



CHAPTER 1

GENERAL CONSIDERATIONS ON CATALYST AND CATALYSIS

1.1 CATALYST DEFINITION.

Catalyst is a substance that initiate and accelerate chemical reaction and affect the direction of chemical transformations [1]. In chemical reactions, bonds between certain atoms are broken and others formed. There are usually many possibilities for this to give a large number of products. However, in biological system as well as in mass transformations performed by catalyst certain single products are desired. This aim is achieved by the presence of a further substance, a catalyst, within the reactive system.

1.2 CONCEPTS OF CATALYSIS.

The term "catalysis" was coined by Berzelius in 1835 when writing his annual report on advances in physical sciences and used to cover a number of physiological and chemical reactions, discovered at that time, all with the common features that they proceeded in the presence of a further substance which did not itself change during the course of the reaction. Berzelius defined a catalyst as a substance which by its mere presence evokes chemical actions which would not take place in its absence. This definition simply described the observation of the phenomenon, "catalysis", without making any attempt to interpret or explain its nature. The word was formed from a combination of two greek words, $\kappa\alpha\tau\alpha$ (kata) = down and $\lambda\upsilon\sigma\epsilon\iota\nu$ (lysein) = to split or break. 'By "awaking affinities which are asleep" (Berzelius), a catalyst breaks down the normal forces which inhibit the reaction of molecules' [2]. The chinese word "tsoo mei"

(cui mei) which means "marriage broker" perhaps describes more correctly the idea behind what is commonly thought of as the phenomenon of catalysis. After Berzelius, it took some sixty years until a new definition of catalysis was given by W.Ostwald, based on the knowledge of chemical equilibrium, that all chemical reactions proceed via a number of more or less stable intermediates.

According to Ostwald, the phenomenon catalysis can be understood as an acceleration of a thermodynamically feasible reaction through the presence of a substance, the catalyst, which itself is neither essentially changed nor consumed by this chemical action. Further from thermodynamics, it is obvious that a catalyst which increases rate of forward reaction of a reversible reaction must also increase the rate of the reverse process. The definition of catalysis according to Ostwald focuses too strongly upon the rate increasing action of a catalyst in a thermodynamically feasible reaction.

Thus uniting both catalysis definitions, that of Berzelius and of Ostwald, a catalyst may be described as a substance which evokes chemical reactions that would not take place without it and which controls the direction of the chemical reactions within the framework of thermodynamic rules.

1.3 FUNCTIONS OF CATALYST.

According to the concepts of catalysis mentioned above, the role of catalyst on activation energy was explained. The activation energy is the critical energy that reactant molecules must possess to enable the reaction to take place. This is usually depicted as shown in Fig. 1-1 [1], where the potential energy is plotted against the reaction coordinate. Between the average potential energies of reactants and products, an energy barrier exists which can only be overcome by a small fraction of reactant molecules for which the total

collision energy exceeds the activation energy.

The function of the catalyst is to decrease the activation energy barrier for a certain reaction, thus the rate of that reaction is increased because a larger fraction of reactant collisions accelerates product formation.

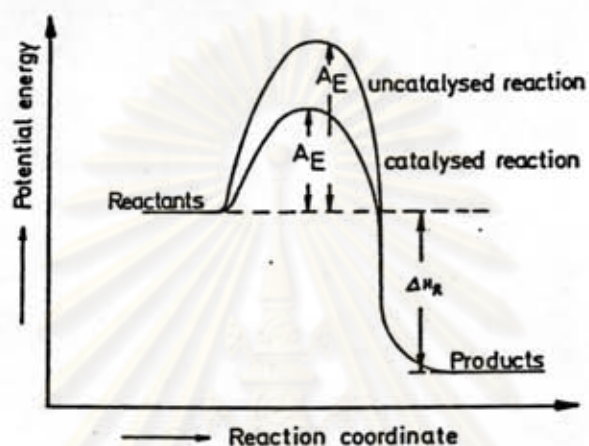


Fig. 1-1 Potential energy profile for a catalyzed and uncatalyzed exothermic reaction.

1.4 CATALYTIC SYSTEMS.

Catalytic systems can be divided into three distinct categories;

- enzyme catalysis, where enzyme is a catalyst which is produced in living cells and evokes and controls a large variety of biochemical reactions,
- homogeneous catalysis, where reactants and catalysts are presented in the same phase, and
- heterogeneous catalysis, where reactants and catalysts are presented in the different phases.

Among these catalytic systems, heterogeneous catalytic reactions are the most important reaction in chemical conversions. In order to understand in more detail the advantages and disadvantages of heterogeneous catalytic reactions, the different catalytic systems will be presented. There are three features which determine predominantly the ~~suitability~~ of catalysts in chemical reactions: activity, selectivity and stability. Differences in catalytic systems give the large differences in these characteristic features.

1.4.1 Enzymes catalysis

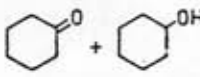
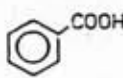
Enzymes are proteins. The most striking feature of these biocatalysts, which are responsible for all chemical reactions in living systems, is the exceptional selectivity and activity. The catalytically active sites in enzymes are specific binding sites which have geometric shapes -very often pockets or grooves- which complement the shapes of reactants (substrates) converted by this enzyme. Thus, besides the principle of catalysis, molecular shape also plays an important role in biochemical reactions; this is also responsible for high selectivity of these reactions. The high rate of enzyme-catalyzed reaction is achieved by the conformational adaptability of the enzyme to each of the intermediate step through which reactants are transformed into products.

Enzyme catalysts are not classified with respect to their chemical natures but according to their catalytic actions. The main application of enzyme catalysts is in the production of antibiotics like penicillins, streptomycins and vitamins like riboflavins, etc. Other important future areas are the production of protein for solving food problems, the treatment of industrial and urban waste, the replacement of less selective catalysts in heterogeneous or homogeneous catalytic reaction systems by highly selective enzymes which have been immobilized in insoluble polymers or in membranes or gels, and the storage and transformation of energy.

1.4.2 Homogeneous catalysis

In homogeneous catalytic reactions, the catalysts and reactants are presented in one phase and, from the engineering view point, a major disadvantage of this reaction arises from the difficulty in separating products from the catalyst; this is a particular problem in large-scale conversions with open reaction systems. Homogeneous catalytic reactions are classified according to the type of catalytically active species. The homogeneous catalytic reactions are used nowadays in about 20 major industrial processes, some typical examples being given in Table 1-1 [1] and in numerous small-scale reactions.

Table 1-1 Typical industrial homogeneous catalytic reactions.

Reactants	Catalyst	Products	Reaction conditions
<u>Ziegler-Natta process</u>			
$\text{CH}_2=\text{CH}_2$	$\text{TiCl}_4/\text{Al R}_3$	polyethylene	10-160 atm, 130-270°C
$\text{CH}_3\text{CH}=\text{CH}_2$	$\text{TiCl}_3/\text{Al R}_3$	polypropylene	20-40 atm, 50-85°C
<u>Wacker process</u>			
$\text{CH}_2=\text{CH}_2+\text{O}_2$	$\text{PdCl}_2/\text{CuCl}_2/\text{HCl}_{\text{aq}}$	CH_3CHO	4 atm, 120-130°C
<u>Oxo-process</u>			
$\text{CH}_2=\text{CH}_2+\text{CO}+\text{H}_2$	$\text{Co}_2(\text{CO})_8$	$\text{CH}_3\text{CH}_2\text{CHO}$	100-200 atm, 140-170°C
$\text{CH}_3\text{CH}=\text{CH}_2+\text{ROOH}$	$\text{Mo}(\text{CO})_6$	$\text{CH}_3\text{CH}-\text{CH}_2$ O	1 atm, 110°C
$\text{CH}_3\text{OH}+\text{CO}$	$\text{RhCl}_3/\text{CH}_3\text{J}$	CH_3COOH	30-40 atm, 180°C
$\text{C}_6\text{H}_{12} + \text{air}$	$\text{Co}(\text{OAc})_2$		10-15 atm, 125-165°C
$\text{ArCH}_3 + \text{air}$	$\text{Co}(\text{II}) \text{ salt}$		2-3 atm, 120-130°C
p-Xylene + air	$\text{Co}(\text{OAc})_2/\text{Mn}(\text{OAc})_2/\text{NaBr}$	terephthalic acid	15 atm, 225°C

Further developments in homogeneous catalysis are concerned with the demands of chemical and energy transformation-industries and on the other hand, with continuous research for more active and more selective catalysts and the combination of advantages in different catalytic systems. Thus, the feedstock basis for the application of homogeneous catalytic conversions changed in the past from acetylene to olefins and synthetic gas and will also incorporate in the future to the conversion of biomass [3].

1.4.3 Heterogeneous catalysis

Heterogeneous catalytic reaction systems, in which fluid reactants are passed over solid catalysts, are at present the most widely used catalytic processes. A number of these processes are listed in Table 1-2 [1] which indicates that much higher temperatures are used in heterogeneous catalytic reactions than in homogeneous catalytic ones. Enzyme catalyzed reactions, on the other hand, are usually performed at or just above room temperature. For example, the optimum temperature for penicillin production is 25°C and above 26°C a deactivation of the enzyme system, *Penicillium chrysogenum*, is observed [4].

Solid catalysts are classified according to their chemical natures into metals, semiconductors, insulators and solid acids. Table 1-3 shows the classification of heterogeneous catalysts [2]. Heterogeneous catalytic reaction systems are preferred for large-scale industrial conversions. The four basic reactor types for performing heterogeneous catalytic reactions are the fixed bed reactor, the fluidized bed reactor, the trickle bed reactor and the slurry reactor

Table 1-2 Industrial heterogeneous catalytic processes.

Processes/ Reactants	Catalyst	Products	Reaction conditions
<u>Petroleum refining processes</u>			
Catalytic re-forming/naphtha	Pt/Al ₂ O ₃ -Cl or Pt/Re/Al ₂ O ₃ -Cl	naphtha with increased octane number	15-30 bar, 470-510°C
Hydrodesulfurization/petroleum fractions	sulfided Co-Mo/Al ₂ O ₃ or sulfided Ni-W/Al ₂ O ₃	sulfur-free petroleum fractions	30-200 bar, 300-430°C
Catalytic cracking large petroleum molecules	Zeolite/silica-alumina	smaller petroleum molecules	3-5 bar, 500-550°C
<u>Petrochemical processes</u>			
ethylene, O ₂	supported Ag	ethylene oxide	10-20 bar, 250-300°C
H ₂ C=CH ₂ , HCl, O ₂	supported CuCl ₂	ClCH ₂ -CH ₂ Cl	2-4 bar, 220-240°C
benzene, O ₂	V ₂ O ₅ -MoO ₃ -H ₃ PO ₄	maleic anhydride	2-5 bar, 350-450°C
<u>Inorganic chemical processes</u>			
N ₂ , H ₂	Fe/Al ₂ O ₃ /K ₂ O/CaO	NH ₃	200 bar, 380-550°C
SO ₂ , O ₂	V ₂ O ₅	SO ₃	500°C, 1 bar
NH ₃ , O ₂	Pt/Rh	NO	1-10 bar, 850-900°C
CO, H ₂	ZnO-Cr ₂ O ₃	CH ₃ OH	100-350 bar, 240-380°C

Table 1-3 Classification of heterogeneous catalysts.

Class	Catalyzed reactions	Examples
Metals	hydrogenation dehydrogenation hydrogenolysis isomerization cyclization	Pt, Pd, Fe, Ni
Semiconductors	oxidation dehydrogenation desulfurization denitrogenation	NiO, ZnO, MnO ₂ , Cr ₂ O ₃ , Bi ₂ O ₃ -MoO ₃ , WS ₂ , NiS, CoS, MoS ₂
Insulators	dehydration	Al ₂ O ₃ , SiO ₂ , MgO
Solid acids	polymerization cracking isomerization alkylation	zeolites amorphous SiO ₂ -Al ₂ O ₃

as shown in Fig. 1-2 [1]. In such systems, mass and energy fluxes are coupled with chemical reactions which occur on the active centers of the catalyst surface. Hence, a kinetic analysis of these systems must include the concurrence of rates of surface reactions, the adsorption and desorption rates of reactant molecules on active sites at surface, and the rate of physical and mass energy transport processes.

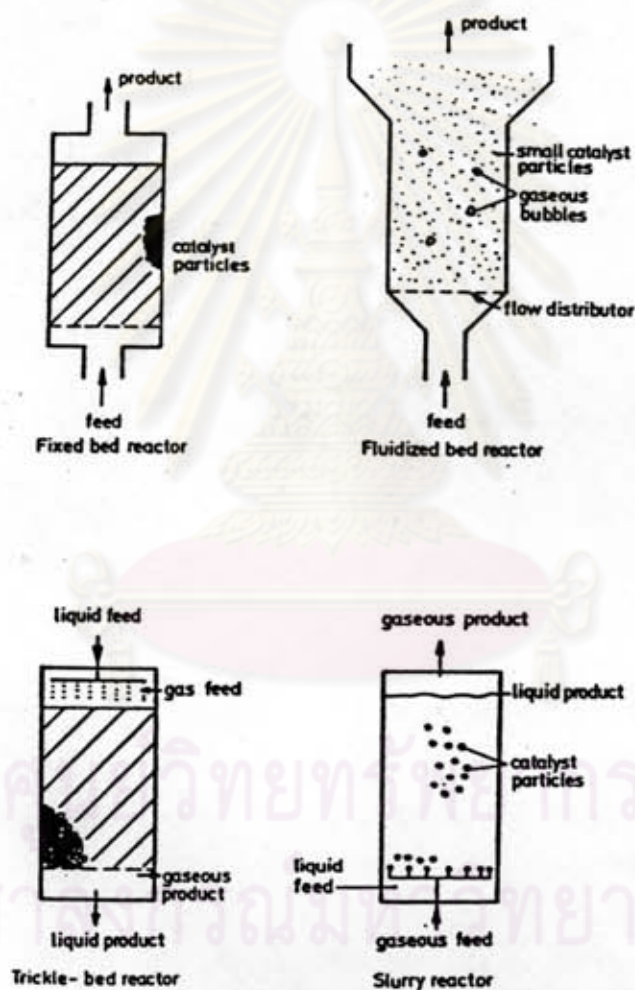


Fig. 1-2 Industrial reactors for performing heterogeneous catalytic reaction.

Usually with isothermal reaction systems, the following steps are considered :

1. Diffusion of reactants from the bulk fluid to external surface of catalyst particle
2. Diffusion of reactants to pores.
3. Adsorption of reactants on surface of solid catalyst.
4. Surface reaction.
5. Desorption of products.
6. Diffusion of products out of pores.
7. Diffusion of products from external surface of catalyst particle to bulk fluid.

Solid catalysts, when used in chemical reactions, must usually be activated to display the desired activity and selectivity; the actual activity and selectivity under operating conditions depends not only on this activation procedure but also on the total history of catalyst including all preparation procedures.

In heterogeneous catalytic reaction systems, the analogous phenomenon to enzyme inhibition is catalyst deactivation. This, however, usually serves not to establish a certain desired activity and selectivity but to determine the long-term stability of a catalyst. One of the aims in investigating the characteristics of solid catalysts is to find catalysts with long-term stability or find procedures that will restore the original activity and selectivity of solid catalysts after some degree of deactivation. Catalyst deactivation is caused either by changes in catalyst structure due to extreme (or even normal) operating conditions, by impurities in reactant feed, or by side or following reactions during reactant conversion.

In order to preserve the catalysts without additional separation procedures, the majority of large-scale processes in the chemical industry are based on heterogeneous catalytic reactions. The improvement of existing or the introduction of new processes is mostly a result of developing new catalysts or modifying existing ones.



1.5 LAYER SILICATE CLAY MINERALS.

Layer lattice silicates commonly found in natural clay minerals are composed of silicate sheets which are stacked one above the other. In the swelling clay minerals, the silicate sheets have negative charges due to their chemical compositions and alkali or alkaline earth metal ions, usually Na^+ or Ca^{2+} , are interlamellarly incorporated into the structure to counterbalance the negative charges. Metal ions in a swelling layer lattice silicate are easily exchangeable with any desired cations, including organic and inorganic cations by a simply ion exchanged method. They can be replaced even with bulky cations such as cationic metal chelate complex, because the interlayer spacing is expandable. Water and other polar molecules of many different kinds can be also intercalated into interlayer spaces.

Smectite clay minerals

Smectite clay minerals have layer lattice structures in which two dimensional oxyanions are separated by layers of hydrated cations. Fig. 1-3 [5] is the schematical illustration of oxygen framework of layer lattice structure which was established crystallographically by Toraya et.al [6]. The oxygen atoms defined upper and lower sheets of tetrahedral sites and a central sheet of octahedral sites. The 2:1 relation between tetrahedral and octahedral sheets within a layer allows the smectite clays to be classified as listed in Table 1-1 [5] for three dioctahedral smectites and two trioctahedral smectites. In montmorillonite, the most familiar and common member of smectite groups, the substitution of octahedral Al^{3+} by Mg^{2+} or Fe^{2+} gives each silicate layer a net negative charge. This negative charge is usually compensated by Na^+ and Ca^{2+} together with small amount of K^+ and Mg^{2+} . Hectorite and laponite, which is a synthesis clay within the same chemical formula as hectorite, the substitution of Mg^{2+} by Li^+ occurs in the octahedral sheet. But for beidellite and saponite, the substitution of Si^{4+} by Al^{3+} occurs in the tetrahedral sheet.

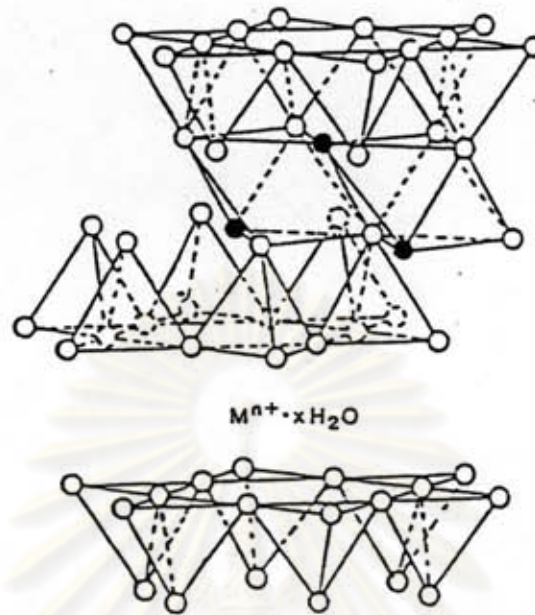


Fig. 1-3 Idealized structure of smectite clay mineral. (o)Oxygen atoms; (●) Hydroxyl groups. Silicon and sometimes aluminum normally occupy tetrahedral positions in the oxygen framework. Al, Mg, Fe, or Li may occupy octahedral sites. $M^{n+} \cdot xH_2O$ represents the interlayer exchange cation.

Table 1-4 Idealized structural formulas for some dioctahedral and trioctahedral 2:1 phyllosilicates. In each formula the cations enclosed in brackets occupy octahedral sites and the cations in parentheses occupy tetrahedral sites.

Mineral group	Dioctahedral	Trioctahedral
Pyrophyllite-talc	Pyrophyllite: $[Al_4](Si_8)O_{20}(OH)_4$	Talc: $[Mg_6](Si_8)O_{20}(OH)_4$
Smectites	Montmorillonite: $M^{n+}_{x/n} \cdot yH_2O [Al_{4-x} Mg_x] (Si_8) O_{20} (OH)_4$	Hectorite: $M^{n+}_{x/n} \cdot yH_2O [Mg_{6-x} Li_x] (Si_8) O_{20} (OH)_4^*$
	Beidellite: $M^{n+}_{x/n} \cdot yH_2O [Al_4] (Si_{8-x} Al_x) O_{20} (OH)_4$	Saponite: $M^{n+}_{x/n} \cdot yH_2O [Mg_6] (Si_{8-x} Al_x) O_{20} (OH)_4$
	Nontronite: $M^{n+}_{x/n} \cdot yH_2O [Fe_4] (Si_{8-x} Al_x) O_{20} (OH)_4$	
Micas	Muscovite: $K_2 [Al_4] (Si_6 Al_2) O_{20} (OH)_2$	Phloosonite: $K_2 [Mg_6] (Si_6 Al_2) O_{20} (OH)_2$

* In this mineral some framework hydroxyls are replaced by fluoride ion.

The layer charge in octahedrally charged smectites is distributed overall oxygens in the framework. These smectites tend to be randomly stacked with respect to in-plane a and b axes of adjoining layers. Negative charge on layer of tetrahedrally charged smectites is more localized and these derivatives tend to exhibit three dimensional aggregation[7-8]. Smectite clays have a combination of cation exchange, intercalation and swelling properties, which make them unique. The cation exchange capacity is fundamental to the intercalation and swelling properties. Thus, compensating cations on the interlamellar surfaces of smectites can be replaced with almost any desired cation by utilizing simple ion-exchange method.

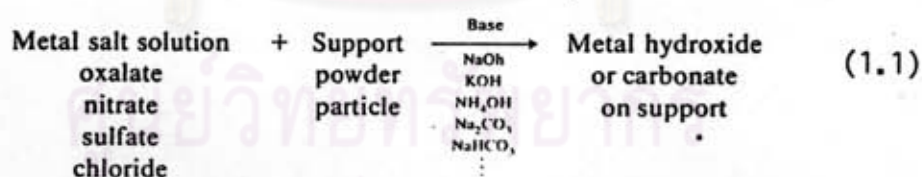
Layer lattice silicate had been used widely in early petroleum industries as a cracking catalyst to produce gasoline with a high octane value. However, their catalytic properties have not been investigated extensively, since they were completely replaced with a synthetic silica-alumina or zeolite catalysts. Recently, interest in the layer lattice silicate has been focused largely on preparation of new catalytic materials by utilizing the intercalation phenomenon. Brindley and his co-workers[9] and Lahav et.al.[10] created new type of molecular sieve by dehydrating smectite intercalates of hydroxy aluminum and hydroxy zirconium cations. Pinnavaia and his co-workers [11-13] reported that intercalation of metal complexes into clay mineral was successful as an immobilized catalyst and showed the shape selectivity caused by the interlayer spacing. Thomas and his co-workers [14-15] demonstrated that the clay intercalated of hydrated metal ions, especially Al^{3+} and Cu^{2+} , promoted numerous acid catalyzed reactions remarkably. Yamanaka et.al. [16-17] and Endo. et.al. [18-19] prepared new type of molecular sieves, namely "pillar clays", in which oxide pillars keep the silicate sheets apart and make pores stable up to $500^{\circ}C$. In conclusion, special interest in a layer lattice silicate as a catalytic mineral has been revived, because of the ion exchange property and the expandable layer structure.

1.6 CATALYST PREPARATIONS.

The deposition of active components on the support is carried out by one of these four methods : (1) precipitation, (2) adsorption, (3) ion exchange, and (4) impregnation. Each technique has advantages and disadvantages. Often preference for one method over another is a matter of compromise. The support is either in powder or in particle form. Depositing active components on the internal surface of porous particles require special attention to avoid pore diffusional limitations that give uneven distributions. This must be weighed against the advantages of better control of pore size distribution and easier handling operations. Active components deposit in large concentration onto powder change mechanical and surface properties. In laboratory preparations, deposition onto powders is usually practiced. Commercial manufactures find preformulation more convenient, efficient, and economical.

1.6.1 Precipitation

In precipitation, the objective is to achieve a reaction of



The choice of salt or alkali depends on factors similar to those considered for single oxide precipitations. Powders or particles are slurred with an amount of salt solution sufficiently to give the required loading. It is helpful to carry out preliminary heating or evacuation to ensure that the pores are properly filled with solution. The sequence of steps is shown in Fig. 1-4.

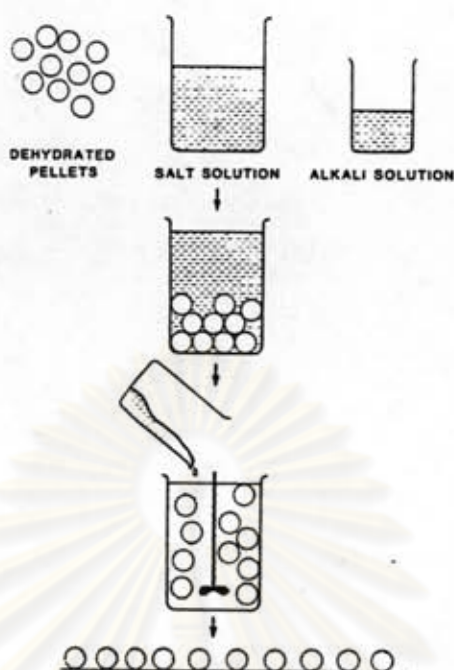


Fig. 1-4 Steps in the precipitation of the active component.

Enough alkali solution is added to cause precipitation, the powder is then filtered or otherwise separated and washed to remove alkali ions, reagent anions, and excess deposit on the outside of particles. Two processes are involved in the deposition:

- (1) precipitation of sols in bulk and pore fluid, and
- (2) interaction with the support surface.

Best results occur when the OH groups of the support surface enter into the reaction(1.1) so that the pH of the surface region is higher than in the bulk solution. Precipitation then occurs preferentially and uniformly on the surface.

Rapid nucleation and growth in the bulk solution must be avoided, since sols are then too large to enter the pores easily and associate only with the outside of the particle. This is most likely to occur in the vicinity of alkali droplets entering the solution.

Rapid mixing is essential. Sometimes cooling, which lowers nucleation and growth rates, is effective. At other times, boiling the solution to introduce turbulence seems to work. Usually, mixing is no problem in laboratory devices. Dilute alkali may be added, drop by drop, with rapid agitation to disperse the droplets before local concentrations become excessive. Alternatively, both the salt and alkali solution may be added simultaneously in a controlled manner to a well-mixed container of water. Mixing is more difficult in commercial operations. Vessels are larger and mixing of reagents takes longer time. This is one of the many perplexing problems faced during scale-up [20].

One effective solution to control uniform precipitation is to use urea rather than conventional alkali. Urea dissolves in water but decomposes very slowly above 90°C. Appropriate amounts of urea is added to the metal salt-support slurry and the mixture heated with stirring. At 90°C, urea hydrolyzes and OH groups are formed uniformly throughout the vessel and in the pores. Precipitation takes place homogeneously over the surface. Since hydrolysis is slow and precipitation is rapid, OH groups are consumed as fast as they are formed and the pH of the solution remains unchanged. Although requiring longer times, this technique yields very uniform products. Loading is controlled by the time of reaction. Scale-up also poses no difficulties [21]. Variations of this procedure are practiced in which alkali solution is slowly injected through the hyperdermic syringe into the turbulence of the mixer.

After washing, the treated support is dried to remove excess moisture from pores. This operation is not as critical as in support preparation, since the active component is firmly anchored to the surface. However, precautions should be taken to avoid rapid heating that generates large internal steam pressures. Calcination decomposes the deposited hydroxides and carbonates into stable oxides or metals, depending on the atmosphere. Calcination temperatures are determined

by the conditions necessary for decomposition. Side reactions also occur, either parallel or series, between the original deposit, the oxide, and the support. Unlike coprecipitation systems, interaction is restricted to surface layers and may be only few atomic dimension thick. Precipitation is the preferred deposition route for loadings higher than 10%-20%. Below this value, other techniques are usually practiced.

1.6.2 Adsorption

Adsorption is an excellent method for depositing small amounts. Support materials exposed to metal salt solutions adsorb equilibrium quantities of salt ions and obey adsorption isotherms as shown in Fig. 1-5. Powders or particles are dehydrated and saturated

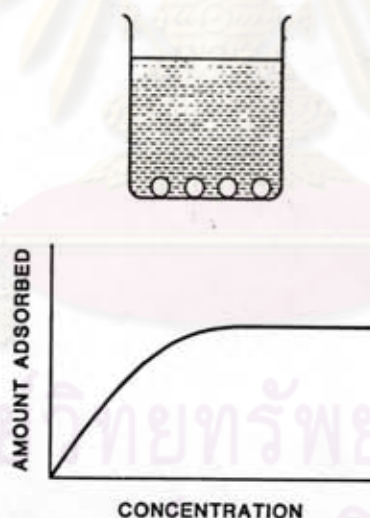


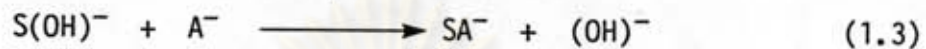
Fig. 1-5 Isotherm for adsorption of catalytic ions.

in the appropriate solution for suitable periods. Deposition is uniform, providing all pores are penetrated during the saturating time. Adsorption from solutions may be either cationic or anionic depending on the properties of surface. In general, zeolite are strongly cationic exchanger, silica is weakly cationic adsorber, alumina adsorbs both cations and anions weakly, magnesia is a strongly

anionic adsorber and carbon prefers to form charge-transfer complexes with electron donation but also weakly adsorbs cations [22]. With the exception of zeolites, that follow a different mechanism, the governing processes for ionic adsorption involve equilibrium reactions of :



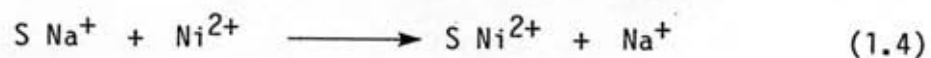
and



Equilibrium is determined by the concentration of C^+ and A^- in the solution and by pH. Unfortunately, saturation amounts are generally small. For example, with nickel solutions and alumina only loadings up to 2%-3% are possible. Multi-adsorptions with intermediate calcination give higher loadings, but this is time consuming. With platinum and other expensive noble metals, amount of less than 1% are often needed. Low loading with high dispersion give satisfactory results. Supports are saturated in solutions of chloroplatinic acid, H_2PtCl_6 , to yield desired levels of adsorbed $(\text{PtCl}_4)^{2-}$. Washing is not necessary, nor desirable, since it induces desorption. Drying and calcination are carried out as usual, with the chloroplatinic ion decomposing to platinum oxide or platinum. Transport effects are encountered when using large particles. Adsorption of chloroplatinic acid is so rapid that diffusion of the solute into the pores controls the rate. Deposition takes place in an outer surface.

1.6.3 Ion Exchange

Ion exchange in catalyst preparation is very similar to ionic adsorption but involves exchange of ions other than protons. Lower valency ions, such as Na^+ , exchange with ions having higher charge, for example Ni^{2+} , according to the stoichiometric equation of :



Ion exchange is useful in removing harmful agents and adding promoters. During washing with ammonia solutions, NH_4^+ ions are exchanged with impurities such as Na^+ to remove potential poisons. For controlled loadings of active components or promoters, the catalyst is saturated in excess solutions containing the exchange ions. Loading or extent of exchange is controlled with saturating time. Even multiple exchange is possible.

Because of the large number of ion exchange possibilities, this method promises to be important for the modification of catalytic materials.

1.6.4 Impregnation

Also Known as "incipient wetness", impregnation is the simplest and most direct method of deposition [23]. The object is to fill the pores with a solution of metal salt of sufficient concentration to give the correct loading.

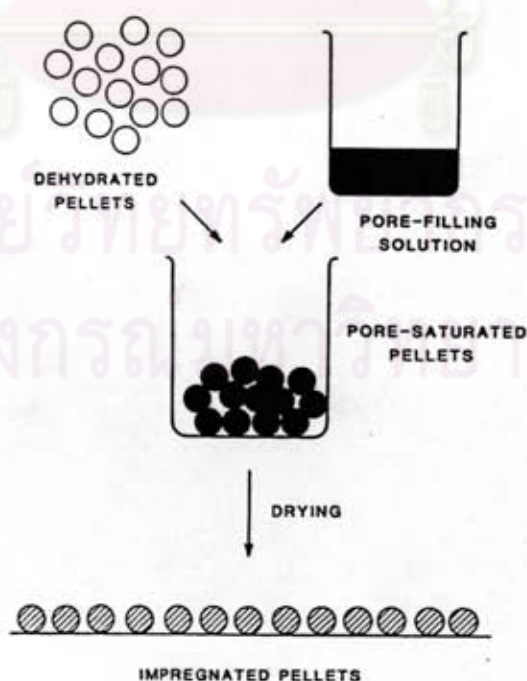


Fig. 1-6 Steps in impregnation of the active component.

Figure 1-6 shows the sequence of steps. The support, usually in particle form, is heated or evacuated to remove pore moisture. This is not essential but speed diffusion of the solute into the pores. Solution, in an amount just sufficient to fill the pores and wet the outside of the particles, is introduced. Although this may be calculated from measured pore volumes, it is sometimes more reliably determined with preliminary tests on aliquot samples. Drying is necessary to crystallize the salt on the pore surface. If not performed properly, this step can result in irregular and uneven concentration distributions. For example, Fig. 1-7 demonstrates how the rate of drying affects pore and particle profiles [24]. If the

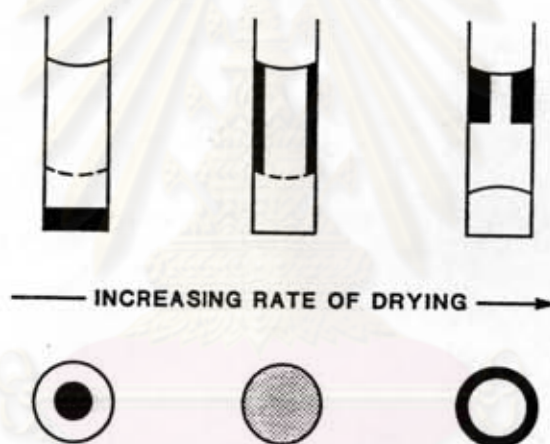


Fig. 1.7 Pore and particle profiles after drying.

rate is too slow, evaporation occurs at the meniscus, which retreats down the pore, some salt deposition occurs but most of the solute merely concentrates deeper in the pore. When finally crystallized, the salt is located at the bottom of a pore or at the particle center. When the drying rate is too fast, a temperature gradient occurs. Vaporization deep in the pore forces solution toward the outside, where most of the deposition takes place. The ideal situation is when crystallization is slow enough to form uniform deposits. However since the support exists with a distribution of pore sizes, it is impossible to satisfy optimum condition for each. Only experiment can

establish the best procedures, but some nonuniformity must always be expected. When concentration profiles are desired for process reasons, these effects may be used to good advantage [25,26].

Calcination is important in these circumstances. Crystallite salt dissolves when the dehydrated catalyst is exposed to moist environments and subsequent process drying may violate optimum conditions. Calcination converted the salt to an oxide or metal and essentially freezes the distribution. Other calcination effects, such as solid state reaction, also take place.



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