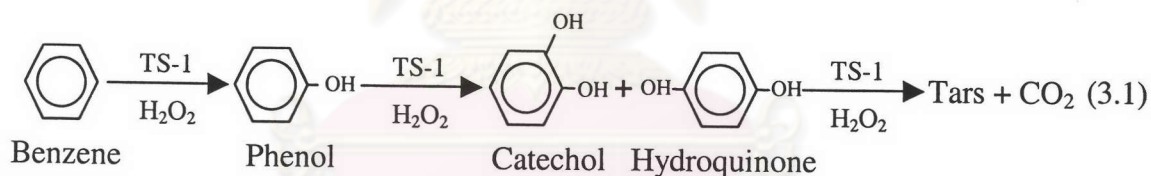


CHAPTER III

THEORY

3.1 Hydroxylation of benzene

The hydroxylation of benzene on TS-1 produces phenol as the primary product. Conversion is generally kept low, because introduction of a hydroxyl group activates the aromatic nucleus to further oxidation to hydroquinone, catechol, and eventually to tarry products (Eq. 3.1). Acetone, methanol, 2-butanone or just water are suitable reaction media (Romano *et al.*, 1990; Khouw *et al.*, 1994; Thangaraj *et al.*, 1990). In aqueous solution, benzoquinone was also found, in appreciable amounts, among the products. Hydroxylation of benzene with a mixture of hydrogen and oxygen, an in situ source of hydrogen peroxide, can be achieved on Pd-containing TS-1 (Tatsumi *et al.*, 1992). This is, in principle, an easier route to phenol than that based on the preformed oxidant (Clerici and Ingallina, 1998). In practice, it proved less effective, because of faster catalyst decay.



3.2 Molecular sieve and zeolite

Zeolite, or crystalline aluminosilicates having pore of molecular dimension, occur naturally in the vugs and vesicles of basaltic lava, in volcanic deposits from saline, alkaline lake and nonmarine tuff beds. These naturally occurring zeolites, the first known examples of molecular sieves, were studied scientifically as early as 1760, whereas their selective adsorption and ion-exchanged properties have been known for decades. Today, zeolites and other molecular sieves, the crown jewels of catalysis, promise to revolutionize chemicals manufacture, petroleum refining and coal and/or natural gas conversion processes through the concept of catalysis by molecular design.

3.2.1 Composition of molecular sieves

Strictly speaking, the term molecular sieve refers to a class of crystalline materials having a range of compositions that exhibit shape-selective adsorption and reaction properties, whereas the term zeolite refers to the shape-selective materials composed only of aluminosilicates. The range of materials that make up molecular sieves includes carbon, silica, aluminosilicates, aluminophosphates, metallosilicates (e.g. gallosilicates, chromo silicates, borosilicates, and ferrisilicates) and metalloaluminates (e.g. germanium aluminates). In fact, the list of cations that can be incorporated into molecular sieve frameworks has been expanded to include 16 or more elements (Si, Al, Ga, Ge, Be, Li, Mg, Ti, Cr, Mn, Fe, Co, Zn, B, C, P etc.).

3.2.2 Composition and structure of zeolites

Zeolites or aluminosilicates have the general formula $M_v(\text{AlO}_2)_x(\text{SiO}_2)_y \cdot z\text{H}_2\text{O}$; the AlO_2 and SiO_2 species are the fundamental units that share oxygen ions to form tetrahedral AlO_4 and SiO_4 building blocks for the zeolite unit cell. Thus, the framework of a zeolite is made up of aluminum and silicon tetrahedral, while metal or hydrogen cations (M) occupy exchangeable cationic sites. Table 3.1 shows the unit cell composition for several important Na-exchanged zeolites along with aperture size (limiting pore size). Note that because the silicon ion has a charge of +4 and aluminium +3, the number of Na^+ ions required for charge equalization is equal to the number of aluminum ions.

The synthesis of zeolites from its basic building blocks is illustrated in Figure 3.1. A typical aluminosilicate is formed by polymerization of SiO_4 and AlO_4 tetrahedra to form sheet-like polyhedra (squares and hexagons) which in turn form cubes, hexagonal prisms and truncated octahedral (14-sided). These three-dimensional tertiary building blocks in turn are arranged regularly to form a superstructure inside which exist pores and a supercage. Each supercage has a characteristic window size aperture which blocks entry of sufficiently large molecules, i.e. the sieve effect.

Table 3.1 Composition and limiting pore diameters for common zeolites (Farrauto and Bartholomew, 1997)

Type	Composition per unit cell				Aperature Size (Å)
	Na	AlO ₂	SiO ₂	H ₂ O	
A	12	12	12	27	4.2
Faujasite X	86	86	106	264	8.0
Faujasite Y	56	56	136	264	8.0
Erionite	4.5	9	27	27	4.4
Mordenite	8	8	40	24	6.6
Pentasil (ZSM-5)	9	9	87	16	5.5
Pentasil (Silicate)	0	0	96	16	5.5

3.2.3 Pore structure of molecular sieves

The zeolites listed in Table 3.1 are just a few of the many possible molecular sieve structures. According to Vaughan, 1988: 'few fields of chemistry offer such chemical diversity; although only about 60 structures are known, tens of thousands of theoretical structures are possible.'

Probably the simplest level of classifying molecular sieve structure is in terms of pore diameter and ring size. By convention, ring size is specified by the number of T atoms or TO₄ units where T = Si, Al, P or B. Pore diameters of aluminosilicate molecular sieves (A, erionite, pensil, mordenite and faujasite) range from 3 to 8 Å, whereas ring sizes range from 8 Å for erionite to 12 Å for Y-Zeolite.

3.2.4 Acidity

Acidity in zeolites increases with decreasing Si:Al ratio, since acid sites are associated with Al ions; acidity is also a function of cation. H-sieves are strong acids but often too unstable for commercial use. Nevertheless, zeolites exchanged with di- and trivalent ions are sufficiently acidic; for example, Ca²⁺ is thought to be present as Ca(OH)⁺ plus H⁺. ALPOs are mildly acidic relative to the aluminosilicates. The

Bronsted and Lewis acidities of zeolites play important roles in their abilities to catalyze various hydrocarbon reactions, e.g. cracking and isomerization.

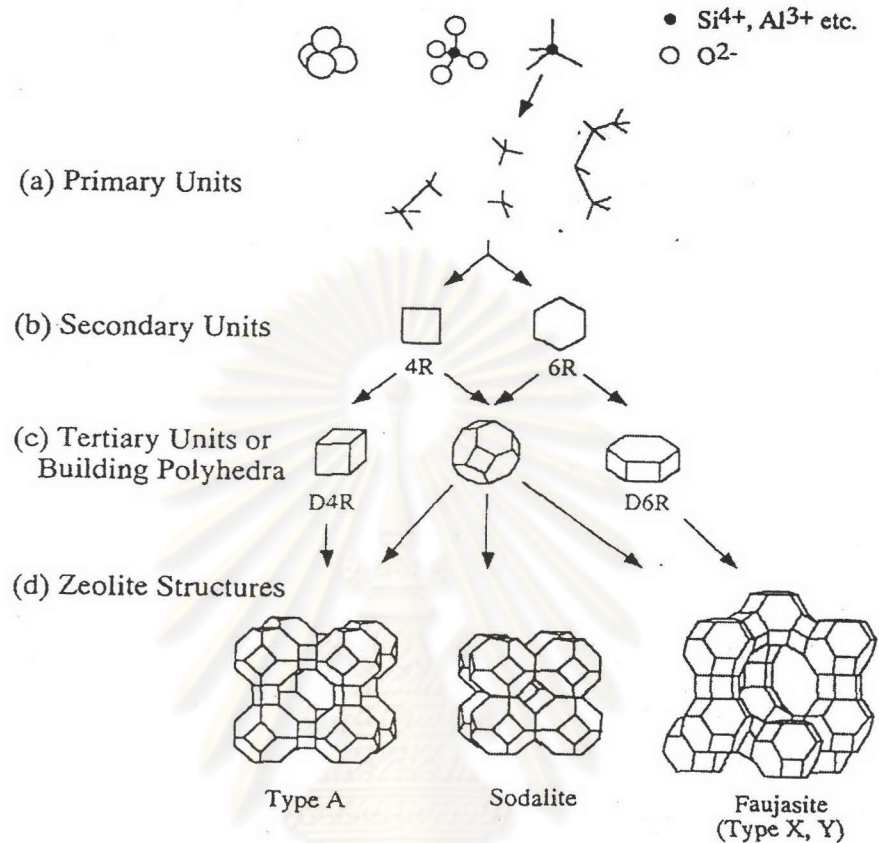


Figure 3.1 Formation of three common zeolites from primary SiO₄ and AlO₄ tetrahedral units through a combination of secondary ring units, and ultimately different mixes tertiary polyhedra; note, however, that all three use the same structural polyhedron (cubo-octahedron) in the final construction (Farrauto and Bartholomew, 1997)

3.2.5 Thermal stability

The thermal stability of zeolites increases with increasing silica content and by exchange with rare earth cations. Most sieves are uncharged by dehydrating to 400 °C; high silica (ultrastabilized forms prepared by steam pre-treatment) and rare earth-exchanged sieves are stable to 700-800 °C. Generally, extensive dehydration causes loss of Bronsted acidity due to the removal of OH or silanol surface groups.

Thermal treatment of zeolites in the presence of water normally leads to dealumination. In fact, it is one of the recommended methods for preparing ultrastable zeolites. Moderate dealumination generally increases catalytic activity or leaves it unchanged, whereas advanced dealumination leads to a decrease in activity due to a loss of active sites and ultimately collapse of the zeolite structure. For example, dealumination of mordenite significantly changes important chemical and physical properties such as crystal structure, thermal stability, sorption capacity and acidity, as well as catalytic properties. Maximum thermal stability is reached for an $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio of about 19. The sorption capacity towards water is highly reduced after dealumination because of the absence of strong polarizing cations which can dissociate water to strongly adsorbed hydroxy groups; accordingly, the number of Bronsted acid sites also decreases. Nevertheless, the hydrocarbon cracking activity of mordenite increases with increasing Si:Al ratio. For further details on zeolite stability, the reader is referred to the comprehensive review of McDaniel and Maher, 1976.

3.2.6 Shape selectivity

Many reactions involving carbonium intermediates are catalyzed by acidic zeolite. With respects to a chemical standpoint the reaction mechanisms are not fundamentally different with zeolites or with any the acidic oxides. What zeolite add is shape selectivity effect. The shape selective characteristics of zeolites influence their catalytic phenomena by three modes shape selectivity: reactants shape selectivity, products shape selectivity and transition states shape selectivity. These types of selectivity are illustrated in Figure 3.2.

Reactants of charge selectivity results from the limited diffusibility of some of the reactants, which cannot effectively enter and diffuse inside crystal pore structures of the zeolites. Product shape selectivity occurs as slowly diffusing product molecules cannot escape from the crystal and undergo secondary reaction. This reaction path is established by monitoring changes in product distribution as a function of varying contact time.

Restricted transition state shape selectivity is a kinetic effect from local environment around the active site, the rate constant for a certain reaction mechanism is reduced if the space required for formation of necessary transition state is restricted.

The critical diameter (as opposed to the length) of the molecules and the pore channel diameter of zeolites are important in predicting shape selective effects. However, molecules are deformable and can pass through opening, which are smaller than their critical diameters. Hence, not only size but also the dynamics and structure of the molecules must be taken into account.

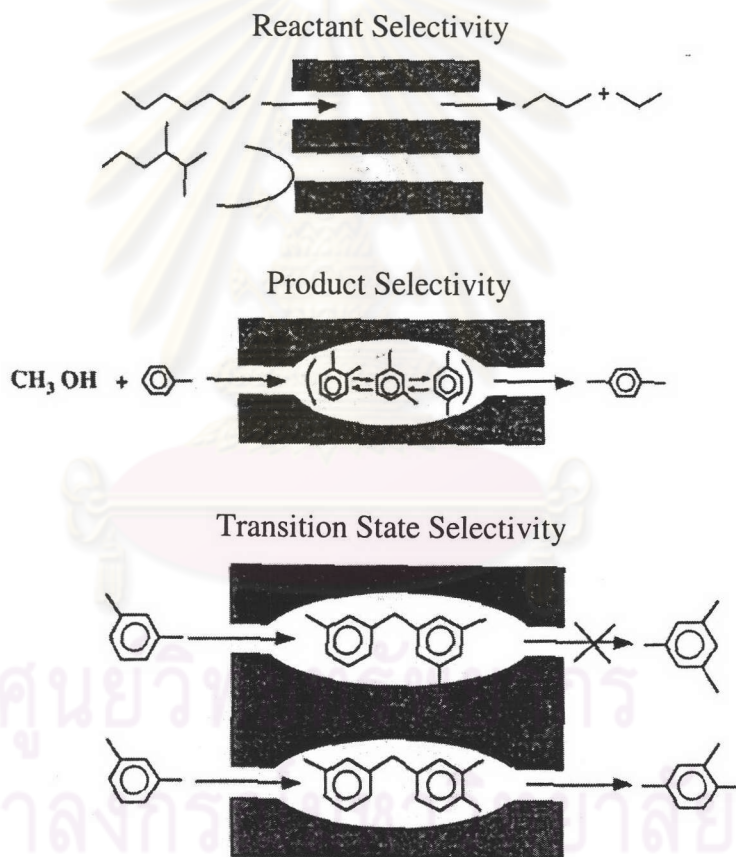


Figure 3.2 Diagram depicting the three type of selectivity (Farrauto and Bartholomew, 1997)

3.3 Titanium silicalite (Notari, 1989)

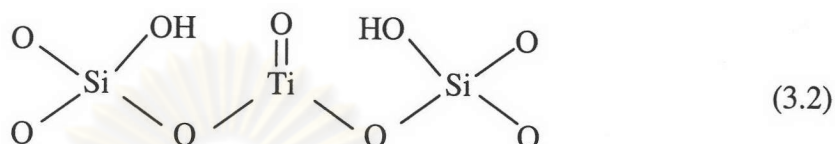
Titanium silicalite is an interesting material obtained by isomorphic substitution of trivalent metals or tetravalent metals in the framework of crystalline aluminosilicates or silicates. Titanium silicalites with MFI (TS-1) and MFI/MEL (TS-2) structures have been used in several oxidation reactions with H_2O_2 as the oxidizing agent (Centi *et al.*, 2001).

Titanium has a stable valence of 4 and in an oxidizing medium it is very likely that this valence is maintained. An examination of the chemistry of Ti^{IV} compounds immediately shows that Ti^{IV} has a strong tendency to assume a high coordination number: with oxygen, six groups in octahedral coordination form a stable and very frequently observed configuration, but to do this Ti^{IV} must have near neighbours capable of increasing their coordination number to satisfy at the same time titanium valency of four and coordination of six. When bulky groups are linked to Ti^{IV} , tetrahedral coordination is also observed. Coordination of seven in a pentagonal pyramidal arrangement like in peroxo compounds and of eight like in $\text{Ti}(\text{NO}_3)_4$ are also observed.

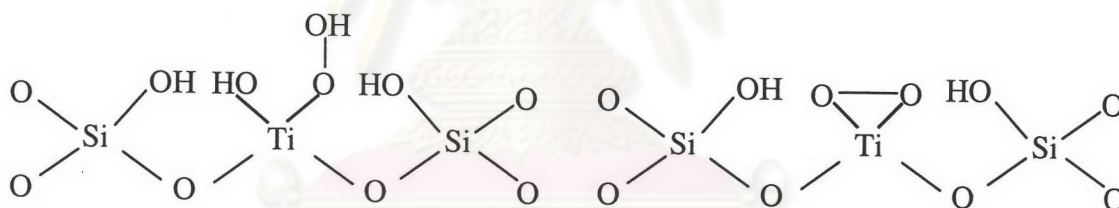
From the crystalline structure and the regular change in unit cell parameters which are consistent with isomorphous substitution of Si^{IV} with Ti^{IV} it seems justified to represent TS-1 as a silicalite in which few Ti^{IV} have taken the place of Si^{IV} . The interpretation of the catalytic activity of TS-1 must take into consideration the role played by these few Ti^{IV} : in fact pure silicalite is totally inactive, and other phases containing Ti have not been identified. Due to the fact that TS-1 crystallizes from a homogeneous solution, it is reasonable to assume that the distribution of Ti^{IV} in the crystal lattice is at random; since the Si/Ti ratio is in the range 40 - 90 in typical preparations, most Ti^{IV} must be isolated from each other by long sequences of -O-Si-O-Si-O-. If Ti^{IV} replaces a Si^{IV} it should be tetrahedrally coordinated by O^- : however, the presence of a band at 980 cm^{-1} closely corresponds to the band observed in other titanium compounds containing the $\text{Ti}=\text{O}$ group, whose stretching frequency is 975 cm^{-1} with bond distances of $1.66 - 1.79\text{ \AA}$; furthermore, hydroxyl

groups are present at the surface as shown by the increase in selectivity which is obtained upon silylation.

Finally, near neighbour positions of Ti^{IV} are occupied by Si^{IV} which in a field of O^- is stable only in tetrahedral coordination. A simple representation of the sites where substitution has occurred which takes into consideration the various pieces of experimental evidence could be

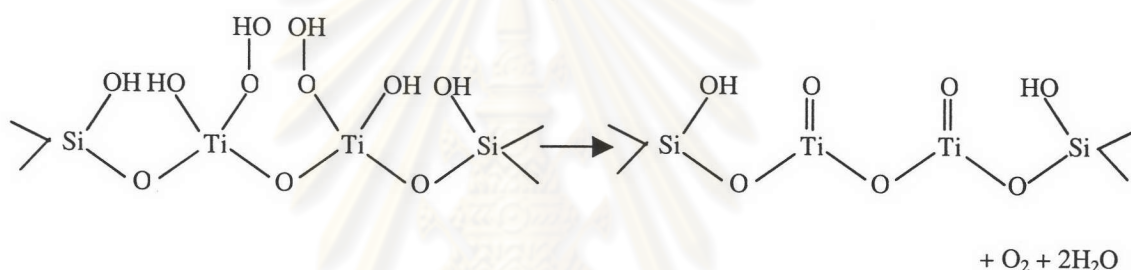


Other more elaborated and detailed representations could be given, should the present model prove inadequate to interpret all experimental facts. Ti^{IV} in TS-1 maintains the strong affinity of soluble Ti^{IV} salts for H_2O_2 and in fact the addition of H_2O_2 gives rise to a strong yellow colour which can be attributed to the formation of surface titaniumperoxocompounds which can be in the hydrated or dehydrated form and which constitutes the actual oxidants.



Work carried out on Mo(VI) and W(VI) peroxocompounds (Amato *et al.*, 1986) has demonstrated that peroxocompounds can act as oxidants in stoichiometric epoxidations involving a nucleophilic attack of the substrate to the peroxidic oxygen: in the presence of excess H_2O_2 the peroxo compound is regenerated and this accounts for the catalytic nature of the reaction. It seems reasonable to assume that a similar mechanism operates in the case of Ti(IV) peroxocompounds. The relevance of isolated Ti^{IV} and the connection with catalytic performances appears to hold also for the $\text{TiO}_2/\text{SiO}_2$ catalyst. In fact high epoxide selectivities are obtained when TiO_2 is distributed on high surface area SiO_2 and its concentration is limited to 2% (Sheldon, 1980). It is very likely that at this low concentration Ti^{IV} are isolated and surrounded by Si^{IV} . Furthermore, SiO_2 or TiO_2 alone, or physical mixtures of SiO_2 and TiO_2 or various metal titanates exhibit no significant activity. Similarly, supporting TiO_2 on

carriers different from SiO_2 like Al_2O_3 , MgO or ZrO_2 leads to catalysts whose activity is lower or nil. One piece of evidence seems very convincing: when the TiO_2 concentration on the catalyst is reduced from 4% to 0.4%, all other conditions being equal, an increase in epoxide selectivity is obtained. The only effect that a reduction in the concentration of TiO_2 can have is an increase in the degree of dispersion of each Ti^{IV} : chances for each Ti^{IV} of having Si^{IV} as near neighbours increase, as does the selectivity of the catalyst. The correlation between the isolated Ti^{IV} and selectivity of the catalyst in epoxidation could be due to the fact that on Ti^{IV} having other Ti^{IV} as near neighbours, a mechanism proceeding through a bimolecular interaction of surface peroxy species could be operating which would give rise to a high decomposition rate of H_2O_2 or hydroperoxides to O_2 . This mechanism could not operate on perfectly isolated Ti^{IV} .



Low decomposition of H_2O_2 (or hydroperoxides as well) means greater stability of titanium peroxy compound whose reduction can only be carried out by the organic substrate with increased yields of useful oxidized products. When the different results between TS-1 and $\text{TiO}_2/\text{SiO}_2$ in the hydroxylation of phenol are analyzed the existence of a “restricted transition state selectivity” must be assumed to explain the small amount of tars formed.

3.4 Three-phase Catalytic Reactions (Gas-Liquid-Solid)

In fine-chemical productions three-phase reaction systems are common for the hydrogenation and hydrogenolysis of different organic functional groups. Other reactions, such as heterogeneously catalyzed catalytic oxidations, hydrodesulfurizations, and reductive aminations are encountered less frequently.

The three phases present in this kind of reaction are a gas phase, containing, e.g., hydrogen or oxygen, a liquid phase, often consisting of a solvent, containing the

dissolved reactants, and the solid catalyst. Besides dissolving the reactants, the solvent also provides a liquid layer around the catalyst particles, which might help to:

- avoid deactivating deposits and thus ensure higher catalyst effectiveness;
- achieve better temperature control because of the higher heat capacity of liquids; and
- modify the active catalyst sites to promote or inhibit certain reactions.

Besides these positive effects there is, however, a disadvantage—an extra barrier is introduced between the gaseous reactants (e.g., hydrogen) and the catalyst (see Figure 3.3). Mass transfer of the gaseous reactant to the liquid phase is often, but not always, the limiting step.

The organic substrate is usually present at much higher concentrations than the hydrogen dissolved in the liquid; hydrogen is the ‘limiting’ reactant. Therefore, the rate of mass transfer of hydrogen is of predominant significance. As shown in Figure 3.3, a number of steps must occur before hydrogen can be converted to products. The major steps are: (i) mass transfer from the gas bubble to the liquid, (ii) mass transfer from the liquid to the external surface of the catalyst particle, and (iii) diffusion inside the pores of the catalyst particle, accompanied by chemical reaction.

Therefore, in the choice and design of three-phase reactors, not only must the intrinsic kinetics be considered, but also the mass-transfer characteristics. For example, it is useless to try and improve the reaction rate by using a more active catalyst or increasing the catalyst load, when the overall rate of reaction is determined by mass transfer from the gas bubbles to the liquid phase, i.e. when the latter is slow compared with the intrinsic rate of reaction. Instead, one should try to increase the gas-to-liquid mass transfer rate, for example by improving mixing conditions. When the diffusion in the interior of the catalyst particles is rate determining, not only are the rates often reduced but selectivities are also affected. In this circumstance one should consider using smaller catalyst particles to improve liquid-to-solid mass transfer. Egg-shell catalysts, in which the active catalyst species is located in the outer shell of the catalyst particle, might also be used to improve selectivity.

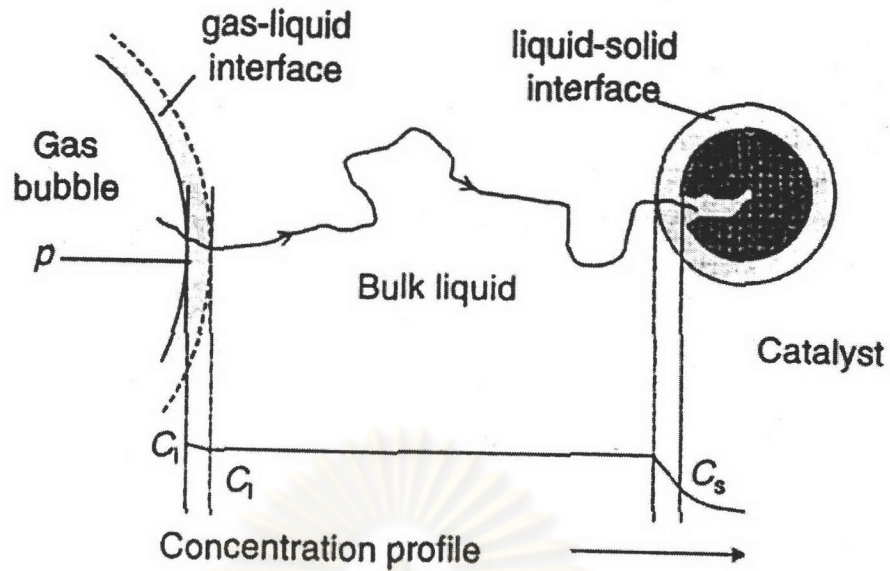


Figure 3.3 Mass transfer of hydrogen in gas/liquid/solid catalyst system; transport of H_2 limiting; $p = H_2$ pressure; $C = H_2$ concentration, C_i at interface, C_1 in bulk liquid, C_s at catalyst surface. (Sheldon and van Bekkum, 2001)

3.5 Periodic operation of catalytic reactors (Silveston *et al.*, 1995)

The terms periodic operation, cycling or cyclic operation, modulation and forcing or periodic forcing are used interchangeably, reflecting the wide range of terminology used in the current literature. All of these terms refer to an operation in which one or more inputs into a chemical reactor vary with time, but in such a way that each input 'state' is revisited after a time corresponding to the period. This mode of reactor operation is shown schematically in Figure 3.4. Here, two inputs, the volumetric flow rates of reactants 'A' and 'B', are switched periodically between two values so as to generate a chain of step-changes representing a square-wave variation of reactant concentrations in the reactor feed. In most of the systems studied in the laboratory, the flow rate variations are matched so that the space velocity in the reactor remains constant, but this is not a necessary condition. The figure typifies the system most frequently studied; however, other inputs may be varied, such as reactor temperature, flow rate, and flow direction.

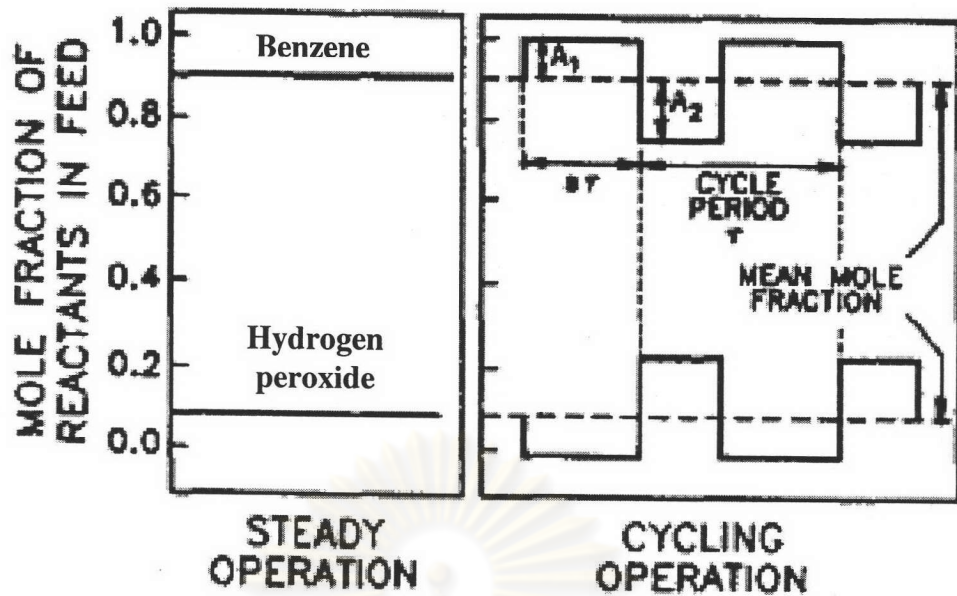


Figure 3.4 Comparison of steady state (left side) and periodic (right side) operation showing definition of the cycling variables: cycle period (frequency), τ , cycle split (duty fraction), s ; amplitudes, A_1 , A_2 . (adapted from Silveston *et al.*, 1995)

Figure 3.4 illustrates most of the variables that arise in periodic operation: period (τ) – the time between repetitions of a change in an input condition; split (s) – the duration of one part of cycle relative to the period; amplitude (A) – the change in the value of an input condition from its mean, and mean composition.

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