

CHAPTER – 1

INTRODUCTION

The available experimental facilities enable one to probe the behaviour of individual molecules under various environments. This is especially true in the elucidation of the surface species, surface intermediates or even the dynamics of surface transformations. A variety of experimental techniques are available for each of these investigations and at times one is at a loss to know what technique to use and what information to look for. There is a number of text books available dealing with the fundamentals of each of these techniques and it is not our intention to repeat them. The primary purpose of this monograph is to highlight the specific features of the techniques with respect to elucidation of catalytic materials, catalytic surface, and catalytic surface transformations and also lead one to understand and appreciate what technique to use when and what information to look for. There are a number of important and fundamental questions one has to clarify before one enters into a research programme in the field of surface science and catalysis and unfortunately no straight forward answers to these questions are available.

For example, one has to define what is meant by a surface, the top monolayer of the material or top few layers of the material which is at the interface between the bulk material and the surrounding medium. This brings us to the concept of interface.

- How do interfaces behave?
- Do they behave as an algebraic sum of the behaviour of the two phases?
- Do the phases at the interface retain their identity?
- If the phases are changed in configurations and structure, what is the driving force for such changes?
- To how many layers in each of these phases, these configurational changes are felt?
- From what depth or number of layers deep down from the surface or interface the bulk properties of these phases are manifested?
- If the surfaces and interfaces are a dynamic one, why do we need the study of the surfaces in static mode?
- Is it for the qualitative and quantitative elemental composition?
- Is it to assess whether there is any accumulation or depletion of species from other phases?
- Is there any accumulation of the species from one phase thus leading to binding at the surface.?
- What is the nature of this adsorption?
- What is the adsorption strength?
- What is the structure of the adsorbed state as compared to the free molecules in its own state?
- How do the properties of these molecules in the adsorbed state differ from that they exhibit in their free state?

One can easily see that not only the static properties but also the dynamics of these species present at the interface is altered in such a way that one has to reformulate his

expressions for transformation kinetics. This means that we are entering an area of chemistry which is different from that of the bulk properties or that of individual molecules, both of which are familiar and are easily amenable for study by chemists using a number of experimental tools at the disposal.

There are a variety of interfaces, like solid/solid, solid/liquid, liquid/liquid, solid/gas, liquid/gas and possibly gas/gas. All of them, though can be classified generally as interfaces, their interface properties can be quite different and hence may require independent treatment. Ideally, it will be good if one can treat all interfaces under one framework, but due to various limitations, we will be confining ourselves mainly to the solid/gas interface though some of the studies that we consider here can be extended to other interfaces like gas/liquid and solid/liquid interfaces as well.

The solid/gas interface is unique in many respects. Many of the chemical industrial processes that are practiced today, like cracking of petroleum crude, hydrogenation of fatty acids, oxidation of organic substrates are all reactions that take place on the surface of a solid catalyst by contacting the vapours of the reactants, even though some heterogeneous reactions are also carried out in solid/liquid interfaces. It appears, generally the principles involved in the surface catalytic reactions whether the substrate is in vapour state or in condensed liquid state to be the same and hence, it is necessary that one considers the adsorption of adsorbates on the surface of the solid by a suitable means. Since the surface on an atomic or molecular scale is heterogeneous with each of the sites being coordinatively unsaturated not to the same extent (refer to **Fig.1** reproduced from Ref.1.) each of these sites can exhibit totally different reactivity

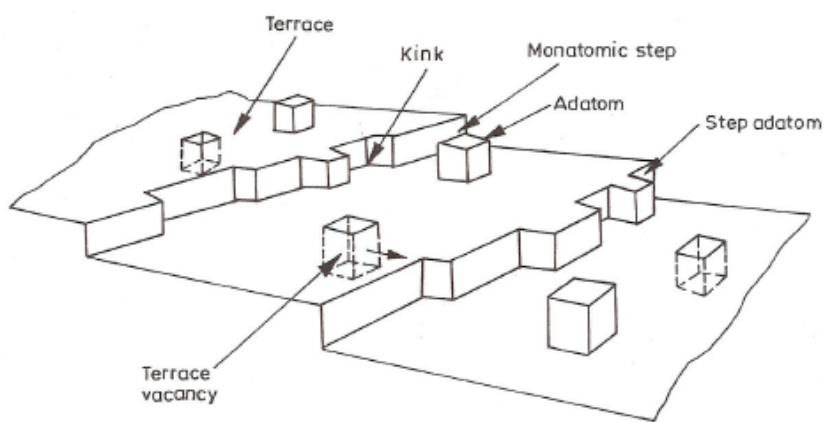


Fig. 1. Model of a heterogeneous solid surface, depicting different surface sites. These sites are distinguishable by their number of nearest neighbours

At this stage one is tempted to name these sites where the reactant molecules are formed into product molecules following the designation of Taylor [2] as the “active sites”. It is natural that one will ask what these active sites are?

- Are they defined in terms of geometry and surrounding coordination or in terms of energetic considerations?
- Are these active sites *a priori* formed on the surface before the surface comes into contact with the substrate or are they generated at the call of the substrate molecules?
- Are these so called “active sites” a dynamic concept or a static pictorial representation?

Many of the heterogeneous catalytic phases are usually supported on some (supposedly inert for the substrate) matrix like oxides which do not participate directly in the catalytic reaction. However, one has been encountering situations where the support interacts with the active metallic component and this state has been termed as (MSI). One such interaction has been well studied, termed as strong metal support interaction (SMSI) originally proposed by Tauster *et al* [3]. Metal support interactions or as a matter of fact, the combination of two solid phases have been shown to give rise to interesting electronic properties, a concept originally developed by Shawab and his coworkers [4]. This solid/solid interface and the consequent electronic properties have been addressed in terms of hetero junctions for solid state electronic applications. Another important observation that needs our attention is the possibility of the support acting as sink for the active species generated on metal sites at a fast rate compared to the desired catalytic reaction and the re-supply of these active species from the support to metal at a rate comparable to that of the catalytic reaction. This phenomenon is termed as “spill over” by Boudart [5]. Though spillover is considered with respect to hydrogen and oxygen, the concepts developed can be definitely extended to a number of adsorbed species which can be transported to and re-transported from the support with the help of suitable activation species. This means that one has to enlarge the scope of the definition of active sites, since these support oxide sites which act as sink for holding these active species and for their subsequent release, are they active sites or not? It appears that one has to start with the definition of the active site on which the reactant molecules are activated. When a substrate molecule interacts on such an active site, it can do so in a number of ways geometrically and this can result in various modes of adsorption. The possible modes of adsorption of CO and N₂ on typical well defined metallic surfaces are shown in **Fig.2**.

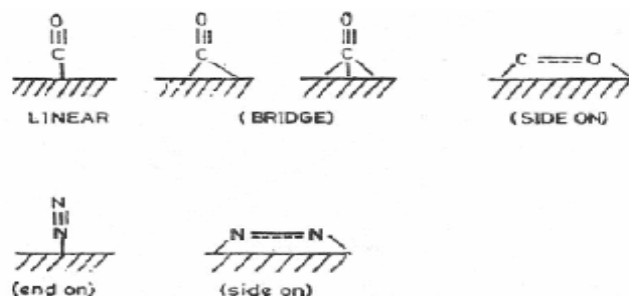


Fig. 2. Adsorbed states of CO and N₂ on metal surface

Similarly for many other molecules one can imagine multiple modes of adsorption [6] and the adsorption energy and adsorption geometry may also contribute to the product selectivity one observes in surface catalyzed reaction. Since the adsorption mode and energies decide which bonds are to be broken and which bonds are to be made, activation of substrates by adsorption always leads to product selectivity. However, there are other selectivities that are most often discussed in catalysis by zeolites. They are termed as reactant or product or transition state shape selectivity, in these cases, the selectivity is governed by the shapes of the species formed or taken so as to fit in the zeolite cages and channels. Since the void space in zeolites is similar to the molecular volumes it is necessary that only certain molecules are able to be accommodated or passed through the channels. Others without the particular shape or bigger molecules are trapped inside the cages and undergo transformations till they are able to pass through the zeolite channels. A pictorial representation of these three shape selectivities which are particularly applicable to micro porous systems are given in **Fig.3**. This brings us to the question of the surface area of a given solid. The actual surface area accessible to molecules may be greater than the geometrical area for the given shape of a catalyst. The particles constituting the catalyst pellet or ring or any other preformed shape may arrange themselves randomly so as to give rise to void volumes which are accessible to the reactant and product molecules. Even while forming the solid from suitable precursors like hydroxides, carbonates, sulphates, the elimination of water, CO, CO₂ or SO₂ and their expulsion from the solid oxide mass obtained could give rise to a porous structure.

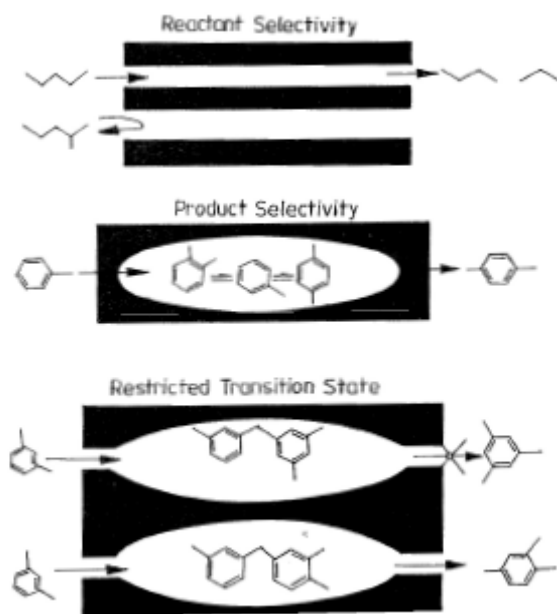


Fig. 3. Mechanism of shape selective catalysis

A third possibility is that the deposition or precipitation of the inorganic substances can take place on individual template molecules or on a preformed template structure. One of the typical mechanisms proposed for the generation of mesopores in materials is shown in **Fig.4**.

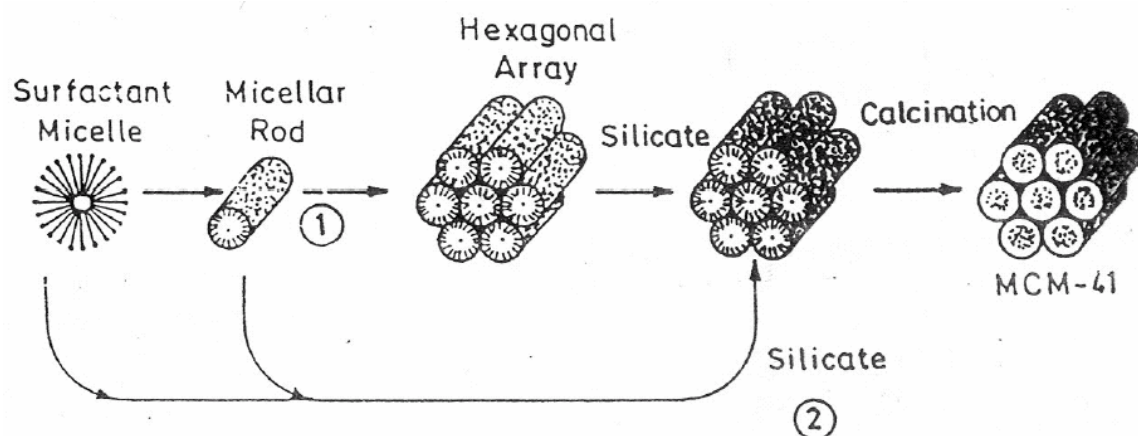


Fig. 4(a) Possible mechanistic pathways for the formation of MCM-41 : (1) liquid crystal initiated and (2) silicate anion initiated [7].

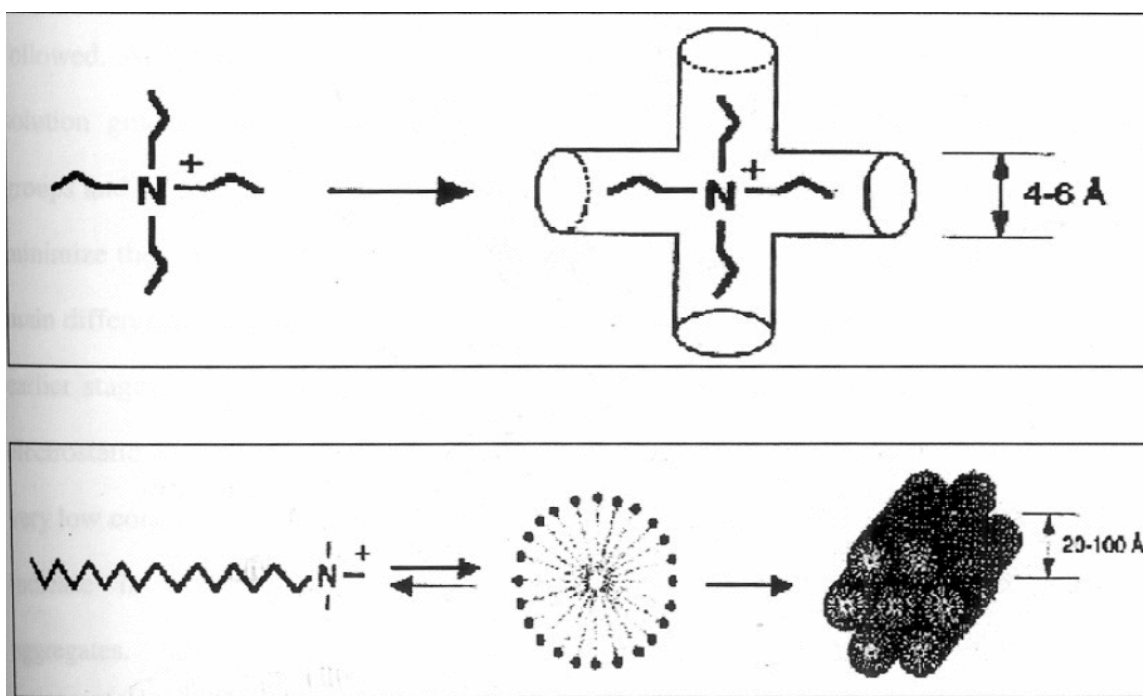


Fig. 4(b) Formation of micro-porous and mesoporous molecular sieves using small (top) and long (bottom) alkyl chain length (quaternary salts) directing agents

It is conceived that the individual template molecules gives rise to a micelle at a critical concentration of the surfactant used and these micelles aggregate to give rise to a preformed arrangement (hexagonal or cubic in this case) at another critical concentration on which the deposition of inorganic species take place. The other alternative is that once the micelles are formed at the first CMC (Critical Micelle concentration) the simultaneous presence of the inorganic species in the medium aids the formation of the

aggregates in particular geometries (cubic or hexagonal in this case) over which the inorganic phase builds up. Whatever is the sequence of events, one ends up in a system from the removal of the template molecules by suitable means (either by combustion or by solvent extraction) with regular uniform porous structure. Thus, it is possible to generate a porous texture with uniform narrow pore size distribution, as is often the case for zeolites or a wide pore size distribution (normally encountered in the oxides prepared from precipitated precursors). Typical pore-size distribution curves obtained for these extreme cases are shown in Fig.5.

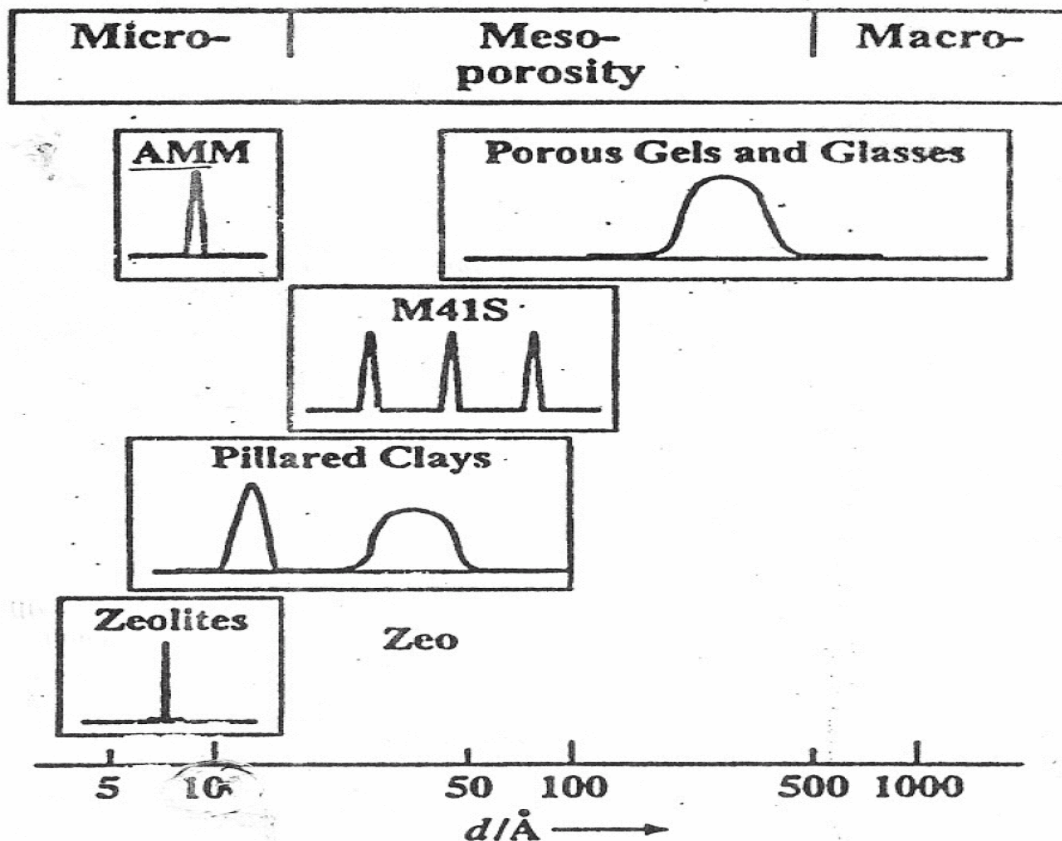


Fig.5 Pore size distribution curves: Porous solid materials are classified according to IUPAC as Microporous $d < 20 \text{ \AA}$ ---Zeolites, ALPO's; Mesoporous $20 \text{ \AA} < d < 500 \text{ \AA}$ ---M41S, HMS, MSU ; and Macroporous $d > 500 \text{ \AA}$ --- Perovskites, Glasses

The available pore architecture in many of these solids can modify the dynamics of surface reactions and the reaction sequence one observes may be resulting from traffic control of reactants and products inside the pores. Therefore, one has to carefully consider whether one is carrying out the reaction on the surface under a crowded situation or not. That is the extent of surface coverage (θ). As the molecules occupy the most reactive sites first and then occupy the other less reactive sites, the activation of molecules is a function of coverage. As coverage increases (i.e. as $\theta \rightarrow 1$) the adsorbed

molecules interact among themselves laterally and this interaction is superimposed on the interaction of reactant molecules with the surface atoms or species. The consequence of all these effects is manifested in the variation of the heat of adsorption or adsorption geometry as revealed by the LEED (Low Energy Electron Diffraction) patterns as a function of coverage. Ideally if the surface were to be homogeneous with all sites having equal adsorption potential then the heat of adsorption should be a constant up to $\theta = 1$.

In the case of supported catalysts there are yet other variables like the crystallite sizes and dispersion. For an efficient catalyst the ideal situation would be to disperse the active phase as a uniform monolayer on the surface of the support. Such a situation is shown in **Fig.6**. This situation is an ideal situation and what one achieves is a thin film consisting of a few layers of the active material on the support phase.

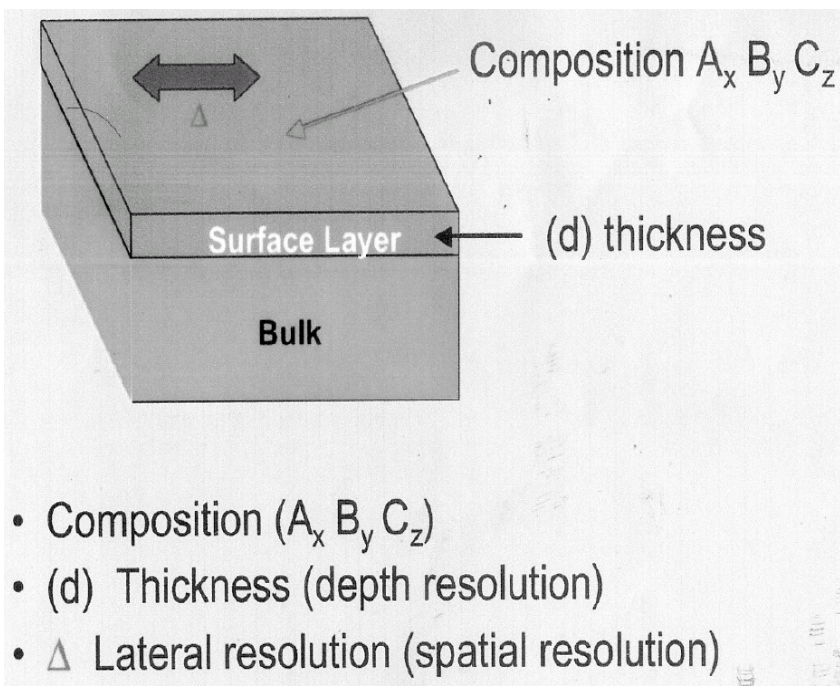


Fig. 6. Pictorial representation of dispersion of the active phase as a uniform monolayer

Thin films of this kind have various other important applications and these will not be considered in the present context. When the supported species crystallize and form a crystallite, then the number of atoms exposed will decrease with the total number of particles in the crystallite as well as the shape of the crystallite. One will be formation of clusters of atoms into simple cubic packing 8, 27, 64, 125, 216, 343, 512 atoms. In the 8 atom cluster all the atoms are present on the surface, however dispersion, D , defined as the ratio of the number of atoms on the surface to the total number of atoms in the

crystallite, decreases rapidly with increase in the total number of atoms in the clusters. The values of dispersion is also dependent on the shape of the cluster formed, and as an example, for a cubo-octahedral arrangement the variation of dispersion as a function of crystallite size is shown in **Fig. 7**.

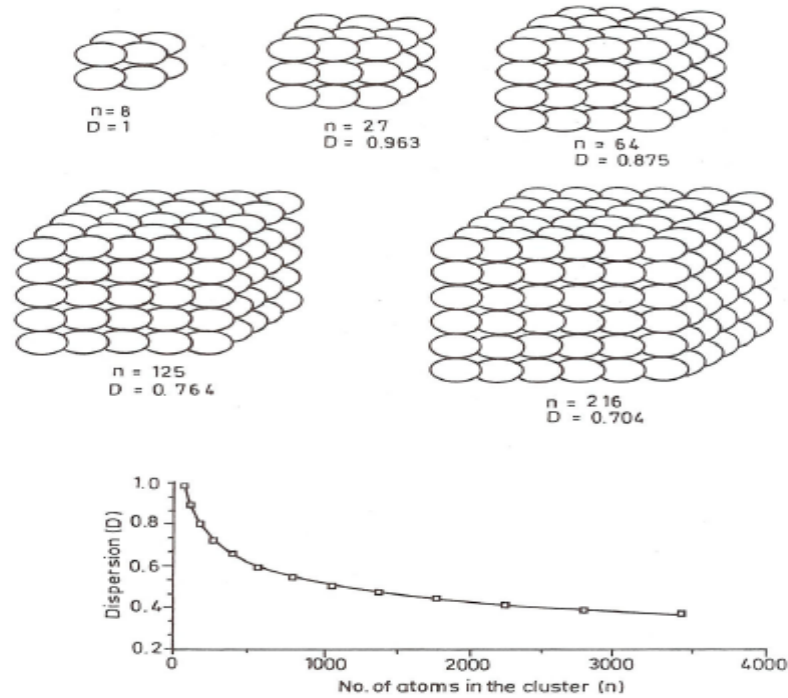


Fig. 7(a) Clusters of atoms with single cubic packing having 8, 27, 64, 125 and 216 atoms. In an eight-atom cluster, all of the atoms are on the surface. However, the dispersion D , defined as the number of surface atoms divided by the total number of atoms in the cluster, declines rapidly with increasing cluster size, this is shown in the lower part of the figure.

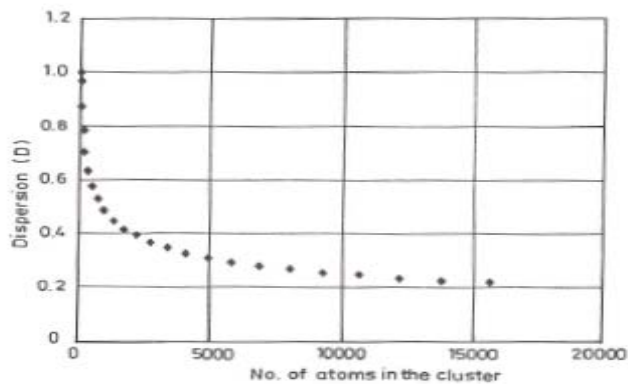


Fig. 7(b). Variation of dispersion as a function of number of atoms in the cluster

The most common variation of heat of adsorption as a function of coverage is shown in **Fig.8**.

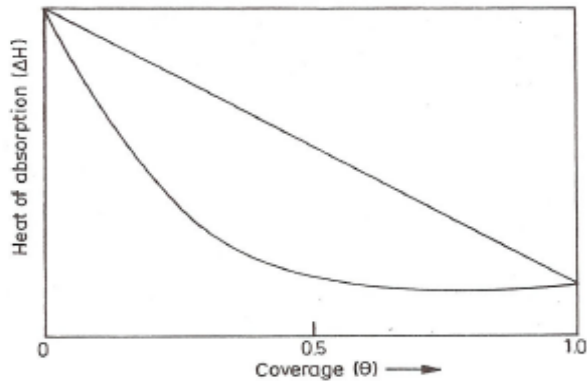


Fig. 8. Variation of heat of adsorption as a function of surface coverage

Typical data for the adsorption of CO and N₂ on different planes of single crystal metallic surfaces are assembled in **Tables 1 and 2**. It is seen that the LEED patterns changes typically from simple [1X1] to [$\sqrt{3}$ X $\sqrt{3}$ R 30] with increase in coverage. The data given in Tables 1 and 2 are meant to be representative ones. Depending on the type of surface and nature of substrates used, there can be many other adsorbate structures as revealed by LEED patterns. The electronic properties of the adsorbates also change on adsorption. Let us consider as example the adsorption of CO. The molecular orbital diagram in its ground state is shown in **Fig.9** and the appropriate molecular properties of neutral CO, CO⁺, CO⁻ and CO* are given in **Table 3**.

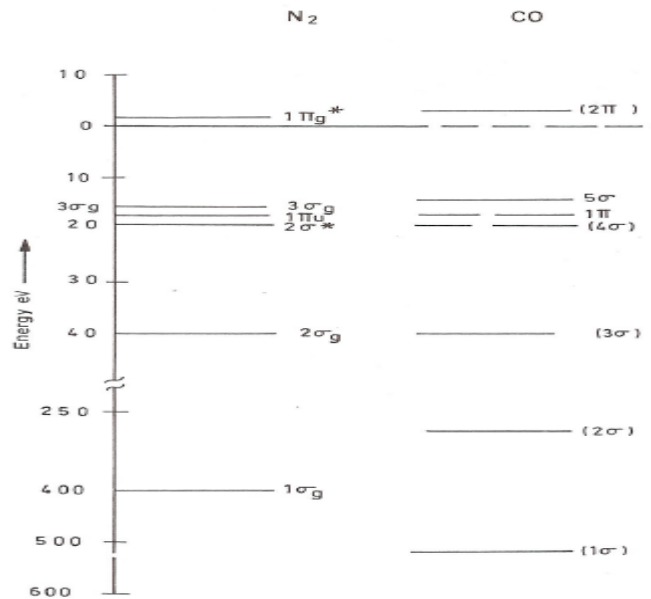


Fig. 9. The MO diagram of the ground state N₂ and CO

It is seen that the highest occupied states in free CO molecule are 5σ and 1π in this order. However, on adsorption the ordering 5σ and 1π is inverted or the photoemission from these two states overlap meaning that 1π level is shifted to lower binding energies or the energy required for ionization from 5σ level has increased. This aspect is normally

considered in terms of ($4\sigma - 1\pi$), the separation between 4σ and 1π levels. The relevant data for this $|4\sigma - 1\pi|$ separation between free molecules as well as for CO in the adsorbed state are assembled in **Table 4**. It is to be recognized that the position of the various energy levels in the free molecule is

Table 1 Parameters for the adsorption of carbon monoxide on single crystal metal surfaces(Data from S.Ishi, Y.Ohno and B.Viswanathan, J.Sci.Ind.Res., **46**, 541 (1987).)

Metal surface	Adsorbate structure	E kJ/mol	Work function change eV	N (C-O) cm ⁻¹
Fe(110)	C(4x2)	147	1.2	1890
Fe(111)	Diffuse (1x1)		1.6	1800
Ni(100)	C(2x2)	126	1.1	1916
Ni(110)	C(2x2)	126	1.3	1960
Ni(111)	($\sqrt{3}\times\sqrt{3}$)R30	113	1.1	1817
Ru(0001)	($\sqrt{3}\times\sqrt{3}$)R30	126	0.65	1984
Os(0001)	($\sqrt{3}\times\sqrt{3}$)R30	138.6		
Co(0001)	($\sqrt{3}\times\sqrt{3}$)R30		1.35	
Rh(111)	P(2x2)	134		1890
Ir(111)	($\sqrt{3}\times\sqrt{3}$)R30	142.8	0.18	
Pd(111)	($\sqrt{3}\times\sqrt{3}$)R30	142	1.0	1813
Pt(100)	C(2x2)	155.4	0.4	2080
Pt(111)	($\sqrt{3}\times\sqrt{3}$)R30	138.6	0.15	2065

Table 2 Typical parameters for the chemisorption of nitrogen on single crystal metal surfaces (Data from S.Ishi, Y.Ohno and B.Viswanathan, J.Sci.Ind.Res., **46**, 541 (1987).)

Metal surface	Temperature range	Adsorbate structure	Adsorption energy kJ/mol	Work function change eV	ν (N-N) cm ⁻¹
Fe(100)		C(2x2)	31.5		
Fe(111)	<100		31.5	0.14	
Ni(100)		C(2x2)			2200
Ni(110)	80-125	(2x1)	<47	0.1	2194
Ni(111)	20-100		20		2186
Cr(110)	100		14		
Ru(0001)	95	($\sqrt{3}\times\sqrt{3}$)R30	31.5		2252
Re(1120)	80		21-29		
W(110)	100		25		
Rh(111)			33.6	-0.15	
Ir(111)				-0.2	
Ir(100)			33.6		
Pt(100)			37.8	-0.3	
Pt(111)			38.6		2230

Table.3 Summary of molecular states of CO in neutral, ionic and excited states

	CO	CO ⁺	Co ⁻	CO*		Co*	
configuration	... $(1\pi)^4$ $(5\sigma)^2$... $(1\pi)^4$ $(5\sigma)^1$... $(1\pi)^4$ $(5\sigma)^2(2\pi)^1$... $(1\pi)^4$ $(5\sigma)^1(2\pi)^1$	 $(1\pi)^3(5\sigma)^2(2\pi)^1$	
				(↑↑)	(↑↓)	(↑↑)	(↑↓)
State	$^1\Sigma^+$	$^2\Sigma^+$	Π	A $^1\Pi$	A' $^3\Pi$	$^3\Sigma^+$	I' $^2\Sigma^+$
R _e A	1.13	1.12	1.17	1.21	1.24	1.35	1.39
N (CO) cm ⁻¹	2143	2214	~1850	1743	1518	1229	1092
D (eV)	11.2	8.4	8.1	5.21	3.17	4.32	3.17
M(Debye)	0.1 (CO ⁺)			1.38 +CO ⁻		1.06 -CO ⁺	
I (eV)	14.01	26.8	-1.5				

Reproduced from S.Ishi, Y.Ohno and B.Viswanathan, Surface Sci., 161, 349(1985).

Table.4. Peak positions of valence levels with respect to E_F and energy separation for 4 $\tilde{\sigma}$ and 1 $\tilde{\pi}$ and $(\Delta | (4\tilde{\sigma} - 1\tilde{\pi}) |)$ for CO adsorption on group VIII metals

	Peak positions eV				
	5 $\tilde{\sigma}$	Overlapping 5 σ and 1 π	1 $\tilde{\pi}$	4 $\tilde{\sigma}$	$(\Delta (4\tilde{\sigma} - 1\tilde{\pi}))$
Fe(110)	8.1		6.9	11.0	4.1
Fe (100)		7.0		10.5	3.5
Fe(111)		7.6		10.8	3.2
Ru(0001)		7.6		10.7	3.1
Co(0001)		7.5		11.0	3.5
	7.9		7.7	10.7	3.0
Rh(111)	8.3		7.8	11.2	3.4
Rh(100)		7.6		10.8	3.2
Rh(110)	7.6		8.7	10.6	1.9
Ir(111)	9.2		8.6	11.7	3.1
Ir(100)	9.2		8.6	11.7	3.1
Ni(111)	8.1		7.1	11.2	4.1
Ni(100)	8.3		7.8	10.8	3.0
Ni(110)	8.4		6.5	11.7	5.2
Pd(111)	8.2		7.5	11.2	3.7
Pd(100)		7.9		10.8	2.9
Pd(110)		7.		10.8	2.9
Pt(111)	9.2		8.4	11.9	3.5
Pt(100)		8.8		11.4	2.6
Pt(110)	9.2		8,2	11.7	3.5
CO (gas)	14.0		16.9	19.7	2.8

Data extracted from S.Ishi, Y.Ohno and B.Viswanathan, Surface Sci., 161, 349(1985).

altered as a result of adsorption. This alteration can be explained with respect to the unoccupied LUMO state. This aspect has to be probed by techniques which can monitor unoccupied states like ‘inverse photo emission’ or by probing the satellite features of the core levels of CO in the adsorbed state. Such an experimental data for emission from 1σ and 2σ levels of CO are given in **Fig.10** and the corresponding data extracted from these figures are given in **Table 5**.

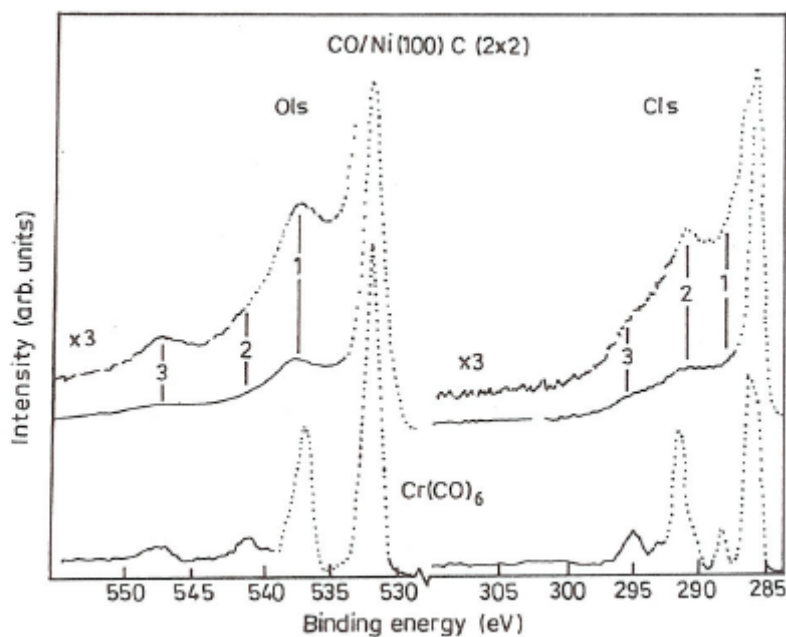


Fig.10. C 1s and O 1s XP spectra for CO/Ni(100) c(2x2) and Cr(CO)₆. (Suitable background correction to the adsorbate spectra has been provided for and the resultant adsorbate spectra alone are shown.)

The satellite features appear because of the excitations from 5σ to $2\pi^*$ or 1π to $2\pi^*$ levels and the energy loss of photo emitted electrons with respect to the main emission denotes the $5\sigma \rightarrow 2\pi^*$ or $1\pi \rightarrow 2\pi^*$ separation values which have to be compared with the corresponding values of free gas phase CO. The consequence of the perturbations of the electronic energy levels of molecules in the adsorbed state is manifested in the vibrational properties of these molecules in the adsorbed state. The free gas phase CO molecule gives rise to an IR absorption band at 2143 cm^{-1} . This band is shifted to lower values of the wave number indicating the weakening of the C–O bond as a result of adsorption. A compilation of the position of the IR absorption bands of adsorbed CO on various metal surfaces is given in **Table 6**. Though one can generally consider that greater is the shift of this IR band to lower values with respect to the value of 2143 cm^{-1} corresponding to gas phase CO, ($\Delta\nu$) the weaker is the C–O bond. This statement holds well only when CO is adsorbed on top mode. If CO were to be adsorbed in bridged configuration as bidentate or tridentate species (See structures in **Fig.2**.) then also one would observe the IR bands at lower frequency. Some typical data for the position of IR bands for CO bonded in various configurations are given in **Table 7**.

Table 5 Positions of shake up features in adsorbed CO or N₂ on Ni(100)

Cl _s (eV)	O1s (eV)	Inner Nitrogen (1s) (eV)	Outer Nitrogen (1s) (eV)
2.1 (sh)	5.5		2.1
5.5	8.0 (sh)	5.3	5.8
9.5	15.0	~15	8.5
	16.0		~15.0
	26.0		
33 (σ to $n\sigma^*$)	35.0		
	45.0		
	55.0		

Data extracted from Anders Nilsson and Nils Mårtensson, Phys. Rev. B 40, 10249 - 10261 (1989); Anders Nilsson, Hlena Tillborg and Nils Mårtensson, Phys.Rev.Lett., 67, 1015(1991)

Adsorption generally means the residence of the molecules at the surface of a solid. With in its residence time, the bond activation takes place so as to provide bond transformation in the desired directions. This reaction yield can be represented in terms of turn over number TON or turn over frequency (TOF). TON is defined as specific rate multiplied by the time for which the reaction is carried out. Specific rate denotes the number of molecules converted per unit site per second at a given pressure,

Table 6 Typical IR frequencies of adsorbed CO on single crystal metal surfaces

surface	Peak positions (cm ⁻¹)			
	ν (C-O)		ν (M-CO)	
	$\Theta=0$	$\Theta \geq 0.5$	$\Theta=0$	$\Theta \geq 0.5$
Fe(110)	1890	1985	456	360,440
Fe(111)	1800	1850,2000	550	515
Ru(0001)	1984	2060	445	445
Rh(111)	1990	2070,1870	480	420
Ni(111)	1817	1915,2045	380	380
Ni(100)	2000	2070		480,365
Ni(110)	1990,1880	2015,1935		450,345
Pd(111)	1813	1936,2092		
Pd(100)	1985	1950,2096	347	315
Pt(111)	2065	2100,1872	498	365
Pt(100)	2080,1950	2096		
Cu(111)	2078	2070		
Cu(100)	2079	2088		
Cu(110)	2088,2104	2094		

Extracted from S.Ishi, Y.Ohno and B.Viswanathan, Surface Sci., 161, 349(1985).

Table 7. Typical IR frequencies for various types of bonded CO

Type of Co bonded	IR Frequency cm^{-1}
Uncoordinated or "free" CO	2143
Terminal M-CO	2125 to 1850
Doubly bridging (μ -2)	1850 to 1750
Triply bridging (μ -3)	1675 to 1600
Semi-bridging	between terminal and μ -2.

concentration, temperature conditions. This is a figure of merit of the activities of catalysts for comparison purposes and it can range from 10^{-4} to 10 per site per second. Similarly, TON's must be greater than 1, for catalytic reactions and it will be less than 1 when one is dealing with stoichiometric reactions. Long residence time of molecules on the surface may lead to migration of adsorbed species (if surface diffusion is a feasible process) over long distances on the surface from 10 to 10^4 \AA , wherein these adsorbed molecules may meet a number of catalytically active sites where they can undergo consecutive reactions or molecular rearrangements and thus reducing the desired selectivity.

Normally the (coverage) number of adsorbed molecules per unit area (σ) molecules (cm^2) is given by $\sigma = F \times \tau$,

Where F is the incidence flux of molecules $\text{cm}^{-2} \text{ sec}^{-1}$ and τ is the surface residence time

$$\tau = \tau_0 \exp [\Delta H_{\text{ads}} (\theta) / RT]$$

Where τ_0 is typically 10^{-17} to 10^{-13} sec. The adsorbate-adsorbate interaction decides the magnitude of ΔH and the incidence flux is given by

$$F = P (2\pi MRT)^{-1/2}$$

While on the point of selectivity, one wish to consider varying levels of selectivity and the selectivity order that is currently being pursued by chemists is given in **Fig.11**.

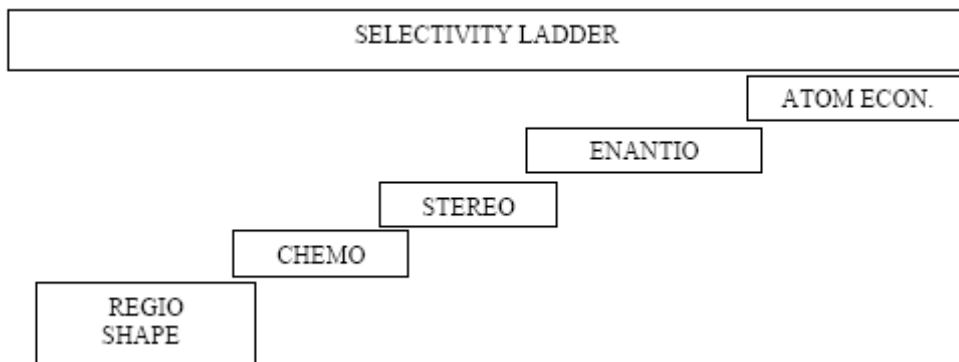


Fig. 11. Selectivity ladder presumed by chemists (www.sc.doe.gov/bes/BESAC/CatalysisMarks05-15-02.ppt)

Though the ideal situation would be total atom economy, wherein the total number of atoms that were introduced as reactant should appear in the desired product, such a realization of all the atoms of the reactant molecules being present in the product molecule implies that the reaction is 100% selective with out the formation of any product arising out of side reactions. We seem to have most of these types of selectivity realizable in catalytic reactions.

It is appropriate that we have some time line for the developments in the field of surface science and catalysis. One such conceptual time line is shown in Fig.12.

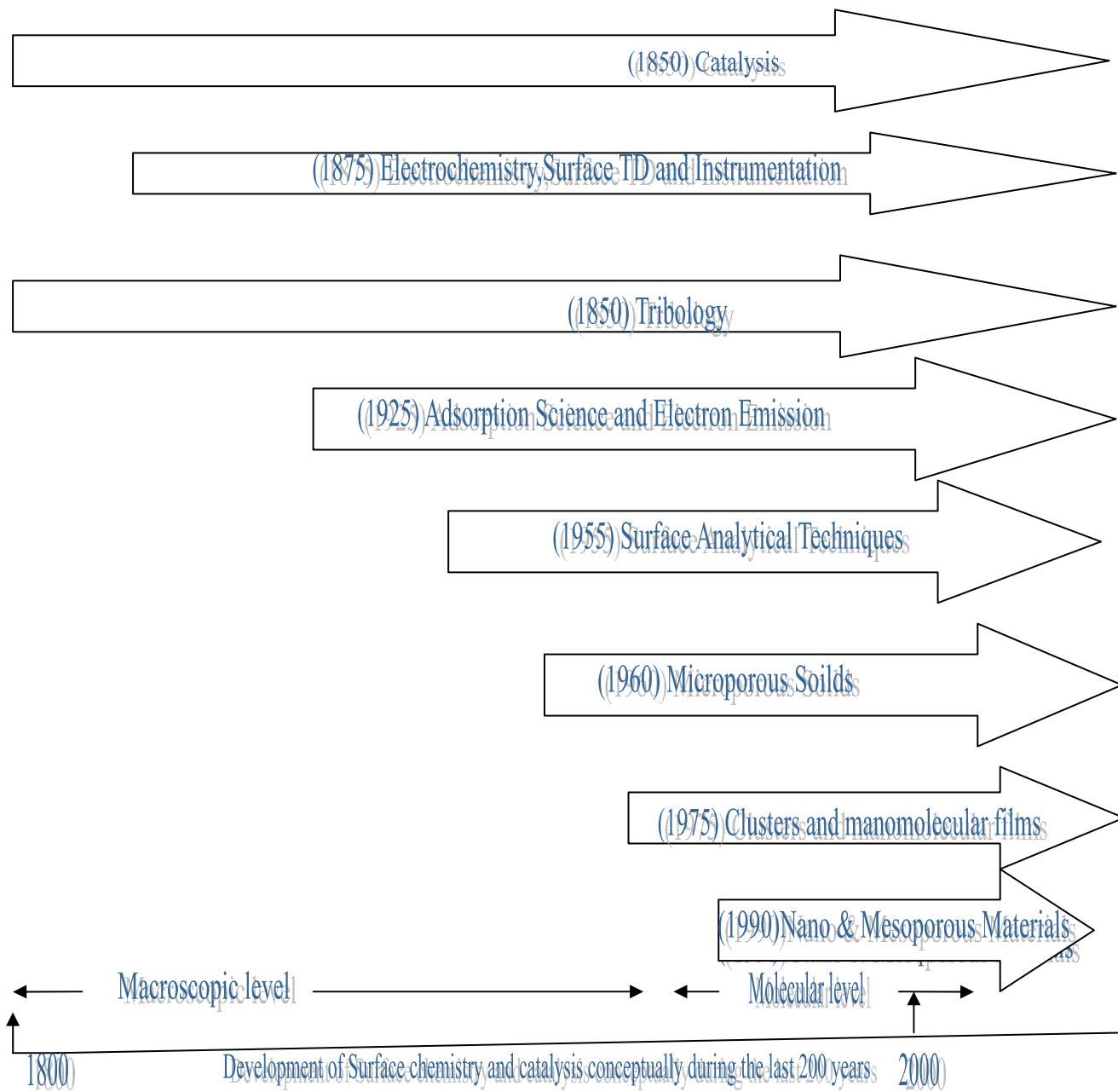


Fig. 12. Conceptual time line for the development in the field of Surface Science and Catalysis

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