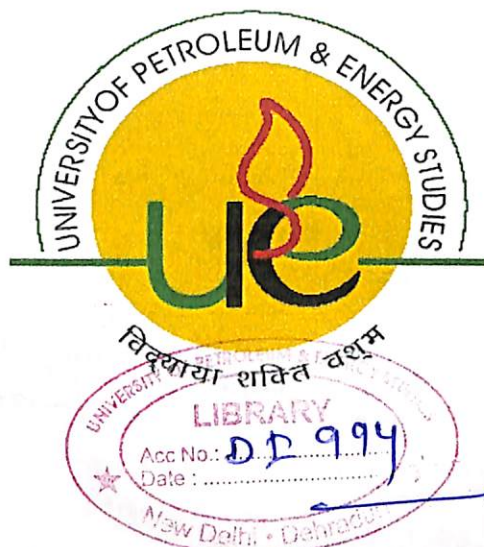


**METAL DISPERSION AND POROSITY ON ACTIVE  
SITES FOR REFORMING OF HYDROCARBONS  
- A COMPARISON**

By  
**ABHIMANYU SINGH**  
&  
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**College of Engineering**  
**University of Petroleum & Energy Studies**  
**Dehradun**  
**May, 2009**

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FOR REFORMING OF HYDROCARBONS  
- A COMPARISON**

**A dissertation submitted in partial fulfillment of the requirements for the Degree of  
Bachelor of Technology**

**Under the guidance of  
Dr. R. P. BADONI  
(Project Guide & Professor COE)  
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Dehradun  
May, 2009**



## UNIVERSITY OF PETROLEUM & ENERGY STUDIES

### CERTIFICATE

This is to certify that the work contained in this thesis titled “METAL DISPERSION AND POROSITY ON ACTIVE SITES FOR REFORMING OF HYDROCARBONS –A COMPARISON” has been carried out by *Abhimanyu Singh and Jitesh Kumar* under my supervision and has not been submitted elsewhere for a degree.

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## Chapter 1

### INTRODUCTION

Basically catalysts are considered as chemical compounds capable of directing and accelerating thermodynamically feasible reactions while remaining unaltered at the end of the reaction, whose thermodynamic equilibrium they consequently cannot change.

Catalysis is homogeneous when the catalyst is soluble in the reaction medium and heterogeneous if the catalyst exists in a phase distinctly different from the phase of reaction medium. In most instances of heterogeneous catalysis, the catalyst is a solid that is brought in contact with gas or liquid reactants to bring about a transformation.

#### 1.1 MECHANISM OF CONTACT CATALYSIS

The chemical reaction of heterogeneous catalysis occurs between compounds adsorbed on the surface of solid catalyst. The entire cycle comprises of five consecutive steps, each of which can have more or less influence on the overall reaction rate, depending on its relation to the others. The steps are

1. Diffusion of reacting substance over the catalyst particle.
2. Adsorption of reacting substance on catalyst.
3. Interaction of reacting substances on the surface of the catalyst.
4. Desorption of the reaction products from the catalyst particle.
5. Diffusion of the reaction products into the surrounding medium.

Steps 1 and 5 correspond to physical processes of mass transfer to and from the catalyst particles into and out of its pores. Steps 2, 3 and 4 involve chemical phenomena that comprise the chemical transformation.

#### STEP1: DIFFUSION OF REACTANT OVER THE CATALYST PARTICLE

Surface and not mass affects the activity of solid catalyst; the specific activity of a unit weight of catalyst is a direct function of its intrinsic activity and of its specific surface, with the intrinsic activity measured as the activity per unit surface of catalyst and the specific surface measured as the surface per unit weight.

However high intrinsic activity and high specific surface area are not in themselves enough; the reactants must be able to reach the active surface quickly and the products to quickly leave it, in order for the active surface to achieve its maximum potential. These movements of the molecules through the fluid surrounding the solid catalyst is governed by laws of diffusion, i.e., by Fick's law. The physical process of diffusion tends to equalize concentrations. Consequently a rapid disappearance of reactants undergoing transformation on the catalyst surface brings about a concentration gradient. Diffusion acts to equalize that gradient through a flow of molecules



towards the surface, and this flow of molecules can be calculated according to laws of diffusion. Furthermore, catalyst particles have internal pores that are accessible to the reactant molecule so that diffusion proceeds in two steps, external and internal.

### **STEP2: CHEMISORPTION OF REACTING SUBSTANCES**

As the inward diffusing reactants arrive in the neighborhood of the catalyst surface, they are chemisorbed, i.e. they react with the surface to give birth to new chemical species, which react with each other according to the mechanisms that are energetically more favorable than the chemistry of the same reaction induced by heat alone.

This step itself is a complex process and takes place in two steps, physical adsorption and chemical adsorption. First the reactant molecule undergo physical adsorption in which Vander Waal forces of attraction bind the molecule to the surface of that catalyst. This physical adsorption is characterized by both low heat of adsorption and reversibility, so that merely heating or lowering pressure will cause the adsorbed molecules to be liberated. Physical adsorption exhibits little selectivity beyond the tendency of molecules with higher boiling points to adsorb more readily on the surfaces of all solids. Thus physical adsorption makes only one contribution to catalytic action: it reduces the energy of activation of the subsequent chemical adsorption.

By contrast chemisorption exhibits the same characteristics as a true reaction, it brings about the formation of covalent bonds of the same kind that hold together the atom of a molecule, except that the chemisorption bond exists between solid surface and the adsorbed molecule. Like chemical reaction chemisorption is subject to laws of thermodynamics and kinetics. The nature of molecule adsorbed from the surrounding field causes chemisorption in two different manners dissociative and associative. Saturated molecules tend to be adsorbed in dissociative manner with molecules cleaving into radicals or ions that have free valences of the adsorbing surface. Unsaturated molecules tend to be adsorbed in the associative manner by opening the double bond and forming two new covalent bonds.

Chemisorption is an exothermic process with the heat of adsorption directly proportional to the adsorptive force i.e. to the stability of bonds formed between adsorbed molecule and the surface of solid. This adsorptive force or stability plays an important role in predicting the activity of various minerals in the catalysis of given reaction.

### **STEP3: TRANSFORMATION OF ADSORBED SPECIES**

The chemisorbed complex of atoms and radicals formed from the original molecules does not remain frozen in the bi-dimensional adsorbed layer; if the temperatures are high enough it in turn becomes active and acquires greater mobility over the solid surface, and the subsequent chemical reaction proceed from that. However, it is not possible to identify the complicated mechanism



involved in the rearrangement of the surface complex for interaction of the adsorbed molecule, except in the case of some simple reactions such as hydrogenation of ethylene.

#### **STEP4: DESORPTION OF PRODUCTS**

The reaction products have not been much studied and we limit ourselves to three observations:

1. This step is reverse of adsorption process, and it therefore follows the same laws.
2. The reaction products cannot be too strongly adsorbed on the surface of catalyst, or they will prevent the reactants from reaching the surface thus play the role of catalyst poison.
3. When the desired product is an intermediate product, it should be desorbed rapidly in order to avoid degradation.

#### **STEP5: DIFFUSION OF REACTANT PRODUCT INTO THE SURROUNDING**

The diffusion is similar to the one described in step1.

### **1.2 PROPERTIES AND CHARACTERISTICS OF INDUSTRIAL CATALYST**

In addition to fundamental properties that come from the very definition of a catalyst i.e. activity, selectivity and stability industrial application requires that a catalyst should be regenerable, mechanically and thermally stable, economical, and possess suitable morphological characteristics.

**1.2.1. ACTIVITY:** A high activity will be reflected either in high productivity from relatively small reactors and catalyst volumes or mild operating conditions, particularly temperature that enhances the selectivity and stability if thermodynamics is more favorable.

**1.2.2. SELECTIVITY:** high selectivity produces high yields of a desired product while suppressing undesirable competitive and consecutive reactions. This means the texture of catalyst particularly pore volume and pore distribution should be improved towards reducing limitations by internal diffusion, which in case of consecutive reaction rapidly reduces selectivity.

**1.2.3 STABILITY:** a catalyst with good stability will change only very slowly over the course of time under conditions of use and regeneration. It is only in theory that a catalyst remains unaltered during the reaction. In actual practice it is far from ideal. Some of the things that lead to progressive loss of activity or selectivity mechanical strength are as follows:

- Coke forms on some catalyst through the intervention of parasitic reactions of polymerization, cyclization.
- Reactants, products or poison may attack active agents or supports.
- Volatile agents may be lost during the reaction for example chlorine may be lost during reforming.



- The crystals of a deposited metal may become enlarged or regrouped. A change in the crystalline structure of the support can cause a loss of mechanical strength.
- Progressive adsorption of trace poison in the feed or products may reduce activity. It can be pointed that industrial feedstocks are rarely pure products, but mixtures containing portion of impurities that must sometimes be eliminated beforehand so that the catalyst can be used.

1.2.4. **MORPHOLOGY:** the external morphological characteristics of a catalyst, that is its form and grain size, must be suited to the corresponding process. For moving bed and fluidized bed reactors spherical form is recommended for reducing problems of attrition and abrasion. In a fluid bed, a spherical powder is preferred for limiting attrition, and its grains should have well determined size distributions for obtaining good fluidization. In a fixed bed, beads, rings, pellets, extrudates or flakes can be used; but their form and dimension will have an influence on the pressure drop through the bed. This for equivalent diameter, catalysts can be classified according to the relative pressure drops the cause as follows

Rings < beads < pellets < extrudates < crushed

This pressure drop must be high enough to ensure even distribution of the reaction fluid across the catalytic bed, but it must not be too high as to cause an increase in the cost of compressing and recycling any gases.

- 1.2.5. **MECHANICAL STRENGTH:** The mechanical strength of a catalyst is demonstrated by its resistance to crushing, which enables the catalyst to pass undamaged through the strains, both foreseen and accidental, that occur within the catalyst bed. Mechanical strength is also demonstrated by the resistance of the grains to attrition through rubbing, which produces fines and can cause an increase in pressure drop in a catalytic bed, for endothermic or exothermic reactions, by improving heat transfer. For other catalysts, the specific heat assumes more importance a high specific heat permits a catalytic cracking catalyst to carry a large thermal load from the combustion of coke back to endothermic cracking reaction.
- 1.2.6. **REGENERABILITY:** it is only in theory that a catalyst is found intact at the end of the reaction. All catalysts age; and when their activities or their selectivities have become insufficient, they need to be regenerated through a treatment that will return a part of their catalytic properties. The most common treatment is burning off of carbon, by scrubbing with suitable gases is also frequently done to desorb certain reversible poisons. When treatment does not include burning off of coke it is often called rejuvenation. The shorter the cycle between two regenerations, the more important is the regeneration. It becomes apparent that it is not enough for the catalyst to recover its activity and selectivity, it must also preserve its mechanical strength during successive regeneration.
- 1.2.7. **REPRODUCIBILITY:** reproducibility characterizes the preparation of the catalyst itself; it is of concern to industrial users who want to be assured of the quality of successive charges of catalyst; and it also preoccupies the various engineers responsible for



developing the cost from the laboratory on to industrial manufacture. Indeed the manufacture of a catalyst takes place in several rather complex stages dependent on a large number of variables difficult to control simultaneously.

- 1.2.8. **ORIGINALITY:** It is also important that the catalyst and the process in which it will be used can be exploited legally through licenses. This is possible only if the catalyst is original, which is rare or if it belongs to the public domain, which is more frequent. In the first case, it can be protected by fundamental patents; in the second case the possible patents can apply only to improvements. The greater the originality, higher the potential royalties associated with the catalyst or the process for which it is the controlling part.
- 1.2.9. **COST:** even when the catalyst possesses all the required properties and characteristics just enumerated there remains one last requirement: it must withstand with competitive catalysts or possess with equal functions from the point of view of cost; or at least its cost should not place too heavy a burden on the economics of the process for which it will be used.

### **1.3. THE IDEAL AND OPTIMUM CATALYST**

All of the above properties and characteristics are not independent; when one among them is changed with the view of improvement the others also get modified, and not necessarily in the direction of overall improvement. As a result, the industrial are never ideal. Fortunately, however the ideal is not altogether indispensable. Certain properties, such as activity and reproducibility are always necessary, but selectivity, for example has hardly any meaning in reactions like ammonia synthesis and the same holds true for thermal conductivity in an isothermal reaction. Stability is always of interest but becomes less important in cases where the catalyst is continuously regenerated in this case regenerability must be maximized.

The goal therefore is not an ideal catalyst rather an optimum catalyst, which may be defined by economic feasibility studies concerning not only the catalyst but also the rest of the process. And when the catalytic process is established and the catalyst in question must compete as a replacement catalyst's cost and method of manufacture predominate in arriving at the optimum formula.

Depending on the use and the economic competition, therefore, the optimization studies establish a hierarchy among the properties and characteristics of a catalyst; and the knowledge of this hierarchy helps to better orient the efforts of the research team responsible for creating and developing catalyst and its process.



## Chapter 2

### PHISIO-CHEMICAL CHARACTERSTICS OF THE CATLYST

For many years, even decades, study in the field of applied catalyst was often limited to immediately exploitable properties i.e. the catalytic, mechanical and physical properties. Catalytic behavior was studied in the framework of its function without attempt to probe its reason for this behavior as they pertain to the physical and chemical characteristics of the solid.

Admittedly, these physical and chemical characteristics are numerous; the method for studying them are many and complex; certain methods have only recently been developed; the equipment needed is expensive; interpretation of the result requires confirmed specialists; and in addition, the catalytic performance of most catalysts does not stem from a single chemical or physical characteristics, but several that must all be measured pre-selected. These difficulties shoe that an effective approach to the explanation of catalysis techniques that are within the budgets of only a few laboratories.

The interpretation of catalytic performance through the mechanism of catalytic action depends on a study of the intrinsic chemical and physical characteristics and catalytic performance. It does not enter into practical scope of this book to describe in detail all the research equipment and methods presented in table 2.1.

Table 2.1

Physio-Chemical Properties of Catalytic and Method of measuring them

Properties	Measurement method
1. Composition of chemical elements	Standard chemical analysis X-ray fluorescence Emission spectrometry Atomic adsorption Flame spectrometry Neutronic activation
2. Nature and structure of the catalytic chemical species	X-ray diffraction Electron diffraction



	Nuclear magnetic resonance (NMR)
	Electron paramagnetic resonance (EPR) Infrared and Raman spectrometry Visible and ultraviolet spectrometry
3. The texture of the catalyst: Texture of the support ( porosity, specific surface, pore distribution)  State of the dispersed active agents	BET methods Porosimetry Chemisorption X-ray diffraction Electron microscopy Scanning electron microscopy Magnetic methods Chemical methods Electron microprobe analyser
4. The quality of the active surface	Chemisorptions kinetics Flash desorption Heats of adsorption Color doping EPR, infrared spectrometry
5. Electronic properties	EPR Conductivity, semi-conductivity Electron extraction work function





## 2.1. ELEMENTARY COMPOSITION OF CATALYST

The catalytic properties of activity, selectivity and stability will vary due to the variation when the concentrations of the various elements are systematically modified from one catalyst to another within a family of the catalyst. The shapes of curves for such relations can reveal synergetic effects and hence chemical interaction between various compounds of the catalyst, as illustrated in the Fig. 2.1. In other cases, the relation between the activity and composition will suggest an approach to the reaction mechanism and reveal the limiting step as shown in Fig. 2.2. For other reactions the relation will be simpler and interpretation easier, as can be seen in Fig. 2.3, 2.4, where the linear relation between activity and concentration of active agent suggest that an increase in concentration of this active agent does not effect the availability of the reactants, and signifies also that diffusional limitation do not intervene.

Such correlations are not surprising; and their interpretation constitutes only an initial step in the approach to the manner in which the catalyst acts. Further interpretation requires that one finds out which chemical or physical property of the solid is responsible for the variation in catalytic properties observed when the elementary composition of the catalyst is systematically modified.

During the catalyst preparation or manufacture, the procedure is generally such that the obtained composition is very close to the one wanted; but that does not eliminate the need to control the composition through analysis of the solid, on one hand, and of the different impregnation and washing solutions on the other. It is also essential to do this analysis at certain critical moments in the life of the catalyst, as for example, after it has been put to use in the reactor before and after regeneration and at the end of its life to do this, chemical method of analysis are still in use, but they are generally laborious; and they require bringing the catalyst into solution, which does not lend itself to automation. Consequently physical methods have been developed, particularly methods of spectral analysis. For major elements whose concentration is over 1%, or minor elements whose content is between 1 and 0.1% the recommended methods will be in either cases measurements of X-ray fluorescence or the emission spectrum in an electric arc or spark.

For the content of trace elements in solid sample, emission spectroscopy will be used, and possibly mass spectrometry and spectrum analysis of activated sparks. If the sample is in solution, the methods most used are flame and atomic absorption spectroscopy.

These various methods are not universal and each has its features, as is shown in table 2.2.

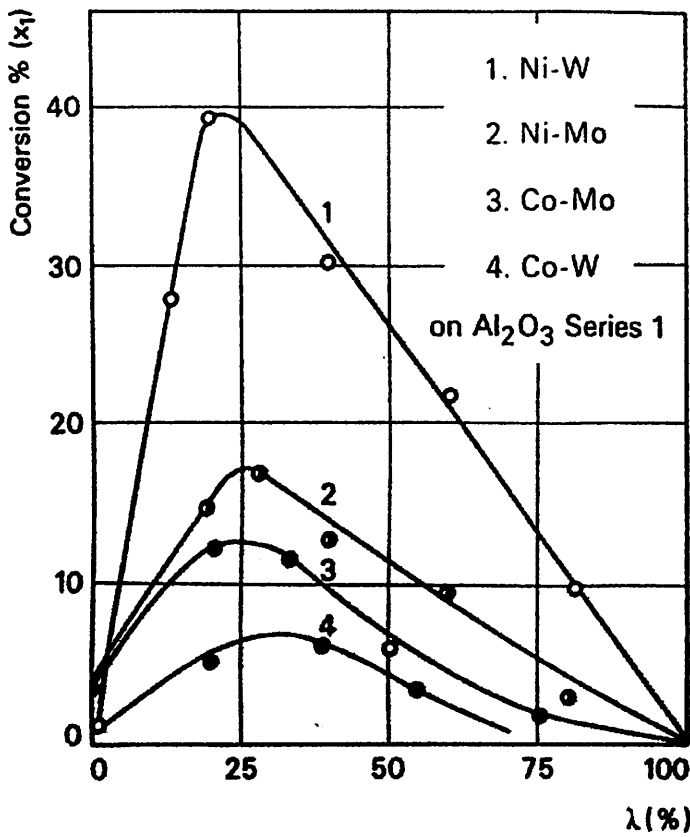


Figure 2.1

The effects of active phase composition on catalytic performance. Tests on model molecules.

(X1) represents hydrogenation of toluene.

The composition of feed was 10% cyclohexane, 40% toluene, 50% cyclohexane.

The operating conditions were T=350°C, P=60 bar amount of catalyst =30gm, supported catalyst.

Ref: Ahuja S., Thesis

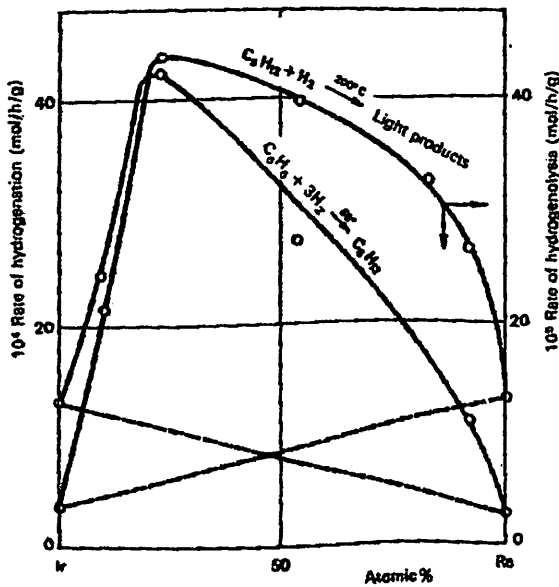


Figure 2.2 Optimum composition of the iridium/rhenium pair in the hydrogenation of n-pentane and hydrogenation of benzene at atmospheric pressure.

Ref: Brunelle J. P. ICC London

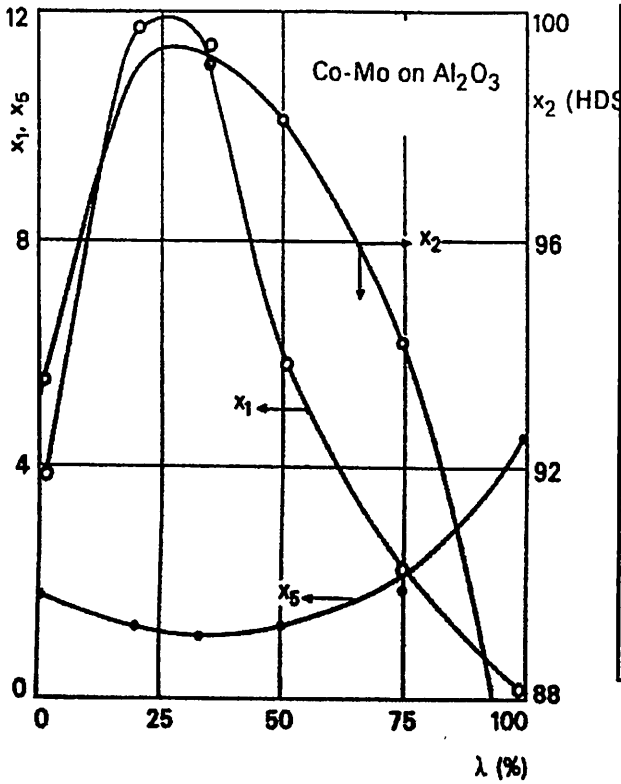


Figure 2.3

The effects of active phase composition on catalytic performance. Tests on model molecules.

(X1) represents hydrogenation of toluene.

The composition of feed was 10% cyclohexane, 40% toluene, 50% cyclohexane.

The operating conditions were T=350°C, P=60 bar amount of catalyst =30gm, supported catalyst.

Ref: Ahuja S., Thesis

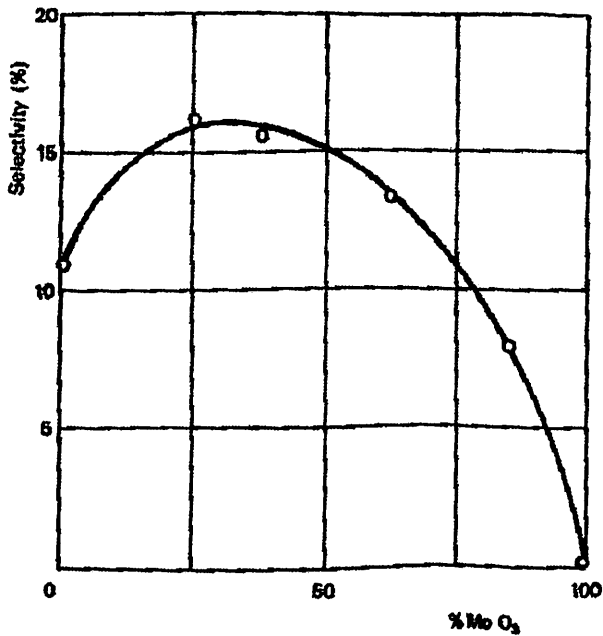


Fig 2.4

Influence of MoO<sub>3</sub> on the selectivity of V<sub>2</sub>O<sub>5</sub> for the oxidation of butene to maleic acid.

Ref Delgrange, J.C., Blanchrd

Table 2.2

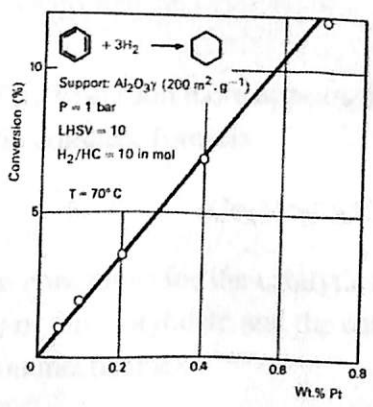
PHYSICAL METHODS OF ANALYSIS FOR CATALYTIC ELEMENTS

Period	Group																				
	I <sub>A</sub>	II <sub>A</sub>	III <sub>A</sub>	IV <sub>A</sub>	V <sub>A</sub>	VI <sub>A</sub>	VII <sub>A</sub>	VIII					I <sub>B</sub>	II <sub>B</sub>	III <sub>B</sub>	IV <sub>B</sub>	V <sub>B</sub>	VI <sub>B</sub>	VII <sub>B</sub>	O	
1	H																				
2	Li	Be																			He
3	Na	Mg*													B	C	N	O	F		Ne
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn*		Al	Si	P	S		Cl		A
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd*		Ga	Ge	As*	Se*		Br		Kr
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg		In	Sn	Sb	Te*		I		Xe
7	Fr	Ra	Ac											Pb	Bi	Po			At		Rn

LANTH III <sub>B</sub>	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
ACTINIDES	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	E	Fm	Mv	No	Lw

- Elements analyzed by flame spectrometry
- Elements analyzed by atomic absorption
- Elements analyzed by the two methods (\* more sensitive by atomic absorption)



Surface area of active agent independent of concentration.  
 In the hydrogenation of benzene catalyzed by platinum deposited from chloroplatinic acid on alumina, the conversion increases linearly with the platinum content, at least for the contents studied. For these catalysts prepared by ion exchange, the quality of the dispersion remains almost constant as the metal content increases.  
 Cosyns J., Le Page, J. F., IFP unpublished results.

Fig. 2.5



## 2.2 THE NATURE AND STRUCTURE OF CHEMICAL COMPONENTS IN A CATALYST

Active elements very often do not act in their elementary form but in the form of definite compounds, amorphous or crystallized, which is important to characterize.

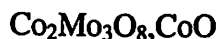
### 2.2.1 CRYSTALLINE COMPONENT

The best method for identifying and determining the presence of new or established structures related to the catalytic properties is X-ray diffraction. This method should be considered routine and will be illustrated with some examples mostly taken from work done at *Institut Français du Pétrole (IFP)*.

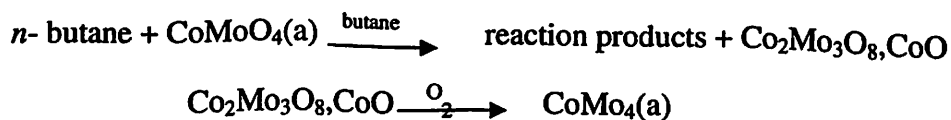
- The catalyst for the oxidation of benzene to maleic anhydride is based on  $V_2O_5$  with the addition of  $MoO_3$  as promoter. X-ray diffraction has been able to show that this catalyst acts in the form of a solid solution of  $MoO_3$  in  $V_2O_5$  and that the solid solubility limit 30% of  $MoO_3$  in  $V_2O_5$ , corresponds to the maximum of catalytic performances.
- The catalytic oxidation of butane to butene and butadiene can be done on a solid catalyst based on cobalt molybdate. Study by X-ray diffraction has afforded a precise definition of the various phases present in the catalytic solid and the oxidation-reduction cycle operated on the surface of the catalyst.

At the beginning, the catalyst is in an oxidized form corresponding to the phase (a) of cobalt molybdate and characterized by its monoclinic structures with 4 coordinates for molybdenum and 6 for cobalt.

In the presence of hydrocarbon there appears a reduced phase, called "catalysis molybdate," with the complex formula:



Under the reaction conditions for the catalytic oxidation of *n*-butane, the catalyst evolves between phase (a) of the molybdate and the catalysis molybdate according to the following oxidation-reduction mechanism:



Evidence for this mechanism is illustrated in Table 2.3 showing the changes of the catalyst depending on whether it is in the oxidizing atmosphere at the top of the catalytic bed or in the reducing atmosphere at the bottom.



- Some reduction catalysis for the nitrogen oxides in automotive exhaust gas initially consist of nickel oxide combined with one or more transition-metals oxides,

Table 2.3

Evidence for the mechanism of catalytic oxidation of *n*-butane to butene and butadiene

Position in the reactor	Color	X-ray diffraction spectrum
Entrance	Violet	CoMoO <sub>4</sub> (phase a)
First layer	Blue	CoMoO <sub>4</sub> (a) + trace molybdite
Second layer	Gray	0.6.CoMoO <sub>4</sub> +0.4.molybdite
Outlet	Black	Molybdite

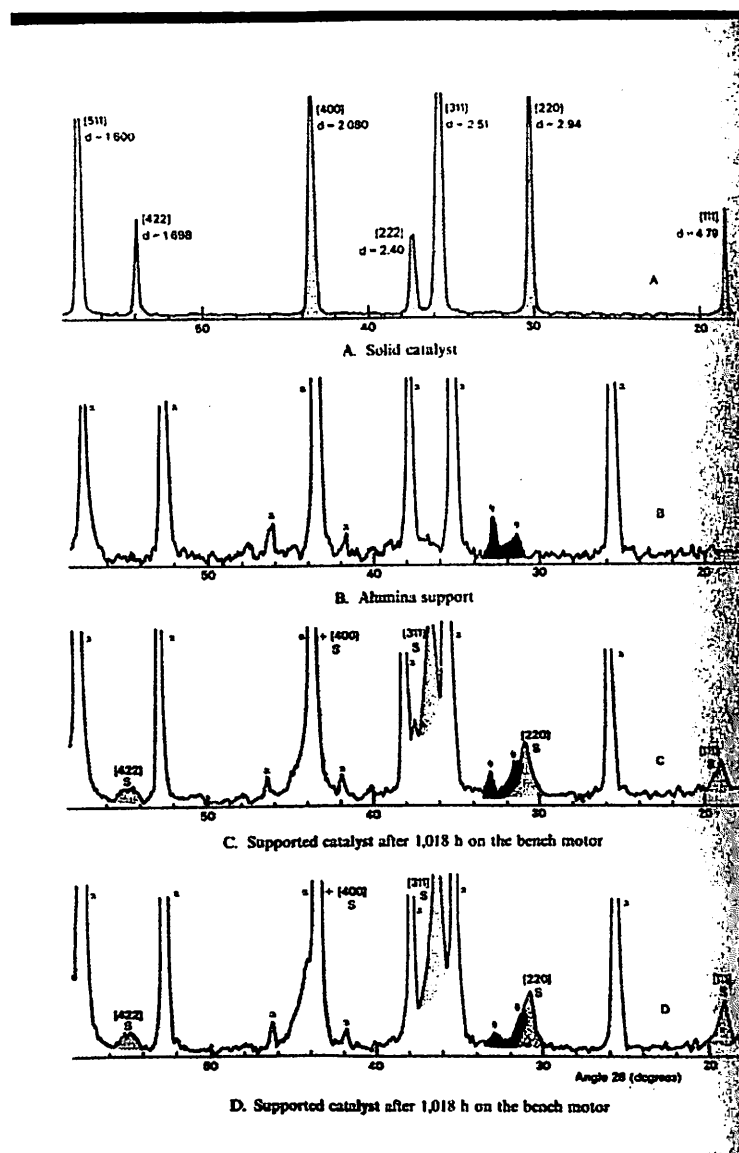


Fig. 2.6

$\text{Ni}(\text{A}_{2-x}\text{B}_x)\text{O}_4$  in the form of a mixed oxide with well determined spinel structure deposited on low-surface alumina that gives good stability to the catalyst. If there is insufficient evolution of this support toward  $\alpha$  alumina, X-ray diffraction will show the presence of a certain amount of transition  $\theta$  alumina on the starting support, along with the  $\alpha$  alumina and some of the active species deposited on the support. During high temperature operation, a rather abrupt reaction in the activity of the catalyst is observed, corresponding to a reaction of the nickel oxide with the transition alumina to form an inactive nickel aluminate, which is produced when the emission gas contains enough oxygen to oxidize the nickel that normally operates in the reduced state with a rich combustion mixture.



- In hydrodesulphurization on  $\text{MoS}_2$  promoted by  $\text{Co}_9\text{S}_8$ , an optimum of desulfurizing, denitrogenizing, and hydrogenating activity is observed for an atomic ratio of  $\text{Co}/(\text{Co} + \text{Mo})$  close to 0.25. Attempt have been made to relate this optimum to modification of the crystal structure of  $\text{MoS}_2$ , as the content of  $\text{Co}_9\text{S}_8$  increases. **Figure** shows the variation for a value of  $\text{Co}/(\text{Co} + \text{Mo})$ ; while parameter  $a$  remains constant, parameter  $c$  undergoes a series of variation for a value of  $\text{Co}/(\text{Co} + \text{Mo})$  less than 0.3 that contributes to the interpretation of the observed catalytic performance.

### 2.2.2 AMORPHOUS OR POORLY CRYSTALLIZED COMPOUNDS

When active agents are present are present in the form of amorphous or poorly crystallized compounds. Their identification becomes difficult and requires a combination of several methods both general and specific.

The general methods, which are capable of furnishing information for any types of catalysts, include, first, thermogravimetric and differential thermal analyses that reveal changes in structure and composition. One can also mention infrared and Raman spectrometry, which can indicate the existence of a given type of certain bond or symmetries, allowing description of the arrangement of certain elements within the catalytic solid.

The specific methods, which can be applied only if some particular elements are present in the catalytic solid, include, first, various magnetic methods: nuclear-magnetic resonance; electron-paramagnetic resonance for characterizing the valence state of transition metal ions; and thermo magnetic analysis, which serves to reveal the presence of certain ferromagnetic species. Also, there are chemical methods for selectivity extracting certain ions of determined valence, such as the  $\text{Cr}^{6+}$  ions extracted by 0.5 normal  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$ . With a few drops of sulfonated biphenyl amine added.

### 2.2.3 COMBINATION METHODS

The usefulness of combining physical and chemical techniques for the purpose of identifying the chemical nature of the active species in relation to the iron molybdate used for the complete oxidation of methanol into formaldehyde at low temperature ( $T=300^\circ\text{C}$ ). For this purpose of catalysts a performance optimum is observed at an atomic of  $\text{Mo}/\text{Fe}$  between 1.5 and 1.7. Diagrams of X-ray diffraction have revealed the presence of only ferric molybdate,  $\text{Fe}(\text{MoO}_4)_3$  at the optimum ratio, while other ratio show lines of both  $\text{MoO}_3$  and  $\text{Fe}_2\text{O}_3$  simultaneously. Likewise electron-paramagnetic resonance study of a family of catalysts, in which the ratio  $\text{Mo}/\text{Fe}$  equals 1.5. The nature of this signal identifies it unequivocally with  $\text{Fe}^{3+}$  ion, which support the X-ray diffraction result. The signal cannot be attributed to  $\alpha\text{-Fe}_2\text{O}_3$ , which is artiferromangetic





and give the white signal that is not detectable, any more than two  $\text{MoO}_3$  where  $\text{Mo}^{6+}$  is diamagnetic.

Infrared absorption can show characteristic bands of ferric molybdate when the ratio Mo/Fe equals to 1.5 is approached whereas at higher ratio it shows the spectrum of  $\text{MoO}_3$  more or less modified by the presence of ferric molybdate. Finally, the diagram of thermal analysis confirms perfectly to the stoichiometric ratio 1.5, by the appearance first at  $350^\circ\text{C}$  of an exothermal crystallization peak for  $\text{Fe}_2(\text{MoO}_4)_3$  and then at  $955^\circ\text{C}$  of the exothermic melting peak for this compound. Catalysts with other composition shows other peaks that can also be interoperated.

## 2.3 TEXTURE OF A CATALYST

Heterogeneous catalysis is a surface phenomenon; and it is not enough for the ideal catalyst simply to have the required elementary composition formed during preparation and start-up. There must also be largest possible active surface for any given mass of catalytic agent and this active surface must be topographically arranged through an optimized pore distribution so as to facilitate the access of reactants and the departure of products, in order words, in such a way as to limit diffusional phenomena as much as possible. Therefore, we are going to examine following characteristics:

- (1) The total specific area of a catalyst.
- (2) The dispersion of the active agents: the size of aggregates and crystallites and gradients of dispersion inside the grains.
- (3) The pore distribution on which the intragranular diffusional phenomena depend.

### 2.3.1 The total specific area of the catalyst

The external surface is negligible compared to the internal surface comprising the walls of the pores, which are considered to be cylindrical as the first approximation; as the size of the surface can be approximated by the following relation:

$$S = 4V_{PT}/\Phi$$

Where

$S$  = specific area of the catalyst ( $\text{m}^2 \cdot \text{g}^{-1}$ )

$V_{PT}$  = total pore volume ( $\text{cm}^3 \cdot \text{g}^{-1}$ )



$\Phi$  = average diameter of the pores

In practice, the method most used for determining specific area is the BET method (Brunauer, Emmett, Teller) based on the physical adsorption of an inert gas at constant temperature, usually nitrogen at the temperature of liquid nitrogen. The principle of measurement consists in determining the point when a mono-molecular layer of gas covers the surface of the catalyst. If the layer corresponds to the quantity  $V_m$ , for a gas whose molar volume is  $V_M$ , the surface studied will be written:

$$S = \sigma \cdot V_m / V_M N_A$$

where  $\sigma$  is the area covered by the adsorbed molecule, and  $[V_m/V_M N_A]$  the number of molecules constituting the single layer when  $N_A$  is the Avogadro number.

Experimental methods used for determine  $V_m$  are numerous and described at length in specialized articles. We are limited here to noting that the most frequently used methods are thermogravimetry, volumetry and sorptometry.

It must be pointed out that the specific area of catalysts with small surfaces can advantageously be derived from the pore distribution curve obtained through mercury porosity measurement. The specific area can also be estimated through measuring the dimensions of the catalyst particles by X-ray diffraction or diffraction (diffusion at small angles or broadening of the X-ray diffraction lines).

In the case of bulk catalysts composed solely of active agents, the total specific area can be taken as the measure of the active specific area; this is not the case, however, if the catalysts is supported, since the support plays the role of dispersing agent, diluent or binder. But even in this latter case knowledge of the total surface of the active agent (or of the support) can still be useful, if only for judging the dispersing role of the support in relation to the active agent during the impregnating operation.

### 2.3.2 DISPERSED STATE OF THE ACTIVE AGENTS

When the active species are supported or diluted, there is no longer a direct relation between the total specific area and the observed catalytic performance, particularly the activity; and it is necessary to determine the available active surface, i.e., the number of molecules or atoms of active agents accessible to the reactants. Defined in this way, the characteristics designated as "active specific surfaces" remains an overall characteristics in the sense that all the atoms or molecules making up the active surface are considered as equivalent from the point of view of their catalytic properties. The actual case is generally more



complicated; it is reasonable to think that the various atoms of a nickel crystallite, for example, offer different catalytic activities for certain reactions according to their different coordination indices, depending on whether they are situated on the corners, the correlations between the catalytic phenomena. Nevertheless such correlation hold some interest, as will be shown in describing current methods of measuring surfaces of active agents by some examples relative to industrial catalysts.

### 2.3.2.1 CHEMISORPTION

Contrary to physical adsorption, which precludes differentiating between support and active agents, chemisorptions is generally specific. The method of measurement consists of adsorbing on the surface atoms of the active agent a compound capable of a complete surface reaction leading to the formation of a single chemisorbed layer of molecules; the measurement of the adsorbed quantity then indicates the state of dispersion of the active agent.

This method is frequently used when the active agent is a metal the nature of which dictates chemisorbed molecule as well as the conditions of chemisorptions. The number of metallic surface atoms  $N_s$  and the surface of the active metal, ( $S_m$ ) can be derived the following equations:

$$N_s = (v/V_M) \cdot N_A \cdot n$$

Where

$v$  = volume of gas chemisorbed,

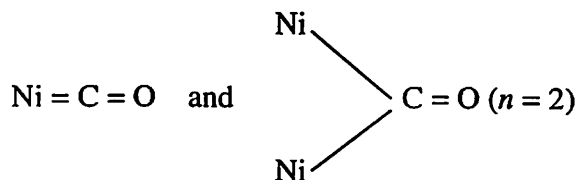
$V_M$  = molar volume of the gas,

$s$  = surface occupies by a metallic atom,

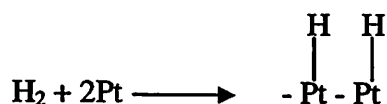
$n$  = stoichiometry of the chemisorptions reaction,

$N_A$  = Avogadro number

The value of  $n$  is not evident from the valences, but depends on the particular nature of the gas and the metal. Thus it has been possible to show at least two chemisorbed forms for the adsorption of carbon monoxide on nickel depending on the operating conditions:



In the case of platinum, either direct chemisorptions of hydrogen on the reduced metal at 250°C according to the following scheme has been recommended:



or the chemisorption of O<sub>2</sub>, according to the following more complex scheme which has the advantage of being three times more sensitive than the simple chemisorptions of hydrogen:

Measurement of the chemisorbed quantity,  $\nu$ , is done by the same techniques: thermogravimetry, volumetry or chromatography, as used for physical adsorption.

In order to show the usefulness of chemisorptions measurements, the relations between the rates of various reactions of pentane on platinum at 250°C and the chemisorptions of CO on this same metal. The rates increase as the chemisorbed quantity of CO per gram of platinum increases, i.e., when the surface of the metal accessible to the reactants increases. However, it must be noted that the isomerization increases linearly with the chemisorptions of carbon monoxide, but that this is not the case for hydrogenolysis. This can be interpreted by assuming that isomerization, an easy reaction, uses all the metal atoms accessible indiscriminately, while hydrogenolysis takes place preferentially on metallic sites at the corners and edges of the crystallites.

Variation of accessible metallic surface with the reduction temperature of catalysts for selective hydrogenation of the acetylene bonds in C<sub>3</sub>, C<sub>4</sub>, and C<sub>5</sub><sup>+</sup> fraction from steam pyrolysis. The catalyst is palladium deposited on suitably neutralized alumina.

The usefulness of chemisorptions is not limited to metal catalysts; the chemisorptions of CO has been related to properties of hydrodesulphurization catalyst based on the sulfides of metals in group VI<sub>A</sub> and VIII of the periodic table. At the ambient temperature at which this chemisorptions takes place, an interaction of the CO with the alumina support is also observed; despite this parasitic adsorption it is still observed that the hydrodesulphurization activity increases with the volume of CO chemisorbed.

Even though all the above are based on the chemisorptions of a gas, the chemical adsorption of a molecule from the liquid-phase can also be used to study active surfaces. Thus the adsorption of pyridine on Raney nickel suspended in liquid heptanes affords in isotherm for determining the



number of moles of pyridine adsorbed in a single layer and hence for determining the surface accessible to reactants.

Finally, the application of chemisorptions of both liquid and gaseous ammonia to measuring the acid sites of solid catalysts should be mentioned. In this case, however, one is usually aiming at simultaneously determining the number of sites and their distribution according to their acidity strength.

#### 2.3.2.2 X-RAY DIFFRACTION: BROADENING OF X-RAY DIFFRACTION LINES

The width at mid-height of X-ray diffraction lines can also be used to obtain the dimensions of crystallites. This method is applicable only to active agents that are well crystallized and whose particles have dimensions between 3nm and 100nm, with certain nuances depending on the proportion of active agent in the catalyst and the characteristics of the apparatus. With platinum, for example, one can go down to 5nm for 1% metal content, but only to 30 nm if the metal content is less than 0.1%.

#### 2.3.2.3 ELECTRON MICROSCOPY

The difficulties often encountered in preparation of the samples and interpretation of the photograph with this technique is offset by the picture it gives of reality. For example, shows the dispersion of platinum on a zeolite support. The sizes of the platinum crystallites on this sample of catalyst vary; but enough of these crystallites appear in the image to make it possible to establish their size distribution and derive the average dimensions.

Suitably applied, this techniques can be used to determine crystallite dimensions comparable to those obtained by chemisorptions or X-ray diffraction. Where the three techniques have been used to measure crystallite sizes in silica based catalyst impregnated with palladium have been used in the synthesis of vinyl acetate, from acetic acid plus ethylene in the presence of oxygen.

The continual improvement in the power of resolution of modern electron microscopes has heightened interest in this technique; today one can see the actually see the aggregates of active agents of active agent whose dimensions are close to 0.5 nm, the size of the smallest aggregates platinum in the reforming catalysts prepared by anionic of  $\gamma$  alumina.

#### 2.3.2.4 OTHER METHODS FOR MEASURING THE STATE OF DISPERSION

Magnetic properties exhibited by certain active agents on a support can also be used to estimate the dimensions of the aggregates of those agents. Ferromagnetism and diamagnetism are both related to the presence of a crystalline structure, while paramagnetism is an atomic property. The magnetic permeability changes with the dimension of the particles, and this change is expressed by the shape of the thermomagnetic analysis of nickel dispersed on the surface of a support.

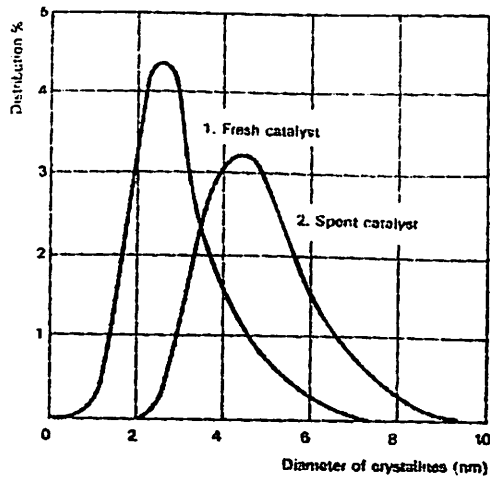


Although its application requires great care, small-angle X-ray scattering is also used for evaluating the dispersion of active agent. Figure 2.6 illustrates the possibilities of this method as the basis of comparing the size of Pt crystal before and after use in a catalyst based on  $\eta$  alumina impregnated with 0.6% of the metal.

As a last approach to the state of dispersion of active agents, there must also be mentioned certain chemical reactions that take place between a specific reactant and some atoms or surface-atoms groups that can be the active sites of a catalyst. For example, supported precious metals can be attacked by HF,  $\text{SnCl}_2$ , and  $\text{H}_2\text{SO}_4$  and acetylacetone. Figure 2.6 relates to the extraction of palladium by a solution of  $\text{SnCl}_2$ ; the metal, which was deposited on the silica by cationic exchange, exhibits a decreasing solubility in the extraction solution as the calcinations temperature of the catalyst is increased, although conditions of a reduction remain unchanged ( $\text{H}_2$  at  $150^\circ\text{C}$ ). Without going into the exact nature of this soluble palladium, we note that the correlation between the dispersion of the metal and its solubility is the straight line in Figure 2.6

Another measure by chemical reaction of the sum of sites capable of being catalytically active is the analysis by triethyl aluminum of hydroxyl present on the surface of certain catalyst acid catalyst such as alumina, alumina silica, silica.

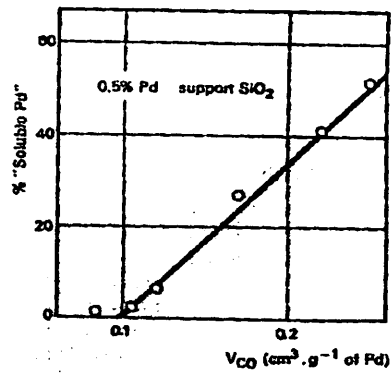
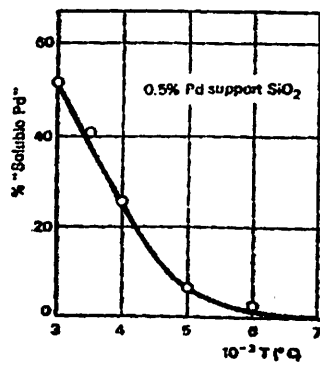
In summary, this method described can be put into two categories. In the first category, chemisorptions method afford direct measurement of the atoms or molecules of catalytic agents; and if these agents are metals, it is then possible to determine the dimension of the crystallite or aggregates that they form by means of certain hypothesis about their geometry. In a second category are the methods that afford a direct determination of the dimensions of the aggregates of the active agents; and from these dimensions reasons hypothesis concerning a geometry of these aggregates which are generally crystallized, provide a basis for estimating the surface offered to the reactant.



Dispersion of platinum on a reforming catalyst by the Small Angle X-ray Scattering (SAXS) method.

The figure shows the crystallite distribution according to dimension for both a fresh catalyst and a spent catalyst that has undergone six regenerations. The support is  $\eta$  alumina; and unwanted diffusion of the alumina pores is suppressed by previous adsorption of  $C_2H_4I_2$ , whose electronic density is close to that of alumina.

White, T. E., Kirklia, P. W., Gould, R. W., Heinemann, H., *J. Catalysis*, 25, 407, 1972.



Correlation between the chemical solubility of deposited palladium and its dispersion.

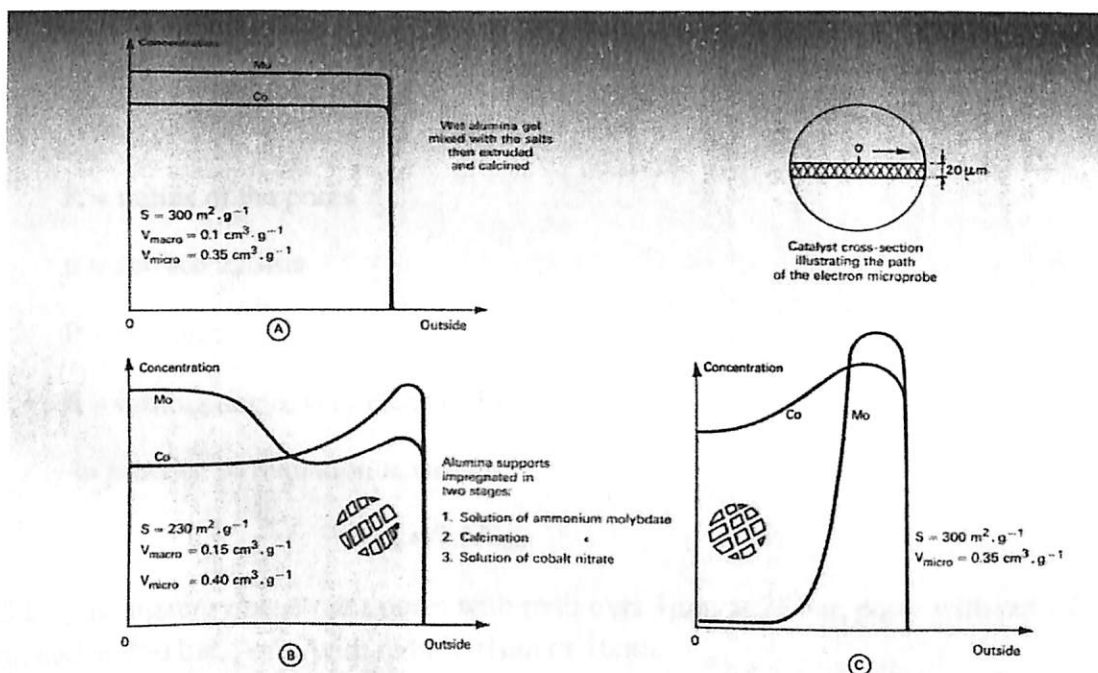
shows that the solubility of palladium in a solution of 5%  $SnCl_2$  decreases as the calcination temperature increases. The linear relation between the percentage of soluble Pd and the quantity of CO chemisorbed in Fig. 7.21 shows that solubility reflects the dimensions of the crystallites.

Samanos, B., Thesis, Paris, 1971.

Figure 2.7

### 2.3.2.5 THE ELECTRON MICROPROBE

When catalyst grains can be several millimeters in diameter, it is not always enough for active agent merely to be in the form of crystallites of optimum size; this active agent must also be dispersed suitably within the volume of grain. If the internal diffusion presents problem to the active agents is sometimes best deposited at the external surface of the grains; at the other time, it is preferable to have the active agents dispersed homogeneously through out the volume of the grain the electron microprobe is a valuable tool for evaluating such dispersions down to dimensions of micron as shown in Fig. 2.7 , which analyze the distribution of cobalt and molybdenum inside a grain of an hydrodesulphurization catalyst prepared by successive impregnation of cobalt nitrate and ammonium molybdate.



(A) Homogeneous distribution such as is obtained by mixing salts with the wet gel before forming. (B) The distribution obtained by impregnating a catalyst with two pore systems,  $\varnothing < 15$  nm and  $\varnothing > 100$  nm. A fairly homogeneous distribution is obtained. (C) The distribution obtained by impregnating a microporous support (average  $\varnothing = 4.6$  nm).

The small diameter of the micropores and the absence of macropores block diffusion of the large highly adsorbed molybdate ion, and molybdenum is deposited in a layer at the exterior of the grain. (The curves for Mo and Co are drawn with different scales).

Jacquin, Y., Chenebaux, M. T., IFP unpublished results.

Figure 2.8

### 2.3.3 PORE DISTRIBUTION





A Knowledge of the composition of the total pore volume in terms of the diameter of the individual pores is indispensable of kinetic interpretation of experimental results whenever the restrictions of internal diffusion are in evidence. This "pore distribution" can be obtained either through a physical adsorption-desorption isotherm for nitrogen or through the curve of volume versus diameter made by mercury porosimetry. The first method was adopted for diameter between 1 nm and 30 nm; the second for diameters between 7 nm and 10  $\mu\text{m}$ , with porosimeter able to operate under the maximum pressure of 2000 bar.

As for the mercury porosimeter, it is based on the property that mercury has of not wetting the walls of the pores where it penetrates only through the pressure. Following Jurin's law

$$R = (2\sigma\cos\theta/P)$$

Where

R = radius of the pores

$\sigma$  = surface tension

P = pressure

$\theta$  = wetting angle, very close to  $140^\circ$

In practice the equation is written:

$$R_{\mu\text{m}} = 7.5/P_{\text{bar}}$$

Thus at 7.5 bar, the mercury penetrates pores with radii over  $1\mu\text{m}$ ; at 75 bar, pores with radii over  $0.1\mu\text{m}$ ; and at 750 bar, pores with radii  $0.01\mu\text{m}$  or 10nm.

As we have already mentioned the total surface of the catalyst, specially small surfaces can also be determined of pore distribution.

The determination of pore distribution must currently be considered a routine procedure in those laboratories developing industrial catalysts. The diameter of the pores of a given support indeed of the controlling variables of the impregnation operation. During the reaction it takes on even more important limiting step of the reaction process is internal diffusion.

## 2.4 THE QUALITY OF THE ACTIVE SURFACE



#### 2.4.1 HETEROGENEITY OF THE ACTIVE SURFACE

As soon as we attempt to analyze the reaction mechanism of the catalyst in greater detail, it is no longer sufficient to know merely the active surface of all the atoms with the same catalytic properties. Catalytic action is a succession of chemical reactions in which the catalyst is a transitory partner; and each of the successive reactions is controlled by the properties of the electrons on its catalytic partner. The various atoms or groups of the atoms on the catalytic surface do not exhibit the same electron environment in terms of valence, coordination and degree of polarization; consequently, they are not identically active or selective.

Results from kinetic studies and physico-chemical determination of the hydrogenation of aromatics and olefins on tungsten sulfide or on nickel-tungsten sulfides, for example, can be interpreted on the basis of existence of the two types of active centre on the catalyst surface bathed in the reaction medium:  $W^{3+}$  ions and pentacoordinated  $W^{4+}$  ions.

The rate at which the tungsten catalysis of the hydrogenation of benzene can be correlated with the intensity of the electron paramagnetic resonance (EPR) signal, which is attributed to the presence of  $W^{3+}$  ions.

There is no correlation between the EPR signal and the rate of reaction for the hydrogenation of cyclohexane and olefins; but a more detailed study of the crystalline structure of tungsten sulfide indicates that the sites responsible for this type of hydrogenation are not only the  $W^{3+}$  ions previously mentioned but also pentacoordinated  $W^{4+}$  ions probably situated on the lateral faces of crystallites for energetic reasons.

Tungsten sulfide has a lamellar-type prismatic structure where the tungsten atoms are sandwiched between the two layers of sulfur atoms. These various S-W-S sandwiches constituting the structure are held very compactly by the van der Waals forces between the two superimposed layers of sulfur atoms.  $W^{3+}$  ions responsible for the hydrogenation of benzene would be tetra coordinated and probably situated on the corner of the crystallites, as it deduced from steric analyses showing that it is only on such sites that benzene can be adsorbed for forming a pi-type complex. Cyclohexane on the other hand, could be adsorbed both on these sites and on  $W^{4+}$  pentacoordinated ions situated on the edge of S-W-S sandwich.

Nickel promoters for this catalyst are probably inserted between the sheets of S-W-S and its promoting effect is simply due to an increase in the concentration of electrons within these sheets, that in turn brings on an increase in  $W^{3+}$  ions on the surface. Indeed, in the case of sulfided tungsten-nickel catalysts, X-ray diffraction does not show the formation of the ternary compounds, but only the presence of  $WS_2$  and  $Ni_3S_2$  phases, the latter being inactive. This leads to the conclusion that the active sites are localized on the surface of  $WS_2$  sheets and that the promotion by nickel is of the electronic type.



In a very different area the acid supports in current industrial use can also serve as an example of heterogeneity of the active centres, both in their nature and in their strength. The silica-alumina of this catalyst is characterized by bronsted type acidity i.e., protonic but the acid strength of the various active centers is very much spread out. The alumina is even more complex and the numerous studies of this support show that strong lewis-acid sites at its surface would co exist along with weak bronsted sites and even certain base sites, depending upon the degree of dehydration of the surface.

The same thing occurs with vanadium oxide catalyst for the oxidation of a aromatic hydrocarbons of where it is well established that only those vanadium atoms whose degree of oxidation is less than 5 are capable of promoting the catalytic reaction. From this arises the need of promoter to displace  $V^{5+}$  balances towards  $V^{4+}$  balances whenever the reducing power is not enough. In the oxidation of benzene to the maleic anhydride the promoter will be  $MoO_3$ ; in the oxidation of naphthalene to phthalic anhydride,  $K_2SO_4$  will be added to the  $V_2O_5$ ; but the oxidation of the o-xylene takes place under the effect of reaction atmosphere are often only the precursors of the active centers that reveal themselves only on the presence of the reactants.

Faced with this heterogeneity of the active surface, one can wonder just how much significance ought to be given to the correlation between the catalytic activity and the total active surface. This is only the simple probability that, at least for the example mentioned, the average quality of the active surface would remain unchanged as it is extended not.

The problem of the quality of the active surface is therefore very complicated, and the methods of studying are often laborious and require much more care. Among these methods, of particularly useful depend on chemisorptions, in relation to the selection of the active species.

#### 2.4.2 MEASURING SURFACE ACTIVITY THROUGH CHEMISORPTION

We examine here those methods which can classify active centers according to their "quality". Taking into account the specificity of the different types of the catalysts and adsorbent used, these methods are many and varied; merely show their value through some practical examples.

We have already shown how it was possible to determine the total active surface of a reduced nickel catalyst by hydrogen chemisorptions that achieved saturation of the surface under pressure, say, of 10 torr at ambient temperature. However it is convincible that at a low coverage the adsorption would occur preferentially on atoms or pairs of atoms whose electronic environment or geometric arrangement are the most favorable. In other words, the most important metallic atoms are those with the strongest energy of adsorption.

From the practical point of view, chemisorption has certainly been most used in the study of the activity of the catalyst. Acidity-performance correlation date from a quarter of a century ago; and they have proven utility in the study of catalyst for cracking, polymerization, alkylation,



isomerization and cyclization. The technique, which are different and varied, consist of chemisorbing a wide variety of basis in most general sense of the term either in liquid or gas phase, and of measuring such characteristic of the chemisorption as

- (a) Total quantity adsorbed.
- (b) Heat of adsorption; entropy of adsorption.
- (c) Controlled desorption of the adsorbate.
- (d) Chemisorbing basis in the presence of colored indicators to classify the acid sites according to their force and type of acidity.
- (e) Physico-chemical study of the surface complex by infrared, nuclear magnetic resonance, electron paramagnetic resonance, etc.

Among methods relevant to direct study of the adsorbed phase, "flash desorption" must also be mentioned. This shows how various type of adsorption for a given reactant-catalyst pair corresponds to different bond energies. Thus it has been possible to observe that a filament of tungsten first saturated with nitrogen then submitted to an increase in temperature will release its gas in three stages corresponding to the existence of three types of adsorption.

In general way, those method related to a determination of the heat of adsorption should be particularly emphasized. As a function of the proportion of a saturation, heat of adsorption of the reactant-catalyst pair on a given catalytic surface can identify active center of different quality; and measured at low proportion of saturation, the heat of adsorption affords a comparison of the various active surface even to the extent of classifying them by order or activity.

If, finally, there are any criticisms to make about method related to chemisorption, they are first, that the adsorbate used is very often not the reactant itself, but molecules more or less analogous; and second, that the condition of the reaction, which are the condition most helpful toward understanding of the catalytic mechanism. These criticism nevertheless appears secondary when one consider the multitude of correlation established between the characteristics of chemisorptions and catalytic performance, even when they have often been determined under different operating conditions



## CHAPTER 3

# STIMULATION TECHNIQUES FOR THE CHARACTERIZATION OF STRUCTURAL AND TRANSPORT PROPERTIES OF CATALYST PELLETS

### 3.1 INTRODUCTION

An essential requirement in heterogeneous catalysis is the diffusion of reactants and products within complex porous structures. Catalytically active components are typically dispersed on high surface area support materials to provide high site density and volumetric activity for chemical reactions. However, the small pores required to achieve a high surface area often limit the arrival of reactants and removal of products from the pore structures; they often lead to reaction rates much lower than those of their intrinsic reactivity values (site turnover rates) and can also lead to poor selectivity. A proper balance between these competing effects- high volumetric activity and low diffusivity – is the key aspect of catalyst design.

An optimum balance between diffusion and reaction processes is difficult to define because effective diffusivity can not be estimated a priori from standard measurements of pore volume properties. For example, the connectivity of pore space is essential for transport, but it cannot be measured experimentally. Also, when diffusing through the pore structure, solid obstacles force the molecules into irregular and tortuous trajectories cannot be described adequately with closed formed expressions; these trajectories ultimately determine effective diffusivities by controlling the mean squared displacements of molecules within such structures. Structural pore models are therefore required to provide the missing information. To be useful, these models must be tractable and realistic. They must allow simulations in reasonable computing times and must account for key geometrical and topological properties of randomly disordered porous structures; we also illustrate the use of these properties in the design of catalyst pellets. We do not review here the extensive literature available in this area. We focus specifically on two approaches that we have developed and used effectively to interpret diffusion and reaction phenomena within porous catalytic materials.



The first approach uses Bethe networks as convenient descriptions of the void space in disordered pore structures as network of randomly interconnected pores of varying diameter and specific topological arrangement. These random pore networks allow adequate descriptions of standard pore volume properties of porous solids; more important, their associated physical and transport properties can be obtained in analytical form.

The second approach uses two types of Monte Carlo physical and transport properties of such structures. These simulations address a specific class simulations: one for the creation of disordered three dimensional porous solid materials and the other for the creation of disordered porous solid materials and the other for the characterization of of such structures. These simulations address a specific class of sol-gel-derived porous materials, and capture important geometrical and topological properties of the diffusing channels in porous solids commonly used for diffusivity characterization.

In many cases, Bethe networks and simulated 3-D structures have complementary applications and inherent advantages and disadvantages. Both networks are easy to use; they must be calibrated to simulate experimental data and their trends are consistent with those obtained using more detailed 3-D representations the latter require more costly simulations and provide more realistic structural characterization than that of cylindrical pore networks. Consequently, they predict experimental data more accurately and without adjustable parameters. Here, both approaches are described in detail and the properties of the two model structures compares.

We show that it is possible to develop optimization frameworks, based on these structural pore models, which can be used in the optimal selection of structural catalyst properties.

## **3.2 BACKGROUND**

### **3.2.1 PHYSICAL CHARACTERISTICS OF POROUS MATERIALS**

The pore space morphology of porous materials varies widely. Unlike zeolite catalyst, whose internal structure is highly regular, amorphous catalyst supports exhibit complex internal void structures. for example, porous metal oxides, such as silica or alumina, which are widely used in catalysis, contain broad pore size distributions and irregular pore branching patterns that vary locally within microscopic dimensions. Adequate characterization of this local geometry, which



depends critically on specific synthesis procedures, is essential to describe transport across macroscopic pellet dimensions.

Several techniques are available for experimental characterization of the physical properties of porous support structures. Porosity and internal surface area are typically measured by He pycnometry and Gas adsorption (BET) techniques, respectively. Both of these techniques are well established and accurately measure such properties of porous materials. Pore sizes are usually measured by capillary condensation and mercury porosimetry; characteristic pore sizes are sometimes also measured with small angle X- ray or neutron scattering (SAXS or SANS). The choice of technique depends upon the characteristic pore dimension of the sample under study; porosimetry is suitable for larger pores ( $>50 \text{ \AA}$ ), adsorption of intermediate- sized pores (10 to 300  $\text{\AA}$ ), and scattering for the smallest pores ( $<20 \text{ \AA}$ ). Unlike porosity and surface area measurements, characterization of pore size depends upon the model that is assumed to describe the structure; interpretation of results requires a priori assumption for pore space and connectivity. The usual assumption is adsorption and porosimetry, cylindrical pores sequentially connected in order of increasing/ decreasing size, is in most cases inaccurate.

In general, pore volume characterization techniques provide very useful details of pore space morphology in catalyst support structures, but they are not sufficient. They do not describe the connectivity of the pores, a key property that controls transport. For e.g. small pores in a porous material affect macroscopic transport differently when they are found as narrow passages between the larger voids then when they appear as non-conducting dead ends within the structure. Structural pore models are required to provide this typical topological information.

### 3.2.2 DIFFUSION PROCESSES IN CATALYST AND SEPARATION SYSTEMS:

Diffusion of gases in porous material is difficult to describe because the pores typically vary in size, shape, and orientation, and exhibit irregular interconnection patterns. These features differ significantly from the conventional descriptions of porous structures such as networks of cylindrical capillaries.

Two limiting diffusion mechanisms control molecular displacement within void spaces. In one mode, molecules diffuse by successive collisions with their molecules. This is known as Bulk



Diffusion; its associated diffusivity ( $D_b = \lambda v/3$ ) is proportional to mean free path ( $\lambda$ ) and mean molecular velocity ( $v$ ) of the diffusing molecule. It applies rigorously to molecular motion in unconstrained space but it is also valid within pores when the mean free path is much smaller than the characteristic pore dimensions ( $r_p$ ). When  $\lambda \gg r_p$ , however, molecules collide preferentially with the surrounding pore walls. This is known as Knudsen Diffusion; as exact diffusivity can only be obtained for long cylindrical capillaries. When  $\lambda$  and  $r_p$  are similar, an equivalent diffusivity can be obtained from an expression derived by Bosanquet for long cylindrical capillaries.

Several methods exist for estimating effective diffusivities in actual porous structures. The approach used most frequently simply modifies the single capillary equations to include the most relevant microscopic structural properties affecting transport. This typically involves a porosity and tortuosity correction. The porosity correction is needed to account for the presence of solid obstacles that usurp void volume. Such a correction is entirely not adequate because accessible porosity within pendant pores does not contribute to net macroscopic transport; only porosity within interconnected backbones participates in transport. Also the tortuosity factor, is an intrinsic property of the pore structure, cannot be measured independently. It frequently becomes an adjustable parameter.

Other approaches describe the size and connectivity of the pores by randomly connected macroscopic capillary networks. Effective diffusivity estimates are obtained by Monte Carlo simulations or closed-form integration procedures. These approaches are more involved than simply correcting single pore equations but allow explicit incorporation of dead ends, tortuous trajectories, and local fluctuations in pore sizes. Some shortcomings of the latter approach are that the mapping of the pore space into an equivalent network is only approximate and that the pores are still assumed to be cylindrical.

A third, more accurate and realistic approach uses Monte Carlo simulations to create porous structures and to calculate their associated effective diffusivities. This requires an accurate representation of the pore space in the solid and efficient simulation of molecular displacements within the resulting structures. In this approach, tracer molecules explicitly probe relevant geometrical and topological properties that control transport because such features are naturally built into simulated structure. Clearly, a concern here is whether the actual pore structure is





properly represented. The level of morphological detail needed to describe transport can be achieved with reasonable accuracy and effort in only a few cases. Fortunately an important class of catalyst support structures, prepared by sol-gel processes, in one such special case. Below, we show that this family of solids can be represented and characterized accurately by computer simulation.

### 3.2.3. PORE STRUCTURE MODELS FOR DIFFUSION/REACTION

Pore structure models are needed to quantify the interplay of diffusion and reaction within disordered porous materials. The scope of models varies widely depending upon their application. The most comprehensive models include descriptions of dynamic pore structures. Their development was motivated primarily by description of non-catalytic gas-solid reactions where solid structures change with time. These models can also be used for a priori design of catalyst support structures and for describing heterogeneous catalytic systems that are affected by structural changes arising from physical processes or by deactivating coke decomposition reactions. The latter case is frequently observed in the catalytic processing of hydrocarbon mixtures.

Early models described the structures as bundle of straight, non intersecting, cylindrical capillaries of varying diameter. These models were later improved to account for pore intersections and random orientations. The highly disordered structure makes random interconnection models very useful. Random pore models adequately capture key structural features of the void space within disordered porous materials. Model descriptions of their physical properties are, however, not straight forward; analytical solutions exist only in a few special cases. They generally do not allow analytical diffusivity estimates, a major obstacle in their use to describe diffusion – limited chemical reactions.

Empirical diffusivity relationships are sometimes used with models. Another popular approach is the use of percolation theory; here pore structures are described as subdivisions of space into solid and void cells that obey certain geometrical and topological arrangements. Physical and transport properties are obtained by direct probing of the structure using Monte Carlo simulations. In many cases these percolation theory models provide a better porous solid representation than that of random pore models but require more extensive compute simulation.



Subdividing the space (solid/voids) into the appropriate size and shape- filling subparts is not straight forward.

### 3.2.4 OPTIMUL DESIGN OF POROUS CATALYST SUPPORTS

Extensive literature exists in the general area of optimal catalyst design. The strategies vary widely in the variables chosen for optimization and in the objective functions (selectivity, activity, stability) that are minimized or maximized. The most comprehensive formulations search for an optimal catalyst loading profile within a pellet, one that maximizes rate/selectivity arbitrary kinetic schemes and nonisothermal conditions. A basic assumption in these approaches is that the structure (porosity and pore sizes) is fixed and not subject to optimization; therefore much of the complexity involved in relating diffusion-reaction processes to pore space morphology is avoided.

Structural features bring additional complexity to the design process and limit our ability to address these problems theoretically. In practice, the process of selecting a suitable porous material to support catalytically active components involves an empirical approach. This is because in most cases it is not apparent which support properties (porosity, pore size and surface area) are required to maximize a given reaction rate or selectivity.

As the structure becomes part of the design process, we must analyze coupling of diffusion and reaction in terms of the catalyst volumetric activity (molecules reacted per unit time and per unit volume of catalyst). This volumetric activity becomes a key parameter in the design of heterogeneous catalyst, it represents reciprocal of a characteristic reaction time; it can be described as a product of three quantities: turnover rate ( $v$ , molecules/site-s), site density ( $\Theta$  sites/m<sup>2</sup>), and surface area per unit volume ( $a_v$ , m<sup>2</sup>/m<sup>3</sup>). These quantities characterize the catalyst intrinsic kinetics, the catalyst loading effectiveness, and the pore volume properties of the support respectively.

This definition of volumetric activity suggests that several combinations of its defining properties can lead to the same catalyst productivity. However, changes in the volumetric activity caused by changes in the support surface area also affect the pore size distribution, the porosity and thus the characteristic diffusion times. As a result, high volumetric activities tend to cause diffusional limitations. When this occurs, the characteristic length scale over which



reaction takes place become much shorter than pellet dimensions, leading to concentration gradient. Depletion of reactants or build up of products affects the rate and selectivity of chemical reactions; therefore, the design of catalyst pellet requires proper balance of characteristic reaction and diffusion times. Theoretical estimates of such a balance requires realistic and tractable pore structure models that describe accessible surface area and effective diffusivity in terms of support porosity and pore sizes.

### **3.3 METHODS/ PROCEDURES**

#### **3.3.1 SIMULATION OF CATALYST SUPPORT STRUCTURES**

##### **3.3.1.1 RANDOM PORE NETWORKS (BETHE NETWORKS)**

Here we discuss the use of Bethe Networks as models of the void space within disordered porous solids. In conventional random pore models, connectivity among pore arises from the random placement of the inter-penetrating pores of various dimensions within a control volume until a specified porosity level is achieved. In Bethe networks, we begin instead with a well defined topological network that we can modify to match the porosity and pore size in a given structure. These networks allow analytical evaluation to its topological and transport properties.

Bethe networks are infinite branching trees without reconnecting branches and fully characterized by a coordination number or connectivity  $z$ . the connectivity  $z$  is the number of bonds emanating from each branching point. A related topological network is obtained by randomly removing a fraction of the initial bonds in the network to match the experimental porosity. The resulting network contains structural features that closely resemble those in actual pore structures: isolated bonds or clusters of bond, tortuous trajectories, and dead ends. A diameter can be assigned at random to each of the remaining bonds according to an arbitrary distribution function. This introduces random fluctuations of pore sizes within local pore dimensions, an important feature of porous materials.

These random pore networks reproduce many of the connectivity and diffusivity properties of more complex three dimensional model structures. In particular, the fraction of original branches that remains reflects the experimental porosity, and the size distribution function is given by the experimentally measured pore size distribution. Only the connectivity  $z$  remains to be specified;



it can be used as adjustable parameters or estimated indirectly from mercury porosimetry or particular fragmentation measurements

### 3.3.1.2 THREE DIMENSIONAL STRUCTURES (SPHERICAL AGGREGATES)

In this section we describe the use of Monte Carlo simulation as an alternative procedure for creating three-dimensional model porous structures. This approach allows more realistic representation of pore space than that of random pore model. In particular, we describe structures in an important class of porous materials obtained by sol-gel processes and commonly used as catalyst supports. They can be described by random assemblages of spheres, structures well suited for computer simulations, because these materials are prepared by aggregating and coalescing spherical micro-particles. We have developed a flexible algorithm for the random packing of spherical particles and for the subsequent modification of the solid porosity; the resulting structures closely resemble porous supports obtained by compression and sintering of spherical aggregates.

The sol-gel technique for preparing porous ceramic materials is well known. Typically, a solution of metal salt is converted by controlled pH precipitation into a colloidal dispersion of spherical particles of micrometer or sub-micrometer dimension. The colloidal dispersion is aged into a gel that is ultimately formed into granules, pellets, tablets, extrudates of desired dimension. Mechanical strength and pore volume characteristics are controlled by the size of the micro-particles and by the degree of compression and sintering during the subsequent treatments. As in actual synthesis procedures, a computer model of these materials is addressed in two stages. First, we create a loose gel structure by randomly assembling spherical particles in three dimensions. Then we modify the porosity to capture structural changes that occur during compression and sintering. There are several ways of assembling spherical particles randomly in three dimensional. Random-poured (RP), random close (RC), and random loose (RL) are the packing arrangements that differ only in how spheres cluster around each other in gravitational field. The simultaneous dropping of many spheres into a containers leads to RP packing. Vigorous shaking converts such aggregates into RC structures. Slow settling of spheres, one at a time at random locations, leads to RL packing. For monosize spheres, RC, RP and RL packings have void fractions of about 0.36, 0.39 and 0.42, respectively. These values are comparable to void fractions found clusters of dried gel like structures. Thus any of these packing arrangements



can provide a reasonable description of sphere aggregates before porosity modification. Computationally, however, RL packings offer clear advantages over RP and RC structures; sequential random placement processes involves simpler algorithms than descriptions of the many particles interactions in RP and RC packings.

### **3.4 RESULTS**

#### **3.4.1 POROSITY**

Porosities in catalyst supports typically range between 10% and 60%. Inaccessible porosity in compressed aggregates of microsphere is usually low. Porosity is an important catalyst design variable; it has a major impact on mechanical strength but also affects the diffusion rates and internal surface area. The porosity of sol-gel derived materials is controlled primarily by the level of compression and sintering of the microspheres that form the solid. In our simulations, the highest porosity level in compressed solids is that of starting random loose structure, which is about 0.42 for monosize spheres; it is slightly lower in aggregates of multisize spheres because smaller spheres can fill interstices between larger ones. It can also be greater than 0.42 in simulated solids with bimodal pore size distribution. The solids consist of spheres of uniform size unless otherwise noted. The lower porosity limit is theoretically zero in compressed structure because porosity can be simply destroyed by growing the radii of the microspheres to large dimensions. The growth process is carried out at random; the level of growth obeys a Gaussian function. The growth process is carried out until the porosity of about 5% is reached; this also provides a starting material for simulated sintered structures. In the latter the porosity is increased by simply removing the microspheres at random.

In both model structures, actual porosities at any stage of compression or sintering are computed by a simple algorithm. It consists of randomly throwing points within a representative porous sample and monitoring how often the points fall within the voids. The porosity level is simply the probability that points fall within voids. A few hundred thousand points within a macroscopic sample are typically required to calculate porosities with an accuracy of 99%.



### 3.4.2 SURFACE AREA

The surface area of the support provides a measure of the amount of active catalyst sites that can be placed within the pore structure. Surface area depends on pore size; thus it affects not only the volumetric activity of the ultimate catalyst sample but also the diffusivities of molecules within it. Here we report surface areas per unit volume for compressed and sintered structures as a function of porosity. We compare such results with those of simple surface area porosity relationship that we have used previously to describe the evolution of surface area in dynamic structures described by Bethe network. The maximum surface area arises at an intermediate porosity due to creation and destruction of pore surfaces as porosity increase.

Using Bethe network surface area per unit volume ( $a_v$ )

$$a_v = K [ \{ \Phi * (\Phi - 1) \} - \{ \Phi^I ( 1 - \Phi^I ) \} ]$$

$a_v$  – surface area per unit volume

K – constant

$\Phi$  – porosity

$\Phi^I$  – inaccessible porosity

For simplicity we have assumed that  $\Phi^I=0$  (i.e.  $z$  is large ) and adjusted the constant K to match the maximum surface area value in three dimensional sphere aggregates.



## Chapter 4

### PROGRAMS TO SIMULATE THE NOBLE METALS ON ALUMINA BED

THIS PROGRAM GIVES THE CONVERSION FOR HYDROGENATION OF TOLUENE ON GAMMA ALUMINA SUPPORT.

#### 4.1 THE COMPOSITION OF FEED (wt%) IS

FEED	PERCENTAGE
Cyclohexane	10%
Toluene	40%
Hexane	50%

#### 4.2 THE OPERATING CONDITIONS ARE

TEMPERATURE	350°C
PRESSURE	60 bar
LHSV	2
Amount of Catalyst	30 gm
P <sub>H2</sub>	40bar

#### 4.3 DATA REFERENCE:

Ahuja S. Thesis



#### 4.4 PROGRAM I

```
# include <iostream.h>
# include <conio.h>
# include <math.h>
void main()
{
int choice,pt,pd,re,ni,mo,w,co,x;
float con;
clrscr();
cout<<"          THE SUPPORT IS GAMMA ALUMINA";
cout<<"\n          CHOOSE CATALYST FOR HYDROGENATION";
cout<<"\n\n\nENTER 1 FOR PLATINUM AND RHENIUM";
cout<<"\n\n\nENTER 2 FOR PALLADIUM AND RHENIUM";
cout<<"\n\n\nENTER 3 FOR PLATINUM";
cout<<"\n\n\nENTER 4 FOR PALLADIUM";
cout<<"\n\n\nENTER 5 FOR NICKLE AND TUNGSTEN";
cout<<"\n\n\nENTER 6 FOR COBALT AND MOLYBDNUM";
cout<<"\n\n\nENTER 7 FOR NICKLE AND MOLYBDNUM";
cout<<"\n\n\nENTER 8 FOR COBALT AND TUNGSTEN";
cout<<"\n\n\nENTER YOUR CHOICE";
cin>>choice;
clrscr();
if(choice==1)
    {
    cout<<"\n\n\nENTER THE PERCENTAGE OF PLATINUM\n";
    cin>>pt;
    re=100-pt;
    if(pt==100)
        con=90;
    else if(pt==75)
        con=90;
    else if(pt==50)
        con=90;
    else if(pt==34)
        con=34;
    else if(pt==0)
        con=0;
    else if(pt>33)
        con=90;
    else if(pt<=33)
        {
```





```
        x=pt;
        con=(90/33)*x;
    }
    cout<<"THE BEST CONVERSION OF 90% IS OBTAINED AT 34%
    PLATINUM\n ";
    cout<<"FOR CONCENTRATION OF PLATINUM GREATER THAN 34% THE
    CONVERSION IS SAME";
    }

else if(choice==2)
{
    cout<<"ENTER THE PERCENTAGE OF PALLIDIUM\n";
    cin>>pd;
    if(pd==100)
        con=61;
    else if(pd>=75 && pd<100)
    {
        x=pd-75;
        con=61+(0)*x;
    }
    else if(pd>=50 && pd<75)
    {
        x=pd-50;
        con=59+(0.08*x);
    }
    else if(pd>=34 && pd<50)
    {
        x=pd-25;
        con=61-(0.08*x);
    }
    else if(pd>=0 && pd<34)
    {
        x=pd;
        con=(61/25)*x;
    }
    cout<<"THE BEST CONVERSION OF 61% IS OBTAINED 34%
    PALLIDIUM\n";
    }
if(choice==3)
{
    cout<<"\n ENTER THE PERCENTAGE OF PLATINUM\n";
```



```

cin>>pt;
    if(pt==100)
        con=91;
    else if(pt>=75 && pt<100)
        {
            x=pt-75;
            con=67+(24/25)*x;
        }
    else if(pt>=50 && pt<75)
        {
            x=pt-50;
            con=43+(24/25)*x;
        }
    else if(pt>=25 && pt<50)
        {
            x=pt-25;
            con=19+((24/25)*x);
        }
    else if(pt>=0 && pt<25)
        {
            x=pt;
            con=0+((19/25)*x);
        }

```

cout<<"\nA MAXIMUM CONVRSION OF 91% IS OBTAINED WHEN PLATINUM IS 100%\n";

cout<<"\nTHE SAME CONVERSION CAN BE ATTAINED WITH 34% PLATINUM AND 66% RHENIUM\n";

```

}
if (choice==4)
{
cout<<"\nENTER THE PERCENTAGE OF PALLIDIUM\n";
cin>>pd;
    if(pd==100)
        con=61;
    else if(pd>=75 && pd<100)
        {
            x=pd-75;
            con=45+((16/25)*x);
        }
    else if(pd>=0 && pd<75)
        {

```



```
        x=pd;
        con=(45/75)*x;
    }
    cout<<"\nTHE MAXIMUM CONVERSION OF 61% IS OBTAINED WHEN Pd IS
100%\n";
    cout<<"\nTHE SAME CONVERSION CAN BE OBTAINED WITH 34%Pd IN
PRESENCE OF Re\n ";
    }
    if(choice==5)
    {
        cout<<"\nENTER THE PERCENTAGE OF TUNGSTEN\n";
        cin>>w;
        if(w==100)
            con=4;
        else if(w>=88 && w<100)
        {
            x=w-88;
            con=28-((24/22)*x);
        }
        else if(w>=80 && w<88)
        {
            x=w-80;
            con=41-((13/8)*x);
        }
        else if(w>=75 && w<80)
        {
            x=w-75;
            con= 37.5+ ((3.5/5)*x);
        }
        else if(w>=0 && w<75)
        {
            x=w;
            con= (37.5/75)*x;
        }
        cout<<"\nTHE MAXIMUM CONVERSION OF 41% IS OBTAINED WITH 80% W
and 20% Ni\n ";
    }
    if(choice==6)
    {
        cout<<"\nENTER THE PERCENTAGE OF MOLYBDNUM\n";
```



```
cin>>mo;
    if(mo==100)
        con=5;
    else if(mo>=79 && mo<100)
        {
            x=mo-79;
            con=11-((6/21)*x);
        }
    else if(mo>=75 && mo<79)
        {
            x=mo-75;
            con=12-((1/4)*x);
        }
    else if(mo>=67 && mo<75)
        {
            x=mo-67;
            con=11+((1/8)*x);
        }
    else if(mo>=50 && mo<67)
        {
            x=mo-50;
            con=6.5 +((4.5/17)*x);
        }
    else if(mo>=25 && mo<50)
        {
            x=mo-25;
            con= 3+((3.5/25)*x);
        }
    else if(mo>=0 && mo<25)
        {
            x=mo;
            con= 0+((3/25)*x);
        }
}
```

cout<<"\nTHE MAXIMUM CONVERSION OF 12% IS OBTAINED FOR COMBINATION  
75%Mo and

25%Co ";

```
}
if(choice==7)
```

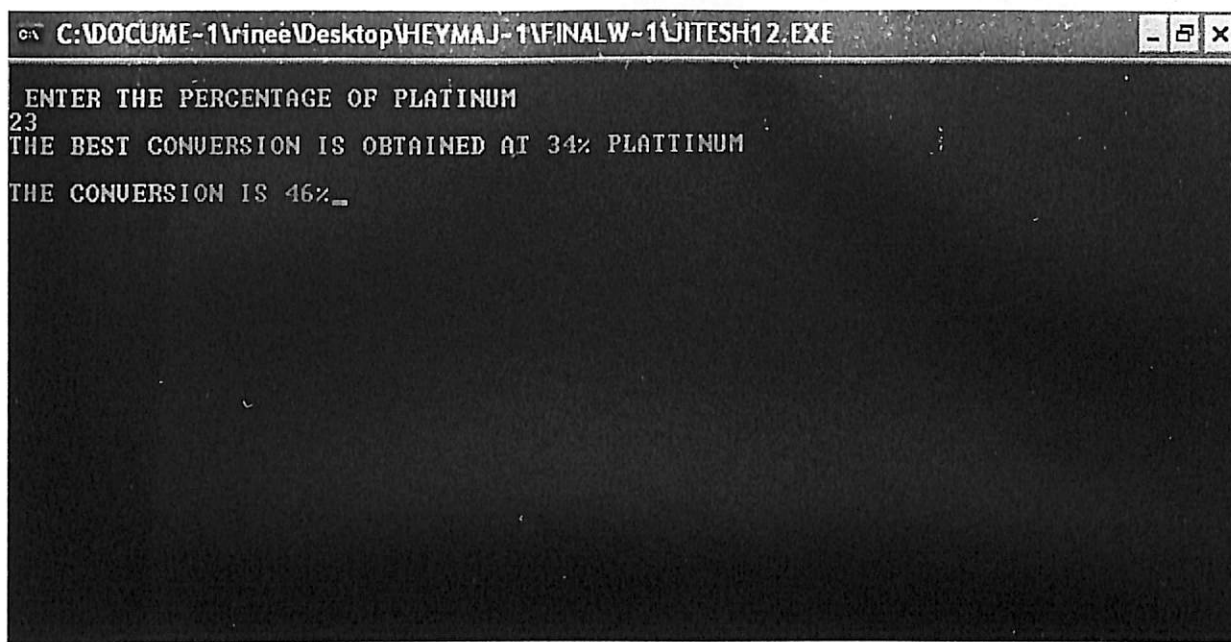


```
{
cout<<"\nENTER THE PERCENTAGE OF MOLYBDNUM";
cin>>mo;
    if(mo==100)
        con=3;
    else if(mo>=90 && mo<100)
        {
            x=mo-90;
            con=12-((9/10)*x);
        }
    else if(mo>=80 && mo<90)
        {
            x=mo-80;
            con=15 -((3/10)*x);
        }
    else if(mo>=75 && mo<80)
        {
            x=mo-75;
            con=14 +((1/5)*x);
        }
    else if(mo>=67 && mo<75)
        {
            x=mo-67;
            con=12.5 + ((1.5/8)*x);
        }
    else if(mo>=50 && mo<67)
        {
            x=mo-50;
            con=6.5+ ((6/17)*x);
        }
    else if(mo>=25 && mo<50)
        {
            x=mo-25;
            con=4+((2.5/25)*x);
        }
    else if(mo>=0 && mo<25)
        {
            x=mo;
            con=(4/25)*x;
        }
}
```



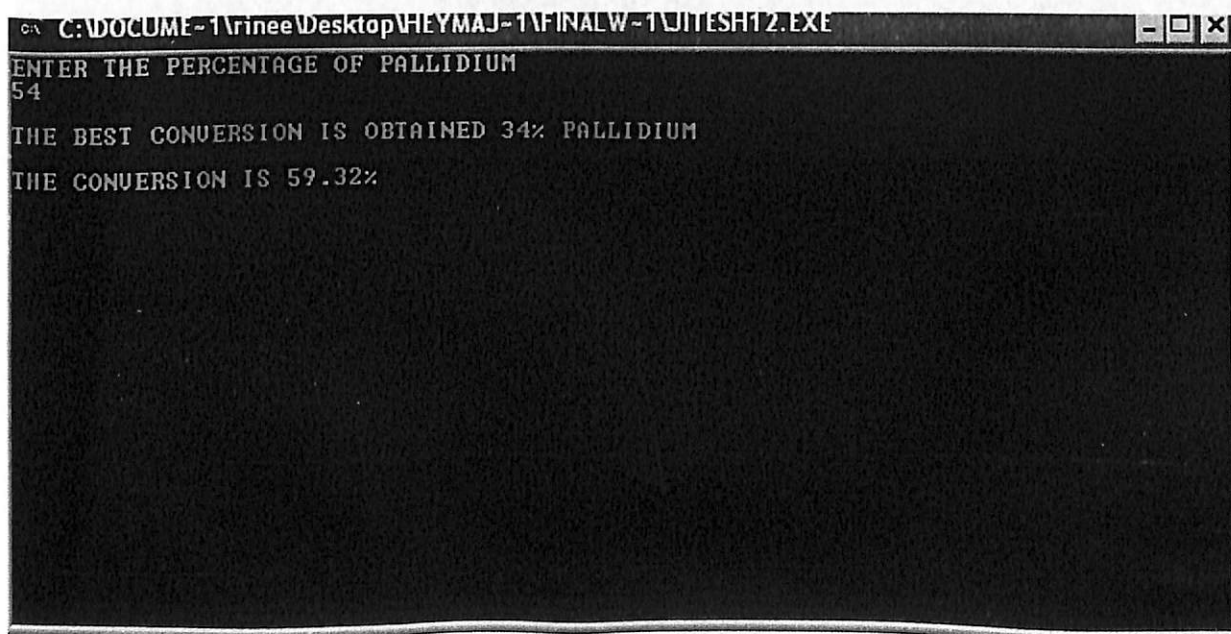
```
cout<<"\nTHE MAXIMUM CONVERSION OF 15% IS OBTAINED WITH
80%Mo and 20%Ni";
}
if(choice==8)
{
cout<<"\nENTER THE PERCENTAGE OF TUNGSTEN";
cin>>w;
if(w==100)
con=2;
else if(w>=90 && w<100)
{
x=w-90;
con=12-((9/10)*x);
}
else if (w>=80 && w<90)
{
x=w-80;
con=15-((3/10)*x);
}
else if(w>=75 && w<80)
{
x=w-75;
con=6.5+((1.5/5)*x);
}
else if(w>=50 && w<75)
{
x=w-50;
con=2 + ((4.5/25)*x);
}
else if(w>=0 && w<50)
{
x=w;
con=((2/50)*x);
}
cout<<"\nTHE MAXIMUM CONVERSION OF 8% IS OBTAINED WITH 80%W
and 20%";
}
cout<<"\nTHE CONVERSION IS "<<con<<"%";
getch();
}
```

#### 4.5 RESULT



```
C:\DOCUME-1\vinee\Desktop\HEYMAJ-1\FINALW-1\JITESH12.EXE
ENTER THE PERCENTAGE OF PLATINUM
23
THE BEST CONVERSION IS OBTAINED AT 34% PLATTINUM
THE CONVERSION IS 46%_
```

Fig 4.5



```
C:\DOCUME-1\vinee\Desktop\HEYMAJ-1\FINALW-1\JITESH12.EXE
ENTER THE PERCENTAGE OF PALLIDIUM
54
THE BEST CONVERSION IS OBTAINED 34% PALLIDIUM
THE CONVERSION IS 59.32%
```



```
C:\DOCUME-1\rinee\Desktop\HEYMAJ-1\FINALW-1\JITESH12.EXE
ENTER THE PERCENTAGE OF PLATINUM
45
A MAXIMUM CONURSION OF 91% IS OBTAINED WHEN PLATINUM IS 100%
THE SAME CONVERSION CAN BE ATTAINED WITH 34% PLATINUM AND 66% RHENIUM
THE CONVERSION IS 19%_
```

```
C:\DOCUME-1\rinee\Desktop\HEYMAJ-1\FINALW-1\JITESH12.EXE
ENTER THE PERCENTAGE OF PALLIDIUM
67
THE MAXIMUM CONVERSION OF 61% IS OBTAINED WHEN Pd IS 100%
THE SAME CONVERSION CAN BE OBTAINED WITH 34%Pd IN PRESENCE OF Re
THE CONVERSION IS 0%
```



```
C:\DOCUME-1\rinee\Desktop\HEYMAJ-1\FINALW-1\JITESH12.EXE
ENTER THE PERCENTAGE OF TUNGSTEN
87
THE MAXIMUM CONVERSION OF 41% IS OBTAINED WITH 80% W and 20% Ni
THE CONVERSION IS 34%
```

```
C:\DOCUME-1\rinee\Desktop\HEYMAJ-1\FINALW-1\JITESH12.EXE
ENTER THE PERCENTAGE OF MOLYBDNUM
56
THE MAXIMUM CONVERSION OF 12% IS OBTAINED FOR COMBINATION 75%Mo and 25%Co
THE CONVERSION IS 8.088235%
```



```
C:\DOCUME~1\rinee\Desktop\HEYMAJ-1\FINALW-1\JITESH12.EXE
ENTER THE PERCENTAGE OF MOLYBDNUM67
THE MAXIMUM CONVERSION OF 15% IS OBTAINED WITH 80%Mo and 20%Ni
THE CONVERSION IS 12.5%
```

```
C:\DOCUME~1\rinee\Desktop\HEYMAJ-1\FINALW-1\JITESH12.EXE
ENTER THE PERCENTAGE OF TUNGSTEN 63
THE MAXIMUM CONVERSION OF 8% IS OBTAINED WITH 80%W and 20%
THE CONVERSION IS 4.34%
```



Bethe network permit the evaluation of topological and diffusivity properties in analytical form, a distinct advantage over random capillary network models. A useful property of Bethe networks is that they exhibit classical percolation behavior: a minimum fraction of bonds is required to find a connected path spanning a large region of space. This fraction is defined as percolation threshold  $\phi_c$ ; it is related to connectivity  $z$  by

$$\phi_c = 1/(z-1)$$

the percolation threshold gives the minimum fraction of the bonds required for the network to have conductivity; below  $\phi_c$ , the bonds remain as isolated bonds and cluster of bonds. The percolation threshold is also a measure of connectivity of pore spaces; the smaller the threshold is, the more connected the pores I the network.

Another property of Bethe network that is relevant to reaction and transport is pore accessibility within the network. That is, what is the probability that a given bond belongs to a cluster that spans the sample? This quantity is defined as accessible porosity  $\phi^A$ ; it measures the fraction of pores in the network that can be reached from a distant peripheral location.

$$\phi^A = 0 \text{ if } \phi < \phi_c \quad \text{if } \phi > \phi_c$$

Thus the fraction of closed or isolated pores ( $\phi^I$ ) in a Bethe network having porosity  $\phi$  and connectivity  $z$  is simply given by

$$\phi^I = \phi - \phi^A(\phi, z)$$

Clearly,  $\phi^A$  is critical to describe dynamic structures because it detects isolated pores that become accessible ( and accessible pores that become isolated) because of chemical reactions or physical processes taking place within the pore space. To describe transport properties, it is convenient to separate the accessible porosity into conducting backbones ( $\phi^B$ ) and dead-end regions ( $\phi^D$ ):

$$\phi^D = 2[\phi^A - \phi + (\phi(\phi - \phi^A))^{1/2}]$$

$$\phi^B = \phi^A - \phi^D$$

Using Bethe network surface area per unit volume ( $a_v$ )

$$a_v = K [ \{ \phi * (\phi-1) \} - \{ \phi^I ( 1 - \phi^I) \} ]$$

$a_v$  – surface area per unit volume



K – constant

$\Phi$  – porosity

$\Phi^I$  – inaccessible porosity

For simplicity we have assumed that  $\phi^I=0$  (i.e. z is large ) and adjusted the constant K to match the maximum surface area value in three dimensional sphere aggregates.

#### 4.6 PROGRAM II

```
# include <iostream.h>
# include <conio.h>
# include <math.h>
void main()
{
float p, critp, accessp, deadp, isolp, backp, av, n,m;
int z=4,a;
clrscr();
cout<<"ENTER THE POROSITY ";
cin>>p;
critp=0.33;
if(critp>=p)
accessp=0;
else if(p>=critp && p<0.4)
accessp=0.33*p;
else if (p>=0.4 && p<0.5)
accessp=0.80*p;
else if(p>=0.5 && p<0.6)
accessp= 0.833*p;
```



```
else if (p>=0.6 && p<0.7)
accessp=0.86*p;
else if (p>=0.7 && p<0.8)
accessp=0.88*p;
else if (p>=0.8 && p<0.9)
accessp= 0.89*p;
else if (p>=0.9 && p<1)
accessp=0.95*p;
else if (p==1)
accessp=1;
isolp=p-accessp;
n=isolp*p;
m=pow(n,0.5);
deadp=2*(accessp-p+m);
backp=accessp-deadp;
av=6.5*(1-p)*p;
cout<<"\n THE POROSITY ENTERED IS "<<p;
cout<<"\n\n THE CRITICAL POROSITY IS "<<critp;
cout<<"\n\n THE ACCESSIBLE POROSITY IS "<<accessp;
cout<<"\n\n THE ISOLATED POROSITY IS "<<isolp;
cout<<"\n\n THE DEAD POROSITY IS "<<deadp;
cout<<"\n\n THE BACKBONE POROSITY IS "<<backp;
cout<<"\n\n THE SURFACE AREA PER UNIT VOLUME IS "<<av;
getch();
}
```



## CHAPTER 5

### CONCLUSION

Porosities in catalyst supports typically range between 10% and 60%. Inaccessible porosity in compressed aggregates of microsphere is usually low. Porosity is an important catalyst design variable; it has a major impact on mechanical strength but also affects the diffusion rates and internal surface area.

The actual porosities at any stage of compression or sintering are computed by a simple algorithm. It consists of randomly throwing points within a representative porous sample and monitoring how often the points fall within the voids. The porosity level is simply the probability that points fall within voids. A few hundred thousand points within a macroscopic sample are typically required to calculate porosities with an accuracy of 99%.

This fraction is defined as percolation threshold  $\phi_c$ ; it is related to connectivity  $z$  by

$$\phi_c = 1/(z-1)$$

This quantity is defined as accessible porosity  $\phi^A$ ; it measures the fraction of pores in the network that can be reached from a distant peripheral location.

$$\phi^A = 0 \text{ if } \phi < \phi_c \quad \text{if } \phi > \phi_c$$

Thus the fraction of closed or isolated pores ( $\phi^I$ ) in a Bethe network having porosity  $\phi$  and connectivity  $z$  is simply given by

$$\phi^I = \phi - \phi^A(\phi, z)$$

Clearly,  $\phi^A$  is critical to describe dynamic structures because it detects isolated pores that become accessible ( and accessible pores that become isolated) because of chemical reactions or physical processes taking place within the pore space. To describe transport properties, it is convenient to separate the accessible porosity into conducting backbones ( $\phi^B$ ) and dead-end regions ( $\phi^D$ ):

$$\phi^D = 2[\phi^A - \phi + (\phi(\phi - \phi^A))^{1/2}]$$

$$\phi^B = \phi^A - \phi^D$$



## Metal dispersion and porosity on active sites for reforming of hydrocarbons - A comparison

The surface area of the support provides a measure of the amount of active catalyst sites that can be placed within the pore structure. Surface area depends on pore size; thus it affects not only the volumetric activity of the ultimate catalyst sample but also the diffusivities of molecules within it. Here we report surface areas per unit volume for compressed and sintered structures as a function of porosity. We compare such results with those of simple surface area porosity relationship that we have used previously to describe the evolution of surface area in dynamic structures described by Bethe network. The maximum surface area arises at an intermediate porosity due to creation and destruction of pore surfaces as porosity increase.

Using Bethe network surface area per unit volume ( $a_v$ )

$$a_v = K [ \{ \phi * (\phi - 1) \} - \{ \phi^I ( 1 - \phi^I ) \} ]$$

$a_v$  – surface area per unit volume

K – constant

$\Phi$  – porosity

$\Phi^I$  – inaccessible porosity

For simplicity we have assumed that  $\phi^I = 0$  (i.e.  $z$  is large ) and adjusted the constant K to match the maximum surface area value in three dimensional sphere aggregates.

Thus if porosity is known and the connectivity is known all other porosities namely Accessible porosity, Dead porosity, Backbone porosity and surface area per unit volume can be found out for particular network.



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