



Catalysts of the preparation and industrial importance of catalysis and catalyst deactivation

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Abstract

A catalyst is a substance which increases the rate at which a chemical reaction approaches equilibrium without becoming itself permanently involved, Types of Catalysis (homogeneously catalyzed and Heterogeneous catalysis), Industrial Importance of Catalysis: Catalysts are the workhorses of chemical transformations in the industry.

Classification of Catalysts :(Unsupported (Bulk) Catalysts, Supported Catalysts). General Methods of Preparation for Supported Catalyst Systems: (Impregnation, Adsorption from Solution, Chemical Vapour Deposition (CVD), Co-precipitation, Deposition, Regenerability).

Catalyst design parameters: (Activity, Stability, Selectivity).

Catalyst deactivation: deactivation leads to a shortened catalyst lifetime, and the replacement of an aged catalyst to a new one is determined by the industrial processes for which the catalyst is used.

Keywords: catalysts of the preparation and industrial importance of catalysis and catalyst deactivation

1. Introduction: Essential principle of catalyst

The term catalysis was coined by Berzelius over 150 years ago when he had noticed changes in substances when they were brought in contact with small amounts of certain species called "ferments". Many years later in 1895 Ostwald came up with the definition that we use until today: A catalyst is a substance *that changes the rate of a chemical reaction without its appearing into the products*. This means that according to Ostwald a catalyst can also slow down a reaction! The definition used today reads as follows: *A catalyst is a substance which increases the rate at which a chemical reaction approaches equilibrium without becoming itself permanently involved* ^[1].

The catalysis as a scientific discipline originated in the early part of the last century. Earlier, the unique feature of a catalytic substance, namely that when added in small quantities to a reaction it affects its rate and selectivity but is not consumed, had become widely recognized, and many applications had been developed. Only after chemical thermodynamics had been defined did a rational approach to discover new catalytic processes become possible. Thermodynamics would define the proper conditions at which a material should be tested as a catalyst and catalytic turnover would be expected. Ostwald, one of the founding fathers of chemical thermodynamics, introduced thermodynamics into the physical chemical definition of a catalyst, specifying that it is a material that will leave the equilibrium of a reaction unchanged ^[2, 3].

Catalysis plays a central role in chemical transformations and lies at the heart of countless chemical protocols, from academic research at laboratories level to the chemical industry level ^[4, 5]. By using catalytic reagents, one can reduce the temperature of a transformation, reduce reagent-based waste and enhance the selectivity of a reaction that potentially avoids the unwanted side reactions leading to a green technology.

1.2. Types of Catalysis

If the catalyst and reactants or their solution form a common physical phase, then the reaction is called homogeneously catalyzed. Metal salts of organic acids, organometallic complexes are typical homogeneous catalysts.

Heterogeneous catalysis involves systems in which catalyst and reactants form separate physical phases. Typical heterogeneous catalysts are inorganic solids such as metals, oxides, sulfides, and metal salts, but they may also be organic materials such as organic hydro peroxides, ion exchangers, and enzymes ^[6, 7].

1.3. Industrial importance of catalysis

Catalysts are the workhorses of chemical transformations in the industry. Approximately 85–90% of the products of chemical industry are made in catalytic processes. Catalysts are indispensable in Production of transportation fuels in one of the approximately 440 oil refineries all over the world.

Production of bulk and fine chemicals in all branches of chemical industry.

Prevention of pollution by avoiding formation of waste (unwanted byproducts).

- Abatement of pollution in end-of-pipe solutions (automotive and industrial exhaust).

A catalyst offers an alternative, energetically favorable mechanism to the noncatalytic reaction, thus enabling processes to be carried out under industrially feasible conditions of pressure and temperature ^[8].

The industrial production of precipitated catalysts usually involves the following steps ^[6, 9, 10, 14]:

- (1)-Preparation of metal salt solution and of precipitating agent (dissolution, filtration)
- (2)-Ageing of the precipitate
- (3)-Precipitation
- (4)-Washing of the precipitate by decantation
- (5)-Filtration
- (6)-Washing of the filter cake (spray drying)
- (7)-Drying
- (8)-Calcining
- (9)-Shaping
- (10)-Activation

3. Classification of Catalysts

Catalysts are extremely important in largescale processes [163-167] for the conversion of chemicals, fuels, and pollutants. Typical industrial catalysts, however, consist of several components and phases. This complexity often makes it difficult to assess the catalytic material's structure.

In the following a variety of families of existing catalysts are described, and selected examples are given. These families include (1) unsupported (bulk) catalysts; (2) supported catalysts; (3) confined catalysts (ship-in-a-bottle catalysts); (4) hybrid catalysts; (5) polymerization catalysts, and several others. The selected examples not only include materials which are in use in industry, but also materials which are not yet mature for technological application but which have promising potential.

3.1. Unsupported (Bulk) Catalysts

3.1.1. Metal Oxides

Oxides are compounds of oxygen in which the O atom is the more strongly electronegative component. Oxides of metals are usually solids. Their bulk properties largely depend on the bonding character between metal and oxygen.

Metal oxides make up a large and important class of catalytically active materials, their surface properties and chemistry being determined by their composition and structure, the bonding character, and the coordination of surface atoms and hydroxyl groups in exposed terminating crystallographic faces. They can develop acid base and redox properties.

Metal oxides can have simple composition, like binary oxides, but many technologically important oxide catalysts are complex multicomponent materials.

3.2. Supported Catalysts

Supported catalysts play a significant role in many industrial processes. The support provides high surface area and stabilizes the dispersion of the active component (e.g., metals supported on oxides). Active phase – support interactions, which are dictated by the surface chemistry of the support for a given active phase, are responsible for the dispersion and the chemical state of the latter. Although supports are often considered to be inert, this is not generally the case. Supports may actively interfere with the catalytic process.

Active phase – support interactions, which are dictated by the surface chemistry of the support for a given active phase, are responsible for the dispersion and the chemical state of the latter. Although supports are often considered to be inert, this is not generally the case. Supports may actively interfere with the catalytic process. Typical examples for the active interplay between support and active phase are bifunctional catalysts such as highly dispersed noble metals supported on the surface of an acidic carrier.

3.2.1. Supports

Many of the bulk materials described in Section Unsupported (Bulk) Catalysts may also function as supports. The most frequently used supports are binary oxides including transitional aluminas, α - Al_2O_3 , SiO_2 , TiO_2 (anatase), ZrO_2 (tetragonal), MgO etc., and ternary oxides including amorphous $\text{SiO}_2 - \text{Al}_2\text{O}_3$ and zeolites. Additional potential catalyst supports are aluminophosphates, mullet, kieselguhr, bauxite, and calcium aluminate. Carbons in various forms (charcoal, activated carbon)

can be applied as supports unless oxygen is required in the feed at high temperatures [6, 15, 16, 17].

Table 1: Properties of typical catalyst supports

Support Crystallographic Properties/ phases applications	
Al_2O_3 mostly α and γ	SA up to 400; thermally stable Three-way cat., steam reforming and many other cats.
SiO_2 amorphous	SA up to 1000; thermally stable Hydrogenation and other cats.
Carbon amorphous	SA up to 1000; unstable in oxide environm., hydrogenation cats.
TiO_2 anatase, rutile	SA up to 150; limited thermal Stability; SCR cats.
MgO fcc	SA up to 200; rehydration may be problematic; steam reforming cat.
Zeolites various	Highly defined pore system; Shape selective; bifunctional cats.
(faujasites, ZSM-5) alumina amorphous	Silica/ SA up to 800; medium strong acid sites; dehydrogenation cats. Bifunctional catalysts.

SA = surface area in m^2/g

4. General methods of preparation for supported catalyst systems

The principal catalyst-preparation technique involves two stages. First, rendering a metal-salt component into a finely divided form on a support and secondly; conversion of the supported metal salt to a metallic or oxide state.

The first stage is known as dispersion and is achieved by impregnation, adsorption from solution, co-precipitation, or deposition, while the second stage is variously called calcination or reduction [18]. It is brought about by a thermal treatment in either an inert atmosphere or an active atmosphere of either oxygen or hydrogen. When the active atmosphere is hydrogen the process is known as reduction. Although calcination/reduction can cause major problems in catalyst preparation on a large scale, it is a generalization to say that once the metal species has been bound to the support surface its degree of dispersion and location will be retained during subsequent treatments.

The primary aim of applying a catalytically active component to a support is to obtain the catalyst in a highly dispersed form and hence in a highly active form when expressed as a function of the weight of the active component.

This feature of supported catalysts is especially important with regard to precious-metal catalysts, because it allows more effective utilization of the metal than can be achieved in bulk-metal systems. However, in the case of base-metal catalysts the use of the support is often primarily aimed at improving the catalyst stability. This can be achieved by suitable interaction between the active material and the support.

A wide range of techniques has been employed for the incorporation of a catalytically active species onto a support material. The most widely used techniques is given more important chemical and physical factors involved in the dispersion of metal salts onto supports and their influence on the activity, selectivity, and durability of the catalyst system.

Impregnation. Impregnation as a means of supported catalyst preparation is achieved by filling the pores of a support with a solution of the metal salt from which the solvent is subsequently evaporated. The catalyst is prepared either by spraying the support with a solution of the metal compound or by adding the support material to a solution of a suitable metal salt, such that

the required weight of the active component is incorporated into the support without the use of excess of solution. This is then followed by drying and subsequent decomposition of the salt at an elevated temperature, either by thermal decomposition or reduction. With this method of preparation it is essential to have an understanding of both chemical and physical properties of the support and the chemistry of the impregnating solution in order to control the physical properties of the finished catalyst. When used for the preparation of mixed metal catalysts, care has to be taken to confirm that a component in an impregnating solution of metal salts is not selectively adsorbed, resulting in an unexpectedly different and undesirable concentration of metals in a mixed-metal catalyst. This technique has been widely used for the preparation of small amounts of catalyst for basic studies.

Adsorption from Solution. Adsorption is defined as the selective removal of metal salts or metal ion species from their solution by a process of either physisorption or chemical bonding with active sites on the support. Depending upon the strength of adsorption of the adsorbing species, the concentration of the active material through the catalyst particle may be varied and controlled. This technique is widely used in the preparation of industrial catalysts as it permits a greater degree of control over the dispersion and distribution of the active species on the support. In some systems, however, the weight of the active component that can be incorporated into the support is limited. Although multiple adsorption is often possible it is not recommended when close control of physical parameters is required.

Adsorption occurs whenever a solid surface is exposed to a gas or liquid: it is defined as the enrichment of material or increase in the density of the fluid in the vicinity of an interface. Under certain condition there is an appreciable enhancement in the concentration of a particular component and the overall effect is then dependent on the extent of the interfacial area. For this reason, all industrial adsorbents have large specific surface areas (generally well in excess of $100 \text{ m}^2 \text{ gm}^{-1}$) and are therefore highly porous or composed of very fine particles.

Adsorption is of great technological importance. Thus, some adsorbents are used on a large scale as desiccants, catalysts or catalyst supports; Others are used for the separation of gases, the purification of liquids, pollution control or for respiratory protection. In addition, adsorption phenomena play a vital role in many solid state reactions and biological mechanisms. Another reason for the widespread use of adsorption techniques is the importance now attached to the characterization of the surface properties and texture of fine powders such as pigments, fillers and cements [20].

Co-precipitation. The preparation of supported catalysts by the co-precipitation of metal ions with the support ions usually produces an intimate mixing of catalysts and support. An example of this technique is the co-precipitation of metal ions with aluminium ions to produce a precipitated alumina gel containing the metal hydroxide. This precipitate when calcined produces a refractory support with active component dispersed throughout the bulk as well as at the surface. However, in the preparation of multicomponent catalysts, it is possible under improper conditions to obtain a heterogeneous product because of the different solubility products of the constituents. Care should be taken therefore to avoid this undesirable situation by appropriate forethought.

Deposition. Deposition, as used in preparing supported catalysts, is the laying down or placing of the active components on the exterior surface of a support. One means by which this may be achieved is the preparation of catalysts by sputtering, which involves condensing the metal vapour onto an agitated finely dispersed support. However, as this process is performed under a high vacuum, the technique is probably only useful for the preparation of 'model' catalysts. Alternatively, the process may be performed in the liquid phase by the deposition of a metal sol onto a suspended support.

Chemical Vapour Deposition (CVD). Another example of deposition is the vapour plating of the support with a volatile inorganic or organometallic compound. The process requires only a moderate vacuum and is currently one of the methods under research in industry [19] as a means of preparing catalysts with a purely surface deposition. Also included in this preparation category is the addition of a precipitating agent for the metal ion to a suspension of the support in an impregnating solution. A layer of precipitated metal ion adheres to the support material, which can be thermally decomposed as before.

In the case of vapour-phase processes for metal deposition on the support, only limited control of dispersion and distribution of the metal crystallites is possible. In the case of liquid-phase systems, they do not provide as wide a range of catalysts as is possible with techniques based on adsorption from solution. However, the technique does provide a means of preparing well characterized surface-impregnated supports.

5. Catalyst design parameters

For catalyst design purposes it is first necessary to translate the catalyst performance parameters into a physical picture of catalyst structure. As them shall see, different performance parameters can give rise to different structural features and so a compromise is generally required. For example it is commonly found in industrial applications that initial catalyst activity may be sacrificed in favour of improved catalyst stability, since a lower activity and a prolonged operating catalyst life is in general preferable to a higher initial activity that decays rapidly. First, we should therefore discuss some of the relationships between the catalyst performance parameters and physical structure.

Activity: In general activity arises from maximizing both the dispersion and availability of the active catalytic material. Ideally, from an activity viewpoint, the catalyst material should be highly dispersed and concentrated on the external surface of the support. Already, however, there is an inherent conflict as high concentrations of active material become progressively more difficult to disperse.

Stability: By stability we refer to the loss in activity with time. This is due to one or several of four main causes; fouling of the active surface with involatile reaction by-products, sintering or crystal growth of the active material, poisoning of the active surface by feed impurities, and blockage of the support pore structure.

Selectivity: Catalyst selectivity can change due either to physical or chemical reasons. For sequential reactions diffusivity and mass transport through the pore structure can lead to apparent loss in selectivity in the formation of intermediate products. Location of active ingredients and pore-size distributions are therefore again of importance. Changes in selectivity can also arise from changes

in intrinsic chemical activity of the active component. Typically this can be affected by use of multicomponent catalysts in which case, as we saw earlier for stability improvement, the location of the difference components ideally should be the same. A specific example of this type of selectivity arises in the case of multifunctional catalysts in which a hydrogenation function is combined with an acid function. Since the latter is typically provided by the support and the former by the impregnated material, a uniform impregnation is required.

Regenerability: Regenerability refers to the reactivation of a catalyst, which typically will involve an air calcination followed in some cases by a redispersion of the active components. From the catalyst design viewpoint this will generally imply of the active components under the high temperature oxidizing environments required for the oxidation of the deactivating carbonaceous deposits. It is now generally recognized that many metals sinter more readily under oxidizing conditions and in extreme cases may even dissolve in the underlying support and become effectively removed from the reaction system. A further complication arises with multicomponent catalysts in which the combination ratio is all important, since such combinations frequently are destroyed under oxidizing conditions.

The activity, stability, and selectivity are determined by the correct dispersion and location of the active ingredients. Dispersion, location, and Regenerability are each in their turn determined by the interaction of the active components with the support surface and with each other during preparation, activation, use and regeneration.

5. Catalyst deactivation

Catalyst deactivation, the loss over time of catalytic activity or selectivity, is a problem of great economical concern in application of commercial catalytic processes. Catalyst deactivation is attributed to interaction between the catalyst and the impurities present in process effluent in which the catalyst is used. Any chemical or physical interaction that reduces catalyst activity or selectivity is classified as catalyst deactivation phenomena. In general, deactivation leads to a shortened catalyst lifetime, and the replacement of an aged catalyst to a new one is determined by the industrial processes for which the catalyst is used. Industrial catalytic deactivation can range from short term to several years. Given that reduced catalyst lifetime has a strong negative impact on the process economics improved catalyst lifetime is of great commercial value^[21].

The causes of catalyst deactivation can be grouped into: chemical deactivation through reversible or irreversible poisoning; physical deactivation through fouling; thermal deactivation through sintering; loss of active material by vaporization; and mechanical deactivation through attrition or erosion (Petersen *et al.*, 1987, Bartholomew, 2001, Forzatti *et al.*, 1999, Chen *et al.*, 1992, Moulijn *et al.*, 2001).

The loss over time of catalytic activity and/or selectivity, is a problem of great and continuing concern in the practice of industrial catalytic processes. Costs to industry for catalyst replacement and process shutdown total billions of dollars per year. Time scales for catalyst deactivation vary considerably; for example, in the case of cracking catalysts, catalyst mortality may be on the order of seconds, while in ammonia synthesis the iron catalyst may last for 5–10 years. However, it is inevitable that all catalysts will decay.

Catalyst deactivation is inevitable for most processes, some of its immediate, drastic consequences may be avoided, postponed, or even reversed. Thus, deactivation issues (*i.e.*, extent, rate, and reactivation) greatly impact research, development, design, and operation of commercial processes. Accordingly, there is considerable motivation to understand and treat catalyst decay. Over the past three decades, the science of catalyst deactivation has been steadily developing, while literature addressing this topic has expanded considerably to include books^[22-25], comprehensive reviews^[26-29], proceedings of international symposia^[30-35], topical journal issues (e.g.,^[36]), and more than 20,000 U.S. patents for the period of 1976–2013. (In a U.S. patent search conducted in November 2013 for the keywords catalyst and deactivation, catalyst and life, and catalyst and regeneration, 14,712, 62,945, and 22,520 patents were found respectively.)

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