CATALYSTS

Ph.D course/ Physical Chemistry
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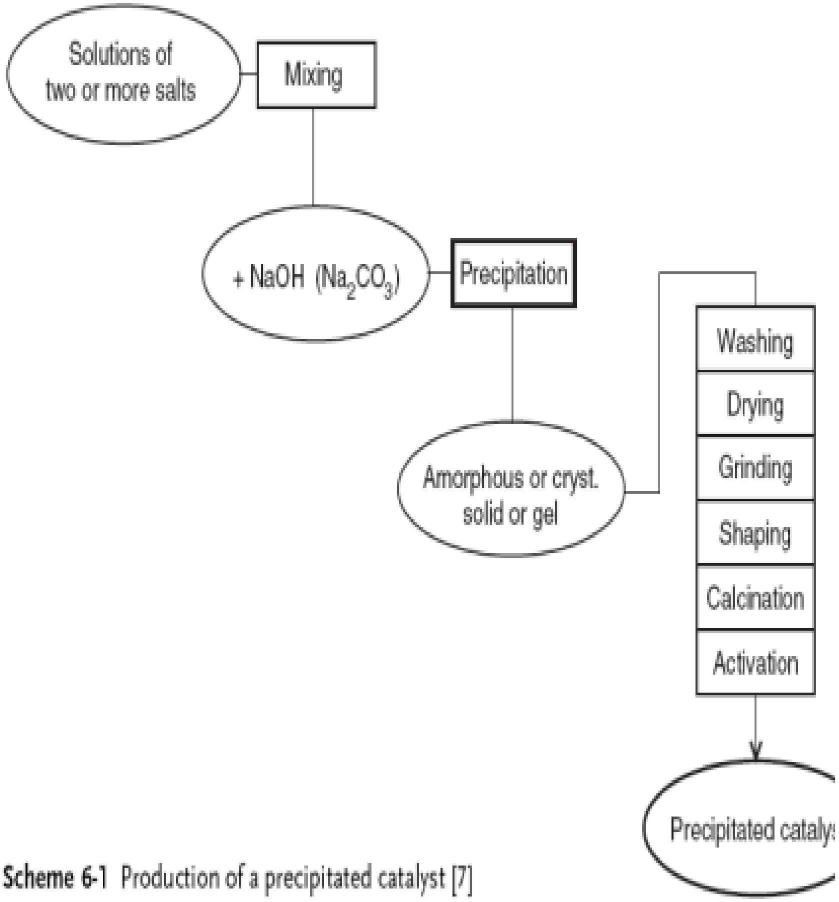
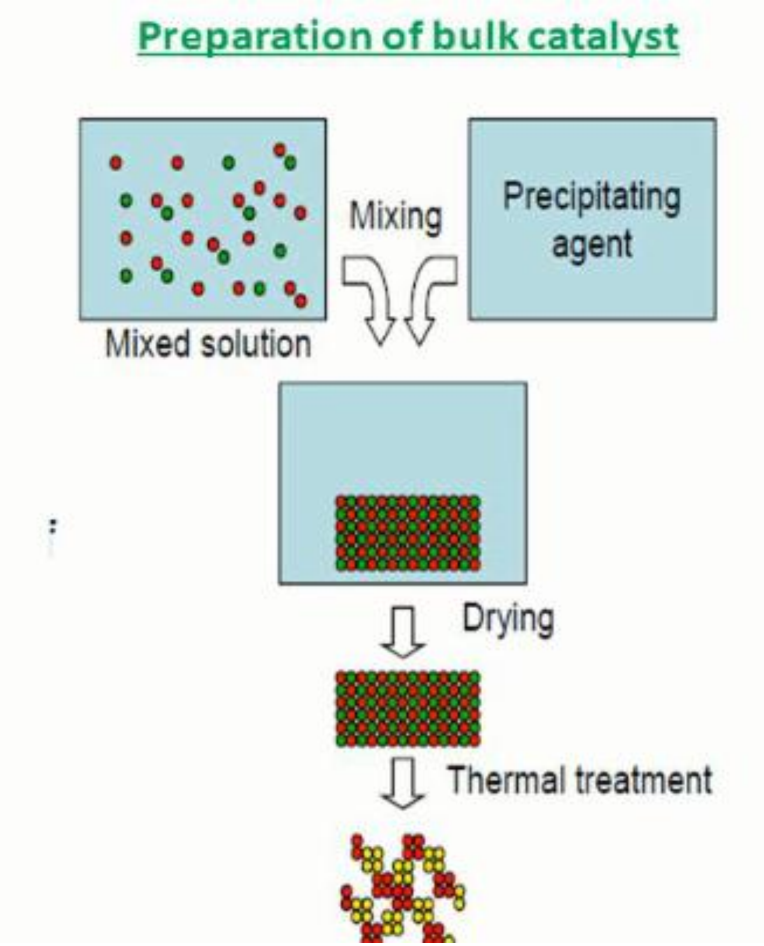
Preparation of Solid Catalysts:

- Depending on their structure and method of production, catalysts can be divided into three main groups:
- – Bulk catalysts
- – Impregnated catalysts
- – Shell catalysts
- **Bulk catalysts**
- - Bulk catalysts are mainly produced when the active components are cheap. Since the preferred method of production is precipitation, they are also known as precipitated catalysts.

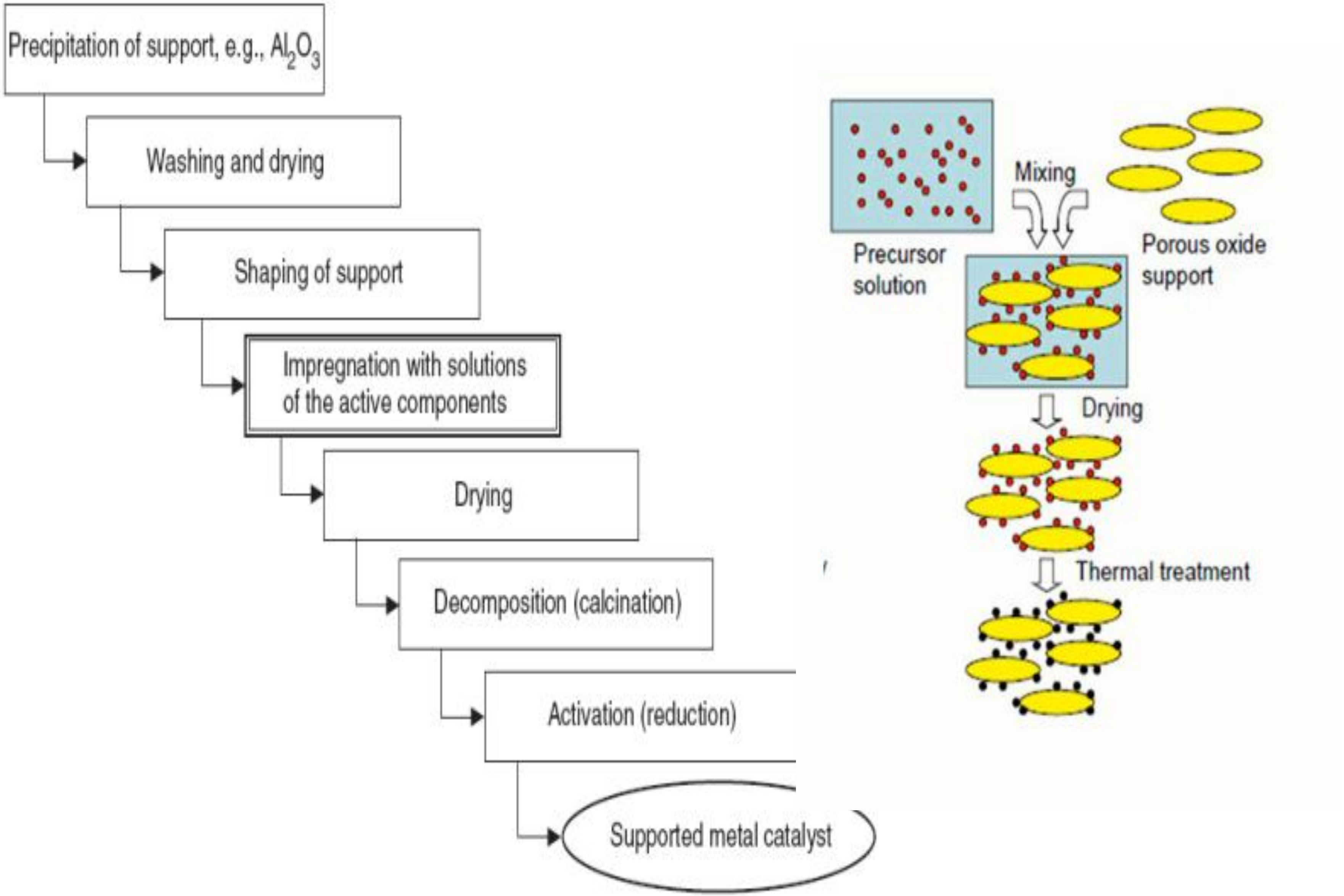
One or more components in the form of aqueous solutions are mixed and then precipitated as hydroxides or carbonates. An amorphous or crystalline precipitate or a gel is obtained, which is washed thoroughly until salt free. This is then followed by further steps: drying, shaping, calcinations, and activation (Scheme 6-1):



Scheme 6-1 Production of a precipitated catalyst [7]



- Typical examples of precipitated catalysts are:
- – Iron oxide catalysts for high-temperature CO conversion (Fe_2O_3 with addition of Cr_2O_3).
- – The silica/alumina hydrocracking catalysts, zeolites, and the ammonia synthesis catalyst.
- **Impregnated catalysts**
- \- One of the best known methods for producing catalysts is the impregnation of porous support materials with solutions of active components. Impregnation as a means of supported catalyst preparation is achieved by filling the pores of a support with a solution of a metal salt. Especially catalysts with expensive active components such as noble metals are employed as supported catalysts. A widely used support is Al2O3, Activated carbon and silica gel. After impregnation the catalyst particles are dried, and the metal salts are decomposed to the corresponding oxides by heating. The process is shown schematically in Scheme 6-2.



Scheme 6-2 Production of supported metal catalysts by impregnation

- \- In the impregnation process, active components with thermally unstable anions (e. g., nitrates, acetates, carbonates, hydroxides) are used. The support is immersed in a solution of the active component under precisely defined conditions (concentration, mixing, temperature, time). Depending on the production conditions, selective adsorption of the active component occurs on the surface or in the interior of the support. The results is non uniform distribution.
- \- To achieve the best possible impregnation, the air in the pores of the support is removed by evacuation, or the support is treated with gases such as CO_2 or NH_3 prior to impregnation. After impregnation, the catalyst is dried and calcined.
- \- Calcination is heat treatment in an oxidizing atmosphere at a temperature slightly higher than the intended operating temperature of the catalyst.

- In calcination numerous processes can occur that alter the catalyst, such as;
- - formation of new components by solid-state reactions,
- - transformation of amorphous regions into crystalline regions, and
- - modification of the pore structure and the mechanical properties.
- In the case of supported metal catalysts, calcination leads to metal oxides as catalyst precursors, and these must subsequently be reduced to the metals. This reduction can be performed with hydrogen (diluted with nitrogen), CO, or milder reducing agents such as alcohol vapor. In some cases reduction can be carried out in the production reactor prior to process start-up.

- Examples of industrial impregnated catalysts are:
- – Ethylene oxide catalysts in which a solution of a silver salt is applied to Al_2O_3.
- - The Pd/C hydrogenation catalysts, the $Pt/Sn/Al_2O_3$ dehydrogenation catalysts.
- – Catalysts for the synthesis of vinyl chloride from acetylene and HCl: $HgCl_2$/activated carbon; $HgCl_2$ is applied from aqueous solution.

The advantages of impregnated catalysts compared to precipitated catalysts

1- Pore structure and surface of the catalyst can be controlled.

2- More economic, since the content of the expensive active components is often low.

3- The distribution and crystallite size of the active components can generally be varied over a wide range.

4- Multiple impregnation is possible.

Shell catalysts

- -Shell catalysts consist of a compact inert support, usually in sphere or ring form, and a thin active shell that encloses it. Since the active shell has a thickness of only 0.1–0.3 mm, the diffusion paths for the reactants are short.
- There are many heterogeneously catalyzed reactions in which it would be advantageous to eliminate the role of pore diffusion. This is particularly important in selective oxidation reactions, in which further reactions of intermediate products can drastically lower the selectivity. An example is acrolein synthesis: two catalysts with the same active mass but different shell thicknesses differed greatly in selectivity at the high conversions desired in industry. Therefore, if acrolein synthesis is to be operated economically, the shell thickness must be optimized.

-The best known method for producing shell catalysts is the controlled short-term immersion of strongly adsorbing support materials. A well-known example is the platinum shell catalyst, which can easily be prepared with low loading and a high degree of dispersion. The support is immersed in solution of hexachloroplatinic acid (H_2PtCl_6), and an outer layer of adsorbed $PtCl_2^{-4}$ ions is formed. The treated catalyst particles are then dried without washing and calcined to generate the metal. Figure 6-6 shows how different impregnation techniques can be used to obtain supported catalysts with special distributions of the metal.

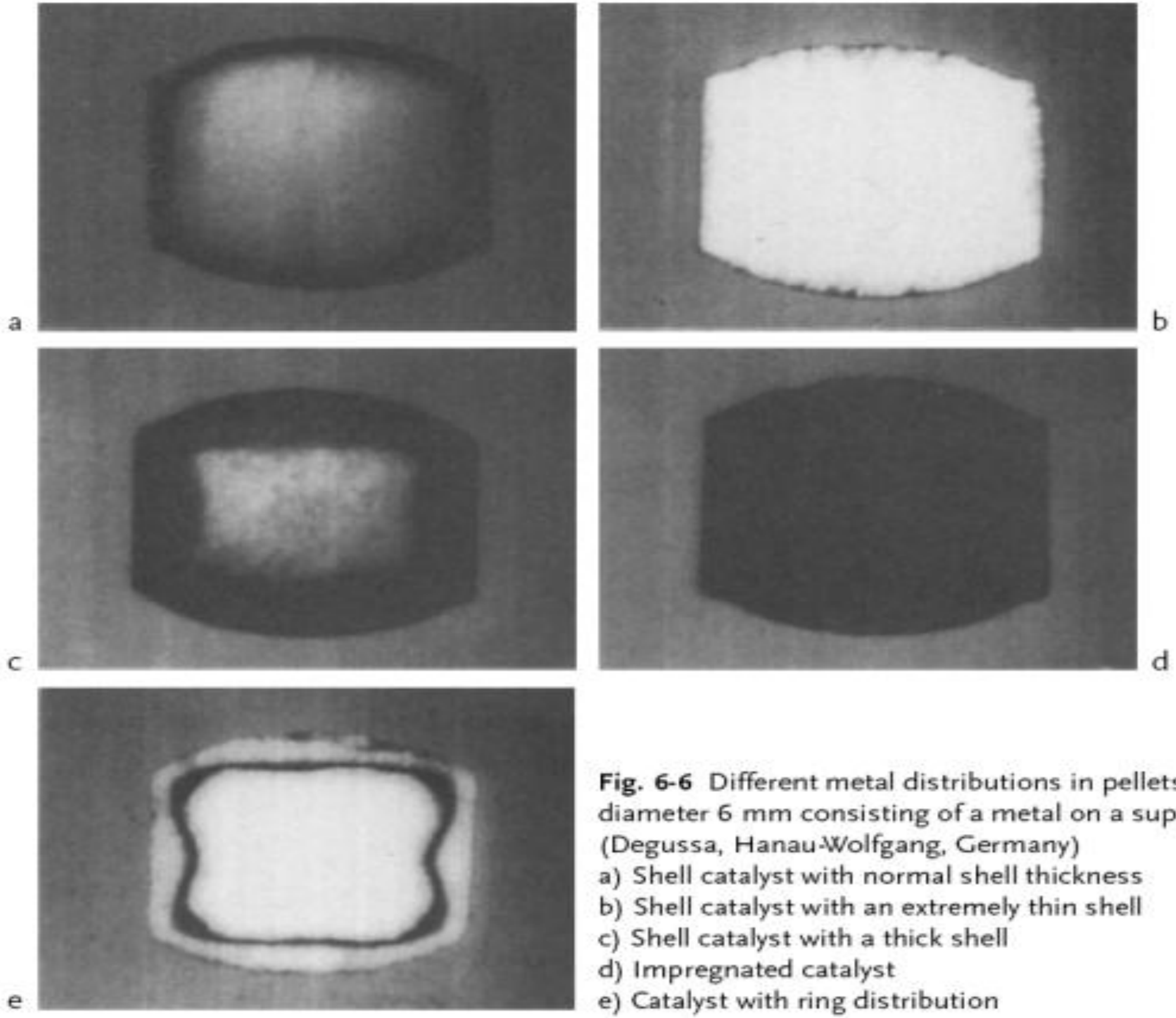


Fig. 6-6 Different metal distributions in pellets of diameter 6 mm consisting of a metal on a support (Degussa, Hanau-Wolfgang, Germany)

a) Shell catalyst with normal shell thickness
b) Shell catalyst with an extremely thin shell
c) Shell catalyst with a thick shell
d) Impregnated catalyst
e) Catalyst with ring distribution

Examples of industrial applications of shell catalysts are:

- – Selective oxidation reactions, e. g., production of acrolein from propene and of phthalic anhydride from *o*-xylene
- – Purification of automobile exhaust gases
- – Selective oxidation of benzene to maleic anhydride (catalytically inactive support without pores)
- – Autothermal decomposition of liquid hydrocarbons on NiO/α-Al_2O_3 shell catalysts (high selectivity for lower alkenes.
- In this chapter we have seen how the different steps of catalyst production can affect the functional properties of catalysts, such as activity and selectivity, and their morphology.
- Because of the numerous influencing parameters, prediction of the catalytic properties is not possible. They can only be determined by measurement of the reaction kinetics. This makes it clear why catalyst production is based on special company know-how and that not all details are publicized.

Immobilization of Homogeneous Catalysts

- The industrial use of homogeneous catalysts often leads to problems with:
- - catalyst separation and recycling,
- - recovery of the often valuable metal,
- - and short catalyst lifetimes.
- Therefore, extensive studies have been carried out on the development of heterogenized homogeneous catalysts (or **heterogenized catalysts**), which are intended to combine the advantages of homogeneous catalysts, in particular high selectivity and activity, with those of heterogeneous catalysts (ease of separation and metal recovery).
- Hence attempts are made to convert organometallic complex catalysts to a form that is insoluble in the reaction medium. This is generally achieved by anchoring a suitable molecule on an organic or inorganic polymer support.

- In the following, we will discuss such methods for obtaining immobilized homogeneous catalysts, which are also known as **fixed catalysts or hybrid catalysts**, and the potential applications of this interesting class of catalysts.
- To come to the most important point first: the ideal immobilized metal complex for industrial applications has not yet been found, as is shown by weighing up the advantages and disadvantages of this type of catalyst.
- ***Advantages:***
- 1) Separation and recovery of the catalyst from the product stream is possible easily. This is the main advantage of heterogenization.
- 2) Mutifunctional catalysts can be obtained in which more than one active component is bound to a carrier.

- 3) Highly reactive, coordinatively unsaturated species that cannot exist in solution can be stabilized by heterogenization.
- ***Disadvantages:***
- 1) The immobilized homogeneous catalysts are not sufficiently stable. The valuable metal is continuously leached and carried away with the product stream.
- 2) The problems of homogeneous catalysts, such as corrosion, catalyst recovery, and catalyst recycling, have so far not been satisfactorily solved.
- 3) Lower catalytic activity than homogeneous catalysts because of: poor accessibility of the active sites for the substrate, steric effects of the matrix, incompatibility of solvent and polymer, deactivation of active centers.
- 4) Inhomogeneity due to different linkages between support matrix and complex.

Particularly intensive investigations have been carried out on catalysts for reactions with CO or alkenes. These reactions, which are typical transition metal catalyzed conversions, provide the best possibility for assessing the properties of heterogenized catalysts. Examples are given in the following overview (Table 6-1).

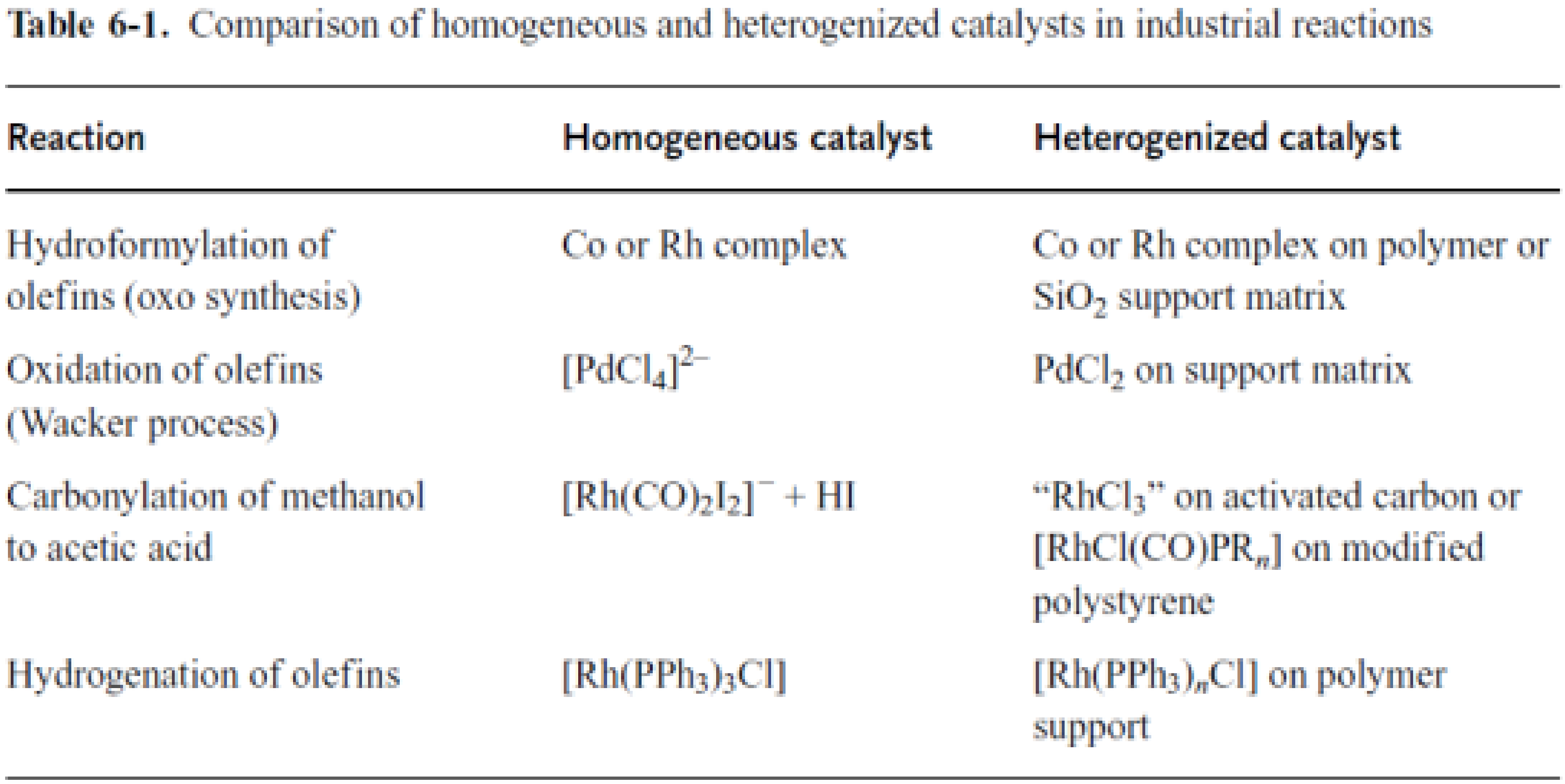


Table 6-1. Comparison of homogeneous and heterogenized catalysts in industrial reactions

Reaction	Homogeneous catalyst	Heterogenized catalyst
Hydroformylation of olefins (oxo synthesis)	Co or Rh complex	Co or Rh complex on polymer or SiO_2 support matrix
Oxidation of olefins (Wacker process)	$[PdCl_4]^{2-}$	$PdCl_2$ on support matrix
Carbonylation of methanol to acetic acid	$[Rh(CO)_2I_2]^- + HI$	"$RhCl_3$" on activated carbon or $[RhCl(CO)PR_n]$ on modified polystyrene
Hydrogenation of olefins	$[Rh(PPh_3)_3Cl]$	$[Rh(PPh_3)_nCl]$ on polymer support

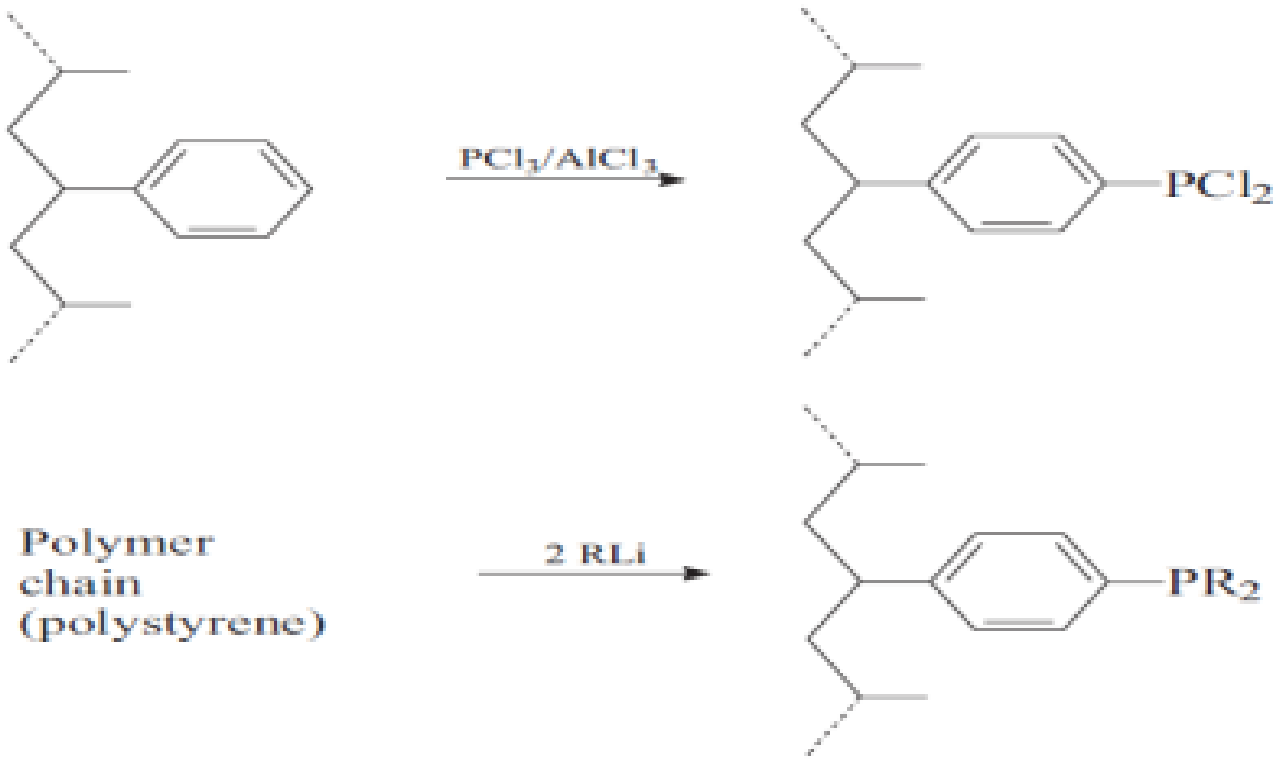
- **There are four basic ways of fixing transition metal complexes on a matrix:**
- 1) Chemical bonding on inorganic or organic supports.
- 2) Production of highly dispersed supported metal catalysts.
- 3) Physisorption on the surface of oxidize supports (supported solid phase catalysts, SSPC).
- 4) Dissolution in a high-boiling liquid that is adsorbed on a porous support (supported liquid phase catalysts, SLPC)

1- Chemical bonding:

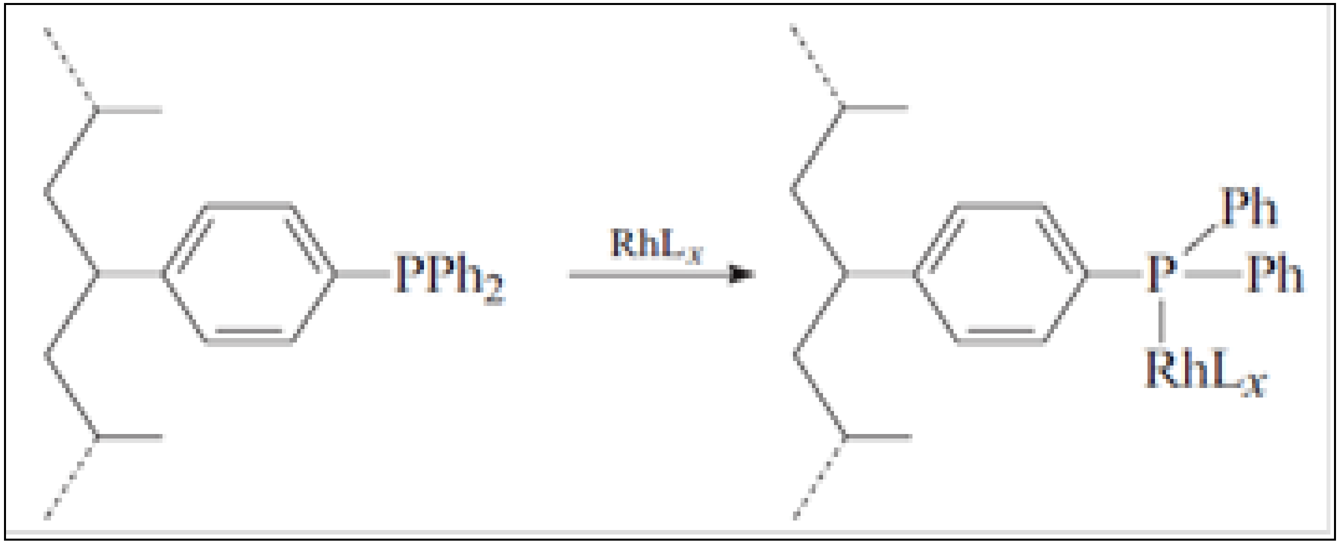
The immobilization of organometallic complexes on inorganic or organic supports is the most widely used method. Basically the supports act as high molecular mass ligands and are obtained by controlled synthesis. The bonding can be ionic or coordinative.

- The main aim of the process is to bind the complexes on the solid surface in such a manner that its chemical structure is retained as far as possible.
- A common method is the replacement of a ligand by a bond to the surface of the solid matrix. This means that a reactive group must be incorporated in the surface during production of the support.

Numerous polymer syntheses and orgamometallic syntheses are available for the construction of functionalized supports; the equation below gives just one example;

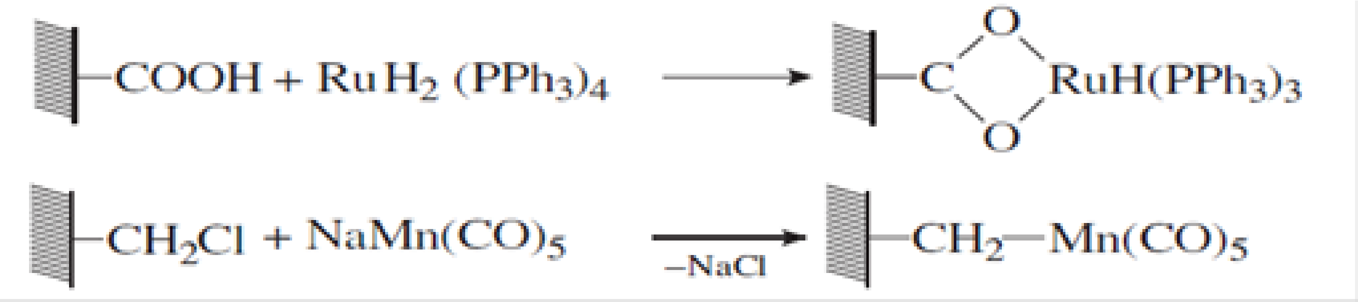


- Here triphenylphosphine, the most important ligand in organometallic catalysis, is coupled to the benzene rings of cross-linked polystyrene.



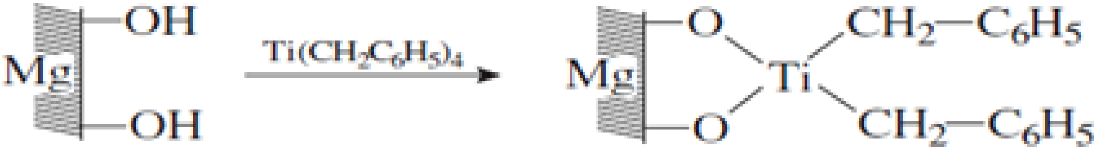
Hard copolymers of this type take up metal complexes only on the surface. The physical properties of the support can be varied by means of the polymerization method; the metal loading can also be controlled well.

There are many reactions available for applying the organometallic complexes to the surface, such as:



Disadvantages of the organic polymer supports are low mechanical durability (e. g., in stirred tank reactors), poor heat-transfer properties, and limited thermal stability (up to max. 150°C).

- There are also several methods available for producing inorganic supports. Here we will discuss a few basic methods. The most important method is the reaction of inorganic supports having surface hydroxyl groups with metal alkyls;



- Alkoxides and halides can also be attached to surfaces. Subsequent hydrolysis and dehydration lead to terminal metal oxo structures;

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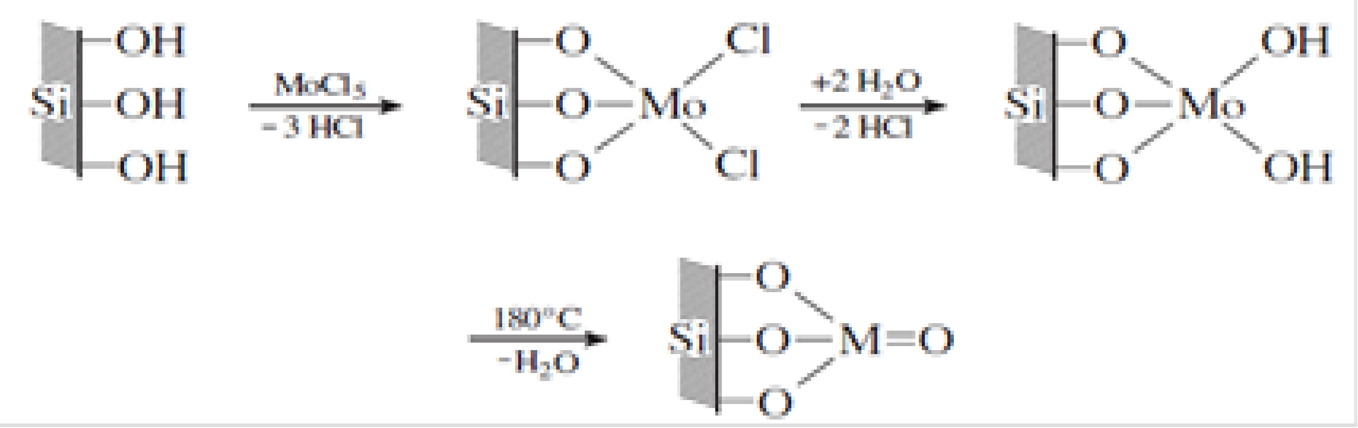
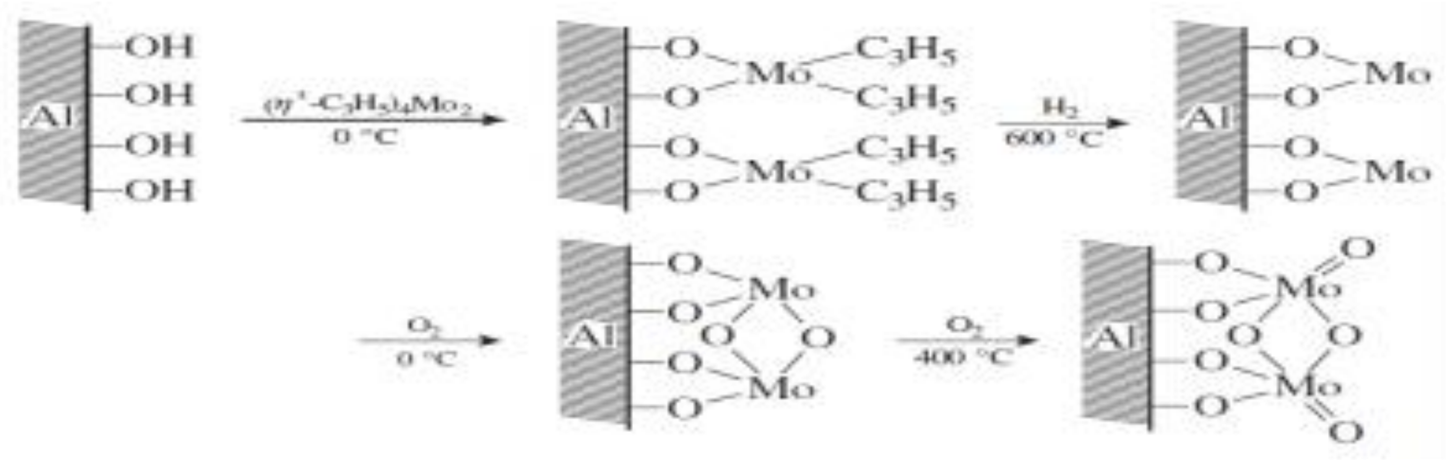
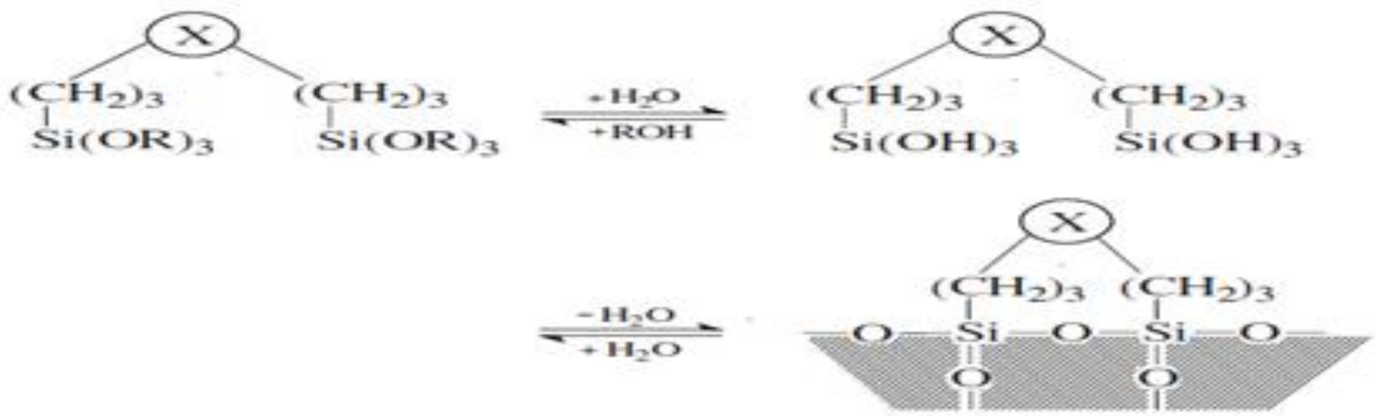


- Such immobilized molybdenum oxide catalysts are active in selective oxidation reactions. For example, methanol can be oxidized with air to methyl formate at ca. 500 K with 90–95 % selectivity.
- The catalyst obtained from ɣ-Al_2O_3 and tetrakis(η^3-allyl)dimolybdenum is considerably more active in ethylene hydrogenation and olefin metathesis than the catalysts prepared by conventional fixation of $[Mo(CO)_6]$ followed by calcination.



- Organofunctional polysiloxanes are a versatile group of catalysts developed by the company Degussa. These are solids with a silicate framework obtained by hydrolysis and polycondensation of organosilicon compounds.



X = functional group: sulfane, phosphine, amine

- This class of substances is characterized by broad chemical modifiability, a high capacity for functional groups, high temperature and ageing resistance, and insolubility in water and organic solvents.
- The heterogenized organopolysiloxane catalysts are marketed as abrasion-resistant spheres of various particle sizes. In particular the phosphine complexes of Ru, Pd, Ir, and Pt are interesting catalysts for hydrogenation, hydroformylation, carbonylation, and hydrosilylation.