

APPLIED INDUSTRIAL CATALYSIS

VOLUME 3

Edited by

Bruce E. Leach

Applied Industrial Catalysis

Volume 3

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BRUCE E. LEACH

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Preface

The objective of these volumes is to provide a practical description of catalysis by industrial scientists. Each chapter gives examples of current industrial practice. Catalysts merit high attention in industry, and a few examples will illustrate this point. Industrial research is concerned with catalyst invention, theory, and development. Profit centers are concerned about catalyst costs, replacement schedules, regeneration, and competitive trends. Chemical plants and refineries are concerned about the physical properties of catalysts, catalyst poisoning, and catalyst disposal.

This last of three volumes begins with a description of unit operations and process schemes used in commercial catalyst manufacturing. Commercial catalysts require highly sophisticated preparation techniques that must be applied in a well-defined series of operations. N. Pernicone and F. Traina in Chapter 1 explain the use of different commercial equipment in making catalysts.

In Chapter 2, R. E. Ellingham and J. Garrett answer the question, If a catalyst dies, can it live again? Catalyst reprocessing and regeneration is a growing business. Often, but not always, a catalyst can be regenerated or the metals reprocessed.

Physical properties of silica can vary widely depending on the method of preparation. M. E. Winyall in Chapter 3 explains how slight changes in procedure produce large differences in silica properties.

Alumina is another catalyst or catalyst carrier for which the generic term is almost meaningless. R. K. Oberlander in Chapter 4 describes how aluminas are made and how their preparation and treatment influences their ultimate use.

Chapter 5 by J. S. Merriam and K. Atwood traces the development of ammonia synthesis and ammonia-synthesis catalysis from its discovery by Fritz Haber early in this century to the present.

Catalytic oxidation reactions convert hydrocarbon substrates to many of the high-volume monomers that contain only elements of carbon, hydrogen, and oxygen. J. E. Lyons in Chapter 6 describes a number of these commercial reactions and the kinetic control required for high product selectivity.

Metathesis of olefins technology and applications are given in Chapter 7 by R. L. Banks. The development of processes and catalysts since the discovery of the metathesis reaction in 1959 are detailed.

An important catalyst application is emission control for the automobile. W. S. Briggs in Chapter 8 traces the 25-year development of the catalysts and governmental regulations.

During the last 20 years, molecular sieve zeolites have had a revolutionary impact on both fundamental and applied catalysis. J. W. Ward in Chapter 9 characterizes the structures of catalytically important molecular sieve zeolites and their modification for catalyst use.

The editor acknowledges Drs. M. L. Shannon and J. B. Winder who assisted with the reviewing. Dr. C. M. Starks, who encouraged me to edit this work, and Sherry Head and Sandy Hunt, who assisted with communications with the authors, deserve special recognition. I thank my wife, Sharon, who supported me in this long project.

It is the editor's hope that this volume will contribute to an understanding of industrial catalysis and be a valuable resource to all those active in catalysis or preparing for a career in industrial catalysis.

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Commercial Catalyst Preparation

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I. Introduction

Commercial catalysts are included among the fine chemicals that require highly sophisticated preparation techniques. In most cases, their industrial production is carried out in fairly small tonnages, so that a highly versatile manufacturing plant is required. Fortunately, the preparation of a catalyst involves a well-defined series of unit operations; therefore, equipment able to perform such unit operations can be combined in different ways to arrange the manufacture of any commercial catalyst.

The different unit operations generally used in catalyst manufacturing will be described and discussed separately, with special emphasis on practical and technological aspects. In particular, for each unit operation we will discuss

the experimental variables relevant in practice and describe the industrial equipment usually employed. Then, some typical examples of how such unit operations can be combined for the production of commercial catalysts will be given. Unfortunately few general treatments of catalyst manufacturing are available in the literature [1-6]; moreover these hardly concern the industrial aspects.

More information is available on laboratory-scale preparation, for instance, in the proceedings of certain symposia [7-9].

II. Unit Operations in Catalyst Manufacturing

A. PRECIPITATION

1. General Principles

Precipitation is the most widely used method for the industrial manufacture of oxide-based catalysts. Though it is basically a very complex phenomenon, the working procedures are relatively simple. The medium used is generally water, for obvious economic reasons. Very often a preliminary operation is needed, namely, dissolution of solid parent compounds in water.

The parent compounds should be chosen very carefully. In practice, ions that are not precipitated and that may remain occluded as traces after washing should be known not to poison the final catalyst or, otherwise, should be removed during thermal treatments. As anion sources, nitrates are usually preferred, though sulfates are sometimes used when possible, for economic reasons. As cation sources, alkali compounds are widely employed, ammonium compounds being used when there is some risk of poisoning by bases.

2. Main Variables Influencing Precipitation

The main variables that can influence the final result of precipitation are temperature, stirring procedure and rate, rate and order of addition of precipitating agents, ionic concentration of the parent solutions, pH, aging time and conditions.

All these variables can influence the particle size of the precipitate. A small particle size must be obtained when a high surface area of the catalyst is required (however, filtration may become difficult); in this case, for instance, lower temperatures, higher stirring rates, and shorter aging times should be adopted.

Homogeneity is an important property when a mixed precipitate consisting of two or more compounds has to be prepared. In fact, in most cases the precipitation of different compounds is not simultaneous. The stirring rate, pH control, order of addition of parent solutions, and time and temperature of aging can be relevant factors in this respect. Simultaneous addition of parent solutions is sometimes used when homogeneous precipitation at a constant pH is not possible by other procedures (for example, many hydroxides from ammonia and metal nitrates).

3. *Industrial Procedures and Equipment*

Precipitation is usually performed in a large tank. One auxiliary tank (two in some special cases) is often required for dissolution of the precipitating agent. Excessively large tanks may present problems (reasonable volumes are 20–50 m³). As corrosive solutions are quite usual, stainless steel or resin-bonded fiber glass tanks are usually employed (sometimes also glass- or Teflon-lined iron tanks). A general view of stirred tanks is shown in Fig. 1. The temperature is usually increased up to the desired value and then kept constant by direct injection of steam into the liquid phase. Obviously,

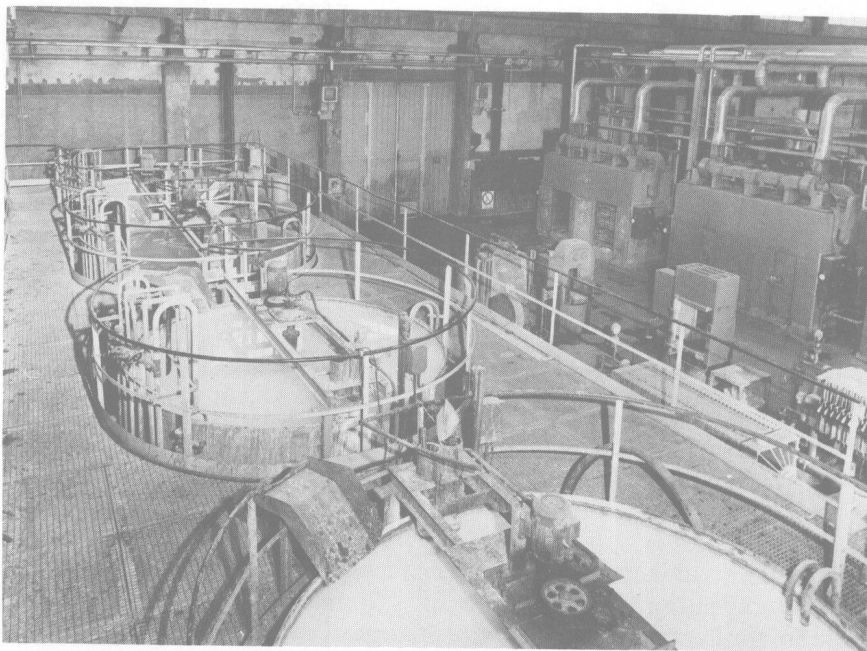


Fig. 1. Top view of stirred tanks used in catalyst precipitation. (Courtesy of Ausind S.p.A., Montedison Group, Novara, Italy)

the increase in volume of the aqueous solution should be properly taken into account. This steam injection produces some agitation too. Automatic temperature control through the regulation of steam addition can be easily arranged. Indirect heating by steam-heated coils is also possible, but less effective.

Usually the precipitation temperature does not exceed 100°C. Preferred values lie in the range 50–70°C. Higher temperatures could require venting systems in the room, unless precipitation in closed vessels under pressure is adopted.

Fixed power-driven stirrers are used for agitation. Baffles are usually needed on the walls of the tank. Stirrer shape is preferably determined from laboratory experiments. Turbostirrers may be necessary when very strong agitation is required.

The rate of addition of the precipitating solution can be kept constant by the insertion of a calibrated disk at the exit of the pump or, less precisely, by manual regulation of a valve. If precipitation at a constant pH is required, the controlled addition of small volumes of a third solution must be provided. Aging of the precipitate could require several hours, with or without either stirring or steam injection.

B. GEL FORMATION

In catalyst manufacturing hydrogels are mainly involved, as water is the usual medium. Some oxides, especially silica, alumina, and their mixtures, must be prepared by gel formation in order to obtain the desired properties in the final catalyst. Gelation times can vary within very wide limits; they can depend on micellar concentration, temperature, ionic strength of the solution, pH, nature of the starting compounds, etc. Subsequent hydrothermal treatments of the gel are often employed to induce transformations relevant to the final properties of the catalyst.

In some special cases the gelation of an amorphous precipitate can be performed by strong agitation of the slurry with a turbostirrer. If the foreign ions can be eliminated during the thermal treatments, filtration and washing may be bypassed.

C. FILTRATION AND WASHING

Filtration is an almost obligatory step after precipitation, and sometimes after impregnation also. The principles of this operation on an industrial scale are similar to those that control laboratory filtration. The main equipment used in catalyst manufacturing includes the following:

(1) Filter press—very widely used. The area of each plate is about 1 m^2 , and 40–50 plates are currently employed. It allows countercurrent washing, provided the cake has no cracks. The filter cake can be subsequently pressed hydraulically to decrease the water content. A view of a typical filter-press used in catalyst manufacture is given in Fig. 2.

(2) Rotary filter—in effect vacuum filtration. It has the advantage of ensuring continuous operation but does not work efficiently when fast sedimentation occurs; moreover, in some cases washing is not very effective (colloidlike precipitates). It can be advantageously used when subsequent reslurrying is needed.

(3) Centrifuge—recommended where fast, effective washing is required. However, its capacity is limited (much less than that of a filter press of equivalent dimensions). Continuous centrifuges are also available. Recycling is often necessary at the beginning of the filtration. A general view of a centrifuge used in catalyst manufacturing is given in Fig. 3.

(4) Vacuum filter—quite similar to that used in the laboratory. Filter diameters of about 1 m are usually employed. Cake depth can reach 50 to

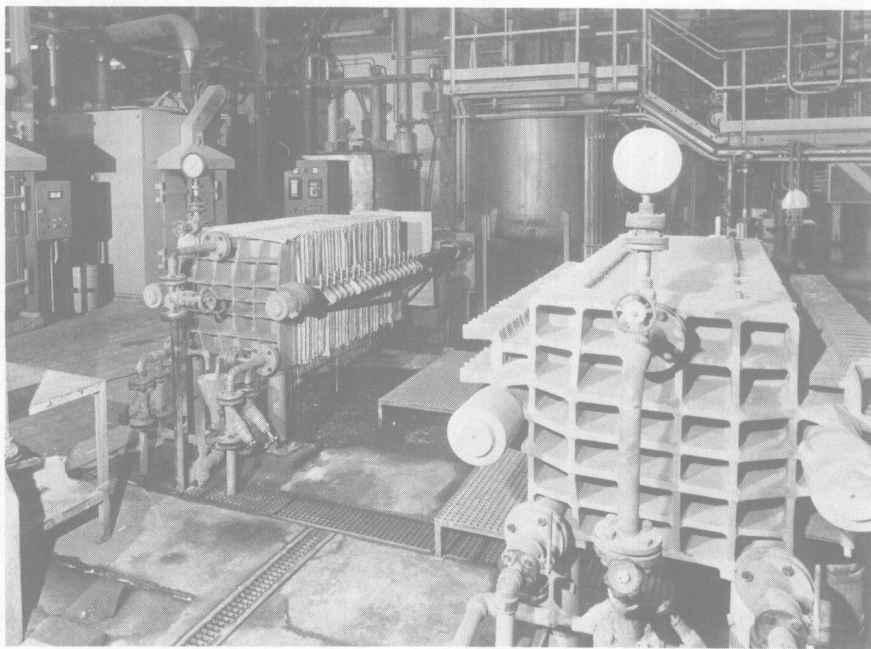


Fig. 2. Filter presses used in catalyst manufacturing. (Courtesy of Ausind S.p.A., Montedison Group, Novara, Italy)

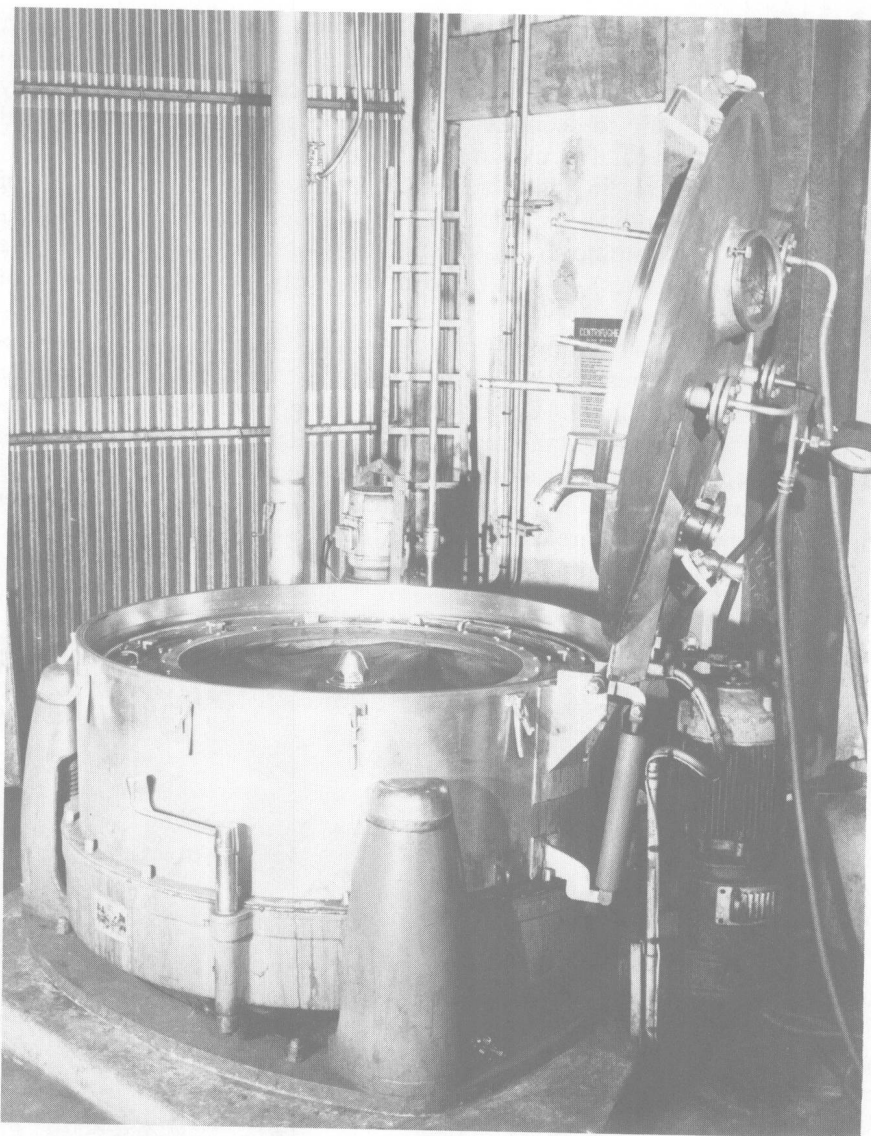


Fig. 3. Centrifuge used for fast washing in catalyst manufacturing. (Courtesy of Ausind S.p.A., Montedison Group, Novara, Italy)

60 cm. The capacity of such a filter is relatively small but, if operated with care, it provides good washing efficiency.

Whichever filtration equipment is employed, the choice of the correct cloth is very important for the success of the operation.

When colloidlike precipitates are processed, it is very difficult to obtain fast, effective washing. In these cases one or more redispersing steps are required to eliminate impurities from the cake. This obviously increases the operating costs, so that one resorts to this operation only when it is unavoidable.

It is worth noting that, when sedimentation is sufficiently fast, it is usually convenient to wash the precipitate by decanting, so that washing after filtration will be minimized if not completely eliminated. This requires a greater number of tanks, but this larger investment cost is more than counterbalanced by shorter filtration times. The mother liquor is removed either by siphoning or through exit tubes placed at various levels in the tank wall. Water is then added (the pH can be varied by the addition of suitable compounds), usually with stirring.

The sedimentation rate can be increased by heating or by the addition of ammonia or of flocculants, if compatible with the catalyst. The number of decanting steps is usually dictated by the level of impurities to be reached and by the working times of the precipitation–decanting–filtration sequence.

A special case is represented by gel washing, where the gel has to be broken down by stirring and then water added. Most of the washing is carried out by decanting. For the filtration a filter press is usually employed. In other cases (for instance, cogelled silica–alumina) simple washing is not sufficient, and ion exchange with ammonium salts is needed for complete elimination of the alkaline ions.

D. IMPREGNATION

1. General Principles

Impregnation, that is, deposition of a suitable compound on a carrier from a solution (usually aqueous), is very widely used in catalyst manufacturing. It is usually chosen when a predetermined pore structure is needed for the catalyst or when the cost of the active component is very high (for instance, noble metals). Often the carrier is not inert, and quite strong interactions between it and the active component may occur, so that it must be selected taking into account not only its porous structure but also its surface chemistry.

Powdered or preformed carriers (pellets, spheres, granules) may be used, depending on the final use of the catalyst. When preformed carriers are used, special attention must be paid to the distribution of the active component after impregnation. For instance, diffusion-controlled reactions require that the active phase be placed mainly on the outer surface of the pellets (sometimes this is needed also for powdered supported catalysts). Impreg-

nation is also used to introduce additional components into a previously prepared catalyst (for instance, when promoters cannot be coprecipitated or added during kneading).

2. Working Procedures

Impregnation may be carried out in different ways. In one of these (dry impregnation) the carrier is evacuated and then moistened, while being appropriately stirred, with a volume of solution of active component not larger than its pore volume.

In other cases (wet impregnation), it is preferable to use an excess of solution and then to remove the excess liquid by filtration. In this case the final concentration of the active component in the catalyst will depend on its concentration and on the adsorption capacity of the solid. Successive impregnations, with interposed drying steps, are sometimes used to obtain higher contents of the active component and also when more than one of them is to be deposited. Another simple procedure consists in completely evaporating the solution in contact with the carrier, though in this way a

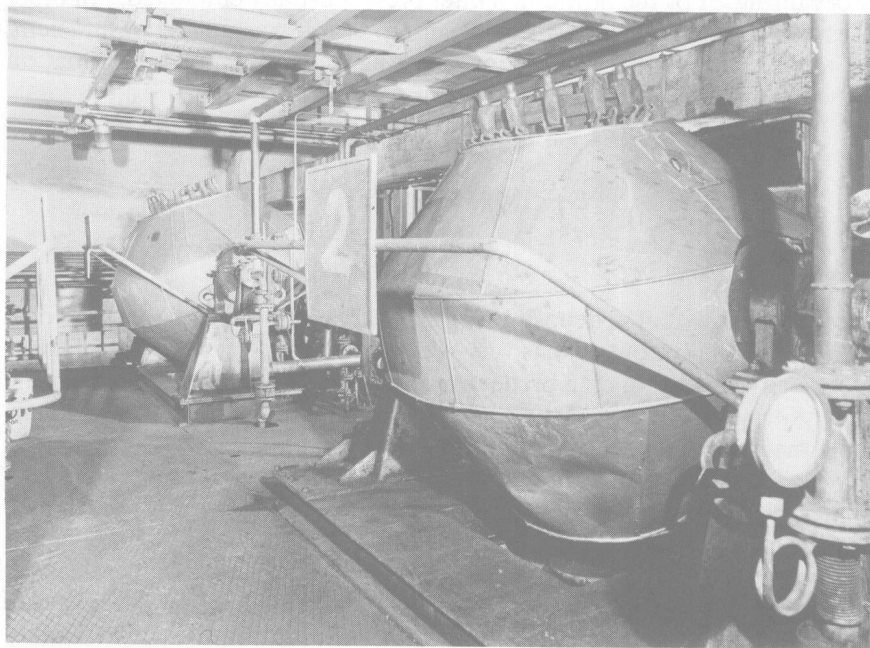


Fig. 4. Steam-heated rotating vessels used for wet impregnation. (Courtesy of Ausind S.p.A., Montedison Group, Novara, Italy)