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CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Adsorption of Reactant on Adsorbent or Catalyst

Two types of adsorption phenomena, physisorption and chemisorption, have been recognized in principle for many years. Physisorption is caused by secondary attractive forces such as dipole-dipole interaction and induced dipoles and to similar to condensation of vapor molecules onto a liquid of the same composition. Chemisorption involved chemical bonding, is similar in character to a chemical reaction and involves transfer of electrons between adsorbent.

Frequently, two or three kinds of chemisorption have been observed between one adsorbent (solid) and one adsorbate (fluid), but it is doubtful that more than one is actually involved in the chemical reaction; other chemisorbed molecule may just "sit" on the catalyst. Chemisorption on pure metals is simpler than chemisorption on oxides; however, the behavior of the same metal when supported on a carrier, as in a commercial catalyst, may be significantly different. It is occasionally useful, especially in developing kinetic mechanisms, to distinguish ***nondissociative chemisorption*** in which the molecule adsorbs without fragmentation from ***dissociative chemisorption*** in which two or more fragments are formed, all of which remain momentarily adsorbed on the surface [5].

Propylene adsorbs on certain metal oxides by dissociation, splitting off a H atom to form a π-allyl complex with the surface, where the asterisk represents a surface site.

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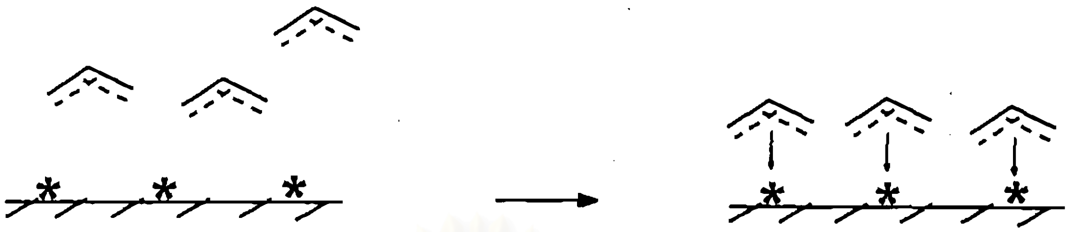

Hydrogen sulfide adsorbs on a metal site without dissociation, which may be symbolized as:

Polar substances are generally more strongly adsorbed than nonpolar substances, with the consequence that in hydrogenation reactions the product is usually least strongly adsorbed than the reactant.

Adsorption can also be affected by various specific interactions. Thus, molecule with lone-pair electrons or π-electrons can chemisorb without dissociation with rehybridization of molecular orbitals. On most metal, in general the strength of adsorption for some simple gases and vapors falls in the sequence:

$O_2 > C_2H_2 > C_2H_4 > CO > H_2 > CO_2 > N_2$

Carbonyl sulfide (COS) in which has 2 positions of bonding is also chemisorbed without dissociation, that may be symbolized as:

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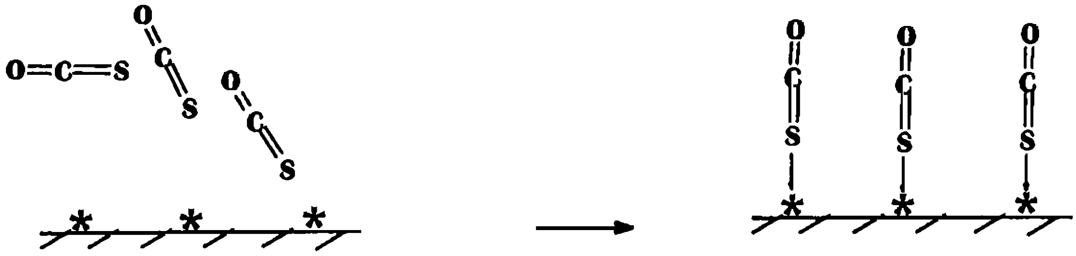

2.2 Kinetics of Adsorption of Reactant on Adsorbent or Catalyst

2.2.1 Empirical Correlations

For studies of homogeneous gas-phase reactions, an elementary ***unimolecular reaction*** has elementary steps are naturally written as below: [5]

$$A \longrightarrow B \tag{2.1}$$

$$A \longrightarrow B + C \tag{2.2}$$

Bimolecular reactions, which have a molecularity of two and are by for the most common type of elementary reaction, are those reactions which proceed as a result of collisions between two reactant molecules, free radicals or other species. The rate of an elementary reaction is given by,

$$A + B \longrightarrow C \tag{2.3}$$

$$\text{Rate, molecules reacted / (time) (volume)} = k\,C_A C_B$$
$$= Ae^{-Ea/RT} C_A C_B \tag{2.4}$$

By analogy a simple expression for the rate, r of heterogeneously catalyzed reaction between A and B is,

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$$(-r_A)\text{Rate, molecules reacted / (time) (area)} = k_0e^{-Ea/RT}f(C_AC_B) \qquad (2.5)$$

where k_0 is taken to be independent of temperature and surface area of catalyst. The function of the concentration which usually is easiest to use in correlating rate data, comprised of simple power function: C_AC_B , where ***a*** and ***b*** are empirically adjusted constants. Hence:

$$-r = k_0e^{-Ea/RT}C_A\,C_B \qquad (2.6)$$

2.2 Langmuir Hinshelwood Model

Five assumptions of the Langmuir adsorption isotherm are homogeneous surface (all sites identical), localized adsorption sites, at must one adsorbed species per site, constant heat of adsorption and equilibrium between surface species and gas phase [5].

Reaction is assumed to occur between adsorbed species on the catalyst. if a single reactant is decomposed the process may be assumed to be either unimolecular or bimolecular, depending upon the number of product molecular formed per reactant molecule and whether or not the products are adsorbed. The reaction is then ***bimolecular*** in the sense that it is proportional to the product of the concentration of adsorbed reactants and of empty sites [5].

The rate of adsorption depended upon three factors; rate of collision between gas molecules and surface that is directly proportional to pressure, number of unadsorbed sites as well as activation energy.

Case 2.1 Decomposition, product not adsorbed.

$$\text{A} \longrightarrow \text{product} \qquad (2.7)$$

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The reaction rate is taken to be proportional to the quantity of adsorbed a molecules. Then,

$$-r = k\theta_A \tag{2.8}$$

The value of θ_A, fraction of surface adsorb, is given by the Langmuir adsorption isotherm:

$$\theta_A = KP_A / 1 + KP_A \tag{2.9}$$

Combining these two equations,

$$-r = kKP_A / 1 + KP_A \tag{2.10}$$

If the system follows this model, the reaction rate should be first order at sufficiently low value of P_A. As P_A increases, the order of reaction should gradually drop and become zero order.

Case 2.2 Bimolecular reaction

$$\mathrm{A + B} \longrightarrow \mathrm{C} \tag{2.11}$$

Assumptions :

1. A, B, C all may be appreciably adsorbed
2. The reaction rate is proportional t the concentration of adsorbed A and adsorbed B.
3. No dissociation of A molecules occurs on adsorption.
4. Reverse reaction is negligible

The rate expression then becomes

$$-r = k\theta_A\theta_B \tag{2.12}$$

$$-r = k\,K_AK_BP_AP_B / (1+K_AP_A+K_BP_B+K_CP_C)^2 \tag{2.13}$$

2.2.3 Apparent Activation Energy

If the kinetic expression is of a complex form as Equation 2.8, the overall apparent activation energy as determined from the effect of temperature on reaction rate at constant reactant composition will change with temperature. An Arrhenius-type plot of ln rate versus 1/T will not be a straight line. For some simpler kinetic expression, the apparent activation energy will be independent of temperature, as in case 2.1 for low surface coverage. Then the kinetic expression reduces to:

$$-r = k_S K_A P_A \tag{2.14}$$

The experimentally adsorbed reaction rate constant k_{exp} equals $k_s K_A$, where k_s is the reaction rate constant for the surface reaction, assumed to follow the Arrhenius equation K_A is the adsorption equilibrium constant, which decreases exponentially with increased temperature by the factor e. Here is the heat of chemisorption, take to be independent of temperature. The effect of temperature upon the experimentally observed reaction rate constant for a rate expression at the type 1 (Equation 2.9) is given by:

$$k_{exp} = Ae\text{-}(Es\text{-}\lambda)/RT \tag{2.15}$$

The apparent activation energy E_a as calculated from a plot of $\ln k_{exp}$ versus $1/T$ equals $E_s - \lambda$. Since E_s and will normally both have positive value, (Adsorption process is almost always exothermic, in which case λ is a positive number). E_a will be less than the so called true activation energy for the surface process, E_s [5].

2.3 Kinetics in Continuous Flow Tube Reactor

In the dynamic mode, the reactants in the gaseous state flow through a bed of catalyst particles, a *continuous- flow* reactor. The ratio of the volumn flow-rate to the volumn of the bed determines the *space velocity*, which thus has the dimension of reciprocal time, while the reciprocal of the space velocity gives the contact time. In a dynamic reactor, conversion increases along the catalyst bed, and distance through the bed is thus equivalent to the time dimension in a static reactor. Once again, order of reaction are best obtained by altering the concentrations of reactants or products entering the catalyst bed [6].

For a constantly continuous flow tube reactor, fluid compositions will change in accordance with distance of flow. The mass balance is necessary to consider. The partial volume of catalyst or adsorbent in the reactor, dw. the mass balance give by,

[Flow rate of reactant (input)] = [Flow rate of reactant (output)] +
[Rate of reactant loss in chemical
reaction or rate of reaction]

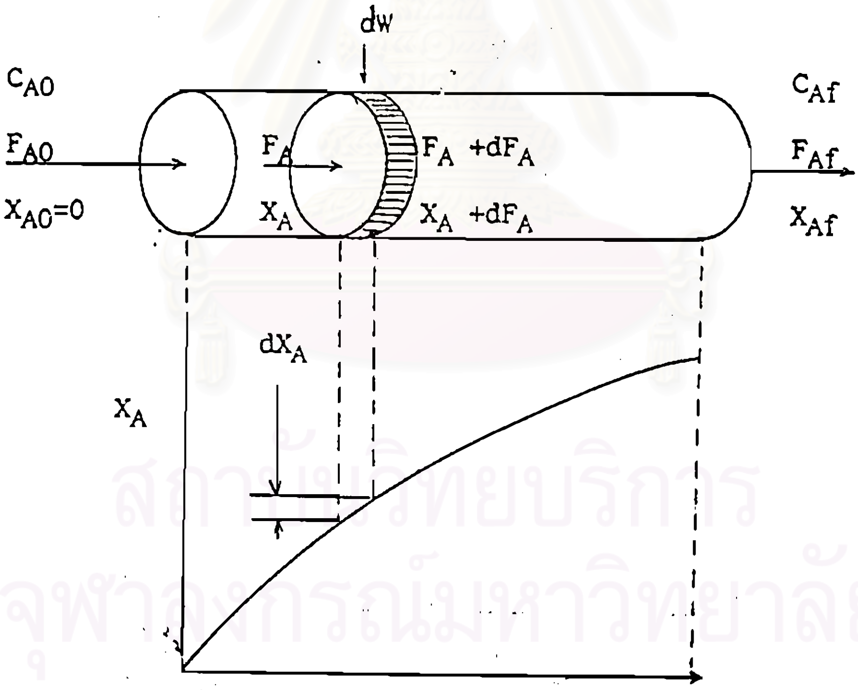

Figure 2.1 Symbol for continuous flow tube reactor [6].

where F_A is the input flow rate of A

$F_A + dF_A$ is the output flow rate of A

$(-r_A)dw$ is the rate of reaction

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$(-r_A)dw$ = moles of A reacted per weight of catalyst/adsorbent per second X weight of catalyst/adsorbent at dw

$$F_A = (F_A + dF_A) + (-r_A)dw \qquad (2.16)$$

From, $$dF_A = d[F_{A0}(1-X_A)] - F_{A0}dX_A \qquad (2.17)$$

Therefore, $$F_{A0}dX_A = (-r_A)dw \qquad (2.18)$$

If considering total amount of catalyst/adsorbent, the integration of Equation 2.13 is shown,

$$dw/F_{A0} = dX_A/(-r_A) \qquad (2.19)$$

$$W/F_{A0} = \tau/C_{A0} = dX_A/(-r_A) \qquad (2.20)$$

where τ is space time that is the time of A in on volume of reactor feeded to react at defined condition.

2.4 Determination of Kinetic Parameters

2.4.1 Chemical Reaction Rate

The rate law for bimolecular reaction of homogeneous reaction

$$A + B \longrightarrow C \qquad (2.21)$$

During reaction, a and b was converted gradually. Therefore, the concentration of A and B decrease while the concentration C increase

Rate and reaction rate at any time show in the term of variation of product concentration as variation of reactant concentration at any time

$$\text{rate of reaction} = d\,[C]/dt \qquad (2.22)$$

or

$$\text{rate of reaction} = -\,d\,[A]/dt = -\,d[B]/dt \qquad (2.23)$$

$$\text{rate of reaction}\ \#\ [A]\,[B] \qquad (2.24)$$

or

$$-\,d\,[A]/dt = -\,d[B]/dt = d[C]/dt = k\,[A]\,[B] \qquad (2.25)$$

Equation 2.19 called rate low or rate equation where as k is the specific reaction rate constant [7].

2.4.2 Determination of Order of Rection and Rate Constant

From unimolecular rection;

rate of reaction, $r = d\,[C]/dt$

$$r = k\,[C]^n \qquad (2.26)$$

$$\ln r = \ln k + n\,\ln\,[C] \qquad (2.27)$$

from Equation 2.21, the partial order of reaction with respect to [C] is represented to n ,or the slope of the plot of ln [C] versus ln r . Moreover the rate constant, k is y-intercept of this ralation.

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2.4.3 Activation Energy

The temperature effect is dependent upon the rate coefficienct or rate constant and it can be derived that an activation energy, Ea from the Arrhenius equation :

$$k_a = k_{a\,0} \exp (-E_a / RT) \quad (2.28)$$

and

$$k_d = k_{d\,0} \exp (-E_d / RT) \quad (2.29)$$

from which is obtained :

$$b \;=\; b_0 \exp ([- E_a - E_d] / RT) \quad (2.30)$$

It modifies the position of the adsorption equilibrium (b) or K in Langmuir Model, with variations of this coefficient having the same significant as an equilibrium constant and related to the temperature by the classic equation.

The situation that might be observed if a reaction of this kind were studied over a wide range of temperature is shown in Figure 2.2. The broken line indicates the rates that would have been observed had the surface coverage not fallen below unity. It is important to distinguish this cause of apparent change in activation energy from a quite different cause that has a very similar affect.

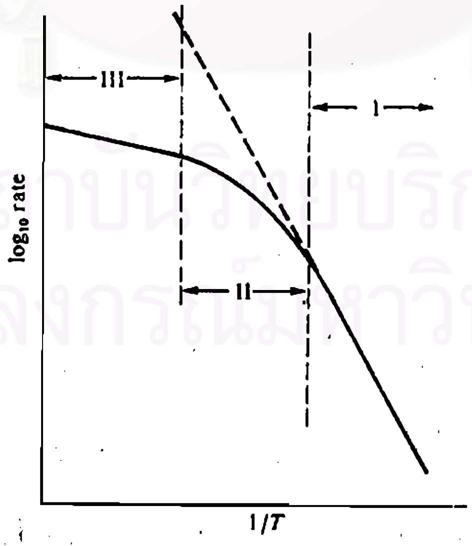

Figure 2.2 Arrhenius plot for a catalysed reaction [8].

For homogeneous reaction, the rate constant can be also determine from Arrhenius equation

$$k \quad = \quad k.e^{(-Ea/RT)} \qquad (2.30)$$

The plot of 1/T and ln k, the slope is ($-E_a/R$) and k_0 calculated from y- intercept.

2.5 Mechanisms of Heterogenous Catalysis

The sequence of events in a surface- catalyzed reaction comprises (1)(external mass trasfer) of reactants to the surface (usually considered to be fast) ;(2) diffusion into pore ; (3) adsorption of the reactants on the surface (slow if activated) ; (4) surface diffusion of reactants to active sites (if the adsorption is mobile); (5) reaction of the adsorbed species (often rate determining) ; (6) desorption of the reaction product (often slow) ; and (7)diffusion of the products away from the surface and mass transfer from external surface to bulk fluid phase.

Three of these steps are considered part of the catalytic reaction mechanism. They are adsorption, surface reaction and adsorption.

Process 1 and 6 may be rate determining where one is dealing with a porous catalyst. The model most often used to describe catalytic reaction is the Langmuir - Hinshelwood model [10].

2.6 Diffusional Limitations

There are two type of transports within porous catalyst or adsorbent particles, i.e., external diffusion and internal diffusion of which detecting limitation may be considered both analytical solution and graphical solution.

2.6.1 Diffusional Limitation Inside the Granule

If r is the reaction rate on the catalyst granule, an effectiveness factor, η is defined as the ratio of the observed rate of reaction, r, to the rate r^*, that would have been obtained without limitations by intragranular diffusion. In the simple case of an irreversible ; isothermal, apparently first order reaction taking place in gaseous phase on a granule of spherical catalyst, the expression η, takes the following form:

$$\eta_l = r_l / r_l^* = (3/\phi_1).[(1/\tanh\phi_1) - (1/\phi_1)] \qquad (2.32)$$

where ϕ_l is a dimemsionless number, called the Thiele module, and a measure of the reaction rate relative to the rate of diffusion, as represented in the following expression :

$$\phi_l = (d_p/2).(\surd k_i \rho_g S.C/\mathcal{D}_e C) = (d_p/2).(\surd k_i \rho_g S/\mathcal{D}_e C) \qquad (2.33)$$

k_i = constant for the intrinsic rate,

d_p = diameter of the spherical granule of volume v,

ρ_g = density of the spherical granule,

S = specific surface of the granule

$\mathcal{D}_e$ = coefficient of effective diffusion of the reactant in the porous

Figure 2.1 give the variation of η_l as a function of ϕ_l, Low valves of ϕ_l define an area where the reaction is limiting, whereas high valves define the area where diffusion is limiting . The plot can be devided into three ranges of ϕ_l , according to whether the chemical reaction limits (range A) or diffusion limite (range C), or both chemistry and diffusion effect the rate (range B) [8].

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2.6.2 Diffusional Limitations Outside the Granule

The expressions of the apparent rate are written as a function of concentration, C_s, and temperature, T_s, at the external surface of the granule ; and in the absence of external diffusion limitations, the valves of C_s and T_s are equal to C_h and T_h of the homogeneous phase, and consequently able to be measured. However, if there are extragranular limitations, it is necessary to cross the limiting layer and express of C_s and T_s as a function of C_h and T_h.

If $\mathcal{A}_s$ represents the external surface of catalyst contained in a unit of volume of a catalytic bed, the rate of reaction (r) can be written for that unit of volumn as equal to the flow of reactant traversing $\mathcal{A}_s$ Accordingly, for a isothermal reaction the first order, ther is the follewing series of equalities:

$$r = [\,C_h/[(\,1/k_s\mathcal{A}_s) + (\,1/\,\eta_l\,k_i S\rho_r)] = C_h/[\,(1/\,k_s\mathcal{A}_s) + (\,1/k_c)] \qquad (2.34)$$

where $k_c = \eta_l\,k_i\,S\rho_r$ is the apparent rate constant related to the unit reacting volume and determined in the absence of extragranular diffusional limitations.

If $k\mathcal{A}_s >> k_c$, the absence of extragranular diffusion are negligible ; and the following equations evolve for the apparent rate:

$$r = k_c C_h = \eta_l\,k_i S\rho_r C_h \qquad \text{(per unit volume of catalytic bed)}$$
$$V = r/\rho_r = \eta_l\,k_i S C_h \qquad \text{(per unit weight)}$$

If $k_s\mathcal{A}_s << k_c$, the transfer phenomena of the laminary film are limiting in stationary beds; and the apparent rate of reaction is represented by the following expresions:

$$r = k_s\,\mathcal{A}_s C_h \qquad (2.35)$$

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2.6.3. Detecting a Limitation in External Transfer

It is always possible to detect the intervention of internal or external diffusional limitation, either appoximately by menes of calculation or more definitely by means of some rather simple experiments

The gradients of extragranular diffusion can be estimated by calculation. Unfortunately, this type of correlation based on dimensionless numbers is generally reliable only for valves of Reynold's number over 40; and such valves are rarely attained in the laboratory reactors. Thus, it is preferable to detect external diffusional limitations through experiment.

Two types of test deserve attention, both consisting of varying the mass flow, G, of reacting gas in a straight section of catalytic bed in which the diameter of the catalytic pellets (on which the internal transfer depend) is uniform. By varying G, the linear rate, u, of the reacting gas of density, ρ, is modified since $G = u\rho$; and two tests can be applied as follows :

(1) In a given reactor section with changing flow rates to provide a constant contact time, and consequently a constant space velocity (LHSV= $1 / \theta$ volume of reactant per volme of catalyst per unit time), the quantity of catalyst is changed from one run to the next (Figure 2.2a). Then, if the conversion $4C_h$ does not vary as the mass flow, G, changes, it can be concluded that the apparent rate is not limited by the external transfers.

(2) In a given reactor section two series of tests are run (Figure 2.2b),firston a catalytic bed of volume V, and second on a bed of volume $5V$. . In each series, contact time, θ, is varied and consequently,G, and the two curves are traced for conversion, vs. θ; if the two curves match, there is no external diffusional limitation.

Finally, that if an external diffusion limitation is suspected, the apparent energy of activation for the reaction should be very low, less than 5 kcal. mol, and can be determined.

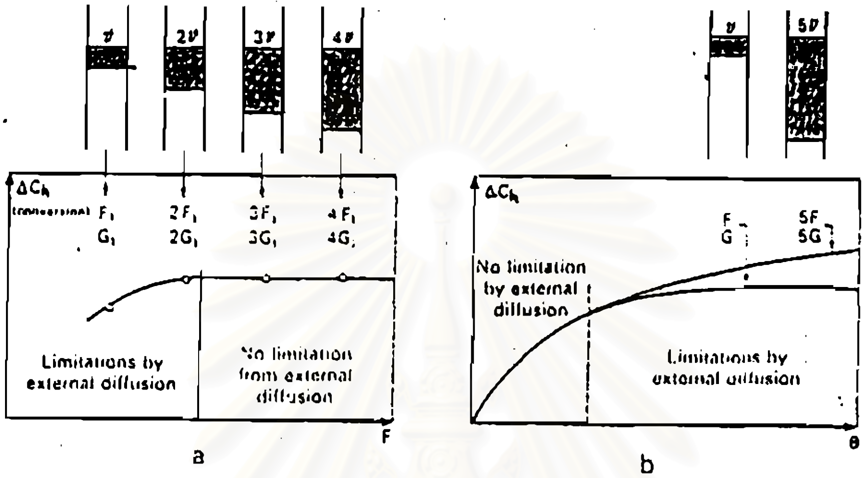

Figure 2.3 Two tests to indicate if a reation is limited by external diffusion [10].

2.6.4 Detecting a Limitation in Internal Transfer

Consequently η depend on unknown kinetic variable that are procisely those being sought : the order of the catalytic chemical reaction, the intrinsic rate constant and the energy of activation for any reaction involving heat.

The procedure for getting around this difficulty has been to introduce an experimental Thiele module that is dimentionless and valid for any order of reaction :

$$\Phi = \eta\phi^2 = (d_p^2 \rho_g V/(4\mathcal{D}_e C_h) \tag{2.36}$$

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where all the terms are accessible to measurement from the rate per gram of catalyst, V, which is experimentally determined. Nomographs have been constructed for determining η as a function of this modified .Thiele module (Ref. [3]); these are similar to Figure 2.3 and take into account the heat of reaction and the energy of activation. Figure 2.17 shows one of these nomographs for a spherical catalyst.

If $\Phi = \eta\phi^2 \ll 1$, then no diffusion limition .

By graphical solution maintain all operating variable (volumetric gas flow, F; mass velocity, G ; contact time, θ ; temperature, T ; inlet gas composition, and catalyst volume, V ;) as the particle size of the catalyst are progessively varied, as d_p, $d_p/2$, $d_p/3$ and $d_p/4$. Then plot conversion against particle size; and if the conversion varies, internal diffusion is limiting, where as a constant conversion indicates limitation of reaction kinetic only.

The most uncompleted experiment is considered by calculation of the Weisz-Prater criterion, if

$$\frac{(\text{rate}) . (V_p/S_{p,\text{ext}})^2}{\mathcal{D}_e . Cg} > 1 \qquad (2.37)$$

Then pore diffusion resistance appears significant.

Where rate = Rate of reaction interested

Vp = Total pore volume

Sp,ext = External surface area

$\mathcal{D}_e$ = Coefficient of effective diffusion of the reactant in the pores.

Cg = Concentration gradient

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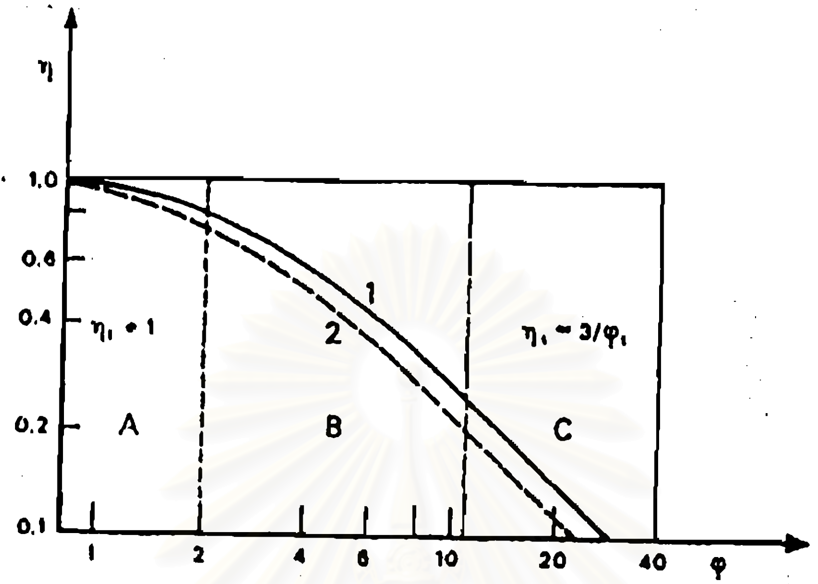

Figure 2.4 Variation of the catalytic effectiveness factor, η, as a funtion of the dimensionless Thiele moduule, ϕ, for first order reactions (curve 1) and second order reactions (curve 2) [10].

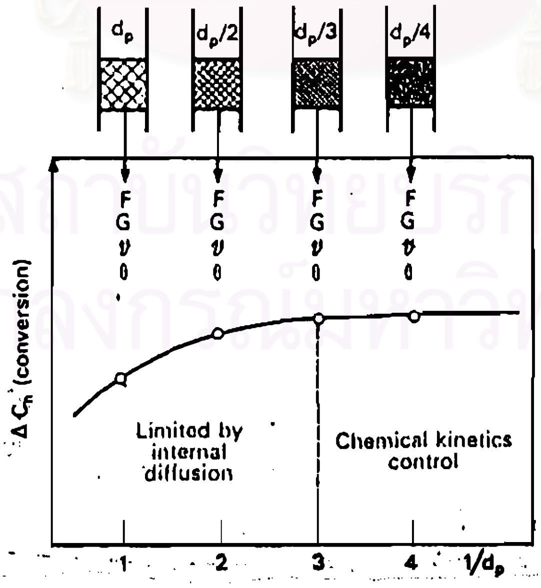

Figure 2.5 Experiment to find out whether reaction kinetics or internal diffusion limit a conversion [10].

2.7 Literature Review

The sulfur removal from liquid or gas hydrocarbons has been developed periodically by various techniques such as desulfurization, hydrodesulfurization, adsorption onto metal-supported catalysts or selective adsorbents as well as absorption into some proper liquid chemicals.

Wakker, J. P., et al, [11] studied about a process developed to remove H_2S and COS at high temperatures (675 - 1075 K) from fuel gases produced by a coal gasification plant. The process uses MnO or FeO on gamma - Al_2O_3 acceptors which can be regenerated after sulfidation with can be regenerated after sulfidation with a gas containing steam. The acceptors should be used in a fixed bed or moving bed reactor. Experiments are carried out in a laboratory setup to determine these influences. After an initial deactivation the acceptors can be used over 400 sulfidation regeneration cycles. Water adversely affects the capacity, whereas CO favors the capacity due to the water - gas shift reaction. Trace compounds can influence the capacity negatively as, e.g. HCl, whereas hydrocarbons do not influence acceptor performance. An optimum between capacity and stability is reached at a operating temperature of 875 K. An increasing pressure does not influence the sulfidation reaction, but the water - gas shift reaction may be positively influenced.

Vannisselrooy-PFMT and Lagas, J.A. [12] used a new selective oxidation catalyst to reduce SO_2 emission in sulfur recovery process. The recovery of sulphur in a two or three stage conventional Claus plant is limited due to the thermodynamics of the Claus equilibrium reaction. Typical Claus plant and 95 - 98 % for a three stage reactor plant. As SO_2 emission limitations are being tightened, higher recoveries are needed to meet the new regulations. SUPERCLAUS, a newly developed sulphur recovery process, increases the sulphur recovery to more than 99 % and reduces the SO_2 emission by more than 50 %

SUPERCLAUS is based on bulk sulphur removal in a conventional Claus section, followed by selective oxidation of the remaining H_2S by O_2 to elemental sulphur. The selective oxidation of H_2S us achieved by means of a newly developed catalyst. This catalyst does not promote the elemental sulphur formed. The new catalyst is insensitive to high water vapor concentrations and excess oxygen, It is extremely selective for the oxidation of H_2S Other compounds in the process gas, such as COS, CS_2, and CO are not oxidized.

The catalytically active material is a mixture of iron and chromium oxides on an alpha-alumina support.This is a low surface area, wide pore material.The selectivity for the formation of sulphur is achieved by kinetic control of the reaction of sulphur is achieved by kinetic control of the reaction sequence : $H_2S \longrightarrow S \longrightarrow SO_2$. The SUPERCLAUS process is a continuous one, with no waste streams, it has a low utility consumption, produces bright yellow sulphur and can easily be incorporated in new as well as in existing claus plants.

As a result, the carbonyl sulfide is not oxidized in sulfur recovery unit . It is therefore required COS removal unit before the sulfur recovery process.

The study of sulfur cycle of each environment was successfully monitored carbonyl sulfide in atmosphere that was described by Protoschillkrebs, G. and Kesselmeier, J. [13] that is the enzymatic pathways for the consumption of COS by Higher - Plants. Carbonyl sulfide COS is an important trace gas of the atmosphere. Considerable uncertainties remain concerning the global sinks of COS. Vegetation is believed to be an unquantified sink in the global cycle of COS. It was investigated whether there is an enzymological background for the consumption of COS by higher plants in analogy to CO_2. Photomentric measurements demonstrated that all enzymes involved in CO_2 assimilation by higher plants can also metabolize COS. The key enzyme for COS metabolism in higher plants is carbonic anhydrase, an enzyme which probably directly splits COS into CO_2 and H_2S. Such a pathway would explain the observed deposition of COS to vegetation.

Even though this study is not concerned about COS contaminated in hydrocarbons; nevertheless, COS removal using biochemical reaction may become useful in petrochemical plant.

The study of solubility and diffiusivity data for the absorption of COS, CO_2, and N_2O in amine solutions is the importance data for COS removal by absorption technique that was achieved by Littel, R. J. et al [14]. Absorption data for COS and N_2O in aqueous solutions of N-methyldiethanolamine (MDEA), ethylene glycol, and sulfolane (tetrahudrothiophene 1,1 - dioxied) at 298 K and solubility data for COS in water at temperatures ranging from 298 to 338 K are presented. Also density, viscosity, N_2O solubility, and N_2O diffusivity data are reported for a wide range of aqueous alkanolamine, solutions, aqueous mixtures of aklanolamines, and solutions of MDEA in water/ethanol. It is shown that an analogy betreen COS and N_20 with respect to gas solubility in aqueous solutions of ethylene glycol and sulfolane holds up to about 25 mass % This seems to justify, for engineering purposes, the application of this analogy for the estimation of COS solubilities in diluted aqueous amine solutions. Direct verification of a COS - N_2O analogy was provided by absorption of N_2O and COS into aqueous MDEA solutions in a laminar film reactor .

Littel, R.J.,. et al [2] studied of kinetics of COS with primary and secondary - amines in aqueous - solutions at temperature 283-333 K by means of the stirred cell technique. Kinetic experiments were carried out with MEA, DGA, DEA, DIPA, MMEA, AMP, and MOR .All kinetic experiments could be described by a zwitterion reaction mechanism similar to the mechanism proposed by Caplow (1968) for the reaction between $C0_2$ and secondary amines :

$$COS + R_2NH \longleftrightarrow R_2NH^+COS^-$$

$$R_2NH^+COS^- + B \longleftrightarrow R_2NCOS^- + BH^+$$

Analysis of concentrated amine solutions at high COS concentrations by various analytical techniques confirmed the conclusions form the kinetic experiments. For all amines except for MEA, the overall reaction rate was found to be determined entirely by the zwitterion deprotonation rate.

The study of kinetics of absorption COS using amine solution should be required the new identification of products resulting from carbonyl sulfide-induced degradation of diethanolamine. Dawodu, O. F. and Meisen, A. [15] studied the degradation of aqueous diethanolamine (DEA) solutions due to carbonyl sulphide (COS) by contacting the solutions (10-40 wt. %) in a well stirred, 600-ml stainless steel autoclave with COS - nitrogen mixtures at temperatures ranging from 120 to 180 °C. Combined gas chromatography mass spectrometry, melting point

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determinations and elemental and infrared analyses were used to identify most of the major reaction products, i.e., monoethanalamine, ethylamino- ethanol, ethyldiethanolamine, hydroxyethylacetamide, hydroxy-ethylpiperazine, ethanethioic acid S - hydroxyethyl

aminomethyl ester, bis (hydroxyethyl) ethylenediamine, bis (hydroxyethyl) piperazine, hydroxyethyloxazolidone, hydroxyethyloxazolidone, tris(hydroxyethy) ethylenediamine, bis (hydroxyethyl) imidazolidone, acetaldehyde, acetone, butanone, acetic acid, ethanol, diethyl disulphide, dithiane and pyridines. In addition, a solid product containing sulphur was formed. The practical implications of the studies for gas plant operators are discussed .

Bhatt, B. L. et al [16] used Calgon FCA as adsorbent for COS removal and used Cu/Zn catalyst for H_2S removal from coal - gas for methanol synthesis.

As an integral part of the liquid - phase methanol (MeOH) process development program, the present study evaluated adsorptive schemes to remove traces of catalyst poisons such as iron carbonyl, carbonyl sulfide, and hydrogen sulfide from coal gas on a pilot scale. Tests were conducted with coal gas from the Cool Water gasification plant at Daggett, California. Iron carbonyl. carbonyl sulfide, and hydrogen sulfide were effectively removed from the coal gas. The adsorption capacities of linde H - Y zeolite and Calgon BPLcarbon for Fe $(CO)_5$ compared well with previous bench - scale results at similar CO_2 partial pressure. Adsorption of COS by Calgon FCA carbon appeared to be chemical and non-regenerable by thermal treatment in nitrogen. A Cu/Zn catalyst very effectively. With the adsorption system on - line, a methanol catalyst showed stable activity during 120 h of operation, demonstrating the feasibility of adsorptive removal of trace catalyst poisons from the synthesis gas. Mass transfer coefficients were estimated for Fe $(CO)_5$ and COS removal which can be directly used for design and scale up.

Most COS removal was usually converted to hydrogen sulfide or sulfurdioxide; hence, the their removals should be concerned couple to COS removal.

Jing Jiang Yu [1] studied the reduction of sulfur dioxide by methane to elemental sulfur over supported cobalt catalysts-cobalt oxides supported on several types of carriers (silica, molecular sieves 5A and 13X, and γ-alumina) were evaluated for the reduction of sulfur dioxide by methane to elemental sulfur. Results showed that γ-alumina is the most effective carrier and that, with a molar ratio of 2 to 1 of sulfur dioxide to methane in a feed gas, the sulfur yield reached a maximum value of 87.5% at a space velocity of 5000 h^{-1} and a temperature of 840° C. X-ray diffraction results revealed that mixtures of cobalt oxide and cobalt sulfide components were observed. The effects of temperature, space velocity, and molar ratio of sulfur dioxide to methane in the feed on the activity of the cobalt catalyst supported on γ- alumina were investigated. The effect of feed gas was performed to determine the influence of the internal diffusion .

To some extent, carbonyl sulfide is not as reactive as its companion in hydrocarbons, hydrogen sulfide. Carbonyl sulfide reacts slowly with the aqueous alkalimetal hydroxides and is only slowly hydrolyzed to carbondioxides and hydrogen sulfide. This relatively unreactive characteristic of carbonyl sulfide makes it extremely difficult to remove from petroleum streams by conventional desulfurization techniques.

The presence of COS, even at very low concentration, oftentimes renders olefins valueless for many purposes. For example, high purity olefins are required for the satisfactory production of many polymeric products especially those useful as plastics, including polymers of ethylene, propylene and the like. As a result, there has been a real need to improve techniques for removing COS from hydrocarbons, especially those used for polymer production.

Some of the known methods for removing carbonoxysulfide (COS) from hydrocarbon streams include the following. In British Patent Specification No. 1,142,339, published Feb. 5, 1969, the inventors teach a process for the removal of COS from gas mixtures in which unsaturated compounds such as propyne and propadiene are present, comprising passing said mixtures in liquid phase at atmospheric or superatmospheric pressures over a substance which contains one or more of the oxides of cadmium, zinc, nickel or cobalt supported on a carrier. It is stated that this process reduces the COS concentration to less than 1 ppm.

Molayem, B., and Garrett, D. [17] described to a method and composition for catalytically converting unburned hydrocarbons and carbonmonoxide to carbondioxide and reducing nitrogenoxides to nitrogen during or subsequent to the combustion of fossil while adsorbing sulfuroxides. The method and composition of the invention are also useful for treating reducing gases containing one or more of hydrogen sulfide, ammonia, and carbonyl sulfide to reduce these gaseous components to non-polluting components such as nitrogen. and water while adsorbing sulfur so that it can be removed from the system. The method and composition of the invention are especially characterized by their use to remove polluting gaseous component form fossil fuels during combustion or subsequent to combustion or from reducing gases and in various stages as long as the catalyst adsorbent system of the invention is brought into contact with the gaseous contaminants being removed.

Nozue, I. ,Fujli . S.,and Hanada, M. [18] studied a catalyst which comprises titanium oxide reinforcing material and oxides of one or more metals selected from Group IA, Group IIA, GroupIIB and Group IVB of the periodic table. The weight of said oxides corresponding to at least 0.5 wt.% of the weight of a final catalyst exhibits an excellent activity in hydrolysis of carbonyl sulfide. said catalytic activity has no possibility of deterioration even in the presence of hydrogen sulfide and /or carbon dioxide coexist with feed gas.

Lui, P. K. T. [3] described an adsorption process for removal of carbonyl sulfide (COS) from a liquid hydrocabon which comprises providing an activated alumina adsorbent which has preferaby impregnated with a compound selected from the class consisting of one or more alkali metal compounds, one or more alkaline earth metal compounds, or a mixture of such compounds; passing a liquid hydrocarbon containing COS through the activated alumina at a flow rate sufficient to adsorb enough COS in the liquid hydrocarbon to lower the COS content of the liquid hydrocarbon to less than 1 ppm; monitoring the effluent liquid hydrocarbon to determine when the capacity of the adsorbent to adsorb COS has been reached; and then regenerating the activated alumina adsorbent by passing the gas, heated to the temperature of from about 150 °C to about 300 °C ., through the adsorbent for a

Debras, L.G., et al, [19] described a process for removing carbonyl sulfide from a liquid hydrocabon feedstocks, that comprising the steps of (a) passing hydrocarbon feedstocks over an adsorbent material comprising nickel deposited on a support material wherein nickel is present as both nickel oxide and metallic nickel and wherein the adsorbent material has been conditioned by passing an inert gas flow containing a minor amount of propylene; and (b) recovering a liquid hydrocarbon stream having substantially reduced carbonyl sulfide content.

Lahousse, C. , et al . [20] was studied about acidic and basic properties of Ti-Al_2O_3 mixed catalyst for propan-2-ol dehydration and carbonyl sulfide hydrolysis. As for basicity, the good agreement between COS hydrolysis and CO_2 adsorption points out the hydrxy basicity of TiO_2-Al_2O_3 mixed oxides.

Radel, R. J. [21] described herein discloses the use of silica gel as the catalyst for the efficient oxidation of hydrogen sulfide to elemental sulfur by nitric oxide. Concomitantly, this catalyst also promotes the hydrolysis of carbonyl sulfide to hydrogen sulfide and cabon dioxide which then can be oxidized further by nitric oxide in the same reactor to produce elemental sulfur.