberts, Catalysis Lett. 67,1 (2000)

Ammonia Synthesis

Großer Kontaktofen
Werk Oppau

- Fe/K catalyst
- double-wall system

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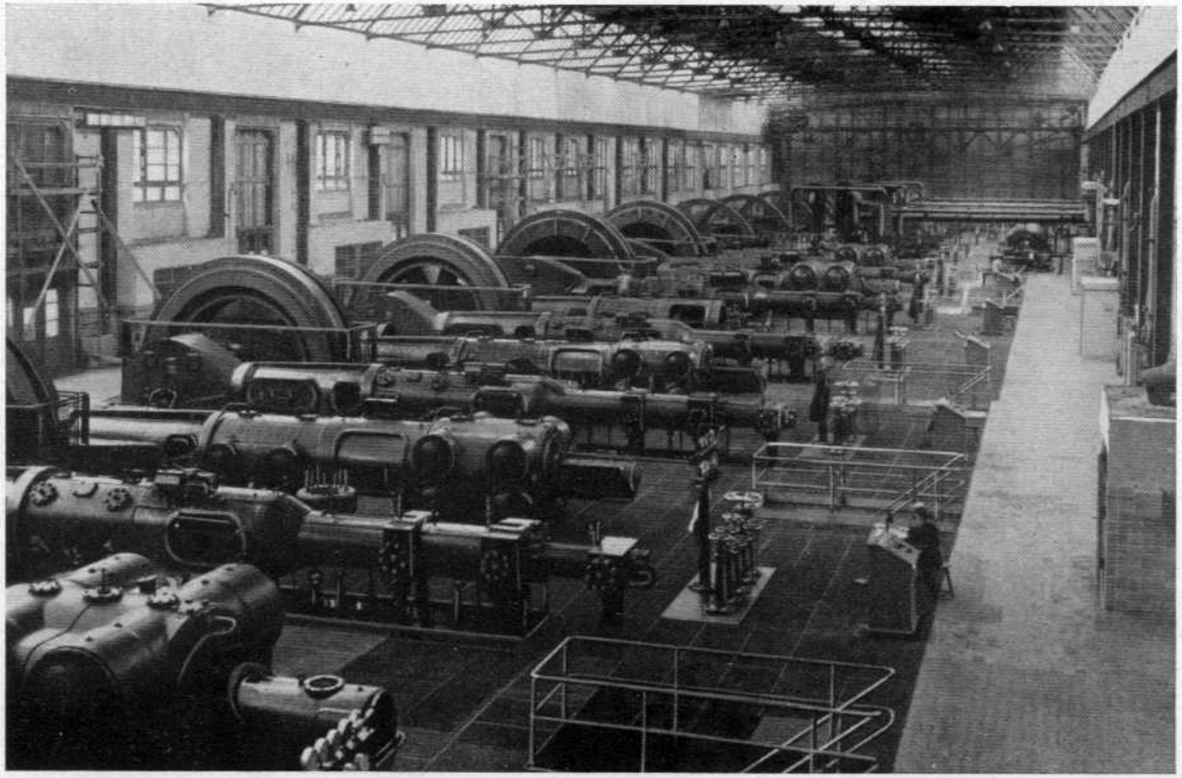
Ammonia Synthesis



Kompressor-Anlage
Werk Oppau

Fritz Haber (1868-1934)

- Nobel Prize in Chemistry 1918
  “for the synthesis of ammonia from its elements"

Carl Bosch (1874-1940)

- Nobel Prize in Chemistry 1931 together with F. Bergius
  "in recognition of their contributions to the invention and development of chemical high pressure methods"

Outline - Part II

Heterogeneous / surface catalysis

Adsorption (1916)

Adsorption isotherms and surface area

Active Sites (1925)

Industrial catalysis

New processes

The Schwab Handbook

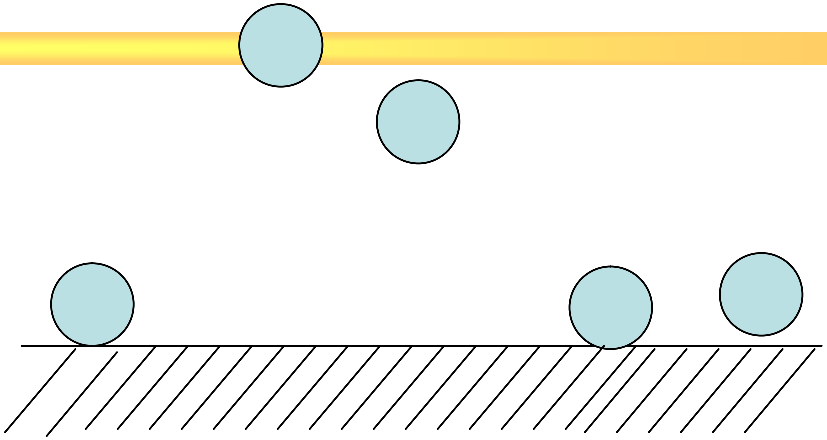
Irving Langmuir (1881-1957)

- ❖ Metallurgical engineer, physical chemist (worked with Nernst)
- ❖ Researcher at General Electric
- ❖ Nobel Prize in Chemistry 1932 "for his discoveries and investigations in surface chemistry"

Langmuir's Experiments

- Filaments in gases, invention of gas-filled incandescent lamp, discovery of atomic hydrogen
- Monoatomic films on W and Pt filaments
- Oil films on water
- proposed that single crystal surfaces be studied (1922)!

Adsorption Theory by Langmuir (1916)



rate of adsorption

$$r_{ad} = a p (1 - q)$$

rate of desorption

$$r_{des} = a' q$$

p= pressure
θ = coverage

$$q = \frac{N}{N_M}$$

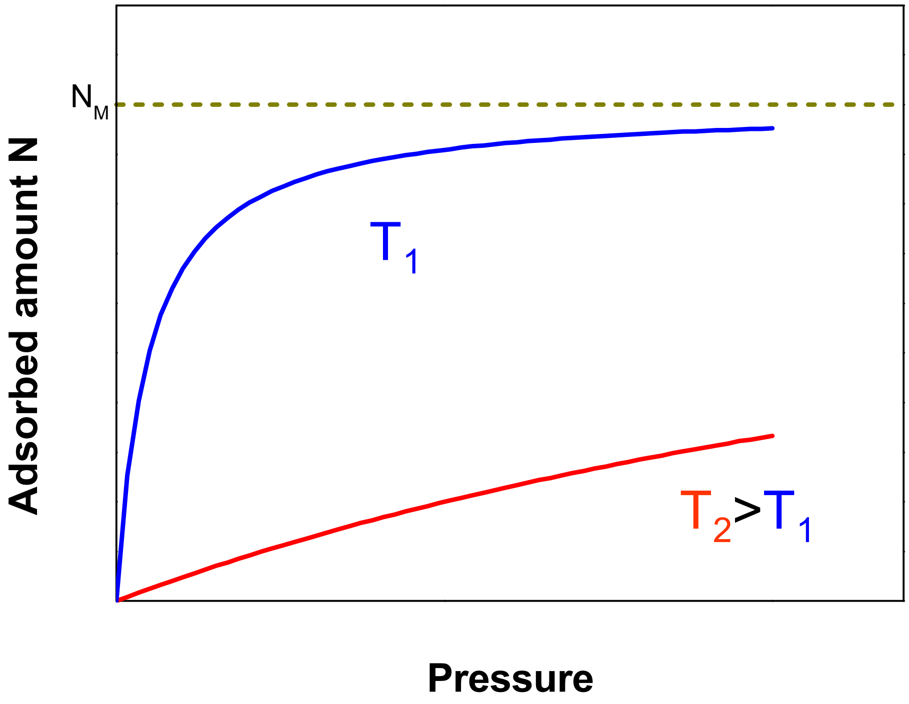
rates are equal in equilibrium, with b = α'/ α

$$N = \frac{N_M p}{b + p}$$

Langmuir isotherm

I. Langmuir, J. Am .Chem. Soc. 38 (1916) 2221

Langmuir Isotherm



- ❖ monolayer only
- ❖ all sites are equal
- ❖ at small pressures: N ~ p

Adsorption Isotherms

- Freundlich isotherm 1923 (logarithmic decrease of adsorption enthalpy with increasing coverage)

$$N = ap^{1/m}$$

- Temkin isotherm....

The BET Method (1938)

- BET-isotherm 1938 - Brunauer, Emmett, Teller
  multilayers: 1st layer chemisorption, others physisorption

$$\frac{P/P_0}{n(1-P/P_0)} = \frac{1}{n_m C} + \frac{C-1}{n_m C}\frac{P}{P_0}$$

- important for surface area measurement by physisorption

S. Brunauer, P. H. Emmett, E. Teller, JACS, 60 (1938) 309

Hugh Stott Taylor (1890-1974)

- Professor of Physical Chemistry in Princeton
- deducted from the small amount of CO adsorbed on quartz that “only a small fraction of the surface is active”

Taylor’s Observations (1925)

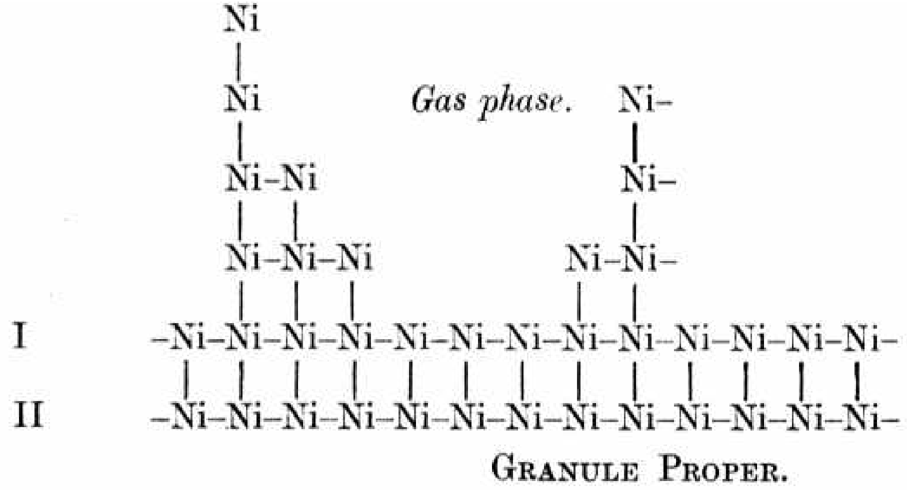


Fig. 1.—Diagrammatic representation of a portion of a Granule Surface in Cross-section.

❖ discussed the CO adsorption on Ni, “a concept of metal atoms detached to varying extents from the normal crystal lattice“ - “capable of adsorbing several molecular reactants”

Taylor’s Observations (1925)

- “the amount of surface which is catalytically active is determined by the reaction catalyzed”
- active sites / centers

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

Reaction Steps in Heterogeneous Catalysis

- Diffusion of reactant to catalyst
- Adsorption of reactant on catalyst surface
- Reaction
- Desorption of products from catalyst surface
- Diffusion of products away from catalyst

The Schwab Handbook

"Handbuch der Katalyse" 1940 - 1957

Ed. Georg Maria Schwab

1. Allgemeines und Gaskatalyse (General & Gas Catalysis)
2. Katalyse in Lösungen (Catalysis in Solutions)
3. Biokatalyse

4.-6. Heterogene Katalyse I-III

7.-8. Katalyse in der organischen Chemie I-II

“Intermediates” or Catalysis & Society

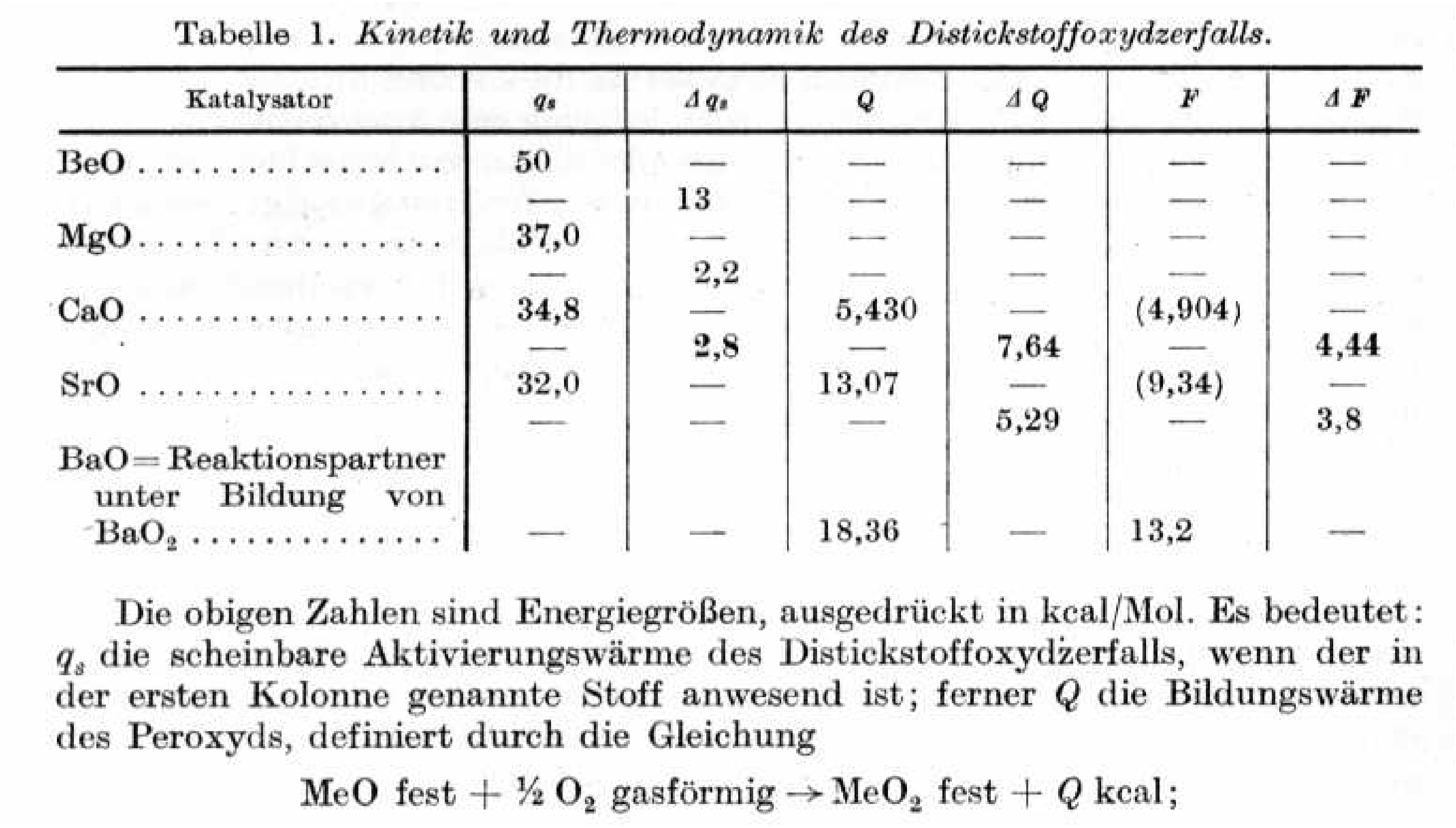


Tabelle 1. *Kinetik und Thermodynamik des Distickstoffoxydzerfalls.*

Katalysator	q_s	Δq_s	Q	ΔQ	F	ΔF
BeO	50	—	—	—	—	—
	—	13	—	—	—	—
MgO	37,0	—	—	—	—	—
	—	2,2	—	—	—	—
CaO	34,8	—	5,430	—	(4,904)	—
	—	2,8	—	7,64	—	4,44
SrO	32,0	—	13,07	—	(9,34)	—
	—	—	—	5,29	—	3,8
BaO = Reaktionspartner unter Bildung von BaO_2	—	—	18,36	—	13,2	—

Die obigen Zahlen sind Energiegrößen, ausgedrückt in kcal/Mol. Es bedeutet: q_s die scheinbare Aktivierungswärme des Distickstoffoxydzerfalls, wenn der in der ersten Kolonne genannte Stoff anwesend ist; ferner Q die Bildungswärme des Peroxyds, definiert durch die Gleichung

$$\mathrm{MeO}\ \text{fest} + \tfrac{1}{2}\,O_2\ \text{gasförmig} \rightarrow \mathrm{MeO_2}\ \text{fest} + Q\ \text{kcal};$$

- compares it to “Einundzwanzig” (17+4, Black Jack, Trop)

G.F. Hüttig, in Handbuch der Katalyse, Vol. 6, Ed. G.M. Schwab, Springer, 1943

The Sabatier principle

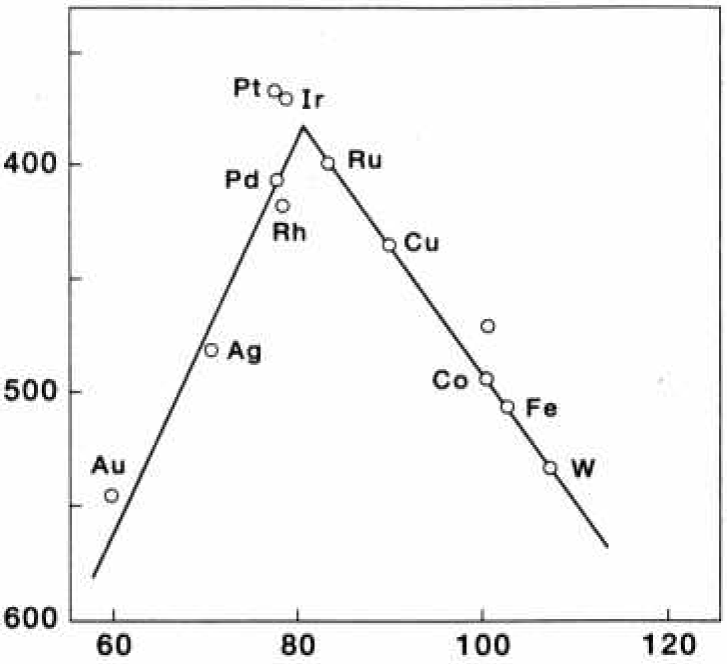
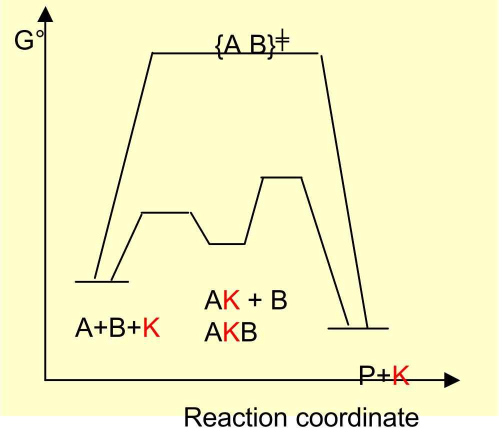
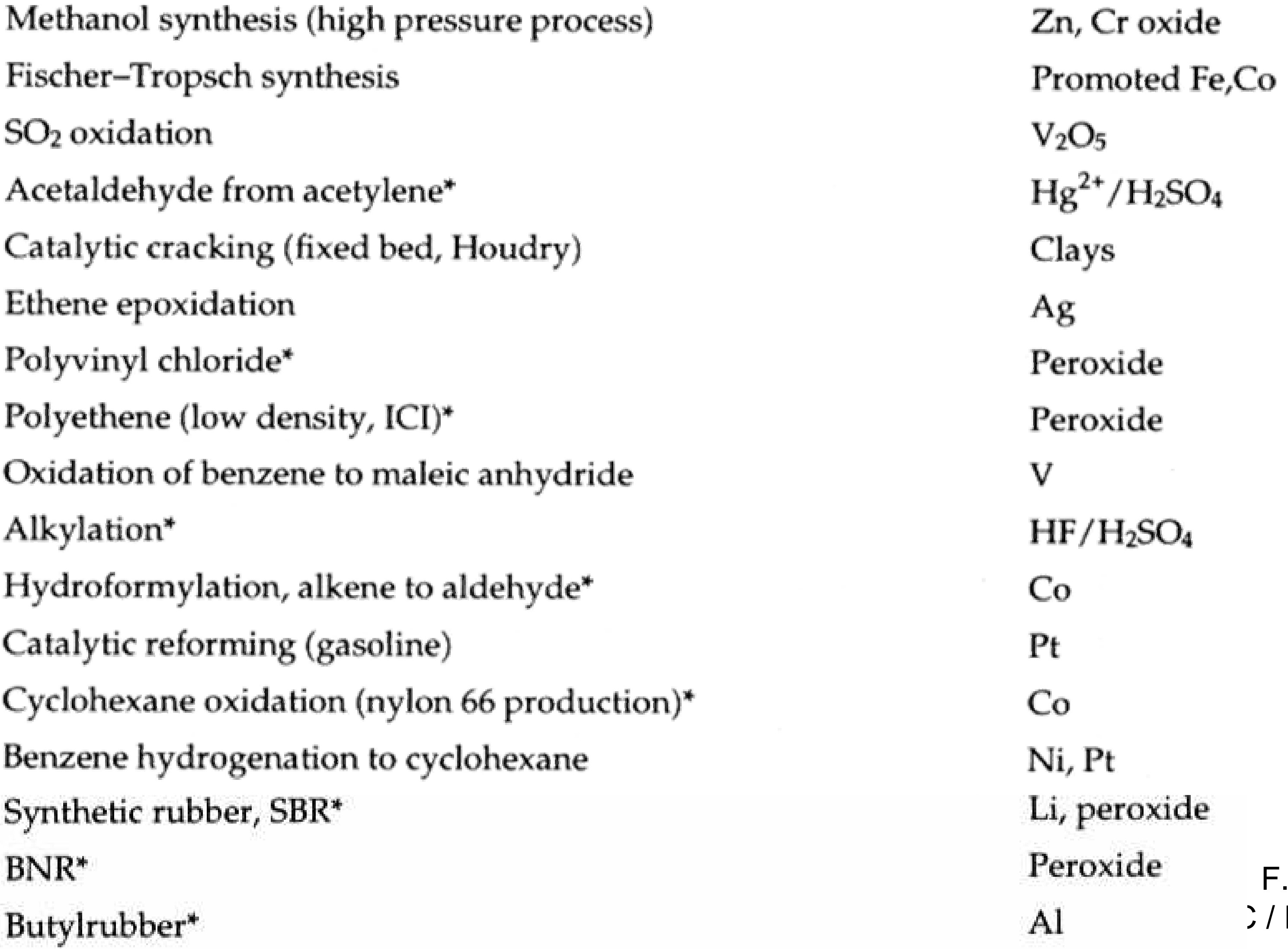


Figure 2. Sabatier's principle: volcano curves T_v/K. The temperature at which the rate of decomposition of formic acid (vertical axis) has a set value v, correlated with the heat of formation of the bulk metallic formate, in kcal per equivalent (horizontal axis) [17].

- Catalyst must have affinity to reactant
- ....but not too much!



Industrial Chemistry



1920	Methanol synthesis (high pressure process)	Zn, Cr oxide
	Fischer–Tropsch synthesis	Promoted Fe,Co
	SO_2 oxidation	V_2O_5
	Acetaldehyde from acetylene*	Hg^{2+}/H_2SO_4
1930	Catalytic cracking (fixed bed, Houdry)	Clays
	Ethene epoxidation	Ag
	Polyvinyl chloride*	Peroxide
	Polyethene (low density, ICI)*	Peroxide
	Oxidation of benzene to maleic anhydride	V
	Alkylation*	HF/H_2SO_4
1940	Hydroformylation, alkene to aldehyde*	Co
	Catalytic reforming (gasoline)	Pt
	Cyclohexane oxidation (nylon 66 production)*	Co
	Benzene hydrogenation to cyclohexane	Ni, Pt
	Synthetic rubber, SBR*	Li, peroxide
	BNR*	Peroxide
	Butylrubber*	Al

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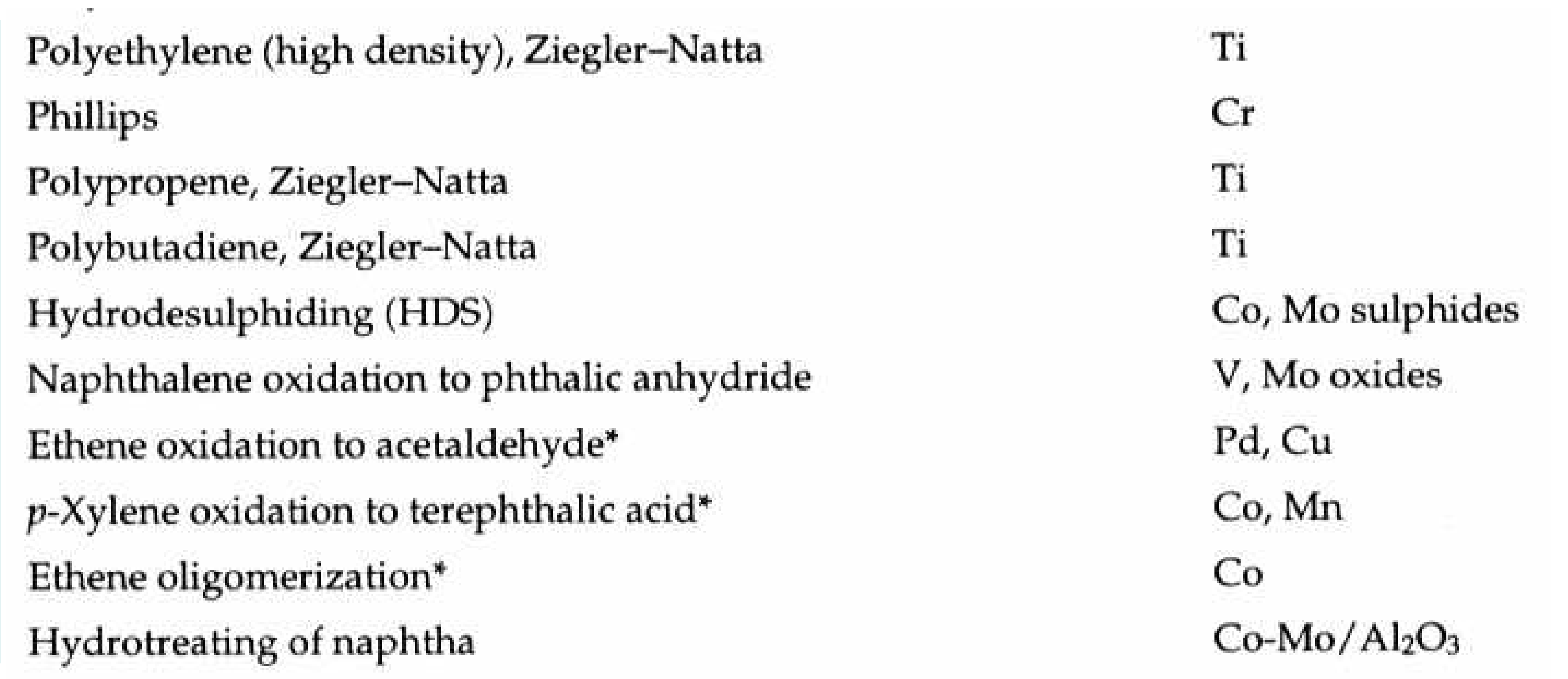
New Processes

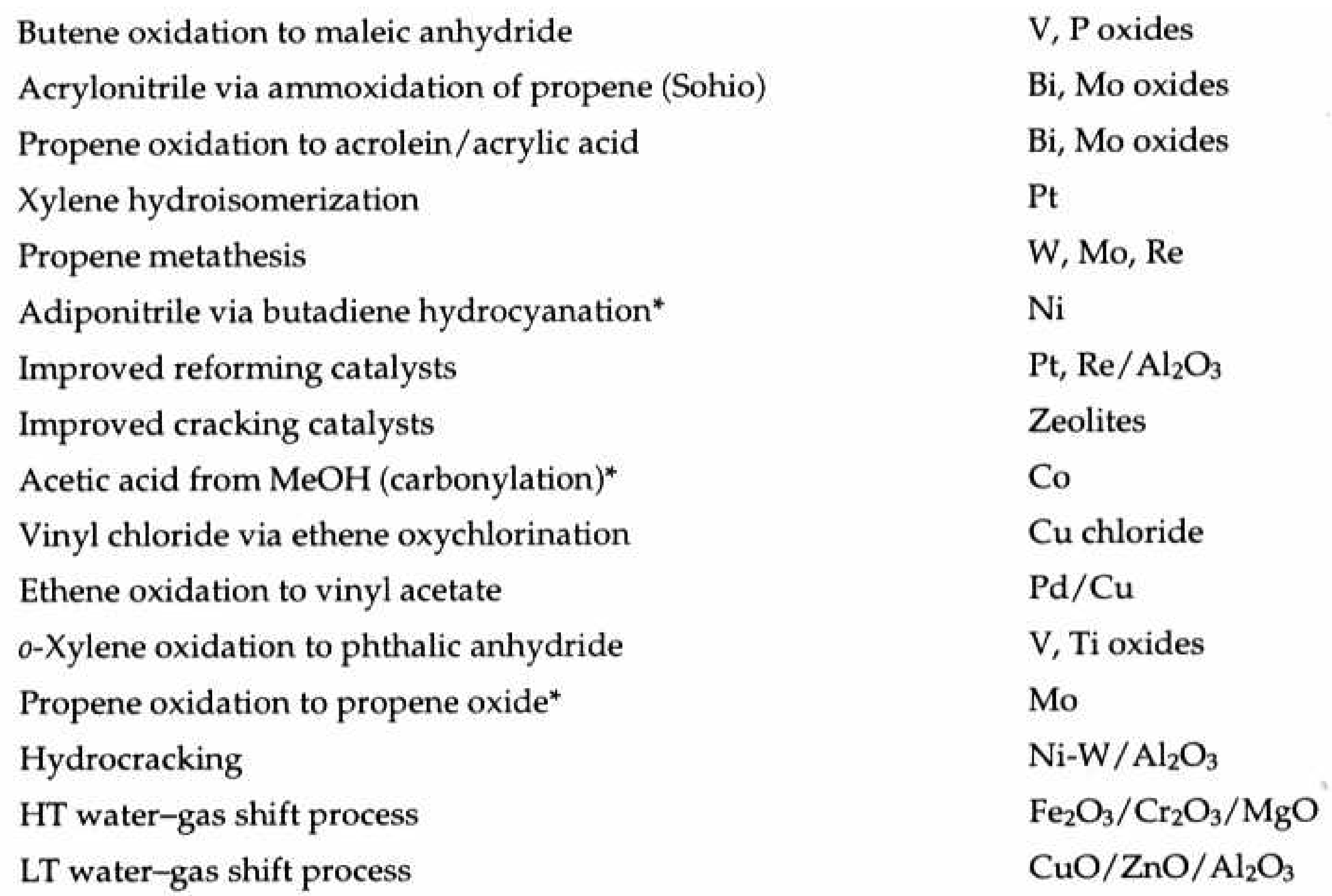


1950	Polyethylene (high density), Ziegler–Natta	Ti
	Phillips	Cr
	Polypropene, Ziegler–Natta	Ti
	Polybutadiene, Ziegler–Natta	Ti
	Hydrodesulphiding (HDS)	Co, Mo sulphides
	Naphthalene oxidation to phthalic anhydride	V, Mo oxides
	Ethene oxidation to acetaldehyde*	Pd, Cu
	p-Xylene oxidation to terephthalic acid*	Co, Mn
	Ethene oligomerization*	Co
	Hydrotreating of naphtha	Co-Mo/Al_2O_3

Ziegler (1898-1973) and Natta (1903-1979)

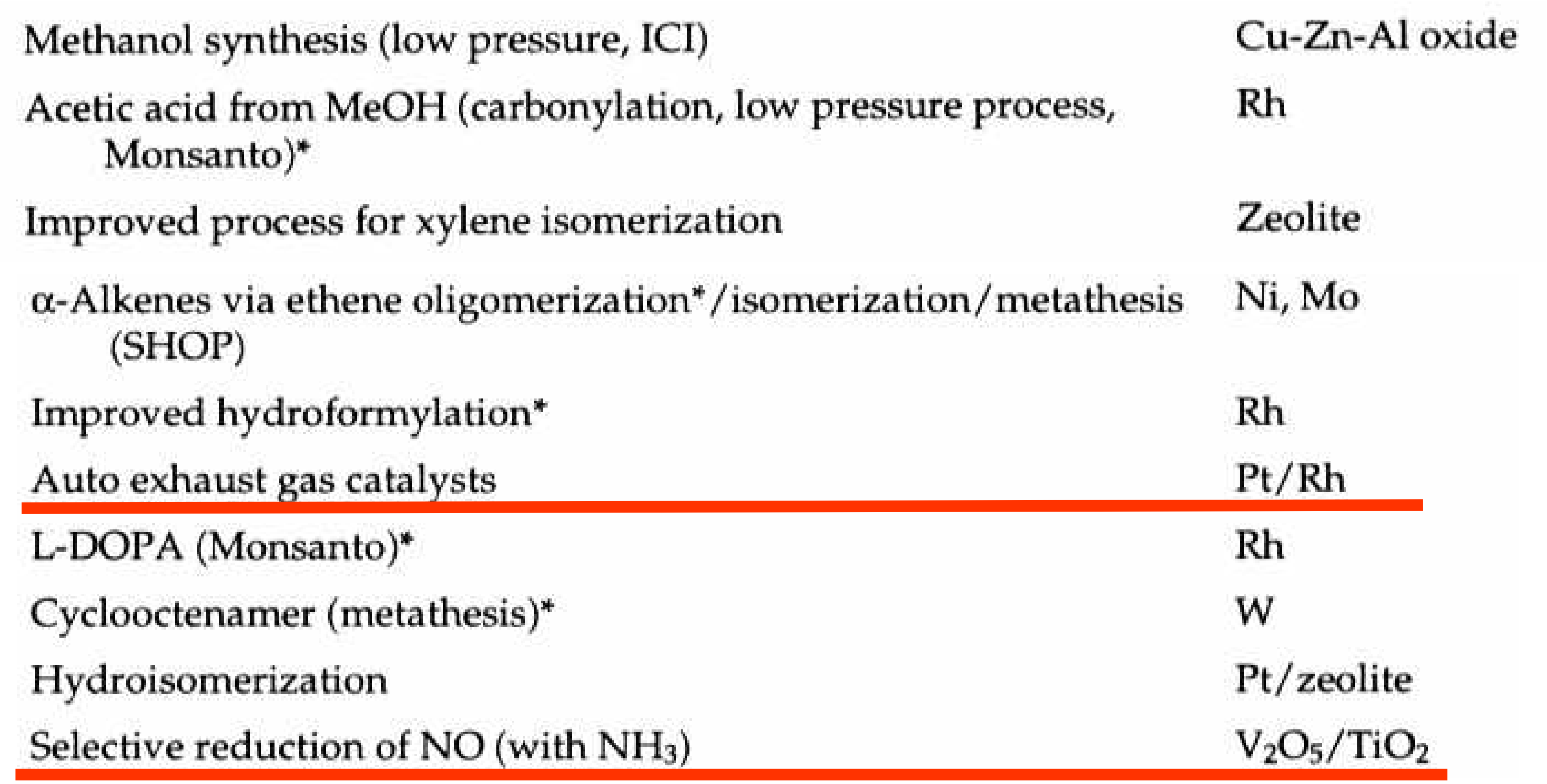
- Nobel Prize in Chemistry 1963
  "for their discoveries in the field of the chemistry and technology of high polymers"

New Processes



1960	Butene oxidation to maleic anhydride	V, P oxides
	Acrylonitrile via ammoxidation of propene (Sohio)	Bi, Mo oxides
	Propene oxidation to acrolein/acrylic acid	Bi, Mo oxides
	Xylene hydroisomerization	Pt
	Propene metathesis	W, Mo, Re
	Adiponitrile via butadiene hydrocyanation*	Ni
	Improved reforming catalysts	Pt, Re/Al_2O_3
	Improved cracking catalysts	Zeolites
	Acetic acid from MeOH (carbonylation)*	Co
	Vinyl chloride via ethene oxychlorination	Cu chloride
	Ethene oxidation to vinyl acetate	Pd/Cu
	o-Xylene oxidation to phthalic anhydride	V, Ti oxides
	Propene oxidation to propene oxide*	Mo
	Hydrocracking	Ni-W/Al_2O_3
	HT water–gas shift process	$Fe_2O_3/Cr_2O_3/MgO$
	LT water–gas shift process	$CuO/ZnO/Al_2O_3$

New Processes



1970	Methanol synthesis (low pressure, ICI)	Cu-Zn-Al oxide
	Acetic acid from MeOH (carbonylation, low pressure process, Monsanto)*	Rh
	Improved process for xylene isomerization	Zeolite
	α-Alkenes via ethene oligomerization*/isomerization/metathesis (SHOP)	Ni, Mo
	Improved hydroformylation*	Rh
	Auto exhaust gas catalysts	Pt/Rh
	L-DOPA (Monsanto)*	Rh
	Cyclooctenamer (metathesis)*	W
	Hydroisomerization	Pt/zeolite
	Selective reduction of NO (with NH_3)	V_2O_5/TiO_2

- Environmental catalysis

Environmental Catalysis: TWC in cars

- ❖ unwanted products
  C_xH_y, CO: incomplete combustion
  NO_x: nitrogen from air reacts at high temperatures
- ❖ products depend on air/ fuel ratio
  typical stoichiometric ratio 14.7 (by mass)
- ❖ Lambda value

$$l = \frac{air/fuel_{actual}}{air/fuel_{stoich.}}$$

Performance and Emissions

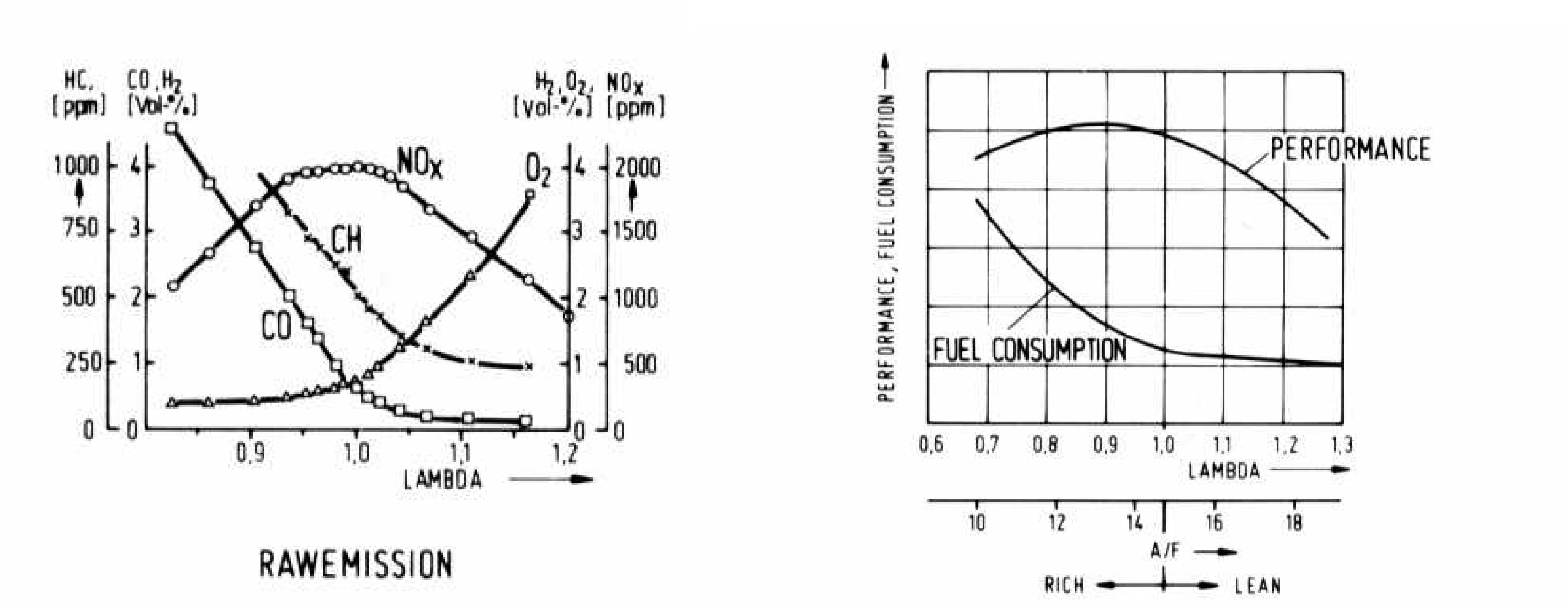


Figure 18. Engine out emission of CO, HC and NO_x: fuel consumption and power output of a gasoline fueled spark ignition engine as a function of the lambda value.

Regulations

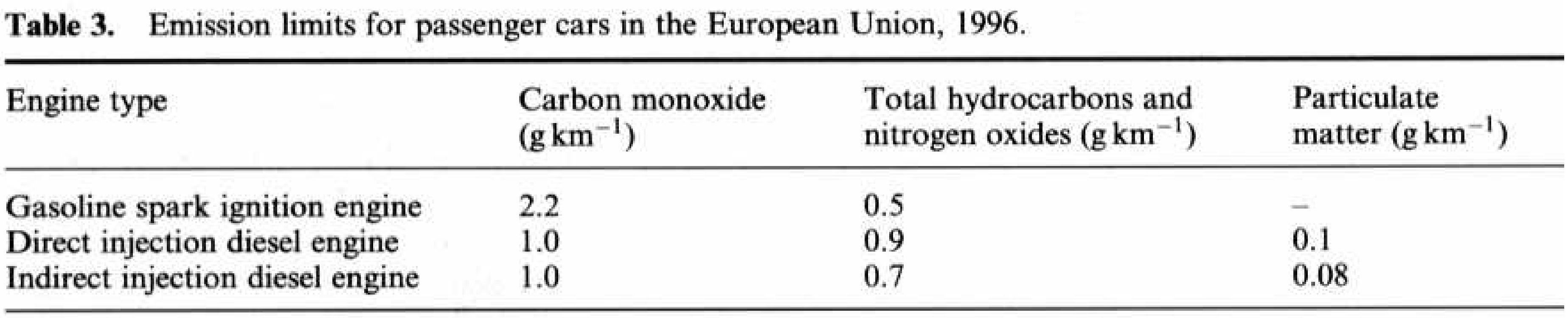


Table 3. Emission limits for passenger cars in the European Union, 1996.

Engine type	Carbon monoxide ($g\,km^{-1}$)	Total hydrocarbons and nitrogen oxides ($g\,km^{-1}$)	Particulate matter ($g\,km^{-1}$)
Gasoline spark ignition engine	2.2	0.5	–
Direct injection diesel engine	1.0	0.9	0.1
Indirect injection diesel engine	1.0	0.7	0.08

Three Way Converter

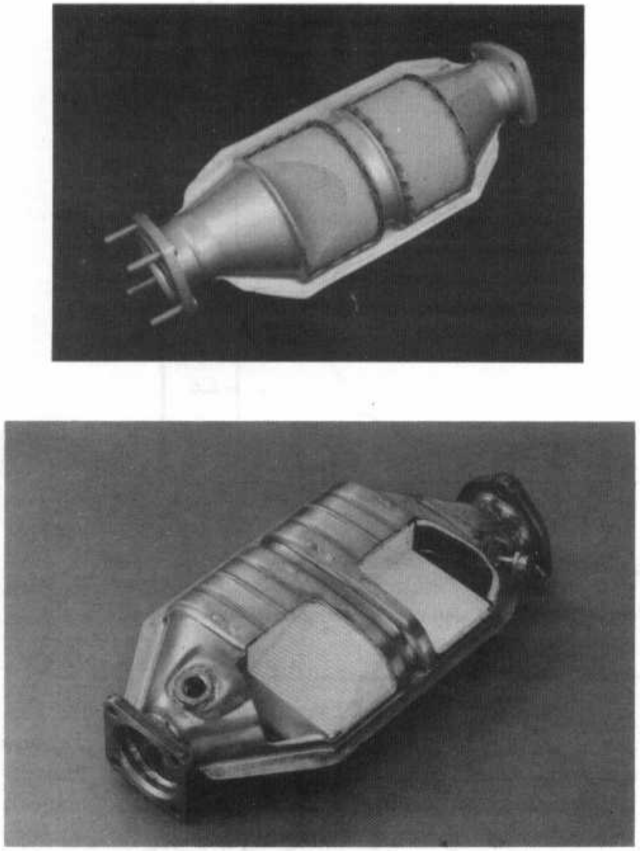
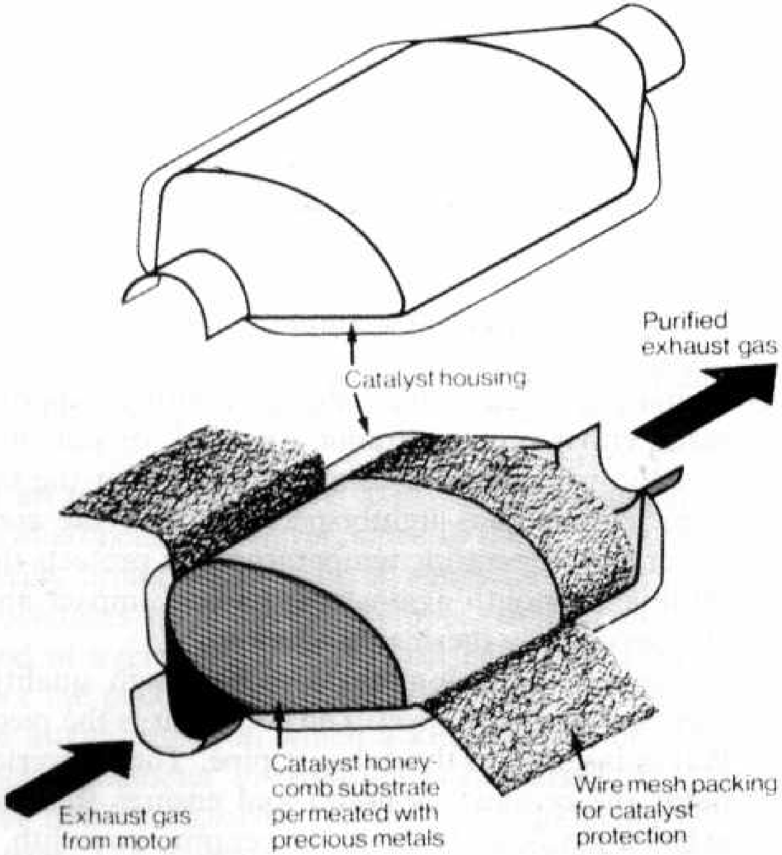


Figure 27. Cutaway view of ceramic monolith based converters for the catalytic aftertreatment of exhaust gases.



Three Way Converter

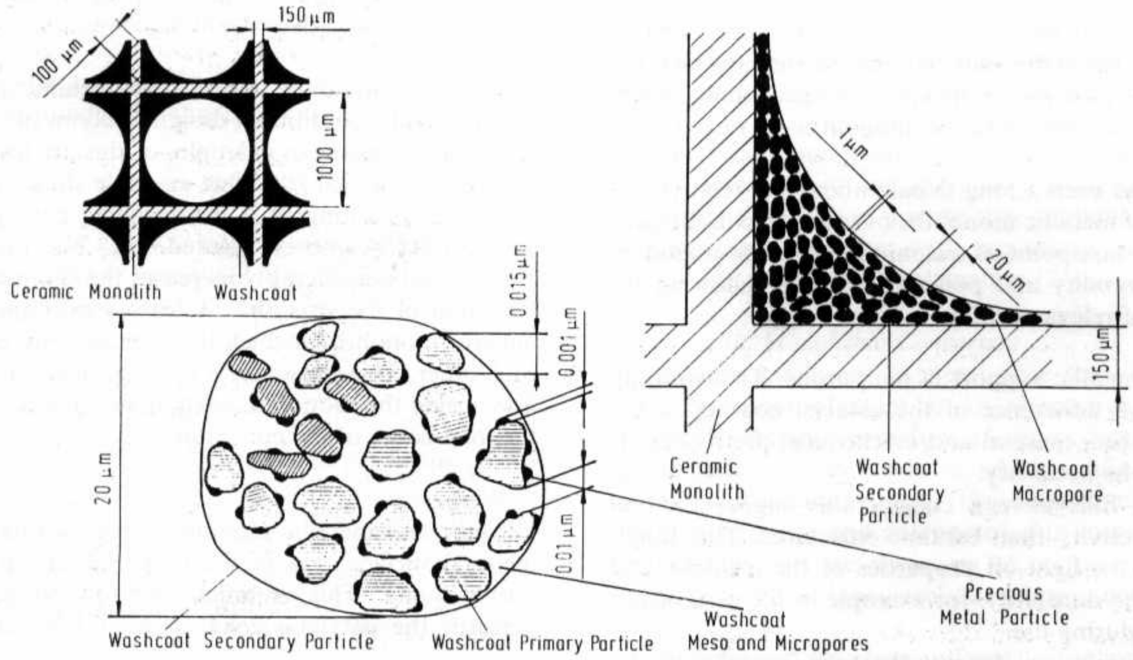


Figure 37. Dimensional relationships of a washcoat on a ceramic monolith.

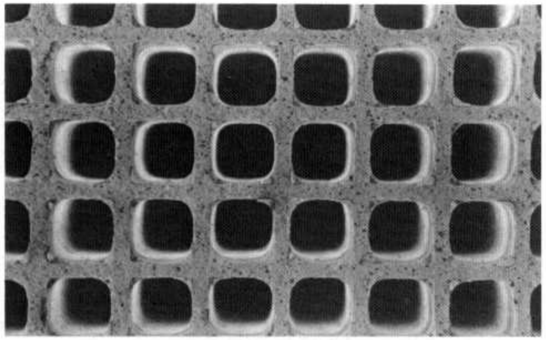


Figure 31. Close-up view of a ceramic monolithic support with 62 cells cm^{-2}.

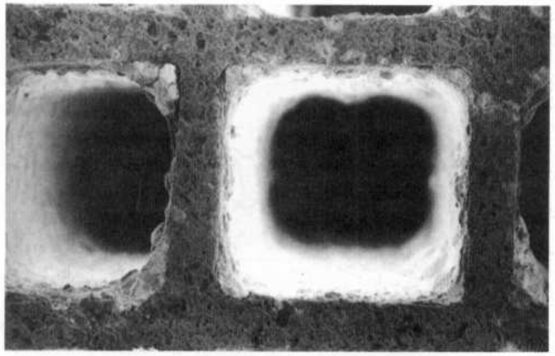


Figure 36. Close-up view of a channel of a washcoated ceramic monolith.

Catalyst

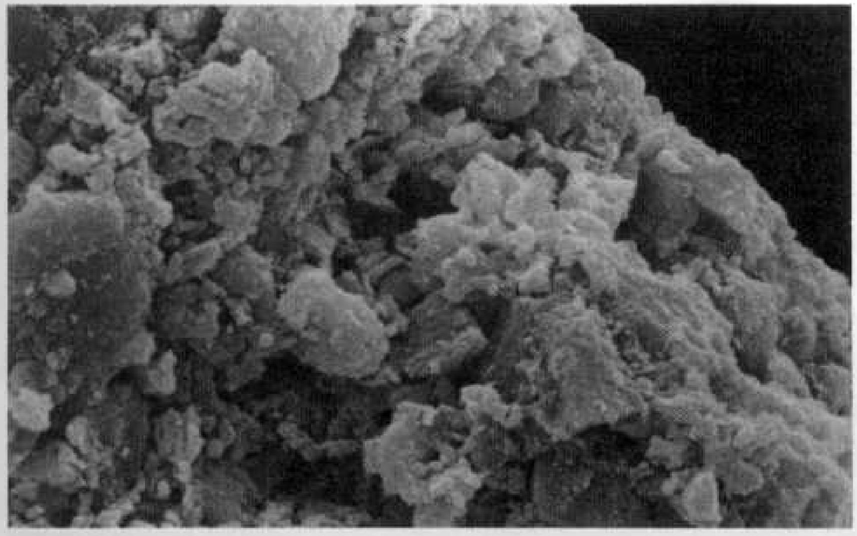


Figure 38. Scanning electron microscope view of a washcoat layer.

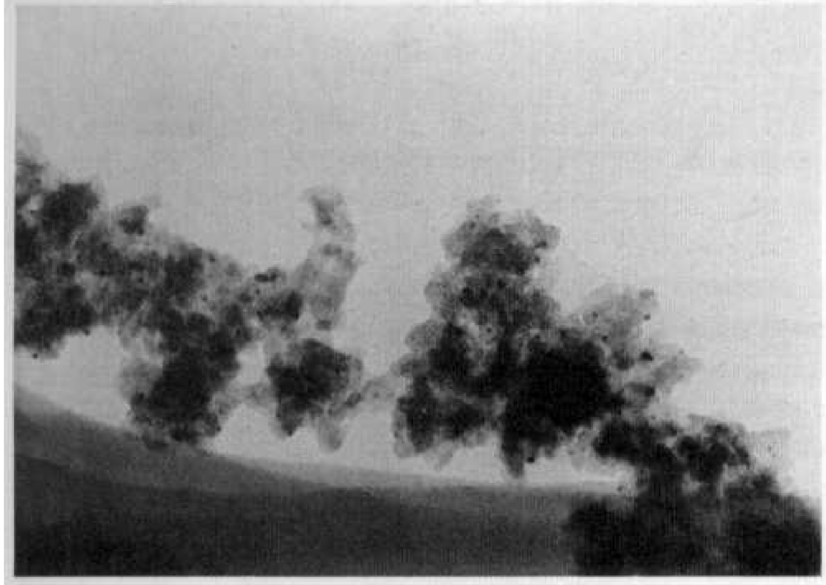


Figure 39. Transition electron microscope picture of precious metals on a washcoat particle.

The Air / Fuel Ratio

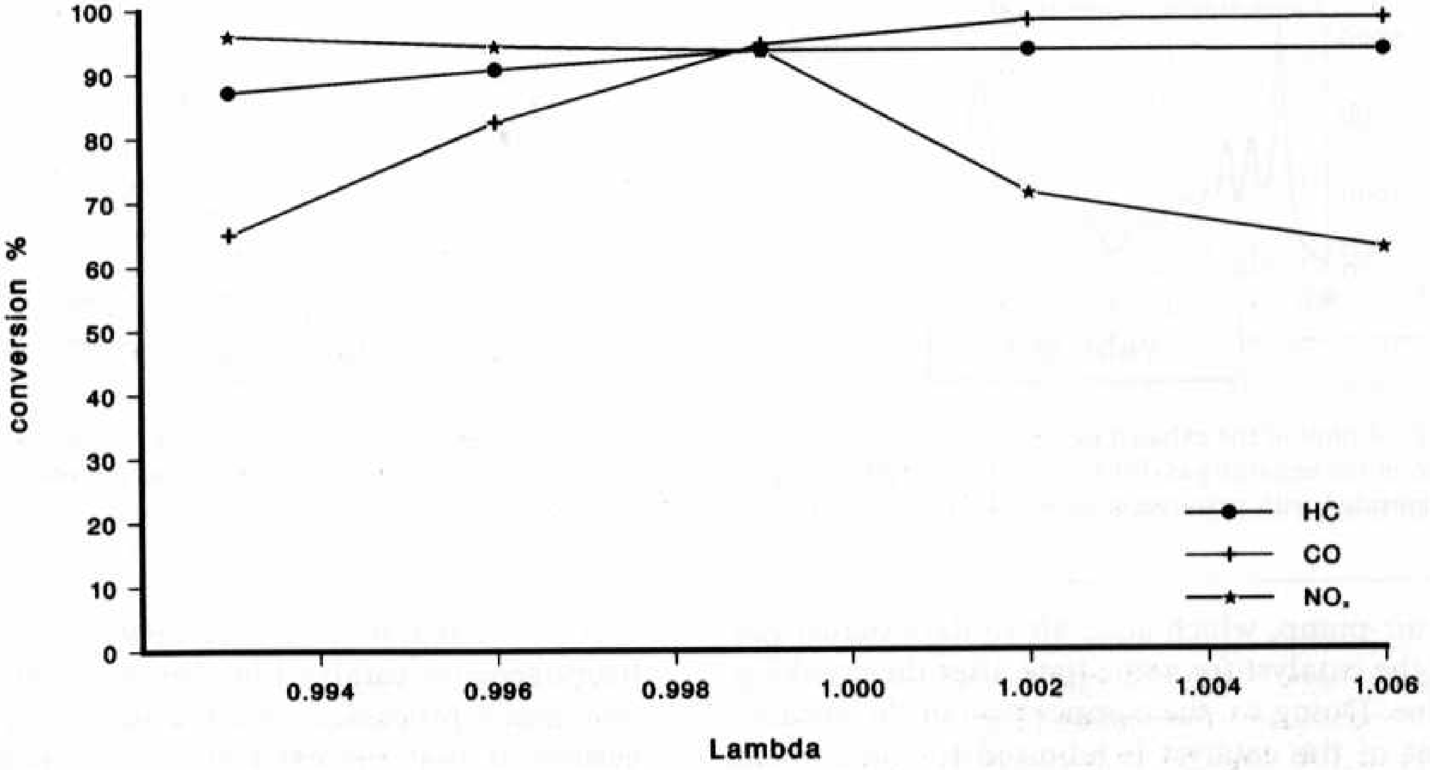


Figure 51. Conversion of CO, HC and NO_x over a three way catalyst as a function of the exhaust gas lambda value (monolith catalyst with 62 cells cm^{-2}, three-way formulation with Pt: 1.42 $g\,l^{-1}$, Rh: 0.28 $g\,l^{-1}$), fresh; engine bench test A/F scan at 623 K exhaust gas temperature; space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

Speed and Emissions

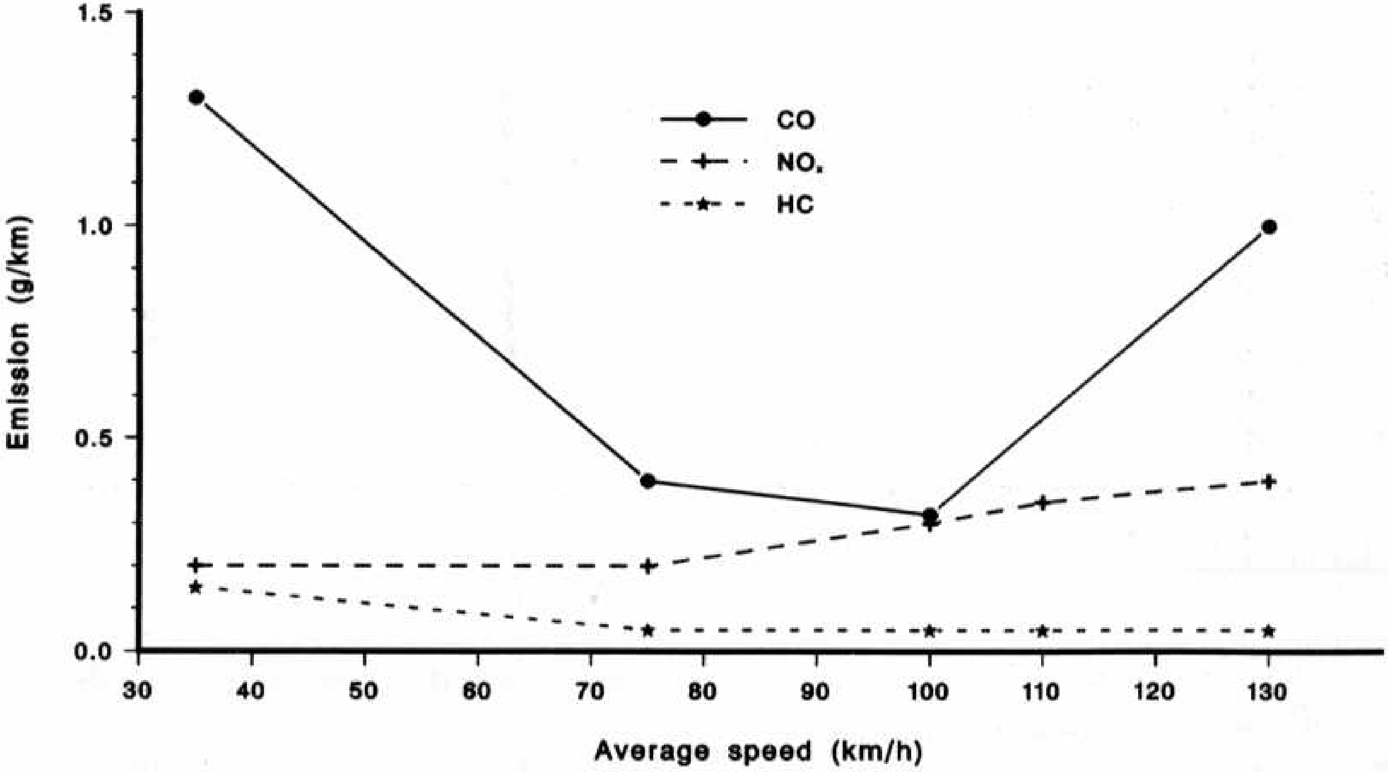


Figure 57. Tailpipe emission of CO, HC and NO_x for a vehicle with gasoline fueled spark ignition engine, equipped with a three-way catalyst, as a function of vehicle speed. Adapted from [40].

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Catalyst

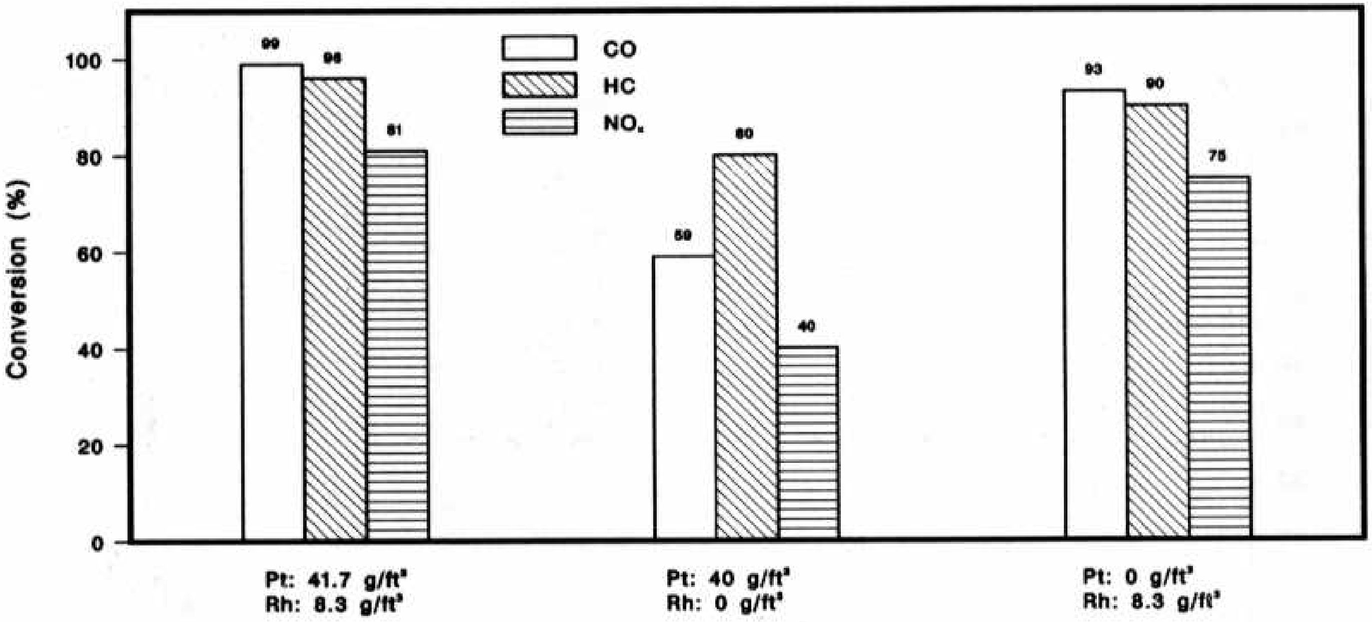
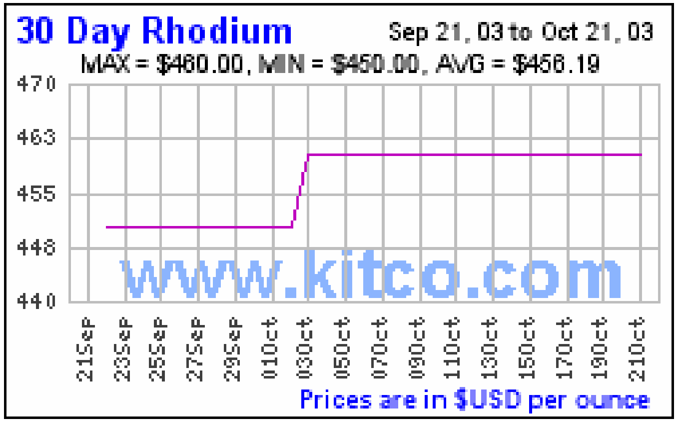
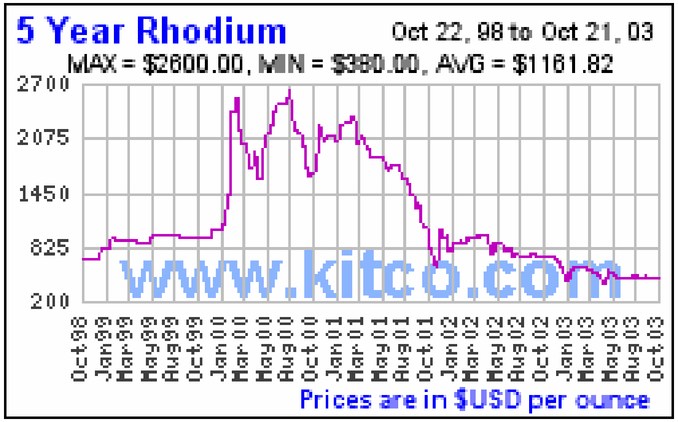


Figure 68. The function of platinum and rhodium on a fully formulated three-way catalyst washcoat in the conversion of CO, HC and NO_x (monolith catalyst with 62 cells cm^{-2}; three-way formulation, aged on an engine bench for 20 h; engine bench test at a space velocity of 60 000 $Nl\,l^{-1}\,h^{-1}$; exhaust gas temperature 673 K; exhaust gas composition lambda 0.999, dynamic frequency 1 Hz; amplitude 1 A/F). Reprinted with permission from ref. [34], © 1991 Society of Automotive Engineers, Inc.

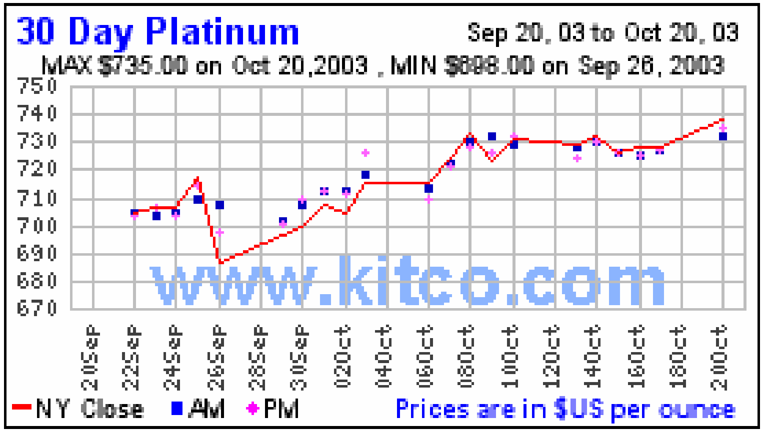
Rh Price

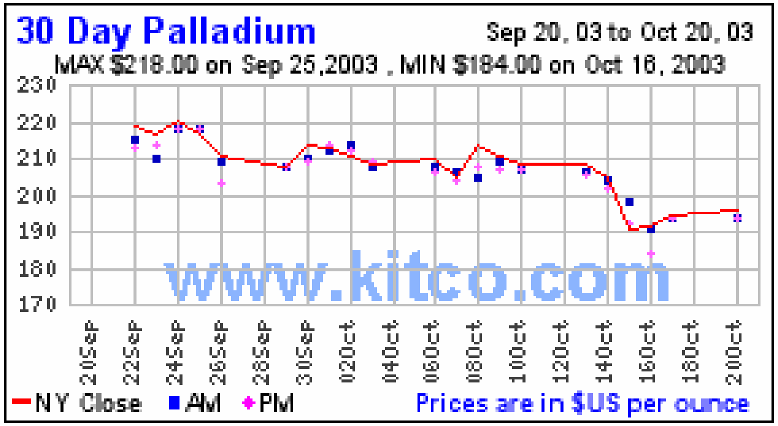


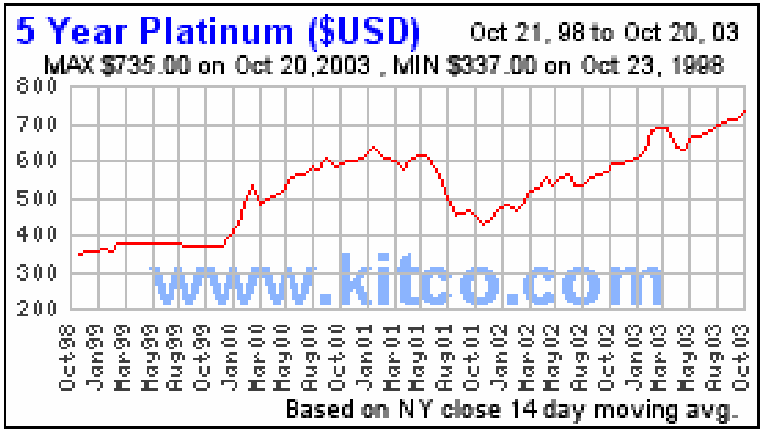


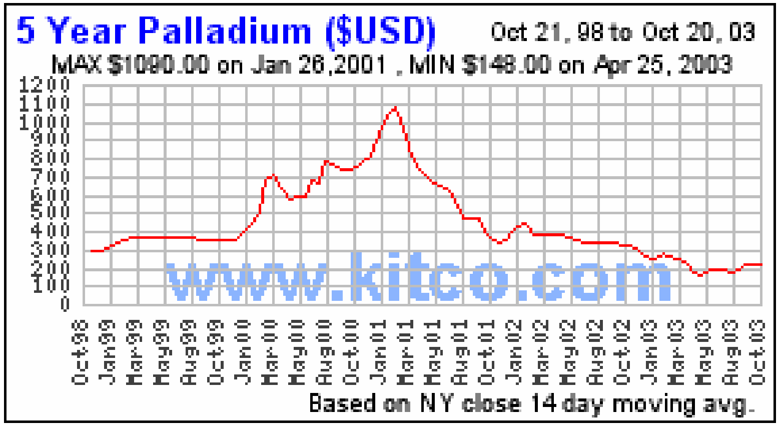
- 1 troy ounce = 31.1 g

Pt vs Pd Price









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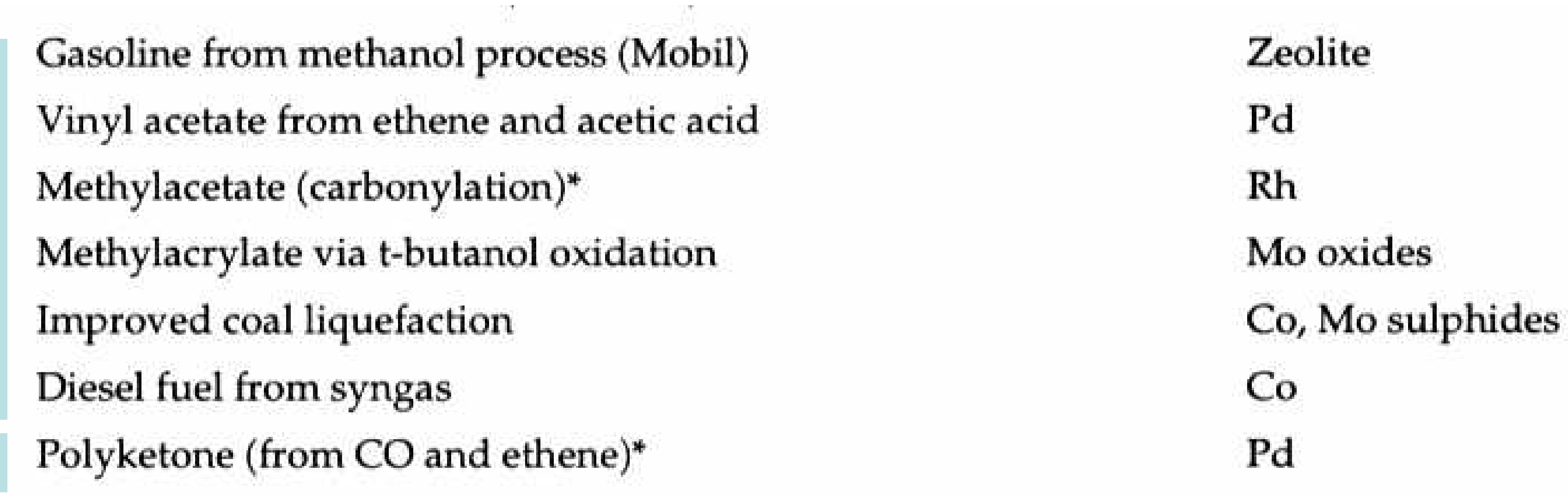
Recent Processes



1980	Gasoline from methanol process (Mobil)	Zeolite
	Vinyl acetate from ethene and acetic acid	Pd
	Methylacetate (carbonylation)*	Rh
	Methylacrylate via t-butanol oxidation	Mo oxides
	Improved coal liquefaction	Co, Mo sulphides
	Diesel fuel from syngas	Co
1990	Polyketone (from CO and ethene)*	Pd

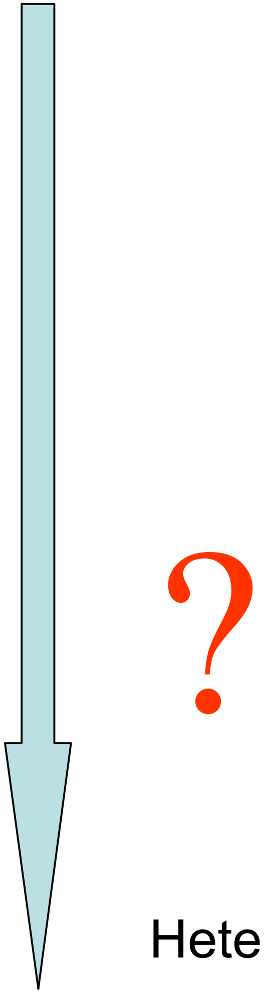
The Handbook of Heterogeneous Catalysis

"Handbook of Heterogeneous Catalysis" 1997

Ed. G. Ertl, J. Weitkamp, H. Knözinger

1. Introduction - Preparation of Solid Catalysts
2. Characterization of Solid Catalysts - Model Systems
3. Elementary Steps and Mechanisms - Kinetics and Transport Processes - Deactivation and Regeneration - Special Catalytic Systems - Laboratory Reactors - Reaction Engineering
4. Environmental Catalysis - Inorganic Reactions - Energy-Related Catalysis
5. Organic Reactions

End & Beginning



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