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Chapter 18

Scale-up of catalyst production

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1. Introduction and literature sources

According to Alvin B. Stiles, catalytic science, which involves the invention, development and manufacture of the catalysts, is probably one of the most interesting and rewarding scientific fields. As a consequence more and more young people are entering the field, as this seminar proves, while people having been for many years in catalysis usually do not change their job. The writer is a practical example of this behavior. The economical importance of catalysis reinforces this situation. In fact, the catalyst is the key point for the success of any catalytic chemical process. Deterioration of catalyst properties during use will cause the process to become soon uneconomical.

As a large gap exists between a laboratory catalyst and the corresponding industrial product, it is easy to understand the enormous industrial importance of catalyst manufacturing development from bench to commercial scale.

Procedures for catalyst manufacturing are usually developed in an empirical way, through time-consuming and costly work, though some attempts of a scientific approach begin to appear in the literature.

Preparation details are not easily available, as patenting is not a common practice for real industrial catalysts. So the preparation of catalysts having good industrial performances can show insurmountable difficulties even for catalytic researchers, if not skilled in manufacturing practice. This mainly because even small changes in manufacturing procedure may have large effects on catalytic properties.

Direct catalyst production from bench experimentation is quite unusual: currently one or more intermediate steps are necessary to get all the information required for a correct choice of the industrial machines. On a very rough basis, the situation can be summarized as follows, referring to a batch production:

bench or lab scale	minimum quantity	10 g
intermediate or pilot scale	minimum quantity	1 kg
industrial or commercial scale	minimum quantity	100 kg

The availability of a catalyst-processing laboratory equipped with both bench-scale and intermediate-scale facilities, reproducing as strictly as possible the industrial machines, is a key-point in the successful development of catalyst production. In most cases the final catalyst optimization occurs on pilot scale, obviously on the basis of the information collected during laboratory work. This means that, for each relevant step of the manufacturing process, relatively small changes of the experimental variables are tried, to find the best mix of them and also to check if some variable is critical. It is clear that this requires a large amount of work.

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Another very important aspect in the development of catalyst manufacturing is the choice of the raw materials. In bench preparations usually very pure compounds are used, but this practice cannot be followed in industrial production, for obvious economic reasons. In fact purity is important, but it should not be overestimated. As a rule of thumb, oxide systems are less demanding about purity of raw materials than metallic ones.

As raw materials, water-soluble compounds of wide commercial availability are preferred. The anions should be easily removable and not poisonous. There are really few degrees of freedom in the choice. Nitrates and ammonium salts apparently are preferable. But the strongly exothermic decomposition of ammonium nitrate should be taken into account. In practice the most common choice appears to be metal chlorides and sodium basic compounds, in view also of the problems of waste water disposal.

Scientific and technical literature on catalyst manufacturing is not easily available; most of it is very generic and concerns a relatively old state of the art. Personal experience and "reading between the lines of the patents" are still the best source of information. Anyway, the following general literature could be referred to advantageously.

1.1. A.B. Stiles, Catalyst Manufacture, Dekker, 1983.

Describes very many pieces of equipment for industrial manufacturing and reports recipes allowing skilled people to prepare sufficiently good but in some cases obsolete catalysts, roughly similar to the commercial ones. It contains photos of various machines, but mainly from supplier source.

1.2. J.F. Le Page et al, Catalyse de contact, Ed. Technip, 1978, Chapter 5.

In 60 pages the main unit operations of catalyst manufacturing are discussed, with special attention to impregnation. Application of basic principles is commendably tried.

1.3. N. Pernicone and F. Traina, Commercial Catalyst Preparation, in Applied Industrial Catalysis, Vol. 3, Academic Press, 1984.

A concise description (23 pages) of 16 unit operations involved in catalyst manufacturing, with many photos showing real industrial machines.

1.4. B. Delmon et al. Eds., Preparation of Catalysts (vol. 1 1976, Vol. 2 1979, Vol. 3 1983, Vol. 4 1987, Vol. 5 1991, Vol. 6 1995), Elsevier.

A mine of information, mainly on laboratory preparations, but subjects connected to pilot and industrial scales can be occasionally found.

1.5. J. Petro in Contact Catalysis (Z.G. Szabo and D. Kallo Eds.), Vol. 2, p.44, Elsevier, 1976.

A non-systematic discussion of some unit operations, reporting experience from the Hungarian catalysis school (15 pages).

1.6. C.N. Satterfield, Heterogeneous Catalysis in Practice, p. 68, Mc Graw-Hill, 1980.

A clear and easily readable treatment of catalyst preparation on various scales (30 pages).

1.7. E.F. Sanders and E.J. Schlossmacher, Catalyst Scaleup, in Applied Industrial Catalysis, Vol.l, Academic Press, 1983.

Contrary to the title, in this chapter Calsicat people discuss only some principles concerning the manufacture of custom catalysts (10 pages).

1.8. M.S. Spencer in Catalyst Handbook, 2nd edn., p. 34, Wolfe Publishers, 1989.

A short discussion (15 pages) of ICI experience in manufacture of industrial catalysts. A few photos of industrial machines.

1.9. F. Traina and N. Pernicone, Chimica Industria, 52, 1 (1970). Preparation Techniques and Their Influence on the Properties of the Solid Catalysts

Though old, it contains a wide discussion of tableting mechanism.

1.10. T. Beecroft and A.W. Miller, Repts. Progr. Appl. Chem., 55 (1970) 385. Preparation and Characterization of Solid Catalysts.

A summary of what was known about 30 years ago, with extensive references.

1.11. G.W. Higginson, Chem. Eng. September 30 (1974) 98. Making Catalysts. An Overview.

Though non-systematic nor up-to-date, this paper contains interesting information on various aspects of catalyst manufacturing.

1.12. A.H. Thomas, Chem. Tech., April (1977) 228.

A short discussion of problems in the development of custom catalysts.

1.13. J.T. Richardson, Principles of Catalyst Development, Chapter 6, Plenum Press, 1989.

A wide (40 pages) and interesting discussion of various aspects of catalyst manufacturing on different scales.

1.14. A.B. Stiles and T.A. Koch, Catalyst Manufacture, Dekker, 1995.

An extension and renovation of Ref. 1.

2. Unit operations in catalyst manufacturing

The manufacture of a catalyst always involves a well-defined series of unit operations. A hopefully complete list of them is reported in Table 1. Sufficient information about each unit operation can be found in the Refs. 1 and 3 listed in the Introduction. Moreover, some of them are discussed in Chapter 3 of this book.

Table 1
Unit operations in catalyst manufacturing

Unit operations in catalyst manufacturing
Dissolution
Precipitation
Gel formation
Dry impregnation
Wet impregnation (absorption)
Wet impregnation (precipitation)
Decanting
Wet mixing
Filtration and washing
Reslurrying
Reduction
Coating
Kneading
Drying
Spray drying
Calcination
Grinding and sieving
Dry mixing
Tableting
Extrusion
Beading
Leaching
Melting and cooling
Activation

3. Scale-up requirements during laboratory research

It is quite common that laboratory researchers aiming at finding new catalysts for industrial use perform their work trying to optimize activity and selectivity, but paying not so much attention to the means adopted to reach the objective. Unfortunately, when scaling-up has to be done for catalyst production, a lot of problems arise, both technical and economical, so that only a fraction of the advantages of the laboratory catalyst can be saved and a lot of further laboratory experimentation is required.

It should be stressed here that during laboratory research for catalyst development it is absolutely necessary to think from the beginning in terms of the subsequent scale-up, so that the solution of many problems can be anticipated and routes impracticable on larger scale are not pursued.

Commercial raw materials should be used very early on laboratory scale and the influence of the most common impurities should be tested. Raw materials having only one supplier should be avoided, if possible.

Critical steps when using large-scale equipment, if known or forecastable, should be investigated already on laboratory scale (for instance, stirring rate, heating rate, etc.). Formation of gelatinous precipitates should be avoided whenever possible and, in any way, filtration should be as fast as possible.

In particular, for drying and calcining it is recommended to simulate in laboratory equipment the working conditions of the industrial ovens, especially for heating rate, gaseous atmosphere, cooperative effects in the catalyst volume.

Industrial forming, contrary to the laboratory one, always requires the addition of various types of compounds, mainly organic, but sometimes also inorganic. It is strongly recommended that such additives are used also on the laboratory scale, because they could change even strongly the catalytic properties.

When the final step of catalyst production is activation, often by reduction, to be performed in the reactor itself, this step must be carefully studied on laboratory scale, even if, strictly speaking, it is beyond the responsibility of the manufacturer. The reduction methods to be tested should be obviously suited to industrial reactors.

Also disposal of waste water and abatement of gaseous emissions during large-scale manufacturing must be taken into account in laboratory experimentation. Preparation procedures giving minimum water and air pollution should be looked for, when not harmful to catalytic performances. Toxic chemicals and flammable solvents should be avoided, whenever possible.

The problem of disposal of the spent catalyst should be also considered from the beginning of the research. Eventually the customer should be provided with instructions on how to proceed for this operation. As an optimal choice, the spent catalyst could be reprocessed in the manufacture of the fresh one, but this will require a lot of laboratory and development research work.

As a general conclusion, it is recommended that, when definite ideas are available about the main properties of the final catalyst and/or about the equipment to be used for industrial manufacturing, a sort of scale-down process will be tried, so that laboratory research will be carried out within well-defined routes, with appreciable saving of time and money.

4. Catalyst scale-up with a manufacturer of custom catalysts or inhouse

Chemical and petrochemical companies, which usually develop their own catalytic processes, but do not have facilities for catalyst manufacturing, have very often to do with the classical problem: make or buy the catalyst? It is very likely that such companies possess even large groups of catalytic researchers very skilled in catalyst preparation and characterization on laboratory scale, sometimes also equipped with small pilot plants for catalyst testing, but unfortunately the manufacture of industrial catalysts is a very different thing. Moreover, techniques and pieces of equipment and also the conceptual approach are very different from those used for the development of petrochemical and organic plants, but more resemble mineral and fine inorganic processing. This situation should suggest to commit an external company for catalyst manufacturing. But inhouse production could be also attractive. On the whole risks and disadvantages on one side and advantages on the other side should be considered. They could be summarized as follows, for custom manufacturing:

(a) if the process gives large economic advantage over competitors, the risk of disseminating information cannot be overlooked, in spite of secrecy agreement obligations;

(b) a fraction of the profit is to be shared with catalyst manufacturer;

(c) the external manufacturer could not like to build a new plant for this catalyst, but would produce it with multipurpose facilities, with the connected risk of contamination;

(d) prompt supply of catalyst charges, when needed, could not be guaranteed;

(e) interactions between different company structures and people could give problems;

(f) the cost of scale-up work could result very high for the customer.

As concerns inhouse production the problems consist in the lack of experience in catalyst scaling-up and in the need for projecting and installing a production unit. The company should therefore recruit skilled personnel and rely on the assistance by the companies that commercialize the required machines.

The alternative between production for captive use only or also for future sales should be carefully considered to correctly size the plant. In any case a larger plant used for campaigns is probably the best choice.

Though on many aspects self-production seems to be preferable, except for very small companies, nevertheless custom catalysts manufacturing is widely practised. In fact, there are some companies specialized in this kind of business.

5. Catalyst characterization in the course of scale-up

Obviously the catalytic system, which is being scaled-up, has been already studied very deeply on laboratory scale, so that both physico-chemical and catalytic properties that are most relevant for it have been identified. They strongly depend on the catalytic system and mostly on the type of process the catalyst has to be used in (fixed-bed, fluid-bed, slurry reactors). The main physical and catalytic properties that are usually measured during scale-up work are summarized hereinafter.

5.1. Physical properties (see chapter 4 of this book)

Surface area
Pore volume (total, micropores, mesopores, macropores)
Bulk density
Particle size distribution (for powders and irregular granules)
Abrasion resistance (formed catalysts and irregular granules)
Attrition resistance (powders)
Crushing strength, pellet (formed catalysts)
Crushing strength, bulk (irregular granules)
Metal dispersion, or metal surface area, or metal average particle size (for supported metal catalysts)
main techniques: selective chemisorption
X-ray diffraction (WAXS)

Metal distribution (for supported metal catalysts)
main techniques: optical microscopy (formed supports, not black)
electron microprobe (black formed supports)

	metal chemical analysis on different particle size fractions (powders, irregular granules)
Crystal phases by XRD (mainly for oxide systems)	
Surface acid sites by TPD of chemisorbed bases	
Thermogravimetry (to check thermal treatments)	
TPR (to check activation by reduction)	

5.2. Catalytic properties (see chapters 5 and 6 of this book)

The measurements of activity and, when required, of selectivity are of the utmost importance during catalyst scale-up. Also an evaluation of catalyst life is recommendable, when an accelerated test is available. During the first steps of scale-up, when the chemical factors are mainly considered, the use of microreactors for activity tests, as for laboratory experimentation, is recommended, so that changes from laboratory preparation can be clearly pointed out.

When the forming techniques are developed, the use of semi-technical reactors (100–1000 ml) is necessary to test the catalyst in its real particle size.

Such considerations hold obviously for catalysts to be used in fixed-bed reactors. For slurry catalysts the same small-scale tests can be used for both laboratory and scale-up work. For fluid catalysts semi-technical reactors are needed from the beginning of laboratory work.

6. Criteria for catalyst sizing and shaping

During the whole work to develop a new catalyst or to improve an already existing one, the bench-scale experimentation is usually not involved with the problem of catalyst size and shape, as its main objective is to optimize chemical composition and some basic physical properties. But as soon as the time of pilot manufacturing comes, a decision must be taken about catalyst size and shape, depending on the type of process. It is necessary to distinguish between fluid bed and slurry processes on one side (powdered catalysts) and fixed bed processes on the other side (formed catalysts).

6.1. Fluid bed and slurry reactors

In this case the choice is very restricted, as it is well known that the range of acceptable particle size is 20–200 μm for both types of reactors and that the shape should be as spherical as possible for fluid beds, while not very relevant for slurries.

In fluid beds a too small size will give problems in fines collection by cyclones, while a too large size will cause bad fluidization.

In slurries a too small size will give problems in filtering, while a too large size will make difficult obtaining a good suspension in the liquid. Obviously, a smaller particle size gives higher activity in many cases, but the above-mentioned requirements have priority.

6.2. Fixed bed reactors

It could be necessary to take into account the following restrictions (for each of them forming criteria are indicated).

* Internal diffusion phenomena

Catalyst with small particle size and large external area (rings, stars, granules). High catalyst porosity (macro pores). Best forming technique: extrusion.

* Low pressure drop.

Catalyst with large particle size and not too regular shape (preferably rings).

Forming technique: any.

* Low catalyst cost.

Catalyst with large particle size. Forming technique: extrusion.

* Poisons in the feed.

Catalyst with large external area (small particle size and irregular shape). Best forming technique: extrusion.

* High pressure applied on bottom catalyst layer.

Catalyst with high mechanical strength and regular shape (pellets). Best forming technique: tableting.

* Reactor loading from appreciable height and/or movement of catalytic bed during plant operation.

Catalyst with high abrasion resistance and regular shape (pellets). Best forming technique: tableting.

Usually one has to do with opposite restrictions at the same time, so that priorities have to be defined. Restrictions are obviously stronger in the case of catalyst development for already existing plants. High priority is often assigned to pressure drop and catalyst strength restrictions, sometimes even with respect to activity.

7. Main unit operations in pilot and industrial scale and related scale-up problems

7.1. Precipitation

At first sight scale-up for precipitation should be straightforward, but in practice phenomena difficult to rationalize can make the situation very complex in industrial tanks (even more than 50 m^3).

The main differences from bench scale can be found in temperature gradients, stirring geometry and connected geometry of precipitate formation. Scaling-down of the industrial tank to pilot scale (10–100 l) can be tried, but the success is uncertain.

Precipitation is often carried out as a batch process, also on industrial scale. The precipitating agent can be simply poured into metal salt solution, or viceversa, if pH is not a problem. Homogeneity will be ensured by vigorous stirring. When pH has to be kept constant during precipitation, a second solution, acid or basic, should be added at the same time.

Alternatively, both metal salt and precipitating agent solutions can be added continuously always under stirring. Continuous precipitation, with feeding and withdrawing the same amount of liquid in the tank, could help to have constant pH, but it is rarely practised.

The particle size of the precipitate can be regulated like in bench experiments. So a high stirring rate will give a finer precipitate, but this is not so easy to obtain on industrial scale; in practice, industrial precipitates will likely show larger particle size but better filterability than the bench ones. Anyway, a high ionic concentration will help for faster filtration. Scale-down of stirring intensity and geometry to bench scale is recommended.

Hydroxides, carbonates and hydroxycarbonates are the preferred precipitates on industrial scale, because they are cheap, give no environmental problems during thermal treatments and easily form mixed compounds. Chlorides are usually preferred as metal salts, but in some cases chlorine is a poison for the catalyst. In such case nitrates are recommended, even if they could give some environmental problem during calcination when washing was insufficient.

When the formation of a crystalline precipitate has to be sped up, seeding is a common industrial practice; it is also useful to direct the process towards the requested crystalline phases.

The phenomenon of aging is very important in most cases. While on bench scale it is only intentional, on industrial scale it can be forced by the process. For instance, time is needed to pump a slurry to the filtering equipment (due attention should be paid on bench scale to this case). Moreover on large scale batch precipitation, the aging time is different for early and late precipitates. Even if a good stirring will ensure sufficient homogeneity, the average aging time will be usually higher than on bench scale. Intentional aging is sometimes used, in spite of the waste of time, to increase filterability or, more seldom, to improve interactions between different precipitated compounds.

Additional problems can be found on large scale in the case of mixed coprecipitates. Different products can be obtained depending on how the metal salt solution is mixed with the precipitating agent. To overcome this, it is necessary sometimes to precipitate separately the two compounds and then mix their slurries.

Stainless steel tanks can be employed for precipitation on pilot and industrial scale only when there are no corrosion problems, because possible contamination of precipitate must be avoided. Previous bench experiments with the same steel should be done. In the case of corrosion problems, Teflon-lined or glass-lined steel tanks should be used, in spite of their higher cost.

If the same pilot or industrial tank has to be used for different catalysts, it should be arranged so that clean-up will be easy, to avoid contamination.

Heating can be performed through a steam jacket or through steam-heated internal coils. However, direct steam injection is also used, because faster and cheaper, but it requires previous bench experiments.

7.2. Filtration and washing

When sedimentation is sufficiently fast, it is common practice on industrial scale to wash the precipitate by decanting and then filter. This operation can be easily checked on bench scale. Obviously it cannot be employed with gel-like precipitates, whose washing has to be done completely on the filter.

Industrial filters can be divided in press-type and vacuum-type.

The former group consists of the filter press and the centrifuge, the latter mainly of Nutsche, rotary and belt filters. On bench scale only the Nutsche filter, called buchner, and the centrifuge are widely used; therefore scale-up problems are not expected, when due attention is paid to the filter clothes. In the other cases pilot experimentation with commercial semi-technical equipment is recommended.

Filtering length is not a problem in laboratory, but on industrial scale any method should be applied to speed up filtration and washing. This frequently forces to come back to laboratory for further experiments. It is recommended to take into account these problems since the beginning of bench work, by using all the possible tricks in the precipitation step for a fast filtration.

When difficulties in washing on industrial scale lead to occlusion of poisons in the precipitate, it is common practice to dry and calcine, then disperse the powder in water and make ionic exchange with ammonium salts, preferably carbonate.

7.3. Extrusion

Among the various forming methods extrusion is the most widely used, in particular when a high porosity is required. Moreover, it is also the cheapest method and often it does not require calcination before forming.

On industrial scale only screw and ring-roll extruders are used. Ring-roll extruders are fed with a paste previously prepared in a kneading machine. This can be done also with screw extruders, but in most of them a kneading section is incorporated, so that it is possible to feed directly the powder and water.

On bench scale a big syringe is commonly used for extrusion: this method gives no problems, but has not much to do with what happens in industrial extruders. Therefore in scaling-up it is absolutely necessary to make experimentation on semi-technical machines, which are commercially available. Usually they are to be fed with a paste, so that additional experiments must be done with the industrial machine, if a powder has to be used.

Starting from a powder of definite characteristics, the main factors influencing extrusion are: water content of the paste, duration of kneading the powder with water, kneading and extrusion temperatures, addition of extrusion aids. Water content is often exceptionally critical: a change as small as 1% (in the usual range 30–50%) could be sufficient to make extrusion impracticable. In general the water content should be as low as possible (but not so low to give paste hardening), because in this way the mechanical strength of the pellets will be higher.

The rotation speed of the cutting device should be variable, to allow for extrusion inhomogeneities. The main problems will be given by paste softening during extrusion (longer pellets and sticking together) and by paste hardening (overheating of the paste and in some cases blocking of the extruder). Therefore a lot of attention should be paid to the kneading step.

As extrusion aids both organic (starch, methylcellulose) and inorganic compounds (nitric acid, kaolin, clays, cements) can be used. Obviously the addition of not-removable compounds should be carefully checked for catalytic performances.

It should be finally remarked that the drying step of extruded pellets is exceptionally critical.

7.4. Tableting

Tableting is an expensive forming method, which is adopted for industrial production when high mechanical strength of the catalyst pellets is required. On bench scale very often a catalyst powder is pressed with some elementary device, then ground and sieved to get a particle size fraction suitable for activity tests.

But this operation has not much to do with industrial tableting.

Semi-technical tableting machines are not easily available, so that the development work for this unit operation is usually performed directly on the industrial machine. Fortunately, some kilos of powder are sufficient for each run.

Powders coming from previous drying or calcining operations in most cases are not suitable for tableting (except sometimes from spray-drying), due to their low density and/or small particle size (sizes below 50 μm usually give problems). Therefore a densification step is required, which is performed by mixing the powder, in a kneading machine or in special granulators, with water or with solutions of sugars, polyglycols, starch, and similar compounds.

After drying, the granulated powders must be carefully mixed, in a dry-mixing machine, with a lubricant, like graphite (for high mechanical strength) or stearic acid (for high porosity). Ideally, the resulting powder to be fed to the tableting machine should flow like a sand.

The above-mentioned operations (granulation and addition of various compounds having nothing to do with the catalytic system) may have a large influence on both textural and catalytic properties, mostly of the adverse type. It is clearly unsound to reach the level of the industrial scale development without any knowledge about such problems. It is therefore necessary to devote sufficient work during bench scale experimentation to study the effects of these industrial-scale operations, if it is expected that tableting will be chosen for catalyst forming.

Obviously, when an organic compound has been added, a final calcination of the pellets is necessary, except for graphite; this is a very critical step in many cases.

When difficulties in tableting arise, mostly with very crystalline or strongly calcined powders, one could resort to:

- pretableting with subsequent grinding and sieving
- addition of more lubricant
- optimization of water content of the powder.

7.5. Thermal treatments (drying and calcination)

On bench scale drying and calcination are performed in small static ovens, where heating rate, catalyst temperature and gaseous atmosphere can be easily controlled as the amount of catalyst treated is relatively small (typically in the range of 10 grams), so that mutual interactions in the catalyst mass are negligible. This is not the case on industrial scale, with some exceptions. For instance, in continuous belt or tunnel dryers and calciners, if the catalyst is sparsely placed on the tape, it is possible to reproduce sufficiently well the ideal laboratory conditions. On the contrary in large static ovens, where the catalyst is placed on trays arranged in a pile, interactions are difficult to avoid. So inhomogeneities in catalyst temperature and in local gaseous atmosphere are very likely, even in gas-circulated ovens. To decrease such phenomena, it is recommended to load the catalyst on the trays in a shallow layer and to leave a sufficient distance between the trays, in order to improve removal of the evolved gases. However, experimentation in semiscale ovens is recommended before choosing the industrial equipment.

For high-temperature calcination (more than 500°C) direct-flame heating, using a methane burner, is often used in both static and belt ovens, as in ceramics fabrication. In this case the effects of the specific gaseous atmosphere should be previously checked.

As concerns spray-drying, small-scale and industrial-scale machines seem to be strictly related each other, but in practice scaling-up is not an easy problem. It is frequently said that spray-drying is really an art, so that specialists of this technique should be called for to manage scale-up problems. A treatment of the subject can be found in K. Masters, Spray Drying, Wiley (1985).

8. Development of quality control system

After the catalyst manufacturing process has been brought to the industrial scale, the development of an effective quality control system is a must nowadays. In fact the achievement of ISO 9000 certifications, for which quality control is a key point, is necessary to get orders from the most qualified customers.

In catalyst manufacturing quality control consists of three steps:

- for raw materials
- during manufacturing process
- for final product

8.1. Raw materials

Specifications for each raw material should be agreed with the vendor and vendor certificate required. Inspection of incoming materials should be always done. The raw materials, whose chemical and/or physical properties are known, from bench or pilot work, to be relevant to catalytic performances, must be controlled, with statistical sampling, through analytical methods to be preferably agreed with the vendor.

8.2. Intermediates in manufacturing process

During bench or pilot-scale experimentation the results could show critical importance, for catalyst performances, of chemical or, more frequently, physical properties of the material coming from some specific unit operation of the manufacturing process. Typical case could be the bulk density of a powder to be tableted. Quality control during manufacturing requires obviously very fast techniques, but, when they are available, it should be done.

When the analysis cannot be done in real time, nevertheless the development of a data bank of relevant physical properties of intermediate materials can be useful to resolve manufacturing problems, when they arise.

Apart from analyses, the visual control of key process parameters by skilled personnel is invaluable to detect problems as soon as they arise and is integrating part of the quality control procedure.

8.3. Final product

Chemical, physical and catalytic properties that must be checked on the final catalyst are usually agreed with the customer. In addition, the manufacturer sometimes adopts some specific control of his own interest. It is recommended that well-consolidated and simple techniques are used for such controls, so that reproducible and not very expensive measurements can be done.

The following controls are the most frequently adopted:

- activity and selectivity in standard tests
- accelerated life tests
- bulk density
- mechanical strength (attrition, abrasion, crushing)
- content of poisonous elements
- particle size
- surface area and pore volume

Also in this case the development of unified testing procedures with customers is strongly recommended.

9. Some practical examples

In the previous sections some general principles were outlined about the various steps of catalyst scaling-up work and about the related problems. Now it will be tried to apply such principles to a few selected cases of real industrial catalysts.

9.1. Catalyst for maleic anhydride from benzene

In this process benzene is oxidized to maleic anhydride by air at 400–450°C. A multitube reactor is used, where heat exchange is ensured by melted salts circulation.

The basic catalyst consists of supported and promoted V_2O_5–MoO_3 system. Supporting is not performed by impregnation, but by coating. The reason is that strongly exothermic processes, having selectivity requirements, like this one, need low surface area catalysts to moderate the reaction rate, thus avoiding large amounts of consecutive byproducts. Unsupported catalysts, even of low surface area, are not suitable, because internal diffusion phenomena should decrease selectivity. So a thin layer of active phase is deposited over an inert low-area, ceramic-type support. As impregnation of a low-area support cannot give a sufficiently high concentration of the active phase, coating is the only way to obtain such type of catalyst.

The catalyst preparation consists of the following steps.

* Dissolution of ammonium metavanadate in aqueous HCl.

* Dissolution of ammonium eptamolybdate and salts of promoters (Na is always included) in water.

* Addition of eptamolybdate solution to the vanadate one (a clear green solution is obtained).

* Heating of the green solution at 80–90°C and addition of the ceramic supports (coarse spheres or preferably rings).

* Slow evaporation of the liquid under continuous rotation of the vessel until dryness. During this operation the active powder sticks on the macropores of the support.

* Calcination at 400–420°C.

Bench-scale coating can be done in a small rotavapor equipment, using ground and sieved ceramic support (maximum size 1 mm). But it is preferable that the major part of the research work is done with real-size supports, using, for coating, special rotating pans of few liters capacity, electrically heated.

Subsequent scale-up is to quartz rotating vessels with capacity of many hundreds of liters, equipped with venting system.

Dissolution steps and mixing of solutions do not give any scale-up problem. The coating step fortunately is very well simulated in the intermediate scale (preparations of hundreds of grams, maximum some kilos), so that no unexpected problem usually occurs on the industrial scale.

The critical step is calcination, where changes in vanadium oxidation state should occur. In fact the active state of vanadium appears to be V(IV). The equilibrium between ions V(III), V(IV) and V(V) strongly depends on the composition of the gaseous atmosphere, which is conditioned by the evolution of ammonium chloride during calcination, shifting the equilibrium towards V(III). On the contrary an excess of air can shift the equilibrium towards V(V). So critical parameters are rate of NH_4Cl evolution and oxygen concentration in the final period of calcination. In such circumstances it is clear that in a laboratory oven the course of calcination will be completely different than in an industrial calciner.

When static tray ovens are used for this operation, it is necessary that the oven is provided with facilities for fast removal of the evolved gases during the first period of calcination and for effective internal gas circulation later on. For further improvement the pavement of the trays could consist of a net. The arrangement of the trays in the oven and the depth of catalyst layer in the trays should be carefully optimized, preferably by experiments with the industrial equipment, that is really difficult to scale-down.

Of course, most of these problems are less relevant in continuous belt calciners.

9.2. Catalyst for low-pressure ammonia synthesis

The currently used ammonia synthesis catalyst (promoted iron) is manufactured by melting (at 1700°C) a magnetite powder including various oxide promoters, cooling, grinding and sieving to the requested size. Reduction to iron is performed in the reactor. For the development of low-pressure processes, catalysts with higher activity are required. Among the various catalysts proposed until now, one very promising is still based on iron, but is manufactured by precipitation (Eur. Pat. 174078, 1988). It could be instructive to briefly discuss the problems expected when this catalyst is being scaled-up.

The final catalyst (not yet reduced to iron) consists of magnetite plus about 4% of promoting oxides (Al_2O_3, MgO, K_2O).

Hydrous iron oxide is precipitated in a stirred tank from iron nitrate and ammonia solutions. In a different stirred tank hydrous Mg–Al oxide is precipitated from Mg nitrate and Na aluminate, the pH being controlled by HNO_3 addition. The two slurries are then mixed under stirring. Mixing is a critical step and its procedure should be carefully checked on bench and pilot scale. The subsequent filtration is also critical, due to the gel-like nature of the material.

The precipitation temperature should be optimized from the point of view of filterability: aging of the mixed slurry in the range 50–90°C could be also tried. A filter-press or a belt filter could be used. Washing should be very effective for complete removal of ammonium nitrate. The panel coming from the filter is now dried and calcined at 250°C, using a static tray oven or a belt calciner. The powder obtained is put in a kneading machine, where a K_2CO_3 solution is added. The resulting paste is then dried. The powder is mixed with graphite in a dry mixer and tableted. No special problem is expected during the scale-up of these operations. The Fe_2O_3-based pellets are now reduced to magnetite by a hydrogen–water mixture at 300°C. A fixed bed reactor or a rotary furnace could be used for this step: pilot-scale experiments are required for this choice. The reduced pellets are now ground, the resulting powder mixed with graphite in a dry mixer and tableted. This second tableting operation could give many problems, because magnetite-containing powders are not easy to tablet and are also very abrasive, so that special materials are required for punches and dies. If the mechanical strength of the resulting pellets is not satisfactory, then a subsequent calcination under inert atmosphere has to be done.

9.3. Catalyst for hydrogenation of organic compounds (slurry reactors)

The hydrogenation of organic compounds in slurry reactors is carried out very often with powdered supported noble metal catalysts.

Among them palladium on active carbon (5–10% Pd) is one of the most widely used. These catalysts are mostly used by the pharmaceutical industry.

The first step in the manufacturing procedure is mixing of an acidified palladium salt (usually chloride) solution with a slurry of active carbon, where sometimes a suitable alkali compound is added.

Completely different catalyst performances can be obtained, depending on:

- chemical and physical properties of active carbon
- procedure of mixing
- pH of Pd solution and of carbon slurry
- final pH after mixing
- type of alkali compound.

Pilot-scale experimentation is recommended to investigate these points.

After impregnation, filtration and washing are performed, usually by a centrifuge, as the industrial batches are not very large (hundreds of kilos). Washing should be very effective, especially when chlorides are used as raw materials. The panel is then reslurried and the hydrous Pd oxide is reduced to metal by a suitable reducing agent (formaldehyde, formic acid, hydrazine, hydrogen, alkali salts like formate, hypophosphite, borohydride). The choice of the reducing agent and the reducing conditions are very critical, so that also this point should be checked on pilot scale.

The final catalyst can be used either in the wet or in the dry form. In the latter case drying can be performed around 100°C without any problem.