

Preparation of Solid Catalysts

Edited by G. Ertl, H. Knözinger,
J. Weitkamp

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Foreword

The Handbook of Heterogeneous Catalysis was published in 1997. This book is part of the Handbook, now published as a monograph. Publisher and Editors felt that the Handbook of Heterogeneous Catalysis, which is only available as a full set of five volumes covering almost all aspects of heterogeneous catalysis, might not always be accessible to individuals interested in narrower areas of this field of chemistry. Therefore, the chapters dealing with aspects of preparation of catalysts were selected and put together in this monograph. Catalysis is a rapidly growing field of both academic and technological interest; this Handbook aims to cover the concepts without an encyclopedic survey of the literature, so – although the chapters chosen could not be updated for the present volume – we believe that it will prove most useful to all readers interested in the chemical and physicochemical basis of the preparation of catalysts.

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1 Introduction

Nature has developed the most efficient and selective catalysts known today. Workers in academia and industry still have a long way to go to reach nature's sophistication in the synthesis of catalysts. For many decades, catalysts were prepared by an empirical approach based on the experience and knowledge of the particular period. Perhaps the best known success story of the development and preparation of a technical solid catalyst by empirical methodologies is that of the ammonia synthesis catalyst by Alwin Mittasch [1–3]. In February 1909 he wrote in his laboratory journal: (i) the search for a suitable catalyst necessitates carrying out experiments with a certain number of elements together with numerous additives; (ii) the catalytic substances must be tested at high pressures and temperatures just as in the case of Haber's experiments; (iii) a very large number of test series will be required [3]. For the optimization of the actual promoted iron catalyst which is still used today, Mittasch ultimately carried out more than 10,000 tests, the number of catalyst formulations exceeding 4,000 [3].

Catalyst preparation lacked a reliable scientific basis until recently and perhaps still does, although catalytic chemists have slowly moved from alchemy to what is now called the science of catalysis. Even in 1940, Raney stated: "It is in the preparation of catalysts that the chemist is most likely to revert to type and to employ alchemical methods. From all evidence, it seems the work should be approached with humility and supplication, and the production of a good catalyst received with rejoicing and thanksgiving" [4, 5].

The catalyst is often, if not always, the heart of a chemical process, and thus, synthesis strategies for technical catalysts are proprietary knowledge of catalyst producers. Therefore, those strategies are either not accessible or protected by patents. This situation, which unfortunately severely hampers the flow of knowledge and information, was strikingly formulated by Richardson: "Catalyst preparation is the secret of achieving the desired activity, selectivity and life time" [6, 7].

Recently combinatorial methodologies were introduced into catalyst development [8, 9]. In this approach, large libraries of materials are synthesized as potential catalysts and examined by microanalysis techniques, and the results are evaluated statistically. This methodology permits an efficient material screening in the case of multi-parameter problems such as the development of solid catalysts. Combinatorial methodologies may be considered as modern versions of Mittasch's approach toward catalyst development that are faster and more cost-efficient than the tradi-

tional methodologies. It seems that potential catalyst formulations can be determined by the combinatorial approach, while technologically important parameters, such as catalyst morphology, texture and forms, mechanical and thermal properties, long-time stability, environmental friendliness, regenerability and disposal of spent catalysts, etc., will still have to be tested independently.

One of the major difficulties in rational preparation of solid catalysts is the fact that catalytic materials are “living” materials, i.e. the active catalyst is often formed from the synthesized precursor material during an induction period under catalytic conditions. Hence, in general the goal of catalyst development must be the synthesis of a suitable catalyst precursor for the chemical process under consideration.

A wealth of information has been accumulated in recent years in various research areas which are relevant to the preparation of bulk and supported solid catalysts. Of high importance for the synthesis of bulk materials is the controlled synthesis of solids including e.g. precipitation and co-precipitation, solid-state reactions, hydrothermal synthesis of zeolites, sol-gel techniques, etc. Great progress has been made in interface chemistry, guest-host interactions, grafting and heterogenization techniques, deposition-precipitation etc., which are extremely important in the synthesis of supported catalysts. This increased understanding of relevant areas of research can now be used as a basis for rational preparation of solid catalysts, and is documented in this monograph. The important parameters of the formation of the final catalysts, catalyst forming and strategies for the development of industrial catalysts are also covered.

References

1. A. Mittasch, *Geschichte der Ammoniak-Katalyse*, Verlag Chemie, Weinheim, 1951.
2. A. Mittasch, *Adv. Catal.* **1950**, 2, 81.
3. B. Timm, *Proc. 8. Intern. Congr. Catal.*, Berlin 1984, Verlag Chemie, Weinheim, and Dechema, Frankfurt, **1984**, Vol. 1, p. I-7.
4. M. Raney, *Ind. Eng. Chem.* **1940**, 32, 1199.
5. M. S. Wainwright, in *Handbook of Heterogeneous Catalysis* (Eds.: G. Ertl, H. Knözinger, J. Weitkamp), Wiley-VCH, Weinheim, **1997**, Vol. 1, p. 64.
6. J. T. Richardson, *Principles of Catalyst Development*, Plenum Press, New York, **1989**, p. 134.
7. M. Che, O. Clause, Ch. Marcilly, in *Handbook of Heterogeneous Catalysis* (G. Ertl, H. Knözinger, J. Weitkamp), Wiley-VCH, Weinheim, **1997**, Vol. 1, p. 191.
8. B. Jandeleit, H. W. Turner, T. Uno, J. A. M. van Beck, W. H. Weinberg, *Cattech*, **1998**, 4, 101.
9. R. Schlögl, *Angew. Chem.* **1998**, 110, 2467; *Angew. Chem. Int. Ed. Engl.*, **1998**, 37, 2333.

2 Developing Industrial Catalysts^{×)}

J. F. LePAGE

Once an active species and perhaps its support have been selected, the task is to construct from precursors of these active species a catalytic structure whose properties and characteristics will meet the demands of an industrial user. One must avoid creating a structure that is only a laboratory curiosity which for technical or economic reasons can not be manufactured on industrial scale.

2.1 Properties and Characteristics of Industrial Catalysts

In addition to the fundamental properties that come from the very definition of a catalyst, i.e., activity, selectivity, and stability, industrial applications require that a catalyst be regenerable, reproducible, mechanically and thermally stable, original, economical, and possess suitable morphological characteristics.

2.1.1 Activity

A high activity will be reflected either in high productivity from relatively small reactors and catalyst volumes or in mild operating conditions, particularly temperature, that enhance selectivity and stability if the thermodynamics is more favorable.

2.1.2 Selectivity

High selectivity produces high yields of a desired product while suppressing undesirable competitive and consecutive reactions. This means that the texture of the catalyst (in particular pore volume and pore distribution) should be improved toward reducing limitations by internal diffusion, which in the case of consecutive reactions rapidly reduces selectivity.

^{×)} Reprinted with permission from J. F. Le Page, *Applied Heterogeneous Catalysis – Design, Manufacture, Use of Solid Catalysts*, Editions Technip, Paris, 1987.

2.1.3 Stability

A catalyst with good stability will change only very slowly over the course of time under conditions of use and regeneration. Indeed, it is only in theory that a catalyst remains unaltered during reaction. Actual practice is far from this ideal. Some of the things that lead to a progressive loss of activity or selectivity or mechanical strength are as follows:

- (a) Coke forms on some catalysts through the intervention of parasitic reactions of hydrogenolysis, polymerization, cyclization, and hydrogen transfer.
- (b) Reactants, products or poisons may attack active agents or the support.
- (c) Volatile agents, such as chlorine, may be lost during reactions such as reforming.
- (d) The crystals of a deposited metal may become enlarged or regrouped. A change in the crystalline structure of the support can cause a loss of mechanical strength.
- (e) Progressive adsorption of trace poisons in the feed or products may reduce activity. It has been pointed out that industrial feedstocks are rarely pure products, but mixtures containing portions of impurities that must sometimes be eliminated beforehand so that the catalyst can be used.

2.1.4 Morphology

The external morphological characteristics of a catalyst, i.e. its form and grain size, must be suited to the corresponding process. For moving or boiling bed reactors the spherical form is recommended for reducing problems of attrition and abrasion. In a fluid bed, a spherical powder is preferred for limiting attrition, and its grains should have well determined size distributions for obtaining good fluidization. In a fixed bed, beads, rings, pellets, extrudates, or flakes can be used; but their form and dimensions will have an influence on the pressure drop through the bed. Thus for a given equivalent diameter, catalysts can be classified according to the relative pressure drops they cause, as follows:

Rings < beads < pellets < extrudates < crushed

This pressure drop must be high enough to ensure an even distribution of the reaction fluid across the catalytic bed, but it must not be so high as to cause an increase in the cost of compressing and recycling any gases.

Let us point out again that the grain density and especially the filling density are properties that greatly preoccupy the user; and these depend on the morphology in terms of pore volume. The catalyst is bought by weight with the purpose of filling a given reactor, and the cost of the catalyst charge will depend on its filling density. Finally, with respect to morphology, we point out that catalysts in the form of beads lend themselves better to handling, filling and emptying reactors, as well as any sieving that may appear necessary for eliminating fines after a number of regenerations.

2.1.5 Mechanical Strength

The mechanical strength of a catalyst is demonstrated by its resistance to crushing, which enables the catalyst to pass undamaged through all the strains, both foreseen and accidental, that occur within the catalyst bed. Mechanical strength is also demonstrated by the resistance of the grains to attrition through rubbing, which produces fines and can cause an increase in the pressure drop in a catalytic bed. In the case of powdered catalysts destined for fluid or boiling beds, a resistance to abrasion on the walls or to erosion by the fluids is also required.

2.1.6 Thermal Characteristics

For certain catalysts thermal conductivity and specific heat require consideration. High thermal conductivity of the catalytic mass leads to reduced temperature gradients within the grain, as well as in the catalytic bed, for endothermic or exothermic reactions, by improving heat transfer. For other catalysts, the specific heat assumes more importance; a high specific heat permits a catalytic cracking catalyst to carry a large thermal load from the combustion of coke back to the endothermic cracking reaction, where it is usefully consumed. By contrast, catalysts in catalytic mufflers are more efficient when they are quickly carried to a high temperature by the combustion gases, and a low specific heat can be advantageous.

2.1.7 Regenerability

As we have pointed out in relation to stability, it is only in theory that the catalyst is found intact at the end of the reaction. All catalysts age; and when their activities or their selectivities have become insufficient, they must be regenerated through a treatment that will return part or all of their catalytic properties. The most common treatment is burning off of carbon, but scrubbing with suitable gases is also frequently done to desorb certain reversible poisons; hydrogenolysis of hydrocarbon compounds may be done when the catalyst permits it, as well as an injection of chemical compounds. When the treatment does not include burning off carbon deposits, it is often called rejuvenation.

The shorter the cycle of operating time between two regenerations, the more important the regeneration. It becomes apparent that it is not enough for the catalyst to recover its activity and selectivity, it must also preserve its mechanical strength during successive regenerations or rejuvenations.

2.1.8 Reproducibility

Reproducibility characterizes the preparation of a catalyst as much as the catalyst itself; it is of concern to industrial users who want to be assured of the quality of

successive charges of catalyst; and it also preoccupies the various engineers responsible for developing the catalyst from the laboratory on to industrial manufacture. Indeed, the preparation of a catalyst generally takes place in several rather complex stages dependent on a large number of variables difficult to control simultaneously. The result is that it is indispensable to rapidly verify that the reproducibility of the preparation is feasible, as well as to keep in mind that the formula developed in the laboratory should be capable of extrapolation to pilot scale and to industrial scale under acceptable economic conditions.

2.1.9 Originality

It is also important that the catalyst and the process in which it will be used can be exploited legally through licenses. This is only possible either if the catalyst is original, which is rare, or if it belongs to the public domain, which is more frequent. In the first case, it can be protected by fundamental patents; in the second case, the possible patents can apply only to improvements. The greater the originality, the higher the potential royalties associated with the catalyst or with the process for which it is the controlling part.

2.1.10 Cost

Even when a catalyst possesses all the properties and characteristics just enumerated, there remains one last requirement: it must withstand comparison with competitive catalysts or processes with equivalent functions from the point of view of cost; or at least its cost should not place too heavy a burden on the economics of the process for which it will be used.

2.2 The Ideal Catalyst and the Optimum Catalyst

All of the above properties and characteristics are not independent; when one among them is changed with a view to improvement, the others are also modified, and not necessarily in the direction of an overall improvement. As a result, industrial catalysts are never ideal. Fortunately, however, the ideal is not altogether indispensable. Certain properties, such as activity and reproducibility, are always necessary, but selectivity, for example, has hardly any meaning in reactions like ammonia synthesis; and the same holds true for thermal conductivity in an isothermal reaction. Stability is always of interest but becomes less important in processes that include continuous catalyst regeneration, when it is regenerability that must be optimized. Furthermore, originality can be of secondary importance for certain manufacturing situations such as those relevant to national defense.

The goal, therefore, is not an ideal catalyst but the optimum, which may be defined by economic feasibility studies concerning not only the catalyst but also the rest of the process. And when the catalytic process is established and the catalyst in

question must compete as a replacement, the replacement catalyst's cost and method of manufacture predominate in arriving at the optimum formula.

Depending on the use and the economic competition, therefore, the optimization studies establish an hierarchy among the properties and characteristics of a catalyst; and knowledge of this hierarchy helps to better orient the efforts of the research team responsible for creating and developing the catalyst and its process. Even when the hierarchy is not fixed at the start, it can evolve in the course of developing the catalyst, sometimes even after industrialization.

2.2.1 Catalyst Development

A real-life solid catalyst is something entirely different to its user, its manufacturer, or its creator.

The user considers the catalyst within the framework of its function of promoting a chemical reaction, and its properties.

The engineer responsible for manufacturing the catalyst considers it from a different point of view, although still recognizing the needs of the user. For this engineer, the catalyst is primarily a chemical product characterized by its composition and its method of preparation, from the nature of its precursor salts of the active agents, through the conditions of various unit operations used for constructing the catalytic solid. All these operations, precipitation, ripening, filtration, washing, forming, drying, impregnation, calcination and activation, need to be meticulously controlled so that at the end of the manufacturing process the catalyst fits the range of specifications guaranteed to the user.

Finally, although the physical chemist who designs a solid catalyst will be interested in the two preceding points of view, he or she will concentrate on defining it in intrinsic physicochemical terms, such as its texture (pore distribution, specific surface of the overall solid, surface of the deposited active agents, structural density and grain density), its crystallographic characteristics (X-ray or electron diffraction examination to precisely determine the presence of a definite compound, a solid solution, or an alloy), its electronic properties (energy levels of the electrons, valence state of certain elements, or the *d* character for other elements or metallic alloys), and especially its surface properties either isolated or preferably in its reaction atmosphere (the thermodynamic characteristics of chemisorption, the chemical and electronic modifications of the catalytic surface, state of surface oxidation or reduction, acidity or basicity, and nature of the bonds in the adsorbed phase).

These various aspects of the catalyst are related through cause and effect. The properties sought in the industrial catalyst by the user flow from its intrinsic physicochemical characteristics; and both industrial properties and physicochemical properties closely depend on the method of preparation. Therefore, it is essential that the research team and the engineers in charge of developing a catalyst and its corresponding process be trained for and given the tools for following the development of the catalyst through all its various aspects, economic and legal ones included. Considering this complexity, the approach to an optimum catalyst can only be an experimental procedure advancing step-by-step through trial and error.

2.2.2 Devising the First Catalytic Formulas

An initial hierarchy of required qualities arises out of the detailed analysis of the chemical transformation plus the data from exploratory tests to select the catalytic species. This hierarchy depends on general laws of kinetics and chemical engineering, as well as observations of industrial operations that are more or less analogous. The steps of its articulation are as follows:

- Starting with the selected active species in the laboratory, one prepares a family of catalysts that are related through variations in the manufacturing process, such as sequence of the unit operations, of which certain ones are considered *a priori* critical by reason of their influence on the catalyst properties. The catalysts of this initial family are not chosen at random, but on the basis of general knowledge of inorganic chemistry and chemistry of the solid, plus the know-how acquired from analogous catalysts that seem closest to the fixed objective.
- Subsequently one prepares a list of physicochemical characteristics to be determined for the various catalysts of the family. These characteristics will be those most likely to produce meaningful results from correlations with mechanical and catalytic properties or with the conditions of preparation.

The catalysts of this initial family are then submitted to experiments whose results should permit:

- (a) A good estimation of the predicted performances, the preferred conditions of preparation, and the physicochemical characteristics.
- (b) An identification of critical properties for the catalyst (i.e., those properties most difficult to obtain), as well as the key unit operations (i.e., those essential to the performance of the catalyst), and the physicochemical characteristics on which the performance of the catalyst depends.

Next, a second series of tests is carried out for the purpose of clarifying points shown to be most important at the end of the first series of tests, both in the preparation of the catalysts and in determination of the performance and physicochemical characteristics.

At the end of this second series, and possibly a third, the results should be good enough for the following three partial objectives:

- (a) To establish some correlations between the properties of the catalyst, the intrinsic characteristics of the solid, and the conditions of preparation, as illustrated in Fig. 1. These correlations will provide a basis for perfecting the catalyst, and they can be ultimately used for defining the control tests during industrial manufacture.
- (b) To make an initial selection of some acceptable catalysts to be studied more thoroughly.
- (c) To start using one of the acceptable catalysts for a practical study of the problems of the chemical reaction process. It would be indeed illogical to delay

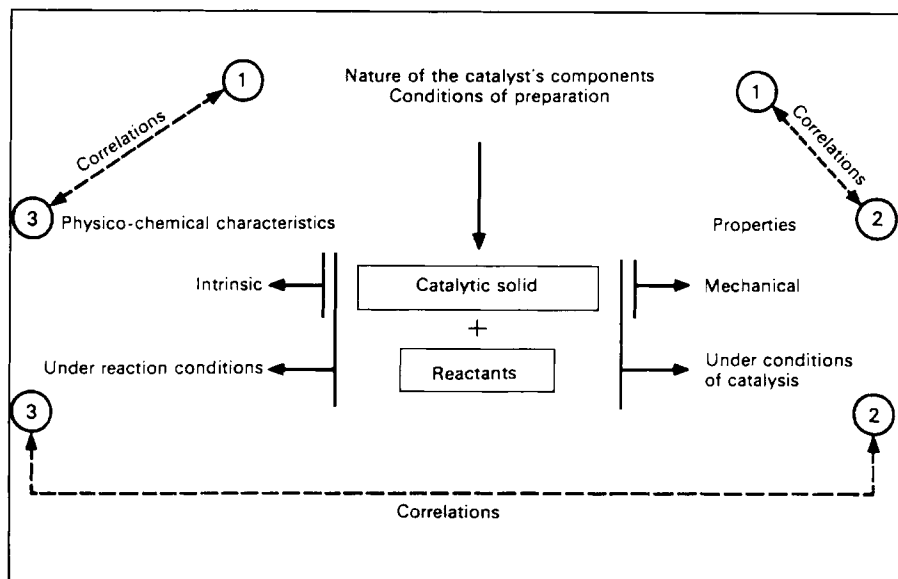


Figure 1. The different aspects of catalysis and their interrelations (adopted from ref [1]).

studying the problems of the overall process for formulation of the optimum catalyst, since according to the economic criteria the idea of an optimum catalyst has meaning only within the framework of the total problems posed by the unit. Thus it is necessary to begin the study of these problems on a catalyst that is judged acceptable, in order to deduce those elements that will orient optimization of the industrial catalyst.

At this stage it is time for a few practical remarks:

- (a) Although the study of catalytic properties can sometimes be made on model molecules for the initial preparation, it is generally preferable to operate with industrially representative feedstocks, and under industrially representative conditions, as early as possible.
- (b) For the initial catalysts, one sometimes omits the study of stability, a property that essentially demands a great deal of time for evaluation. Generally, stability is studied only with formulas that are already acceptable and often after having developed a test for accelerated aging.
- (c) For a catalyst to be regarded as acceptable, a study of its manufacturing process should have been started and advanced to the pilot scale for judging its production feasibility. Indeed, from this point on, experimenting becomes costly, and it is necessary to make sure that the catalyst is not just a laboratory curiosity.
- (d) As soon as the first results from the study of the process are obtained with the initial acceptable formula, an economic analysis and possibly a legal review

should be undertaken for judging more accurately the industrial viability of the proposed process. If the results that one can expect from these reviews deviate too far from commercial requirements, the research project should be abandoned. If the proposed process is shown to be economically viable, one continues on to the optimization of the catalyst, taking into account the problems to be encountered in the course of its use in the proposed process.

2.2.3 Optimization of a Typical Catalytic Formula

This optimization is achieved by exploiting to the utmost the correlations established during definition of the initial catalytic formulas. It should not only take into account the problems raised by the study of use but also the need for a simple and economical preparation that can be expanded to industrial scale. Therefore, the problems of extrapolating to industrial scale the various unit operations perfected in the laboratory have to be resolved in the pilot plant. This study consists of:

- (a) Pilot preparation of a certain number of samples whose performances must be tested. Examination of the results makes it possible to specify the operating conditions for each stage of the future industrial operation.
- (b) Forecasting a price for the industrial catalyst.
- (c) Establishing a manufacturing process using existing equipment as far as possible.
- (d) Production of enough catalyst by the manufacturing process for the catalyst to be representative of industrial production.

One must remember that a catalyst optimized in this way represents only a transitory optimum; experience has shown that hardly is any catalyst industrialized before it is subject to improvements, either for correcting deficiencies revealed through the industrial experience or for improving a competitive position. Sometimes it happens that a change occurs in the very nature of the catalytic agent; and at that point it is a veritable matter of catalyst renovation, involving a procedure identical to that which has just been described for the genesis of the initial formula.

Perfecting an industrial catalyst is thus the culmination of a long and complicated process that requires a knowledge as broad as possible of the methods relative to the preparation of catalysts, to the study of catalytic and mechanical properties, and to the determination of the physicochemical characteristics.

References

1. R. Montarnal, and J. F. Le Page, *La catalyse au laboratoire et dans l'industrie*, 1967, Masson, 1967, 231–287.

3 Bulk Catalysts and Supports

3.1 Fused Catalysts

R. SCHLÖGL

3.1.1 Introduction

A small number of heterogeneous catalysts is prepared by fusion of various precursors. The obvious group of compounds are metal alloy catalysts which are applied in unsupported form like noble metal gauze for the ammonia oxidation to nitric oxide. Melting of the elements in the appropriate composition is the only way to produce bulk amounts of a chemical mixture of the constituent atoms. The process is well-described by thermodynamics and a large database of phase diagrams and detailed structural studies is available. Metallurgy provides the technologies for preparation and characterization of the products [1]. This enables the synthesis of a large number of bulk alloys with well-defined properties. An interesting development in the use of such bulk-phase metallic alloy catalysts is the application of bulk metallic glasses in the form of ribbons with macroscopic dimensions [2–5]. In this class of materials the atomic dispersion in the liquid alloy is preserved in the solid state as a single phase, although the material may be metastable in its composition. This allows the preparation of unique alloy compositions which are inaccessible by equilibrium synthesis. The solidification process by rapid cooling (cooling rates above 10^4 K s^{-1}) creates “glassy” materials with well-defined short range order but without long range order. The difference in free energy between compositional equilibration and crystallization, stored in the metallic glass, can be used to transform the material in an initial activation step from a glassy state into a nano-crystalline agglomerate with a large internal surface interface between crystallites. This still metastable state is the active phase in catalysis and the final transformation into the stable solid phase mix with equilibrium composition terminates the life of such a catalyst.

In oxide materials [2] which are fused for catalytic applications, two additional factors contribute to the unique features of this preparation route. Many oxides in their liquid states are thermodynamically unstable with respect to the oxygen partial pressure present in ambient air, i.e. they decompose into lower-valent oxides and