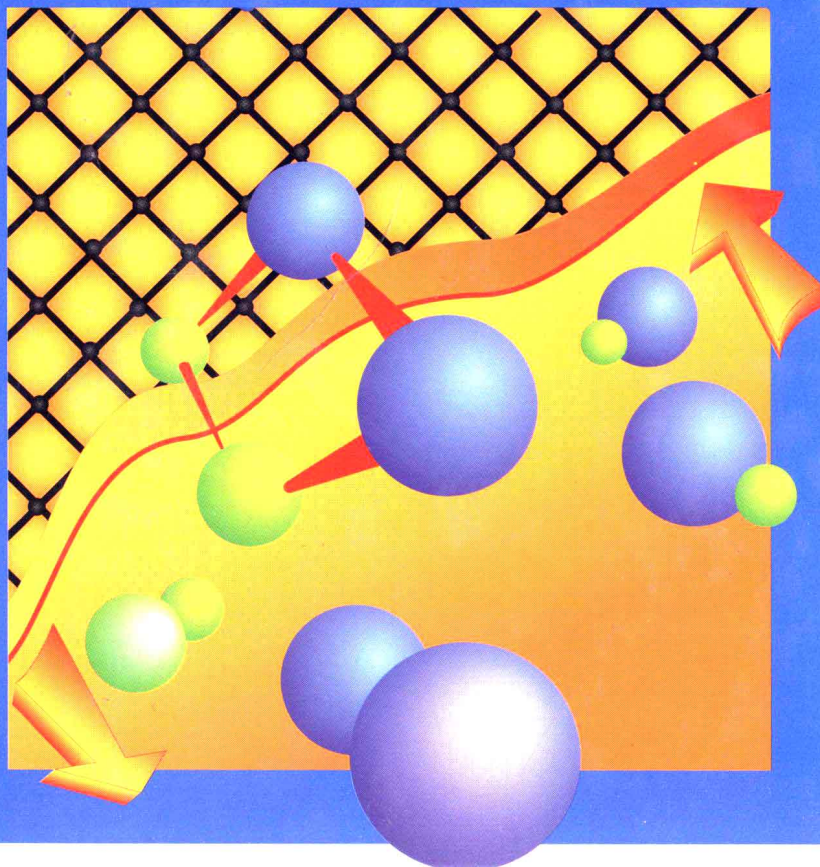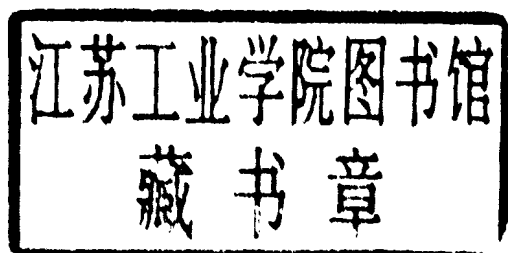WILEY-VCH

Jens Hagen

Industrial Catalysis

A Practical Approach

Jens Hagen

Industrial Catalysis

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fundamental aspects made it necessary to treat certain areas that would be of interest to specialists in concise form or to omit them completely.

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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]
ads	adsorbed (subscript)
AES	Auger electron spectroscopy
aq	aqueous solution (subscript)
bcc	body-centered cubic
bipy	2,2$'$-bipyridine
Bu	butyl C$_4$H$_9$-
c_i	concentration of component i [mol/L]
C.I.	constraint index
Cp	cyclopentadienyl C$_5$H$_5$-
D	diffusion coefficient [m^2/s]
d	deactivation (subscript)
E_a	activation energy [J/mol]
E_F	Fermi level
eff	effective (subscript)
E_i	ionisation energy
Et	ethyl C$_2$H$_5$-
ESCA	electron spectroscopy for chemical analysis
ESR	electron spin resonance spectroscopy
e	electrons
fcc	face-centered cubic
ΔG	Gibb's free energy [J/mol]
G	gas (subscript, too)
H	Henry's law constant
H_{ex}	external holdup
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
HSAB	hard and soft acids and bases
h	hard
hcp	hexagonal close packing
ISS	ion scattering spectroscopy

K	equilibrium constant
K_i	adsorption equilibrium constant of component i
k	reaction rate constant
k_0	pre-exponential factor
$k_L a_L$	gas-liquid mass transfer coefficient
$k_S a_S$	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]
$m_{cat.}$	mass of catalyst [kg]
n	number of moles [mol]
n	order of reaction
$\dot{n}$	flow rate [mol/s]
$\dot{n}_{A,0}$	feed flow rate of starting material A [mol/s]
Oxad	oxidative addition
P	total pressure [bar]
Ph	phenyl C_6H_5-
PPh$_3$	triphenylphosphine
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	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

STY	space time yield [mol L^{-1} h^{-1}, kg L^{-1} h^{-1}]
T	temperature [K]
TEM	transmission electron microscopy
TON	turnover number [mol mol^{-1} s^{-1}]
t	time [s, h]
V	volume [m^3]
$\dot{V}$	volumetric flow-rate
V_R	reaction volume [m^3]
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
η	catalyst effectiveness factor
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

Contents

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.

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].

R (Reactant)

Cat.   Cat.−R

P (Product)
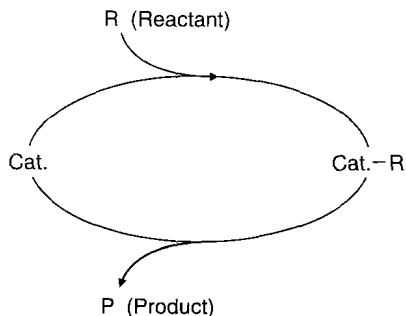
Fig. 1-1. Catalytic cycle

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
Methanol conversion to hydrocarbons	Zeolites	Mobil Chemical Co., 1975

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].

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:

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

$$(1\text{-}1)$$

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

$$\frac{dn_A}{dt} = kV\text{f}(c_A) \qquad (1\text{-}2)$$

k = rate constant

$\text{f}(c_A)$ is a concentration term that can exhibit a first- or higher order dependence on adsorption equilibria (see Section 4.2).

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

$$k = k_0\, e^{-(E_a/RT)} \qquad (1\text{-}3)$$

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 and is defined as the number of reactant molecules reacting per active center per second.

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}:

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

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: