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CATALYSIS

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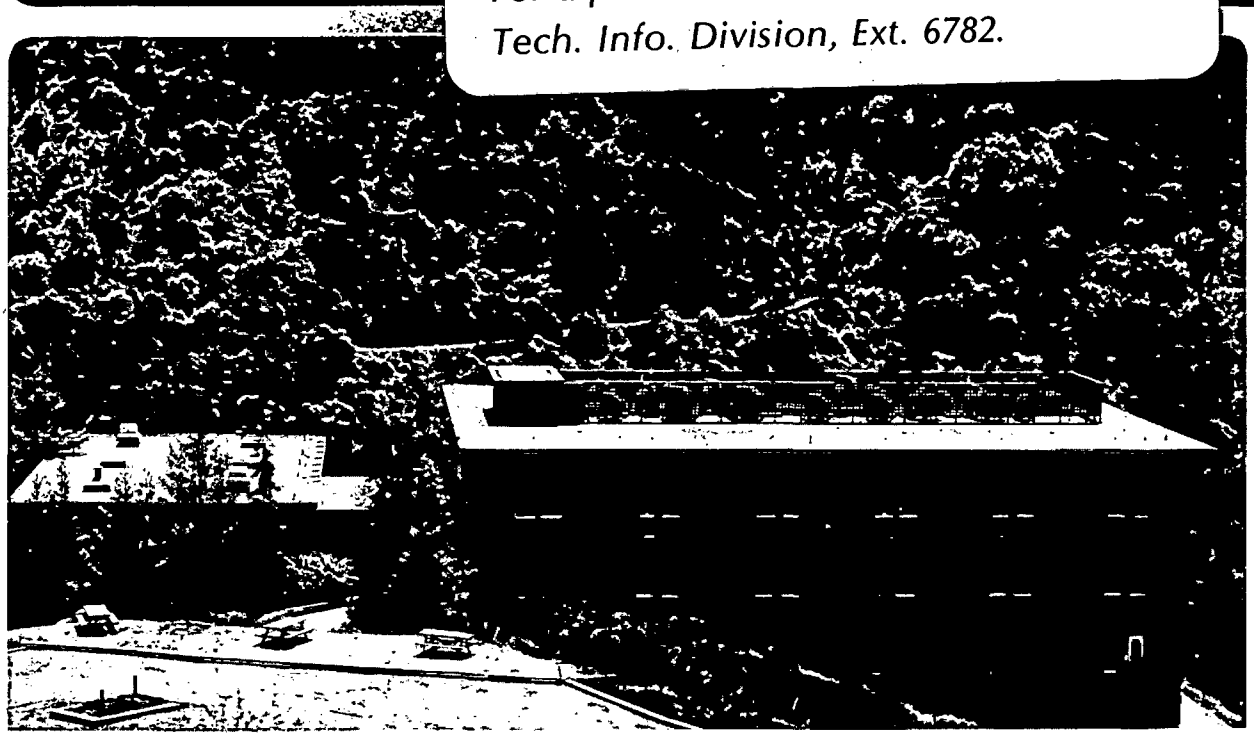

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CATALYSIS

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ABSTRACT

The concepts of heterogeneous catalysis and catalytic science are introduced, and the tools of the modern catalytic scientist's trade are then briefly described. Six detailed "case histories" of important industrial catalytic processes are presented. The application of modern surface science, to scrutinise the catalyst surface and the reaction mechanisms on the molecular scale, is emphasized.

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I. INTRODUCTION

The word "catalyst" was introduced by Berzelius (1836) to describe the property of certain substances which facilitate chemical change without being consumed during the reaction. The original definition has stood the test of time; catalysts aid the attainment of chemical equilibrium by reducing the potential energy barriers in the reaction path. For example, hydrogen and oxygen will remain as an unreacted mixture indefinitely, although in the presence of a platinum or nickel gauze, they react instantaneously to produce water.

Catalysis is a kinetic phenomenon. The speed of a catalysed reaction is often described in terms of a "turnover rate", which reveals how many product molecules form per second at a given temperature and pressure.

Since the catalytic action occurs at specific sites on solid surfaces, often called "active sites", the rate can be increased phenomenally by using very high surface area catalysts. Catalysts with surface areas of $1\text{-}10^2$ m^2/gm are quite common. These are ususally prepared by finely dispersing the active metal or compound catalyst on high surface area "supports", which usually consist of refractory oxides or oxy-hydroxides (alumina, zirconia, silica, etc.). The catalyst dispersion, defined as the number of surface atoms per total number of atoms, may range from unity (all of the atoms are on the surface) to ~ 0.01 and the catalyst particles may range in size between 10-200Å. This dispersed system must maintain structural and chemical stability for thousands of hours under the conditions of high temperature (400-900K) and high pressure ($1\text{-}10^2$ atmospheres) frequently encountered in the chemical technology. The design of new, more stable, catalysts which resist chemical attrition and sintering of the small particles is a constant concern of the catalytic scientist.

The specific rate, the number of product molecules per catalyst unit area per second, (or the number of product molecules per surface site per second)

at a given temperature and pressure provides a figure of merit to compare the "activity" of different catalysts for the same reaction under similar experimental circumstances. Although only a fraction of the catalyst surface is active during the reaction this fraction is usually unknown; thus the specific rate provides a lower limit of the catalyst's activity.

Specific rates must be in the range of 10^{-4}-10 to be part of a viable process in chemical technology. As a consequence, most catalytic reactions that involve the breaking or rearrangements of C-H, C-C, H-H, C=O and N≡N bonds are carried out in the temperature range of 400-900K since activation energies range from a low of 10-15 kcal/mole (for hydrogenation of unsaturated hydrocarbons) to a high of 40-50 kcal/mole (for dehydrocyclisation or hydrogenolysis of hydrocarbons). There are, of course, several exceptions; the catalytic isotope exchange of hydrogen ($H_2 + D_2$ ----> 2HD) occurs at temperatures as low as 77K on most transition metal surfaces and the hydrogenation of ethylene to ethane is readily performed at 300K. The oxidation of ammonia to nitric oxide, a highly exothermic reaction, is ususally carried out in the range 1100-1200K.

By multiplying the specific rate by the reaction time used in a given study, the turnover number, T.N., (number of product molecules per catalyst surface site) can be obtained. The T.N. must be greater than unity to assure that the reaction is catalytic (i.e. that there is more than one "turnover".) If the T.N. is less than unity we may be dealing with a stoichiometric reaction and our solid surface may be acting as a reactant rather than a catalyst. Thus, to demonstrate its catalytic character, the reaction must be carried out for long enough to obtain a turnover number that is greater than unity.

Many chemical reactions of interest lead to the formation of several different, but all thermodynamically feasible, products. It is often of greater interest to produce one of the many different molecules selectively, rather than

increasing the overall rate. A selective catalyst will facilitate the formation of one product molecule while inhibiting the production of other, different molecules, even though the formation of all of the species is thermodynamically feasible. Thus, the blocking of reaction pathways which lead to the formation of unwanted molecules is as important an attribute of a good catalyst as the lowering of the potential energy barrier along the reaction pathway to the desired product molecule.

The reaction probability, R.P., is defined as the number of product molecules formed per number of reactant molecules incident on the catalyst surface. It is readily obtained by dividing the specific rate of catalysis by the incident reactant flux. R.P. is generally very low, and varies in the range 10^{-12}–10^{-6} for most catalytic reactions in the pressure and temperature ranges generally employed in the chemical industry. The reason for this is the long surface residence time for the adsorbed molecules and reaction intermediates, (usually in the range of 10^{-1}–10^{3} sec.) which leads to a surface which is covered and inaccessible to the impinging molecules. The desorption of the product molecules from the catalyst surface frees surface sites, onto which the reactant molecules may adsorb. The desorption is always an endothermic reaction and appears to be the slow step in the catalytic process for most reactions running at high pressures.

The long surface residence times of adsorbed intermediates have another interesting consequence. The molecules may diffuse over long distances (10–10^{4}Å) within their surface lifetime, visiting many catalytic sites where they can undergo consecutive reactions and molecular rearrangements. Thus, a catalyst surface may possess many different active sites, all of which are likely to be accessible to the adsorbed reactants.

The coverage of adsorbed molecules, σ, [molecules/cm^2] is usually determined by multiplying the incident flux, F, [molecles/cm^2 sec] by the surface residence

time, t, [sec].

$$\sigma = F \times t$$

The flux can be estimated from the reactant pressure, $F = P(2\pi MRT)^{-1/2}$, and the residence time $t = t_o \exp[\Delta H_{ads}(\theta)/RT]$ depends on the heat of adsorption, ΔH_{ads}, the temperature, T, and the preexponential factor, t_o, (which varies in the range 10^{-17}-10^{-13} (Ibach, 1980) depending on the degree of mobility of the adsorbed molecules). The heat of adsorption is a measure of the strength of the chemical bond between the adsorbed molecule and the surface. It depends on both the coverage and the structure of the catalyst surface. As the coverage is increased the adsorbed molecules are packed closer together in the surface monolayer. If the interaction among the adsorbates is repulsive, the heat of adsorption per molecule decreases as the coverage in the monolayer is increased. This is the case for molecular CO adsorption on most metal surfaces (Engel, 1979). If the adsorbate-adsorbate interaction is attractive, the heat of adsorption per molecule may increase with coverage. This occurs, for example, during the growth of oxide monolayers on metal surfaces, (Buchholz, 1975).

The surface structure sensitivity of bonding of adsorbed molecules and as a result, the structure sensitivity of catalytic reactions is well documented, (Spencer, 1982, Gillespie, 1981). The surface structure is heterogeneous on the atomic scale (Fig. 1) and there are many surface sites that are distinguishable by their number of nearest neighbours: there are surface atoms can form terraces, steps and kinks, and these structures may, in turn, contain point defects, adatoms and vacancies. The binding of adsorbed atoms or molecules at each site may be different, giving rise to heats of adsorption that vary with the surface structure. This effect is particularly noticeable in adsorption and desorption studies carried out on single crystal surfaces. These surfaces

can be prepared with different relative concentrations of terrace, step and kink sites. The structure sensitivity of bonding can lead to structure sensitivity in many catalytic reactions. These have been described in the literature (Toyoshima, 1979).

It is often thought that the most active catalysts consist of surfaces which can form bonds of intermediate strength with adsorbates. If the surface chemical bonds are too strong, the reaction intermediates either have surface lifetimes which are much too long, or they may simply never come off the surface, forming stable surface compounds such as oxides, carbides or nitrides instead. On the other hand, if the surface bonds to adsorbates are too weak, the needed chemical bond-breaking or rearrangements might not occur before desorption. Chemical experience is in agreement with the contention that intermediate bond strength leads to superior catalyst activity. The structure of the catalyst surface, however, is one of the key factors which control chemical selectivity.

The catalytic process may be subdivided into several elementary reaction steps. These are a) adsorption, b) surface diffusion, c) molecular rearrangements at active surface sites and d) desorption. There are several techniques capable of studying the elementary reaction step. Predominant among them are (1) molecular beam surface scattering and (2) thermal desorption. The reader is referred to recent review papers describing these methods of investigation (Ceyer, 1977; King, 1975).

The catalyst, unfortunately, does not have an indefinite life, but becomes "poisoned" or deactivated after a certain period of time. It is thought to reflect good catalyst performance if seven pounds of products are produced per pound of catalyst before the catalyst must be regenerated. Catalyst deactivation and regeneration are important and major fields of catalysis science. There are many possible reasons for deactivation. For example, the catalyst

may restructure as a consequence of selective adsorption of impurities from the reactant stream, such as sulphur or nitrogen. Alternatively, carbon may be deposited, blocking the active surface, due to side reactions leading to complete dehydrogenation and decomposition of organic molecules during hydrocarbon conversions. The use of additives, (introduced either during catalyst preparation or with the reactants) to prevent restructuring of the catalyst or the blocking of active sites is being explored intensively by many research laboratories.

Catalysis is an exciting and diverse field that has, in recent years, rapidly been converted from an art into a science. This is largely the result of modern surface science, which has permitted molecular level scrutiny of the catalyst surface. The structure, composition and oxidation state of atoms on the catalyst surface can now be correlated with the macroscopic reaction parameters: the specific rate, activation energy and selectivity. As a result, rapid advances in the understanding of many technologically important catalysts are presently being made, and the design of improved catalysts becomes feasible as we utilize the knowledge gained from the study of surface science.

We shall describe several "case histories" of important catalytic processes which will serve to illustrate the rapidly accelerating development of catalysis science over recent years. We hope that this review will stimulate and facilitate the entry of researchers into this exciting field.

II. EXPERIMENTAL METHODS IN CATALYTIC RESEARCH

Practical catalyst systems often consist of millions of small particles dispersed on oxide supports containing many small pores and, as a result, enormous internal surface areas (~ 10^2 m^2/gm). In the past, most of the techniques utilized for the physico-chemical characterisation of catalyst surfaces were intended for use with these highly dispersed systems. In situ analysis by infrared spectroscopy, (Hair, 1967; Blyholder, 1968; Force, 1975; Eischens, 1958) Mossbauer spectroscopy (Dumesic, 1977) and electron spin resonance (Lunsford, 1972) were frequently carried out. H-D exchange studies during the catalytic reaction probed the importance of the breaking or forming of C-H bonds through detection of changes of reaction rates with isotopic substitution (De Jongste, 1980; Mintsa-Eya, 1980). Recently extended x-ray absorption fine structure studies (EXAFS) using high intensity x-ray sources have revealed the coordination number and nearest neighbor bond distances in dispersed catalyst particles (Sinfelt, 1981). Traditionally, the kinetics of catalytic reactions on dispersed catalyst systems have been determined by measuring the concentrations of reactants and products as a function of time, temperature and pressure or as a function of other reaction variables. Detection is usually accomplished by means of a gas or liquid chromotograph or mass spectrometer and the reactions may be carried out in a flow or batch mode.

There are, however, great difficulties inherent in studying the structure, composition and the oxidation states of surface atoms in dispersed high surface area systems. It is not possible to prepare such high area surfaces with reasonable uniformity of structure and composition. Since these parameters have large effects on the catalytic process, reproducibility of results is difficult to obtain. In addition, working practical catalyst systems contain many

additives that are "promoters" for certain desirable side reactions, others that prevent restructuring and still others that selectively block special surface sites which would otherwise facilitate undesirable reactions. In fact, the working system is so complex that its reliable and reproducible study on the molecular scale must be carried out through the use of model systems.

For this purpose small area (~ 1 cm^2) single crystals, polycrystalline fails or thin films are frequently used. These have many advantages for definitive research investigations, since their surfaces can be prepared with structural uniformity, and readily cleaned by ion bombardment or chemical treatment. In addition, the external surface can be exposed to electron, atom or ion beams in high vacuum to determine its structure, composition and oxidation state. All of the newly developed surface science techniques can be used to characterise such a small area catalyst surface at low pressures (~ 10^{-9}-10^{-5} torr). A list of the most frequently used techniques is given in Table 1. Additives may be deposited on the model catalyst surface by deposition from the vapor phase.

After surface characterisation the small area catalyst must be exposed to the high pressure-high temperature conditions of the catalytic reaction. For this purpose a low pressure-high pressure cell technology has been developed (Blakely, 1976a). The catalyst, after surface characterization in high vacuum is enclosed in an isolation cell. This small volume (~ 100 cm^3) chamber can be pressurised and the reaction carried out under conditions that are very similar to that used in the chemical industry. The reactant gases are circulated in the high pressure loop and the products periodically sampled using a gas chromatograph. Figure 2 shows one type of such an apparatus. As long as the reaction rates are in the range of 10^{-4}-1 product molecules per site per second, our present day detectors are sensitive enough to monitor the product distribution and the reaction rates even when using such small surface area catalyst

samples. The reaction may be interrupted by pumping out and subsequently opening the isolation cell to ultrahigh vacuum, where its surface can be scrutinised with the various techniques of surface science. The cell may be closed again and the reaction continued. In this way, the catalyst structure, composition and oxidation state can be correlated with the reaction parameters.

When using model catalysts it is always necessary to compare their catalytic behaviour with those of the large area practical catalysts. Identical reaction rates, activation energies and product distributions were found within experimental error for several system, when such comparisons were performed. These reaction systems include the hydrogenation of CO over rhodium (Castner, 1980) and nickel (Goodman, 1980), cyclopropane ring openings (Kahn, 1974) over platinum and the hydrogenation of cyclohexene over platinum (Davis, 1980).

TABLE 1

Table of some of the frequently utilized surface characterization techniques to determine the structure and composition of solid surfaces. Adsorbed species present at concentrations of 1% of a monolayer can be readily detected.

SURFACE ANALYSIS METHOD	ACRONYM	PHYSICAL BASIS	TYPE OF INFORMATION OBTAINED
Low energy electron diffraction	LEED	Elastic backscattering of low energy electrons	Atomic surface structure of surfaces and adsorbates
Auger electron spectroscopy	AES	Electron emission from surface atoms excited by electron, x-ray or ion bombardment	Surface composition
High resolution electron energy loss spectroscopy	HREELS	Vibrational excitation of surface atoms by inelastic reflection of low energy electrons	Structure and bonding of surface atoms and adsorbates
Infrared spectroscopy	IRS	Vibrational excitation of surface atoms by absorption of infrared radiation	Structure and bonding of adsorbates
X-ray and ultraviolet photoelectron spectroscopy	XPS UPS (ESCA)	Electron emission from atoms	Electronic structure and oxidation state of surface atoms and adsorbates
Ion scattering spectroscopy	ISS	Elastic reflection of inert gas ions	Atomic structure and composition of solid surfaces
Secondary ion mass spectroscopy	SIMS	Ion beam induced ejection of surface atoms as positive & negative ions	Surface composition
Extended X-ray absorption fine structure analysis	EXAFS	Interference effects in photoemitted electron wave function in x-ray absorption	Atomic structure of surfaces and adsorbates
Thermal desorption spectroscopy	TDS	Thermally induced desorption or decomposition of adsorbates	Adsorption energetics and composition of adsorbates

III. "CASE HISTORIES" IN INDUSTRIAL CATALYSIS

A. CATALYTIC SYNTHESIS OF AMMONIA

1. Introduction

By the end of the 19th Century a great demand for fixed nitrogen had been created; this was due both to the widespread use of artificial nitrogeneous fertilizers and to an increasing demand for explosives. The principal sources of fixed nitrogen at the time was sodium nitrate, obtained from salt beds in Chile. This made it strategically sensitive. Several attempts had been made to fix atmospheric nitrogen. These included heating calcium carbide to high temperatures in nitrogen to form calcium cyanamide, and creating an electrical discharge in air to produce small quantities of nitric oxide. Neither method was economically feasible on large scale. A process whereby ammonia could be directly synthesised from its elements seemed particularly attractive, especially after the invention, in 1902, of a catalytic method for the oxidation of ammonia to nitric acid.

In 1904, direct synthesis of ammonia was achieved for the first time when Haber produced 0.004% (vol.) ammonia by passing a mixture of hydrogen and nitrogen over very pure iron at 1000°C (Mittasch, 1950, Haber, 1904). The thermodynamics of the reaction were soon established (Haber, 1905, 1908, Nernst, 1907) and by going to lower temperatures and higher pressures, Haber produced a recycling system with high yields of ammonia (Haber, 1910). The principle of this system, which involves condensing out the sythesised ammonia and returning the unreacted gases to the reactor, forms the basis of all modern ammonia manufacturing plants.

Bosch and Mittasch (working with B.A.S.F. in Germany) carried out several thousands of tests on potential ammonia synthesis catalysts between 1909 and

1912 (Mittasch, 1950). Of the substances tested, osmium (Mittasch, 1951) and uranium were found to have higher activity than pure iron used by Haber, although osmium was too expensive for large-scale use and uranium too susceptible to poisoning. One of the most active catalysts tested during this period was a sample of Swedish magnetite (Fe_3O_4) which, on analysis, was shown to contain traces of alumina (Al_2O_3) and magnesia (MgO) as well as certain alkali metal oxides. It ws found that a catalyst of similar activity could be made by adding alumina and potassium oxide (K_2O) to pure Fe_3O_4. A catalyst of this composition was used in the first ammonia plant which started continuous production early in 1912. The basic composition of industrial ammonia synthesis catalysts has undergone very little change since that time. For a fuller treatment of the early history of ammonia synthesis, the reader is referred to Mittasch (1951).

2. The Structure of the Catalyst

The ammonia synthesis catalyst is usually made by burning pure iron in an atmosphere of oxygen to form powdered Fe_3O_4 which is then mixed with potassium nitrate and alumina, after which the mixture is fused in an electric furnace. After cooling, the resultant solid is crushed and screened to the correct particle size. At this stage, the catalyst would be initially inactive in ammonia synthesis if not first reduced to metallic iron. This is usually accomplished (at ~ 350°C) within the synthesis reactor in a stream of either hydrogen or the reactant gases. Reduction is generally not undertaken outside the reactor, since the reduced catalyst burns spontaneously in air. XPS studies (Ertl, 1979) have shown that prior to reduction, although potassium is present in the bulk at concentrations below 0.5%, it may cover 20% of the catalyst surface. On the other hand, iron constitutes a mere 5% of the surface, whereas it comprises 40% of the bulk. X-ray studies have shown that the unreduced catalyst has the

usual Fe_3O_4 spinel structure (cubic packing of oxide ions with alternate Fe^{2+} and Fe^{3+} ions located in interstices) and that while Al_2O_3 (as γ-alumina) seems to form a solid solution in the Fe_3O_4, K_2O does not enter the oxide matrix, concentrating along the grain boundaries (Nielsen, 1968).

On reduction, the oxygen ions are removed from the Fe_3O_4 lattice, but its external volume changes very little. This is because the iron matrix does not relax, leaving a porous structure of surface area ~ $20m^2g^{-1}$ and average pore radius 240Å (Nielsen, 1970). The XPS spectra (Ertl, 1979) show that far more iron is present on the surface after reduction of the catalyst and that the promoters remain in their oxidised states.

The precise role of the promoters is uncertain, but it has been shown that both K_2O and Al_2O_3 need to be present in order to attain maximum activity. It has been demonstrated (Schafer, 1960) that the alumina forms thin (5-10Å) lamellae around the iron particles, presumably acting as a structural promoter in preventing sintering. The role of the K_2O is more complicated, although there is some evidence to suggest that it functions partially by neutralising acidic sites on the alumina (Brunauer, 1940). The function of potassium in the catalyst will be dealt with more fully below.

Conditions used in ammonia synthesis in industry involve temperatures between 450 and 550°C and pressures of 100-1000 atm. For a description of modern ammonia plant design, the reader is referred to Bridger (1979).

3. The Mechanism of Iron-Catalysed Ammonia Synthesis

Although numerous reactor studies of ammonia synthesis have been undertaken since the beginning of this century, progress in the elucidation of the reaction mechanism has been slow. This is due, in part, to the indirect nature of such experiments, which can often lead to ambiguity in the interpretation of the

results. With the advent of UHV techniques, the basic steps of the synthesis reaction could be probed directly for the first time. The thermodynamics of the reaction do not, however, allow the synthesis of detectable quantities of ammonia under low pressure conditions, since the overall reaction,

$$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)} \qquad \Delta H^{o}_{293} = -46 \text{ kJ mole}^{-1}$$

leads to a decrease in volume and is, therefore, favoured by high pressures. At 720 K, with 10^{-5} torr of a stoichiometric mixture of hydrogen and nitrogen, for instance, the equilibrium ammonia pressure is only 2.8×10^{-16} torr.

The early reactor studies did lead to a greater understanding of the macroscopic kinetics of the reaction as well as producing many valuable spin-offs, such as the BET method of catalyst surface area determination (Brunauer, 1938). The possibility that nitrogen adsorption was the rate determining step in the overall synthesis reaction was first suggested in the early 1930's and confirmed by Emmett and Brunauer (1934) when it was found that ammonia synthesis proceeded at a similar rate to that of nitrogen adsorption. This was further supported by observations of the relatively facile dissociative adsorption of hydrogen (Kozhenova, 1940) on the catalyst. In 1967, Brill (1967) observed the molecular adsorption of nitrogen on the Fe(111) plane in a field emission experiment at liquid nitrogen temperatures. This was followed (Grundy, 1968) by a UHV work function study of nitrogen adsorption on iron films where it was concluded that although nitrogen adsorbed molecularly at low temperatures, it dissociated above 90 K. More recent studies have confirmed this (Kishi, 1977; Ertl, 1976; Bozso, 1977 a&b), and the molecular species is now regarded as a precursor for the atomic state.

Although bulk iron nitride (Fe_4N) is thermodynamically unstable under UHV conditions, Ertl *et al.* (1979 a&b) observed the formation of a few layers of a surface nitride on Fe(111) and Fe(110) after exposure to nitrogen. These stable

surface nitrides had been postulated by earlier workers (Mittasch, 1950; Emmett, 1933). The activation energies and, consequently, the rates of nitrogen dissociation on the three low-index iron crystal planes were found to vary widely (Ertl, 1980), the rate ratio being 60:3:1 for Fe(111):Fe(100):Fe(110) at 550 K. In all cases, the sticking probability of N_2 was found to be of order 10^{-7}.

Hydrogen adsorption was studied in UHV on iron crystals by Bozso et al. (1970 c) and on a polycrystalline sample by Wedler (1976). These results confirmed the earlier studies (Kozhenova, 1940), hydrogen adsorption being found to be non-activated, dissociative (above 100 K), and having a high sticking probability ($S_o \sim 0.16$ at 140 K).

In an effort to identify reaction intermediates in low pressure experiments, the adsorption of ammonia on iron single crystals was also studied. The results of UPS and work function experiments (Grunze, 1978; Weiss, 1979) suggested that ammonia was always bonded to the iron surface through the nitrogen. However, isotopic exchange and decomposition studies (Grunze, 1978, 1979) showed certain differences of behaviour between the low index crystal planes. While the coadsorption of deuterium and ammonia led to deuterium incorporation on the Fe(111) and Fe(100) surfaces (forming NH_2D and NHD_2), this did not occur on the Fe(110) surface. Similarly, on heating ammonia-dosed iron single crystal samples, NH_3, NH_2, NH, N, and H species were all detected on the Fe(111) and Fe(100) surfaces, whereas on the Fe(110) surface, as was confirmed later by SIMS (Drechsler, 1979), NH was the only surface species present. Differences in the activity of the three low index iron crystal planes with respect to the catalysis of ammonia synthesis were first noticed in indirect experiments by Brill and Kurzidim (1969); it was found that ammonia synthesis was occurring only on the (111) plane of the iron whisker under investigation. Experiments on the catalytic properties of small iron particles by Dumesic et al. (1975 a&b) supported Brill's findings

that the (111) plane of iron was the most active in ammonia synthesis and proposed that this was due to the presence of seven-coordinated iron atoms (C_7 atoms) in the Fe(111) surface (see Figure 3).

The face specificity was observed directly by Spencer et al. (1982) who, by the use of a high pressure-low pressure apparatus, were able to show that at 798 K the relative rates for ammonia formation on the (111), (100), and (110) surfaces were 418:25:1, respectively. However, the actual nature of the iron surface during catalysis is still uncertain, although experiments carried out in a UHV system equipped with a preparation chamber (Ertl, 1980) suggest that the nitrogen coverage is low under reaction conditions. Ertl argues that this is clear evidence that the hydrogenation of molecular nitrogen is not involved in iron-catalysed ammonia synthesis, since, if it were, the facile dissociation reaction: $N_{2ads} \longrightarrow 2N_{ads}$ would rapidly saturate the surface with nitrogen. The generally accepted reaction pathway for ammonia synthesis is therefore

$$H_2 \rightleftharpoons 2\,H_{ads}$$

$$N_2 \rightleftharpoons N_{2ads} \rightleftharpoons 2\,N_{ads}$$

$$N_{ads} + H_{ads} \rightleftharpoons NH_{ads}$$

$$NH_{ads} + H_{ads} \rightleftharpoons NH_{2ads}$$

$$NH_{2ads} + H_{ads} \rightleftharpoons NH_{3ads} \rightleftharpoons NH_{3(g)}$$

the step $N_{2ads} \longrightarrow 2N_{ads}$ being rate limiting. At high pressures, and if the conditions are far away from equilibrium (i.e. the rate of NH_3 decomposition is negligible) the rate of NH_3 formation can be given by (Ertl, 1980) $r = k^1 \cdot P_N$. However, at significant conversions, the situation becomes more complicated, and a model involving competitive adsorption must be used. The Temkin equation (Temkin, 1940) uses such a model and is well discussed by Ozaki (1979).

Despite the large number of reactor and UHV studies of the subject, the

role of potassium oxide as a promoter of the real catalyst is still not completely understood. Ertl (1980) has found that, particularly on the less active planes, the presence of potassium on an iron surface facilitates adsorption and dissociation of molecular nitrogen. By lowering the work function of the surface, potassium permits more extensive back-donation from the iron into the antibonding orbitals of N_2 increasing the adsorption energy and dissocation probability.

Potassium is added to the real catalyst as K_2O, but this compound is known to decompose and react with hydrogen to form KOH and KH at temperatures well below those used in the industrial reaction. Although KOH itself has been regarded by some as the active promoter (van Ommen, 1975), this seems unlikely, due to the high vapour pressure of this compound at reaction temperatures. Paal et al. (submitted) infer from their K+O coadsorption studies on iron that the potassium and oyxgen form a uniform single layer on the catalyst during reduction, both constituents being attached to the iron. They suggest that while the role of the oxygen is to stabilise the potassium against thermal desorption, it has the undesirable side effect of blocking sites to nitrogen adsorption, leading to an optimal K_2O concentration in the catalyst. It appears that the electronic structure in the vicinity of potassium atoms is unaffected by the presence of coadsorbed oxygen, facilitating the adsorption of molecular nitrogen as in the case of pure K-dosing (Ertl, 1980). Scanning Auger electron spectroscopy has shown that potassium may also play a role in preventing poisoning of the catalyst surface by sulphur.

For further details on the study of the mechanism of ammonia synthesis, the reader is referred to Emmett (1975), Nielsen (1968), Vancini (1971), and Ozaki (1979). The more recent, low pressure work has been reviewed by Grunze (in press).

B. AUTOMOTIVE CATALYSTS FOR POLLUITON CONTROL

1. The Need for Catalytic Converters.

With the post-war boom in car production, automobile related air pollution became a major problem in many urban areas throughout the industrialised world. The principal pollutants originating from car exhaust are carbon monoxide (CO) and hydrocarbons (HC) arising from incomplete fuel combustion, as well as nitrogen oxides (NO_x) formed from the high temperature oxidation of atmospheric nitrogen in the cylinders of the petrol engine. CO is a well known poison, forming a tightly bound complex with haemoglobin in the blood, which inhibits the transport of oxygen from the lungs. In areas with abundant sunshine, hydrocarbons and nitrogen oxides can undergo a photochemical reaction to produce a mixture of nitrogen dioxide, ozone, and peroxyacyl nitrates: these are responsible for example for the characteristic yellow-brown smog of Los Angeles (Haagen-Smit, 1952) and can cause both eye and respiratory irritation even in low concentrations.

By the early 1960's it had become clear that there was a need to control automobile emissions. Since 1967, U.S. federal emission standards, along with those of the State of California and Japan, have become increasingly stringent (Figure 4) and, although they could be initially met by minor engine modifications, the stricter U.S. federal regulations of 1975 made the more expensive, catalytic methods of pollution control virtually unavoidable. An additional pressure in this direction was the rapidly increasing price of oil, since emission control by engine modification generally reduces the fuel economy of the vehicle.

Research on catalytic converters (which remove CO, HC, and/or NO_x from car exhaust, converting them to harmless carbon dioxide, nitrogen, and water) has been in progress since 1949 (Houdry, 1951). However, the U.S. Emission

standards of the early 1970's provided the impetus for a phenomenal increase in the effort expended in this area. Unlike long standing catalytic systems, such as that used in ammonia synthesis, automotive pollution control has been a field where modern surface science has played a key role in catalyst development.

2. Requirements for Catalysts

The requirements for catalytic converters are severe, since they must be capable of efficiently removing CO, HC, and NO_x for 50,000 vehicle miles at high exhaust gas flow rates and under transient conditions (Hegedus, 1980), with temperatures varying from 300 to 1000°C (Wei, 1975). In addition to this, the catalyst must be resistant both to occasional overheating due to engine malfunction and to small quantitites of poisons (Shelef, 1980). The composition of the exhaust gases can also vary considerably, depending mostly on the air-to-fuel ratio (A/F) of the mixture entering the cylinders (Figure 5). Rich mixtures (A/F=12:1) are used to prevent stalling while idling or on cold starts and to provide maximum power during acceleration, while lean mixtures (A/F=16:1) are best for fuel economy at cruising speeds. Although rich mixtures lead to the emission of larger quantities of CO and HC than lean mixtures, the latter lead to higher concentrations of NO_x in the exhaust gases. The types of hydrocarbon present also vary considerably depending both on the mode of driving and the type of petrol used. In addition to the regulated pollutants, significant quantities of water, sulphur dioxide, carbon dioxide, nitrogen, hydrogen, oxygen, and some oxygenated organic compounds are present in the exhaust gases leading to side reactions in the catalytic converter.

The principal pollutant removal reactions are:

$$2NO_x + xCO \longrightarrow N_2 + xCO_2 \qquad (1a)$$

$$2NO_x + 2xH_2 \longrightarrow N_2 + 2xH_2O \qquad (1b)$$

$$NO_x + \text{"HC"} \longrightarrow xH_2 + yCO_2 + H_2O \qquad (1c)$$

$$2CO + O_2 \longrightarrow 2CO_2 \qquad (2)$$

$$\text{"HC"} + O_2 \longrightarrow 2CO_2 + yH_2O \qquad (3)$$

Although reactions 1a, 1b, and 1c occur readily on many catalysts in a reducing atmosphere, the presence of a significant amount of oxygen (as required for reactions 2 and 3) can be inhibitive, the oxygen being preferentially reduced. Similarly, although many catalysts will facilitate the oxidation of CO and HC, these reactions are suppressed in a highly reducing atmosphere. For certain catalysts, however, there exists a narrow "window" of A/F values (and therefore exhaust composition) where the oxidation and reduction reactions can proceed simultaneously (Figure 6). These are known as stoichiometric or 3-way catalysts and achieve pollution control under conditions which also allow great fuel economy. Unfortunately, despite the testing of many thousands of base metal catalysts, the only formulations which can operate in this manner for the 50,000 miles required by U.S. and Calfiornia State laws contain platinum-group metals which, in addition to being expensive, need to be imported from the U.S.S.R. and South Africa. Car exhaust catalysis has now become the largest scale industrial catalytic process in the U.S., requiring approximately $3x10^5$ oz. of platinum metals per year; cheaper, more readily available substitutes for these materials are still being actively sought.

In order to operate a 3-way catalyst, the A/F ratio must be maintained very close to 14.7:1. This is the stoichiometric ratio, i.e. the amount of air admitted to the cylinders is exactly that needed to burn the fuel. Since with conventional carburettors the A/F can vary by ~ 1 due to change of fuel, humidity or altitude, a feedback system involving a zirconium oxide platinum sensor is used in modern pollution control systems to monitor the oxygen concentration of the exhaust gases and regulate the amount of air admitted to the cylinders (Figure

7). While the standard 3-way catalyst is effective at removing all three regulated pollutants, further HC and CO removal can be achieved by using a dual bed approach. In this system, after passing over a 3-way catalyst, the exhaust gases are mixed with air and passed over an oxidising converter. This arrangment is less effective at NO_x removal, however, since traces of NH_3 formed in the 3-way bed may be re-oxidised to NO by the oxidation catalyst (Shelef, 1975).

3. Catalyst Mechanism and Poisoning

Of the pollution removal reactions mentioned above, by far the most researched has been the catalytic oxidation of CO (Engel, 1979). This reaction appears to ossur in a similar fashion on platinum, palladium, and rhodium surfaces, and little, if any, sensitivity to the structure of the surface has been observed. The individual steps probably involved in the reaction are as follows (Engel, 1979):

$$CO \longrightarrow CO_{ads}$$

$$O_2 \longrightarrow 2O_{ads}$$

$$O_{ads} + CO_{ads} \longrightarrow CO_2$$

i.e. the reacting molecules are both adsorbed on the surface before they react, the oxygen having dissociated. The reaction is highly self-poisoning; it proceeds at a maximum rate at low coverages, slowing down rapidly as the CO coverage increases. This is due to the blocking of sites on the surface due to the dissociative adsorption of oxygen - an essential step in the reaction. An oxygen-saturated surface will, however, adsorb CO and carry out the oxidation, presumably due to a compression of the surface oxygen, making free sites available for CO adsorption.

The other pollution removal reactions have been less rigorously studied. Dubois et al. (1980) have studied the interaction of CO and NO on a rhodium (331) surface using electron energy loss spectroscopy (ELS) and suggested a mechanism:

$$2NO_{(g)} \longrightarrow N_{2(g)} + 2O_{ads}$$

$$2O_{ads} + 2CO_{(g)} \longrightarrow 2CO_{2(g)}$$

the CO serving as a scavenger for the atomic oxygen left by the decomposing NO. Other experiments have been carried out on polycrystalline rhodium (Taylor, 1980) in which the inhibition of the NO decomposition reaction by preadsorbed oxygen was observed, which would be consistent with the above mechanism. The CO oxidation and NO reduction reactions have been studied together on a platinum-alumina catalyst (Chang, 1979) using infrared absorption spectroscopy under reaction conditions. In a net reducing atmosphere, corresponding to a low A/F ratio (rich mixture) the catalyst was found to be covered by strongly chemisorbed CO which inhibited its activity. However, under net oxidising conditions (equivalent to A/F high, lean mixture), the surface was found to be covered by oxygen atoms, inhibiting its ability to adsorb NO. Around the stoichiometric point there was a region where the processes appeared to be in balance and this coincided with the A/F window fo the real 3-way catalyst (Figure 6).

While platinum, palladium, and rhodium can all function as 3-way catalysts, platinum is much less effective than the others at converting HC and NO_x under rich conditions. Rhodium is an excellent NO reduction catalyst; however, its inability to catalyse oxidation reactions when oxidised itself, together with its great scarcity (15-20 times that of platinum) preclude its use as the sole active catalyst in the converter. However, rhodium does have to be incorporated in the catalyst to some extent since platinum and palladium are relatively sensitive to sulphur dioxide poisoning of their NO reduction activity under rich conditions. Sulphur dioxide is typically present at ~ 20 ppm in exhaust gases (Hegedus, 1980); it has been suggested (Somorjai, 1972) that the action of the sulphur is to change the free energy of the platinum surface. This could lead to reconstruction into a surface structure which is inactive in the catalysis

of the ammonia forming reaction.

Other substances often present in petrol which can poison the catalytic converter are lead, halogens, and phosphorus. Oil companies have been adding lead (as a mixture of tetra-ethyl lead and various organic halides) to their petrol for many years at a concentration of about 3g per gallon, in order to mprove the octane rating without the expense of extra refining. However, if used in a vehicle fitted with a catalytic converter, lead-containing petrol will rapidly reduce the activity of the catalyst, particularly with respect to hydrocarbon oxidation. Therefore, it has been necessary to make unleaded petrol available in countries where catalytic converters are in use, and oil companies have been obliged to change their refining procedures in order to produce petrol of a higher intrinsic octane rating. The precise action of the lead is uncertain; it has been observed, however, that at submonolayer coverages, it can actually increase the activity of platinum in the catalytic oxidation of CO while not affecting the adsorption of oxygen (Brunelle, 1980). The organic halide scavengers (usually added with tetra-ethyl lead to facilitate lead removal as volatile halides) are found to be serious poisons of the oxidation activity of platinum and palladium (Shelef, 1978), presumably competing for adsorption on the catalytically active sites. There is also some evidence (Brunelle, 1980) to suggest that most of the catalyst deactivation which occurs when leaded petrol is used with a catalytic converter, is due to the action of the organic halides rather than that of the lead. Phosphorus is a particularly serious poison of CO oxidation activity on platinum and has been eliminated from petrol intended for use in vehicles with catalytic converters. Its specific action, however, is unclear (Shelef, 1978); it appears that the simultaneous presence of phosphorus and lead is less harmful than the presence of either one of them alone due to the scavenging effect of phosphorus, producing

nonpoisonous lead phosphates (Acres, 1975).

4. Three-way Catalyst Design

As mentioned in the previous section, rhodium, platinum and palladium are all used in the 3-way catalyst: rhodium because of its resistance to SO_2 poisoning and its efficiency at NO reduction to nitrogen, platinum because it is a better oxidation catalyst than rhodium (as well as being considerably more abundant), and palladium because it is more resistant to sintering than platinum, giving the catalyst a longer life. Various other factors also have to be considered in the design of this catalyst. Firstly, rhodium is a scarce element which is found in nature alongside platinum and palladium. This means that the cheapest combination of the metals on a large scale is in their mining ratio, namely ~ 19:7:1 for Pt:Pd:Rh. Secondly, although steps are taken to keep lead and phosphorus levels as low as possible in "unleaded" petrol, the catalyst is likely to be exposed to several grams of both elements during its useful life; palladium and rhodium are particularly sensitive to poisoning and so, in the catalyst design, steps have to be taken to protect them. Third, it is necessary to keep platinum, palladium, and rhodium physically separate within the catalyst since platinum alloys with the other metals, losing its resistance to poisoning when coimpregnated with palladium over the same support. A solution which satisfies all these constraints (Hegedus, 1979) consists of using spherical pellets of porous alumina impregnated with rhodium, palladium, and platinum in concentric spheres (Figure 8). The platinum is in the outer sphere and impregnated to the depth of the expected poison penetration during the catalyst's useful lifetime - a figure which can be simply calculated (Hegedus, 1977). The next to outermost layer consists of rhodium, which, although requiring protection from poisoning, needs to be as close as possible to the outside of the

pellet, maximising its efficiency as a rich-side NO reduciton catalyst. The palladium sphere is the innermost layer and the entire pellet is impregnated with cerium, the presence of which markedly improves the catalyst's performance under transient conditions, presumably by storing and slowly releasing oxygen from the surface, thereby smoothing out the effect of A/F fluctuations on the catalyst's activity. Catalysts of this concentric sphere design together with monolithic versions based on similar principles are currently being manufactured for the U.S. and Japanese auto industries.

C. THE CATALYTIC HYDROGENATION OF CARBON MONOXIDE

1. Introduction

The catalytic hydrogenation of carbon monoxide to form methane and oxygenated and long-chain hydrocarbons was initially developed in the first quarter of this century. Until recently, however, it has not been of great industrial importance, except in countries with a lack of domestic petroleum, a desire to be independent of foreign oil sources and with relatively inexpensive labour (and therefore cheap coal-derived CO). These conditions were met in Nazi Germany (where, at the height of World War II, 100,000 barrels of synthetic fuel were being produced per day) and are still met in South Africa, where 100,000 barrels per day is the target of synthetic fuel production for 1985.

In the last decade, however, there has been a reevaluation of CO hydrogenation as an economic fuel source. This is due both to escalating prices, the potential uncertainty of supply of OPEC oil, and to the concommitant increase in the economic attractiveness of other fossil energy sources. These include coal, tar sands and oil shale, all of which can be used to produce carbon monoxide and hydrogen and hence, via catalytic hydrogenation, the higher molecular weight hydrocarbons needed for motor fuels.

2. History

The first reported instance of the catalytic hydrogenation of CO was in 1902, when Sabatier and Senderens (1902) succeeded in producing methane from CO and H_2 using a nickel catalyst. In 1913, Badische Analin und Soda Fabrik (B.A.S.F.) took out a patent on a process to form long chain and oxygenated hydrocarbons from CO and H_2 using alkali-metal promoted oxides of cobalt and osmium (Mittasch, 1950). This method required pressures of over 100 atm and was carried out at 350°C. In 1923, B.A.S.F. patented a technique for the selective hydrogenation of CO to methanol using a catalyst composed of oxides of zinc and chromium. Fischer and Tropsch first managed to produce measurable quantities of higher hydrocarbons at atmospheric pressure and moderate temperatures (250-350°C) in 1925 (Fischer, 1926) using a catalyst consisting of iron and cobalt with K_2CO_3 and copper as promoters. This has been named the Fischer-Tropsch synthesis. In the next few years, the process underwent several modifications, including the addition of ThO_2 to the catalyst and an increase in pressure to 10-15 atm. The standard German catalyst, as used in the 1940's contained cobalt, thoria, magnesium oxide and kieselguhr, the plants being operated at pressures ranging from 1-10 atm. Yields of C_4-C_{11} hydrocarbons were high, providing a source of petrol with an octane number of ~ 50 (Pichler, 1952; Kolbel, 1957; Storch, 1951).

Research on CO hydrogenation continued during the 1940's and 1950's at the U.S. Bureau of Mines (Anderson, 1956; Natta, 1957), but with the availability of cheap foreign oil, research was virtually halted in all countries except South Africa by the late 1950's. As the Fischer-Tropsch process became economically viable once more in the 1970's, synthetic fuel research began again and is presently being actively pursued on both a technological and fundamental level in many countries around the world. With the aid of hitherto unavailable surface science techniques, the basic atomic mechanisms for the catalytic hydro-

genation of CO are finally being unravelled.

3. Thermodynamics

The most convenient source of both CO and H_2 is the gasification of coal by steam. Coal varies in its composition, but for thermodynamic purposes may be considered as graphitic carbon. The reaction of graphite with steam is:

$$C_{graphite} + H_2O \longrightarrow CO + H_2 \qquad \Delta H = +32 \text{ kcal mole}^{-1}$$

This is an endothermic reaction, and, therefore, must be carried out at high temperatures (~ 1100 K). The product mixture (known as "water gas") can subsequently be enriched with hydrogen via a reaction known as the "water-gas shift" reaction:

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad \Delta H = -9.5 \text{ kcal mole}^{-1}$$

This is a useful technique, since varying the $CO:H_2$ ratio of the reactant gases can alter the product distribution of the catalytic hydrogenation reaction.

Alkane-forming reactions are of two overall types:

$$1) \quad (n + 1)H_2 + 2nCO \longrightarrow C_nH_{2n+2} + nCO_2$$

$$2) \quad (2n + 1)H_2 + nCO \longrightarrow C_nH_{2n+2} + nH_2O$$

Both of these reactions are thermodynamically feasible. It is generally found that if catalysts which are effective for the water-gas-shift reaction are used for CO hydrogenation, both CO_2 and H_2O are produced. Catalysts that are poor for catalyzing the water gas shift tend to produce either CO_2 or H_2O as a by-product.

Since the CO hydrogenation reactions are all exothermic, they are thermodynamically favoured by lower temperatures. However, on the catalysts used at pre-

sent, the reaction is typically rather slow (turnover rates of 10^{-6}-10^{1} molecules $site^{-1}$ s^{-1}), hence, temperatures in the range of 500-700 K are required to optimize the rate of product formation.

By Le Chatelier's principle, high pressures favour more associative reactions, so if the reactant pressure is increased, the production of higher molecular weight products is enhanced. For methanation, for example,

$$3H_2 + CO \longrightarrow CH_4 + H_2O$$

ΔG_f at 730 K and 1 atm is -11.42 kcal $mole^{-1}$ yielding an equilibrium constant of 3.68×10^{3}. However, at 10^{-4} torr total pressure, the equilibrium constant is 6.4×10^{-11}, leading to a negligible production of methane. As the molecular weight of the desired product increases, the reactant pressure must also be increased. For example, in the case of benzene synthesis, (figure 9) pressures in excess of 20 atm have to be used in order to synthesize significant amounts of product.

4. Chemisorption Studies of CO and H_2

Many recent surface studies using ultraviolet photoelectron and infrared spectroscopies have led to the conclusion that CO adsorbs molecularly on many transition metals, its major axis being perpendicular to the surface with the carbon atom nearest the metal. Bonding with the surface is widely thought to be synergic in nature, with a mutual enhancement occurring between donation of electrons from the $CO_{5\sigma}$ orbital into unoccupied metal orbitals and a back donation from other metal orbitals into the $CO_{2\pi^*}$ (anti-bonding) system (figure 10). Both linear bonding (one metal site) and multiple bonding (several metal sites) of CO to the metal surface have been observed (figure 11).

The molecularly adsorbed CO species serves, on many transition metals, merely

as a precursor to the dissociative chemisorption of the molecule. This is an activated process, the transition state presumably involving the simultaneous interaction of both C and O with the metal surface. This interaction is achieved during vibrational deformation, and is particularly likely to occur in the case of CO bonded to several metal atoms (Richardson, 1979). The preferential dissociation of multiply-bonded CO was elegantly demonstrated by Aradi and Ponec (1976), who adsorbed CO on nickel-copper alloys. The addition of copper to nickel is known not to affect the electronic properties of the nickel significantly (Ponec, 1975), the effect of alloying the nickel with copper being merely to diminish the surface concentration of large clusters of nickel atoms. It was found that both the concentration of bridge-bonded CO molecules and the extent of CO disproportionation were reduced on addition of copper, while the rate coefficient of disproportionation remained constant.

H_2 has been found to dissociate on many transition metal surfaces, e.g. Pd (Conrad, 1974), Fe (Boszo, 1977) and Ni (Horn, 1978), and a mutual enhancement of adsorption has been observed when CO and H_2 are simultaneously present in the gas phase. This suggests some kind of interaction between the adsorbed H and CO species, and there is much contradictory evidence surrounding the existence and importance of such an interaction. Many IR studies have suggested the formation of an H_2CO species (Kolbel, 1974) on iron after simultaneous adsorption of CO and H_2. The precise bonding in this species is uncertain, however, and it is not now thought to be central to the mechanism of the Fischer-Tropsch rection, as was once believed (Pichler, 1952; Kummer, 1953; Hall, 1960).

5. Selectivity

Although cobalt and iron-based catalysts can be used under conditions which lead principally to the formation of products of a particular molecular weight

range, they are not selective catalysts per se. Selective catalysts do exist for the methane and methanol syntheses, however, and surprisingly, these were among the earliest CO hydrogenation catalysts to be formulated. Nickel (Vannice, 1976) is an excellent methanation catalyst:

$$2CO + 2H_2 \xrightarrow[500\text{-}600\ K]{Ni} CH_4 + CO_2$$

and zinc chromate - copper chromate catalyses the synthesis of methanol (Herman, 1978; Mehta, 1979):

$$CO + 2H_2 \xrightarrow[450\text{-}600\ K]{Zn\text{-}Cr\text{-}Cu} CH_3OH$$

where Cu^+ appears to be the active component, chromium serving to increase the copper solubility in the zinc oxide matrix. Palladium (Poutsma, 1978) has also been found to produce methanol selectively at ~ 12 atm pressure.

The oxidation state of the active metal appears to affect the product distribution of a catalyst very significantly. This is manifested in the effects of promoters and catalyst supports, which may stabilize particular oxidation states of the catalyst metal. Anderson (1953) has shown that the product distribution on CO hydrogenation over iron nitrides is very different from the distribution obtained both over clean iron and iron oxides, suggesting that the oxidation state of the active metal has a significant effect on the selectivity of the catalyst. Sexton and Somorjai (1977) have shown that while clean, unsupported rhodium does not lead to the formation of oxygenated products, preoxidation of the surface leads to the generation of alcohols, aldehydes and acids. Moreover, the use of basic oxide supports with the rhodium catalyst results in the formation of alcohols, whereas more acidic supports favour the production of olefins and methane. The effect of manganese and alkali metals on rhodium catalysts is to enhance the production of oxygenates.

The ability of alkali metals to stabilize an oxidation state is well illustrated by the observation (Somorjai, 1978) that the presence of potassium can prevent the reduction of iron oxides in the reducing conditions encountered during CO hydrogenation. In this system, potassium also fulfills the useful role of removing inactive graphitic carbon from the iron oxide surface, probably via the formation of K_2CO_3 (Verda, 1975) and subsequent desorption of CO_2. If this carbon were allowed to build up, the Fischer-Tropsch activity of the oxide would be greatly diminished.

Another approach to selectivity in the Fischer-Tropsch synthesis has been described by Meisel et al. (1976) and involves the incorporation of zeolite shape-selective catalysts into the same reaction chamber as the metal Fischer-Tropsch catalyst. This has been found to produce aromatic molecules (and therefore high octane petrol) with a high degree of selectivity.

6. Mechanism

It is now widely believed that the initial step in many CO hydrogenation reactions is the disproportionation of CO, otherwise known as the Boudouard reaction:

$$2CO \longrightarrow C + CO_2$$

Experiments on nickel (Araki, 1976), rhodium (Sexton, 1977) and iron (Dwyer, 1978) have shown the formation of an active carbon overlayer during the synthesis reaction. This carbon has been found to react with hydrogen to produce methane at the same rate as does carbon monoxide. The role of surface carbon has also been demonstrated by Biloen (1979), who dissociated ^{13}CO on cobalt, nickel and ruthenium, finding that subsequent ^{12}CO hydrogenation over these surfaces resulted in the formation of some $^{13}CH_4$. The CO-derived active carbon is

prone to graphitisation, however (McCarty, 1979), when heated over 700 K or in an inert environment. Graphitic carbon appears to be unreactive with hydrogen, making 700 K an upper temperature limit for CO hydrogenation.

Methane has been formed on surfaces which do not readily dissociate CO, e.g. palladium (Poutsma, 1978), nickel at 300 K (Rabo, 1978), platinum and iridium (Vannice, 1976) and it is thought that another mechanism operating via an enol species may be operating in these cases (Pichler, 1952; Kummer, 1953; Hall, 1960). This process is thought to be less common, under industrial conditions, than that involvng prior CO dissociation.

Methanation has been shown to occur via two different mechanisms on rhodium and rhodium oxide (Castner, 1980). The activation energy for methane production on clean rhodium was found to be 24 kcal $mole^{-1}$, whereas that obtained for oxidized rhodium was 12-15 kcal mol^{-1}, with a much higher turnover frequency. The reaction of CO_2 with hydrogen also has activation energies in the range 12-15 kcal $mole^{-1}$, suggesting, perhaps, that CO_2 may oxidize the rhodium surface in an initial dissociative step.

The mechanism of methanol formation, which occurs with high selectivity on a catalyst consisting of zinc, chromium and copper oxides (Mehta, 1979) as well as palladium, platinum and iridium at higher pressures (Poutsma, 1978), is not well understood. Unfortunately, this is also true for the formation of all oxygenated products from CO. The activity on palladium, which will not readily dissociate CO, suggests that the reaction occurs via an oxygenated intermediate.

The formation of longer-chain molecules from CO hydrogenation is now thought of as a polymerisation reaction, with methylene groups acting as the monomer, and alkyl groups serving as the chain terminators and initiators. The distribution of products from non-selective catalysts, such as iron and cobalt, has been shown to obey the Schultz-Flory (Schultz, 1939; Flory, 1953) distribution of

molecular weights, which is often encountered in polymerization reactions.

Dwyer and Somorjai (1979) have illustrated the polyermization process by running the Fischer-Tropsch synthesis in a high pressure-low pressure apparatus (Blakely, 1976) on polycrystalline iron. At low conversions (< 1%) the product distribution was heavily weighted towards low molecular weight species, such as methane and ethylene, whereas under industrial conditions, a significant proportion of higher molecular weight species are normally produced. After the addition of small quantities of ethylene or propylene to the reaction it was found to mirror the industrial product distribution more exactly, suggesting that secondary reactions were occurring on the catlayst, with the ethylene or propylene fragments serving as chain initiators. This leads in an industrial reactor to a variation in the product distribution across the catalyst bed, with the weighting of the distribution tending towards larger molecules as the reactor outlet is approached.

A striking example of chain initiation has been shown by Brady and Petit (in press), who passed dilute diazomethane (CH_2N_2) over various transition metals. In the absence of other reactants, the products were solely ethylene (the dimer of CH_2) and nitrogen (N_2). If, on the other hand, hydrogen was present, a FischerTropsch-like product distribution was obtained, suggesting that the methylene (CH_2) groups had reacted with hydrogen to form methyl (CH_3) groups, which in turn serve as chain initiators.

Based on this kind of information, Bell (1981) has suggested the following reaction sequence for the Fischer-Tropsch synthesis:

$$1) \quad CO + S \rightleftharpoons CO_S$$

$$2) \quad CO_S + S \rightleftharpoons C_S + O_S$$

$$3) \quad H_2 + 2S \rightleftharpoons 2H_S$$

$$4a) \quad O_S + H_2 \text{ (or } 2H_S) \longrightarrow H_2O + 2S$$

4b) $O_S + CO \text{ (or } CO_S) \longrightarrow CO_2 + 2S$

5) $C_S + H_S \rightleftharpoons CH_S + S$

6) $CH_S + H_S \rightleftharpoons CH_{2S} + S$

7) $CH_{2S} + H_S \rightleftharpoons CH_{3S} + S$

8) $CH_{3S} + H_S \longrightarrow CH_4 + S$

9) $CH_{3S} + CH_{2S} \longrightarrow CH_3CH_2 + S$

10) $CH_3CH_{2S} + CH_{2S} \longrightarrow CH_3CH_2CH_{2S} + S$

11) $CH_3CH_{2S} + S \longrightarrow CH_2CH_2 + H_S$

12) $CH_3CH_{2S} + H_S \longrightarrow CH_3CH_3 + 2S$

This idealized mechanism would lead to the formation of a Schulz-Flory distribution of straight-chain hydrocarbons. In practice, oxygenation, isomerization and aromatisation side reactions frequently appear to intervene. Unfortunately, the precise mechanistic roles of these site reactions are not well understood, but it would appear that their control, via suitable catalyst formulation, can lead to the selective synthesis of almost any hydrocarbon starting from CO and H_2.

D. CATALYSIS BY ZEOLITES

1. Introduction

Zeolites were discovered in the mid-18th Century by Baron Cronstedt (1756), who observed that certain minerals appeared to boil and melt at the same time. Cronstedt named these substances "Zeolites" after the Greek zeo, meaning "to boil" and lithos, meaning "stone". In 1840, Damour observed that chabazite, heulandite and analcite (all naturally-occurring zeolites) underwent reversible dehydration on heating, and in the 1920's, Weigel and Steinhoff ascertained that while chabazite adsorbed water, methanol, ethanol and formic acid, it was imper-

vious to dimethyl ether, diethyl ether or benzene. This latter observation led to the term "molecular sieve" being coined for zeolites which displayed this property of size-selective sorption.

X-ray diffraction studies in the 1930's showed the existence of large cavities within the structures of naturally-occurring zeolites; in the late '30's, Barrer embarked on a systematic investigation of the sorptive properties of these substances (Barrer, 1967). A decade later, Milton and his colleagues at the Linde Divison of Union Carbide studied the separation of gases with natural zeolites, and reported the first large scale syntheses of zeolites, some with compositions not found in nature. Linde began manufacturing these synthetic zeolites, which are still used as drying agents and for the separation of gases.

The catalytic properties of zeolites were first observed in the late 1950's, and in 1960 Rabo et al. (1960) announced that Linde's synthetic zeolites had considerable activity for isomerization. In the next few years, Plank and Rosinsky (1964) at Socony-Mobil developed a technique for stabilizing the Linde zeolites to withstand the conditions encountered in industrial heterogeneous catalysis of hydrocarbon reactions. In 1964, the chemical industry began to change over from the previous silica-alumina cracking catalysts to the new, highly active, zeolite version. As can be seen in figure 12 (Heinemann, 1981), the U.S. hydrocarbon catalytic cracking capacity actually decreased between 1964 and 1966, in spite of the steadily increasing production of petrol, due to the introduction of the far more active zeolitic catalysts. The greater selectivity of the zeolitic catalysts also contributed to the substantial savings in the amount of crude oil consumed.

Today, 90% of the world's catalytic cracking is carried out over zeolite catalysts. In addition, a large number of other processes in the petrochemical

industry are catalyzed by zeolites, and the reaction mechanisms are becoming sufficiently well-understood so that it is now within the realms of possibility to tailor zeolite catalysts, ab initio, to the needs of a particular process.

2. Zeolite Structure

Zeolites have the general formula $M_{x/n}[(AlO_2)_x\ (SiO_2)_y]\ zH_2O$, where n is the charge of the metal ion, M^{n+}; x, y and z are integers. The structure of zeolites can be divided into two main sections: the rigid zeolitic framework and the semi-mobile internal cations and water molecules. First, we shall deal with the zeolitic framework.

The fundamental building blocks of the zeolites are the SiO_4 and AlO_4^- tetrahedra shown in figure 13. The strength of the Si-O bonds makes catenation of these units energetically very favourable (cf carbon in organic chemistry), leading to the formation of rings of varying sizes. Al-centred tetrahedra are incorporated in the rings, but are always separated by Si-centred units. Meier (1968) has described a set of eight secondary building blocks of zeolite frameworks consisting of rings, prisms and other combinations of tetrahedra. These secondary units can, in turn, be combined to produce cages, such as the sodalite cage shown in figure 14 (In diagrammatic representations of zeolites, a single line (----) is used to represent the Al-O-Si or Si-O-Si linkage). This cage is a tertiary building block found in many zeolites including the industrially-important synthetic X and Y zeolites. The sodalite cage consists of eight 6-membered and six 4-membered rings with common edges, and has a volume of approximately 160$Å^3$, (Turkevich, 1967). The structure of the mineral sodalite consists of a closepacked array of such cages, sharing all 4-membered and 6-membered rings, so as to fill all space. The faujasite structure (figure 15), which is also that of the X and Y zeolite frameworks, consists of sodalite cages joined

by hexagonal prisms attached to four of the 6-membered rings. This structure will be considered in more detail because of its importance in catalysis.

The faujasite unit cell consists of a diamond-type lattice of sodalite units (figure 15). It contains a supercage consisting of 48 atoms of silicon (or aluminium) and 96 atoms of oxygen, which together form four 18-membered, four 6-membered and four 12-membered rings. The 12-membered rings are arranged tetrahedrally around the supercage and have a diameter (pore-opening size) of 8-9Å. The internal diameter of the faujasite cavity is 12.5Å and its volume is about $850Å^3$. It is the existence of these large, interconnecting internal pores in faujasite and in other zeolites, that give them many of their useful characteristics. Because of the openness of the zeolite structure, the internal surface areas in these compounds can exceed 10^2 m^2 g^{-1}. In the type X zeolites, the numbers of silicon-centred and aluminium-centred tetrahedra are equal. This leads to an ordering in the sodalite cages, where aluminium atoms occupy diagonal positions on the square faces thus allowing Si-O-Al catenation. In the case of type Y zeolites, however, there are at least three times as many SiO_4 units as AlO_4^- units, so that there is only one aluminium atom per square face of the sodalite cage. The concentration and distribution of the aluminium atoms is important in determining the catalytic properties of the zeolites, since each aluminium atom carries a single negative charge. The structure and pore arrangement of another important zeolite catalyst, ZSM-5, are shown in figure 16. This zeolite has been prepared with SiO_4/AlO_4^- ratios from 20 up to infinity and, therefore, displays some very different characteristics from the older, X and Y zeolites. For a useful collection of stereodiagrams of other common zeolite structures, the reader is referred to Meier (1971).

While the zeolite framework may be considered to be fairly rigid under the conditions normally encountered in industrial catalysis, the positions of the

other zeolite components, namely cations and water molecules, are much less well-defined. However, there are certain locations relative to the zeolite framework which seem to be energetically favourable for cations, although exchange between many of these locations appears to be facile. In the case of the faujasite structure (Smith, 1976), the centres of the hexagonal prisms (site I) are the most favourable positions for cations that are suited to an octahedral field (figure 17), sine, six O(3) atoms are pulled inwards to a near-octahedral configuration when this site is occupied. Site I' is also favourable, providing one-sided coordination to three O(3) atoms. It would seem unlikely that both sites I and I' would be simultaneously occupied on the same prism. On each free 6-membered ring of the sodalite cage, there are two more possible positions for the cations to occupy; II' is displaced into the sodalite unit, whereas II is displaced into the supercage. In these positions, three O(2) atoms provide bonding to the cations. In hydrated faujasites, cations also appear to be positioned at II*, further out into the supercage. This bonding is not simple, and presumably involves water molecules. Other cation positions include coordination on the walls (e.g. to four oxygens on a bridging 4-ring) as well as many positions within the supercage, which again can only be occupied by heavily hydrated cations.

The cations in X and Y zeolites may readily be exchanged with other Group I or II ions, as well as with some transition metal ions such as Co^{+}, Ni^{2+} and certain rare earth ions. Catalysts are often prepared by replacing metal cations with protons--a process known as "decationation". This cannot be achieved by using acids (such as sulphuric acid) since this procedure would destroy the zeolite framework. The usual technique involves ion-exchanging the zeolite with an ammonium salt. During subsequent heating ammonia is evolved, leaving protons behind in the cation sites.

A knowledge of the diffusion phenomena in zeolites is important in order to understand their catalytic properteis. Below 500°C, diffusion of the framework aluminium and silicon atoms can be neglected, although controlled heating above this temperature can lead to changes (McDaniel, 1976), which enhance the stability of the zeolite. Diffusion of water through the zeolite at room temperature and above is very rapid, although ~ 100 times slower than the self-diffusion of water in water. NMR relaxation studies (Resing, 1971) have shown that intrazeolitic H_2O has a viscosity some 30 times greater than that of pure water, with a proton mobility approximately 1000 times that of ice at 273 K.

Diffusion of molecules through zeolites may be considered simple, in terms of the steric hindrance encountered on passing through pore openings (windows): a 6-membered ring has a diameter of 2.7Å, an 8-membered ring a diameter of 4.4Å, and a 12-membered ring a diameter of 7.7Å, with slight increases in size as the proportion of aluminium in the ring is increased (due to the slightly longer Al-O bond). Every time a molecule reaches a window, it also encounters an energy barrier, due to interaction with the framework oxygen around the window. Another possible obstruction to diffusion of a molecule through a zeolite is the presence of bulky cations in the pore windows (figure 17). This problem can be substantially reduced, however, by decationation via the ammonium zeolite (see above). Cation diffusion in an anhydrous zeolite would seem to involve strong interaction with framework oxygens in the pore windows. However, if the zeolite is hydrated, the picture is very different. In this case, the cations can be viewed as the centres of large hydration clusters, since diffusion of cations inevitably involves the simultaneous diffusion of some water molecules. In large channels, the cations probably drift from one large hydration cluster to another, and diffusion of a cation through a small window must involve the stripping of one hydration cluster, followed by the growth of another on the

other side of the window (Smith, 1976).

For more information on zeolite structure, synthesis and chemical properties, the interested reader is referred to the excellent book by Breck (1974).

3. Catalytic Applications of Zeolites

The largest use of zeolites is undoubtedly in catalytic cracking. This process involves breaking the larger hydrocarbons found in crude oil into smaller, more useful, molecules. Since the products are often highly-branched alkanes or aromatics, they display a higher octane number than the feedstock. Polycyclic aromatics and certain N- and S-containing compounds are, however, not easily processed in this way, although zeolites do have a role to play in the conversion of these substances to high octane number hydrocarbons. The technique most often employed in these cases is "hydrocracking", which, as the name implies, involves carrying out cracking reactions in the presence of hydrogen. The hydrocracking catalyst consists of large-pore zeolites, such as Y or Ultrastable Y (a Y zeolite which has been partially dealuminated, with a consequent increase in pore size), into which small quantities of hydrogenation/dehydrogenation catalysts such as platinum or palladium have been impregnated (Ward, 1973). This technique may be useful in the processing of future hydrocarbon sources such as shale oil and liquefied coal. Platinum has also been added in very low concentrations to zeolite cracking catlysts where it appears to function as a combustion promoter (Oblad, 1972; Burke, 1979), allowing catalyst regeneration to occur at a relatively low temperature. Platinum also appears to oxidize the byproduct CO to CO_2 when used in this way, reducing pollution problems at the same time as providing a useful source of heat.

Perhaps the most exciting development in catalysis in the last decade has been the invention of "Shape-Selective" zeolites (Weisz, 1960 & 1962). These

catalysts force selectivity on hydrocarbon transformation reactions either by hindering the diffusion of certain reactants or products, or by inhibiting the formatin of transition states larger than the maximum pore size of the zeolite. The first process to use this new concept of "molecular engineering" was "Selectoforming" (Chen, 1968), which used a natural zeolite (pore opening ~ 5Å) containing a small quantity of nickel. When a low octane-number hydrocarbon mixture was passed over this catalyst in the presence of hydrogen, the straight-chain alkanes were selectively cracked on the nickel surface, mostly to gaseous hydrocarbons. The branched and aromatic molecules were unable to penetrate the zeolite pores, and remained unaffected; the octane number of the mixture was enhanced due to the removal of the straight-chain alkanes (the lowest octane-number components).

The shape-selective synthetic zeolite ZSM-5, illustrated in figure 16, (Meisel, 1976), contains pore openings with diameters ranging from 5-7Å (cf Faujasite, 8-9Å), and has considerable resistance to coking; the development of this zeolite has led to several new shape-selective catalytic processes. These include an extension of "Selectoforming" to singly-branched alkanes (Heinemann, 1973), the selective cracking of waxy straight-chain alkanes to high octane number petrol (Mobil Distillate De-Waxing (MDDW) Process (Chen, 1977)), the disproportionation of toluene to benzene and xylenes and the isomerization of xylenes. The synthesis of petrol from methanol (Chang, 1977) or even from CO and H_2 (Lechthaler, 1978) over ZSM-5 catalysts, has been shown to be feasible on a laboratory scale, and is very attractive as a route to motor fuels starting from non-petroleum fossil energy sources.

4. Mechanism of Zeolite Catalysis

The aspects of zeolitic structure which appear to be relevant to catalysis

are acidity, electrolytic strength and pore size. The cause of the acidity in decationated zeolites is the electron-withdrawing power of aluminium atoms adjacent to hydroxyl groups (figure 18). This leads to a weakening of the zeolite O-H bond and to consequent acidity of the hydrogen. In the case of zeolites which have been ion-exchanged with multivalent cations, the acidity is due to the hydrolysis of the ion, e.g.

$$La^{3+} \xrightarrow{H_2O} LaOH^{2+} + H^+ \xrightarrow{H_2O} La(OH)_2^+ + 2H^+$$

The subsequent incorporation of hydroxylated multivalent ions into the framework also appears to increase the thermal stability of the zeolite.

Many reactions occurring during zeolite catlaysis may also be catalyzed homogeneously in the presence of strong mineral acids. This suggests that the zeolite acidity is important, probably facilitating the formation of carbonium ions from the reactants. Carbonium ions (sometimes known as carbenium ions) are reactive intermediates of the type R_3C^+, formed by extraction of H^- ions from the C-H bond. Although in homogeneous acid media, tertiary (R_3C^+) ions are easier to form than secondary (R_2C^+H) ions, and these in turn are easier to form than primary (RC^+H_2) ions, this order may be modified or reversed in some zeolites as a result of pore-size constraints, which inhibit the diffusion of tertiary carbon- or secondary carbon-containing molecules to the acid sites.

The electrolytic strength of zeolites leads to a far higher concentration of the polarizable hydrocarbons in the pores than that which is found in the extra-zeolitic gas phase. This has the effect of enhancing concentration-dependent bimolecular reactions (such as hydrogen transfer) over concentration-independent unimolecular steps (such as bond-scission). The hydrogen transfer reactions are favoured on the zeolite catalysts but not on more traditional cracking catalysts; they lead to the formation of alkanes and aromatics, which

are stable with respect to thermally-induced cracking to gas. The latter reaction can substantially lower the yield of petrol, and its inhibition, therefore, accounts for the greater petrol yield of Y-zeolite cracking catalysts, compared to the older silica-alumina gels (Weisz, 1973).

5. Recent Developments in Zeolite Catalysts

Since faujasite and the related synthetic zeolites are very strong electrolytes, they have the disadvantage of cracking polar molecules such as alcohols and alkenes to carbon (Coke). In consequence, in industrial zeolite catalysis, several beds of zeolite are run in parallel, one bed actually being in operation, while the others are being regenerated ("de-coked"). It has been found that, by dramatically increasing the Si/Al ratio of zeolites, the coking problem can be lessened. In addition, feedstocks such as methanol can be used with little loss of the reactant to coke. Reducing the aluminium content of zeolites can be readily accomplished by steam treatment or reaction with silicon tetrachloride, and it has the very desirable side-effect of introducing a network of very large pores into the zeolite structure. This facilitates access of the reactants to the active 5-10Å pores with a consequent increase in activity.

There is little published work on silicon-rich zeolites, although they currently constitute an area of intense research activity in the petrochemical industry.

E. THE CATALYTIC EPOXIDATION OF ETHYLENE

1. Introduction

Ethylene oxide is one of the most important feedstocks in the petrochemicals industry. Its principal use is in the synthesis of glycols, which , in turn, are used in fibre-manufacture, as coolants in motor vehicles, in the pro-

duction of cellophane and, when polymerised, as neutral bases in the cosmetic, pharmaceutical and printing industries. When reacted with ammonia, ethylene oxide yields ethanolamines, which find applicaton as acid gas absorbants and in hair shampoos. Other ethylene oxide derivatives include glycol ethers (used as brake fluids), ethoxylated long-chain alcohols (detergents) and polyols (precursors for polyurethane foams). Ethylene oxide itself is also used as a fumigant for insect control on grain.

Because of the widespread use of ethylene oxide, a considerable research effort has been expended on maximising the efficiency of its synthesis (epoxidation) from ethylene—a commodity readily obtained from petroleum. The older "Chlorohydrin" process, involving the reaction of ethylene with hypochlorous acid:

$$CH_2CH_2 + HOCl \longrightarrow CH_2Cl\text{-}CH_2OH \longrightarrow \underset{\diagdown\,O\,\diagup}{CH_2\text{-}CH_2} + HCl$$

was inefficient in terms of yield, partly because it consisted of two distinct reaction steps. This process has now been superceded by the direct oxidation of ethylene by oxygen, which, in addition to having an efficiency exceeding 70%, has fewer environmental problems than the Chlorohydrin process.

The direct oxidation of ethylene was first carried out successfully by Lefort (1931) in 1931, using a silver catalyst, the process being commercialised by Union Carbide in 1937. Silver seems to be unique in its ability to catalyse ethylene epoxidation and, therefore, all commercial catalysts used in this process are silver-based. Catalyst formulations (Nielson, 1976 & 1977) generally consist of finely-divided silver on an alumina support (so as to maximise the surface area of the expensive silver component) together with traces of alkali and alkaline earth metals, which act as promoters. Small quantities of ethylene dichloride or vinyl chloride are usually added to the oxygen/ethylene feedstock,

since organic chlorine has been found to improve the selectivity of the catalyst, inhibiting the total oxidation of the ethylene to CO_2 and H_2O. The process is usually operated at 250-325°C under 10-50 atm pressure.

2. Mechanism of Ethylene Epoxidation on Unpromoted Silver

Despite (or perhaps because of) the plethora of studies in this area, a universally-accepted reaction mechanism for ethylene epoxidation still remains to be devised. However, most workers would now agree (Voge, 1967) that the relationship that exists between the reactant, ethylene, the desired partially oxidized product, ethylene oxide, and the products of total oxidation, carbon dioxide and water, is as shown in figure 19.

A principal cause of the lack of agreement between different workers, and the vast scatter in the numerical results, has been the ill-defined conditions of the catalysis experiments. For safety reasons, reactor studies have been carried out under conditions either far richer or far leaner than those which could potentially lead to explosion. In the case of lean experiments (O_2-rich) it is conceivable that the silver surfaces are covered by a layer of silver oxide, which may not be present under rich conditions or in the higher pressure environment of an industrial reactor. In addition, reactor studies have been hampered by the presence of trace impurities, such as sulphur and chlorine, which are known (Schwaha, 1979, Kitson, 1980) to form surface compounds on silver that are stable at relatively high temperatures.

The first proposed mechanism for silver-catalyzed ethylene epoxidation was formulated by Worbs (1942), who suggested that it was diatomic oxygen that reacted with ethylene to form ethylene oxide, whereas monatomic oxygen was responsible for the total oxidation of the hydrocarbon to CO_2 and H_2O. Voge (1968) extended this theory to say that after the reaction of the diatomic oxygen with ethylene,

the remaining oxygen atom reacts with ethylene to yield the products of total oxidation. Since, in order to be catalytic, the remaining oxygen atom has to be removed, an upper limit of selectivity to ethylene oxide can be calculated (Kilty, 1974) as 6/7 i.e. a maximum of 85.7% of the ethylene can be oxidized to ethylene oxide by this mechanism, the remainder being totally oxidized to carbon dioxide and water.

There is considerable evidence to support the theory of Worbs (1942). Imre (1970) found that the epoxidation rate of ethylene over a silver catalyst was much greater (17x) than the dissociative adsorption of oxygen under similar conditions. He also found (Imre, 1968 & 1970) that the exposure of a surface in equilibrium with gas phase oxygen at 300°C to ethylene, led to an increase in the concentration of subsurface atomic oxygen. Since this latter species is in equilibrium with surface atomic oxygen, this result implies that the ethylene is actually increasing the concentration of adsorbed monatomic oxygen species, presumably by reacting with diatomic oxygen to form ethylene oxide. If CO was admitted to a similar oxygen-covered silver surface, the result was a decrease in the subsurface oxygen concentration, due to the removal of surface atomic oxygen by CO to form CO_2.

Infrared studies have yielded much information on the ethylene epoxidation mechanism. Gerei (1965) studied the interaction of ethylene and oxygen on Ag/SiO_2 catalysts, first exposing them to oxygen and then to ethylene at 363 K. Subsequent infrared adsorption spectra showed a band at 870 cm^{-1}, which was interpreted as the O-O vibration of an organic peroxide, $CH_2-CH_2-O-O-Ag$. Heating the catalyst to 383 K resulted in a different IR spectrum. It was found to be identical to that obtained when ethylene oxide was adsorbed on clean silver. Kilty et al. (1973) confirmed the work of Gerei, and extended it by using mixtures of $^{18}O_2$, $^{16}\,^{18}O_2$ and $^{16}O_2$. When all three isotopic combinations were pre-

sent in the reactor feed, three bands at 870, 859 and 848 cm^{-1} were obtained in the IR spectrum. However, if the mixed $^{16}\,^{18}O_2$ was absent from the reactant mixture, only two bands appeared (870 and 848 cm^{-1}) showing that there was no isotopic scrambling before the formation of the peroxidic species i.e. the O-O bond remained intact, and it was only diatomic oxygen that was reacting with the ethylene.

Force and Bell (1975 a & b, 1976) took IR spectra of a supported catalyst during the epoxidation reaction itself, thus obtaining a picture of the steady-state population during catalysis. No bands could unambiguously be ascribed to peroxidic species. This, in combination with their kinetic measurements, led the authors to conclude that both ethylene oxide and carbon dioxide were being produced from monatomic oxygen, the interaction of gaseous ethylene with the oxygen leads to epoxidation and the reaction of adsorbed ethylene with oxygen leads to total oxidation. This model was first proposed by Twigg (1946).

An observation which supports the Worbs mechanism and is inconsistent with that of Twigg has been made by Herzog (1970). If a silver catalyst is subjected to conditions which would normally lead to the selective synthesis of ethylene oxide, and the O_2 is replaced by N_2O (which is known to deposit monatomic oxygen on surfaces) epoxidation is not found to occur. If, however, the reaction is performed at a higher temperature (where N_2O is known to decompose into O_2 and N_2), small amounts of ethylene oxide are formed. This result (which has been confirmed by others (Kobayashi, 1977)) suggests very strongly that diatomic oxygen is necessary for ethylene epoxidation. Similarly, Kagawa et al. (1971) have found that while Ag_2O_2 (containing O_2^{2-} ions) will readily epoxidise ethylene, Ag_2O will not do so until reduction has occurred and metallic silver is present.

Recent results have shown that the situation is rather more complicated

than that represented by the mechanism of Worbs (1942). Cant and Hall (1978) made the surprising discovery that the selectivity for epoxidation is higher for C_2D_4 (the totally deuterated form of ethylene) than for C_2H_4. This is not consistent with a mechanism where selectivity is merely determined by the interaction or non-interaction of ethylene with atomic oxygen. It has been suggested (Sachtler, 1981) that this result implies that although the reaction of ethylene with surface diatomic oxygen is necessary for the production of ethylene oxide, it is not sufficient, and that the $O-O-CH_2-CH_2$ complex has a finite chance of decomposing into carbon dioxide and water (figure 20). The substitution of deuterium for hydrogen reduces the likelihood of the decomposition taking place by lessening the chance of a C-H bond cleavage occurring before an ethylene oxide molecule is released.

Sachtler et al. (1981) (using HREELS and TPD) have found three species of oxygen present after low-temperature (110 K) adsorption of oxygen on an Ag(110) surface. These species are adsorbed diatomic oxygen (which dissociates above 173 K), adsorbed monatomic oxygen and subsurface oxygen. The adsorption of ethylene on the Ag(110) surface at 170 K was found to be greatly enhanced by the presence of monatomic oxygen, although no changes in the C-H or O-metal bond energies were observed. This suggests that no rehybridization occurs in the ethylene molecules, which seem to be bonded to the metal rather than the oxygen. The enhancement of ethylene adsorption was probably due to positive charge being induced in the silver atoms neighbouring the adsorbed oxygens. Ethylene desorbed from the oxygen + ethylene-dosed Ag(110) specimen at 170 K, before reaction could occur. However, if the O-covered surface was exposed to a standing pressure of ethylene, the formation of a carbonate species was observed on heating to 320 K.

Sachtler et al. (1981) also carried out some interesting experiments on

carefully-reduced silver powders. As with the single crystal experiments, dosing of oxygen and ethylene at low temperatures (113 K) with subsequent heating led to the desorption of ethylene with no epoxidation. If, however, oxygen-dosed silver was exposed to a standing pressure of ethylene, ethylene oxide and CO_2 were both produced. A remarkable observation in this work was that ethylene oxide was formed only if the temperature during O-predosing was high enough to enable oxygen to diffuse into the subsurface region (while still being below the desorption temperature). This suggests that subsurface oxygen may play a significant role in ethylene epoxidation and that the actual mechanism involved is different from and more complicated than the model of Worbs.

3. The Role of Promoters in Catalytic Ethylene Epoxidation

The promoters used in the ethylene oxide catalyst are chlorine (which is continuously added to the reactant feed as dichloroethane or vinyl chloride) and alkali metals (present in the catalyst itself). Since the epoxidation mechanism is not yet completely understood, the roles of these promoters have also been subject to many interpretations. It is, however, generally acknowledged that chlorine, while lowering catalyst activity, does increase selectivity for the epoxidation reaction. Alkali metals also enhance selectivity, and are either added deliberately during catalyst manufacture, or are present as impurities in the alumina support material.

The role of chlorine in the Sachtler-modified Worbs mechanism (figure 20) (Sachtler, 1981) is to block the pathway from the adsorbed diatomic precursor to adsorbed monatomic oxygen. This is achieved (Kilty, 1974) by the blocking of silver surface sites by tightly-bound chlorine atoms. Since the dissociation mechanism:

$$O_2 + 4Ag_{(adjacent)} \longrightarrow 2O^{2-}_{(adjacent)} + 4Ag^{+}_{(adjacent)}$$

requires four adjacent silver atoms, a surface chlorine coverage of approximately 1/4 is enough to inhibit this process completely. It is likely that at reaction temperatures, the chlorine atoms react with the silver surface atoms to which they are adsorbed, resulting in the formation of AgCl units (Kitson, 1980) on the same sites. Chlorine coverages greater than 1/4 will lead to the inhibition of diatomic oxygen adsorption, with a consequent decrease in catalytic activity.

Force and Bell (1976) favour the Twigg (1946) mechanism, whereby interaction of gaseous ethylene with adsorbed oxygen atoms leads to epoxidation, and adsorbed ethylene reacts with oxygen to produce CO_2. Thus these authors view the role of chlorine as blocking the adsorption of ethylene onto the silver surface--behaviour which they have observed (Force, 1976) on model catalyst systems. Since chlorine adsorption also inhibits dissociative oxygen adsorption, Force and Bell explained the increase in selectivity by the difference in order between epoxidation (1st order) and total oxidation (2nd order).

The exact function of alkali metals as promoters in ethylene epoxidation is far from clear. However, UHV coadsorption experiments have revealed some interesting phenomena. Spencer and Lambert (1981) have shown that rubidium diffuses with a very low activation energy (30 kJ $mole^{-1}$) into the immediate subsurface region, and that the presence of subsurface rubidium can lead to the adsorption of <u>diatomic</u> oxygen on Ag(111) at room temperature, while simultaneously enhancing the sticking probability for oxygen on this face by up to seven orders of magnitude. A room temperature dioxygen species has also been observed by Kitson and Lambert (1981), who coadsorbed potassium + chlorine + oxygen on an Ag(100) specimen. In addition, they found that, in the presence of potassium, chlorine blocks monatomic oxygen adsorption while not affecting the adsorption of the diatomic species to any great extent. Several workers (Marbrow, 1976;

Goddard, 1981; and Kitson, 1980) have observed the mutual enhancement of surface → bulk transport during coadsorption of alkali metals (Na, Rb, K) and oxygen on simple crystal silver surfaces. Again, this suggests that subsurface oxygen may be present and play a mechanistic role in ethylene epoxidation on a promoted catalyst.

Another function of alkali metals may involve the alumina support material. Trace impurities of silica in the support can lead to the presence of acid sites which facilitate the isomerisation of ethylene oxide to acetaldehyde, which, in turn, is readily oxidized to CO_2. It is generally believed that alkali metals can neutralise these acid sites, removing this pathway to carbon dioxide, and thereby improving catalyst selectivity.

Certain alkali metal promoted catalysts have been found to display selectivities higher than the maximum theoretically achievable (85.7%) by a reaction following the Worbs-Sachtler mechanism (figure 20). It is, therefore, quite clear that this mechanism is in need of further modification. One possbility is that the single oxygen atom left on the silver surface after the reaction of ethylene with dioxygen, does not necessarily oxidize ethylene to CO_2, but may be scavenged by alkali metal compounds and redeposited in combination with another oxygen atom, as O_2. If this process could be understood, and controlled more precisely on the real catalyst, a marked improvement in selectivity could be expected.

F. PLATINUM-CATALYSED HYDROCARBON CONVERSION

1. Introduction

Platinum is of tremendous importance in the modern petroleum and chemical industries. It can catalyse the restructuring of organic molecules contained in petroleum feedstocks (Mills, 1953) into useful products such as petrol, and

precursors for the chemical industry such as toluene, ethylene or benzene.

Platinum is also an essential component in catalysts that remove pollutants from car exhaust (see Section IIIB) as well as being unique in its ability to catalyse the oxidation of ammonia--a vital process in the manufacture of artificial fertilizers (Dixon, 1960). The dependence of the world's petroleum, chemical and automobile industries on this expensive metal is not desireable, particularly since the platinum supply is concentrated in only two nations: the Soviet Union and South Africa. In order to improve this situation we should make efficient use of platinum by recovering and regenerating the spent catalyst. Using dispersions near unity, all of the atoms may be exposed for increased utility in surface reactions. In addition, research that scrutinizes the catalytic processes on platinum in molecular detail may lead to an understanding of the material that serves as a basis for developing less expensive and more available substitutes.

2. Reactions on Platinum

Platinum can catalyse hydrogenation and dehydrogenation reactions (e.g. ethane ⇌ ethylene) with hgh turnover numbers (10^{-1} - 10^{1} s^{-1} at ~ 500 K in excess hydrogen, total pressure ~ 1 atm.). It can also catalyse more complex reactions such as dehydrocyclisation (e.g. n-heptane to toluene), isomerisation (e.g. n-hexane to 2-methyl pentane) and hydrogenolysis (e.g. n-pentane to ethane and propane), but with much lower turnover numbers ($< 10^{-2}$ s^{-1}). An interesting and very useful property of platinum is that, by suitable pre-treatment, it can be made to catalyse selectively the lower turnover number reactions, such as dehydrocyclisation; i.e., the hydrogenation/dehydrogenation pathway may be virtually switched off. This is of particular value in oil refining, where enhancement of the aromatic and branched hydrocarbon concentrations in

petrol leads to a higher intrinsic octane number.

Platinum catalyst selectivity appears to be influenced by many diverse factors, often including the metal particle size and the nature of its pretreatment. Boudart (1969) has divided catalytic reactions into those which appear to be insensitive to particle size (i.e., structure-insensitive or "facile" reactions) and those for which the size of the particles appears to play a crucial role (i.e., structure-sensitive or "demanding" reactions). This subject has been dealt with more recently by Monogue and Katzer (1974), and will be explored in more detail below. The nature of its pre-treatment can have a drastic effect on the behavior of a given platinum catalyst. This has been exemplified by Boudart (1968), who found a 27-fold increase in selectivity for the isomerisation of neopentane (2,2dimethyl propane) with respect to its hydrogenolysis, when the catalyst was pretreated by heating to 900°C. Preadsorption of foreign atoms on platinum catalysts can also lead to changes in selectivity by several orders of magnitude, and this topic will be dealt with in Section IIIF$_4$. The particle size dependence (and therefore the structure-sensitivity), pressure-dependence and mechanisms of n-hexane skeletal rearrangements have been investigated by many workers. N-hexane has often been chosen because it is the simplest molecule which can undergo the whole range of conversion reactions, including hydrogenolysis, isomerisation, dehydrogenation, C_5-cyclisation and aromatisation (Figure 21). Detailed, but often contradictory information has been obtained concerning the particle-size dependence of these reactions. While Dautzenberg and Platteeuw (1970, 1972) and Lankhorst et. al. (1980) have detected no significant particle-size dependence of n-hexane isomerisation and cyclisation (working on 15-80Å Pt particles supported on Al_2O_3 and SiO_2), Santacessaria (1978) and Anderson (1972) observed increased activity for n-hexane isomerisation, hydrogenolysis and C_5-cyclisation on very small particles (< 10Å).

In these latter experiments, the reactions were carried out on thin films and Pt/SiO_2 catalysts, the particle size being varied between < 10 and > 100Å . The particle size dependence was explained in terms of a change of mechanism from cyclic (Corolleur, 1972) to bond-shift (Anderson, 1966) (see Figure 22) as the particle size was increased. The determination of structure sensitivity can best be undertaken by single-crystal studies, however, since the ill-defined structure and composition of dispersed particle catlaysts can easily lead to misinterpretations due to artefacts. Davis et al. (1982a) have conducted extensive n-hexane conversion experiments on platinum single crystal surfaces, which were prepared in ultrahigh vacuum and then subjected to catalytic conditions in a high pressure cell (see section II). The samples were chosen so that the effects of varying terrace structure, as well as kink and step density could be independently investigated. The n-hexane reaction which displayed the most significant structure sensitivity was the aromatisation to benzene, where the rate and selectivity appeared to be maximised on surfaces containing high concentrations of contiguous (111) microfacets (Figure 23). The product distribution of n-hexane hydrogenolysis also showed a marked terrace structure sensitivity, where (100) terraces appeared to favour internal C-C bond scission, surfaces with (111) terraces being more selective for terminal hydrogenolysis (Figure 22). Post-reaction Auger spectroscopy always showed the presence of a carbonaceous overlayer after catalytic reactions on single crystal platinum surfaces. The origins and function of this overlayer will be dealt with in the following section.

Davis et al. (1982 b) have also investigated the conversion of light alkanes (n-butane and isobutane (2-methyl propane)) on platinum single crystals. In contrast to their results with n-hexane, isomerisation displayed a significant structure sensitivity (Figure 24), high concentrations of (100) microfacets

appearing to be necessary for high catalytic activity in butane isomerisation. These results compare well with the oriented film studies of Anderson and Avery (1966), who found that (100)-oriented platinum displayed higher activity for butane isomerisation than films with a (111) orientation. The difference in structural sensitivity behavior between the isomerisation rates of n-hexane and the light alkanes can be related to mechanistic differences; a cyclic mechanism is operative in the hexane case, where the rates for C_5-cyclisation and isomerisation showed identical temperature and hydrogen pressure-dependence. This mechanism is not available to the smaller light alkanes, which react via a bond-shift mechanism (Figure 22).

3. The Carbonaceous Overlayer - its Properties and Role

The hydrogenation/dehydrogenation of cyclohexene over platinum single crystal surfaces at low pressure has been investigated extensively (Blakely, 1976, Smith, 1979). At pressures between 10^{-8} and 10^{-5} torr these reactions display considerable structure sensitivity. Working at pressure in excess of 10 torr on Pt/SiO_2, Segal et al. (1978) have shown that hydrogenation of cyclohexene is structure insensitive. In an effort to reconcile these disparate observations, Davis and Somorjai (1980), using a UHV chamber invorporating a high pressure cell, have investigated platinum-catalysed cyclohexene hydrogenation over a ten-orderof-magnitude pressure range (10^{-7} to 10^{2} torr). Their results confirm the changes in structure sensitivity behaviour as well as demonstrating a change in selectivity from mostly dehydrogenation at low pressures to mostly hydrogenation at high pressures. The steady-state reaction probability was also observed to decrease with increasing pressure. These observations are explained by the presence of a near monolayer of carbonaceous species, which was found to be present on the platinum surface after reaction. The carbon apparently has the

effect of "smoothing out" surface irregularities such as steps and kinks, thereby reducing the effect of the underlying platinum surface structure.

The carbonaceous overlayer has been observed in all high-pressure platinum-catalysed hydrocarbon interconversion reactions studied so far. It does not, however, always mask structure sensitivity, as is illustrated by the preferential aromatisation of n-hexane on (111) microfacets at high pressure. Davis (1981, 1982 b) has carried out a series of experiments involving the radioactive labelling of the carbonaceous deposit, the titration of bare platinum sites with carbon monoxide and the investigation of the temperature-dependence of hydrocarbon conversion reactions. These experiments have shown that there are three distinct temperature regimes where the bond-strength, bond-multiplicity and catalytic behaviour of the metal-carbonaceous layer are different:

1) Low temperatures (< 300 K), where reversible adsorption of hydrocarbons seems to occur, and catalysis at high hydrogen pressures is characteristic of a clean metal surface.
2) High temperatures (> 750 K), where multilayer carbon build-up has been observed. Under these conditions, the catalyst rapidly becomes poisoned by graphitic coke.
3) Intermediate temperatures (350-700 K), where both reversible and irreversible hydrocarbon adsorption can occur, with sequential bond-breaking, skeletal rearrangement and intermolecular hydrogen transfer.

Thus, depending on reaction temperature, hydrocarbon adsorption on platinum can be totally reversible, totally irreversible or a combination of these two extremes, the last of these being the most interesting and relevant to industrial catalysis. In this intermediate temperature regime, the surface can be represented by the model shown in Figure 25. Bare metal sites are still exposed, and account for the unique properties of platinum and the structural sensitivity displayed by

reactions such as n-hexane aromatisation. The rest of the surface consists of active C_xH_y polymers with approximately 1-1.5 hydrogen atoms per surface carbon atom. These fragments are present as both 2-D and 3-D structures, the latter predominating at higher reaction temperatures. The principal property of the carbonaceous deposit is to poison the surface non-selectively, simply by hindering the access of reactants to the metal sites. However, it is clear from H-D exchange studies (Davis, 1982 b) that the deposit also has the important role of exchanging hydrogen with reacting surface species. This property may alter the selectivity of skeletal rearrangements at high temperatures. Davis (1981) has clearly established that the dissociatively chemisorbed intermediates of catalysed hydrocarbon reactions have surface residence times on the order of seconds, permitting diffusion over many different surface sites.

Industrial reforming catalysts rarely contain platinum alone, since the inclusion of metals such as rhenium and gold appears to improve the catalyst's resistance to poisoning by coke. This is quite understandable in terms of the model just described, since these diluent metals do not form strong bonds with hydrocarbons, thereby reducing the chance of adsorbed molecules forming multiple bonds with several adjacent sites. A multiply-bonded configuration is essentially irreversible, and therefore of no catalytic value, since the probability that hydrogenation would occur simultaneously on adjacent sites is extremely small. Platinum is probably unique in its formation of stable, strongly-bound polymeric residues, because of its very low activity as a hydrogenolysis catalyst. On metals with high hydrogenolysis activity, continuous C-C bond-breaking and subsequent removal of hydrocarbon fragments as light alkanes could reasonably be expected to occur, leading to a continuously regenerated clean metal surface.

4. The Action of Foreign Atoms on Platinum Catalysts

a) Oxygen

If platinum is heated in oxygen at elevated temperatures (> 1000 K), a strongly-bound surface oxygen species is formed (Smith, 1980, Gland, 1978). This species shows greater thermal stability than oxygen chemisorbed at lower temperatures or of the bulk platinum oxides. Ion scattering experiments by Niehus and Comsa (1980) have shown that the strongly-bound oxygen is located below the topmost layer of platinum atoms. Salmeron (1981) has very recently carried out LEED studies to show that this Pt/O/Pt structure may be explained in terms of various orientations of platinum oxides, the stability being due to the very slow kinetics of oxygen diffusion to the surface.

If pre-treated with oxygen at high temperature, platinum catalysts show marked changes in their catalytic behaviour. Poltorak et al. (1966) and Mitrafanova et al. (1972) observed that highly dispersed catalysts displayed enhanced activity for cyclohexene hydrogenation following oxidation, while the activity of catalysts with low dispersions was not altered appreciably. This can be understood in the light of experiments reported by Gillespie (1980) and Smith et al. (1979), who investigated the catalytic behaviour of several single crystal platinum surfaces after oxygen pretreatment and observed that strongly-bound oxygen only changed the chemical activity of crystals with high kink concentrations. The more highly dispersed catalysts have far greater concentrations of kinks and are therefore preferentially promoted by oxygen pre-treatment.

Changes which have been observed in the catalytic properties of oxygen-pretreated platinum crystal with high kink concentrations include a ten-fold increase in the hydrogenolysis rate of certain alkanes (Gillespie, 1981), an inhibition of catalyst deactivation, particularly at low temperatures (Smith, 1980) and changes in the selectivity of cyclohexene hydrogenation/dehydrogena-

tion. Differences have been observed (Gillespie, 1980) in the action of oxygen pretreatment on high and low pressure catlaytic reactions: this is probably due to the large differences in the steady state populations of both hydrogen and hydrocarbons. The probable role of strongly-bound oxygen is to modify the local electronic structure of the platinum surface, thereby affecting the binding strength of reactants, intermediates and products, with consequent changes in rates and selectivities. These phenomena are almost certainly important in real platinum catalysts, where strongly-bound oxygen species are either formed during oxygen pretreatment or the reaction of platinum with oxygen in the support materials.

b) Sulphur

Sulphur is added to most commercial reforming catalysts, in order to reduce hydrogenolysis activity relative to isomerisation or cyclisation, and to reduce the rate of coke formation. Its role is that of a selective poison, and it is incorporated into the catalyst by pretreatment in mixtures of hydrogen sulphide and hydrogen. While the precise action of sulphur on platinum is uncertain, some single crystal experiments have been carried out by Davis (1981), who pretreated Pt(111) specimens with sulphur and with thiophene (C_4H_4S). In Figure 26 the effects of sulphur pretreatment on rates of isomerisation, hydrogenolysis and C_5-cyclisation of n-hexane (at high pressure) are illustrated. Although the catalytic activity of the platinum was generally reduced, hydrogenolysis was suppressed to a far greater extent than the (more industrially useful) isomerisation and cyclisation reactions i.e. the presence of sulphur significantly altered the selectivity of the reaction. Similar effects have been observed by Biloen et al. (1980) for n-hexane reactions carried out over Pt/SiO_2 catalysts.

Davis (1981) explains the changes in selectivity caused by sulphur treat-

ment in terms of a simple ensemble effect. Although hydrogenolysis requires multiple atomic sites (Gillespie, 1980, Clarke, 1976), isomerisation and cyclisation reactions can occur on single atoms of platinum (Anderson, 1972). The effect of sulphur pretreatment is to increase the relative number of monatomic sites, thereby increasing the rates of cyclisation and isomerisation relative to the rate of hydrogenolysis.

c) Metals

Platinum is always alloyed with other metals such as gold, palladium, iridium or rhenium when used as a reforming catalyst. These bimetallic (and multimetallic) catalysts can be more selective for certain reactions (e.g., dehydrocyclisation or isomerisation) than pure supported platinum. Moreover, they display a slower rate of deactivation (i.e., have longer lifetimes) than the one-component catalyst. The latter property is particularly important, since the reactivation of platinum catlaysts can be a very time-consuming and expensive process.

The catalytic effects of dosing gold onto single crystals of platinum have been extensively investigated by Sachtler et al. (1981). While these workers found that adsorbed gold merely caused a linear decrease n the platinum catalytic activity with coverage, they observed strikingly different behaviour when the gold was allowed to diffuse into the platinum at elevated temperatures. This gold-platinum alloy was found to have much higher activity for isomerisation than platinum, whereas dehydrocyclisation and hydrogenolysis appeared to decrease exponentially with gold coverage. This can be explained in terms of the tendancy of gold to break up high coordiantion number sites sequentially, thus inhibiting reactions involving three-fold sites to a greater extent than those which merely require one or two platinum atoms. The increase in activity

is probably due to a decrease in the amount of carbonaceous deposit on the catalyst surface when gold is present--this effect also explains the increased lifetime of bimetallic catalysts. By breaking up the deposit into smaller units, the presence of surface gold appears to facilitate the rehydrogenation of the carbonaceous overlayers, and may also decrease the rate of conversion of these carbonaceous fragments into inactive, graphitic carbon.

IV. SUMMARY

Catalysis is at the heart of most chemical and energy production technologies. In recent years, the application of surface science techniques has permitted the scrutiny of catalyst surfaces on the atomic scale. The structure, composition and oxidation state of surface atoms may now be determined and correlated with the reaction parameters, such as the rate, activation energy and product distribution. The molecular understanding gained permits the design of improved catalyst formulations and holds the promise that one may "build" new catalysts for carrying out specific chemical functions. The art of catalysis is rapidly being converted to catalysis science.

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VII. FIGURE CAPTIONS

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

Figure 2: A high pressure-low pressure apparatus, which enables industrial-type reactions to be run on model catalysts, as well as permitting scrutiny of the catalyst surface by the techniques of surface science.

Figure 3: The three low-index planes of iron, showing the coordination numbers of atoms in the surface and near surface regions.

Figure 4: U.S. Federal and California State maximum permissable automobile emissions of hydrocarbons (HC), carbon monoxide (CO) and oxides of nitrogen (NO) from 1971-1983.

Figure 5: The dependence of emissions of hydrocarbons (HC), carbon monoxide (CO) and oxides of nitrogen (NO_x) on the air/fuel ratio of the mixture entering the cylinders of an automobile engine.

Figure 6: The air/fuel "window" at which point pollution control reactions involving oxidation and those involving reduction may take place simultaneously.

Figure 7: Feedback system used in modern U.S. automobiles to maintain a near-stoichiometric air/fuel ratio.

Figure 8: A poison-resistant design of automobile catalyst pellet containing alumina, cerium, platinum, rhodium and palladium.

Figure 9: The effect of increasing reactant pressure on the hydrogenation of carbon monoxide to benzene.

Figure 10: Synergic bonding of carbon monoxide to a transition metal (in this case, platinum), showing donation of electrons from 5σ orbital of CO into metal, and back donation of electrons from the 5d metal orbitals into the CO 2π^* antibonding orbitals.

Figure 11: a) Linear bonding of carbon monoxide on a nickel surface.
b) Multiple ("bridge") bonding of carbon mnoxide on a palladium surface.

Figure 12: Change in U.S. catalytic working capacity from 1960 to 1970, showing impact of zeolitic catalysts on actual capacity needed. (Springer Verlag)

Figure 13: SiO_4 and AlO_4^- tetrahedra--the fundamental building blocks of zeolites.

Figure 14: The sodalite cage ("——" represents an Si-O-Si or Si-O-Al linkage).

Figure 15: The faujasite strucutre, showing a tetrahedral arrangement of sodalite cages, linked by hedagonal prisms.

Figure 16: ZSM-5 structure (Structure Commission of IZA).

Figure 17: Most favoured positions for cations in the faujasite structure (American Chemical Society).

Figure 18: The cause of acidity in decationated zeolites.

Figure 19: The interrelation of ethylene, ethylene oxide and the products of total combustion.

Figure 20: The Sachtler-modified Worbs mechanism for the silver-catalysed epoxidation of ethylene.

Figure 21: Rections of n-hexane on platinum in the presence of excess hydrogen.

Figure 22: Bond-shift and cyclic mechanisms for isomerisation, and the distinction between terminal and internal bond-scission during hdyrogenolysis.

Figure 23: Structure-sensitivity for the platinum-catalysed aromatisation of n-hexane.

Figure 24: Structure-sensitivity of light alkane isomerisation over platinum.

Figure 25: Model for the working platinum reforming catalyst.

Figure 26: The effects of sulphur pretreatment on the rates of isomerisation, hydrogenolysis and C_5-cyclization of n-hexane over platinum (111).

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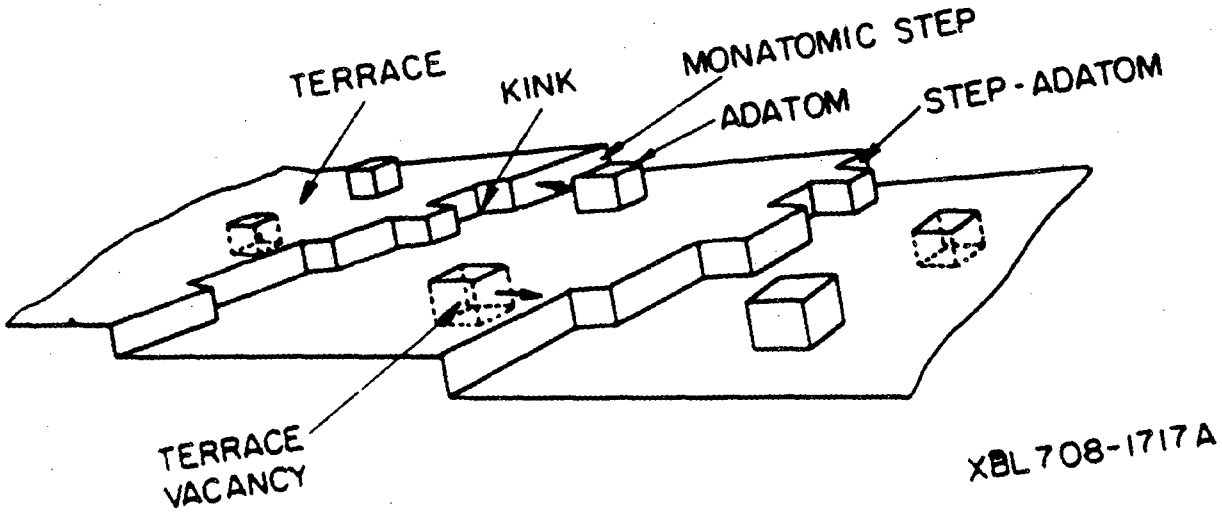

TERRACE
KINK
MONATOMIC STEP
ADATOM
STEP-ADATOM
TERRACE VACANCY
XBL708-1717A

Fig. 1

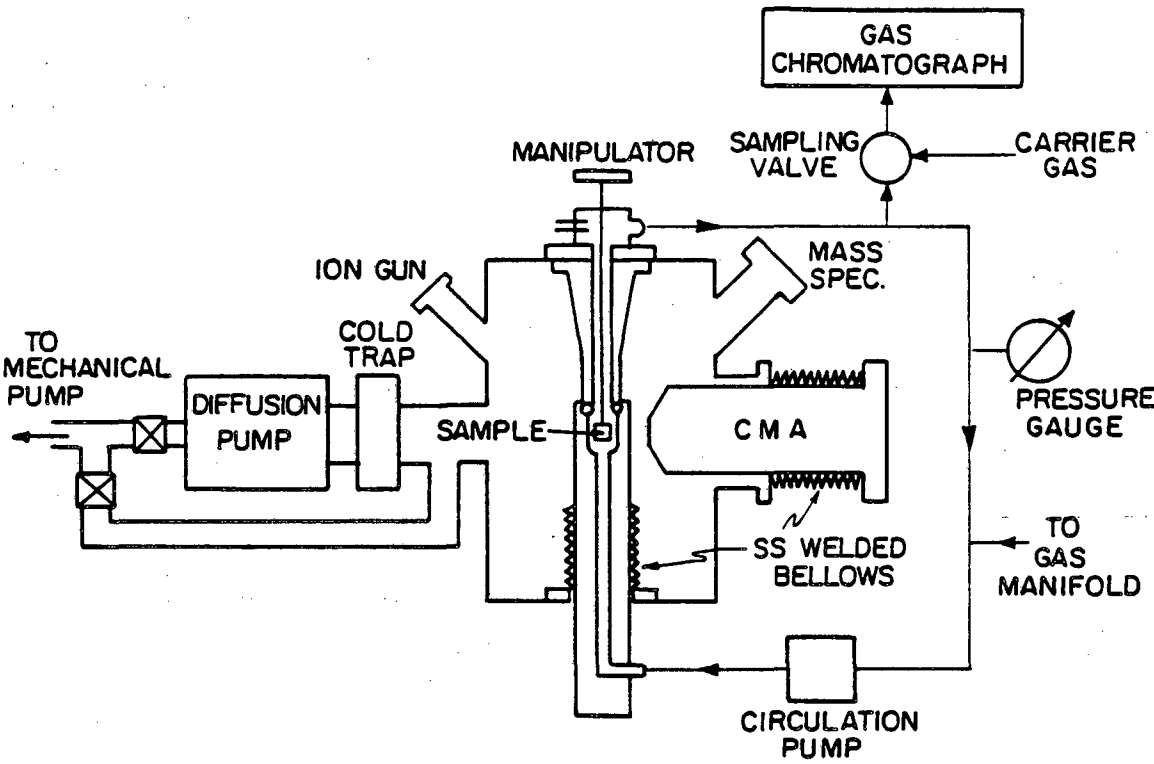
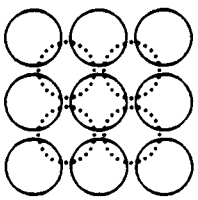

GAS
CHROMATOGRAPH
MANIPULATOR
SAMPLING
VALVE
CARRIER
GAS
ION GUN
MASS
SPEC.
TO
MECHANICAL
PUMP
COLD
TRAP
DIFFUSION
PUMP
SAMPLE
CMA
PRESSURE
GAUGE
SS WELDED
BELLOWS
TO
GAS
MANIFOLD
CIRCULATION
PUMP
(a)
SAMPLE
CMA
(b)
XBL 814-5584

Fig. 2

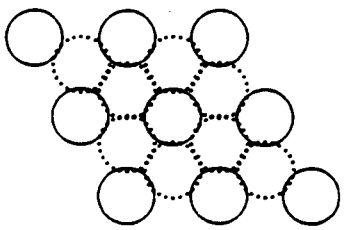
LOW-INDEX PLANES OF IRON



C_4 ATOMS (SOLID)

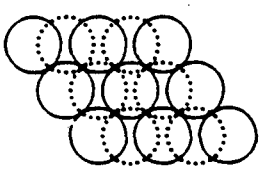
C_8 ATOMS (DOTTED)

(100) PLANE



(111) PLANE

C_4 (SOLID) AND C_7 ATOMS (DOTTED)



(110) PLANE

C_6 (SOLID) AND C_8 ATOMS (DOTTED)

XBL 819-1842

Fig. 3

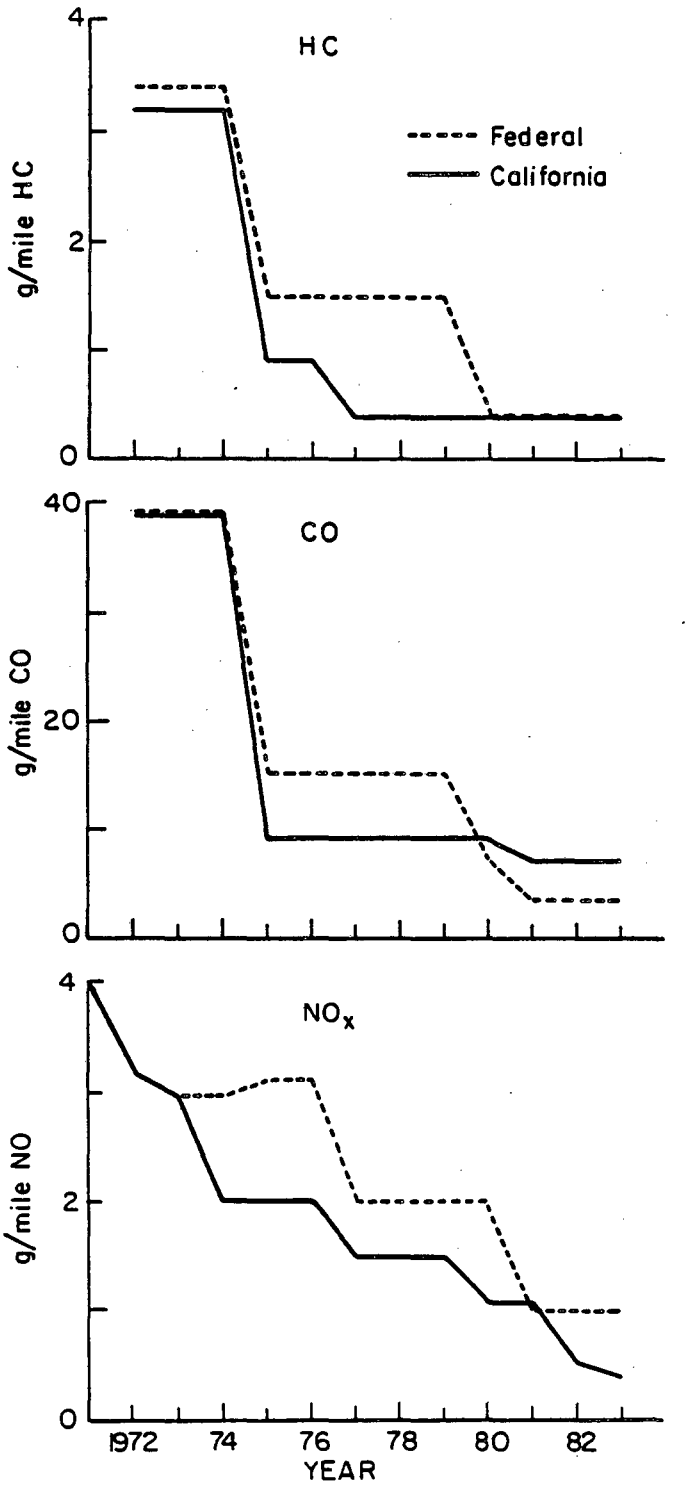

HC
Federal
California
g/mile HC
4
2
0
CO
g/mile CO
40
20
0
NOx
g/mile NO
4
2
0
1972
74
76
78
80
82
YEAR
XBL 8111-6945

Fig. 4

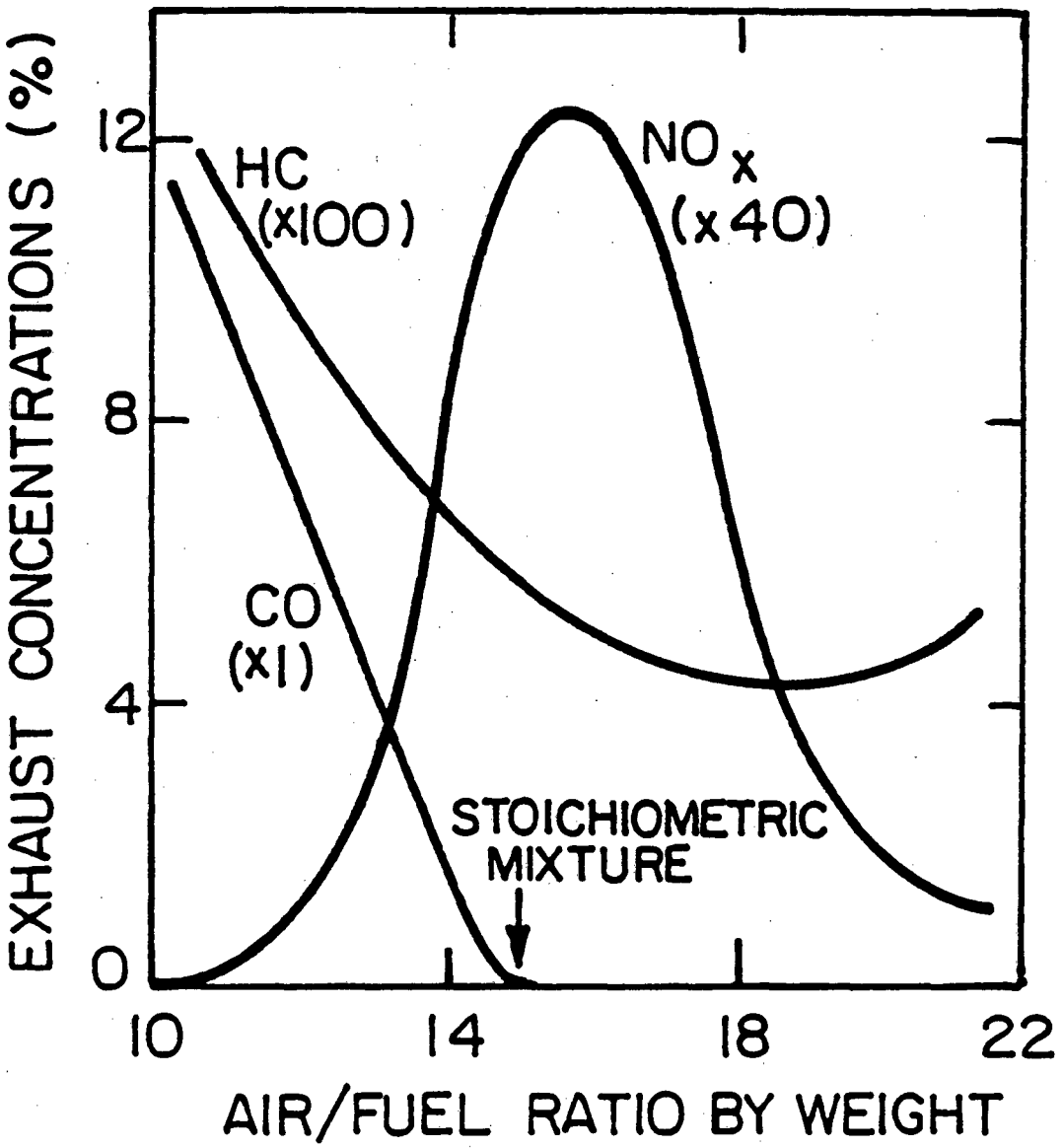

EXHAUST CONCENTRATIONS (%)
12
8
4
0
HC
(x100)
NO x
(x40)
CO
(x1)
STOICHIOMETRIC
MIXTURE
10
14
18
22
AIR/FUEL RATIO BY WEIGHT
XBL8111-6946

Fig. 5

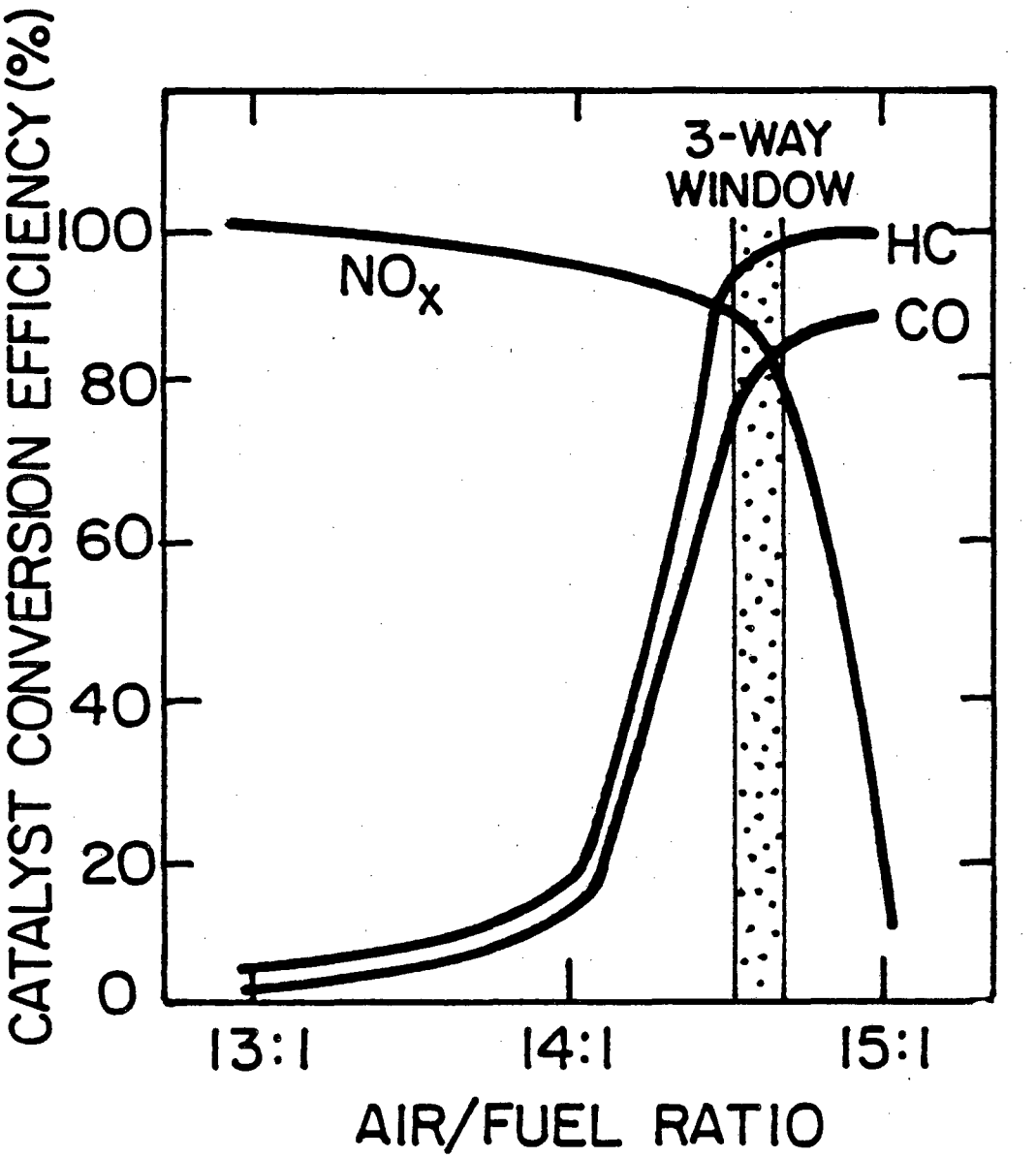
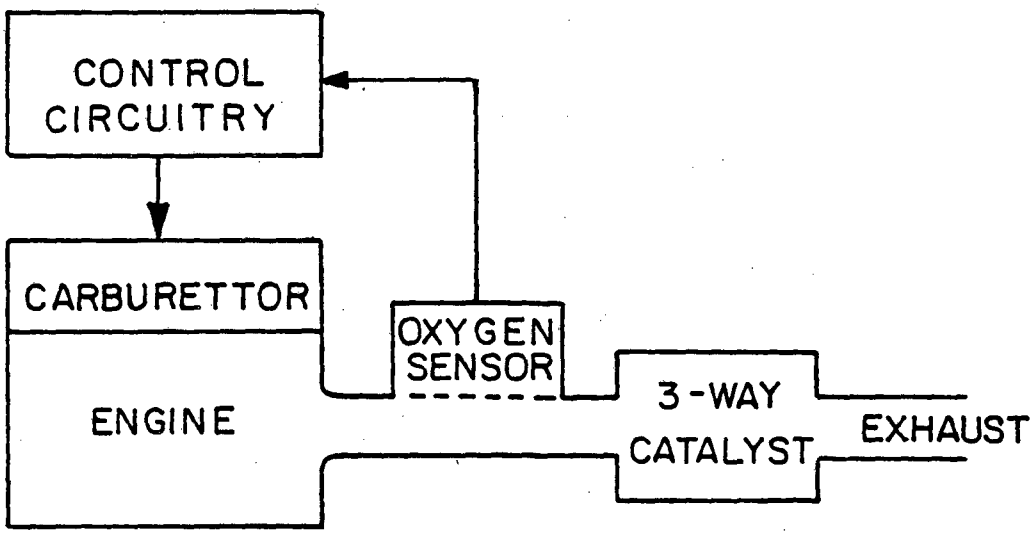
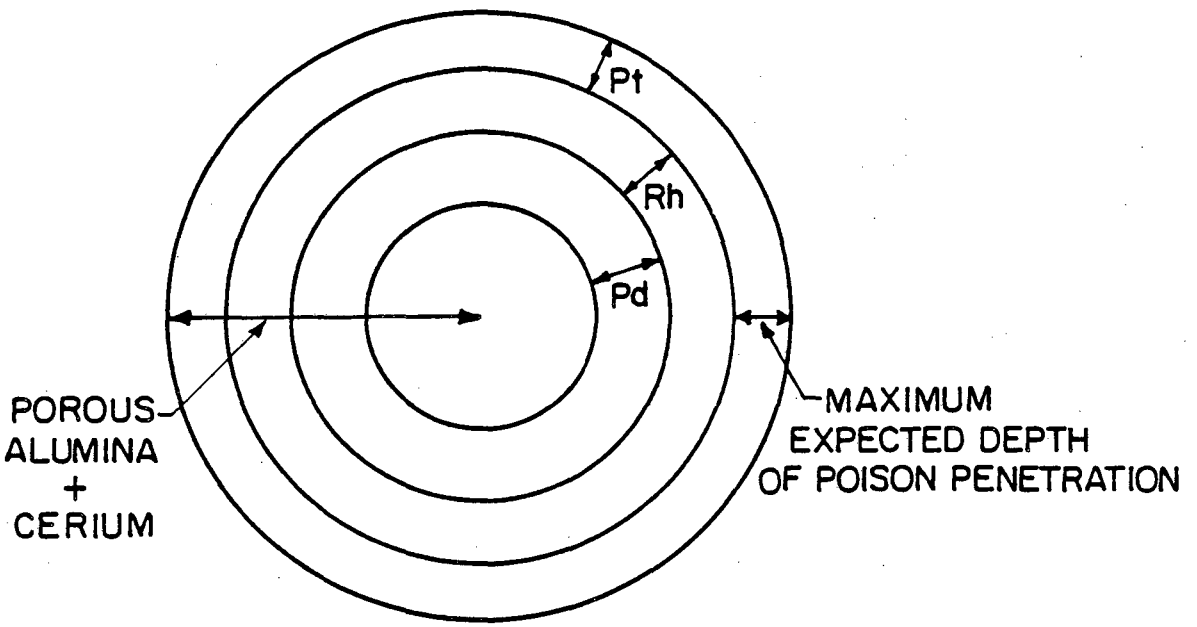

CATALYST CONVERSION EFFICIENCY (%)
100
80
60
40
20
0
3-WAY
WINDOW
NOx
HC
CO
13:1
14:1
15:1
AIR/FUEL RATIO
XBL8111-6947

Fig. 6



XBL 8111-6948

Fig. 7



XBL8111-6949

Fig. 8

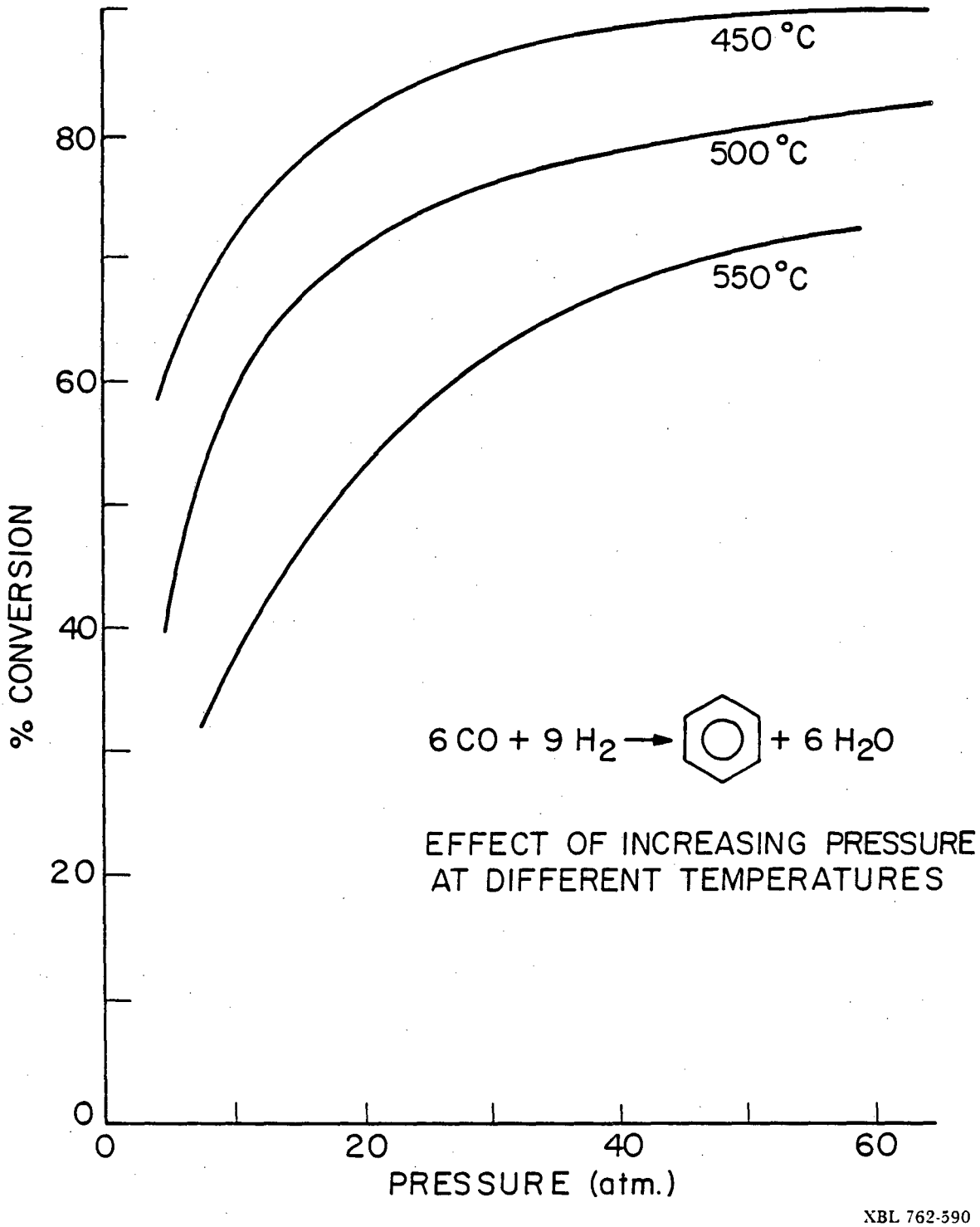
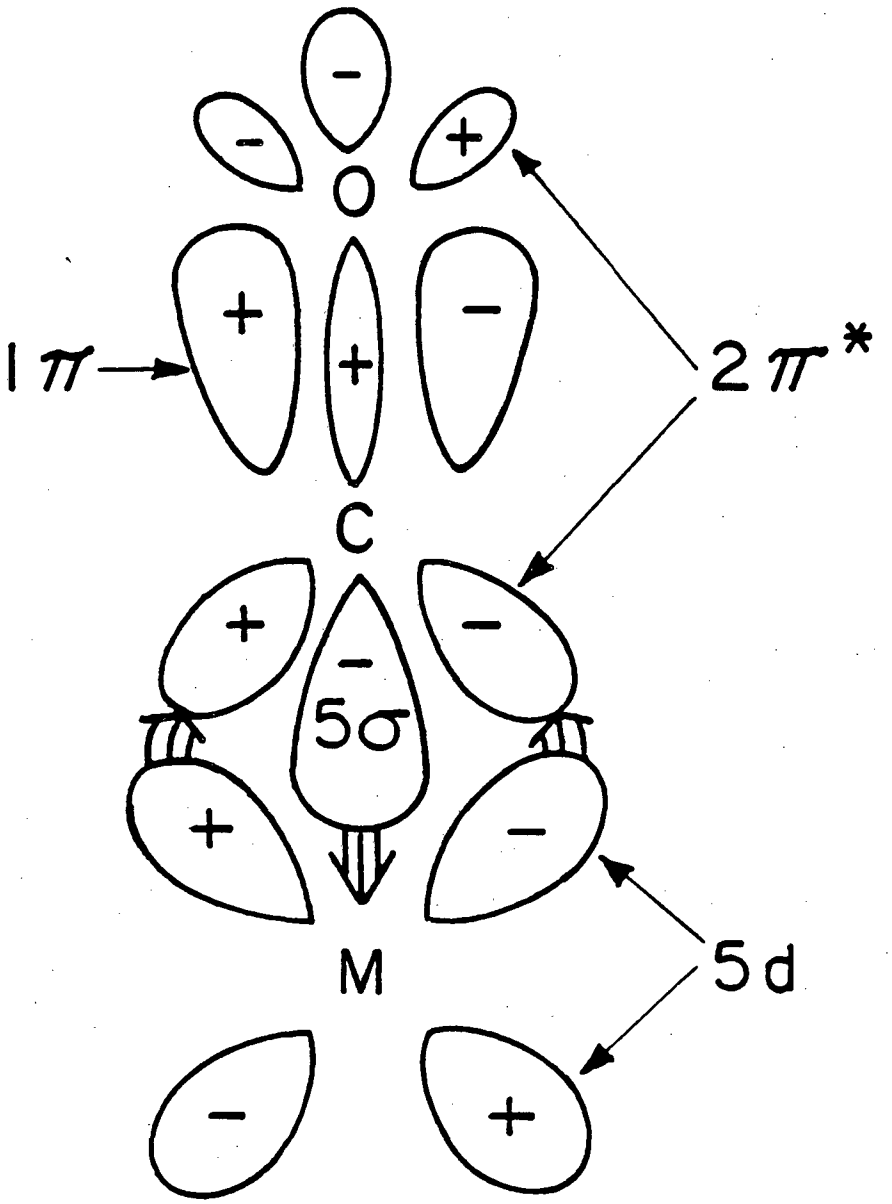
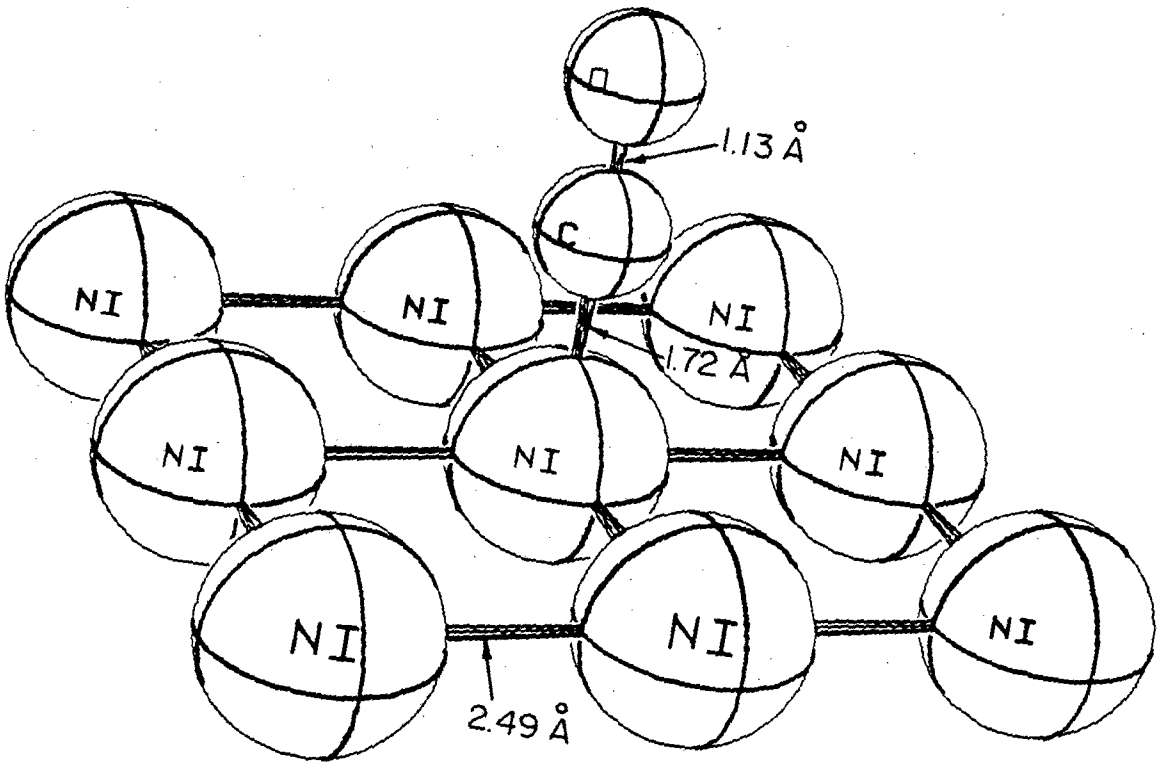

450 °C
500 °C
550 °C
80
60
40
20
0
% CONVERSION
0
20
40
60
PRESSURE (atm.)
6 CO + 9 H2 → + 6 H2O
EFFECT OF INCREASING PRESSURE
AT DIFFERENT TEMPERATURES
XBL 762-590

Fig. 9



XBL 823-8332A

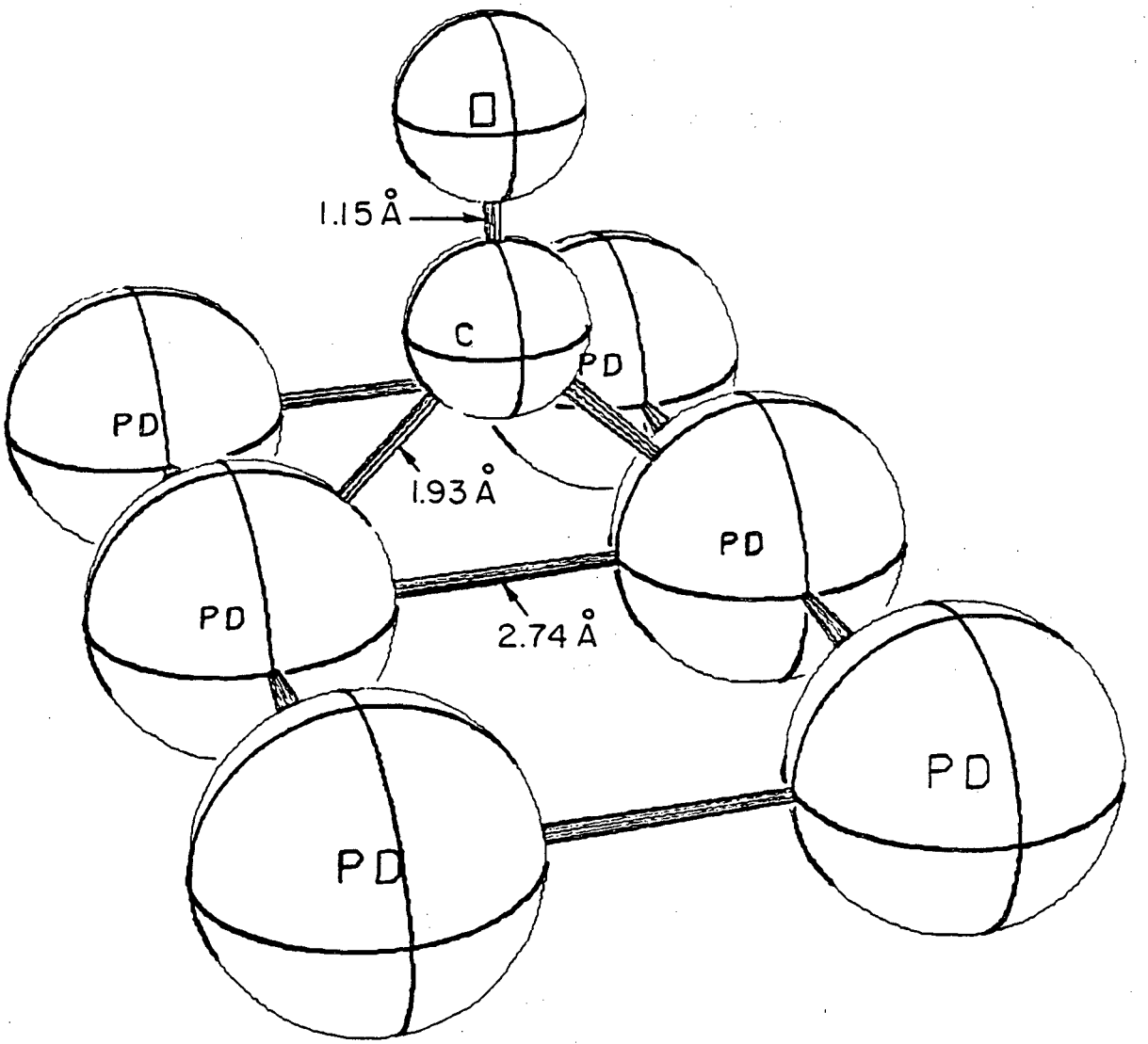
Fig. 10



Ni (100) + c (2x2) CO

XBL 794-6169

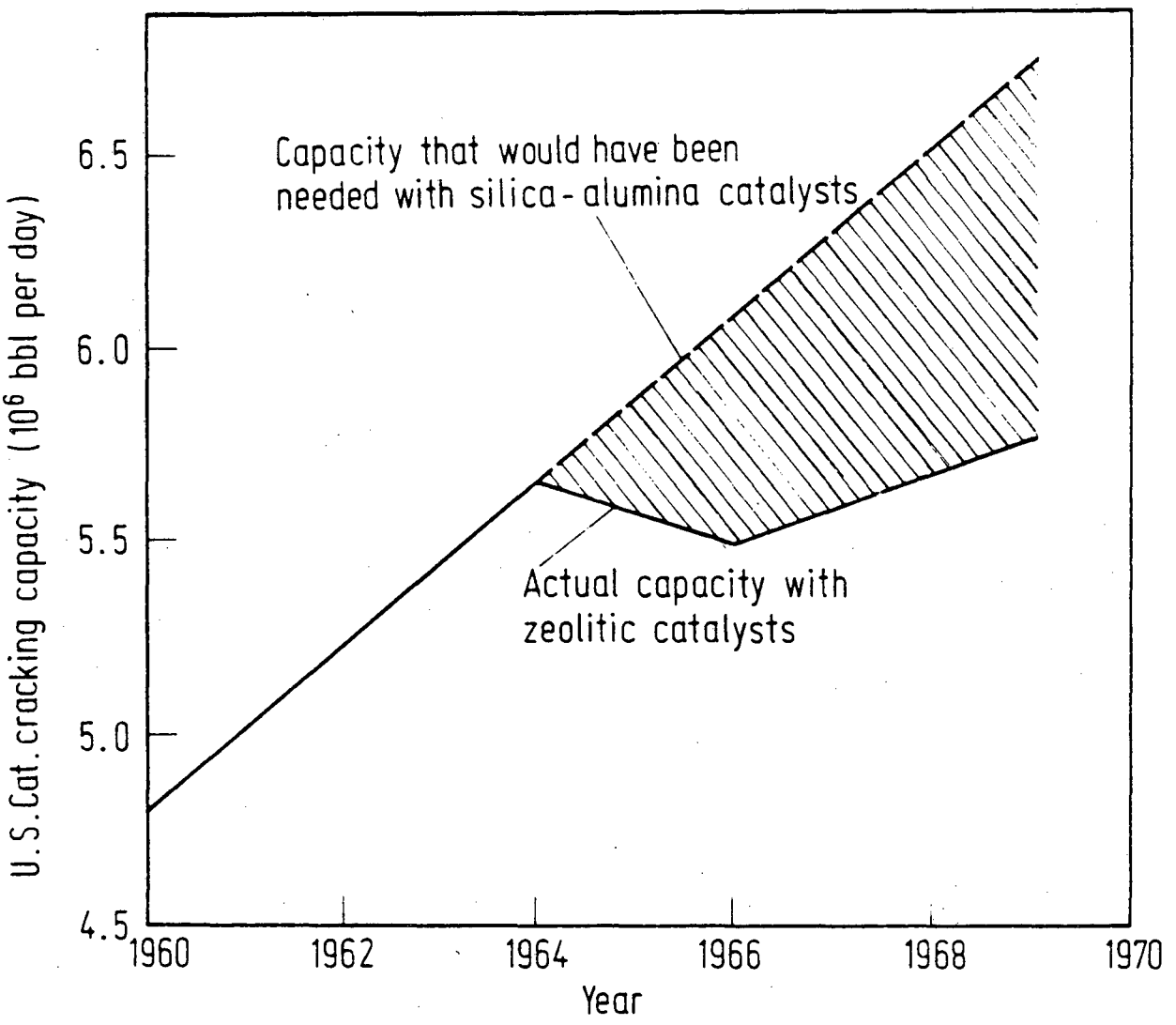
Fig. 11a



Pd (100) + $(2\sqrt{2}\times\sqrt{2})$ R 45° 2 CO

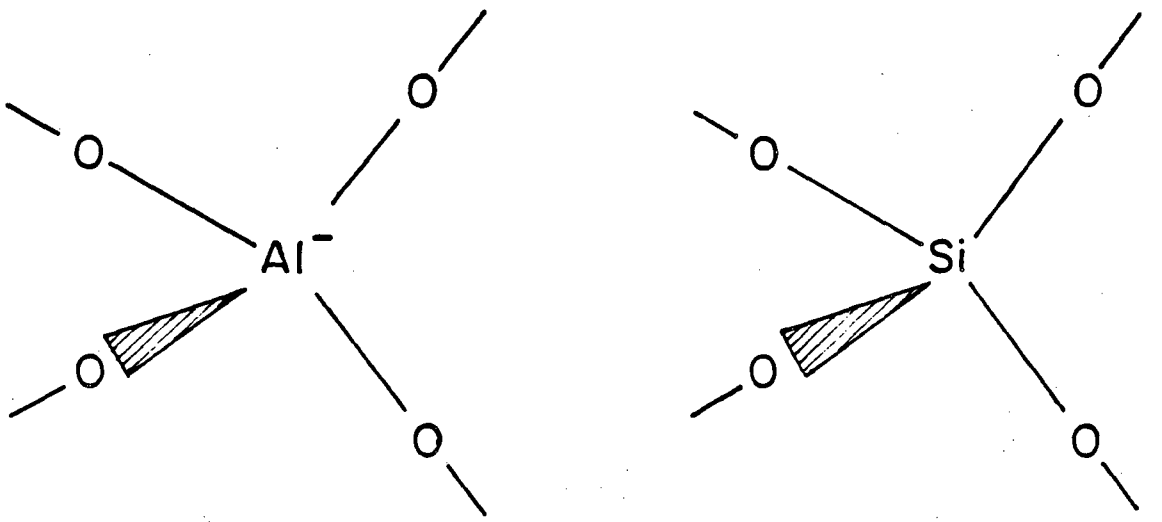
XBL794-6170

Fig. 11b



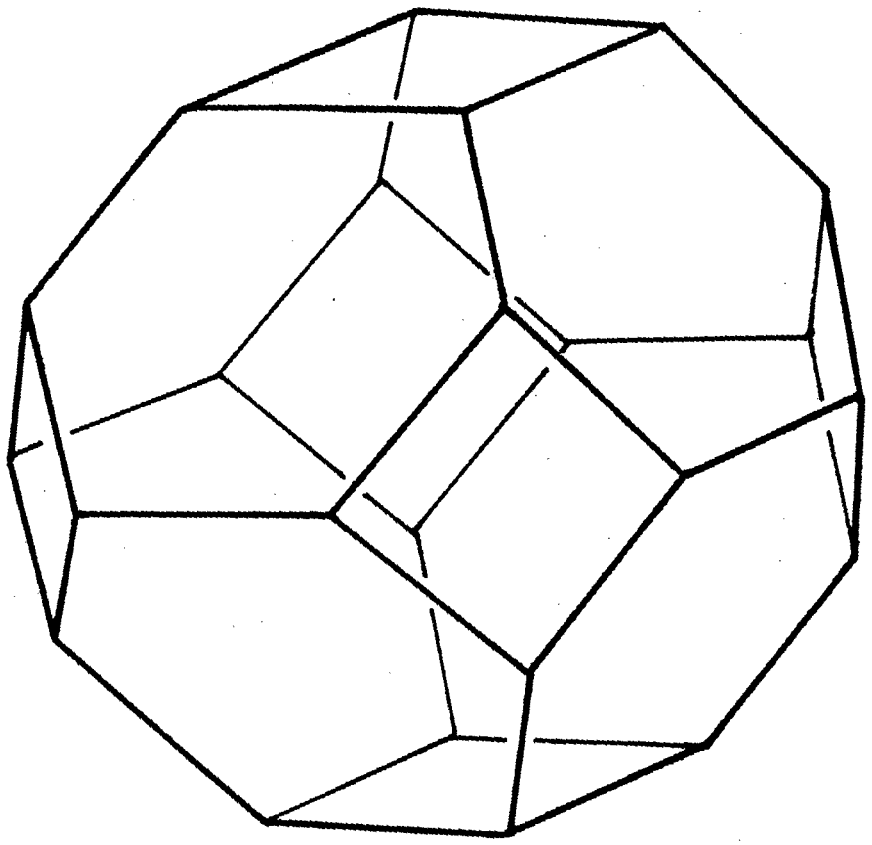
XBL 823-8360

Fig. 12



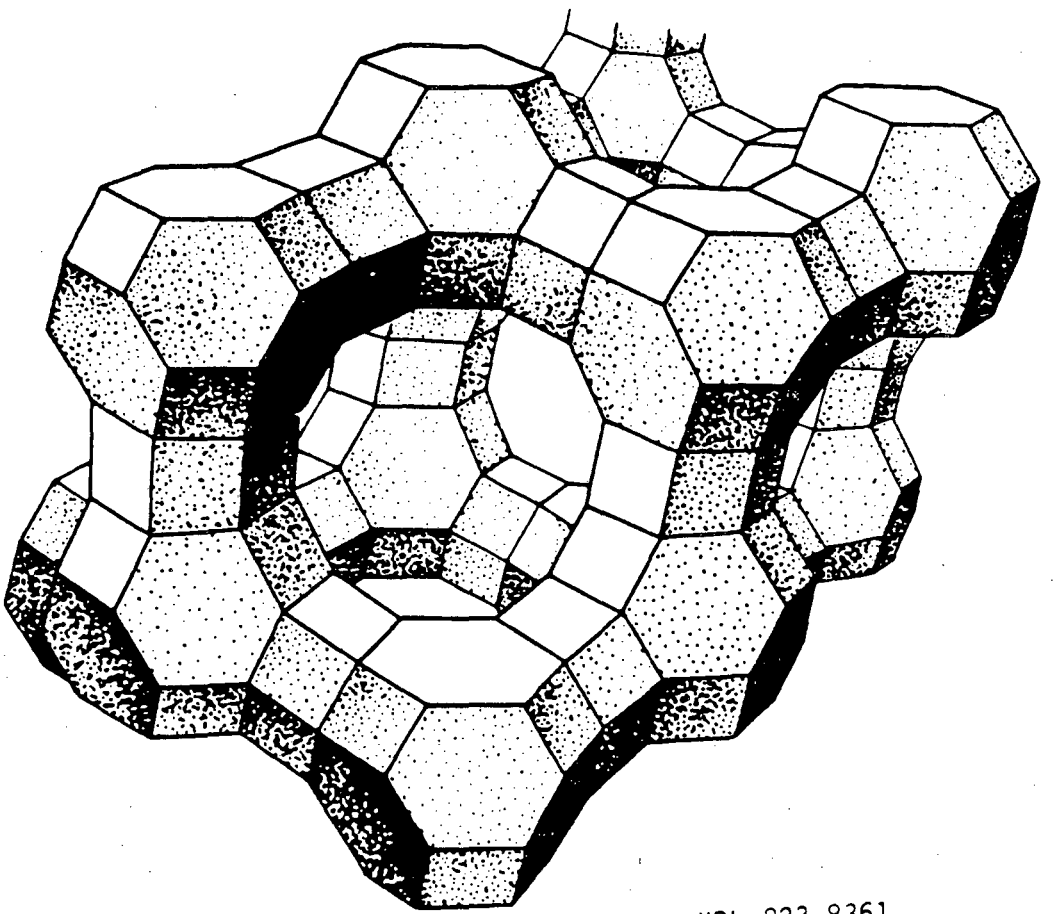
XBL 8111-12854

Fig. 13



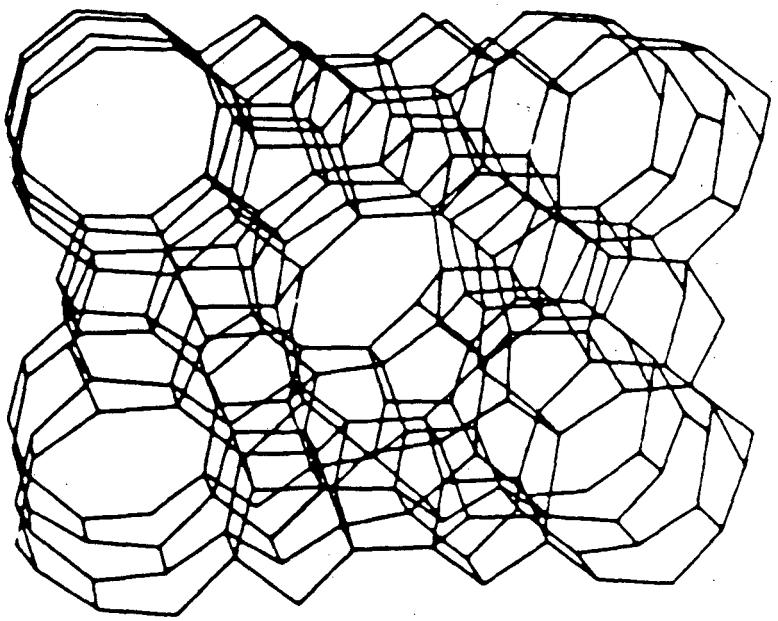
XBL 8111-12853

Fig. 14



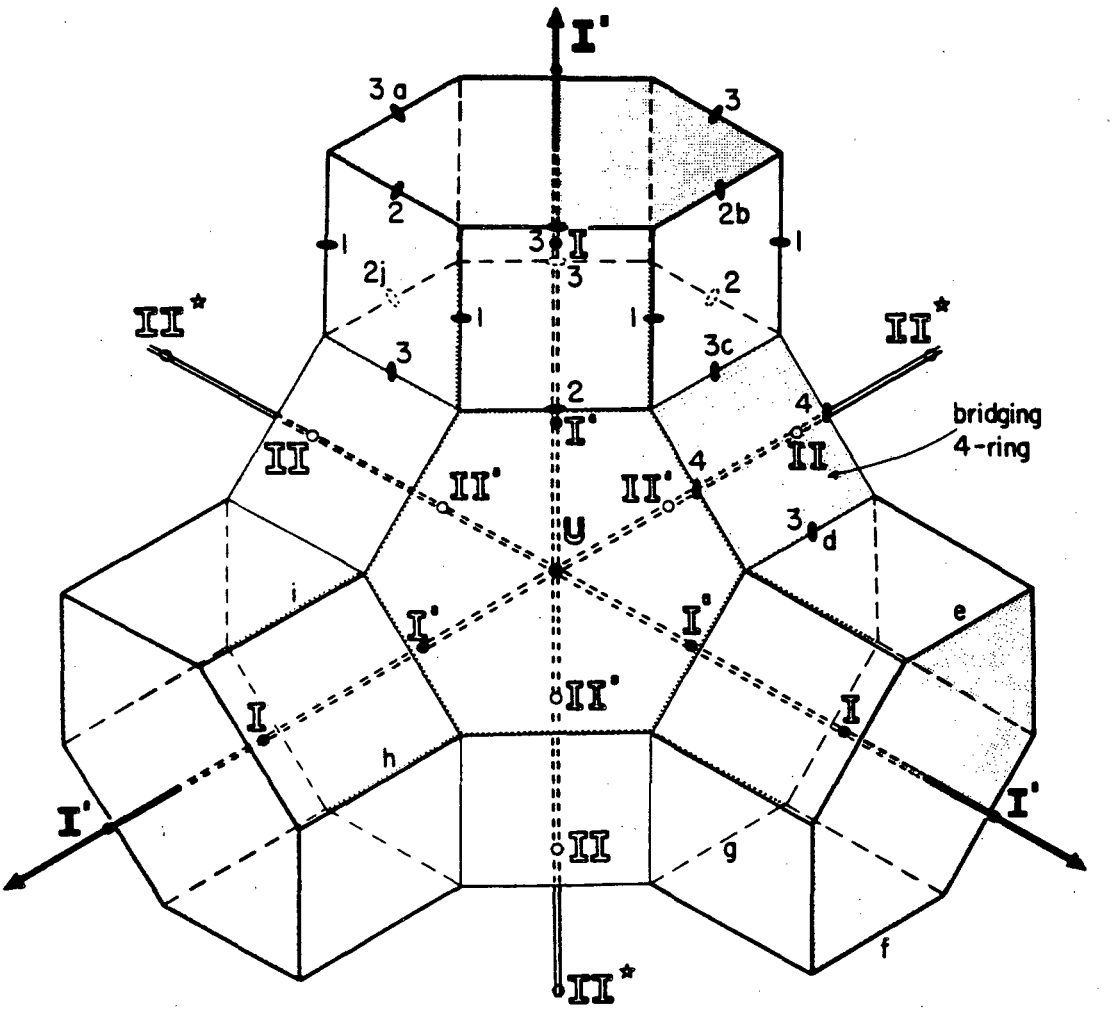
XBL 823-8361

Fig. 15



Zeolite ZSM-5

Fig. 16


I'
3a
3
2
2b
1
3
I
2j
2
II*
II*
3c
bridging
4-ring
II
II'
II'
II
U
3
d
i
e
h
g
f
II*

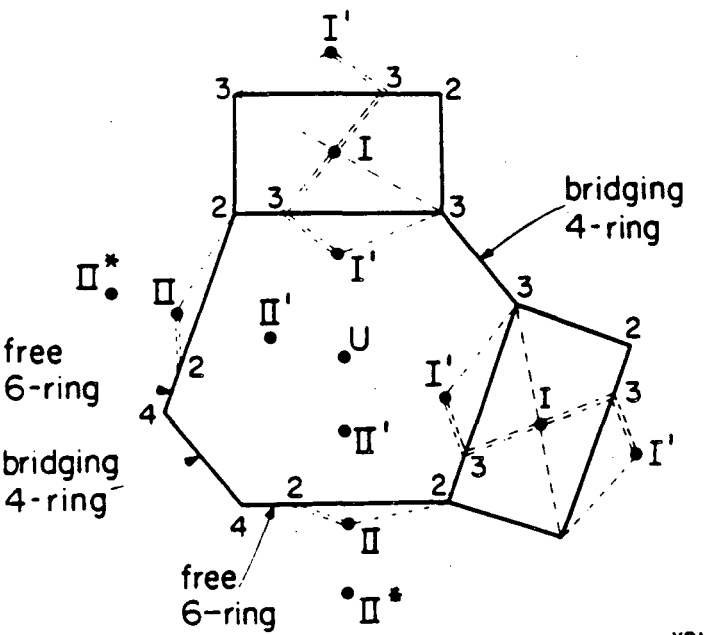
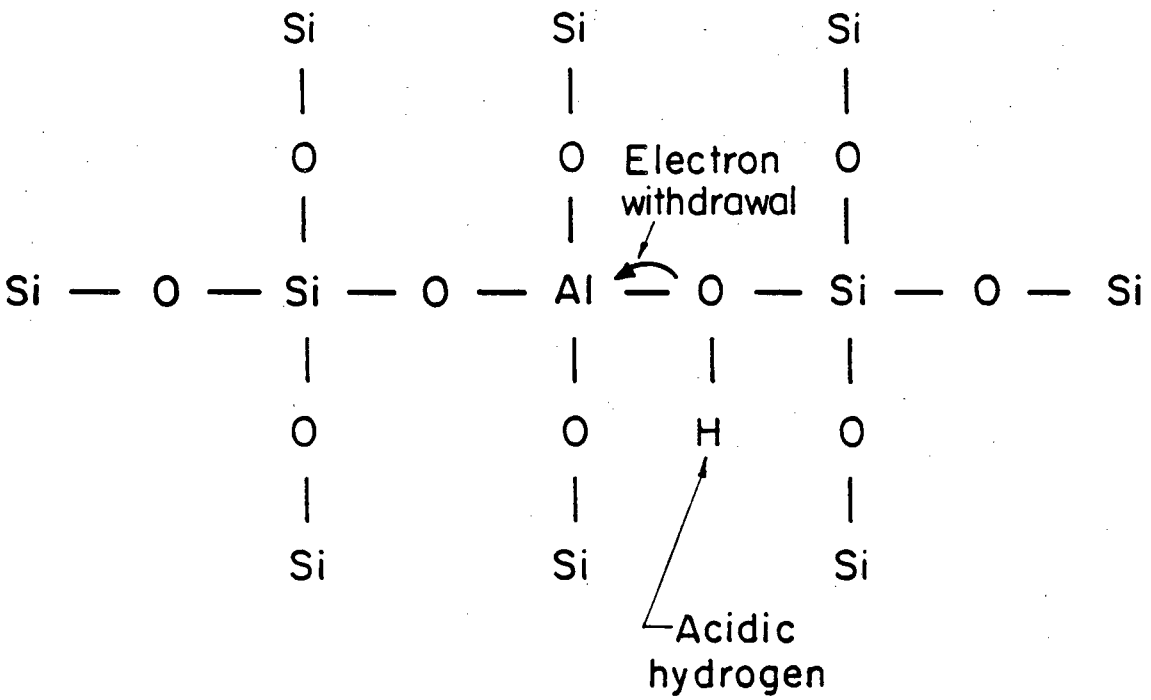
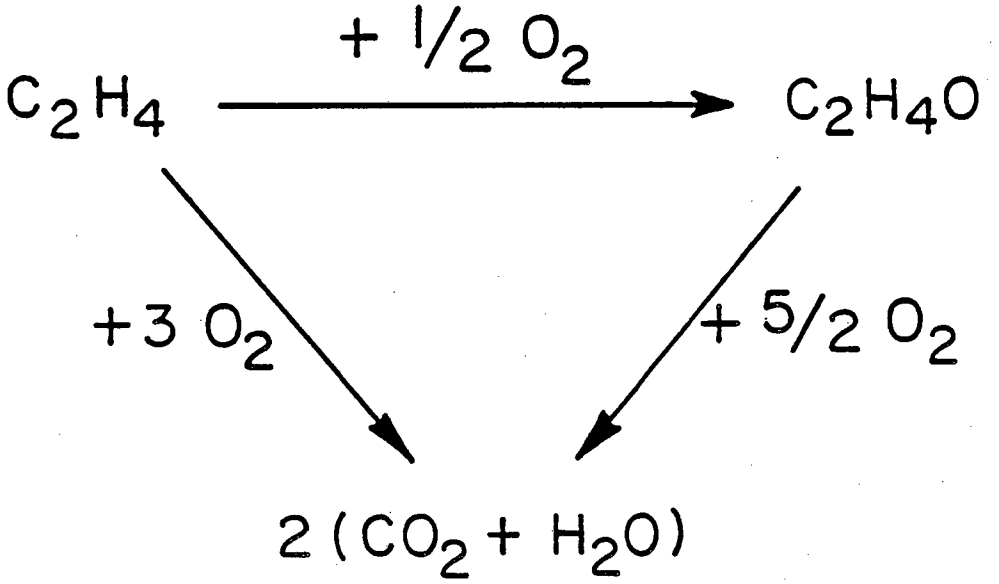

I'
II*
II
II'
U
free
6-ring
bridging
4-ring
bridging
4-ring
free
6-ring
II*
XBL 823-8363

Fig. 17



XBL8111-12855

Fig. 18



XBL825-5654

Fig. 19

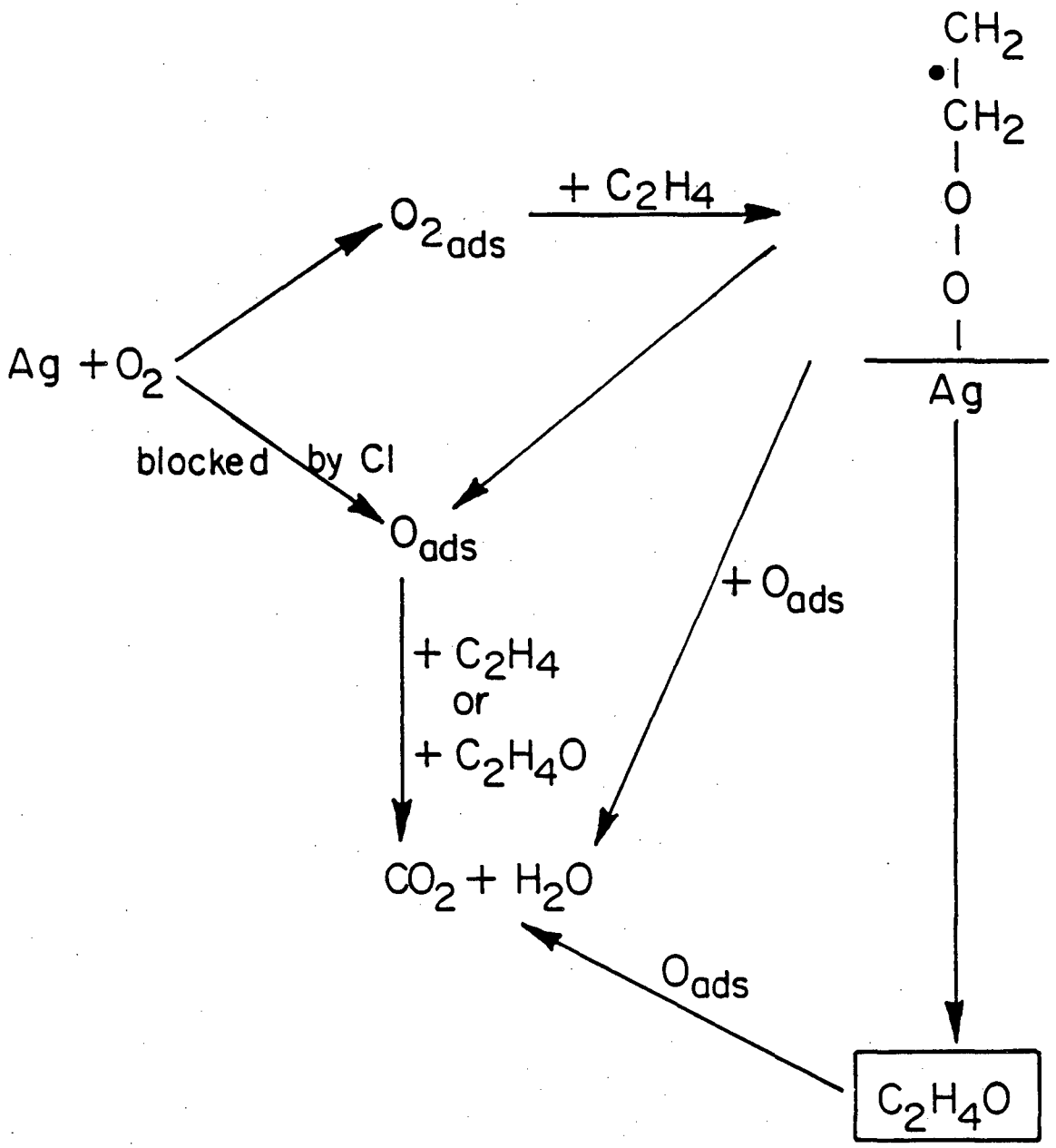

Ag + O2
O2ads
+ C2H4
blocked by Cl
Oads
+ Oads
+ C2H4
or
+ C2H4O
CO2 + H2O
Oads
C2H4O
Ag
XBL825-5655

Fig. 20

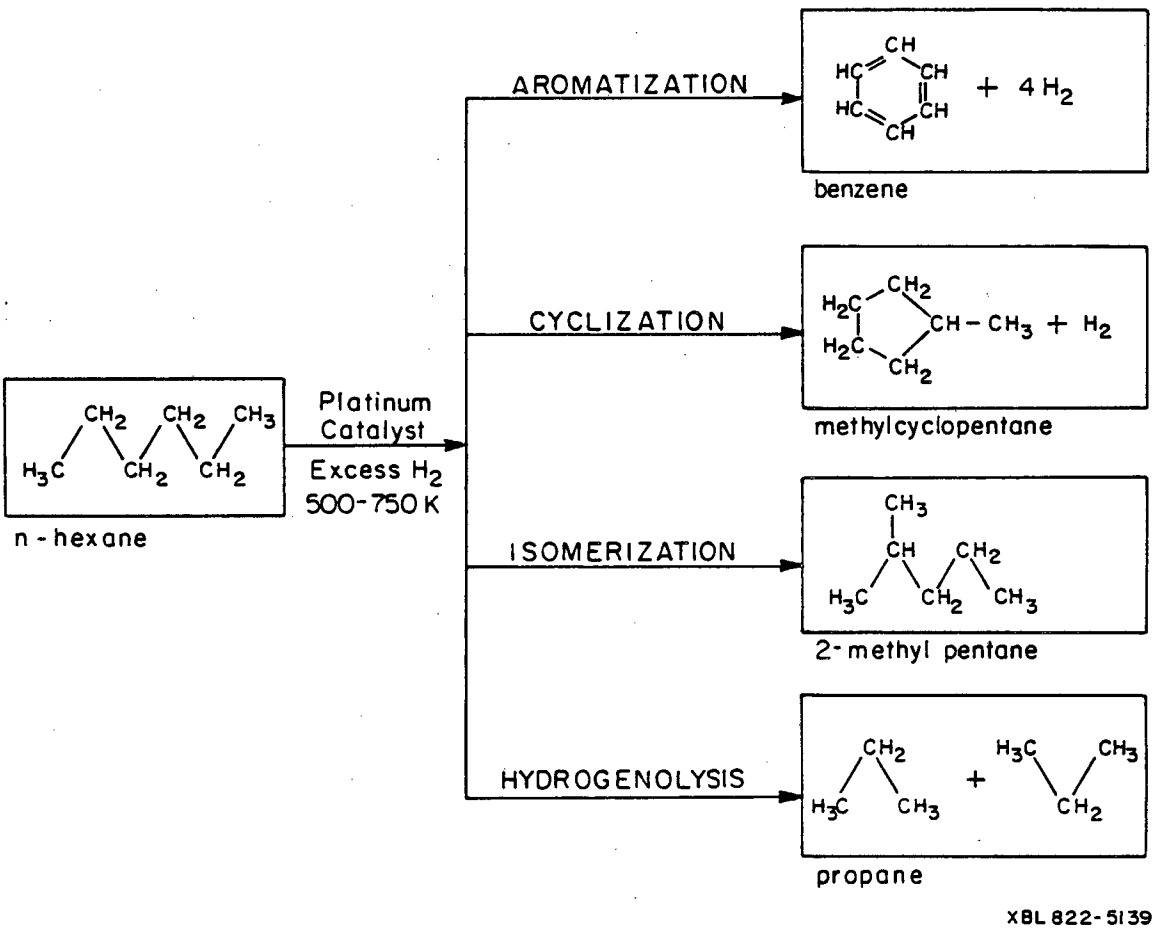
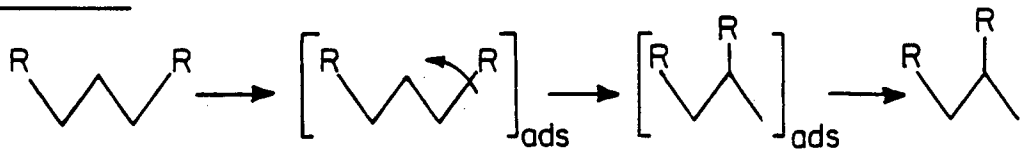
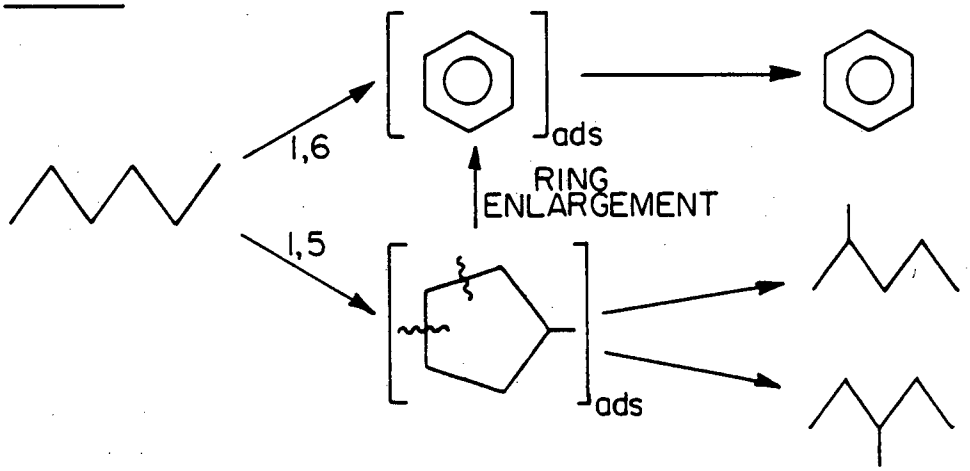

AROMATIZATION
+ 4 H2
benzene
CYCLIZATION
+ H2
methylcyclopentane
ISOMERIZATION
2-methyl pentane
HYDROGENOLYSIS
+
propane
Platinum Catalyst
Excess H2
500-750 K
n-hexane
XBL 822-5139

Fig. 21

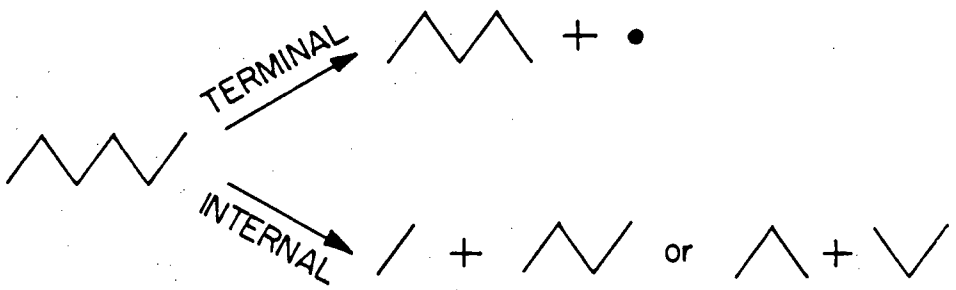
BOND SHIFT:



CYCLIC:



BOND SCISSION:



XBL822-5249

Fig. 22

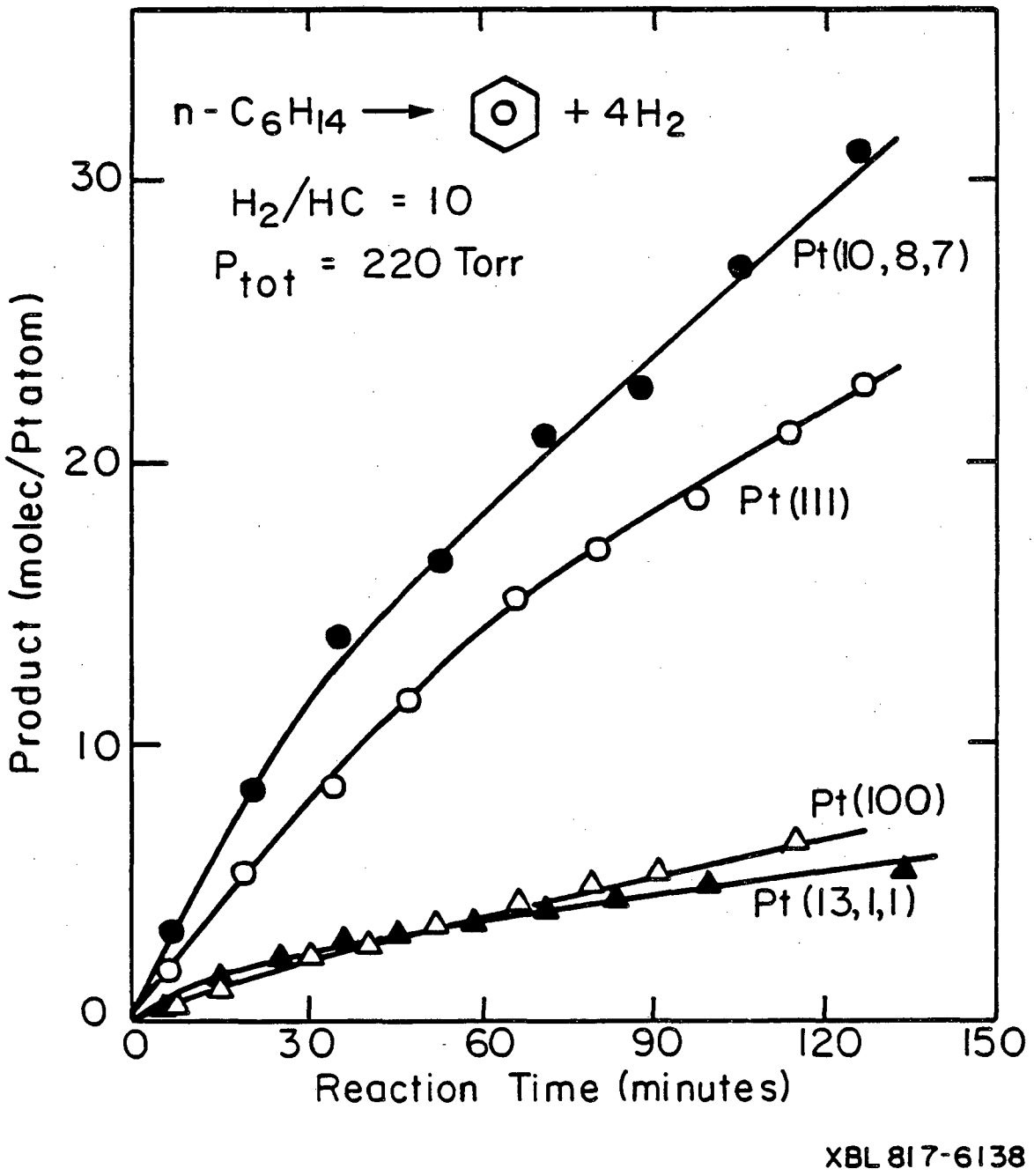

n-C6H14 → + 4H2
H2/HC = 10
Ptot = 220 Torr
Pt(10,8,7)
Pt(111)
Pt(100)
Pt(13,1,1)
Product (molec/Pt atom)
Reaction Time (minutes)
0
10
20
30
0
30
60
90
120
150
XBL 817-6138

Fig. 23

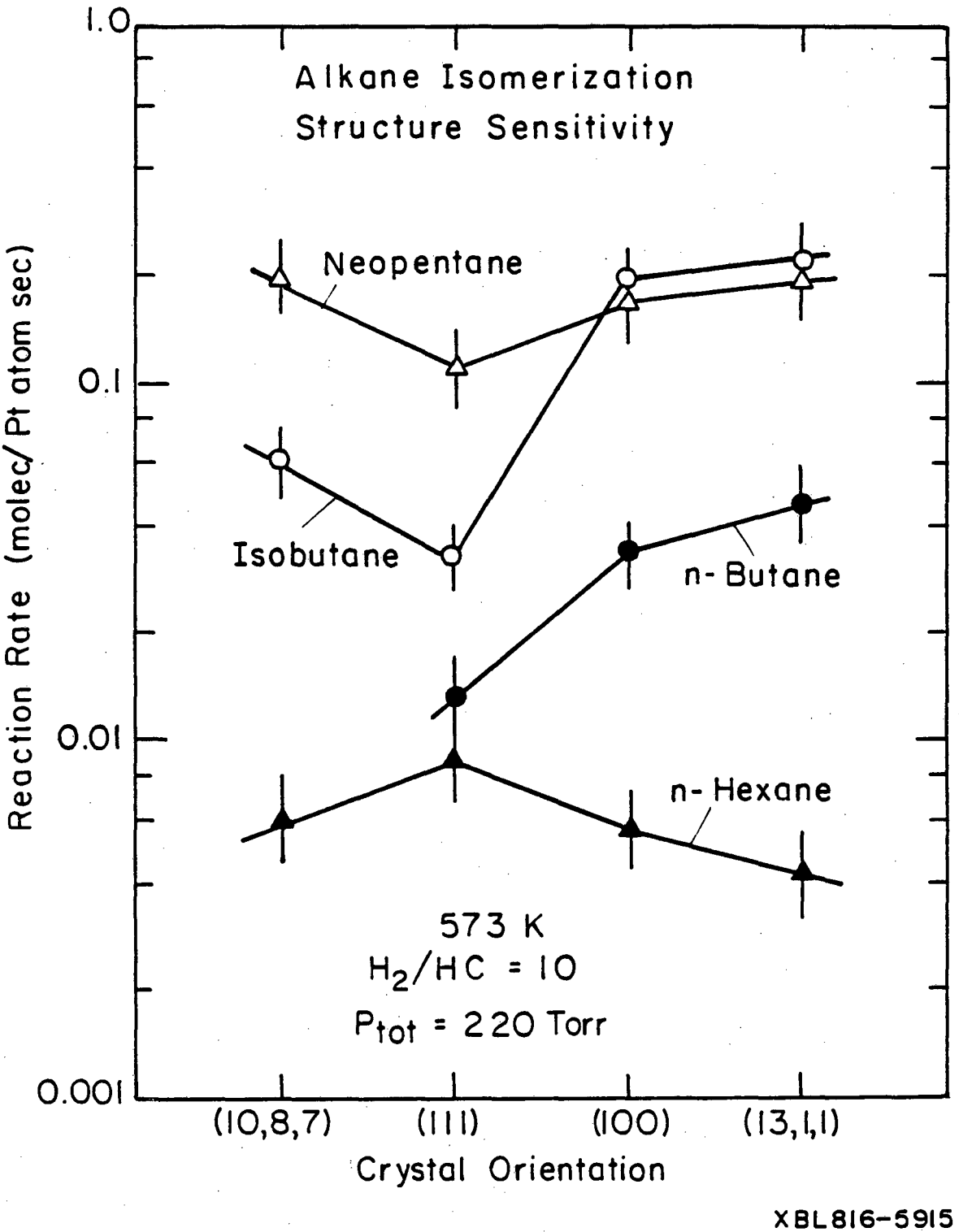

Alkane Isomerization
Structure Sensitivity
Neopentane
Isobutane
n-Butane
n-Hexane
573 K
H_2/HC = 10
P_{tot} = 220 Torr
Reaction Rate (molec/Pt atom sec)
1.0
0.1
0.01
0.001
(10,8,7)
(111)
(100)
(13,1,1)
Crystal Orientation
XBL816-5915

Fig. 24

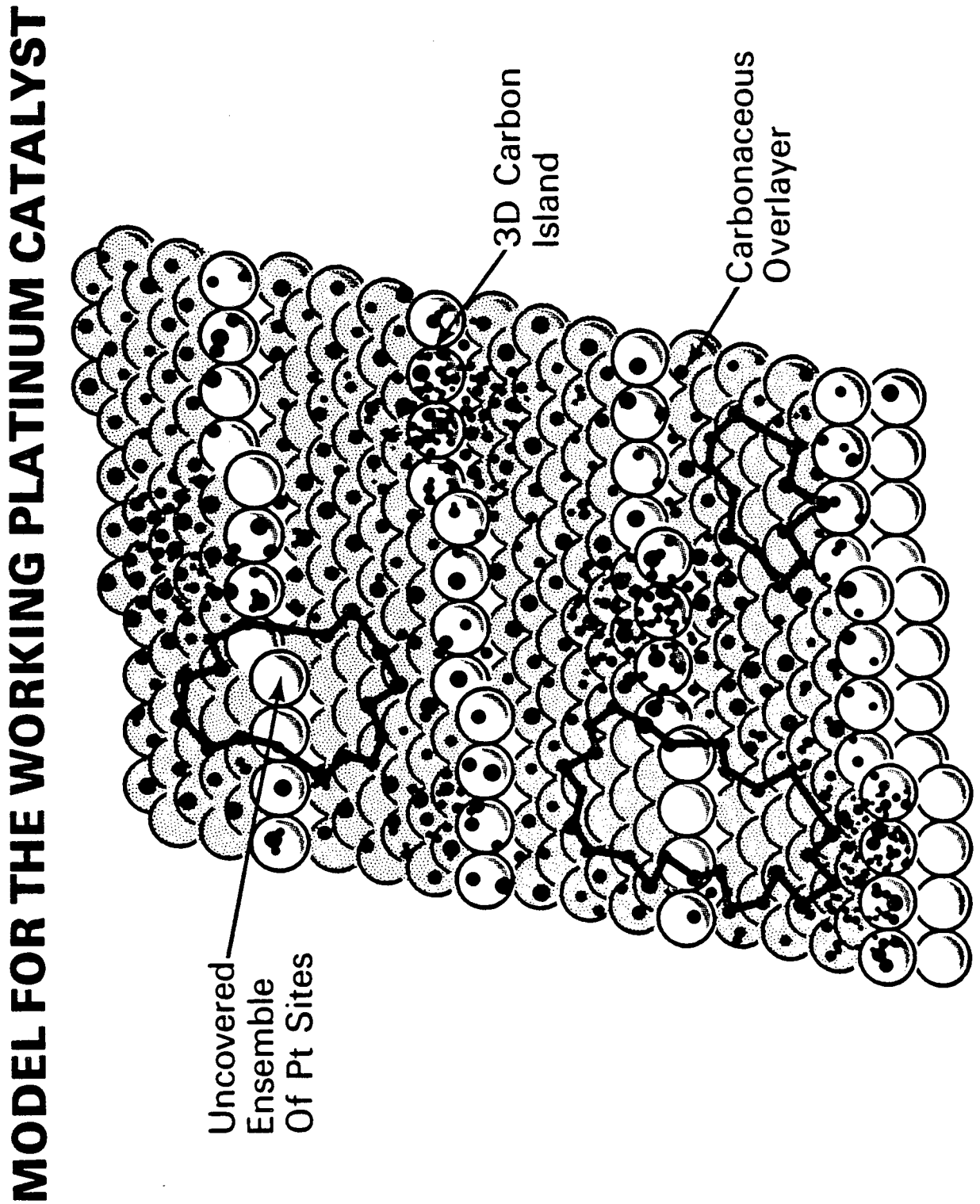

MODEL FOR THE WORKING PLATINUM CATALYST
Uncovered Ensemble Of Pt Sites
3D Carbon Island
Carbonaceous Overlayer

Fig. 25

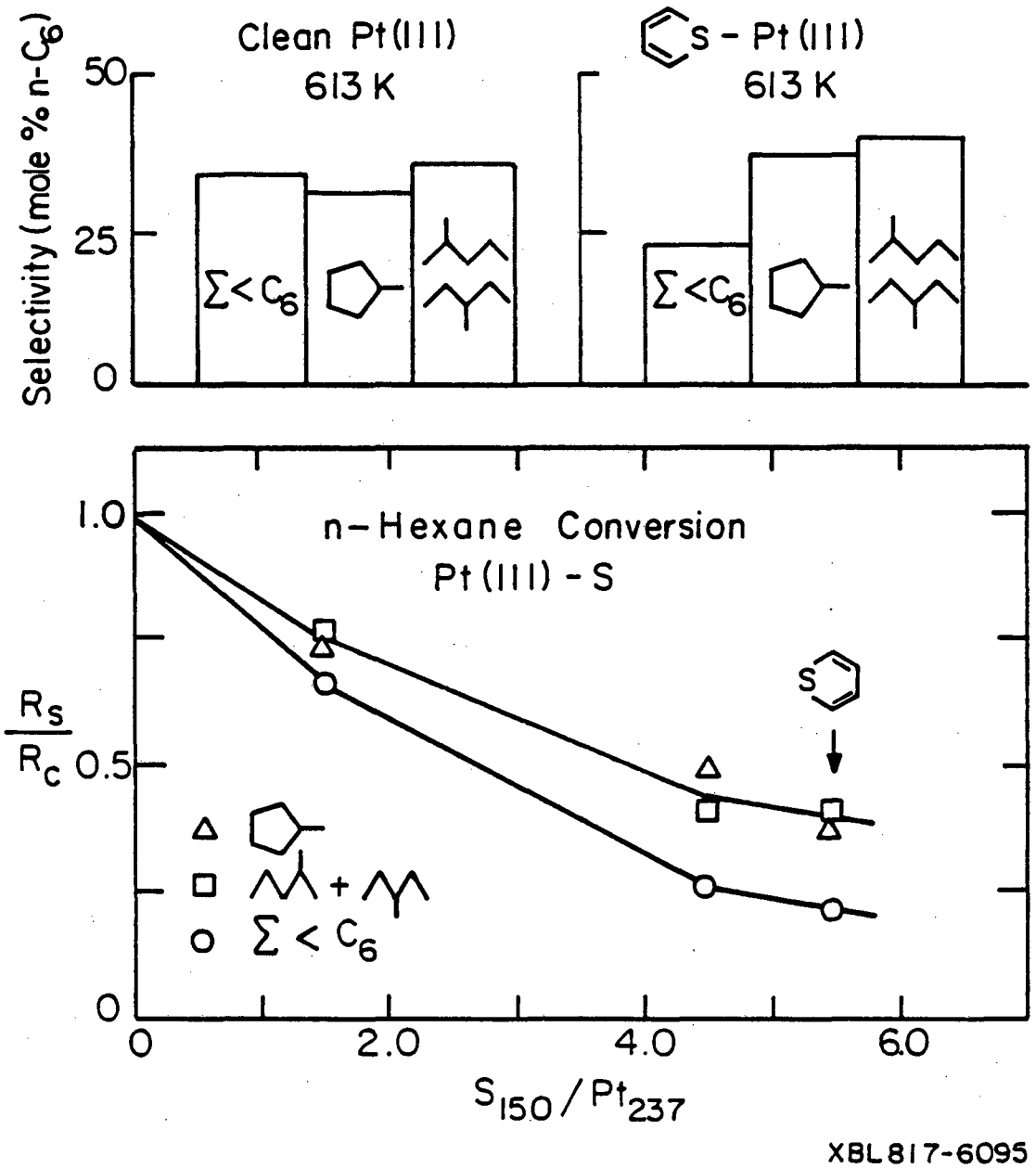

Clean Pt(111)
613 K
S - Pt(111)
613 K
Selectivity (mole % n-C6)
50
25
0
Σ<C6
Σ<C6
n-Hexane Conversion
Pt(111) - S
1.0
0.5
0
Rs/Rc
S
Σ < C6
0
2.0
4.0
6.0
S150 / Pt237
XBL817-6095

Fig. 26

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