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Chapter 2

Classification of industrial catalysts and catalysis for the petrochemical industry

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1. Introduction

Catalysts are used in all sectors of the chemical industry:

in basic chemistry, for the synthesis of nitric acid, sulfuric acid, ammonia, methanol and aromatics;

in petrochemistry, for the synthesis of intermediate chemicals and polymers;

in refining, essentially in reactions of fluid-catalytic-cracking and hydrotreatments;

in technologies for the abatement of pollutants, for removal of NO, CO and hydrocarbons in emissions of stationary and mobile combustors;

in the production of fine chemicals, for the synthesis of intermediates and active compounds.

In this paper of an issue dedicated mainly to the engineering aspects of catalysis, only a brief description of the several classes of industrial catalysts is presented. Emphasis is placed on the synthesis of intermediates for the petrochemical industry, and on the processes used in refineries. Catalysis for fine chemicals, polymerization reactions and pollutant abatements are not treated.

2. Properties of an industrial catalyst

A catalyst is a substance, or a mixture of substances, which increases the rate of a chemical reaction by providing an alternative, quicker reaction path, without modifying the thermodynamic factors. The catalyst remains, in general, unaltered at the end of the catalytic process.

The properties of a catalyst which determine its choice are the following:

(1) The activity, which can be expressed either in terms of rate (moles of product per volume of catalyst per hour), or of turnover number (mole of product per mole of catalyst or of active site), or of conversion (mole of transformed reactant per mole of inlet reactant). The higher the activity, the higher the productivity, and/or the lower the volume of the reactor and the milder the reaction conditions that can be used.

(2) The selectivity, (chemical, stereo or regio), expressed as mole of desired product per mole of converted reactant. The higher the selectivity, the lower the costs of separation, purification and waste treatments and the lower the amount of reagents necessary.

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(3) The lifetime, expressed in years of use before catalyst unloading or, better, in terms of amount of chemical produced per amount of catalyst. The higher the lifetime, the lower the down-time costs (loss of production due to exhaust catalyst substitution), and the lower the recatalyzing costs.

(4) The ease of regeneration of spent catalysts (in order to increase the lifetime and to reduce the problems related to spent catalyst disposal).

(5) The toxicity, the ease and safety in handling, and the disposal of spent catalysts.

(6) The price.

3. Types of catalysis

The two main types of catalysis, homogeneous and heterogeneous catalysis, can be classified according to the phases involved in the process.

3.1. Homogeneous catalysis

The reactants, the products and the catalysts are in the same phase, usually the liquid phase. The catalysts are soluble acids, bases, salts and organometallic compounds. The catalyst is dissolved in a solvent which can also be the reactant or the product itself. The advantages of homogeneous catalysis can be summarized as follows:

the utilization of almost all the molecules of the catalyst in the catalytic act;

the higher selectivity obtained in some reactions, especially in the synthesis of optically-active compounds;

the easier control of the temperature for highly exothermic reactions;

the higher selectivity achieved due to the fact that it is possible to operate at milder conditions (for instance, in oxidation reactions).

Homogeneous catalysis also have the following disadvantages:

expensive procedures of separation and of catalyst recovery;

serious problems of corrosion (when acid catalysts or solvents are employed);

expensive treatments of toxic liquid wastes obtained after the separation, regeneration and recycling of the catalyst;

the possibility of contamination of the products by the catalyst;

the existence of gas–liquid mass-transfer limitations in cases where one of the reactants is a gas (hydrogen, oxygen).

3.2. Heterogeneous catalysis

In this case, the catalyst, the reactants and the products are in different phases. Usually the catalyst is a solid, and the reactants and products are in the liquid or vapor phase. The catalysts are either inorganic solids, such as metal oxides, sulfides or chlorides, or organic solids, such as modified polymers.

The catalyst can be used (i) as a powder, in slurry reactors, in the presence of a liquid phase; (ii) in the form of pellets, in the presence of a liquid phase in trickle-bed reactors; (iii) as pellets in the presence of gaseous reactants in fixed-bed reactor; and (iv) in small-sized particles in fluid- or transport-bed reactors.

The advantages of heterogeneous catalysis are as follows:

the easier separation of catalysts from reactants and products;

the elimination of corrosion problems and of liquid waste treatments.

The disadvantages are as follows:

the difficulty in the control of temperature for very exothermic reactions;

the mass transfer limitations of reactants and products, both interphase and intraphase (inside the pores of the catalyst);

the requirement of high mechanical and erosion resistance for the catalysts.

4. Design of an heterogeneous catalyst

Heterogeneous catalysis is most widely used in industry, and the transformation of homogeneous catalysis (especially the acid one) to heterogeneous catalysis, by supporting of the catalyst or by developing alternative solid catalysts, is a constant trend of the chemical industry.

A catalyst used in heterogeneous catalysis is a composite material characterized by (i) the relative amount of several components, (ii) its shape, (iii) its size, (iv) its pore size distribution and (v) its surface area.

The components of a catalyst used in heterogeneous catalysis are the following:

The active species, constituted of one or more compounds which either contribute each one with its own different functional properties, or interact between themselves creating synergetic effects at their interfaces.

Physical promoters; elements or compounds added in small amounts that help in stabilizing the surface area of the composite material or that increase its mechanical resistance.

Chemical promoters, which are elements or compounds that modify the activity and selectivity of the active species.

Supports, which are compounds present in the highest amount in the composite material, that can play a multiple role in the catalyst.

The main roles of the support can be summarized as follows:

To reduce the amount of the expensive active species. The active species are in fact deposited on the surface of the support, and constitute a minor fraction of the catalyst.

To give the optimal surface and pore size distribution to the active species (i.e., those ones of the support, already optimized for different applications).

To increase the mechanical resistance of the catalyst composite.

To create a polyfunctional catalyst by introducing new active sites (usually, basic or acid sites).

To increase the heat exchange capacity of the catalyst composite (this is the case of the use of SiC as the support).

To stabilize metal components with a small particle size.

To stabilize metal oxide species in a valence and coordination state different from those typical of the unsupported oxide.

5. Classification of catalysts

It is possible to classify the catalysts on the basis of the key-properties responsible for their catalytic behavior. The following four main classes of catalysts can be singled out:

(1) Redox catalysts. These are catalysts for oxidation, hydrogenation, dehydrogenation and halogenation reactions. The main feature of these catalysts is the presence of transition elements (in the form of salts, complexes, sulfides, chlorides, oxides or metals) as the main component. Exceptions are: Ag, Cu, ZnO, SbO_x and $SbCl_x$.

(2) Acid–base catalysts. These are catalysts for alkylation, dehydration, hydration, oligomerization, cracking, H-transfer and isomerization reactions. The key feature of all the catalysts for these reactions is their acidity or basicity.

(3) Polyfunctional catalysts. They are catalysts for reforming, oligomerization and aromatization of paraffins. They are a mixture of redox and acid–base catalysts.

(4) Catalysts for the transformation of CO. It is the peculiar reactivity of CO that makes it possible to separate the catalysts for its transformation into a separate class.

6. Redox catalysts

6.1. Oxidation catalysts

In the oxidation reactions oxygen atoms are introduced into inorganic molecules or into organic ones with the formation of aldehydes, ketones, anhydrides, acids, hydroperoxides and epoxides. The reactions of N-insertion with formation of nitriles in the presence of ammonia (ammoxidation reactions) also belong to this group, as well as the transformation of C–C bonds into C = C bonds and of C–H bonds into

$C = O$, with the formation of water (oxidative dehydrogenation).

In most oxidation reactions molecular oxygen (air, oxygen-enriched air, oxygen) is used as the oxidizing agent, while a few other processes use organic hydroperoxides, hydrogen peroxide or nitric acid as the oxidant. The oxidation reactions are strongly exothermic and are all thermodynamically favoured at both low and high temperature, with the exception of the oxidation of SO_2, which is favored only at low temperature. Table 1 shows the most important industrial oxidation reactions, aimed to the synthesis of important chemicals, most of them employed as monomers for the polymer industry.

It is possible to single out four types of catalysis:

(1) in the vapour phase, with molecular oxygen and with heterogeneous catalysis, operating at temperatures higher than 250°C;

(2) in the liquid phase, with molecular oxygen and homogeneous catalysis;

(3) in the liquid phase, with hydroperoxide in homogeneous catalysis;

(4) in the liquid phase, with heterogeneous catalysis and either hydrogen peroxide or hydroperoxide.

6.1.1. Vapour phase oxidations

The following three mechanisms have been hypothesized to explain the activity of catalysts in vapour phase oxidations:

6.1.1.1. Redox mechanism. This mechanism has been proposed to explain both selective and unselective catalysis. The production of formaldehyde with Fe/Mo oxides-based catalysts is given here as an example:

$$MoO_4^{2-} + CH_3OH \rightarrow CH_2O + H_2O + MoO_3^{2-}$$

$$2Fe^{3+} + Mo^{4+} \rightarrow Mo^{6+} + 2Fe^{2+}$$

$$2FeO + \frac{1}{2}O_2 \rightarrow Fe_2O_3$$

6.1.1.2. Rideal mechanism. This mechanism has been hypothesized to occur only for the selective epoxidation of ethylene to epoxide on Ag-based catalysts.

$$Ag + O_2 \rightarrow AgO_2$$

$$AgO_2 + CH_2 = CH_2 \rightarrow Ag\text{-}O\text{-} + C_2H_4O$$

6.1.1.3. Langmuir–Hinshelwood mechanism. This mechanism can be postulated for the oxidation reactions which are not selective. As an

Table 1
Main catalytic oxidation processes in petrochemistry

Reagents	Product/coproduct	Het/Hom	Conv. (%)	Sel. (%)
Methanol/air	Formaldehyde	Het	99	94
n-Butane/air	Maleic anhydride	Het	75–80	67–72
Benzene/air	Maleic anhydride	Het	98	75
o-Xylene/air	Phthalic anhydride	Het	100	79
Naphthalene/air	Phthalic anhydride	Het	100	84
Propene/air, NH_3	Acrylonitrile	Het	> 99	73–77
Propene/air	Acrolein	Het	> 90	80–85
Acrolein/air	Acrylic acid	Het	> 95	90–95
Isobutene/air	Methacrolein	Het	> 97	85–90
Methacrolein/air	Methacrylic acid	Het	70–75	80–90
Ethene/oxygen	Ethene epoxide	Het	90	80
Ethene/air, HCl	1,2 Dichloroethane	Het	> 95	> 95
Propene/hydroperoxide	Epoxide/alcohol	Hom	10	90
Cumene/air	Phenol/acetone	Hom	35–40	90
Cyclohexane/air	Cyclohexanone	Hom	5–15	85–90
Cyclohexanone/HNO_3	Adipic acid	Hom	> 95	92–96
Cyclohexanone/NH_2OH,H_2SO_4	Cyclohexanoneoxime, $(NH_4)_2SO_4$	Hom	100	> 98
Cyclohexanone, NH_3, H_2O_2	Cyclohexanoneoxime	Het	> 99	95–98
p-Xylene/air	Terephthalic acid	Hom	90	85–95

example, the total combustion of hydrocarbons (HCR) with Pt-based catalysts is reported here:

$$2Pt + O_2 \rightarrow 2Pt\text{-}O\text{-}$$

$$2Pt + HC\text{-}R \rightarrow Pt\text{-}CR + PtH$$

$$n Pt\text{-}O\text{-} + m Pt\text{-}CR \rightarrow x CO_2 + y Pt$$

6.1.2. *Main properties of key-components in selective catalysts*

With the exception of Ag for ethylene epoxidation, of Pt for the oxidation of NH_3 to NO and for Pd for the oxidation of sugars, all selective catalysts for vapour phase oxidations contain one or more of the following elements in the form of (mixed) oxides: Mo, V, Sb and W.

The key-properties of the oxides of these elements are as follows:

the presence of Me = O bonds;

the acidic nature;

the high binding energy for the metal–oxygen bond;

the formation of non-stoichiometric oxides;

the inactivity (or the very low activity) in CO oxidation, and the high activity in methanol oxidation; oxidation is achieved by abstracting hydrogen rather than by donating oxygen.

6.1.3. *Liquid phase oxidations*

The following three mechanisms and types of catalysis can be singled out for liquid phase oxidations:

6.1.3.1. Radical chain mechanism. The first stages of the mechanism of oxidation occur with the following radical chain mechanism (IN: initiator):

$$RH + IN\cdot \rightarrow R\cdot + INH$$

$$R\cdot + O_2 \rightarrow ROO\cdot$$

$$ROO\cdot + RH \rightarrow ROOH + R\cdot$$

After this stage, the catalyst (a salt of a transition element of the first series) is involved through the following redox mechanism:

$$ROOH + Co^{2+} \rightarrow RO\cdot + Co^{3+} + OH^-$$

$$Co^{3+} + ROOH \rightarrow Co^{2+} + ROO\cdot + H^+$$

6.1.3.2. Oxygen transfer mechanism. The role of the catalyst is to transfer an oxygen atom (through complexation and activation) from the hydroperoxide or hydrogen peroxide to an olefin. Mo complexes, Ti on silica and Ti-silicalite are the catalysts which operate with this mechanism.

Table 2
Main industrial processes of hydrogenation

Reagent	Products	Catalyst	Temp. (°C)	Press. (atm)
N_2	NH_3	Fe	350	300
CO	CH_3OH	Cu/Zn/Al oxides	250	50
Unsat. esters	Unsat. alcohols	Cu/Cr oxides	300	300
Benzene	Cyclohexane	Ni	80	30
Olefins/CO	Alcohols	Rh complexes	80	20
Nitrobenzene	Aniline	Pd/C	80	70
Benzene	Cyclohexene	Ru (Zn)	80	10
Adiponitrile	Hexamethylendiamine	Ni	100–130	30
Aldehydes	Alcohols	Cu/Cr oxides	160	60
Maleic anhydride	Butyrrolactone	Cu/Cr oxides	220	5
CO	Paraffins	Fe	300	60
Fat nitriles	Saturated amines	Ni	140	50
Phenol	Cyclohexanone	Ni	150-250	75–200
Oils, greases	Unsat. alcohols	Cu/Cr oxides	200–300	100–300
Fat acids	Part. satur. acids	Cu/Cr oxides	130–190	4
Diolefins, acetylene	Olefins	Pd	50–80	1–10
Dinitrotoluene	Diamintoluene	Ni	100	50
Glucose	Sorbitol	Ni	140	170

6.1.3.3. Redox mechanism. The oxidation of olefins with molecular oxygen catalyzed by $PdCl_2$-$CuCl_2$ occurs through the following redox mechanism:

$$PdCl_2 + H_2O + CH_2 = CH_2 \rightarrow Pd + 2HCl + CH_3CHO$$

$$Pd + 2CuCl_2 \rightarrow PdCl_2 + 2CuCl$$

$$2CuCl + \frac{1}{2}O_2 + 2HCl \rightarrow 2CuCl_2 + H_2O$$

6.2. Hydrogenation catalysts

It is possible to identify two types of hydrogenation reactions:

(1) addition of H_2 to multiple bonds;

(2) reactions of hydrogenolysis with transformation of C–X bond into C–H and H–X bonds.

Almost all industrial reactions employ molecular hydrogen as the hydrogenating agent. Hydrogenation reactions are exothermic and thermodynamically favored at low temperature (usually, at temperatures lower than 120°C). The most used catalysts are those which contain VIII group elements: Fe, Co, Ni; Ru, Rh, Pd; Os, Ir, Pt.

However other elements also are present in industrial catalysts, such as Cu, Re, Mo-sulfides, ZnO and Cr_2O_3.

The most important hydrogenation reactions are reported in Table 2. Four types of industrial hydrogenation catalysis can be singled out:

(1) Homogeneous catalysis, with metal complexes (e.g. Rh complexes, which are active at temperatures lower than 80°C, or Co carbonyl compounds, active at $T < 180°C$).

(2) Heterogeneous catalysis in the liquid phase, with catalysts in the form of a powder. This is one of the most widely used types of catalysis (e.g. Pd supported on carbon).

(3) Heterogeneous catalysis in the liquid phase, with catalysts in the form of pellets (e.g. for hydrogenolysis of petroleum fractions with Co/Mo sulfides).

(4) Heterogeneous catalysis in the vapour phase, with the catalyst in the form of pellets (e.g. Cu/Cr oxides, Fe).

All the hydrogenation catalysts are able to activate molecular hydrogen, but they can differ in the capacity to activate the several functional groups to be hydrogenated.

The choice of a hydrogenation catalyst is based on a compromise between the following properties:

6.2.1. The activity

The individual group VIII elements show different scales of activity towards the various functional groups. For example, in the hydrogenation of:

(a) olefins, the order of activity is Rh > Ru > Pd > Pt > Ir = Ni > Co > Fe;

(b) acetylenes: Pd > Pt > Ni > Rh > Fe > Co = Ir = Ru

(c) aromatics: Pt > Rh > Ru > Ni > Pd > Co > Fe.

The choice of a more active catalyst makes it possible to (i) operate at lower temperature, with the possibility to obtain higher selectivity due the milder reaction conditions, (ii) use a lower amount of catalyst, and spend a shorter time for filtration, (iii) use a shorter residence time, thus minimizing consecutive reactions.

6.2.2. The chemioselectivity

This property is important when only one functional group has to be hydrogenated in a molecule which has more than one group (e.g. in the hydrogenation of unsaturated aldehydes to unsaturated alcohols).

6.2.3. Stereoselectivity

In the case of synthesis of high-purity optically-active molecules (e.g. in the synthesis of L-Dopa).

6.2.4. Regioselectivity

In the case where hydrogenolysis (i.e. of CCl bonds) reaction are required only in some positions of an aromatic ring.

6.2.5. The price

In the synthesis of ammonia, for example, the most active catalyst is Ru, but Fe is still used because of its lower cost. The same occurs in the hydrogenation of benzene; the most active catalyst is Pt, but Ni is widely employed.

6.2.6. The susceptibility to poisons

The metals are highly sensitive to impurities present in the reactants, and sometimes also to some functional groups. The most common poisons are S, CO, Cl, and N-containing groups. The degree of poisoning is different for the various catalysts (e.g. in the presence of sulfur-containing compounds the hydrogenation of olefins must be carried out with Co/Mo sulfides-based catalysts).

6.2.7. Environmental aspects

In the future, for the hydrogenation of glucose to sorbitol Ru will be the preferred catalyst, even though is much more expensive than the currently employed Ni-based catalyst. However, Ru is 5 times more active than Ni, and can operate at lower temperature with lower formation of by-products. In addition, Ni is easier to dissolve in the reaction medium than Ru. The dissolution of Ni contributes to the high cost of waste water treatment and of product purification to remove Ni impurities (Ni is suspected to cause cancer in humans).

6.3. Dehydrogenation catalysts

The dehydrogenation reactions are endothermic and are favored at high temperature.

The main dehydrogenation reactions, reported in Table 3, can be divided into the following two classes:

(1) Dehydrogenation of alcohols to ketones, carried out at temperatures lower than 450°C with Ag or ZnO. The choice of these catalyst is due to the fact that the transitions elements must be avoided because are too active, and promote further dehydrogenation of the molecule. In addition, acid and basic sites must be minimized, in order to avoid side reactions involving both reactants and products.

(2) Dehydrogenation of paraffins and of alkyl aromatics to olefins, at temperatures higher than 500°C. With the exception of higher paraffins (C_{10}–C_{13}), these are the most difficult reactions, because of the following reasons:

(a) thermodynamic limitations on the reactant conversion;

(b) side reactions of thermal cracking, favoured at the same temperature at which the dehydrogenation occurs;

(c) formation of coke on the catalyst, which consequently requires frequent regeneration;

(d) strongly endothermic reaction, which necessitates that a large amount of heat must be supplied at temperatures above the reaction temperature.

The following catalytic systems have been used for the dehydrogenation of paraffins:

Pt-Sn on γ-alumina, in the presence of hydrogen as a diluent;

Pt-Sn on Mg aluminate, in the presence of steam as a diluent;

K-doped Cr/Al oxide, in vacuum or at atmo-

Table 3
Main dehydrogenation reactions

Reactant	Product	Catalyst	Temp. (°C)	Press. (atm)
sec-Butanol	Methylethylketone	ZnO (Ag)	35	1
Cyclohexanol	Cyclohexanone	ZnO (Ag)	400	1
Ethylbenzene	Styrene	Fe/Cr/K/O	550–650	1–3
Isobutane	Isobutene	Cr/K/Al/O	500–650	1–5
Isobutane	Isobutene	Pt-Sn/Al_2O_3	500–650	1–5
n-Butane, butenes	Butadiene	Fe/Cr/O	620–680	1–2
Isopentane, isoamylenes	Isoprene	Fe/Cr/K/O	600	1–2
C_{10}–C_{13} paraffins	C_{10}–C_{13} olefins	Pt/ Al_2O_3	400–500	2–3

spheric pressure, either in alternating fixed-bed or in fluid-bed reactors.

For the dehydrogenation of ethylbenzene to styrene, only K-doped, Fe/Al oxide has been used as the catalyst, in the presence of steam as the diluent.

6.4. Halogenation catalysts

Chlorination reactions are the most important halogenation reactions.

Chlorinations consist of the addition of chlorine atoms to C = C bonds, and of the transformation of C–H bonds into C–Cl bonds. The chlorination reactions are very exothermic, and favoured at any temperature.

The following three types of technologies for olefins and aromatics chlorination are industrially employed:

(1) Homogeneous catalysis, with Cl_2 as the chlorinating agent, operating at $T < 80°C$, with $FeCl_3$ or $SbCl_5$ catalysts.

(2) Heterogeneous catalysis with Cl_2 and with supported metal chlorides as catalysts.

(3) Heterogeneous catalysis, with $HCl + O_2$ as chlorinating agents, and with γ-alumina-supported $CuCl_2$-KCl catalysts. Both chlorination processes involve a redox-type mechanism.

6.4.1. Chlorination

$$FeCl_3 + Cl_2 \rightarrow FeCl_4^- Cl^+$$

$$FeCl_4^- Cl^+ + CH_2 = CH_2 \rightarrow FeCl_3 + CH_2Cl\text{-}CH_2Cl$$

6.4.2. Oxychlorination

$$CH_2 = CH_2 + 2CuCl_2 \rightarrow CH_2Cl - CH_2Cl + 2CuCl$$

$$2CuCl + 0.5O_2 \rightarrow CuOCuCl_2$$

$$CuOCuCl_2 + 2HCl \rightarrow 2CuCl_2 + H_2O$$

7. Acid–base catalysts

7.1. Acid catalysts

The acid catalyzed reactions include the following reactions: double bond isomerization, skeletal isomerization, hydrogen-transfer, oligomerization, polymerization, alkylation, cracking, hydration, dehydration and etherification. The most important acid-catalyzed industrial reactions, reported in Table 4, fall into one of the following three categories:

(1) Heterogeneous catalysis in the vapor phase, with oxides as catalysts.

(2) Heterogeneous catalysis in the liquid phase, with acid supported on oxides (P_2O_5 on silica), or on polymers (sulfonate polymers).

(3) Homogeneous catalysis, with either organic or inorganic Broensted or Lewis acids.

The catalytic properties of acid catalysts are due to their ability to create carbocations in the organic substrate. The carbocations are reactive intermediates which can drive the transformation of the reactant into another molecule. This is the reason why the acid catalysts are not selective.

Table 4
Main acid-catalyzed industrial processes

Reactant	Product	Catalyst	Temp. (°C)	Press. (atm)
Naphtha, gasoil, LPG	Olefins (Catal. Crack)	H-Y	480–540	1–5
Olefins	Oligomers	Al-Ti-alkyl compl.	100–120	100
Olefins	Dimers, trimers	H_3PO_4/SiO_2	200	30–40
Isobutane/olefins	Higher isoparaffins	HF	40	20
Benzene/ethylene	Ethylbenzene	$AlCl_3/HCl$	160–180	10
Benzene/ethylene	Ethylbenzene	H-ZSM5	420–450	15–25
Benzene/propylene	Cumene	H_3PO_4/SiO_2	220	30–40
Isobutene/methanol	Methylterbutylether	Sulf. resins	65–95	7–15
Ethylene	Ethanol	H_3PO_4/SiO_2	300	70
Propylene	Isopropanol	Sulf. resins	130–150	60–100

In order to increase the selectivity and minimize the by-products formation, which can also deactivate the catalyst, it is possible to intervene with respect to the following factors:

(1) The thermodynamics. Some acid reactions are favoured at low temperature while other ones are favoured at high temperature. For instance, polymerization is favoured at low temperature, cracking at high temperature, while double bond and skeletal isomerizations can occur at any temperatures.

(2) The acid strength. Each reaction requires a particular acid strength. Double bond isomerization and dehydration require sites with a weak acid strength, while cracking or skeletal isomerization require strong acid sites. The acidity of homogeneous catalysts can be varied by varying the catalyst concentration, while for oxide catalysts the acidity increases according to the following scale:

$$Al_2O_3 < SiO_2/H_3PO_4 < SiO_2/Al_2O_3 = \text{acid zeolites}$$

7.2. Shape selectivity with acid zeolites

Zeolites are crystalline acid aluminosilicates. The acid sites are accessible through framework channels and windows 0.4 to 0.8 nm in size, quite similar to the dimensions of many molecules employed in petrochemistry. Several types of zeolites are known, which possess different channels opening, and therefore with different accessibility to organic molecules: A, X, Y, ZSM5, erionite, etc.

Zeolite-based catalysts present three types of selectivity:

7.2.1. Shape selectivity on reactants

Only molecules which are smaller than the opening size have access to the zeolite cages and react with the acid sites localized inside the cavities. This kind of selectivity has been found to occur in the dewaxing reactions: in a mixture of *n*- and isoparaffins only the linear molecules can diffuse in the structural porous network of the zeolite (an erionite), and consequently can be cracked into lower molecular weight hydrocarbons.

7.2.2. Shape selectivity on products

Only molecules which pass through the channels can get out from the cages and can be obtained as products. For example, in the reaction of alkylation of benzene with ethylene, higher selectivity to monoethylbenzene is obtained since diethylbenzenes are too bulky to pass through the channels of the zeolite (H-ZSM5), and equilibrate inside the cages with benzene giving rise to more ethylbenzene (transalkylation).

7.2.3. Shape selectivity on transition state

Heavy hydrocarbons formed by condensation reactions can not be formed due to the small size of the cages, which hinders the formation of bulky transition states (bimolecular reactions). This property allows the use of zeolites in acid-catalyzed reactions without the sensible deactivation which instead occurs with other types of acid catalysts.

7.3. Basic catalysts

Basic catalysts are constituted of KOH, K on carbon, NaOH on alumina, or of basic oxides such as MgO, CaO, ZrO_2. These latter oxides are less basic.

The basic catalysts are not extensively used in industry because they deactivate by exposure to the atmosphere.

In comparison to acid catalysts, basic catalysts (i) catalyze other types of reaction and (ii) exhibit a peculiar selectivity for some reactions.

The first step in the mechanism of a basic-catalyzed reaction is the formation of a carboanion through the interaction of the organic substrate with the catalyst.

The main differences in reactivity between basic and acid catalysts are the following:

(1) Isomerization of double bonds. Basic catalysts isomerize olefins forming the cis isomer;

in addition, they do not possess cracking activity.

(2) Dehydration. Basic catalysts dehydrate secondary alcohols to primary olefins, while acid catalysts produce mixtures of primary and secondary olefins.

(3) Alkylation. Basic catalysts alkylate alkylaromatic compounds in side chains and not in the aromatic rings.

(4) Aldolic condensation and Diels Alder reaction. These are typical reactions catalyzed by basic catalysts.

(5) Polymerization. Basic catalysts catalyze the formation of polymers with very high molecular weights.

8. Polyfunctional catalysts

The first polyfunctional catalyst to be developed was a reforming catalyst. The main reactions which occur in the reforming process are the skeletal isomerization of *n*-paraffins and the transformation of cycloparaffins to aromatics. The reforming catalysts is constituted of 1.2% Pt, 0.01% Re, 97.29 γ-alumina and 1.5% HCl.

The reforming mechanism can be illustrated using *n*-heptane isomerization as an example:

n-heptane ⇔ *n*-heptene → isoheptene ⇔ isoheptane

The key-features of this reaction scheme and of the designed catalyst are the following:

(1) Acid catalysts are not active in paraffin isomerization, but are active in skeletal isomerization of olefins. A dehydrogenation component is therefore introduced together with the acid catalyst, in order to transform the paraffin to an olefin. In a following step, the olefin is isomerized by the acid function of the catalyst.

(2) High temperatures are necessary in order to favour the first step; however, at high temperature cracking reactions become important. In addition, low temperatures (and also H_2 pressure) are necessary to decrease the amount of residual olefins in the product. These contradictions in the optimal reaction conditions of the several steps are overcome by choosing a very active catalyst for the first and final step, driving the dehydrogenation–hydrogenation reaction at equilibrium.

(3) The overall rate-determining step must be the acid one.

(4) The presence of HCl is necessary to increase the acidity of the γ-alumina, while the presence of Re as promoter of Pt is necessary to decrease the hydrogenolysis reaction.

Few polyfunctional catalysts are known, but it is very likely that in many other types of reactions different kinds of functional groups are indeed working. The concept of polyfunctionality can help in the design of new types of catalysts. Polyfunctionality can be obtained by (i) simply mixing two different active components, (ii) by supporting one active component onto a material with different active functionality (i.e. a dehydrogenating component onto an acid support), or (iii) by creating catalysts which have different types of active sites in their structure.

9. Catalysts for the transformation of CO

The most important catalytic reactions of CO transformation are:

(1) Synthesis of methanol from CO and H_2, with Cu/Zn/Al/O based catalysts.

(2) Synthesis of long-chain paraffins from CO and H_2 with supported Fe catalysts.

(3) Synthesis of acetic acid from methanol and CO, with Rh complexes.

(4) Synthesis of aldehydes from CO/H_2 and olefins, with Rh or Co complexes.

(5) $CO + H_2O$, to produce H_2 and CO_2 with Cu/Zn/Al/O based catalysts.

10. For further reading

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