

## CHAPTER II

### THEORY AND LITERATURE REVIEW

Chemistry is an area of vital importance in today's society, and within chemistry, catalysis is a mainstay, not only in many industrial applications, but also in numerous processes in the chemistry of life. Catalysis performs a key role in processes such as the conversion of crude oil into a wide scale of useful products, in the preparation of many nutrients, in the conversion of coal via synthesis gas into products like alcohols, gasoline, and in the removal of noxious components from exhaust gases.

Catalysis is the science of accelerating chemical reactions that under normal conditions proceed only slowly or not at all. The rate of a chemical reaction can be controlled by a few parameters only: temperature, pressure and composition. In addition, the choice of a suitable catalyst may change the reaction pathway. As a consequence, the overall reaction rate may be increased and / or new pathways, and therefore new products, may become feasible. A chemical reaction is the result of a collision of two or more molecules or atoms. The function of a catalyst is merely to capture the participants of the reaction, to bring them in close contact and thus to guide them through some reaction pathway. The combination of catalyst and reactant(s) dictates the pathway. The characteristics are important in describing a catalyst. First of all, its activity that is the rate at which the products are generated. The higher the activity, the better the catalyst. Secondly, there is the selectivity. In most cases, a catalyst produces a wide range of products, some of which are useful and

others are not. By selectivity in general we mean the fraction of useful products, usually expressed as a percentage. A high selectivity indicates that the catalyst produces mainly the desired products.

The concept of catalyst as a method of controlling the rate and direction of a chemical reaction has captured the imagination of scientists and technologists. Berzelius, in 1835, coordinated a number of disparate observations on chemical transformations by attributing them to a "catalytic force" and coined the term catalysis to refer to the "decomposition of bodies" by this force. At about the same time Mitscherlich introduced the term "contact action" for a similar group of phenomena. Ideas of what constitutes a catalyst and the mechanism of catalytic activity have undergone continuous refinement since, spurred by the enormous industrial importance of catalysts as illustrated by the variety of catalytic processes characteristic of modern petroleum refineries and of the chemical industries. Most of these processes involve solid catalysts, and an understanding of catalysis from both the theoretical and practical point of view is essential to chemists and chemical engineers.

### **Theories of Catalytic Reaction**

A basic concept is that a catalyzed reaction involves the transitory adsorption (almost always chemisorption) of one or more of the reactants onto the surface of the catalyst, rearrangement of the bonding, and desorption of the products. This leads to three groups of theories of catalysis: (11)

## 1. The Geometrical Theories

This theories emphasize the importance of the correspondence between the geometrical configuration of the active atoms at the surface catalyst and the arrangement of the atoms in the portion of the reacting molecule that adsorbs on the catalyst, this portion sometimes being called the index group. In one sense the usefulness of this approach is limited in that seldom can one change the geometrical arrangement of atoms in the catalyst surface without changing something else. Studies of reaction rates on different crystal faces of a metal have shown that the rates indeed may change with geometry, and it is found that introduction of defects by cold rolling of a sheet of metal, by grinding, or by radioactive bombardment may substantially change the rate of a reaction if the reaction temperature is sufficiently low that the defects do not rapidly anneal or that the structure does not assume a more stable configuration. An aspect of the geometrical approach of great usefulness is the observation that reaction selectivity may be markedly altered by the number and arrangement of sites required for competing reactions, which leads to the concepts of the importance of "ensembles" or specific grouping of atoms at the catalyst surface and structure sensitivity as affected by particle size, alloying, and other variables.

## 2. The Electronic Theories

This theories proceed from the fact that chemisorption involves the distortion or displacement of electron clouds, and they attempt to relate activity to the electronic properties of the catalyst. This may be in terms of the electronic structure of the solid as a whole, or in terms of the orbital around individual atoms. In the charge-transfer theory of catalysis (11) it is postulated that the reaction rate is controlled by the availability of charge carriers-

electrons or holes-in the catalyst. These are visualized as being nonlocalized; i.e., a sea of electrons or holes is available. Chemisorption is then related to the electronic properties of the catalyst, for example, the ease or difficulty of removal or donation of an electron to or from the lattice-as predicted by applying band theory as developed for metals and semiconductors.

This approach, of considerable interest in the 1950s, is now seen to be too broad and is inadequate or inapplicable for most cases. More recently attention has been directed to the properties of atoms as individual entities and to the electronic effects caused by the nearest neighbors in the solid rather than by the solid as a whole. In many cases it is difficult to separate geometrical effects from localized electronic effects; the relative importance of the two probably varies greatly from case to case.

### 3. Other Theories

The above two theories represent primarily a physical approach in that the catalyst is regarded as essentially a static material having the property of converting reactant to product. The chemical approach on the other hand regards the catalyst as a chemical intermediate that forms an unstable, surface, transitory complex with the reactants. This decomposes into the final products, returning the catalyst to its initial state. The rates of these processes and the structures formed are assumed to obey chemical principals. If the energy of formation of the unstable intermediate is low, the affinity between catalyst and reactants will be weak and the overall rate is limited by the rate of formation of the intermediate. If the energy of formation is high, the intermediate compound will be stable and the rate is limited by the rate of breakup of this intermediate.

This leads to the concept that the maximum rates is obtained when the bonds between the adsorbed complex and the catalyst surface are neither too strong nor too weak. This is a useful concept but limited in that the energetics are generally unknown, more than one intermediate is frequently involved, and one is more generally concerned with selectivity rather than activity as such.

### **Definitions of Catalyst**

The basic concept of a catalyst is that of a substance that in small amount causes a large change. More precise definitions of catalysis and of what constitutes a catalyst have gradually evolved as understanding of the cause of catalytic phenomena has grown. Even today there is no universal agreement on definitions, the point of view varying somewhat depending upon the investigator ; for example, as between the fundamental investigator and the practitioner, and among researchers concerned with heterogeneous catalysis, homogeneous catalysis, polymerization reactions, and enzymes. For purposes however our definition is: A catalyst is a substance that increases the rate of reaction without being appreciably consumed in the process (11).

This basic concept, stemming from the chemical approach to catalysis, is that a reaction involves a cyclic process in which a site on a catalyst forms a complex with reactants, from with products are then desorbed, thereby restoring the original site. This leads to the idea that a catalyst is unaltered by the reaction it catalyzes, but this is misleading. A catalyst may undergo major changes in its structure and composition as part of the mechanism of its participation in the reaction. A pure metal catalyst will frequently change in surface roughness or crystal structure on use. The ratio of oxygen to metal in a metal oxide catalyst will frequently change with temperature and composition

of the contacting fluid. In both cases, however, there is no stoichiometric relationship between such changes and the overall stoichiometry of the catalyzed reaction. Many so-called polymerization catalysts or initiators are not termed catalysts within the above definition. Thus in the use of an organic peroxide consumed to quantity of monomer reacted is indeed nonstoichiometric, but the peroxide becomes completely consumed in the process; hence it cannot be regarded as a true catalyst.

A catalyst is defined as a "substance"; the acceleration of a rate by an energy-transfer process is not regarded as catalysis by this definition. Excluded cases include excitation by thermal energy (increased temperature), by bombardment of reactants by charged or high-energy particles, by electric discharge, or by photochemical irradiation. For example, the reaction of hydrogen and oxygen is increased by irradiation by ultraviolet light and even more so if a small amount of mercury vapor is present and illumination is by a mercury vapor lamp. Here the reaction is accelerated by energy transfer to the reacting gases from mercury atoms, which in turn are activated by irradiation. As a second example, the rate of thermal decomposition of a vapor at low pressure is usually increased by the addition of a second "inert" gas which furnishes activation energy by collisions. These various methods of accelerating the rate of a reaction are more clearly understood as aspects of the mechanisms of homogeneous gas-phase reactions rather than as catalysis. A catalyst cannot change the ultimate equilibrium determined by thermodynamics; its role is restricted to accelerating the rate of approach to equilibrium. This point is developed later.

## Categories of Catalysts

Catalysts are known in many varieties, but in principle they can be classified into two categories (12) : homogeneous and heterogeneous catalysts. Homogeneous catalysts can be mixed perfectly with the reactants. i.e., up to molecular scale. Homogeneous catalysis mainly occurs in the liquid phase. The reactants and the catalyst are liquids or dissolved in the liquid phase. All the enzymes at work in our body are homogeneous catalysts. In heterogeneous catalysis, the catalyst, the reactants, and the products are in separate phases and therefore the mixing is far from perfect. The catalyst is usually a solid and the reactants are liquids or gases. The automotive catalyst is an example of a heterogeneous catalyst. The reactants, hydrogen, carbon monoxide and nitric oxides, and the products, water, carbon dioxide and nitrogen, are gaseous while the active catalyst is a combination of several precious metals supported on some (inert) support.

## Industrial Heterogeneous Catalysts

The first heterogeneous catalytic process of industrial significance, introduced in about 1875, utilized platinum to oxidize  $\text{SO}_2$  to  $\text{SO}_3$ , which was then converted to sulfuric acid by adsorption in an aqueous solution of the acid. This came to replace the lead chamber process for manufacture of  $\text{H}_2\text{SO}_4$ , in which the same series of reactions were catalyzed by a homogeneous catalyst, nitrogen oxides, probably via nitrosylsulfuric acid,  $\text{HNOSO}_4$ . In the contact process platinum in turn was superseded by a catalyst comprising vanadium oxide and potassium sulfate on a silica carrier, which was less susceptible to poisoning, and essentially this same composition is used in present-day  $\text{SO}_2$  reactors.

Other inorganic chemical catalytic processes followed, notably the development by Ostwald in about 1903 of the oxidation of ammonia on a platinum gauze to form nitrogen oxides for conversion to nitric acid and the synthesis of ammonia from the elements during the period of about 1908 to 1914 by a process developed by Bosch utilizing a catalyst developed by Mittasch. The industrial synthesis of methanol from carbon monoxide and hydrogen appeared in about 1923, and the synthesis of hydrocarbons from carbon monoxide and hydrogen by the Fischer-Tropsch process in the 1930s. The catalytic partial oxidation of methanol to formaldehyde as an industrial process started in Germany about 1890, that of naphthalene to phthalic anhydride was commercialized in the 1920s, and that of benzene to maleic anhydride in 1928. The partial oxidation of ethylene to ethylene oxide was commercialized by Union Carbide in 1937 (11).

In the processing of petroleum for fuels the first catalytic process, catalytic cracking, appeared in about 1937. This first used an acid-treated clay, then later a synthetic silica-alumina catalyst, and more recently zeolite crystals incorporated in a silica-alumina matrix. Reforming, using a molybdena/alumina catalyst to increase the octane number of gasoline by cyclization of paraffins and dehydrogenation to aromatics, was introduced in the United States and Germany just prior to World War II. In the early 1950s this was superseded by a reforming process using a platinum/alumina catalyst. Catalytic hydrocracking first came into use in England and Germany prior to World War II; subsequently it became relatively uneconomic, but more recently, with the advent of new types of catalyst, it has been revived. Hydrodesulfurization and hydrotreating processes have grown rapidly during the past two decades and are now of major importance in petroleum processing.



## Classification and Selection of Catalysts

Catalysts effective in practice range from minerals used with little or no further processing, to simple massive metals, to substances of precise and complex composition. The latter may have to be carefully prepared under closely controlled conditions, and their effectiveness in use may also require careful control of the environment in the reactor. The desired catalytic action may range from the acceleration of a simple organic reaction which can go in only one direction to a highly selective organic reaction which may involve complicated interaction among many intermediate species.

In the choosing or developing of a catalyst the difficulty of the problem may vary greatly as indicated by a scheme of the order of increasing complexity, suggested by S.Z.Roginskii, 1968 (11) :

### 1. Selection among known catalysts

- (1) For known reactions
- (2) For reactions analogous to known catalytic reactions
- (3) For new reactions

### 2. Search for new catalysts

- (1) For well-known catalytic reactions
- (2) For reactions analogous to those well-known
- (3) For reactions of new types, having no analogous among well-known reactions

Only a few broad generalizations can be offered at this point about correlations between the nature of a catalyst and the reactions it catalyzes.

More specific correlations within groups of catalysts or groups of reactions will be discussed later.

Solids exhibiting catalytic activity process, in general, strong interatomic fields, such as that involved in ionic or metallic bonding. Organic covalent compounds in general are noncatalytic. A fundamental requirement is that the desired catalytic structure be stable under reaction conditions ; e.g., a desired metal must remain metallic and not be converted to an inactive compound.

The metal that catalyze hydrogenation reactions do so usually because they adsorb hydrogen with dissociation and the bonding is not too strong. These are essentially the elements in group VIII (Fe, Co, Ni and the platinum-group metals) plus possibly copper in group 1B. However, hydrogen adsorption is also affected by impurities in the metal and by various species adsorbed on the surface. Thus under a particular set of circumstances hydrogen adsorption can be low on pure copper but may be considerably enhanced by the presence of impurities, e.g., carbonaceous residues. Almost all of these reactions are of the homolytic type (those involving noncharged intermediates).

Some metals also catalyze oxidations by chemisorbing oxygen, but the base metals in general cannot be used in the metallic form since they usually are converted to the oxide throughout their bulk. Only the platinum-group metals ( Ru, Rh, Pd, Os, Ir, Pt ) and silver and gold are sufficiently resistant. Of these, gold has little adsorptivity in general and hence has little catalytic activity, and within the platinum group osmium and iridium are very scarce. Of the others, Pt and Pd are the most important. Note however that the oxide form of many metallic elements, both base and noble, may be acted for oxidation reactions.

Oxygen is more strongly adsorbed by metals than is hydrogen; apparently the bonds are generally too strong to be easily rearranged, so higher temperatures are generally required for oxidations to occur on metals than for hydrogenations.

The oxide catalysts may be divided into two groups by structure. If the structure is ionic and oxygen atoms can be readily transferred to or from the lattice, the substance may be a good catalyst for partial oxidation reactions. The easy movement of oxygen atoms (it is not clear in some cases whether these are radicals or ions) causes the compounds to be generally nonstoichiometric, and the ratio of oxygen to metal may vary significantly with the composition of the reacting mixture. Examples are the complex molybdates containing several metals and various multimetallic oxide compositions. The second group consists of dehydrogenation catalysts in which the oxygen is more tightly bound and the oxide must not be reducible to the metal by hydrogen at the reaction temperatures. Thus the oxides suitable for partial oxidation reactions are generally not suitable for dehydrogenations. Some oxides such as chromia may be regarded as being intrinsically dual-function in nature, catalyzing acid-type reactions. Metals as such usually are not suitable for dehydrogenations because under representative reaction conditions they become rapidly deactivated by carbonaceous deposits.

A number of solids are acidic (11) and can catalyze a wide variety of reactions similar to those catalyzed by strong mineral acids. These include materials in which two or more elements are tightly linked together in the structure via oxygen atoms, such as in silica-alumina and in various zeolites (crystalline aluminosilicates and related materials). Solid acids may also be formed by treating alumina so as to incorporate a halogen into its structure. Many salts such as metal sulfates and phosphates exhibit little or no acidity as

prepared in the hydrated form but acquire moderate acid strength after heat treatment. The development of acidity here is associated with the gradual removal of water. In the case of acid-catalyzed reactions the strength and nature of the acidity (Lewis or Bronsted acids or both) are of central importance rather than the particular elements present as such.

Paraffin isomerization and hydrocracking are examples of reactions requiring that the catalyst incorporate a metallic and an acid function in order to accelerate each of two different intermediate steps (or groups of steps) in the overall reaction.

A number of industrially significant reactions are catalyzed by metal sulfides, but the mechanisms of action are perhaps not as well understood. A metal sulfide such as nickel sulfide is an effective catalyst for hydrogenation reactions, and this is of particular importance in dealing with feed streams containing sulfur compounds. These can adsorb on other metal catalysts, such as platinum, thereby making them inactive.

Some catalysts, such as a mixture cobalt and molybdenum on a support, actually are more active in the sulfide form than in the metallic form for at least some hydrogenations. Metal sulfides such as those of tungsten, of a mixture of cobalt and molybdenum, or of a mixture of nickel and molybdenum are active for hydrodesulfurization and hydrodenitrogenation. Some sulfides are probably significantly acidic, thereby being bifunctional in themselves and capable of catalyzing both hydrogenation-dehydrogenation reactions and acid-catalyzed reactions.

Many industrial catalysts are very complex. Promoters and carriers play an important role, and the trend is towards more precise tailoring of the catalyst

structure, in which each ingredient and each step in preparation contributes towards better activity, selectivity, or stability.

### **Catalytic Activity**

The activity of a catalyst refers to the rate at which it causes the reaction to proceed to chemical equilibrium. The rate may be expressed in any of several ways. The performance of an industrial reactor is frequently given in terms of a space-time yield (STY), which is the quantity of product formed per unit time per unit volume of reactor.

With Mars and Krevelen mechanism (13) bearing in mind one can expect a relation to exist between the metal-oxygen bond strength and the catalytic activity. Also the coordination of the metal ion (tetrahedral and octahedral), the crystallographic structure of the oxide and the acidity of the oxide, which plays a role in abstraction of H-atoms, can influence the activity of a catalyst (14).

### **Reaction Pathways**

Consider a gas-phase reaction which may occur either homogeneously. The two reaction pathways occur simultaneously, but in order for the catalyzed reaction to be observed it must occur measurably faster than the homogeneous reaction. We know inquire into how the catalyst brings this about.

The rate of a single elementary step of a homogeneous reaction is proportional to a rate constant  $k$  that varies with temperature according to the Arrhenius relationship,  $k = Ae^{-E/RT}$ , where  $E$  is the activation energy and  $R$  is

the gas constant. The preexponential factor  $A$  is a constant that in collision theory is identified as a collision number for bimolecular processes and, for unimolecular processes, as a frequency factor or the probability of reaction of an activated molecule.

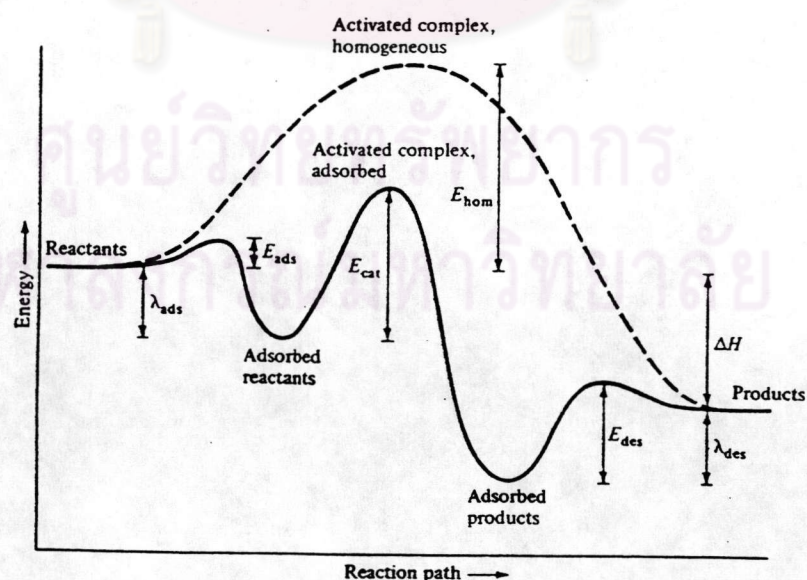
The ability of a catalyst to increase a reaction rate can be ascribed in a general way to its causing a reduction in the activation energy of the reaction. But even for the simplest kind of reaction, the single-step conversion of A to B, the situation is considerably more complicated than this simple statement may imply. The catalyzed reaction involves three rate processes: adsorption, the formation and breakup of an activated complex, and desorption of products. Each of these has its own activation energy. The rate of each is also determined by the total surface area of the catalyst present (or, more precisely, the number of active sites) and by the concentration on the catalyst surface of various adsorbed species. The idealized homogeneous reaction has a single activation energy, and its rate is a function of the gas-phase concentration.

In order for a reaction to be noticeably catalyzed, the various factors that determine the overall rate of the heterogeneous reaction must in the entirety of their interactions outweigh that of the different group of factors that determine the rate of the homogeneous reaction. Generally the most important effect of the catalyst is to provide a pathway whereby the activation energy for the formation of the intermediate surface complex is considerably less than for the homogeneous reaction. Because the activation energy appears in the rate equation as an exponent, a slight change in activation energy has a marked effect on the rate.

The rate of the catalyzed reaction is proportional to the active surface area, and the rate of a homogeneous reaction is proportional to the volume of

fluid. Hence the maximum ratio of the catalyzed rate to the homogeneous rate occurs with the use of high-area (porous) catalyst pellets packed in a reactor. Catalyst such as those frequently utilized in practice have areas of the order of  $100 \text{ m}^2/\text{g}$  or more. Arguments based on the absolute theory of reaction rates show that, although it is not usually observed, it is entirely possible for the observed rate of a catalyzed reaction to proceed faster than the corresponding homogeneous reaction even when the activation energy for the rate-limiting step on the catalyst is no less than that for the homogeneous reaction (15).

The changes in energy associated with the different steps in a simple exothermic reaction can be depicted as shown in Figure 2.1.  $E_{\text{hom}}$  is the activation energy for the homogeneous reaction,  $E_{\text{ads}}$  for adsorption of reactants onto the catalyst,  $E_{\text{cat}}$  for the formation of the activated complex, and  $E_{\text{des}}$  for the desorption of products.  $\lambda_{\text{ads}}$  is the heat of adsorption of reactants, taken to be exothermic, and  $\lambda_{\text{des}}$  is the heat of desorption of products, taken to be endothermic. The overall energy change upon reaction is  $\Delta H$  and is, of course, the same for the two pathways.



**Figure 2.1** Energy changes associated with individual steps of a reaction

From experimental rate data, an "apparent activation energy" can be calculated from the slope of an Arrhenius plot of the log of an observed rate constant as a function of the reciprocal of the absolute temperature. To proceed from this to calculation of the activation energy of a surface process in the general case requires a knowledge or assumption of the mechanism of the surface reaction, identification of the rate controlling step, and heats of adsorption and desorption. This treatment also shows that there is no reason why a straight-line relationship between  $\log k$  and  $1/T$  should be expected to be encountered over a substantial range of temperature. It will usually be found that the apparent or effective activation energy for a catalyzed reaction is less than that for the same reaction proceeding homogeneously, both being determined from the slope of an Arrhenius plot. It is to be emphasized, however, that there is no fundamental reason why this should always be the case. Nevertheless, a consequence of this common behavior is that with increased temperature a point will usually be reached beyond which the rate of a catalyzed reaction will be exceeded by the rate of the homogeneous reaction.

With some endothermic reactions high temperatures are required in order for a substantial amount of the product to be present at equilibrium, and it may be found that these temperatures are so high that no significant increase in rate is achieved by any catalyst. An example is the dehydrogenation of ethane to form ethylene and hydrogen, in which a temperature of about 725 °C is required for 50 percent conversion to equilibrium at atmospheric pressure. Little increase in rate is obtained with a heterogeneous catalyst, For conversion of a higher paraffin such as butene, however, a specified degree of conversion to equilibrium can be obtained at considerably lower temperatures than with ethane, and a substantial increase in rate is observed with use of a catalyst such as chromia-alumina.



## Catalytic Oxidation

Partial oxidation processes using air or oxygen are used to manufacture a variety of chemicals, and complete catalytic oxidation is a practicable method for elimination of organic pollutants in gaseous streams. In the manufacture of organic chemicals, oxygen may be incorporated into the final product, as in the oxidation of propylene to acrolein or o-xylene to phthalic anhydride; or the reaction may be an oxidative dehydrogenation in which the oxygen does not appear in the desired product, as in the conversion of butylene to butadiene. The desired reaction may or may not involve C-C bond scission. Closely related are ammoxidation reactions (also termed oxidative ammonolysis) in which a mixture of air and ammonia is reacted catalytically with an organic compound to form a nitrile, as in the ammoxidation of propylene to acrylonitrile. With the advent of more active and selective catalysts, direct oxidation processes have gradually replaced earlier processes that utilized such oxidizing agents as nitrogen dioxide, chromic acid, and hypochlorous acid.

Catalytic oxidation processes for manufacture of organic chemicals have several features in common.

(1) They are highly exothermic. Heat- and mass-transfer effects may be very important, so multitude heat-exchange reactors on fluidized beds are usually used. An important element of reactor design is to prevent catalyst deactivation by excessive temperature or runaway reaction.

(2) Certain composition regions may be explosive. The ratio of organic compound to air (or oxygen) in the feed stream may be selected in large part to avoid these regions. For the same reason, air may be introduced at multiple points. Operation may be either "fuel-rich" or "fuel-lean".

(3) The desired product must be sufficiently stable relative to the reactant under reaction conditions that it can be removed from product gases in an economic yield, usually involving rapid quenching, before it decomposes or undergoes further reaction. Most of the compounds currently made industrially have ring structures that are highly stable, for example, phthalic anhydride, maleic anhydride, and ethylene oxide ; or a conjugated structure which imparts stability, such as  $C=C-C=C$ ,  $C=C-C=N$ , and  $C=C-C=O$ . In contrast, although there have been many attempts to develop a process for the direct heterogeneous oxidation of methane to formaldehyde, no economic method has been invented since the product is so much less stable than the reactant. Sometimes relatively good selectivity to a desired product can be achieved at low percent conversions. In that case the product is typically removed from the reactor exit gas and the remaining stream sent to a second reactor. Alternately the stream may be recycled, perhaps after purification, to the reactor inlet.

Effective catalysts for oxidation reactions fall into three categories.

(1) Transition metal oxides in which oxygen is readily transferred to and from the structure. Most but not all of the industrial catalysts of this type are mixed oxides containing two or more cations, and the compounds are nonstoichiometric. Examples are an iron molybdate catalyst for oxidizing methanol to formaldehyde, bismuth molybdates for oxidizing propylene to acrolein or ammoxidation of propylene to acrylonitrile, and catalysts based on vanadium oxide for converting benzene to maleic anhydride and naphthalene or o-xylene to phthalic anhydride.

(2) Metals onto which oxygen chemisorbed. Examples are ethylene to ethylene oxide on a supported silver catalyst, ammonia oxidation to nitric oxide on platinum gauze, and methanol to formaldehyde on bulk silver.

(3) Metal oxides in which the active species is chemisorbed oxygen, as molecules or atoms. These may also provide a significant additional mechanism under some conditions with metal oxide catalysts that also contain interstitial oxygen as an active species.

Practical oxide catalysts may be much more difficult to characterize than other types of catalysts. In the case of a supported oxide catalyst, methods for determining active area in contrast to total area, analogous to the use of selective chemisorption for supported metal catalysts or base titration to estimate the number of acid sites on an acidic catalyst, are much more rudimentary. Knozinger (16) has recently reviewed in detail methods of specific adsorption that may be suitable. Many of the oxide catalysts may be more or less amorphous, and even when an X-ray pattern can be observed, the contribution of the crystalline phase to total catalytic properties may be far from clear. Some useful catalyst compositions may contain as many as four or five metal elements, each of which must be present for optimum performance, but their role remains obscure. Defects in a crystal structure appear to play a role, but the extent to which they exist under reaction conditions is speculative.

In a few cases, at reaction temperatures the catalyst appears to be a liquid held in the pores of a support rather than a solid. This is the case under at least some reaction conditions for the vanadium oxide-potassium sulfate catalyst used for oxidation of sulfur dioxide to sulfur trioxide, and also for some metal chloride catalysts used in oxychlorination.

Several general conclusions about the use of this heterogeneous catalytic oxidation of volatile organic compounds are:

(1) Applications of catalytic oxidation for volatile organic compounds control have primarily involved direct transfer of technology from related applications, such as the use of an automotive catalyst downstream of a burner. Little has been done to develop catalyst specifically for this need.

(2) The use of catalytic oxidation as a volatile organic compounds control technique is more widespread in Europe than in the United States, perhaps because of higher energy costs and more stringent environmental regulations.

(3) Very little has been reported on the systematic scientific study of volatile organic compounds mixtures. Reported work (17) tends to be either well characterized research on pure components in air or anecdotal studies of "real" streams where only gross performance is reported.

(4) Both metal oxides and supported noble metals are active for many deep oxidations. The mechanism of deep catalytic oxidation involves both lattice and surface oxygen for metal oxides and probably reduced metal sites for supported noble metals.

(5) Modeling of the catalytic oxidation of volatile organic compounds interest may be complex, especially for mixtures, because of both surface kinetic and mass transfer effects that can vary with experimental conditions. These effects may result in inhibition or enhancement of the oxidation of a given compound.

Heterogeneous catalytic oxidation is a well studied and industrially useful process. Industrial catalytic oxidation of vapors and gases is a very broad field and is dealt with in several texts and review articles (11, 18, 19, 20,

21). Catalytic oxidation, both partial and complete, is an important process for such reactions as the partial oxidation of ethene and propene, ammoxidation of propene to acrylonitrile, maleic and hydride production, production of sulfuric acid, and oxidation of hydrocarbons in automotive exhaust catalysts. By far, the majority of oxidation catalysts and catalytic oxidation processes have been developed for these industrially important partially oxidized products. However, there are important differences between the commercial processes and the complete catalytic oxidation of volatile organic compounds (VOCs) at trace concentrations in air. For instance, in partial oxidation, complete oxidation to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  is an undesirable reaction occurring in parallel or in series to the one of interest. Other differences include the reactant concentration and temperature, the type of catalyst used, and the chemical nature of the oxidizable compound.

### **General Mechanism of Catalytic Oxidation**

A general theory of the mechanism of the heterogeneous catalytic oxidation of low molecular weight vapors at trace concentrations in air does not exist. However, as with many catalytic reactions, certain observations have been consistently made that have led to general hypotheses about how the reaction takes place.

The mechanism of complete catalytic oxidation depends on the type of catalyst used. Basically two types of conventional catalysts are used for oxidation reductions: metal oxides and noble metals (supported or unsupported).

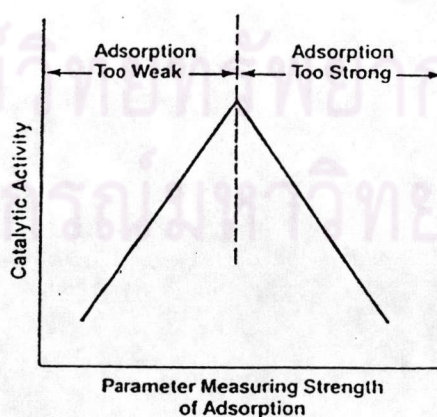
## 1. Metal Oxides

Metal oxide catalysts are defined here in as oxides of occurring in groups III-B through II-B of periodic table. These oxides are characterized by high electron mobility and positive oxidation states. These catalysts are generally less active than are supported noble metals, but they are somewhat more resistant to poisoning. This poison resistance may be due to the high active surface area of metal oxides compared to supported noble metals. The literature on catalytic oxidation over metal oxides is more extensive than is that on noble metals. A variety of single and mixed metal oxides have been evaluated for complete oxidation of trace levels of volatile organic compounds in oxidizing gas streams.

As oxidation catalysts, these oxide are further classified in the literature. Golodets has divided them by the stability of the oxide (22). Those forming the most stable oxides ( $\Delta H^{\circ}_{298} > 65$  kcal/g-mole O) are the alkali and alkali earth metals such as Sc, Ti, V, Cr, Mn ; the rare earth metals ; and the actinides , Ge, In, Sn, Zn, Al. Those oxides with intermediate stability ( $\Delta H^{\circ}_{298} = 40-65$  kcal/g-atom O) include Fe, Co, Ni, Cd, Sb, Pb. Oxides that are unstable ( $\Delta H^{\circ}_{298} < 40$  kcal/g-atom O) are the noble metals Ru, Rh, Pd, Pt, Ir, Au, as well as Ag. The usefulness of this criterion for classifying oxidation catalysts is that presumably the metals that do not form stable bulk oxides remain as reduced metals during oxidation reactions at moderate temperatures. This suggests that the mechanism of oxidation, even when these metals are supported on refractory oxides such as  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$ , may involve only molecular  $\text{O}_2$  in the incoming gas stream.

By contrast, the lattice oxygen of some metals forming stable or intermediately stable oxides is known to be involved in the oxidation of hydrocarbons and other reactants in  $O_2$  - containing gas streams. This has been demonstrated over numerous metal oxides by using  $O_2$  in the gas stream and measuring the  $O^{16}$  and  $O^{18}$  content of the oxidized products.

Another consequence of the classification of oxide catalysts by oxide stability is that there are some optimum level of metal oxygen interaction in an oxide catalyst. This is because “the catalytic activity (of a metal oxide catalyst) is inversely related to the strength of chemisorption of (the volatile organic compound and oxygen), provided that adsorption is sufficiently strong for (the volatile organic compound and oxygen) to achieve a high surface coverage”. This statement suggests the qualitative behavior shown in Figure 2.2, often known as a “volcano” plot. If the chemisorption is too strong, the catalyst will be quickly deactivated as active sites are irreversibly covered (this is one definition of poisoning). If chemisorption is too weak, only a small fraction of the surface is covered and the catalytic activity is very low.



**Figure 2.2 Catalytic activity as a function of adsorption strength (19)**

It is interesting to examine the quantities used for the abscissa of Figure 2.2. Bond suggests using the initial heat of adsorption (22). Satterfield (11), discussing metal oxide catalysts more specifically, suggests using the heat of reaction,  $Q_0$ , for reoxidation of the catalyst. Balandin specified that the maximum volatile organic compound oxidation rate would occur when  $Q_0 \sim Q_{1/2}$  where  $Q_1$  is the overall heat of reaction for conversion of volatile organic compound to products (e.g., VOC,  $O_2$ ,  $CO_2$ , and  $H_2O$ ) (23, 24).

Metal oxide catalysts can be generally divided into three groups insofar catalytic oxidation reactions are concerned. These are n-type semiconductors, p-type semiconductors, and insulators. The basis for this classification is electrical conductivity (which is related to their catalytic properties).

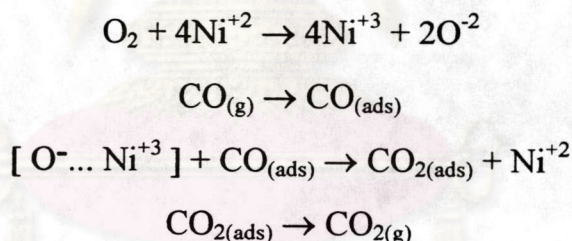
In n-type metal oxides, electrical conductivity arises by means of quasi-free electrons that exist because of an excess of electrons present in the lattice. N-type metal oxides are generally not active oxidation catalysts, although vanadium pentoxide ( $V_2O_5$ ) is a notable exception. P-type metal oxides are electron-deficient in the lattice and conduct electrons by means of positive "holes". These oxides are generally active oxidation catalysts. Insulators have very low electrical conductivities because of the strictly stoichiometric metal-oxygen ratio in the lattice and very low electron (or "positive hole") mobility and are generally not active catalysts. However, insulators are often used as catalyst supports.

One direct result of the different electrical and chemical properties of n- and p-type oxides is that n-type oxides lose oxygen upon heating in air whereas p-type oxides gain oxygen. Fierro and de la Banda (25) discuss the desorption of oxygen from various classes of metal oxides more

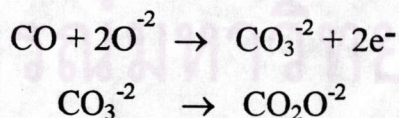


quantitatively, showing that the less stable the metal oxide is (as measured by the heat of formation per oxygen atom), the more easily the surface is reduced to form oxygen adsorption sites. This is important because the difference in their catalytic properties is a direct result of their respective interaction with oxygen at reaction conditions. Oxygen adsorption occurs far more readily on p-type oxides because electrons can be easily removed from the metal cations to form active species such as O, whereas no such mechanism is available on an n-type oxide. On n-type oxides, oxygen adsorption occurs only on pre-reduced surfaces, i.e., replacing oxide ions removed in a reducing pretreatment.

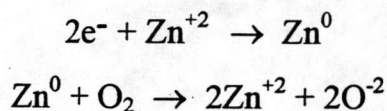
As an example, consider the mechanism of CO oxidation as described by Bond. On p-type oxides such as NiO, adsorbed O, which is formed upon O<sub>2</sub> adsorption, reacts with adsorbed CO via :



On n-type oxides such as ZnO, CO oxidation occurs via lattice O<sup>-2</sup> :



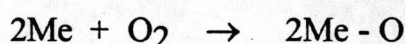
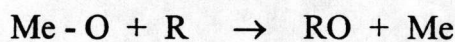
followed by oxide regeneration :



The difference between these mechanisms for the two types of oxides, p-type oxides involving adsorbed  $O^-$  and n-type oxides involving lattice  $O^{2-}$ , leads to profoundly different activity for deep oxidation reactions. Because adsorbed oxygen species are more relative than are lattice oxide ions, p-type oxides are generally more active, especially for deep oxidation.

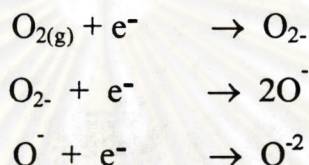
The oxidation of CO over metal oxides demonstrates the differences in these oxide catalysts as opposed to noble metals. First, over noble metals,  $CO_{(ads)}$  is not thought to be active in the catalytic reaction (the mechanism is Eley-Rideal, i.e., involving abreaction between adsorbed oxygen and gas phase CO). Second, and partly as a consequence of this, the formation of an adsorbed carbonate intermediate does not occur over noble metals (22) but has been shown to be present at least on NiO at some conditions (18). This adsorbed carbonate intermediate, in a related study on formaldehyde oxidation on NiO, is shown to be autocatalytic; i.e., the presence of  $CO_2$  in the feed to the catalyst increases the reaction rate by forming carbonate sites that oxidize formaldehyde directly (26).

As shown by Golodets (19), the formation of the carbonate intermediate also may be interpreted in terms of the more conventional redox or Mars and van Krevelen cycle (27), which explicitly involves the oxidation and reduction of the metal oxide (11). The Mars and van Krevelen mechanism of catalytic oxidations over metal oxides is a redox mechanism involving both gas phase and lattice oxygen :



where Me is a metal cation and R is a hydrocarbon reactant.

The activity of the catalyst for deep oxidation may depend on the type of oxygen involved in the reaction. The various types of oxygen present on the surface of metal oxide catalysts have been the subject of much study. The existence of  $O_{2\cdot}$ , atomic  $O\cdot$ , and of the regular  $O^{2-}$  ions in the oxide lattice is beyond doubt (28, 29). Low-temperature ESR studies have shown that the interaction of gaseous diatomic oxygen with an oxide surface proceeds through the following steps :



Where  $O^{2-}$  is directly incorporated into the oxide lattice (in the Mars and van Krevelen mechanism above). For complete oxidation of trace contaminants at the conditions (17), the extent to which lattice oxygen ( $O^{2-}$ ) and chemisorbed oxygen ( $O_{2\cdot}$ ,  $O\cdot$ ) participate in the mechanism is not clear. This is in contrast to industrial partial oxidation reactions where selective oxidation is dependent only on lattice oxygen (30). Although complete oxidation to  $CO_2$  is possible when no oxygen is present in the gas stream, the consensus seems to be that both chemisorbed and lattice oxygen can participate in complete oxidation, although lattice oxygen certainly accounts for selective oxidation (25).

Additional views on complete oxidation as compared to selective oxidation center primarily on oxygen mobility which results from so-called "weak" metal-oxygen bonds. Weak metal-oxygen bonds, i.e., low energies of oxygen binding to the oxides surface, are necessary for catalysts that completely oxidize reactants. Haber postulates that "surface adsorbed" oxygen may generally lead to complete oxidation, whereas lattice oxygen is needed for

partially oxidized products. Presumably, this surface-adsorbed oxygen is more mobile than is lattice oxygen. Though in principle either  $O_2$  or  $O^-$  may promote complete oxidation,  $O^-$  may be the more reactive (i.e., "mobile") because it is known to oxidize CO and  $H_2$  even at  $-196^\circ C$ (28). Oxidation on n-type oxides is thought to involve lattice oxygen, while on p-type oxides the reaction involves an adsorbed oxygen. Haber's postulate suggests that p-type oxides are active for complete oxidation, but at least some n-type oxides can be used for partial oxidation. This is generally true.

Finally, Satterfield (11) states that "highly mobile" oxygen should result in a highly active, nonselective catalyst. Germain in fact says that for simple metal oxides there is a direct, but limited, correlation between activity and oxygen mobility. Satterfield also points out, however, that oxygen mobility as a sole criterion for catalyst activity and selectivity is somewhat limited. For instance, this concept does not account for the effect of partially oxidized intermediate adsorption on selectivity in series-type reactions nor for the effects of mixed oxide composition and catalyst surface defects on catalytic reactivity, especially in partial oxidation reactions.

Mixed metals oxide are used quite often in industrial partial oxidation reactions, examples being  $Bi_2O_3$ - $MnO_3$  for the oxidation of propene to acrolein and  $V_2O_5$ - $MoO_3$  for oxidation of benzene to maleic anhydride. Some mixed oxides also are quite active deep oxidation catalysts, a good example being  $MnO_2$ - $CuO$ . The difficulties in understanding mixed oxides are of course more formidable than they are for single metal oxides. It is a well-established empirical fact that mixed oxides behave quite differently than as individual oxides in most catalytic reactions. This situation is further complicated by the often dramatic effect of "promoters", such as alkali metal oxides that are added to the catalyst intentionally.

The mechanism of catalytic oxidation on mixed metal oxides is thought to be similar, at least in principle, to that on single metal oxides. The interesting aspect of these mixed oxides is their generally higher activity compared to the single oxide components. This is thought to be due to the readily available multiple energy levels of the metals and their associated oxygen anions, which makes available to the organic reactant more accessible active oxygen anions. This also may result in higher surface mobility of oxygen and /or the activated complex as well as electron transport through the lattice.

Although many attempts to examine the mechanism of catalytic oxidation have been reported, the exact mechanism even for intensely studied reactions such as CO oxidation is not completely understood. However, certain general statements about p-type oxides and  $V_2O_5$  deep oxidation catalysts can be made :

- 1) High activity catalysts are generally metal oxides in which the metal can assume more than one valence state, are p-type semiconductors, and produce highly mobile chemisorbed surface oxygen (a consequence of this last characteristic is an intermediate heat of adsorption of  $O_2$  that produces the familiar "volcano" plot).

- 2) Mixed metal oxides often have unique properties relative to the individual oxide constituents, primarily in terms of activity and stability (22).

- 3) Lattice oxygen, as well as gas phase oxygen, participates in the catalytic oxidation process. Various attempts to explain exactly how the process occurs usually include a redox cycle at the oxide surface with anionic oxygen from the surface (either chemisorbed or lattice

oxygen) reacting with a chemisorbed or gas phase organic reactant. Whether the reactant is oxidized directly in the gas phase by an adsorbed oxygen species (a so-called Eley-Rideal mechanism) or adsorbed and then reacts (a Langmuir-Hinshelwood mechanism) is especially important in considering mixture effects because the selectivity for a given reactant in a mixture would presumably be different if it must be adsorbed prior to being oxidized. Such mixture effects are difficult to study at the oxide surface, and little is reported.

4) Various attempts have been made to relate the activity of metal oxides for catalytic oxidation with various thermodynamic properties that would seem to be important, knowing that in a continuous system oxygen must adsorb from the gas phase and interact with the metal oxide lattice. Such correlations include comparison of catalytic activity with heat of formation of the oxide from elemental metal (per oxygen atom usually), initial heat of chemisorption of oxygen on evaporated metal films, heat of dissociation of the first oxygen atom from the oxide, grams of oxygen per gram of metal oxide, and others. One of the most widely used comparisons is that of activity versus the heat of reaction for reoxidation of the catalyst. Such a plot has a maximum (see Figure 2.2), suggesting that if oxygen is chemisorbed either too weakly or too strongly, the activity is not as great as for some intermediate strength of chemisorption that might correspond to activated yet mobile surface oxygen species (probably anionic).

5) The most active single metal oxide catalysts for complete oxidation for a variety of oxidation reactions, as calculated from the above techniques and confirmed by experiment, are usually found to be oxides of V, Cr, Mn, Fe, Co, Ni, Cu. The mechanism of oxidation on these p-type oxide catalysts is generally thought to involve strong adsorption of the organic compound at an ionic oxygen site in the oxide lattice leading to the formation

of an activated complex. This complex can then react further to yield products to complete combustion. Some authors have suggested that a degree of oxygen mobility on the surface is necessary for such a mechanism, with the successive desorption of complete oxidation products  $\text{CO}_2$  and  $\text{H}_2\text{O}$  and movement of the remaining activated complex fragment to a nearby available oxygen anion for further reaction.

6) Metal oxides generally have somewhat lower activity than do noble metal catalyst, but they have greater resistance to certain poisons (especially halogens, As, Pb, and P).

## 2. Noble Metals

Noble metals are defined herein as Pt, Pd, Ag, and Au. These noble metals are frequently alloyed with the closely related metals Ru, Rh, Os, and Ir, and they are usually supported on an oxide support such as  $\gamma\text{-Al}_2\text{O}_3$  or  $\text{SiO}_2$ . Although in principle any of these metals may be used as oxidation catalysts, in most practical systems only Pt, Pd, and a few alloys are used because the generally high temperatures employed for most oxidation catalyst applications (e.g., catalytic incineration, automotive exhaust catalysts) can cause sintering, volatility loss, and irreversible oxidation of the other metals. Limited supply and the resulting high cost of these other metals also minimizes their use. As a result, most reported research deals with supported Pt and Pd (and alloys of these with other metals).

In general, much less research has been reported on catalytic oxidation at conditions of interest herein on noble metals than has been reported on metal oxides, especially research dealing with the mechanism of

complete oxidation. Although supported noble metal oxidation catalysts (apparently based on formulations developed for automotive applications) have been widely applied for control of exhaust from various industrial processes, most reported information deals primarily with overall performance, not the mechanism of oxidation.

One reaction over noble metals that has been extensively studied is the oxidation of CO. Although is not within the scope of this review to examine the vast literature dealing with this reaction, others who have done so have reached several general conclusions of interest : (31)

1) A change in reaction order in CO from positive at low CO concentrations to negative at high CO concentrations and multiple steady states have been both predicted and observed.

2) Several surface species of adsorbed CO have been observed during oxidation on Pt/Al<sub>2</sub>O<sub>3</sub>. Barshad et al. conclude that CO adsorbed on oxidized Pt was not taking part in the reaction, but that CO adsorbed on a Pt atom sharing an adsorbed oxygen with a neighbor accounts for their results (32).

3) Apparently, O<sub>2</sub> adsorbed onto adjacent Pt atoms, and CO diffuses along the surface to the active O-containing sites. O<sub>2</sub> adsorption have been postulated as being rate-determining in at least some cases (32).

Despite the extensive research on this specific reaction, it is unclear whether these results can be directly extended to oxidation of other organic compounds. However, it is interesting that, at moderate CO concentrations (10vol%CO in 15%O<sub>2</sub> / 75%N<sub>2</sub>) and low temperatures (150 °C,



the rate-determining step is  $O_2$  adsorption adjacent Pt sites (32). Above 230 °C, Langmuir postulated that the mechanism of CO oxidation over Pt changed to a reaction between adsorbed  $O_2$  and gaseous CO (an Eley-Rideal mechanism) (33). Further, in a large excess of  $O_2$ , above 350 to 400 °C. Sklyarov et al. and Tretyakov et al. (20) show that on pure Pt metal the rate law is first order in CO and zero order in  $O_2$ . The above observations suggest that, as the temperature is increased, the surface concentration of adsorbed oxygen increases while that of CO decreases.

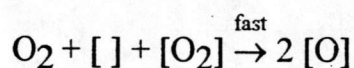
The noble metals Pt and Au are said to function in the reduced state at all conditions. This may be true for Pd as well, at least at relatively low temperatures. At temperatures above about 450 °C, prolonged exposure of supported Pd to oxygen has been observed to cause structural changes in the Pd metal that result in a loss of catalytic activity in the oxidation of methane (34). In this same study, supported Pt did not undergo detrimental structural changes at these temperatures. Noble metals generally form quite unstable oxides (e.g.,  $\Delta H_{298}^\circ$  for  $Au_2O_3 = 0$ ). However, oscillatory behavior in catalytic oxidation of n-heptane on Pt/ $\gamma$ - $Al_2O_3$  at 178 °C has been linked to the presence of relatively active reduced metallic Pt sites and relatively inactive oxidized  $[Pt^{IV}]$  (35), suggesting that even at moderate temperatures, there may be a complex interaction between the Pt and oxygen that affects the hydrocarbon conversion. One result of this interaction is the observation that there is a direct relationship between the oxygen adsorption capacity for Pd and Pt, on a variety of oxide supports, and the catalytic oxidation activity, at least for methane. Thus, the mechanism for oxidation on noble metals may be different from that on metal oxides. Literature on the complete oxidation of organic compounds over noble metals or supported noble metals shows that:

1) Noble metals may follow either a Langmuir-Hinshelwood type of mechanism (reaction between adsorbed oxygen and an adsorbed reactant) or an Eley-Rideal mechanism (reaction between adsorbed oxygen and a gas phase reactant molecule). In the case of nucleophilic organic reactants (e.g., CO or alkenes), both the oxygen and reactant are adsorbed and react on the surface.

2) On Ag, oxygen chemisorption is relatively strong, with a transfer of electrons to the oxygen taking place. On Pd, however, oxygen adsorption is relatively weak. This implies that the reaction mechanism on Ag involves a redox mechanism similar to that for metal oxides. On Pd, however, anionic surface oxygen species do not exist and the mechanism may proceed through direct electron transfer between the reactant and oxygen, with the metal surface providing an energy-modifying function. On Pt, Volter et al. (35) show that oxidation occurs faster in air than in pure oxygen due to the formation of a relatively inactive "oxidic" [Pt<sup>IV</sup>] species in highly oxidizing environments.

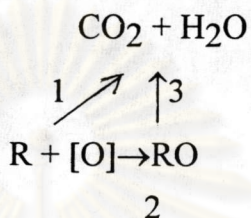
3) Pt and Pd have a high activity for total oxidation of C<sub>2</sub>-C<sub>8</sub> alkenes. As a general rule, these noble metals have a higher activity than do metal oxides for complete oxidation of alkenes on these metals has not been well studied.

4) The general mechanism of oxidation over noble metals is thought to involve the dissociate adsorption of oxygen :



where [ ] represents a "surface site".

This step is then followed by direct reaction of the gaseous organic reactant with [O] or the reactant may be weakly adsorbed first. Both Golodets (25) and Germain (36) have proposed that oxidation often occurs by a parallel-series mechanism :



### Adsorption of CO on Metals

Carbon monoxide is a molecule with an extremely strong C-O bond (1.06 MJ/mol dissociation energy) and only due to the fact that it possesses "reactive" orbitals ( $5\sigma$ ,  $2\pi^*$ ) by which it can very easily interact with metals and ions, the CO-chemistry offers such a variety of reactions. Among them also the CO bond breaking by many metals, since the affinity of many metals to oxygen and carbon is high enough to make the breaking of the CO bond energetically possible.

Carbon monoxide has a dipole with a negative end on carbon. The existence of the almost non-bonding  $5\sigma$ -orbital and of electron-electron interaction is responsible for the dipole orientation and size. With transition metals, CO interacts with C-oriented to the metal and O away from it. According to all available information, the orientation of the molecularly bond CO is always perpendicular to the surface, within a small angle. This orientation is-actually against the intuitive expectation-preserved also when CO is adsorbed on/or in the neighborhood of "steps" on the metal surface or next to an atom of another metal, as e.g. alkali atom.

When CO has to undergo a dissociation on a metal (a pure or promoted one) it is very likely that CO must tilt (an activated movement) and bring O in contact with the surface. However, there are only very few pieces of information on the - possibly - horizontal laying CO. This is a very elusive hard to detect transient state.

Adsorption of CO on a zero valent metal is accompanied by a decrease of the C-O bond strength. A delocalization or partial removal of  $5\sigma$  electrons increases slightly the CO bond strength but this effect is outweighed by the effect of acceptance of electrons into the  $2\pi^*$ (antibonding) CO orbitals, by which step the CO bond is weakened. The interaction of CO with a metal manifests itself by changes in the  $\nu(\text{CO})$  frequency (wave number). Resulting shift  $\Delta\nu = \nu(\text{CO, free}) - \nu(\text{CO, ads})$ , is built up from several contributions which has been roughly estimated for the single-coordinated CO on a metal like Pt as follows: an effect of mechanical bonding to a heavy body:  $+30 \text{ cm}^{-1}$ ; adsorbed dipole-image dipole interaction:  $-50 \text{ cm}^{-1}$ ; effect of chemical binding usually described as direct and back donation of electrons:  $-60 \text{ cm}^{-1}$ ; mutual interaction of adsorbed CO molecule: about  $+30 \text{ cm}^{-1}$ ; all with regard to  $\nu = 2143 \text{ cm}^{-1}$ , of the free CO.

The dynamic dipoles of the adsorbed CO molecules interact with each other and this is the main component of the CO-CO interaction. This interaction leads to an increase in  $\nu(\text{CO})$  with  $\Theta(\text{CO})$ . when a  $^{12}\text{C}^{16}\text{O}$  dipole layer is diluted by dipoles vibrating at a different frequency (e.g., those of  $^{13}\text{CO}$  or,  $\text{C}^{18}\text{O}$ ) the interactions are suppressed, since they are strongest at the resonance frequency. Also alloying causes such dilution effect if CO adsorbed on individual alloy components differs significantly in  $\nu(\text{CO})$  or when one component does not adsorb CO at certain conditions at all.

Carbon monoxide adsorbed on metals and alloys can be visualized as bound to certain "sites". Sites consist of one or more contiguous metal atoms (ensemble of atoms). One can distinguish in the IR spectra regions of  $\nu(\text{CO})$  which can be ascribed to certain ensembles, i.e. to certain coordinations of the adsorbed CO :

single coordinated (linear, terminal)	2000-2130 $\text{cm}^{-1}$
double coordinated (bridged)	1880-2000 $\text{cm}^{-1}$
triple (tripodic), multiply coordinated	1700-1900 $\text{cm}^{-1}$

Carbon monoxide molecules interact with each other and therefore also at very low coverages they form layers of ordered structures observable by surface crystallography (LEED), or they form ordered patches clusters. Crystallographic information together with the IR spectra allowed a very detailed and well supported assignment. The CO-CO interactions cause that CO prefers different sites at different surface coverages  $\Theta(\text{CO})$ . This has even lead to temporary doubts about the site character of CO adsorption but the present generally accepted view is as described.

There has been a discussion whether CO molecules can interact with each other through-the-metal. In principle, a through-the-metal interaction of covalently adsorbed species does exist but estimates of its strength show that this interaction is only of the size of the physical adsorption forces. Blyholder (37) and many authors after him, speculated on "competition" effects : CO molecules compete for the metal  $d$ -electrons and this competition suppresses the extent of back donation from  $d$  into the  $2\pi^*$  -orbitals. However, it appeared that with some surfaces the  $\nu(\theta=1)-\nu(\theta=0)$  difference is exactly equal to that identifiable as a result of the CO-CO dynamic dipole interactions. However,

with some other surfaces the CO-CO interactions leads to the shifts in the position of CO adsorbed and by that an additional  $\nu(\theta=1)-\nu(\theta=0)$  effect is created. This additional effect has been (in our opinion incorrectly) ascribed to the chemical effects, like the mentioned competition for the *d*-electrons. Small particles of metals, with their atomically rough surfaces, restrict shifts in the CO positions. On the other hand small particle adsorbents show a variety of different CO sites. Thus no evidence has been found yet for "competition" or any other strong through-the-metal interaction.

When CO is coadsorbed with species having a dipole or forming a dipole with the metal surface, the dipole of CO is influenced (Stark effect) and to some extent also the occupation of the CO orbitals. These coadsorbed species cause then, next to a dilution effect, additional shifts in the  $\nu(\text{CO})$  by this electrostatic mechanism. This is also probably a part of the  $\nu$ -shift caused by the fragments of hydrocarbon molecules or by benzene molecules. Finally, if the coadsorbed species influences the position of CO on the surface, again an additional  $\Delta\nu(\text{CO})$  effect results from it.

There are several pieces of information in the literature on the different reactivity of CO adsorbed on different sites i.e. differently coordinated. With Ni seems to be very likely that CO in multiply-coordinated form dissociates first. With other metals the information is less complete or less certain.