Jens Hagen

Industrial Catalysis

A Practical Approach

Second, Completely Revised and Extended Edition

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Contents

Preface to the Second Edition

During the last years catalysis has made a rapid progress, there can be observed many new applications of catalysts. For obvious reasons catalysis is the key to the success in developing new processes for various fields in industry. The use of suitable catalysts for new processes requires a basic knowledge of catalytic principles.

In this book, my main objective is to present an overview on catalysis, so that both the student and the experienced practitioner can see the broad picture. It was the intention to compile a text of about 500 pages surveying the whole area of catalysis, that means homogeneous catalysis, heterogeneous catalysis, biocatalysis and special topics of applied catalysis. It is felt that sufficient information is given here for a rational approach to be applied in a basic understanding of the phenomenon catalysis.

In the present edition some space is dedicated to special topics such as electrocatalysis, photocatalysis, asymmetric catalysis, phase-transfer catalysis, environmental catalysis, and fine chemicals manufacture. On the basis of fundamental reaction engineering equations, examples for calculation and modeling of catalysis reactors are given with the easy-to-learn PC program POLYMATH. Well over 170 exercises help the reader to test and consolidate the gained knowledge.

The book is based on my own lecture course for chemical engineers at the University of Applied Sciences Mannheim and several vocational training seminars for chemists and engineers in industry. I hope this book will be useful both to students who have studied chemistry or chemical engineering and to graduates and chemists who work in or are interested in the chemical industry.

Grateful appreciation is given to the following companies which provided photographic material: Degussa AG, Hanau and Marl, HTE AG, Heidelberg, and Süd-Chemie AG, Heufeld. I am particular grateful to Prof. V. M. Schmidt, Mannheim, for his valuable advice in electrocatalysis and additional material. I also want to thank the numerous students who followed my courses in Mannheim.

I thank the publishers, for their kind and competent support. I gratefully acknowledge the help of Dr. Romy Kirsten, who directed the project, Claudia Grössl for production, and Dr. Melanie Rohn for copy-editing. Special thanks and appreciation to my wife Julia for her patience, understanding and the encouragement to stay with this project to its completion.

Mannheim, October 2005 *Jens Hagen*

Preface to the First Edition

Catalysts have been used in the chemical industry for hundreds of years, and many large-scale industrial processes can only be carried out with the aid of catalysis. However, it is only since the 1970s that catalysis has become familiar to the general public, mainly because of developments in environmental protection, an example being the well known and widely used catalytic converter for automobiles.

Catalysis is a multidisciplinary area of chemistry, in particular, industrial chemistry. Anyone who is involved with chemical reactions will eventually have something to do with catalysts.

In spite of years of experience with catalysts and the vast number of publications concerning catalytic processes, there is still no fundamental theory of catalysis. As is often the case in chemistry, empirical concepts are used to explain experimental results or to make predictions about new reactions, with greater or lesser degrees of success.

To date there has been no standard book that deals equally with both heterogeneous and homogeneous catalysis, as well as industrial aspects thereof. The books published up to now generally describe a particular area or special aspects of catalysis and are therefore less suitable for teaching or studying on one's own. For this reason, it is not easy for those commencing their careers to become familiar with the complex field of catalysis.

This book is based on my own lecture course for chemical engineers at the Fachhochschule Mannheim (Mannheim University of Applied Sciences M.U.A.S) and is intended for students of chemistry, industrial chemistry, and process engineering, as well as chemists, engineers, and technicians in industry who are involved with catalysts. Largely dispensing with complex theoretical and mathematical treatments, the book describes the fundamental principles of catalysis in an easy to understand fashion. Numerous examples and exercises with solutions serve to consolidate the understanding of the material. The book is particularly well suited to studying on one's own.

It is assumed that the reader has a basic knowledge of chemistry, in particular, of reaction kinetics and organometallic chemistry. Homogeneous transition metal catalysis and heterogeneous catalysis are treated on the basis of the most important catalyst concepts, and the applications of catalysts are discussed with many examples. The book aids practically oriented readers in becoming familiar with the processes of catalyst development and testing and therefore deals with aspects of test planning, optimization, and reactor simulation. Restricting the coverage to fundamental aspects made it necessary to treat certain areas that would be of interest to specialists in concise form or to omit them completely.

I wish to thank all those who supported me in producing this book. Special thanks are due to Dr. R. Eis for all the hard work and care he invested in preparing the figures and for his helpful contributions and suggestions. I am grateful to the following companies for providing photographic material: BASF, Ludwigshafen, Germany; Degussa, Hanau, Germany; Hoffmann-LaRoche, Kaiseraugst, Switzerland; Doduco, Sinsheim, Germany; and VINCI Technologies, Rueil-Malmaison, France. Interesting examples of catalyst development were taken from the Diploma theses of Fachhochschule graduates, of whom K. Kromm and T. Zwick are especially worthy of mention.

I was pleased to accept the publisher's offer to produce an English version of the book. The introduction of international study courses leading to a Bachelor's or Master's degree in Germany and other countries makes it necessary to provide students with books in English. I am particularly grateful to Dr. S. Hawkins for his competent translation of the German text with valuable advice and additional material.

I thank the publishers, Wiley-VCH Weinheim, for their kind support. Thanks are due to Dr. B. Böck, who directed the project, C. Grössl for production, and S. Pauker for the cover graphics.

Mannheim, January 1999 *Jens Hagen*

Abbreviations

A	area [m^2]
A^*	adsorbed (activated) molecules of component A
a	catalyst activity
a_s	area per mass [m^2/kg]
A	electron acceptor
ADH	alcohol dehydrogenase enzyme
ads	adsorbed (subscript)
AES	Auger electron spectroscopy
aq	aqueous solution (subscript)
bcc	body-centered cubic
bipy	2,2′-bipyridine
Bu	butyl C_4H_9-
c_i	concentration of component i [mol/L]
CB	conduction band
C.I.	constraint index
Cp	cyclopentadienyl C_5H_5-
CSTR	continuous stirred tank reactor
D	diffusion coefficient [m^2/s]
d	deactivation (subscript)
D	electron donor
DMFC	direct methanol fuel cell
E	E factor, rate of waste [kg] per product unit [kg]
E_a	activation energy [J/mol]
E_bg	bandgap energy [eV]
E_F	Fermi level
E	enzyme
e.e.	enantiomeric excess [%]
eff	effective (subscript)
E_i	ionisation energy
E_r	redox potential [V]
Et	ethyl C_2H_5-
ESCA	electron spectroscopy for chemical analysis
ESR	electron spin resonance spectroscopy

e	electrons
F	Faraday constant [96 485 C/mol]
fcc	face-centered cubic
ΔG	Gibb's free energy [J/mol]
G	gas (subscript, too)
GHSV	gas hourly space velocity [h^{-1}]
H	Henry's law constant
H_{ex}	external holdup
ΔH_{ads}	adsorption enthalpy [J/mol]
ΔH_{f}	enthalpy change of formation [J/mol]
H_{m}	modified Henry's law constant
ΔH_{R}	reaction enthalpy [J/mol]
H_0	Hammett acidity function
HC	hydrocarbon
HSAB	hard and soft acids and bases
h	hard
hcp	hexagonal close packing
I	inhibitor
IL	ionic liquid
ISS	ion scattering spectroscopy
j	current density [A/m^2]
K	equilibrium constant
K_{i}	adsorption equilibrium constant of component i
K_{i}	inhibition constant
K_{M}	Michaelis constant
k	reaction rate constant
k_0	pre-exponential factor
$k_{\mathrm{L}} a_{\mathrm{L}}$	gas-liquid mass transfer coefficient
$k_{\mathrm{S}} a_{\mathrm{S}}$	liquid-solid mass transfer coefficient
k_{tot}	global mass transfer coefficient
L	liquid (subscript)
L	ligand
LEED	low-energy electron diffraction
LF	liquid flow [L/min]
M	metal
m	mass [kg]
$m_{\mathrm{cat.}}$	mass of catalyst [kg]
MAO	methylaluminoxane
Med	mediator, redox catalyst
n	number of moles [mol]
n	order of reaction
$\dot{n}$	flow rate [mol/s]
$\dot{n}_{\mathrm{A,0}}$	feed flow rate of starting material A [mol/s]
NAD	nicotinamide adenine dinucleotide cofactor
NHE	normal hydrogen electrode

NSR	NO_x storage-reduction
ODE	ordinary differential equation
Oxad	oxidative addition
P	total pressure [bar]
PEG	polyethylene glycol
PEMFC	proton exchange membrane fuel cell
Ph	phenyl C_6H_5-
PPh_3	triphenylphosphine
PTC	phase-transfer catalysis
p	pressure [bar]
p_i	partial pressure of component i [bar]
py	pyridine
R	ideal gas law constant [J mol^{-1} K^{-1}]
R	recycle ratio
R	alkyl
r	reaction rate [mol L^{-1} h^{-1}]
r_eff	effective reaction rate per unit mass of catalyst [mol kg^{-1} h^{-1}]
rel	relative (subscript)
r_d	deactivation rate
S	Tafel slope (electrocatalysis)
S	surface area [m^2/kg]
ΔS	entropy change [J mol^{-1} K^{-1}]
S_p	selectivity [mol/mol] or [%]
S	solid (subscript, too)
SCR	selective catalytic reduction
SIMS	secondary-ion mass spectroscopy
SLPC	supported liquid phase catalysts
SMSI	strong metal-support interaction
SSPC	supported solid phase catalysts
s	soft
s	sample standard deviation
s^2	experimental error variance
S^{-1}	mass index, ratio of all the materials [kg] to the product [kg]
S	substrate
sc	supercritical
STY	space time yield [mol L^{-1} h^{-1}, kg L^{-1} h^{-1}]
T	temperature [K]
TEM	transmission electron microscopy
TF	time-factor [$m_\mathrm{cat}/\dot{n}_\mathrm{A,0}$]
TOF	turnover frequency [s^{-1}]
TON	turnover number [mol mol^{-1} s^{-1}]
t	time [s, h]
TPD	temperature-programmed desorption
TPR	temperature-programmed reduction
TS 1	titanium(IV) silicalite zeolite catalyst

U	cell voltage [V]
V	volume [m^3]
$\dot{V}$	volumetric flow-rate
V_R	reaction volume [m^3]
VB	valence band
VOC	volatile organic compound
X	conversion [mol/mol] or [%]
$\bar{x}$	mean value of measurements
$\vec{x}$	positional vector (simplex method)
z	tube length [m]
δ	percentage d-band occupancy
$\in$	excitation energy of semiconductors [eV]
$\in_P$	void fraction of particle
$\mathrm{\eta}$	catalyst effectiveness factor
η	overpotential [V]
θ_i	degree of coverage of the surface of component i
v	stretching frequencies (IR) [cm^{-1}]
v_i	stoichiometric coefficient
ρ	density [g/mL]
$\rho_{cat.}$	pellet density of the catalyst [g/mL]
τ	tortuosity
σ	interfacial tension
ϕ_0	work function [eV]
*	active centers on the catalyst surface

1
Introduction

1.1
The Phenomenon Catalysis

Catalysis is the key to chemical transformations. Most industrial syntheses and nearly all biological reactions require catalysts. Furthermore, catalysis is the most important technology in environmental protection, i. e., the prevention of emissions. A well-known example is the catalytic converter for automobiles.

Catalytic reactions were already used in antiquity, although the underlying principle of catalysis was not recognized at the time. For example, the fermentation of sugar to ethanol and the conversion of ethanol to acetic acid are catalyzed by enzymes (biocatalysts). However, the systematic scientific development of catalysis only began about 200 years ago, and its importance has grown up to the present day [2].

The term "catalysis" was introduced as early as 1836 by Berzelius in order to explain various decomposition and transformation reactions. He assumed that catalysts possess special powers that can influence the affinity of chemical substances.

A definition that is still valid today is due to Ostwald (1895): "a catalyst accelerates a chemical reaction without affecting the position of the equilibrium." Ostwald recognized catalysis as a ubiquitous phenomenon that was to be explained in terms of the laws of physical chemistry.

While it was formerly assumed that the catalyst remained unchanged in the course of the reaction, it is now known that the catalyst is involved in chemical bonding with the reactants during the catalytic process. Thus catalysis is a cyclic process: the reactants are bound to one form of the catalyst, and the products are released from another, regenerating the initial state.

In simple terms, the catalytic cycle can be described as shown in Figure 1-1 [T9]. The intermediate catalyst complexes are in most cases highly reactive and difficult to detect.

In theory, an ideal catalyst would not be consumed, but this is not the case in practice. Owing to competing reactions, the catalyst undergoes chemical changes, and its activity becomes lower (catalyst deactivation). Thus catalysts must be regenerated or eventually replaced.

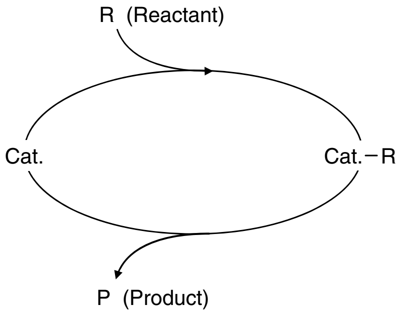


Fig. 1-1 Catalytic cycle

Apart from accelerating reactions, catalysts have another important property: they can influence the selectivity of chemical reactions. This means that completely different products can be obtained from a given starting material by using different catalyst systems. Industrially, this targeted reaction control is often even more important than the catalytic activity [6].

Catalysts can be gases, liquids, or solids. Most industrial catalysts are liquids or solids, whereby the latter react only via their surface. The importance of catalysis in the chemical industry is shown by the fact that 75 % of all chemicals are produced with the aid of catalysts; in newly developed processes, the figure is over 90 %. Numerous organic intermediate products, required for the production of plastics, synthetic fibers, pharmaceuticals, dyes, crop-protection agents, resins, and pigments, can only be produced by catalytic processes.

Most of the processes involved in crude-oil processing and petrochemistry, such as purification stages, refining, and chemical transformations, require catalysts. Environmental protection measures such as automobile exhaust control and purification of off-gases from power stations and industrial plant would be inconceivable without catalysts [5].

Catalysts have been successfully used in the chemical industry for more than 100 years, examples being the synthesis of sulfuric acid, the conversion of ammonia to nitric acid, and catalytic hydrogenation. Later developments include new highly selective multicomponent oxide and metallic catalysts, zeolites, and the introduction of homogeneous transition metal complexes in the chemical industry. This was supplemented by new high-performance techniques for probing catalysts and elucidating the mechanisms of heterogeneous and homogenous catalysis.

The brief historical survey given in Table 1-1 shows just how the closely the development of catalysis is linked to the history of industrial chemistry [4].

Table 1-1 History of the catalysis of industrial processes [4]

Catalytic reaction	Catalyst	Discoverer or company/year
Sulfuric acid (lead-chamber process)	NO_x	Désormes, Clement, 1806
Chlorine production by HCl oxidation	$CuSO_4$	Deacon, 1867
Sulfuric acid (contact process)	Pt, V_2O_5	Winkler, 1875; Knietsch, 1888 (BASF)
Nitric acid by NH_3 oxidation	Pt/Rh nets	Ostwald, 1906
Fat hardening	Ni	Normann, 1907
Ammonia synthesis from N_2, H_2	Fe	Mittasch, Haber, Bosch, 1908; Production, 1913 (BASF)
Hydrogenation of coal to hydrocarbons	Fe, Mo, Sn	Bergius, 1913; Pier, 1927
Oxidation of benzene, naphthalene to MSA or PSA	V_2O_5	Weiss, Downs, 1920
Methanol synthesis from CO/H_2	ZnO/Cr_2O_3	Mittasch, 1923
Hydrocarbons from CO/H_2 (motor fuels)	Fe, Co, Ni	Fischer, Tropsch, 1925
Oxidation of ethylene to ethylene oxide	Ag	Lefort, 1930
Alkylation of olefins with isobutane to gasoline	$AlCl_3$	Ipatieff, Pines, 1932
Cracking of hydrocarbons	Al_2O_3/SiO_2	Houdry, 1937
Hydroformylation of ethylene to propanal	Co	Roelen, 1938 (Ruhrchemie)
Cracking in a fluidized bed	aluminosilicates	Lewis, Gilliland, 1939 (Standard Oil)
Ethylene polymerization, low-pressure	Ti compounds	Ziegler, Natta, 1954
Oxidation of ethylene to acetaldehyde	Pd/Cu chlorides	Hafner, Smidt (Wacker)
Ammoxidation of propene to acrylonitrile	Bi/Mo	Idol, 1959 (SOHIO process)
Olefin metathesis	Re, W, Mo	Banks, Bailey, 1964
Hydrogenation, isomerization, hydroformylation	Rh-, Ru complexes	Wilkinson, 1964
Asymmetric hydrogenation	Rh/chiral phosphine	Knowles, 1974; L-Dopa (Monsanto)
Three-way catalyst	Pt, Rh/monolith	General Motors, Ford, 1974
Methanol conversion to hydrocarbons	Zeolites	Mobil Chemical Co., 1975
α-olefines from ethylene	Ni/chelate phosphine	Shell (SHOP process) 1977

Table 1-1 (continued)

Catalytic reaction	Catalyst	Discoverer or company/year
Sharpless oxidation, epoxidation	Ti/ROOH/tartrate	May & Baker, Upjohn, ARCO, 1981
Selective oxidations with H_2O_2	titanium zeolite (TS-1)	Enichem, 1983
Hydroformylation	Rh/phosphine/ aqueous	Rhône-Poulenc/Ruhrchemie, 1984
Polymerization of olefines	zirconocene/MAO	Sinn, Kaminsky, 1985
Selective catalytic reduction SCR (power plants)	V, W, Ti oxides/ monolith	~1986
Acetic acid	$Ir/I^-/Ru$	„Cativa"-process, BP Chemicals, 1996

1.2
Mode of Action of Catalysts

The suitability of a catalyst for an industrial process depends mainly on the following three properties:

- Activity
- Selectivity
- Stability (deactivation behavior)

The question which of these functions is the most important is generally difficult to answer because the demands made on the catalyst are different for each process. First, let us define the above terms [6, 7].

1.2.1
Activity

Activity is a measure of how fast one or more reactions proceed in the presence of the catalyst. Activity can be defined in terms of kinetics or from a more practically oriented viewpoint. In a formal kinetic treatment, it is appropriate to measure reaction rates in the temperature and concentration ranges that will be present in the reactor.

The reaction rate r is calculated as the rate of change of the amount of substance n_A of reactant A with time relative to the reaction volume or the mass of catalyst:

$$r = \frac{\text{converted amount of substance of a reactant}}{\text{volume or catalyst mass} \cdot \text{time}} \ (\text{mol}\,\text{L}^{-1}\,\text{h}^{-1} \ \text{or} \ \text{mol}\,\text{kg}^{-1}\,\text{h}^{-1}) \tag{1-1}$$

Kinetic activities are derived from the fundamental rate laws, for example, that for a simple irreversible reaction A → P:

$$\frac{\mathrm{d}n_\mathrm{A}}{\mathrm{d}t} = kV\mathrm{f}(c_\mathrm{A}) \tag{1-2}$$

k = rate constant

$\mathrm{f}(c_\mathrm{A})$ is a concentration term that can exhibit a first- or higher order dependence on adsorption equilibria (see Section 5.2).

The temperature dependence of rate constants is given by the Arrhenius equation:

$$k = k_0\,\mathrm{e}^{-(E_\mathrm{a}/RT)} \tag{1-3}$$

E_a = activation energy of the reaction
k_0 = pre-exponential factor
R = gas constant

As Equations 1-2 and 1-3 show, there are three possibilities for expressing catalyst activity, i. e., as:

- Reaction rate
- Rate constant k
- Activation energy E_a

Empirical rate equations are obtained by measuring reaction rates at various concentrations and temperatures. If, however, different catalysts are to be compared for a given reaction, the use of constant concentration and temperature conditions is often difficult because each catalyst requires it own optimal conditions. In this case it is appropriate to use the initial reaction rates r_0 obtained by extrapolation to the start of the reaction.

Another measure of catalyst activity is the turnover number TON, which originates from the field of enzymatic catalysis.

In the case of homogeneous catalysis, in which well-defined catalyst molecules are generally present in solution, the TON can be directly determined. For heterogeneous catalysts, this is generally difficult, because the activity depends on the size of the catalyst surface, which, however, does not have a uniform structure. For example, the activity of a supported metal catalyst is due to active metal atoms dispersed over the surface.

The number of active centers per unit mass or volume of catalyst can be determined indirectly by means of chemisorption experiments, but such measurements require great care, and the results are often not applicable to process conditions. Although the TON appears attractive due to its molecular simplicity, it should be used prudently in special cases.

In practice, readily determined measures of activity are often sufficient. For comparitive measurements, such as catalyst screening, determination of process parameters, optimization of catalyst production conditions, and deactivation studies, the following activity measures can be used:

- Conversion under constant reaction conditions
- Space velocity for a given, constant conversion
- Space–time yield
- Temperature required for a given conversion

Catalysts are often investigated in continuously operated test reactors, in which the conversions attained at constant space velocity are compared [6]

The space velocity is the volume flow rate $\dot{V}_0$, relative to the catalyst mass m_{cat}:

$$\text{Space velocity} = \frac{\dot{V}_0}{m_{\text{cat}}} \quad (\text{m}^3\ \text{kg}^{-1}\ \text{s}^{-1}) \tag{1-4}$$

The conversion X_A is the ratio of the amount of reactant A that has reacted to the amount that was introduced into the reactor. For a batch reactor:

$$X_A = \frac{n_{A,0} - n_A}{n_{A,0}} \quad (\text{mol/mol or \%}) \tag{1-5}$$

If we replace the catalyst mass in Equation 1-4 with the catalyst volume, then we see that the space velocity is proportional to the reciprocal of the residence time.

Figure 1-2 compares two catalysts of differing activity with one another, and shows that for a given space velocity, catalyst A is better than catalyst B.

Of course, such measurements must be made under constant conditions of starting material ratio, temperature, and pressure.

Often the performance of a reactor is given relative to the catalyst mass or volume, so that reactors of different size or construction can be compared with one another. This quantity is known as the space–time yield STY:

$$STY = \frac{\text{Desired product quantity}}{\text{Catalyst volume} \cdot \text{time}} \quad (\text{mol L}^{-1}\ \text{h}^{-1}) \tag{1-6}$$

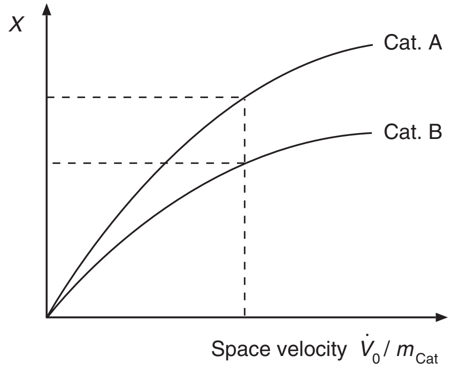


Fig. 1-2 Comparison of catalyst activities

Determination of the temperature required for a given conversion is another method of comparing catalysts. The best catalyst is the one that gives the desired conversion at a lower temperature. This method can not, however, be recommended since the kinetics are often different at higher temperature, making misinterpretations likely. This method is better suited to carrying out deactivation measurements on catalysts in pilot plants.

1.2.1.1 **Turnover Frequency TOF**

The turnover frequency TOF (the term was borrowed from enzyme catalysis) quantifies the specific activity of a catalytic center for a special reaction under defined reaction conditions by the number of molecular reactions or catalytic cycles occuring at the center per unit time. For heterogeneous catalysts the number of active centers is derived usually from sorption methods (Eq. 1-7).

$$\mathrm{TOF} = \frac{\text{volumetric rate of reaction}}{\text{number of centers/volume}} = \frac{\text{moles}}{\text{volume} \cdot \text{time}}\ \frac{\text{volume}}{\text{moles}} = \text{time}^{-1} \tag{1-7}$$

For most relevant industrial applications the TOF is in the range 10^{-2}–10^{2} s^{-1} (enzymes 10^{3}–10^{7} s^{-1}).

Examples:

TOF values for the hydrogenation of cyclohexene at 25 °C and 1 bar (supported catalysts, structure insensitive reaction; Table 1-2):

Table 1-2 TOF values for the hydrogenation of cyclohexene [T 46]

Metal	**TOF (s^{-1})** **Gas phase**	**Liquid phase**
Ni	2.0	0.45
Rh	6.1	1.3
Pd	3.2	1.5
Pt	2.8	0.6

1.2.1.2 **Turnover Number TON** [T 46]

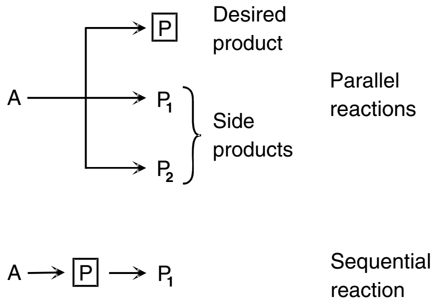
The turnover number specifies the maximum use that can be made of a catalyst for a special reaction under defined conditions by a number of molecular reactions or reaction cycles occuring at the reactive center up to the decay of activity. The relationschip between TOF and TON is (Eq. 1-8):

$$\mathrm{TON} = \mathrm{TOF}\ [\text{time}^{-1}] \cdot \text{lifetime of the catalyst [time] [–]} \tag{1-8}$$

For industrial applications the TON is in the range 10^{6}–10^{7}.

1.2.2
Selectivity

The selectivity S_p of a reaction is the fraction of the starting material that is converted to the desired product P. It is expressed by the ratio of the amount of desired product to the reacted quantity of a reaction partner A and therefore gives information about the course of the reaction. In addition to the desired reaction, parallel and sequential reactions can also occur (Scheme 1-1).



Scheme 1-1 Parallel and sequential reactions

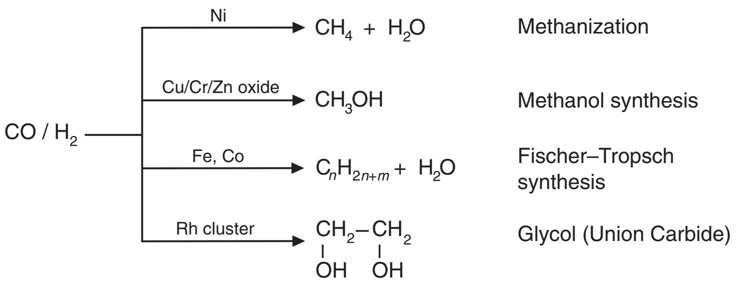
Since this quantity compares starting materials and products, the stoichiometric coefficients v_i of the reactants must be taken into account, which gives rise to the following equation [6]:

$$S_P = \frac{n_P/\nu_P}{(n_{A,0} - n_A)/|\nu_A|} = \frac{n_P|\nu_A|}{(n_{A,0} - n_A)\nu_P} \quad \text{(mol/mol or \%)} \tag{1-9}$$

In comparative selectivity studies, the reaction conditions of temperature and conversion or space velocity must, of course, be kept constant.

If the reaction is independent of the stoichiometry, then the selectivity $S_p = 1$. The selectivity is of great importance in industrial catalysis, as demonstrated by the example of synthesis gas chemistry, in which, depending on the catalyst used, completely different reaction products are obtained (Scheme 1-2) [2].

Selectivity problems are of particular relevance to oxidation reactions.



Scheme 1-2 Reactions of synthesis gas

1.2.3
Stability

The chemical, thermal, and mechanical stability of a catalyst determines its lifetime in industrial reactors. Catalyst stability is influenced by numerous factors, including decomposition, coking, and poisoning. Catalyst deactivation can be followed by measuring activity or selectivity as a function of time.

Catalysts that lose activity during a process can often be regenerated before they ultimately have to be replaced. The total catalyst lifetime is of crucial importance for the economics of a process.

Today the efficient use of raw materials and energy is of major importance, and it is preferable to optimize existing processes than to develop new ones. For various reasons, the target quantities should be given the following order of priority:

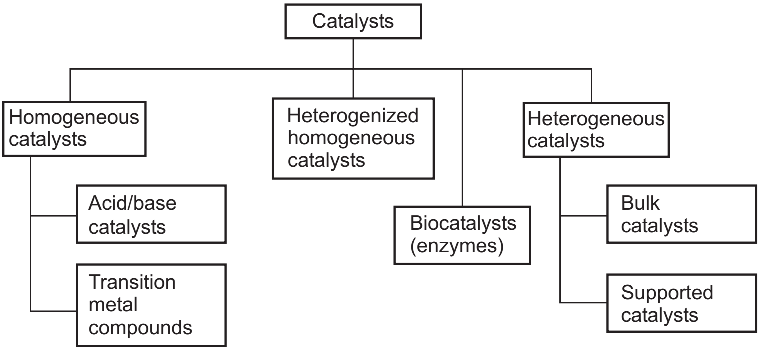
Selectivity > Stability > Activity

1.3
Classification of Catalysts

The numerous catalysts known today can be classified according to various criteria: structure, composition, area of application, or state of aggregation.

Here we shall classify the catalysts according to the state of aggregation in which they act. There are two large groups: heterogeneous catalysts (solid-state catalysts) and homogeneous catalysts (Scheme 1-3). There are also intermediate forms such as homogeneous catalysts attached to solids (supported catalysts), also known as immobilized catalysts [4].

In supported catalysts the catalytically active substance is applied to a support material that has a large surface area and is usually porous. By far the most important catalysts are the heterogeneous catalysts. The market share of homogeneous catalysts is estimated to be only ca. 10–15 % [5, 6]. In the following, we shall briefly discuss the individual groups of catalysts.



Scheme 1-3 Classification of catalysts

Catalytic processes that take place in a uniform gas or liquid phase are classified as homogeneous catalysis. Homogeneous catalysts are generally well-defined chemical compounds or coordination complexes, which, together with the reactants, are molecularly dispersed in the reaction medium. Examples of homogeneous catalysts include mineral acids and transition metal compounds (e. g., rhodium carbonyl complexes in oxo synthesis).

Heterogeneous catalysis takes place between several phases. Generally the catalyst is a solid, and the reactants are gases or liquids. Examples of heterogeneous catalysts are Pt/Rh nets for the oxidation of ammonia to nitrous gases (Ostwald process), supported catalysts such as nickel on kieselguhr for fat hardening [1], and amorphous or crystalline aluminosilicates for cracking petroleum fractions.

Of increasing importance are the so-called biocatalysts (enzymes). Enzymes are protein molecules of colloidal size [e. g., poly(amino acids)]. Some of them act in dissolved form in cells, while others are chemically bound to to cell membranes or on surfaces. Enzymes can be classified somewhere between molecular homogeneous catalysts and macroscopic heterogeneous catalysts.

Enzymes are the driving force for biological reactions [4]. They exhibit remarkable activities and selectivities. For example, the enzyme catalase decomposes hydrogen peroxide 10^9 times faster than inorganic catalysts. The enzymes are organic molecules that almost always have a metal as the active center. Often the only difference to the industrial homogeneous catalysts is that the metal center is ligated by one or more proteins, resulting in a relatively high molecular mass.

Apart from high selectivity, the major advantage of enzymes is that they function under mild conditions, generally at room temperature in aqueous solution at pH values near 7. Their disadvantage is that they are sensitive, unstable molecules which are destroyed by extreme reaction conditions. They generally function well only at physiological pH values in very dilute solutions of the substrate.

Enzymes are expensive and difficult to obtain in pure form. Only recently have enzymes, often in immobilized form, been increasingly used for reactions of nonbiological substances. With the increasing importance of biotechnological processes, enzymes will also grow in importance.

It would seem reasonable to treat homogeneous catalysis, heterogeneous catalysis, and enzymatic catalysis as separate disciplines.

1.4
Comparison of Homogeneous and Heterogeneous Catalysis

Whereas for heterogeneous catalysts, phase boundaries are always present between the catalyst and the reactants, in homogeneous catalysis, catalyst, starting materials, and products are present in the same phase. Homogeneous catalysts have a higher degree of dispersion than heterogeneous catalysts since in theory each individual atom can be catalytically active. In heterogeneous catalysts only the surface atoms are active [3].

Due to their high degree of dispersion, homogeneous catalysts exhibit a higher activity per unit mass of metal than heterogeneous catalysts. The high mobility of the