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SCIENTIFIC BASES FOR THE PREPARATION OF HETEROGENEOUS CATALYSTS

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Aspects of scale-up of catalyst production

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1. SCOPE OF CATALYST PRODUCTION

Catalyst production has a significant influence on the economy, since 80-90% of the chemicals used in a modern society are exposed to a catalyst. The value of the US catalyst market was 2.2 billion $ in 2000 [1]. A number of specialised catalyst companies in the world, many global, produce and supply a large number of products to the industry. It is said that products corresponding to 10% of the GNP of the industrialised countries are dependent on the availability of catalyst. Catalyst plants produce quantities of 0.1-100 t/day of each product dependant on the type. Thus, transfer of new products and implementation in catalyst plants are important technological disciplines for each catalyst company.

2. NATURE OF THE SCALE-UP PROBLEM

Before the decision is taken on transferring a new recipe from research and development departments to an existing catalyst plant or a new investment, considerable work has already been carried out – many test samples have been prepared and activity-tested. All candidates for a new product have one thing in common: in the starting phase they have been prepared and selected from the laboratory processes.

2.1. Description of laboratory prepared samples

Laboratory or bench scale prepared catalyst samples for screening are typically made in gram scale (10-50 g). The catalysts can be prepared in many ways depending on the type, but steps for three commonly used preparation routes are shown below in Fig. 1 and, for each step, examples of the typical laboratory equipment are given.

I. Typical co-precipitated catalyst manufacture

Preparation step	Typical equipment
1. Dissolution of agents	Beaker with stirrer
2. Precipitation	Pump + beaker with stirrer
3. Ageing	Electric heating, thermostatic bath
4. Filtration	Buchner funnel
5. Washing	Demineralised water on Buchner funnel
6. Drying	Drying cabinet
7. Calcination	Muffle furnace
8. Lubricant aid addition	Powder mixer
9. Tabletting	Single station excenter press
10. Calcination	Electrically heated muffle furnace
11. Activation	Small reactor with H/N_2 once through

II. Typical impregnated catalyst carrier process

Preparation step	Typical equipment
1. Forming a support (from another route)	
2. Activation of support	Heated muffle furnace
3. Dissolution of impregnation liquid(s)	Beaker with stirrer (pure chemicals)
4. Impregnation	Net in a beaker
5. Drying	Drying cabinet
6. Decomposition	Muffle furnace
7. Re-impregnation back to 4.	
8. Activation	Reactor sulphidation with H_2/N_2 once through

III. Typical process for mixed/compounded catalyst

Preparation step	Typical equipment
1. Powders	From flasks
2. Dissolution of active metals	Beaker with stirrer
3. Dissolution of extrusion aids	Beaker with stirrer
4. Mixing	Laboratory kneader
5. Extrusion	Laboratory piston extruder
6. Drying	Drying cabinet
7. Calcination/decomposing	Muffle furnace
8. Sieving	Laboratory sieve
9. Activation	Small reactor with H_2/N_2 etc. once through

Fig. 1. Three examples of commonly used preparation methods

The laboratory equipment used is normally characterised by:

- Small dimensions with short mass and heat transport distances
- High energy intensity per volume for stirrer mixers and kneaders
- Pure chemicals
- Small layers in muffle furnaces with low temperature gradients, but long heating cycle
- H_2 activation with low pH_2O
- Drying with low but undefined pH_2O
- Precipitation within small volume dimension
- Filtration without respect of agglomerate size
- Washing without respect of time or leakage of particles or ions
- Tabletting/forming of non-representative granules
- Generated heat during processes easily dissipated to cooling surface

A modern catalyst laboratory will analyse and describe in detail all intermediates and final catalysts from the above three manufacturing routes by means of the methods as follows: main chemical elements and trace elements, phases (if not amorphous), pore distribution and BET or selective surface area. A more complete list of commonly used methods is given in Table 1 below:

Table 1.
Physical and chemical characterisation methods

Chemical	
Main chemical elements	ICP, AAS, XRF and electron micro probe analysis
Trace elements	AAS, ICP
Oxidation state	Electron micro probe analysis, EDS in SEM, EDS
Element distribution	in TEM
Physical	
Surface area	BET (N_2, Ar, K), or specific area, chemisorption of H_2,CO, N_2O
Pore volume - total	Water absorption –Hg intrusion
Pore size distribution	He, or Hg intrusion, N_2 adsorption
Phases, crystallite size	XRD, TEM, Raman Spectroscopy
Surface composition	XPS, SIMS
Surface properties	IR, microcalorimetry, chemisorption/desorption (TPD,TPR)
Particle size distribution	LLD, SAXS, sieves, TEM, SEM
Structure and texture	TEM, SEM, optical microscopy
Thermogravimetry	TGA, DTA, dilatometer
Specially for finished product form	
Abrasion resistance for granules	
Attrition resistance for fluid cat and powders	Attrition loss
Crushing strength	Texture analyser

However, all the above methods in Table 1 cannot give a scientifically exhaustive description of the intermediates nor of the final catalyst. Amorphous phases often obtained from precipitation cannot be characterised sufficiently (how many kinds of amorphous phases exist?) Furthermore, the final catalyst granule is formed from agglomerates of crystallites. Both crystallites (forming primary agglomerates) and the agglomerates have their own particle size distribution and binding properties. Particle size distribution of primary and secondary agglomerates controls the final pore size distribution. The pore size distribution and particle strength will have significant influence on the final performance of the product in the reactor. Even considering the methods listed in Table 1, there is no method or combined methods today that can give a full description of the crystallite-agglomerate multi-parameter system. To further illustrate the problem, it should be mentioned that even if the overall chemical composition is the same for two different manufacturing routes, the pore size distribution is most probably different. *Thus, it is not possible to characterise an intermediate or final catalyst so you can be sure to have the same catalyst without preparing it in the same reproducible way.*

2.2 Catalyst manufacturing – unit operations

The catalyst plant is operating in ton scale (typically 1-100 t/day) with processes and equipment completely different from bench scale as sketched in Fig. 1, even if the preparation steps are the same. In the open literature, description of catalyst manufacturing processes and equipment is sparse. The reference list contains important monographs and papers [2-24]. The patent literature gives some information, but catalyst manufacturing technologies are often not patented but kept secret. The single step in manufacturing is called a unit operation and can be performed by several types of equipment. Table 2 shows most of the unit operations used and examples of equipment for each. Most of the typical equipment will have more different time constants, heat transfer, flow patterns, temperature profiles etc. than bench scale equipment and, therefore, the final catalyst will achieve other properties.

2.3 Optimal combinations

For every commercial catalyst an optimal combination of unit operation sequence exists for the manufacture of that specific catalyst and there will for each unit operation exist preferential process equipment, i.e. fluid bed calciner for calcination. The sequence of unit operations with the special selection of process equipment and all process parameters forms the *know-how* for manufacturing a catalyst product of large commercial value. But know-how does not mean that you always know why the desired properties are obtained due to the insufficient scientific characterisation of the catalyst material as described above under 2.1. Even small adjustments of the process can change strength, pore size distribution, bulk density, crystallite size etc. of the product and, thus, harm the performance in the industrial reactor. It has normally been costly and time-consuming to reach the final recipe and, therefore, all catalyst companies want to keep it secret. *If a single unit operation is changed it will often influence the optimisation of most of the other unit operations, and much of the development will have to be redone.*

Table 2.
List of unit operations with typical equipment

Unit operation	Typical equipment
1. Dissolution	Tanks with stirrer
2. Precipitation	Pumps, specially designed reactors and stirrers
3. Ageing and maturation, gel formation	Temperature-regulated tanks, autoclaves
4. Filtration	Belt filter
	Drum filter
	Centrifuge
	Filter press
5. Washing	Belt filter
	Drum filter
	Centrifuge
6. Drying	Belt conveyor furnace
	Spray drying
	Fluid bed drying
	Rotary kiln
	Vacuum dryer
7. Wet mixing (kneading)	Z-mixer
	Double screw mixer
8. Dry mixing	Nauta mixer
	Double cone mixer
	Ribbon blender
9. Grinding	Jet mill
	Roller mill
	Universal mill
	Pearl mill
10. Sieving	Screen
11. Forming	Tabletting
	Extrusion
	Granulation
	Spray drying
	Corrugation
12. Calcination	Belt conveyor furnace
	Rotary kiln
	Shaft furnaces
	Chamber and muffle furnace
	Tunnel furnace
	Fluid bed
13. Impregnation	Pore filling – incipient wetness
	Immersion in liquid
	Controlled chemisorption
14. Decomposition	See under calcination
15. Fusion	Electrical hearth
16. Activation	Prereduction reactor
17. Cooling and annealing	Fluid bed, chamber and muffle furnace
18. Coating	Washcoater, dragee pan
19. Leaching	Tanks with stirrer
20. Reslurrying	Tanks with stirrer, kneader