TRACER STUDIES IN HETEROGENEOUS CATALYSIS

THESIS

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by

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SUMMARY

The reactions of ethylene, propylene, acetylene and hydrogen over alumina- and silica-supported catalysts from 20°C to 350°C have been investigated using carbon-14 and tritium tracer techniques.

The dissociation of adsorbed hydrocarbon, leading to retention and alkane formation, and hydrocarbon exchange increased with increasing temperature and increasing platinum concentration. With acetylene and, to a lesser extent ethylene and propylene, the extent of these reactions was greater over alumina-supported than over silica-supported catalysts.

The acetylene retention was greatly in excess of mono-layer coverage of the metal surface as determined by carbon-monoxide adsorption and the C_2H_2/Pt ratios were very much greater for an alumina-supported catalyst than for the corresponding silica-supported catalyst.

Tritium, used the reduction, was found to be associated with the support in the form of hydroxyl groups. The presence of platinum was found to enhance the extent of hydrogen exchange with the support and to enhance the formation of OD bands in the infra-red spectrum of the support.

Thermal desorption studies have also emphasised the difference between alumina and silica as catalysts and as supports.

The results have been discussed in terms of activation of the support by the metal and the migration of both hydrogen and hydrocarbon between the metal and the support.

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CHAPTER I

INTRODUCTION.

Section 1.1 A General Introduction.

The surfaces of solids, especially metals and metallic oxides, are important as heterogeneous catalysts for a variety of chemical reactions in which the reactants may be gases or liquids. The empirical use of these catalysts, which has been widespread for many years, has usually been in advance of the theoretical knowledge of processes involved in the reactions.

Modern theories of heterogeneous catalysis are based upon the work of Langmuir[1] who postulated that the intermediates in these reactions were formed by the adsorption of the reactants (adsorbates) onto the surface of the solid (adsorbent).

Section 1.2 Adsorption

Adsorption is usually defined as being either physical or chemical. In physical adsorption, the molecules are held to the surface by dispersion forces. The process is random, non-activated and usually occurs at temperatures near

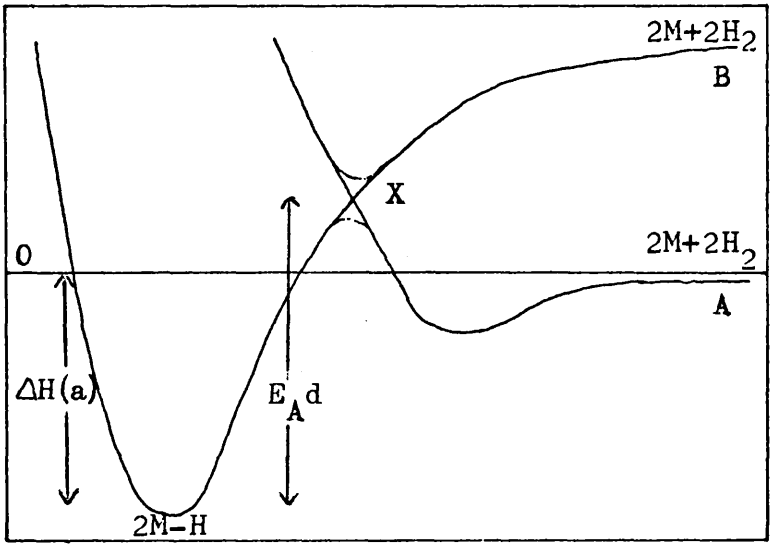


Figure 1.1

the boiling point of the gas. The heat of adsorption is usually less than 6 kcals.mol.$^{-1}$ whereas in the case of chemical adsorption, usually termed chemisorption it is usually greater than 20 kcals.mol.$^{-1}$.

Chemisorption, involving the breaking and reforming of chemical bonds, would be the activating process leading to reaction in heterogeneous catalysts.[2] Since reaction occurs at a particular surface site there will be a limit, monolayer coverage, on the extent of chemisorption depending on the number of surface sites available. In physical adsorption, however, multilayer adsorption is possible.

Adsorption processes can be described by a Lennard-Jones[3] plot which is shown for the case of hydrogen adsorption at a clean metal surface[4] in Figure 1.1. If a physically adsorbed molecule (curve A) can reach X it may transfer to curve B (which refers to the chemisorption of atomic hydrogen) and become chemisorbed.

The extent of adsorption depends very much on temperature. Near the boiling point of the adsorbate both types of adsorbed species may be present. Raising the temperature may either provide the activation energy to convert the physically adsorbed species to a chemisorbed state or to remove them from the surface.

The distinction between physical and chemical adsorption is often not clear. This is particularly true when specific interactions occur between the adsorbate and surface atoms or groups although no chemical bonds are formed. The most common example is hydrogen bonding which may occur between adsorbates containing lone pairs of electrons and surface hydroxyl groups. For chemisorption both covalent and ionic bonding have been recognised.[5]

The strength of the surface bond and hence the heat of adsorption depends both on the nature of the adsorbate and the adsorbent as well as on the degree of surface coverage.

Section 1.3 Surface Heterogeneity, Geometric and Electronic Factors.

In general, the heat of adsorption decreases quite markedly[6] with increasing surface coverage (θ). The merits of various concepts evolved to explain this phenomenon have been discussed by Tompkins.[5] No theory alone appears sufficient to provide an explanation, although the one based on the heterogeneity of the surface[6] itself due to point imperfections, dislocations, impurities etc., seems to be the most satisfactory. It has been shown that different crystal faces[7,8,9] differ in their catalytic activity and thus the heat of adsorption probably also varies.

Attempts have been made to correlate the catalytic activity of transition metals with parameters derived from their bulk properties. The importance of both surface geometry and the electronic properties of the catalyst in relation to its catalytic activity have been widely studied and discussed.[10,11]

Balandin,[12] in his multiplet theory of catalysis, stressed the importance of both the lattice spacing and the arrangement of the atoms at the exposed faces. From his work on the hydrogenation of six-membered rings, he claimed that only crystal faces showing hexagonal symmetry and having spacings within certain limits would be active in these reactions. Later work, however, has tended both to substantiate[13] and to cast doubt[14] upon the validity of this hypothesis.

Using evaporated films of transition metals as catalysts, the rate of hydrogenation of ethylene when plotted as a function of the metal lattice spacing yields a smooth curve.[15] This suggests that the metal lattice spacing may be a parameter in determining catalytic activity. If, however, the same measurements are plotted against the percentage d-character of the metallic bond a similar curve[15] is obtained. Since, as Pauling has emphasised,[16] the d-character controls the lattice spacing, this fact is not surprising.

It has been found that the differences in activity between different faces of one catalyst can be greater than the differences in activity between two catalysts with appreciably different d-character.[7] Both factors, though perhaps necessary, appear to be insufficient to explain metal catalysis although direct correlations between d-character and catalytic activity are still being sought.[17,18]

Sachtler[19] has proposed that regularities observed in catalysis should be related to the properties of metallic compounds rather than directly to basic electronic properties of the metal. This approach has proved profitable in certain cases such as the decomposition of formic acid over transition metals.[20]

Section 1.4 The Form of The Catalyst.

Catalytic processes, such as oxidation and hydrogenation, play an ever increasing role in the chemical and allied industries. Most of the metals of Groups VIII and IB have some use as catalysts since at this point in the periodic table the optimum conditions allowing adsorption of at least one of the reactants in a catalytically active form are to be found.

Most of the fundamental work on catalysis by metals, such as described above, has been carried out using metal films which afford the cleanest surfaces. The importance of which has been emphasised by Gwathmey,[7] who stated that further progress depended on the best definition of the surface being studied. Two main disadvantages are the instability of metal films towards sintering and their inherent reactivity, leading to irreversible adsorption.

Metal films are, however, very different from the industrial forms of catalyst which may consist of metals supported on a substance which is supposedly inert or, as in the case of bifunctional catalysts, may play as important a role as the metal itself in the overall reaction. Additional substances may be added to promote activity, for example K_2O is added to an iron catalyst for the synthesis of ammonia.

Supported metals have certain definite advantages over other forms of metals such as films, wires or powders. The use of a support leads to a high dispersion of the metal in the form of small crystallites. As a result, the metal has a high surface area and is more resistant to sintering at high temperatures. Furthermore, Schuit and Van Reijan have shown[21] that the broad patterns of activity of silica-supported metals are similar to those observed for evaporated metal films, at least for ethylene hydrogenation. This suggests that the results obtained using films may be applied, with some caution to supported metal systems.

Unfortunately, supported catalysts show different activities and kinetics,and appear very irreproducible,since one has brought many more variables into an already complex situation. Restraints on the number of uncertainties are important, for example, it is customary to employ the method devised by Brunauer, Emmett and Teller[22] to give a measure of the specific surface area (metres ^{2}/gm.) of the catalyst in terms of a particular adsorbate. Although this may give an idea of the difference between catalysts, owing to the complexity of the surface structure and the possibility that the catalytic activity is limited to certain regions of the surface, the inferences drawn from the B.E.T. areas have to be used with caution.

The immense practical importance of supported metals combined with the ever increasing availability of new techniques provide an incentive for the investigation of their properties.

A number of complexes of the metals of Groups VIII and IB can act as homogeneous catalysts for a variety of similar reactions to those in which heterogeneous catalysts are used. For example, tris(triphenylphosphine)rhodium chloride[23] is active under mild conditions and is highly specific for the hydrogenation of unsaturated hydrocarbons.

Homogeneous catalysts have the advantage of greater efficiency since every metal atom is available to react and also of greater specificity. The chief disadvantage, however, is the problem of removal of the catalyst at the end of the reaction.

Although much doubt still exists as to many of the mechanisms involved in homogeneous catalysis, the more accessible mechanisms may suggest new ideas in the heterogeneous field.

Section 1.5 Physical Methods

Physical methods employed in catalysis may either be direct, in which studies are made of the catalyst surface during reaction, or indirect, for example, the examination of the products of a particular reaction.

Perhaps one of the most rewarding of the direct techniques has been the application of infrared spectroscopy[24] to adsorption studies. This has expanded considerably since it was first developed by Eischens and Pliskin.[25,26] As well as determining the nature of adsorbed species, deductions about their reactivity may also be drawn. An unequivocal assignment as to the type of adsorption may usually be made. There is, however, no assurance that any species seen by this method are those active in catalysis. Ultraviolet and visible spectroscopy[27] have been applied in a similar manner to infra-red spectroscopy.

Changes in the nuclear magnetic resonance,[28,29] electron spin resonance,[30] magnetic susceptibility,[31] work function,[32] and conductivity of solids[33] have all been measured in an attempt to explain various aspects of the subject. In many of these techniques, however, the physical conditions and physical form have to be carefully chosen in order to obtain satisfactory results.

Radiotracer techniques, developed by Thomson and co-workers,[34,35,36] provide a valuable method of looking directly at the surfaces of either metal films or supported metals during adsorption. The technique has been particularly useful in the study of the reactivity of the adsorbed species under varying conditions. A notable achievement has been to illustrate that only a small fraction of the adsorbed species are reactive in catalytic processes and that poisoning, although apparently complete, may only be affecting part of the surface. It is thus obvious that attempts to relate heats of adsorption, conduction, surface potentials and other concepts to catalysis can only be valid if they apply to the catalytically active fraction of the adsorbed species.

Due perhaps to the practical difficulties associated with many direct methods, many of the important advances in the understanding of catalytic processes have come from the use of indirect techniques. For example, the use of deuterium as an isotropic tracer has provided the most valuable information regarding the mechanism of hydrogen exchange and hydrogenation reactions.[37] Radiotracers, such as carbon-14 and tritium, have also been used in this capacity. Emmett by the use of C-14 carbon monoxide determined the mechanism of the Fischer-Tropsch synthesis of hydrocarbons.[38]

It is, however, profitable to employ many techniques in the study of a particular aspect of catalysis. For example, an understanding of the mechanisms involved in the catalytic reactions of unsaturated hydrocarbons has come in part from kinetic studies and related deuterium tracer work and partly from the study of adsorbed species, particularly by by infra-red spectroscopy.

Section 1.6 Reactions of Unsaturated Hydrocarbons

As well as being very important commercial processes, for example, the hardening of fats and the production of fine chemicals in the drug industry, the reactions of unsaturated hydrocarbons are among the most intensively investigated catalytic reactions. The compounds studied include olefins, particularly ethylene, diolefins, alkynes and aromatic and alicyclic compounds.

Much controversy concerning the mechanisms of these reactions still exists and there is thus much research still to be done in this field before an unequivocal understanding of mechanisms is achieved. It is generally agreed, however, that when an unsaturated hydrocarbon interacts with a metal surface one or more of the following processes may occur.

(1) Hydrogenation of the double or triple bond.

(2) The exchange of a hydrogen atom in the hydrocarbon with another hydrogen of the system.

(3) Double-bond migration or cis-trans isomerism.

(4) Polymerisation or cracking.

The existence and proportion of a particular reaction will depend upon many factors, including the nature and pressure of hydrocarbons, the presence or absence of hydrogen and the pressure of hydrogen. The nature of the catalyst and its history prior to reaction are also very important.

A characteristic of many catalytic reactions are the complex rate laws which apply to them. Many have been explained quite successfully by the Langmuir-Hinshelwood mechanism[39] which postulates that the rate is controlled by the reaction of adsorbed molecules. All adsorption-desorption processes were assumed to be in equilibrium. The rate is thus proportional to the surface coverage which is described by the Langmuir adsorption isotherm θ[40], for one reactant and θ_1, for a reaction in which two reactants compete for the same surface sites:

$$\theta = \frac{bp}{1+bp} \quad , \quad \theta_1 = \frac{b_1p_1}{1+b_1p_1+b_2p_2}$$

where p denotes the reactant pressure and b is a constant termed the adsorption coefficient. For the reaction $A + B \rightarrow C$ the rate is given by

$$\text{Rate} = \frac{dc}{dt} = K\theta_A\theta_B = \frac{Kb_Ab_Bp_Ap_B}{(1+b_Ap_A+b_Bp_B)^2}$$

A mechanism for hydrogen reactions in which reaction occurred upon desorption was proposed by Bonhoeffer and Farkas.[39] It has been shown, however, that the desorption of hydrogen is slow below 400°C.

Both mechanisms require a high desorption rate to account for the high reaction rates observed at low temperatures. These considerations led Rideal[42] to envisage that reaction occurs between a chemisorbed species and molecules which are weakly adsorbed. The kinetics, however, do not distinguish between the mechanisms.

Section 1.7 The Reaction of Ethylene

The reactions of ethylene, particularly hydrogenation over metal catalysts, have been extensively studied for many years and are often chosen as test reactions to characterise the catalytic activity of a system. Many of these considerations also apply for other hydrocarbon reactions. Despite the extent of these studies, no theory has yet been advanced to account fully for all facets of the reactions. Several features of the reaction have been well defined for nickel catalysts[43] which have been most extensively studied, especially up to 150°C. The hydrogenation reaction

$$C_2H_4 + H_2 \longrightarrow C_2H_6$$

is closely related to the exchange reaction

$$C_2H_4 + D_2 \longrightarrow C_2H_3D + HD$$

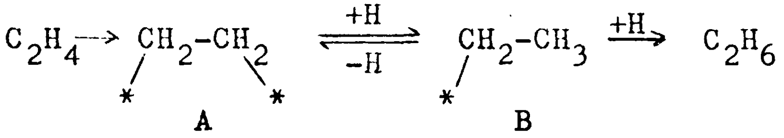
since both reactions follow similar kinetics.

$$\text{Rate} = Kp_{H_2}^{1}\, p_{C_2H_4}^{0}$$

The importance of both hydrogen exchange and ethylene exchange, which have higher activation energies than the hydrogenation reaction, is minimal at -78°C and increases with increasing temperature. With other metals, however, different reaction characteristics have been observed, for example, the order in ethylene is negative over platinum.[37] The heat of adsorption of ethylene is always greater than the heat of adsorption of ethane and hydrogen on any metal.

Mechanisms tend to be based on either dissociative or associative adsorption.

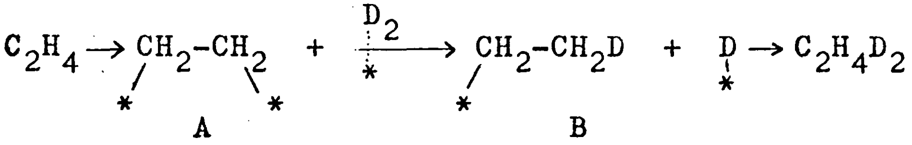
In 1934 Horiuti and Polanyi[44] proposed that, for nickel and platinum ethylene adsorbed by opening of the double bond to give an associatively diadsorbed species A in which (*) denoted a surface atom. Reaction of A with an adsorbed hydrogen atom gave an ethyl radical B (the half-hydrogenated state) which could either add hydrogen and desorb as ethane or alternatively lose a hydrogen atom to give ethylene exchange. This scheme, however, led to a different order for exchange and hydrogenation



$$C_2H_4 \rightarrow \underset{A}{\underset{*\qquad *}{CH_2-CH_2}} \underset{-H}{\overset{+H}{\rightleftharpoons}} \underset{B}{\underset{*}{CH_2-CH_3}} \xrightarrow{+H} C_2H_6$$

Support for the associative mechanism came from the observation that no isotopic mixing occurred when ethylene and deutero-ethylene[45] were exposed to a nickel surface.

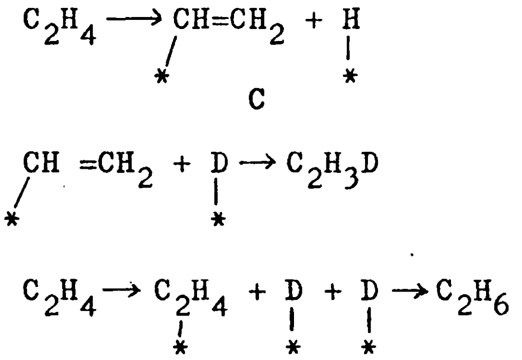
Deficiencies in the above mechanism led Twigg and Rideal[46] to propose that the rate determining step in both reactions was the reaction of chemisorbed ethylene with physically adsorbed hydrogen to give an ethyl radical



$$C_2H_4 \rightarrow \underset{A}{\underset{*\qquad *}{CH_2-CH_2}} + \underset{*}{\overset{D_2}{\longrightarrow}} \underset{B}{\underset{*}{CH_2-CH_2D}} + \underset{*}{D} \rightarrow C_2H_4D_2$$

A facile equilibrium between states A and B was proposed to account for the redistribution of all hydrogen in the system. The existence of such a reaction has been invoked by Kemball[47] to explain ethane exchange. In later work, Twigg[48] showed that the hydrogen must be dissociated before hydrogenation occurs since he found the same deuterium content in product ethane from both an equimolar and an equilibrium mixture of hydrogen and deuterium. The presence of adsorbed ethylene was found[49] to inhibit the equilibration of hydrogen, making the possibility of rapid equilibration before reaction with ethylene unlikely.

At least some dissociative adsorption of ethylene must occur, since the admission of ethylene[15] or of a mixture of ethylene and deuterium[50] results in the immediate formation of gas phase ethane. Farkas[51,52] suggested that the first step for ethylene exchange over platinum and nickel was the loss of a hydrogen atom from ethylene to give C. Hydrogenation was assumed to be independent of exchange, in contrast to the observed kinetic data, and to proceed through the simultaneous addition of a pair of hydrogen atoms.



$$C_2H_4 \longrightarrow \underset{*}{\underset{/}{CH}}=CH_2 + \underset{*}{\underset{|}{H}}$$

C

Exchange

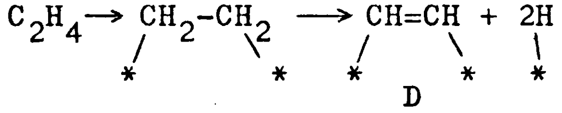
$$\underset{*}{\underset{/}{CH}} =CH_2 + \underset{*}{\underset{|}{D}} \rightarrow C_2H_3D$$

$$C_2H_4 \rightarrow \underset{*}{\underset{|}{C_2H_4}} + \underset{*}{\underset{|}{D}} + \underset{*}{\underset{|}{D}} \rightarrow C_2H_6$$

Hydrogenation

The exchange of saturated hydrocarbons must proceed through a dissociative mechanism. Since, however, the rate is much less than that of the corresponding unsaturated hydrocarbon an associative mechanism seems more probable for unsaturated hydrocarbons. The more sensitive mass spectrometric technique (compared to infra-red used previously) enabled Douglas and Rabinovitch[53] to observe hydrogen exchange between ethylene and deutero-ethylene over supported nickel and over nickel wire thus refuting a major argument against the dissociative mechanism.

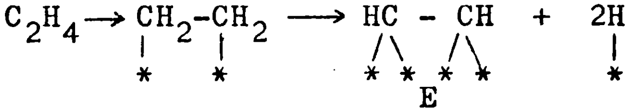
Beeck, from his studies of ethylene hydrogenation on metal films,[9,54] has demonstrated the feasibility of dissociative adsorption and helped to reconcile it with an associative mechanism. He assumed that the adsorption of ethylene would be associative except in the initial stages of adsorption when dissociative adsorption may occur if four adjacent sites are available



$$C_2H_4 \longrightarrow \underset{*}{\overset{}{\underset{/}{CH_2}}}-\underset{*}{\underset{\backslash}{CH_2}} \longrightarrow \underset{D}{\underset{*}{\underset{/}{CH}}=\underset{*}{\underset{\backslash}{CH}}} + \underset{*}{\underset{|}{2H}}$$

The process would account for the instantaneous production of ethane, the irreversible adsorption of ethylene and the inhibiting effect of preadsorbed ethylene on the hydrogenation reaction. The kinetics were also explained by Beeck. Further loss of hydrogen and the combination of the residues to yield polymeric species may occur. Hydrogen removed 20% of the residues to give 10% ethane and 90% saturated C_4-hydrocarbon or higher polymers.

Jenkins and Rideal[55] demonstrated that 80% of the available sites on a nickel film were covered with acetylenic residues with composition $(C_1H_1)_n$. They envisaged that half of the remaining sites could adsorb hydrogen while the rate of reaction was controlled by the diffusion of hydrogen atoms to the remaining sites, where reaction with ethylene may occur. Support for the existence of at least two types of site was found by Selwood[56] from his magnetic studies of ethylene adsorption on nickel-silica catalysts at room temperature. The first were accessible to ethylene and hydrogen. While the second were only accessible to hydrogen. His results were consistent with the slow dissociation of an initially associatively adsorbed species



$$C_2H_4 \rightarrow \underset{*}{\underset{|}{CH_2}}-\underset{*}{\underset{|}{CH_2}} \longrightarrow \underset{E}{\underset{*\;*\;*\;*}{HC - CH}} + \underset{*}{\underset{|}{2H}}$$

Section 1.8 The Adsorbed State of Ethylene

The infra-red spectra of ethylene and other hydrocarbons adsorbed on metals and metallic oxides[24] have been studied in order to determine the nature of the adsorbed species.

Spectra of ethylene on nickel-silica catalysts were thought by Eischens and Pliskin[26] to represent saturated C_2-species attached to nickel. They also noticed weak olefinic absorption and some polymerisation. In the absence of hydrogen the spectra were characteristic of a dissociatively adsorbed species probably of variable composition although on a catalyst covered with hydrogen associative adsorption to give A was inferred. This contradicted the conclusions of Jenkins and Rideal[55]. On addition of hydrogen all the adsorbed species were rapidly and reversibly hydrogenated to give a species corresponding to the half-hydrogenationed state proposed by Polanyi[44]. The rapid equilibrium proposed by Twigg[48] is also substantiated by this work. However, no explanation was advanced to explain the role of adsorbed hydrogen nor why no ethane was produced. The fact that the observed species were not easily removed suggests that they are not intermediates in the hydrogenation reaction.

Little[24] has criticised the fact that olefinic species were not given greater consideration. On 'bare' palladium-silica catalysts evidence has been found for D which gave A and B upon treatment with hydrogen.[57]
Although both Pickering and Eckstrom[58] from their infra-red studies and McKee[59] from his volumetric work could only find evidence of C_2-species for ethylene adsorbed on nickel the later work of Peri[60] suggests that on nickel-silica ethylene dimerises to give butene. This is readily hydrogenated to butane. Recently Sheppard[61] also observed the formation of C_4-species on nickel-silica and platinum-silica catalysts and proposed that the surface retention is caused by the occurrence

of dimerisation rather than simply by dissociative adsorption. Like many workers,[60,62] however, they[63] could find no difference between 'bare' and hydrogen covered nickel. It was suggested that the cause of this disparity in observations by different workers lay in different forms of catalyst giving different results.

Radiochemical studies[35] using alumina-supported metal catalysts indicate at least two modes for ethylene adsorption at room temperature. One type, probably associatively adsorbed, is involved in hydrogenation and molecular exchange whereas the other is an inert retained form. Similar studies[64] using evaporated nickel films showed ethylene to be irreversibly adsorbed.

The above studies were at room temperature. Several workers, however, have emphasised the importance of temperature upon the mode of adsorption. Selwood[65] found that, although associative adsorption was dominant at 0°C, dissociative adsorption and self hydrogenation became more important with increasing temperature and at 130°C a surface carbide was produced. McKee[59] observed effects which could be explained in a similar manner. These results explain the observations of Schissler[49] et al who found that ethylene adsorbed below room temperature has a lower poisoning effect on hydrogen-deuterium exchange than ethylene adsorbed at higher temperatures.

From the infra-red spectra of ethylene adsorbed on nickel-silica and platinum-silica catalysts over the range -78°C to 150°C Morrow and Sheppard[61] deduced that the same chemisorbed species occur on both metals but over different temperature ranges.

On platinum-silica the dominant spectral features were assigned to A with a small contribution from D. Evidence was found for the formation of E at -145°C and the occurrence of self hydrogenation above 95°C. The observed high increase in intensity of absorption on hydrogenation, however, implied that the principle mode of adsorption was dissociative to form surface carbide species.

Only at -78°C were similar spectra observed for both catalysts, although with nickel-silica the spectra changed with time and a marked variation with temperature was found. The change with time was interpreted as being due to the formation of surface n-butyl groups followed by further adsorption of ethylene on the sites made available by the dimerisation process. At 150°C, rapid dissociation to a surface carbide was thought to occur.

It is interesting to note that they found a close correspondence between the nature of the gas phase products after hydrogenation and that of the surface species. For example, production of butane was accompanied by the appearance of butyl groups on the surface. With nickel-silica, ethane was the major product only at the lowest temperatures whilst at room temperature butane formation was dominant and at 150°C methane was observed. No butane was produced below 95°C with platinum-silica although the relative proportion of butane in the products increased with increasing temperature. Greater dissociation, yet lower retention, occurs on platinum than on nickel. Similar results were found for but-1-ene[61] and also, in part for acetylene.[66]

Further work by Morrow[67] demonstrated the improbability that on platinum-silica, the butyl groups were formed by the breakdown of randomly formed high polymers. No redistribution of carbon-13 was observed during the reation of hydrogen with preadsorbed 1-carbon-13 ethylene to give ethane. This work together with thermal desorption[68] studies support the view that on platinum the retained species was in the form of C_2 units. On nickel, however, the work of Peri[60] and Sheppard[61] suggest that the retained species are C_4 units.

In these studies silica itself appeared inert so that any processes were assumed to be occurring on the metal. In the case of porous glass supports, however, the slight acidity was thought to have some bearing on the results and perhaps influence the effect of the metal.

Section 1.9 The Role of the Support.

Bond,[69] however, concluded that the support may provide some chemical action although he did not draw any conclusions as to the nature of the action.

He made an intensive investigation of the reaction of ethylene over different types of platinum catalysts to study the effect of the form of the catalyst in relation to the inherent metal activity. Both hydrogen exchange and olefin exchange appeared to be independent of temperature with platinum-alumina and platinum foil and to increase with temperature on platinum-silica. On platinum-silica-alumina and platinum-pumice, olefin exchange decreased, whereas the extent of hydrogen exchange increased with temperature. He postulated that although the same mechanism was operative for all the catalysts the relative rate constants were dependent upon the form of the catalyst.

If the support does provide chemical action, differences in the behaviour of the catalysts are not unexpected in view of the varying structure and behaviour of silica, alumina and silica-alumina. Silica, although supposedly neutral may exhibit slight acitity.[70] Silica-alumina is supposed to have the same structure as silica except that there has been an isomorphous replacement of some silicon atoms by aluminium atoms leading to the production of either Brönsted or Lewis acid sites such as are found on alumina.

Sinfelt and Yates demonstrated the importance of support effects for the reactions of various hydrocarbons over supported metals and over the supports themselves. At room temperature silica was inert for the adsorption of ethylene whereas on alumina a slow adsorption was observed.[72] Different aluminas, however, gave different results and appeared to give similar infra-red spectra of adsorbed ethylene to those observed with metals. Species corresponding to A and B were observed; the relative amounts were dependent upon the type of alumina which was used. Since no incorporation of deuterium was observed using a fully deuterated catalyst these workers suggested that the ethyl groups were formed by self-hydrogenation.

Acetylene,[73] however, adsorbed onto a silica surface although weakly, and exchanged with both deuterated alumina and silica. Preadsorbed acetylene[74] did not affect ethylene self-hydrogenation and preadsorbed ethylene did not inhibit the interaction of acetylene with surface hydroxyl groups. Thus the acetylene adsorption sites and the ethylene adsorption sites seemed to be mutually independent.

The lack of interaction with hydroxyl groups appears to be a property of ethylene since Hall[75] also found no exchange between ethylene and an exhaustively deuterated zeolite. Although the adsorption of propylene was similar to that of ethylene, it exchanges readily with deuterated hydroxyl groups.

Several studies[76] have demonstrated that the chemisorption of olefins readily occurs on silica-aluminas far below the temperatures at which cracking occurs.

Since similar spectra were found for the adsorption of ethylene on 0·6% Pt/Al_2O_3 and alumina[77] it was suggested that the observed species were adsorbed on the alumina in both cases. The chemical reactivity of the adsorbed species towards hydrogen, however, was very different both for the removal of adsorbed species and the nature of the products. The presence of metal favoured the production of ethane and n-butane over that of methane and propane. It is possible, however, that the species observed are not the catalytically active intermediates since studies of ethylene hydrogenation in a flow reactor[78] have shown that only a small fraction of the surface actually participated in catalysis.

Furthermore, these reactions over a mixture of platinum-silica and alumina gave a significantly higher rate per unit amount of platinum implying, according to Sinfelt,[77] the presence of a co-operative action of separate centres on the two catalysts when compared to the rates over a mixture of platinum-silica and silica. It was suggested that platinum centres activate certain species for further reaction and subsequent desorption and that the reactive species migrate between platinum and alumina centres. No detail as to the mechanism of migration or of the nature of the species were given. The migration of adsorbed hydrogenic species was preferred although the migration of adsorbed hydrocarbon species was also thought to be possible.

It has been postulated that certain reactions over bifunctional catalysts, for example, the isomerisation of hexane and pentane involve the migration of stable intermediates between metal and acidic centres.[79-82] The results are interpreted in terms of olefin intermediates which are present in the gas phase in equilibrium concentrations and which undergo isomerisation on the acidic function by a carbonium ion mechanism.

Although these mechanisms provide a good explanation of bifunctional catalysis they may not be the only possible mechanisms, nor sufficient to explain all the observed facts. For example, certain rapid increases in activity have been observed at critical metal concentrations.[83]

Isomerisation is thought to occur on the acid. However, Anderson and Baker[84] have shown that the isomerisation of saturated hydrocarbons may occur on metal films and Barron et al[85] found that the isomerisation of hexane was similar on both supported platinum and platinum films. It thus appears that the metal may not act simply as a hydrogenating and dehydrogenating agent.

There is much evidence to indicate that there is interaction between the metal and the support. Thus, for example, changing the support from silica to alumina has been shown to give rise to differences in the infra-red spectrum of carbon monoxide adsorbed on platinum[26] and to change the strength and nature of adsorption on nickel.[86] Hirota and Ueda[87] found that when p-xylene and heavy water were reacted over alumina-supported nickel catalysts, both ring and methyl hydrogen atoms underwent exchange. However, when kieselguhr or silica were used as supports only the methyl hydrogen atoms were exchangeable. Different activities for the reaction of p-xylene with deuterium over platinum were observed[88] when the support was changed from γ-alumina to α-alumina or to silica.

It has been stated that alumina, when used as a metal catalyst support, assists the isomerisation of butenes over Group VIII metals in the absence of hydrogen.[89] A correlation appeared to exist between the activity of the support for deuterium-exchange and the isomerisation activity of the supported catalyst.

Other types of interactions between metals and supports have been defined.

When an interface exists between the metal and the support the metal properties may be altered by contact with an insulating or semiconducting support. The reverse effect may also occur and a specific influence on the catalytic activity is indicated.[90]

The support may act as a source of contaminants or it may regulate the particle size and orientation of the metal crystallites. Schuit and Van Reijan[21] concluded that when supported and unsupported metal catalysts were compared per unit area of metal surface their catalytic activities were similar. They stressed the importance of determining the metal surface areas before making comparisons between the activity of different catalysts.

The importance of the effect of particle size has been recently reviewed.[91] There appears to be a critical change in activity at a particular crystallite size ~50 Å. However, no apparent crystallite size effect has been found for ethylene hydrogenation over platinum-silica catalysts. Boudart[92] suggests that certain facile reactions may be insensitive to the precise nature of the catalyst, whereas other less facile reactions may be very sensitive to surface details.

CHAPTER 2

THE AIMS OF THE PRESENT WORK

Although the hydrogenation of ethylene is one of the most extensively studied of all metal-catalysed reactions, it is probably still one of the least well understood catalytic reactions. This deficiency in understanding arises, in part, from a lack of correlation between results obtained from adsorption studies and those obtained from catalytic reaction studies. There are several reasons which might account for this; first, since adsorption studies are not usually carried out under conditions similar to those used for reaction studies, they cannot directly be related. Second, it is now apparent that the physical nature of the catalyst is of critical importance in determining the reaction characteristics, although much of the earlier work has paid no attention to this factor. Third, recent work has shown that the reaction temperature is of importance in determining the type of adsorption and hence the nature of the reaction.

The object of the work described in this thesis was to investigate the interaction of unsaturated hydrocarbons with supported metal catalysts, with a view to (a) simultaneously determining the reactions and retention of these hydrocarbons on the catalyst, and (b) determining the nature and reactivity of the retained hydrocarbon in the temperature range 20° - 350°C. From these studies it was hoped to obtain correlations between the adsorption characteristics of the hydrocarbon and its catalytic reactivity in hydrogenation under comparable conditions. A further aim of this work was to study the role of the support in the reactions of ethylene over alumina- and silica-supported metal catalyst, in particular to establish the nature and reactivity of hydrogen retained by the catalyst.

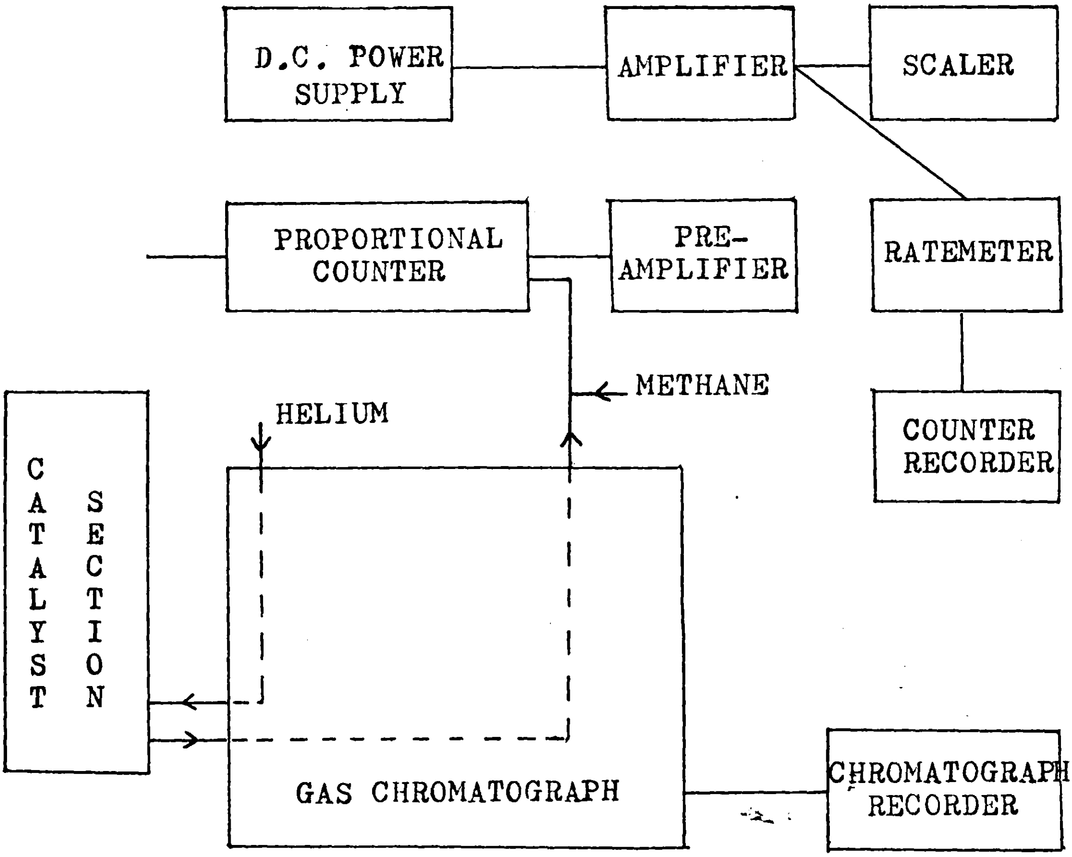


Figure 3.1 Diagram of the Flow System

EXPERIMENTAL

CHAPTER 3.

Section 3.1 The Flow System.

In the present work a flow system (Fig. 3.1) similar to the design of Kokes, Tobin and Emmett[93] was used. It comprised of a microcatalytic reactor coupled to a chromatograph and a proportional counter.

The catalyst vessel (Fig. 3.2) was made of 'Pyrex' glass with a copper to glass seal at each end connecting it to the otherwise metal flow system. It had been found that a pipette shape kept the dead volume of the vessel to a minimum, while allowing the required quantities of catalyst to be used without the catalyst bed acting as a chromatographic column. This effect was especially important in the case of the low density silica-supported catalysts. The packing of the silica wool plug was found to be critical. If it was too tightly packed, the flow of the helium carrier gas was obstructed and if too loose, fine particles of catalyst could be carried through it by the helium stream. A glass sinter was not successful as the fine catalyst particles became embedded in it when the helium flow stream was switched over the catalyst bed. The use of a bed of small glass beads ($\sim$ 1·5 mm. diameter) over the silica

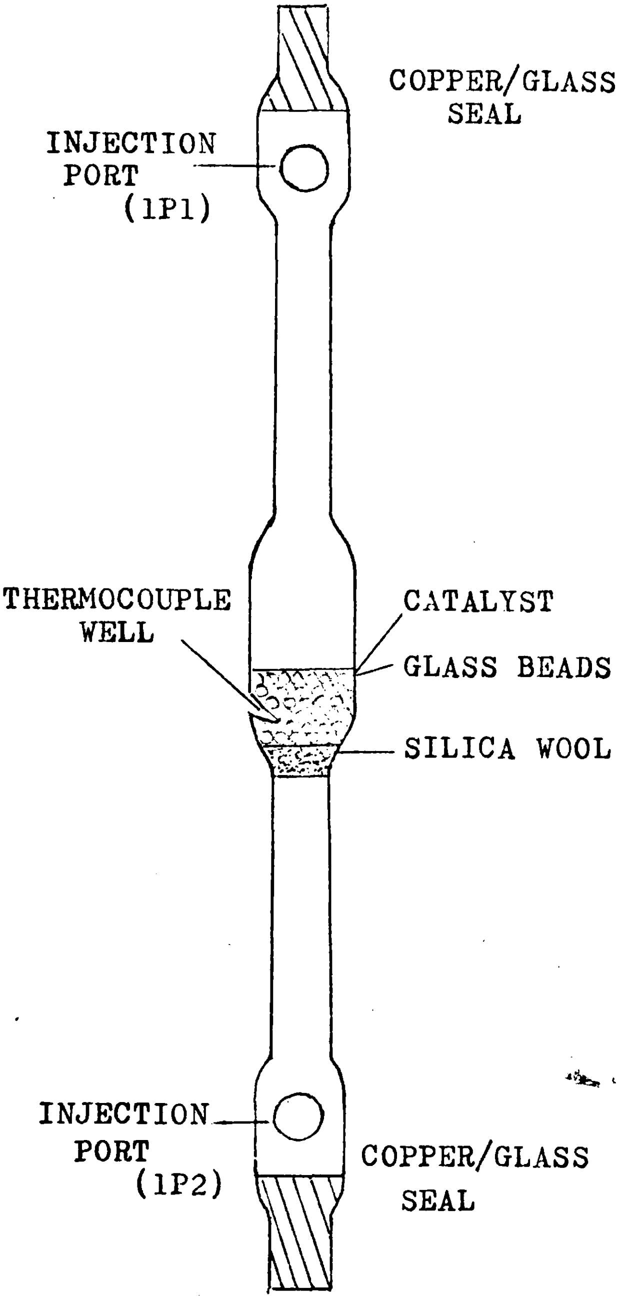


Figure 3.2 The Catalyst Vessel

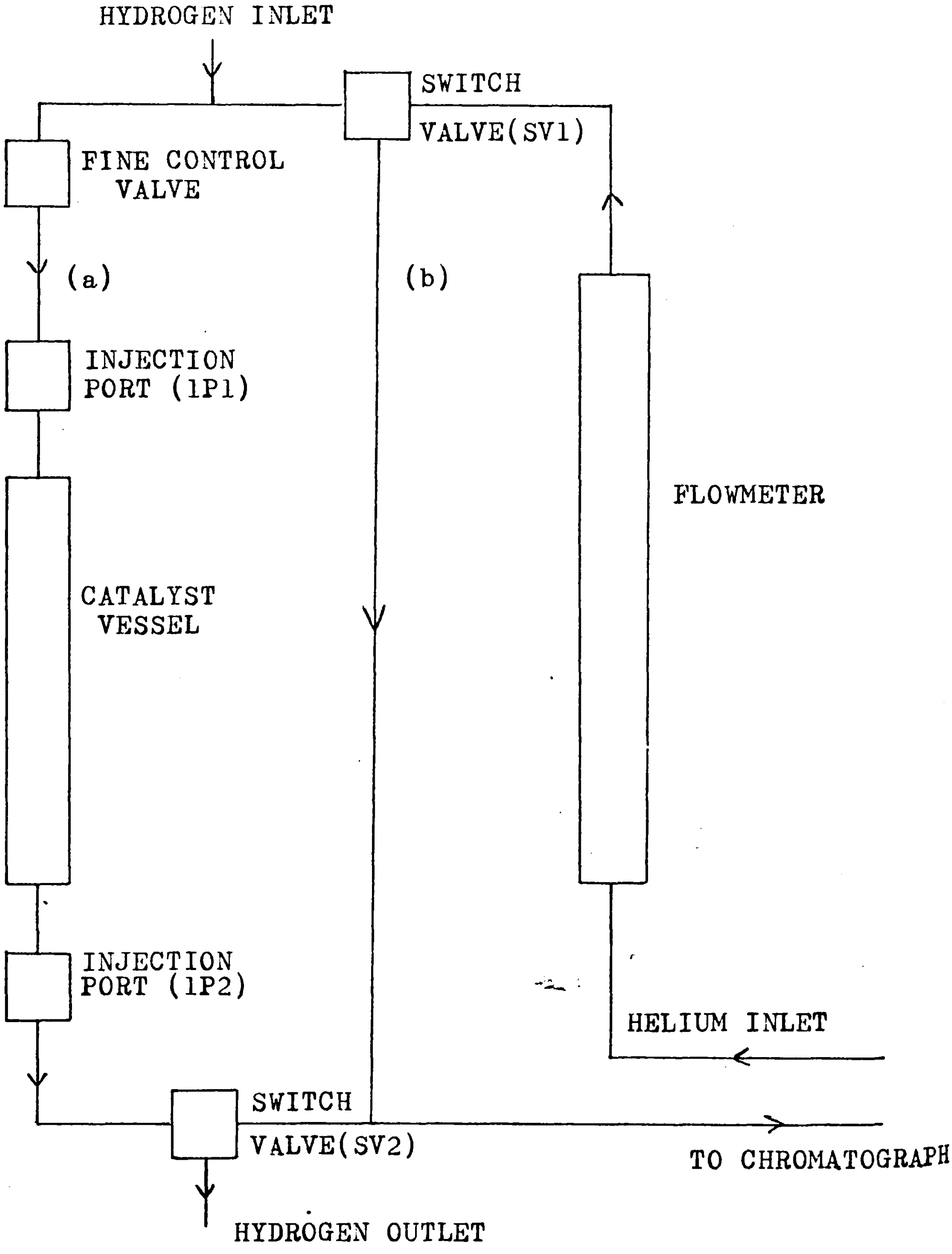


Figure 3.3. Diagram of the Catalyst Section.

wool plug was found to give the best experimental conditions. Injection ports 1P1 and 1P2 for reaction, and calibration injections respectively, were situated 6 cm. above and below the catalyst bulb. Their diameter was such that $^{1}/4''$ serum caps (Subaseal, Esco Rubber Co.) with both internal and external sealing edges gave a tight seal.

The temperature of the catalyst could be raised by a cylindrical electric furnace surrounding the catalyst vessel. The current to the furnace was controlled via a 'Variac' variable transformer and the temperature of the catalyst was measured using a platinum/platinum-rhodium thermocouple. A calibration of temperature against the thermocouple readings in millivolts and variac settings was made.

The helium entered the catalyst section (Fig. 3.3) through a 'Rotameter' gas flowmeter calibrated against a soap bubble flowmeter at the end of the system. From the flowmeter the carrier gas passed through a rotary switch valve RSV1 (Drallim Industries Ltd.) from which it could be led either directly back through the chromatograph and counter via line (a), the by-pass circuit, or through a Nupro fine control valve over the catalyst section (b) and through a second switch valve RSV2. This valve

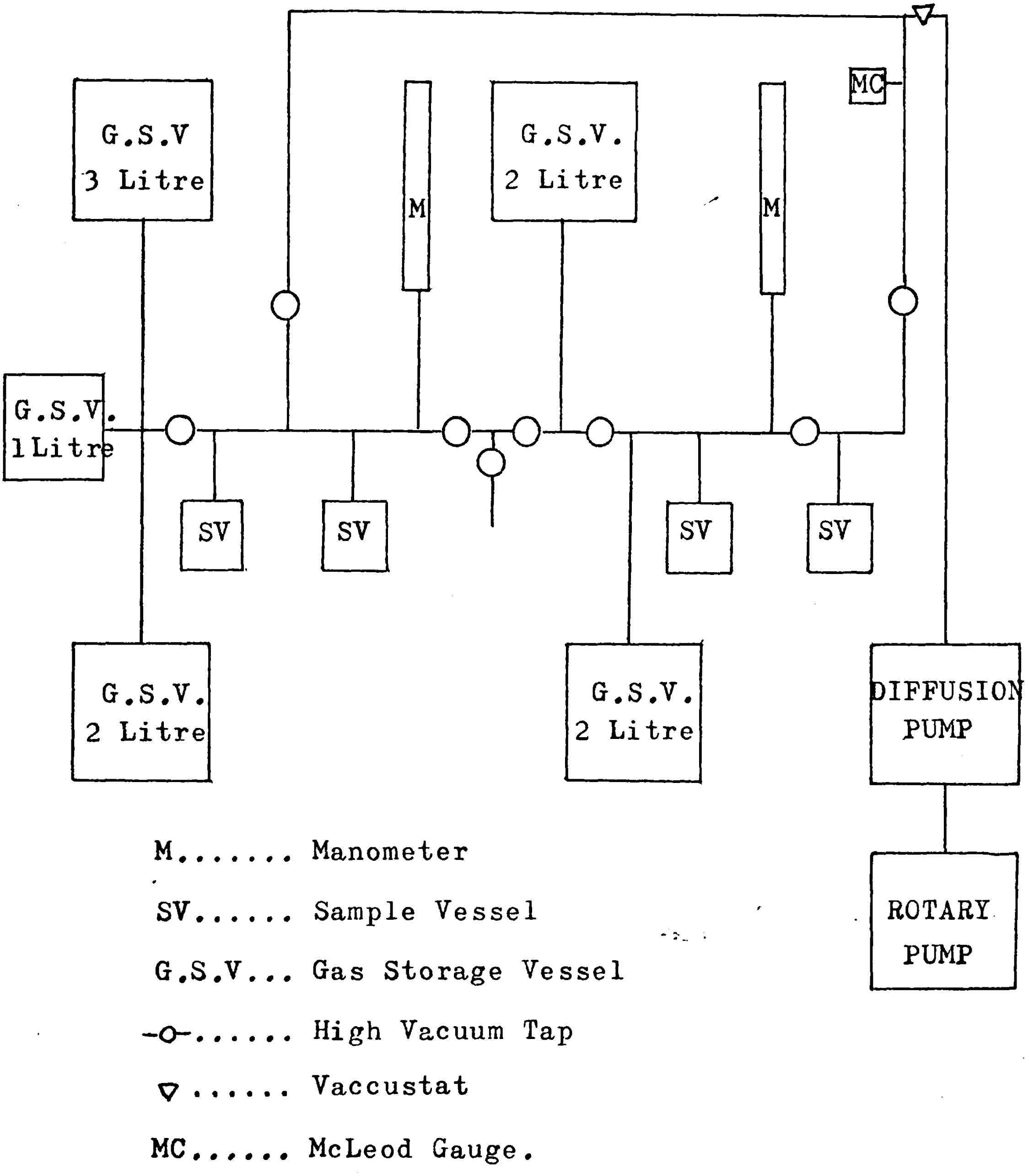


Figure 3.4 Diagram of the Vacuum Apparatus

enabled hydrogen for the reduction of the catalyst to pass from the hydrogen inlet, through the catalyst vessel and out to the atmosphere. In the meantime the carrier gas could flow through the rest of the system via the by-pass circuit.

Gases used in the reactions studied were prepared in a vacuum apparatus (Fig. 3.4) and transferred to the catalyst system by Hamilton Gas-Tight Syringes fitted with 'Chaney Adaptors'. By using syringes of 0·25, 1·0 and 2·5 ml. capacity it was possible to inject quantities of gas from 0·02 to 2 ml. with a high degree of accuracy. 'Cold flow' of the teflon tip occurring after prolonged use, however, resulted in loss of their gas-tightness and was corrected by immersing the tips in boiling water for about half an hour, according to the maker's instructions.

The vacuum system was evacuated by a mercury diffusion pump, backed by a rotary pump with taps and traps to isolate the diffusion pump where necessary. Two connections were made from the main (20 mm. i.d.) line to a secondary manifold (12 mm. i.d.) divided by 2 mm. taps and connected to six gas reservoirs of various capacities, four sample vessels fitted with injection ports and serum caps, two open manometers and an outlet to the atmosphere used to fill the reservoirs with the required gases. All taps were lubricated with 'Apiezon N' vacuum grease. An 'Edwards vacustat' (1-10^{-3} torr.) and a McCleod gauge were also fitted to the system.

Section 3.2 The Chromatograph

From the catalyst section the gas stream passed through a Beckmann GC2A chromatograph which had the gas and liquid sampling inlets removed and replaced by the catalyst section. The resultant increase in the gas flow necessitated the removal of the capilliary restrictor located in the sample line in order to keep the flow rates in this and the reference line constant. The chromatograph was coupled to a Honeywell -0·25 -2·5 mv recorder fitted with an electro-mechanical continuous integration unit. It had been previously found[94] that the integrator was not perfectly linear throughout the range of the recorder, deviations being greatest at outputs of less than 2% full scale deflections. Since the output was continuous, the integrator had to be read and zeroed after every peak. The attenuation was chosen to give a calibration peak for the volume of gas used in a particular run completely on scale on the recorder.

These factors meant that the smaller the quantity of a particular product the greater was the inaccuracy in determining it.

A 9 ft. $^1/4$" O.D. stainless steel column filled with 30-60 mesh silica gel (Perkin-Elmer Ltd.) was used with all, except C_4 hydrocarbons, for the analyses of products.

A flow rate of 60 ml. min.^{-1} for the helium was found necessary to give separation of methane, ethane, ethylene, acetylene, propane and propylene. Since the column was run for long periods at 70°C, accumulation of water from the catalyst on the silica gel column reduced the resolving power. Heating the column up to 130°C and maintaining it at this temperature for several hours until the recorder trace had returned to base line level, reactivated the column.

The chromatograph was used with a filament current of 200 mamps. It operated on the output of an Advance Voltstat CV500/28 constant output transformer which was kept running constantly.

Under the conditions of the flow system, temperature programming of the column was not possible making simultaneous analysis of mixtures of a wide range of components impossible. The column temperature was maintained at 70°C for experiments with ethylene and hydrogen and 130°C for those with acetylene and propylene. It can be seen from Table 3.1, showing the retention times at these temperatures, that the accurate analysis of ethylene and ethane, at the same time as propylene and propane, could not be achieved.

TABLE 3.1

RETENTION TIMES ON SILICA COLUMN.

Column Temperature (°C)	Gas	Retention Time Calibration	Retention Time Catalyst (20°C)
70	Hydrogen	0 min. 58 secs.	1 min. 10 secs.
	Methane	1 min. 17 secs.	-
	Ethane	2 min. 20 secs.	2 min. 25 secs.
	Ethylene	3 min. 25 secs.	3 min. 37 secs.
130	Hydrogen	0 min. 55 secs.	1 min. 10 secs.
	Methane	1 min. 10 secs.	-
	Ethane	1 min. 35 secs.	-
	Ethylene	2 min. 2 secs.	2 min. 10 secs.
	Propane	2 min. 10 secs.	2 min. 15 secs.
	Acetylene	2 min. 45 secs.	2 min. 55 secs.
	Propylene	3 min. 15 secs.	3 min. 42 secs.

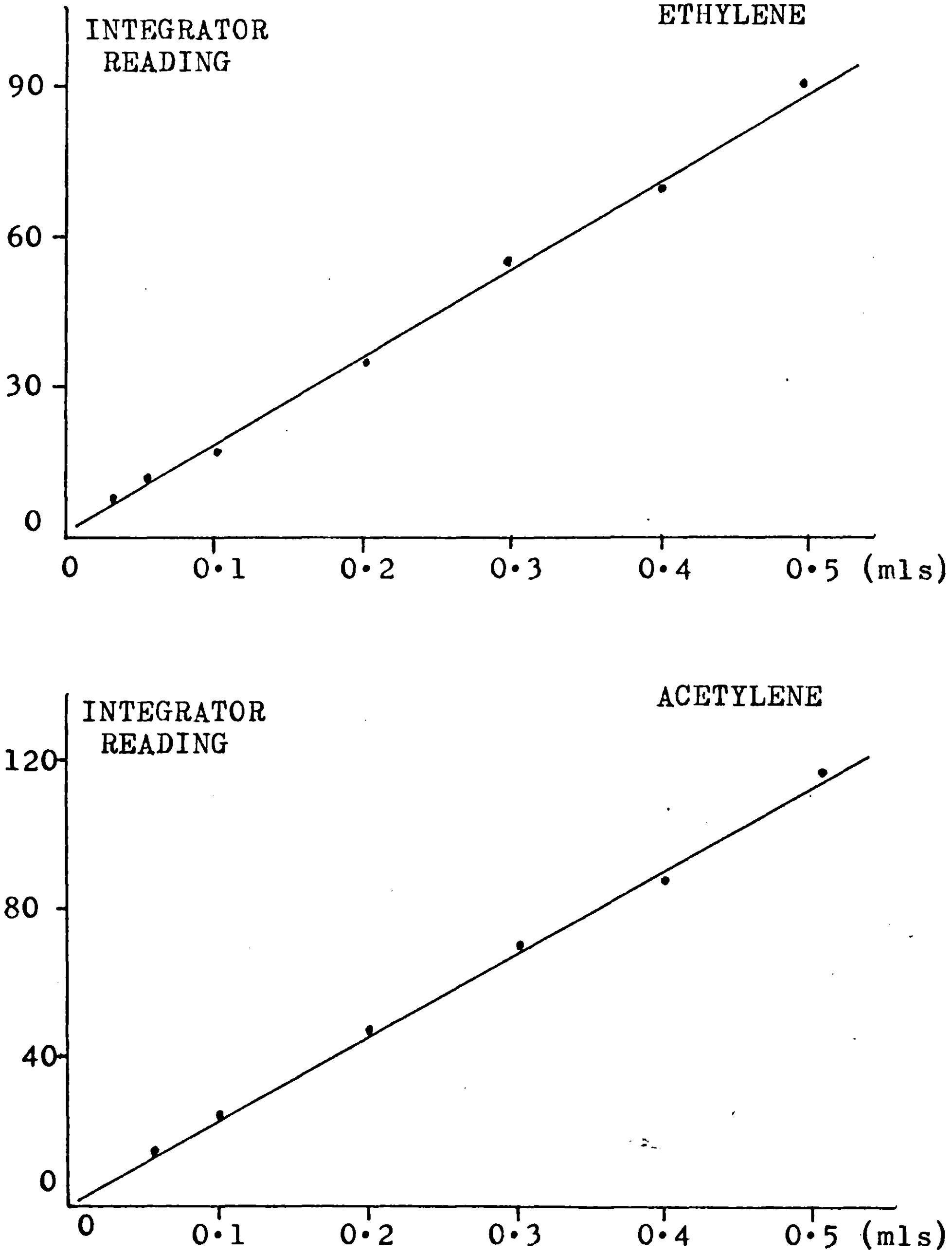


Figure 3.5 · Integrator Calibration

A calibration of the chromatograph integrator reading for different volumes of acetylene and ethylene, gave quite good linear relationships (Fig. 3.5). For hydrogen, however, the volume could not be determined on the chromatograph due to the insensitivity of the detector filament to hydrogen, when helium was used as the carrier gas.

At the start of each run, a number of calibration injections of the volume of the particular gas or gases used in that experiment, were made into the port below the catalyst, to test the sensitivity and reproducibility of the experimental conditions.

From the retention times and integrator counts, the nature and quantity of the reaction products could be determined. Although the depth of the catalyst bed was kept at a minimum, the presence of a certain, 'chromatographic effect' was shown by the increase in the sharpness of the peaks on the chromatograph with increasing catalyst temperature. This was also shown by a comparison of the retention times when a particular hydrocarbon was injected above and below the catalyst. Peak 'tailing' and the increased retention times were most noticeable at 20°C, the lowest temperature at which reactions were studied, but insignificant at and above a catalyst temperature of 100°C.

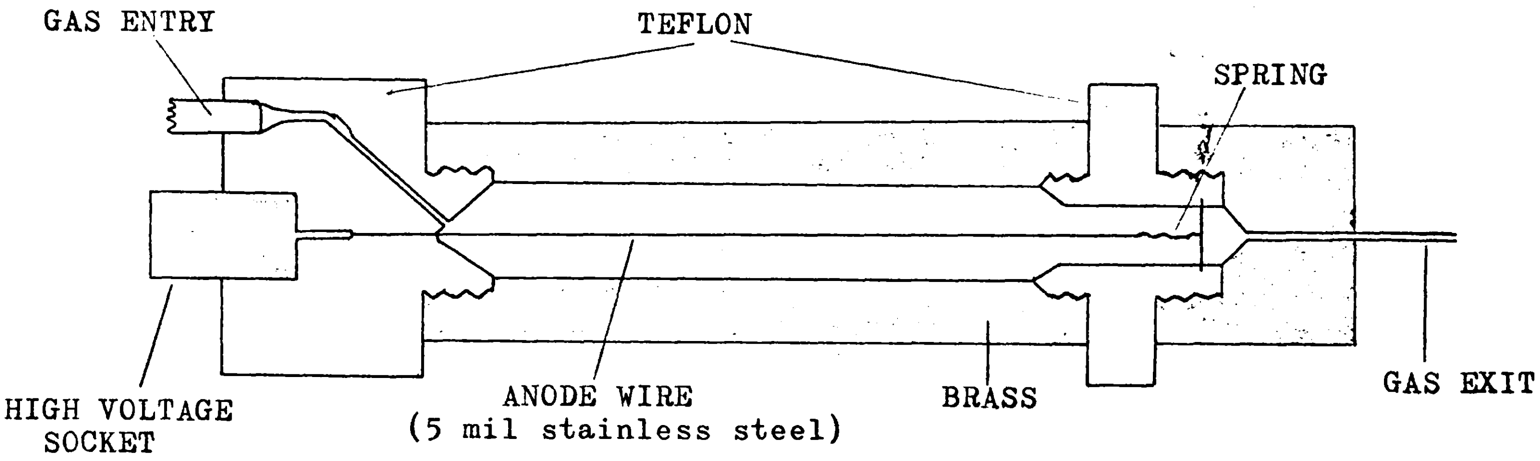


Figure 3.6 The Proportional Counter.

Section 3.3 The Proportional Counter.

The elements used in the counting experiments were carbon-14 and tritium. Since the latter is a very weak β emitter ($E_{max.}$=0·018 MEV), an efficient method of counting had to be used. It also, if possible, had to be incorporated into the flow system, unless a discontinuous method of counting was to be used.

Proportional counters may be used to detect α-particles and have advantages over other techniques in some cases for the measurement of β particles, for example when $E_{max.}$ is low. They are useful when it is necessary to work at or near atmospheric pressure, since most of the common gases can be made to operate at atmospheric pressure in the proportional region with a reasonably low applied potential. They will also give almost 100% efficiency for both tritium and carbon-14.

A proportional flow counter was constructed similar to the design of Schmidt-Bleek and Rowland[95], modified to accommodate different connectors for the gas inlet and the high voltage supply (Fig. 3.6).

The instrumentation associated with it is shown in Fig. 3.1. The power supply was by a Dynatron (type N103) unit, the output from which was continuously variable from

300 to 3300 volts. The amplification was through a dynatron (type 80D) pulse amplifier, consisting of a high gain preamplifier which was connected to the counter by a short lead to minimise interference pick up, and a main amplifier in which the gain could be altered in 2 D.B. steps in the range 0-40 D.B. The output from the amplifier was measured by an EKCO high speed scaler (530D) and recorded by means of an EKCO N522C ratemeter, coupled to a servoscribe potentiometric recorder. Both the scaler and ratemeter had discriminator units by means of which the detection of certain pulses could be optimised.

Though the total number of counts in a particular sample were measured on the scaler, the recorder gave a visual account of the peaks and acted as an aid in the determination of when to start and stop counting with the scaler.

Section 3.4 Operation of the Counter.

It was found[94] that the background noise was at a minimum with the amplifier set as follows:

Attenuation 40 db.; Time constant (differentiation) 3·2 or 1·6 μ secs.; Time constant (integration) 1·6 μ secs.

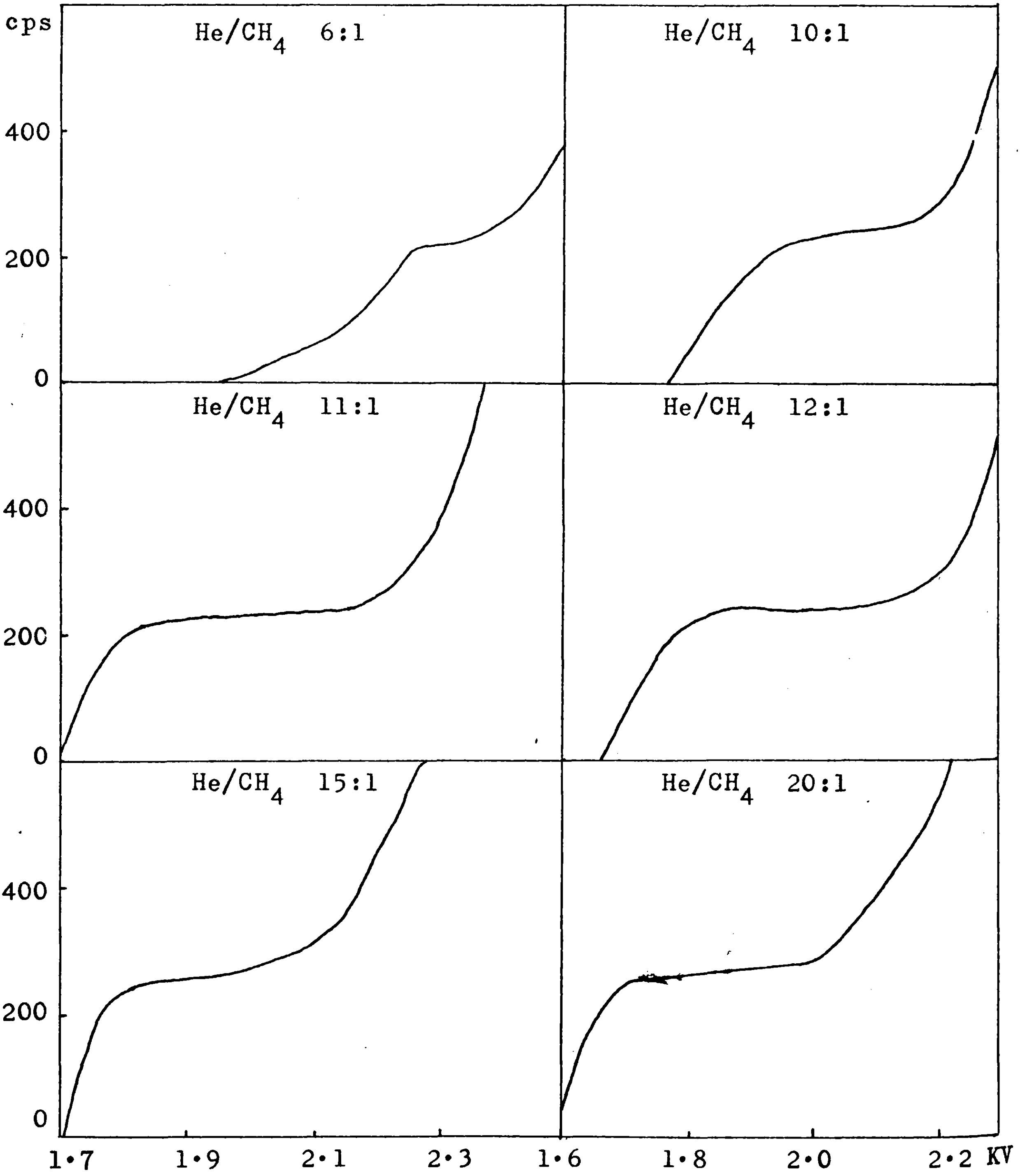


Figure 3.7 Counter Plateaux at Different Helium/Methane Ratios.

A counting mixture of helium and methane was used in all the experimental work and, since the helium flow rate had to be maintained at 60 ml. min.$^{-1}$ to give chromatographic separations, the methane flow was varied. The ratio of helium to methane was found to be critical in the determination of the plateau for which an external cesium -137 source was used. The variation in count rate at a constant discriminator setting against the applied voltage for different ratios of helium to methane is shown in Fig. 3.7. It was found that a ratio of 11:1 or 10:1 helium to methane gave the best plateau both for length and slope.

The background was kept in the order of 2-5 cps. by a shield of lead bricks round the counter.

Once the plateau had been determined the effect of varying the discriminator bias potential was found for both the rate meter and scaler using the Cs-137 source. With the applied potential set at the centre of the plateau the counting rate was measured against the bias potential (Fig. 3.8). It was found that for both the scaler and rate-meter the plateau (where counting is normally performed) had a slope of less than 0·1 per cent and extended over 15-20 mv. The bias potential was set at a value slightly above the noise region ~12-15 mv.

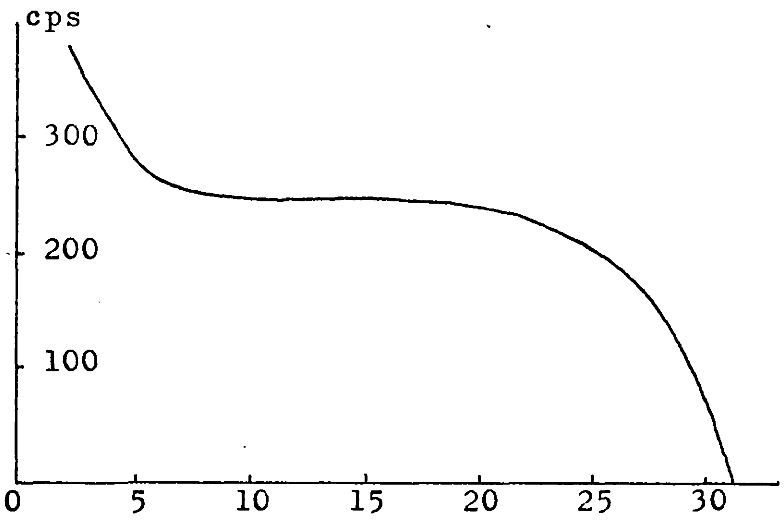


Figure 3.8 Counts v. Discriminator Bias Setting

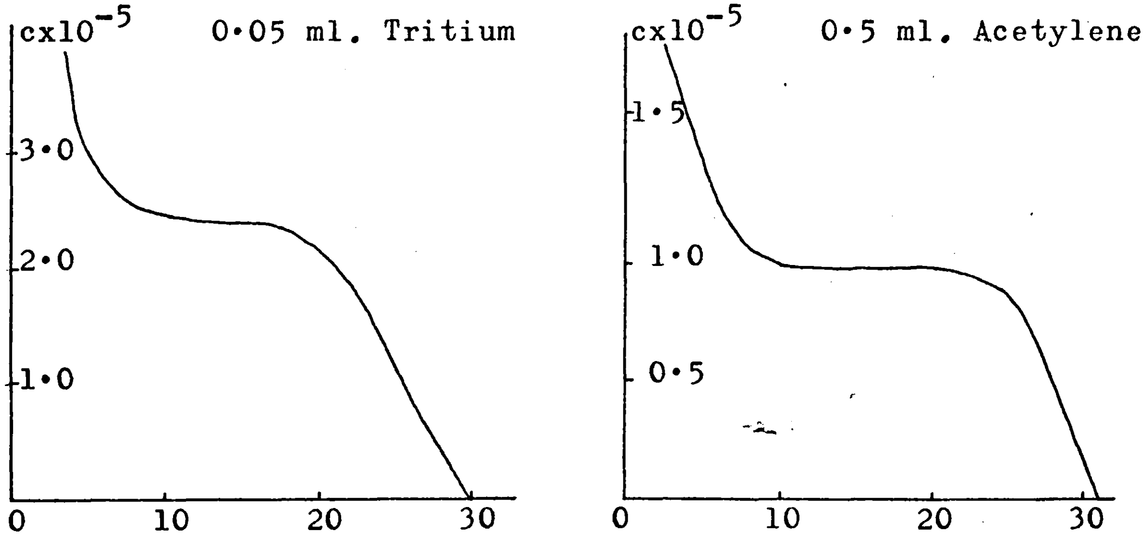


Figure 3.9 Counts v. Discriminator Bias Setting

Since tritium and carbon-14 were used in the counting, the procedure was repeated using samples of tritium (0·05 ml.) and ^{14}C-acetylene (0·5 ml.) Fig. 3.9. For tritium the 'plateau' length was shortened, whereas acetylene gave a curve similar to that found for the standard caesium-137 source. The cut off at lower discriminator settings for tritium, emphasises the relative weakness of the β emission from this nuclide.

Experimental Problems Associated with Counting.

An important factor was the effect of the reactant gases on the counter plateau and on the counting rate at a set applied potential. Since 0·5 ml. of hydrogen and hydrocarbons were almost always used, this quantity of gas was injected into the flow stream with the external source in position. A slight lowering of the counting rate at different applied potentials was observed. Since calibration injections were always incorporated the subtraction of the counts observed for the calibration from the reaction sample gave the net total count for a sample and corrected for the effect of the reactants on the counting rate.

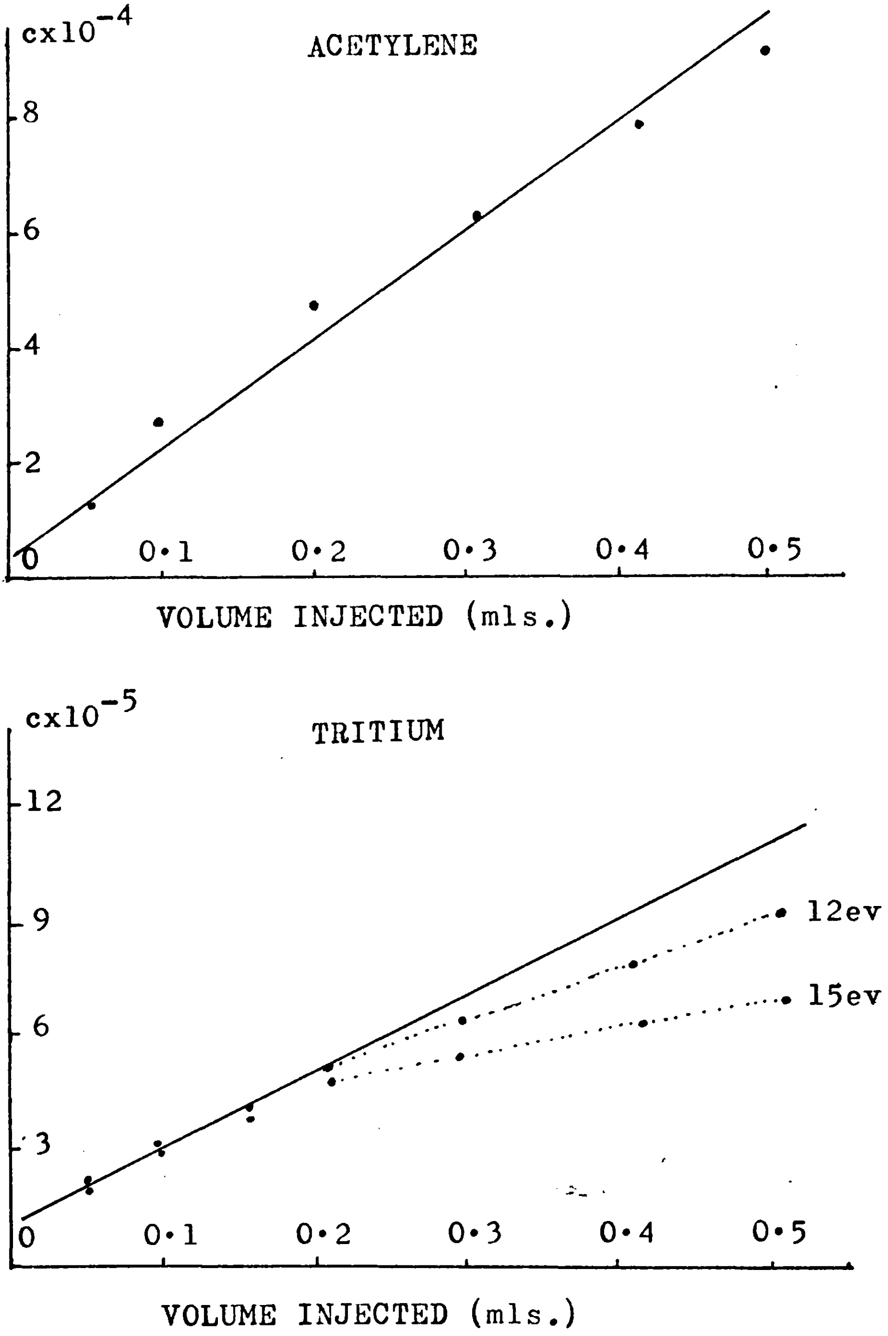


Figure 3.10 Counts Observed v. Volume

The effect of different volumes of gases on the total count recorded was studied by injecting different volumes of tritium and acetylene and determining the specific activity (count per ml.) for each injection. A graph of counts against volume (Fig. 3.10) was almost linear for acetylene but nor for tritium.

The correction of the counts observed for tritium only slightly affected this although a lower discriminator setting produced a more linear graph.

Water retained on the column has been mentioned above. When experiments were conducted with the column at 70°C any water from the catalyst or other sources was retained on the column. When, however, the temperature was raised above 100°C, some water passed through the column and entered the counter. This led to a lowering of the observed count rate by quenching and a disappearance of the plateau which gave much experimental difficulty.

It was found that by disconnecting the counter from the chromatograph while the column was heated to the required temperature, and until the recorder trace had returned to a steady base line, water was prevented from reaching the counter. The leads from the chromatograph were baked out during this time. When the counter was reconnected to the flow line only small changes were noticed in the plateau and count rate, provided the time for this procedure was kept to a minimum.

Another experimental problem which occurred was the adsorption of tritium onto the walls of the counter leading to an increase in the background of 20 cps. or greater.

By baking the counter overnight at ~ 150°C with helium flowing through it, the background could be reduced and water could be removed. The counter was dismantled, cleaned and polished when either of the above effects became serious. After reconstructing the counter, helium was allowed to flow through it for several days at 20 ml. $min.^{-1}$, until it had restabilized and a good plateau had once more been attained.

Section 3.5 Materials

(i) The catalysts were prepared by the impregnation of a solution of chloroplatinic acid on an aqueous slurry of the support. They consisted of 0·1%, 1% and 5% platinum and 5% palladium supported on 'Aerosil' silica (Degussa Ltd.), alumina (Peter Spence type A) or γ-alumina (Degussa Ltd.). Xray powder photographs showed the Peter Spence alumina to be mainly γ-alumina with some k-alumina (see Table 3.2).

TABLE 3.2

XRAY POWDER PHOTOGRAPH OF ALUMINA

d Å	Ion Film	I/I	Mineral
4·56	vvb	40	$\gamma\text{-}Al_2O_3$
2·80	w	20	-do-
2·39	sb	80	-do-
2·28	s	50	-do-
2·13	sb	80	$k\text{-}Al_2O_3$
1·977	s	100	$\gamma\text{-}Al_2O_3$
1·96	w	10	$k\text{-}Al_2O_3$
1·88	w	60	$k\text{-}Al_2O_3$
1·65	w	30	$k\text{-}Al_2O_3$
1·52	vw	30	$\gamma\text{-}Al_2O_3$
1·40)	vsb	100	$k\text{-}Al_2O_3$
1·395)	vsb	100	$\gamma\text{-}Al_2O_3$
1·31	m	20	$k\text{-}Al_2O_3$
1·14	s	20	$\gamma\text{-}Al_2O_3$

(ii) Helium (Fisons Ltd.) was used as the carrier gas in the flow system. Hydrogen could not be used if hydrogenation and hydrogen retention studies were to be made. Since the chromatograph detector depended on thermal conductivity, the quantitative analysis of hydrogen was impossible using helium as the carrier gas since helium (33·6) and hydrogen (39·6) have similar conductivities. The use of argon (3·88) or nitrogen (5·68) having conductivities in the range of the hydrocarbons used (ethane 4·31) would have precluded the analysis of these. Helium was thus chosen as the carrier gas.

(iii) The hydrogen used in the reduction of the catalyst, in the dilution of the tritium and as reactant hydrogen was obtained from the British Oxygen Company Ltd. Before being used it was passed through an Engelhard Deoxo Hydrogen Purifier and a 5 Å molecular sieve maintained at -195°C to remove any oxygen impurity.

(iv) Methane used for a counting gas was C.P. grade Air Products Ltd. with a quoted purity of greater than 99%.

(v) Ethylene and acetylene were obtained from the British Oxygen Company Ltd. and propylene from Matheson Company Inc. They were purified by condensing them and degassing until no impurity was recorded on the chromatograph.

(vi) The ^{14}C-ethylene and ^{14}C-acetylene were obtained from the Radiochemical Centre, Amersham and ^{14}C-propylene from New England Nuclear Inc. The ampoules were glass blown onto the vacuum apparatus and after breaking the seal, the ^{14}C-hydrocarbon was diluted to the desired activity by the transfer of purified non-radioactive hydrocarbon from a storage vessel. Since comparative work was carried out in reactions with the radioactive hydrocarbons, no attempt was made to reproduce the dilution exactly from one run to the next.

(vii) The tritium was also obtained from the Radiochemical Centre, Amersham as a one curie sample, 0·4 cc. at S.T.P., and of 98% isotopic abundance. It was diluted to 1 litre at S.T.P. with hydrogen in a storage vessel. Samples 10 mm. pressure were taken to another storage vessel and diluted further to atmospheric pressure with hydrogen.

(viii) The carbon monoxide was grade X obtained from the British Oxygen Company.

Section 3.6 Experimental Procedure.

(i) Tritium Experiments.

The general procedure was similar for all runs. The catalyst vessel was removed from the flow system at the switch valves. A silica wool plug was inserted into the cleaned catalyst vessel and tested to ensure that there was no blockage to the gas flow. The glass beads and 0·45 gms. of the catalyst were then placed into the vessel and compacted. The furnace was slipped over the vessel, the thermocouple inserted into the well, new serum caps put into the injection points and the section reassembled onto the flow system.

The hydrogen flow-line was completed and the hydrogen was passed over the catalyst at 30-40 ml. min.$^{-1}$. After it had flowed for about 15 minutes to displace the air in the system, the temperature of the catalyst vessel was raised to the reduction temperature.

In the meantime the rate of the helium flowing through the by-pass circuit, at 20 ml. min.$^{-1}$ was increased to 60 ml. min.$^{-1}$ and the methane for the counter turned to a flow rate of 5-6 ml. min.$^{-1}$.

The chromatograph was switched on and column temperature control set to the required valve, usually 70°C or 130°C.

The counter plateau and stability were checked using the Cs^{137} source. A background determination was also made.

The serum caps on the vacuum apparatus were renewed and the sample vessels, manometers and connecting manifolds were evacuated. Tritium was admitted from the storage vessel to one of the sample vessels and contracted by cooling in liquid nitrogen in order to obtain a pressure of 1·2 atmospheres. A working pressure greater than atmospheric was necessary to ensure no contamination by air during the gas transfer.

At the end of the reduction period, the hydrogen flow was reduced to about 5 ml. $min.^{-1}$ and tritium was injected over the catalyst. The hydrogen flow was immediately stopped and the catalyst section isolated with the catalyst at the reduction temperature and left for the tritium to exchange with the catalyst hydrogen.

The reactant gases were then prepared by transferring the gas from the reservoir to a sample vessel and condensing them or contracting them (in the case of hydrogen) until a pressure of 1·2 atmospheres had been achieved. The chromatograph filament was increased to the working current of 250 mA and a steady base line obtained.

At the end of the tritium exchange period the helium flow was diverted over the catalyst. The tritium displaced was measured on the scaler and ratemeter and compared with calibrations for the tritium injected. From the difference, an estimate of the tritium retained on the catalyst could be made. Two peaks were observed on the counter. The first, a short sharp peak, was concluded to arise from the removal of gas phase 'hydrogen' while the second larger and more diffuse peak was taken to be 'hydrogen' that was being removed from the catalyst by the helium.

The helium cleaning period was always taken as the time for the count rate to reach the background level and was usually about one hour. Leaving the helium to flow for up to 6 hours produced no noticeable further removal of tritium.

The catalyst temperature was then adjusted to that required for the reaction series and injections of the reactant were made. At least two injections were made into the calibration port below the catalyst to ensure the reproducibility of the system and thereafter occasionally during the series of reactions.

(ii) Carbon-14 Experiments.

The procedure for these experiments was similar to that described above for the tritium work. The only difference was that no tritium was injected onto the catalyst at the end of the reduction period. The helium cleaning period was taken as that found for the relevant experiment with tritium. In addition to the chromatograph calibration, counter calibrations were made for the ^{14}C-hydrocarbon samples.

(iii) Carbon Monoxide Adsorption Experiments.

In the studies of carbon monoxide retention on the various catalysts the procedure adopted was the same as that used in the carbon-14 experiments. The chromatograph was maintained at 70°C. At this temperature a sharp peak was obtained for carbon monoxide, the retention time being 1 min. 14 secs. for a calibration injection and 1 min. 25 secs. for an injection over the catalyst at 20°C.

(iv) Treatment of the Results.

The nature and quantity of the products from a particular reaction were determined from their retention times on the chromatograph and from the integrator count. The latter, giving a count which was proportional to the volume of gas eluted, has always been converted into millilitres in the results shown in the ensuing tables. Any counts shown in the tables refer to radioactivity measurements.

From the difference between the total volume eluted and the initial volume of an injection, the volume of the reactant gas which was obtained on the catalyst could be determined.

The radioactive content of the samples are shown as the total number of counts recorded during the elution. They have been corrected for background either by suctracting the background total for the period of counting or, more accurately, by subtracting the count observed during a calibration injection of the same volume during the same run. The latter method corrects for the effect of the hydrocarbon or hydrogen on the counter efficienty.

In many cases the specific activity of a product has been determined as counts per millilitre (shown as c/ml. in the tables of results). When either the sensitivity of the gas chromatograph ($<$ 0·01 ml.) or the counter ($<$ 100 counts) was too low to detect the volume or count rate accurately the specific activities have been either omitted or else the approximate values have been shown in brackets.

The radioactive content of the samples are shown as the total number of counts recorded during the elution. They have been corrected for background either by subtracting the background total for the period of counting or, more accurately, by subtracting the count observed during a calibration injection of the same volume during the same run. The latter method corrects for the effect of the hydrocarbon of hydron on the counter efficiency.

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RESULTS

CHAPTER 4.

Section 4.1 Reactions on Palladium Supported Catalysts.

Hydrocarbon reactions on various alumina-supported metal catalysts have been studied previously in this laboratory using a flow system. The catalyst 'hydrogen' was labelled with tritium in order to distinguish it from reactant hydrogen.

(i) Ethylene on 5% Pd/Al_2O_3.

Using the same experimental conditions as used previously, the reaction of ethylene on 5% Pd/Al_2O_3 at 200°C was examined.

After the catalyst (0·5 gm.) had been reduced at 200°C for 1 hour tritium (10 ml.) was injected over the catalyst, which was then isolated to allow the tritium to exchange with the catalyst hydrogen at the reduction temperature. At the end of an hour the helium flow was diverted over the catalyst. When the count-rate of the reaction eluant had returned to the background level the catalyst was allowed to cool to the required temperature, in this case 200°C.

Since low conversions of the reactants had been found, a minimum volume of gas was required to allow the maximum sensitivity in determinations of the product yields. The volume chosen was 0·2 ml. since the retention volumes observed previously were always less than this.

In addition to the retention of ethylene, both the conversion of ethylene to ethane (hydrogenation) and the exchange of ethylene with the tritium retained on the catalyst were observed. The results for the first (1) and second (2) injection are shown in Table 4.1, denoted by A; also shown are the values, denoted by B, obtained previously.

In comparing the values of the two experiments, the similarity in both the percentage of ethane and the specific activity of ethylene support the reliability of the experimental method. The different yields of ethane are a reflection of the different volumes of ethylene injected onto the catalyst in each case.

TABLE 4.1

COMPARISON OF PRESENT & PREVIOUS WORK[94]

ETHYLENE ON 5% PALLADIUM-ALUMINA

Catalyst		Ethane		% of	Ethylene
Temperature (°C)		mls.	(c/ml.x10^{-5})	Product	(c/ml.x10^{-5})
200	1. A.	0·15	1·2	100	-
	1. B.	0·30	1·7	100	-
	2. A.	0·14	1·3	95	0·8
	2. B.	0·29	1·5	93	0·4

TABLE 4.2

ETHYLENE on 5% PALLADIUM-SILICA

Reduction Temp. (°C)	Catalyst Temp.(°C)	Retention (mls.)	Methane (mls.)	Ethane (mls.)	Ethylene (c/ml.x10^{-5})
200	20	1. 0·10	-	-	-
		2. 0·08	-	-	-
		3. 0·09	-	-	-
	100	1. 0·12	-	-	-
		2. 0·13	-	-	-
		3. (0·11)	-	-	-
	200	1. 0·18	-	-	0·05
		2. 0·18	-	-	0·16
		3. 0·11	-	-	0·06

(ii) Reaction of Ethylene on 5% Pd/SiO_2.

The experiment was repeated using 5% Pd/SiO_2 instead of 5% Pd/Al_2O_3.

The less dense silica-supported catalyst had the disadvantage that only small weights, less then 0·2 gm., could be used before the flow of helium was obstructed. Since the catalytic conversions were often low it was preferable to use the maximum weight of the catalyst in order to observe minor products.

This problem was eventually overcome, in the manner mentioned previously (see Section 3.1) by mixing the catalyst with glass beads thereby enabling a maximum of 0·45 gm. of catalyst to be used before any blockage occurred. This weight was chosen as the standard weight throughout the experimental work using the flow system.

In order to test the reproducibility of the results a series of experiments at 20°C, 100°C and 200°C were carried out. The results from three of the experiments at each temperature are shown in Table 4.2.

In contrast to 5% Pd/Al_2O_3, no hydrogenation or ethylene exchange was found at 20°C or 100°C. At 200°C, however, there was some ethylene exchange, although the catalyst still showed no hydrogenation activity. The retention was lower than that on 5% Pd/Al_2O_3 at every temperature.

Apart from the third value shown for the ethylene retention at 200°C, the results were within the experimental error. The specific activity of the ethylene showed a considerable variation from $0{\cdot}05 \times 10^5$ to $0{\cdot}16 \times 10^5$ counts per ml. Since the fluctuations in these results may vary by a factor of 10^6 the error is reasonably low.

In a second series of experiments the catalyst was heated to 100°C after the reaction of ethylene had been studied at 20°C. Several injections of ethylene were made at 100°C until no retention was observed, when the temperature was raised to 350°C. Further injections were then made at this temperature. The results are shown in Table 4.3.

At 100°C the catalytic activity appeared to be enhanced. Both the retention of ethylene and ethylene exchange were greater than before (see Table 4.2) and some hydrogenation was observed. A considerable enhancement in all reactions was observed at 350°C. Some cracking to methane was also observed to occur at 350°C.

TABLE 4.3

ETHYLENE ON 5% PALLADIUM-SILICA

Reduction Temp.(°C)	Catalyst Temp.(°C)	Retention (mls.)	Methane (mls.)	Methane (c/ml x 10^{-5})	Ethane (mls.)	Ethane (c/ml x 10^{-5})	Ethylene (c/ml x 10^{-5})
200	20	0·09	–	–	–	–	–
	100	0·16	–	–	0·01	0·09	0·11
	350	0·10	(0·01)		0·15	0·11	0·06
350	350	0·04	0·01	2·95	0·10	0·74	1·24

(iii) The Effect of Reduction Temperature.

The effect of the reduction temperature on the activity of the catalyst was investigated by repeating the above experiments on catalysts reduced at 350°C. Little change in the activity of the catalysts at the lower temperatures was found (see Table 4.3) although at 350°C the specific activity of ethane and ethylene was greater on the catalyst reduced at 350°C than on catalysts reduced at 200°C. The reduction temperature in most of the following experiments was 350°C.

(iv) The Effect of Time.

A surprising effect was observed in experiments in which successive volumes of ethylene were injected onto the catalyst at a particular temperature. The specific activity of the ethylene decreased with each successive injection although when the catalyst was left for an hour at the reaction temperature, this exchange had increased. The results for an experiment at 200°C using a catalyst reduced at 200°C and 350°C using a catalyst reduced at 350°C are shown in Table 4.4. The numbers refer to the series of injections in which A represents the first injection and B the final injection for that series.

TABLE 4.4

ETHYLENE ON 5% PALLADIUM-SILICA (TIME EFFECT)

Reduction	Catalyst			Methane	Ethane		Ethylene
Temp.(°C)	Temp.(°C)			(mls.)	(mls.)	(c/mlx10^{-5})	(c/mlx10^{-5})
200	200	1	A	-	-	-	0·060
			B				0·021
		2	A				0·045
			B				0·026
		3	A				0·037
			B				0·006
350	350	1	A	(0·01)	0·10	0·74	1·24
			B		(0·006)	0·04	0·15
		2	A		0·02	0·05	0·21
			B		0·006	0·02	0·05

At 350°C an enhancement of the hydrogenation activity was also observed, the product ethane also had a higher specific activity.

(v) Ethylene-Hydrogen Mixtures.

Since 5% Pd/SiO_2 appeared less active in hydrogenation than 5% Pd/Al_2O_3, the activity towards ethylene-hydrogen mixtures was investigated at 20°C, 100°C and 200°C. An injection (0·4 ml.) of an equimolar mixture of ethylene and hydrogen was made at each temperature onto a freshly reduced catalyst. In every case there was a high conversion to ethane and some radioactivity was observed in both the product ethane and ethylene. A second injection of ethylene alone was made which gave both radioactive ethane and ethylene at 20°C and 200°C. At 100°C no ethane was observed. The results are shown in Table 4.5.

(vi) Molecular Exchange of Ethylene.

The exchange between gas phase ethylene and retained ethylene has been studied in the following manner. After reduction of the catalyst at 200°C ^{14}C-ethylene was injected onto the catalyst until no further retention was observed. At this point inactive ethylene was injected onto the catalyst and the radioactivity in the products (expressed as counts ml.) was determined. The results are shown in Table 4.6.

TABLE 4.5

ETHYLENE ON 5% PALLADIUM-SILICA

Catalyst Temperature (°C)		Ethane mls.	Ethane c/ml.	Ethylene c/ml.
20	1.	0·12	x	x
	2.	0·02	x	x
100	1.	0·19	x	x
	2.	-	-	x
200	1.	0·07	x	x
	2.	0·01	x	x

TABLE 4.6

MOLECULAR EXCHANGE ON 5% PALLADIUM-SILICA

Catalyst Temp.(°C)	Retention (mls.)	Methane (mls.)	Ethane (mls.)	Ethylene ($c/ml.x10^{-5}$)	Exchange (mls.)
20	0·04	-	-	0·004	0·01
100	-	-	-	-	-
200	0·06	-	-	0·002	0·004
350	0·04	0·01	0·14 (0·006)	(0·001)	0·01

$0\cdot2$ ml. ${C_2H_4}^{14} \equiv 0\cdot02 \times 10^5$ counts

Reduction Temperature = 200°C

From the specific activity of the ^{14}C-ethylene the counts could be converted into the volumes of retained ethylene undergoing molecular exchange.

Only a low fraction appeared to be active in molecular exchange; this fraction tending to decrease with increasing temperature.

(vii) Comparison of 5% Pd/Al_2O_3 and 5% Pd/SiO_2.

The reactivity of ethylene appeared different on 5% Pd/Al_2O_3 and 5% Pd/SiO_2, for example the former catalyst was active for the hydrogenation of ethylene at 20°C whereas no ethane was formed at this temperature on 5% Pd/SiO_2. Although no hydrogenation or ethylene exchange was observed for ethylene alone on 5% Pd/SiO_2, the catalyst was active for both reactions at 20°C when a mixture of hydrogen and ethylene was studied.

The presence of hydrogen thus appears to enhance the reactivity of the retained tritium.

Since palladium absorbs hydrogen the apparent activity of the retained tritium may be affected by absorbed tritium.

To find our if these effects were common to other metals the reactivity of ethylene on alumina and silica-supported platinum has been investigated.

In order to ensure, as far as possible, uniformity in all experiments the following conditions were used unless otherwise specified.

The catalyst (0·45 gms.) was reduced for four hours at 350°C. At the end of this period, tritium (2 ml.), when it was used, was injected over the catalyst and allowed to exchange at 350°C for one hour.

Since conversions were greater than 0·2 ml. in some cases, the volume of each injection was chosen to be 0·5 ml. as this usually gave complete coverage after one injection.

In each series of experiments the complete results for one run are usually shown and the results from the complete series are presented in summary form.

Section 4.2 Ethylene on Tritiated Platinum Catalysts.

(i) Reactions on 5% Pt/Al_2O_3, 1% Pt/Al_2O_3, 5% Pt/SiO_2 and 1% Pt/SiO_2.

A platinum catalyst was treated with tritium as described above (see Section 3.6(i) and 4.1(vii)). From the difference between a calibration injection and the volume removed by the 'helium' cleaning, the volume retained by the catalyst could be determined.

Ethylene (0·5 ml.) was injected onto the catalyst at 20°C. Both hydrogenation of the ethylene to ethane and the incorporation of tritium into the ethylene (ethylene exchange) were observed.

The injections were continued at this temperature until, for a given sample, only ethylene was observed on the chromatograph and the count rate recorded by the counter corresponded to background or, after many injections, was substantially reduced. The temperature was raised to 100°C and the eluent gas monitored. A peak was sometimes observed on the counter recorder, whereas the chromatograph recorder remained at base line level, even when set at the highest sensitivity. Injections were then made at 100°C, after which the process repeated at 200°C and 350°C.

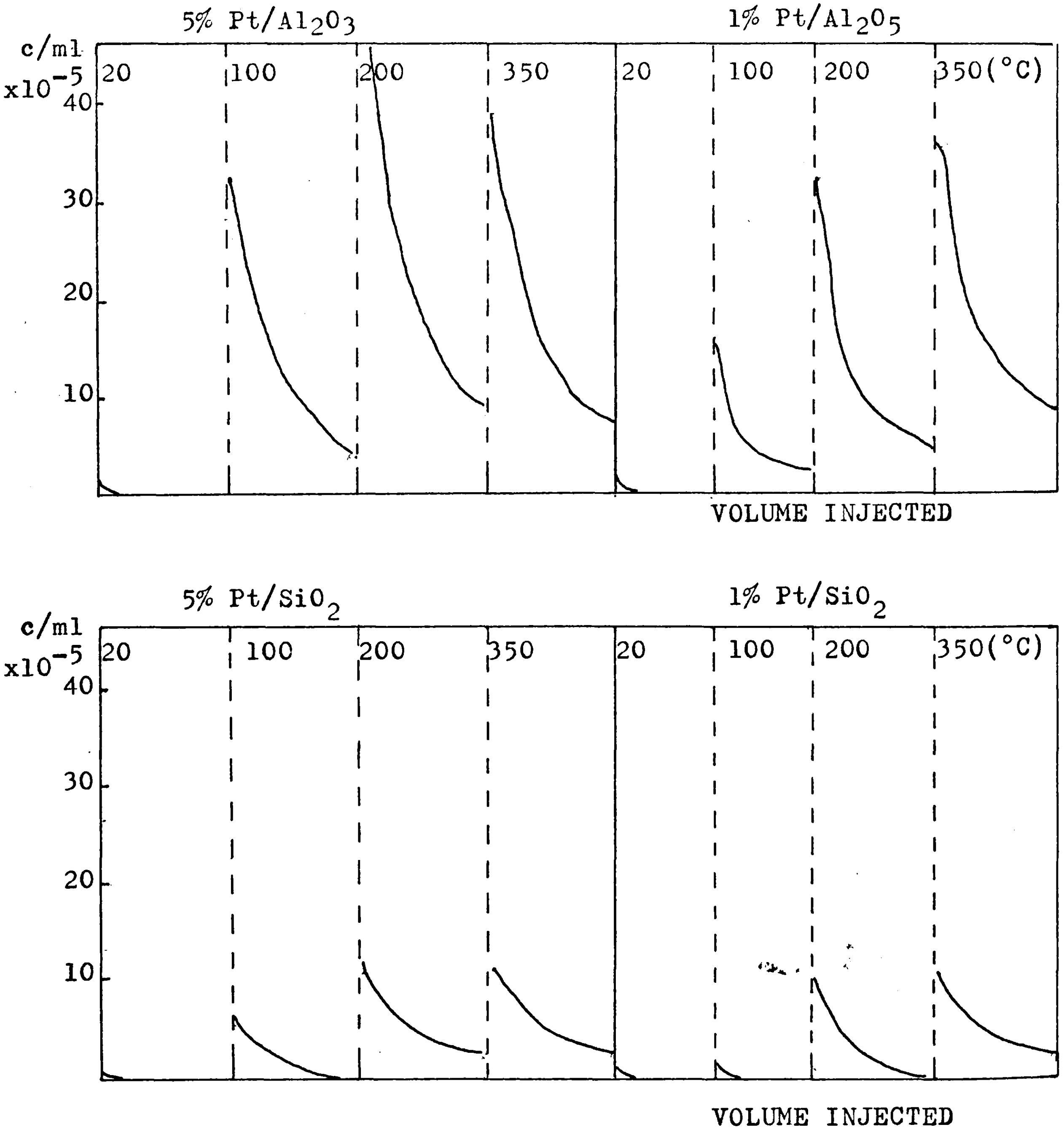


Figure 4.1 Ethylene Exchange.

This procedure was carried out for 5% Pt/Al_2O_3, 1% Pt/Al_2O_3, 5% Pt/SiO_2 and 1% Pt/SiO_2. The complete results for a typical run on 5% Pt/SiO_2 are shown in Table 4.7. The results for the first injection at each temperature, for all the catalysts, are summarised in Table 4.8. They are shown graphically in Figures 4.1(a-d), which clearly show the differences in behaviour of the catalysts and the marked effect of temperature.

The only products observed were ethane and ethylene except at 350°C where some cracking to give methane was observed.

The production of ethane, which will be subsequently referred to as the hydrogenation activity, diminished quickly after the first injection of ethylene at 20°C, but was restored, either fully or partially, by increasing the catalyst temperature to 100°C. At 200°C and 350°C the hydrogenation activity was considerably enhanced.

A similar pattern was observed for the exchange of ethylene with tritium (termed the exchange activity), although a more gradual decrease in exchange activity was observed at each temperature. For example, on 1% Pt/Al_2O_3 at 100°C the initial specific activity of the ethylene, 4×10^5 counts/ml., had decreased to $5{\cdot}6 \times 10^4$ counts/ml.

TABLE 4.7

ETHYLENE ON A TRITIATED 5% PLATINUM ON SILICA CATALYST

Temp. (°C)	Injection No.	Ethane			Ethylene			Methane			Retention
		mls.	counts	c/ml*	mls.	counts	c/ml*	mls.	counts	c/ml*	mls.
20	1	0·06	500	0·08	0·35	1000	0·03	-	-	-	0·09
	2	<0·005	25	-	0·44	1200	0·025	-	-	-	0·05
	3	-	-	-	0·44	900	0·02	-	-	-	0·06
	4	-	-	-	0·45	450	0·01	-	-	-	0·05
	5	-	-	-	0·49	300	0·006	-	-	-	0·01
	6	-	-	-	0·5	200	0·004	-	-	-	-
	7	-	-	-	0·5	150	0·003	-	-	-	-
	8	-	-	-	0·5	(110)	(0·002)	-	-	-	-
	9	-	-	-	0·5	(50)	(0·001)	-	-	-	-
	10	-	-	-	0·5	-	-	-	-	-	-
100	1	0·04	2550	0·64	0·35	21500	0·60	-	-	-	0·11
	2	0·02	550	0·28	0·41	14000	0·34	-	-	-	0·07
	3	0·01	250	0·25	0·45	8000	0·18	-	-	-	0·04
	4	0·01	-	-	0·48	6500	0·15	-	-	-	0·01
	5	>0	-	-	0·48	5500	0·12	-	-	-	0·01
	6	>0	-	-	0·48	5900	0·12	-	-	-	0·01
	7	>0	-	-	0·5	5700	0·11	-	-	-	-
	8	-	-	-	0·5	5000	0·10	-	-	-	-
	9	-	-	-	0·5	3500	0·07	-	-	-	-
	10	-	-	-	0·5	3200	0·06	-	-	-	-
	11	-	-	-	0·5	2900	0·06	-	-	-	-
	12	-	-	-	0·5	2700	0·05	-	-	-	-
	13	-	-	-	0·5	2000	0·04	-	-	-	-
	14	-	-	-	0·5	1900	0·04	-	-	-	-
	15	-	-	-	0·5	1700	0·03	-	-	-	-

cont'd.

TABLE 4.7 (cont'd.)

Temp.	Injection	Ethane			Ethylene			Methane			Retention
(°C)	No.	mls.	counts	c/ml*	mls.	counts	c/ml*	mls.	counts	c/ml*	mls.
200	1	0·12	16000	1·33	0·29	31700	1·12	-	250	-	0·09
	2	0·06	3600	0·6	0·41	24500	0·60	-	150	-	0·03
	3	0·04	2000	0·5	0·44	20400	0·46	-	100	-	0·02
	4	0·03	1050	0·35	0·46	17200	0·39	-	-	-	0·01
	5	0·02	700	0·35	0·47	15500	0·33	-	-	-	0·01
	6	0·02	550	0·28	0·47	12500	0·27	-	-	-	0·01
	7	0·02	500	0·25	0·48	10000	0·21	-	-	-	-
	8	0·01	400	(0·22)	0·49	9400	0·19	-	-	-	-
	9	<0·01	350	-	0·49	8900	0·18	-	-	-	-
	10	<0·01	300	-	0·5	9000	0·18	-	-	-	-
	11	>0	280	-	0·5	7000	0·14	-	-	-	-
	12	>0	260	-	0·5	6500	0·13	-	-	-	-
	13	>0	200	-	0·5	6400	0·13	-	-	-	-
	14	>0	(100)	-	0·42**	5000	0·12	-	-	-	-
	15	>0	-	-	0·5	5600	0·12	-	-	-	-
	16	>0	-	-	0·5	4700	0·09	-	-	-	-
	17	>0	-	-	0·4	3500	0·09	-	-	-	-
	18	-	-	-	0·5	3500	0·07	-	-	-	-
	19	-	-	-	0·5	3200	0·06	-	-	-	-
	20	-	-	-	0·5	3000	0·06	-	-	-	-
350	1	0·22	30000	1·36	-	500	-	0·22	46000	2·09	0·06
	2	0·23	30000	1·30	0·10	9000	0·90	0·11	13600	1·24	0·06
	3	0·17	15000	0·88	0·21	17500	0·83	0·06	5000	0·83	0·06
	4	0·13	7800	0·60	0·28	17300	0·62	0·04	2300	0·58	0·05
	5	0·10	4400	0·44	(0·25)	12000	0·48	0·03	1200	0·40	(0·03)
	6	0·08	2000	0·25	0·35	10500	0·30	0·02	850	0·43	0·05
	7	0·06	1700	0·27	0·41	10000	0·24	0·01	500	0·60	0·02
	8	0·05	1250	0·25	0·44	9800	0·22	<0·01	-	-	-
	9	0·04	870	0·22	0·45	9500	0·21	<0·01	-	-	-
	10	0·04	800	0·20	0·46	8900	0·19	-	-	-	-

* Counts/ml$\times 10^{-5}$ ** Faulty Injection

TABLE 4.8

ETHYLENE ON TRITIATED 5% and 1% PLATINUM CATALYST
(Results from 1st Injection at each Temperature)

Tritium Retained	Catalyst	Retention	Methane		Ethane		Ethylene
(Counts & mls.)	Temp.(°C)	mls.	mls.	c/mlx10^{-5}	mls.	c/mlx10^{-5}	c/mlx10^{-5}
5% Pt/Al_2O_3							
5x10^6 counts	20	0·36	-	-	0·06	0·10	0·04
(1·40 mls.)	100	0·22	-	-	0·07	2·85	2·85
	200	0·10	-	-	0·14	5·19	4·98
	350	0·32	0·27	4·0	0·11	5·40	(3·8)
1% Pt/Al_2O_3							
5x10^6 counts	20	0·13	-	-	0·01	(0·1)	0·01
(1·42 mls.)	100	0·04	-	-	0·05	6·71	4·17
	200	0·12	-	-	0·12	3·70	3·25
	350	0·11	0·24	2·8	0·12	4·01	(3·5)
5% Pt/SiO_2							
6x10^6 counts	20	0·26	-	-	0·06	0·08	0·03
(1·65 mls.)	100	0·24	-	-	0·04	0·64	0·60
	200	0·17	-	-	0·12	1·33	1·12
	350	0·28	0·22	2·1	0·22	1·36	(1·1)
1% Pt/SiO_2							
6x10^6 counts	20	0·14	-	-	0·01	0·04	0·01
(1·64 mls.)	100	0·02	-	-	0·02	0·25	0·10
	200	0·05	-	-	0·04	0·20	0·10
	350	0·18	0·04	1·6	0·25	1·20	0·98

after the injection of 6 ml. of ethylene. However, the specific activity, $2{\cdot}6 \times 10^4$ counts/ml., after the addition of 15 ml. was still quite high. The yield of ethane, however, had decreased one hundred times after 2 ml. of ethylene had been injected.

On the silica-supported catalysts the specific activity of the ethane was always greater than that found for ethylene. In some cases, however, the alumina-supported catalysts gave ethylene with a higher specific activity than that of ethane.

For all the catalysts at 20°C and 100°C and for the Pt/SiO_2 catalysts at each temperature, the hydrogenation activity appeared to be dependent, to some extent, on the metal content of the catalysts. For example, at 20°C the 5% Pt catalysts gave approximately a five times greater yield than that given by the 1% Pt catalysts. At the higher temperatures, however, Pt/Al_2O_3 showed virtually the same hydrogenation and cracking activity on both the 1% and 5% platinum catalysts. The comparison at 350°C is further complicated by the fact that, except for 1% Pt/SiO_2, the only hydrocarbon products from the first injection were methane and ethane.

The appearance of methane at 350°C is not unexpected in view of the known cracking activity of Pt/Al_2O_3 and $Pt/SiO_2-Al_2O_3$ reforming catalysts at these temperatures.

At 20°C the 5% Pt/Al_2O_3 and 5% Pt/SiO_2 catalysts gave higher ethylene exchange than the 1% Pt/Al_2O_3 and 1% Pt/SiO_2 catalysts as judged by the specific activities of ethylene obtained. Above this temperature ethylene had a similar specific activity on both alumina-supported catalysts although 5% Pt/SiO_2 showed greater exchange activity than did 1% Pt/SiO_2.

The figures for adsorption of ethylene shown in the tables of results were calculated from the difference between the volume injected and the volume recovered as products. Adsorption should strictly be referred to as the volume of hydrocarbon retained on the catalyst, since the ethylene observed to undergo exchange and hydrogenation must have been reversibly adsorbed onto the catalyst surface.

Two other interesting features emerge from these results. First, the extent to which tritium is retained by the catalysts. Taking the experimental error as being at least $\pm 0{\cdot}5 \times 10^6$, the retention values are constant for all the catalysts. They correspond to ~1 and ~·6 hydrogen

TABLE 4.9

EFFECT OF TEMPERATURE ON THE COUNT RATE OF THE REACTOR ELUENT (COUNTS RECORDED x 10^{-4})

Catalyst	20°C 100°C	100°C 200°C	200°C 350°C
5% Pt/Al_2O_3	1·8	15·0	5·9
1% Pt/Al_2O_3	1·7	1·9	7·1
5% Pt/SiO_2	0·5	0·6	1·2
1% Pt/SiO_2	0·3	0·9	0·9

atoms adsorbed per platinum atom for the 5% and 1% platinum catalysts respectively. The second feature is the appearance of peaks on the counter recorder as the catalyst temperature was raised (Table 4.9) indicating the removal of tritiated species from the catalyst. The absence of any peak on the chromatograph, even at its highest sensitivity, indicated that only a small volume of material was being removed. No indication as to the nature of this species could be found under the conditions used in these experiments.

(ii) Ethylene on Tritiated 1% Pt/Al_2O_3 and 1% Pt/SiO_2.

The temperature of the catalyst markedly affects its activity. To study more carefully the effects observed above (Section 4.2(i)), the runs were repeated at $50^{o}C$ intervals over the same temperature range with three injections at each temperature. 1% Pt/Al_2O_3 and 1% Pt/SiO_2 were chosen as examples of each type used previously. Table 4.10 shows the results for the initial injection at each temperature, except for the second column of retention values which refers to the total retention.

TABLE 4.10

ETHYLENE ON TRITIATED 1% Pt/Al_2O_3 and 1% Pt/SiO_2

Catalyst	Catalyst Temp.(°C)	Retention mls.1*	Retention mls.2*	Methane mls.	Methane $c/ml x 10^{-5}$	Ethane mls.	Ethane $c/ml x 10^{-5}$	Ethylene $c/ml x 10^{-5}$
1% Pt/Al_2O_3	20	0·13	0·04	-	-	0·01	>0	0·01
	50	0·0	0·0	-	-	-	-	0·03
	100	0·03	0·03	-	-	0·02	1·67	0·56
	150	0·01	0·01	-	-	0·04	3·81	1·36
	200	0·03	0·03	-	-	0·08	2·91	2·12
	250	0·04	0·04	0·01	2·79	0·15	4·33	2·96
	320	0·07	0·08	0·25	4·00	0·17	4·45	4·33
1% Pt/SiO_2	20	0·11	0·12	-	-	0·02	0·12	0·02
	50	0·00	0·00	-	-	-	-	0·03
	100	0·05	0·05	-	-	0·01	0·12	0·05
	150	0·00	0·00	-	-	0·03	0·15	0·06
	200	0·02	0·02	-	-	0·05	0·25	0·10
	250	0·01	0·01	-	-	0·09	0·20	0·13
	320	0·05	0·05	0·03	0·42	0·19	0·32	0·28

1* Initial retention from 1st injection

2* Total retention

Unless otherwise stated the number of injections at each temperature and the form of the subsequent tables in this section will be the same as that for the experiments in this section.

At 50°C there was no apparent enhancement of the hydrogenation activity or any further ethylene retention although the exchange activity increased slightly over that found at 20°C. At 100°C and above the catalytic activity for each of these processes was enhanced with every temperature increase although the specific activity of ethane remained relatively constant. Below 100°C the behaviour of the two catalysts was virtually identical, although it tended to differ above this temperature.

Apart from the high values obtained previously for the specific activity of ethylene on 1% Pt/Al_2O_3 at 100°C the results for each experiment are of a similar order of magnitude. No methane was produced below 250°C. Only at 320°C on the Pt/Al_2O_3 catalyst did it constitute a major product.

A comparison of the sum of the initial hydrogenation activities on a particular catalyst shows the ethane yield to be greater in this series of experiments than was observed in the previous rum on the same catalyst. Since the time taken to reach a certain temperature would be greater for these experiments, the relatively constant activity at each temperature may mean that a time factor as well as a temperature factor is involved in promoting the catalyst activity for hydrogenation.

The removal of a tritiated species on heating the catalyst was observed for each catalyst. The total counts which are shown in Table 4.11 are also expressed as a percentage of the tritium retained on the catalyst.

(iii) Ethylene on Tritiated 0·1% Pt/Al_2O_3, 0·1% Pt/SiO_2, Al_2O_3 and SiO_2.

From the preceding experiments certain differences in catalytic behaviour have been observed using the same concentration of platinum on either alumina or silica supports. Furthermore, certain processes, particularly ethylene exchange, appeared to be almost independent of the metal concentration.

To investigate these effects further, catalysts with lower metal content, namely 0·1% Pt/Al_2O_3 and 0·1% Pt/SiO_2, were studied under identical conditions to those described previously (section 4.2(i)) for other catalysts at temperatures of 20°C, 50°C, 100°C, 200°C and 350°C. The results are shown in Tables 4.12 and 4.13.

TABLE 4.11

EFFECT OF TEMPERATURE INCREASE UPON THE COUNT-RATE OF THE REACTOR ELUANT

	1% Pt/Al_2O_3		1% Pt/SiO_2	
	Count$\times10^{-5}$	%	Count$\times10^{-5}$	%
20°C → 50°C	0·005	(0·006)	(0·004)	(0·007)
50°C → 100°C	0·10	0·10	0·02	0·03
100°C → 150°C	0·25	0·27	(0·005)	0·01
150°C → 200°C	0·29	0·31	0·02	0·03
200°C → 250°C	0·36	0·38	0·02	0·03
250°C → 320°C	0·74	0·86	0·04	0·06

Apart from the ethane yield at 20°C and 200°C on 0·1% Pt/SiO_2 the extent of retention and hydrogenation of ethylene appeared to be less on these catalysts than on the 1% Pt catalysts. The exchange activity was of a similar order of magnitude on both alumina-supported catalysts. On the silica catalysts, however, a slight increase was noticed on 0·1% Pt/SiO_2 compared to 1% Pt/SiO_2.

The metal concentration thus seems to be a factor in determining the retention and hydrogenation activity although it appears to have no direct effect on the exchange activity.

The same series of reactions was repeated using the same weights of the supports themselves. Alumina and silica were treated in a similar manner to the platinum catalysts except that, of course, no chloro-platinic acid solution was added to a slurry of the support. From these experiments any activity of the supports towards ethylene could be determined. The results are also shown in Tables 4.12 and 4.13.

Apart from slight ethylene retention at 50°C, 200°C and 350°C silica appeared to be inert at all temperatures, as also did alumina up to 200°C. At this temperature slight exchange activity was observed with the alumina and this increased at 350°C where traces of methane and ethane were also observed.

TABLE 4.12

ETHYLENE ON 0·1% Pt/Al_2O_3, 0·1% Pt/Al_2O_3, Al_2O_3 and SiO_2

Catalyst	Catalyst Temp.(°C)	Retention mls.$_1$	Retention mls.$_2$	Methane mls.	Methane c/mlx10^{-5}	Ethane mls.	Ethane c/mlx10^{-5}	Ethylene c/mlx10^{-5}
0·1% Pt/Al_2O_3	20	0·02	0·03	-	-	-	-	0·01
	50	0·07	0·07	-	-	-	-	0·03
	100	0·06	0·06	-	-	-	-	0·06
	200	0·07	0·07	-	-	0·01	(5·6)	1·52
	350	0·07	0·07	(0·02)		0·10	7·22	4·41
0·1% Pt/SiO_2	20	0·06	0·06	-	-	0·05	0·71	0·34
	50	0·03	0·03	-	-	-	-	0·33
	100	-	-	-	-	-	-	0·23
	200	0·07	0·08	-	-	0·08	0·31	1·25
	350	0·04	0·06	0·03	4·80	0·23	2·58	1·68
Al_2O_3	20	-	-	-	-	-	-	-
	50	0·03	0·03	-	-	-	-	-
	100	0·04	0·04	-	-	-	-	-
	200	0·03	0·03	-	-	-	-	0·04
	350	0·03	0·05	>0·0		>0·0		0·40
SiO_2	20	-	-	-	-	-	-	-
	50	0·02	0·02	-	-	-	-	-
	100	-	-	-	-	-	-	-
	200	(0·02)	(0·02)	-	-	-	-	-
	350	(0·02)	(0·02)	>0·0		-	-	-

TABLE 4.13

THE EFFECT OF TEMPERATURE INCREASE UPON THE COUNT-RATE OF THE REACTOR ELUANT

	0·1% Pt/Al_2O_3		0·1% Pt/SiO_2	
	Countx10^{-5}	%	Countx10^{-5}	%
20°C → 50°C	0·02	0·02	0·02	0·02
50°C → 100°C	0·02	0·03	0·06	0·07
100°C → 200°C	0·87	1·00	0·44	0·47
200°C → 350°C	0·23	0·25	0·10	0·11

	Al_2O_3		SiO_2	
	Countx10^{-5}	%	Countx10^{-5}	%
20°C → 50°C	-	-	-	-
50°C → 100°C	-	-	-	-
100°C → 200°C	-	-	-	-
200°C → 350°C	0·04	0·04	-	-

No tritiated species were removed from the supports on heating except with alumina in the range 200°C - 350°C. This result contrasts markedly with the behaviour of 0·1% Pt catalysts where, for every temperature increase, a tritiated species was removed, though it tended to be greater on the 0·1% Pt/Al_2O_3 than on 0·1% Pt/SiO_2.

The results from these experiments are shown in the summary tables (Tables 4.14 and 4.15).

Section 4.3 ^{14}C-Ethylene on Platinum Catalysts

Following the observation that tritiated species were removed from the catalyst as the temperature was raised, an attempt has been made to determine if these species originated from retained ethylene. ^{14}C-ethylene was used in these experiments. The reactivity of the retained ethylene towards gas phase ethylene, termed molecular exchange, has been investigated.

1% Pt/Al_2O_3 and 1% Pt/SiO_2 were chosen for these studies and were pretreated exactly as before (Section 4.2(i)) except that the tritium exchange procedure at the end of the reduction period was omitted.

TABLE 4.14

COMPARISON OF RESULTS ON PLATINUM-ALUMINA CATALYSTS

Catalyst Temp.(^{o}C)	5% Pt/Al$_2$O$_3$	1% Pt/Al$_2$O$_3$	0·1% Pt/Al$_2$O$_3$	Al$_2$O$_3$
Retention (ml.)				
20	0·36	0·13	0·03	-
50	0·02	0·0	0·07	0·03
100	0·12	0·04	0·06	0·04
200	0·18	0·12	0·07	0·03
350	0·34	0·11	0·07	0·05
Methane (ml.)				
20	-	-	-	-
50	-	-	-	-
100	-	-	-	-
200	0·01	-	-	-
350	0·27	0·25	(0·02)	(>0)
Ethane (ml.)				
20	0·06	0·01	-	-
50	-	0·0	-	-
100	0·07	0·04	-	-
200	0·14	0·12	(0·01)	-
350	0·11	0·15	0·10	(>0)
Methane (c/ml.x10^{-5})				
350	(4)	(4)	(20)	-
Ethane (c/ml.x10^{-5})				
20	0·10	(0·10)	-	-
50	-	-	-	-
100	2·85	4·71	-	-
200	5·19	3·70	-	-
350	7·50	4·02	(7·2)	-
Ethylene (c/ml.x10^{-5})				
20	0·04	0·01	0·01	-
50	1·27	0·03	0·03	-
100	2·35	1·50	0·06	-
200	5·05	3·25	1·52	0·04
350	(3·8)	(3·5)	4·41	0·40

cont'd.

Table 4.14 (cont'd.)

Catalyst Temp.(°C)	5% Pt/Al_2O_3	1% Pt/Al_2O_3	0·1% Pt/Al_2O_3	Al_2O_3
Temperature Increase				
20 → 50	0·18	0·01	0·02	–
50 → 100	0·34	0·10	0·02	–
100 → 200	2·20	0·19	0·87	–
200 → 350	0·60	0·71	0·23	0·04

TABLE 4.15

COMPARISON ON RESULTS ON PLATINUM-SILICA CATALYSTS

Catalyst Temp.(°C)	5% Pt/SiO_2	1% Pt/SiO_2	0·1% Pt/SiO_2	SiO_2
Retention (ml.)				
20	0·26	0·14	0·06	-
50	-	-	0·03	0·02
100	0·24	0·02	-	-
200	0·17	0·05	0·07	(0·02)
350	0·28	0·18	0·04	(0·02)
Methane (ml.)				
20	-	-	-	-
50	-	-	-	-
100	-	-	-	-
200	-	-	-	-
350	0·22	0·04	0·03	(>0)
Ethane (ml.)				
20	0·06	0·01	0·05	-
50	-	-	-	-
100	0·04	0·02	-	-
200	0·12	0·04	0·08	-
350	0·22	0·25	0·23	-
Methane (c/ml.x10^{-5})				
350	(2·1)	(1·6)	(4·8)	-
Ethane (c/ml.x10^{-5})				
20	0·08	0·12	0·71	-
50	-	-	-	-
100	0·64	0·25	-	-
200	1·33	0·26	0·31	-
350	1·36	1·20	2·58	-
Ethylene (c/ml.x10^{-5})				
20	0·03	0·02	0·34	-
50	-	0·03	0·33	-
100	0·06	0·10	0·23	-
200	1·12	0·10	1·25	-
350	(1·10)	0·98	1·68	-
Temperature Increase				
20 → 50	0·05	0·01	0·02	-
50 → 100		0·02	0·06	-
100 → 200	0·06	0·09	0·44	-
200 → 350	0·12	0·09	0·10	-

^{14}C-ethylene (0·15 ml.) was injected onto the catalysts at 20°C until no further retention was observed. Usually two injections were necessary. The reactivity of the retained ethylene towards gaseous ethylene was then studied by injecting 0·5 ml. of inactive ethylene onto the ^{14}C-ethylene precovered catalyst and determining the radioactivity of the products. The injections of inactive ethylene were continued until no further exchange was observed to occur. Further ^{14}C-ethylene injections were then made until the specific activity of the ethylene eluted from the reactor was that of the initial calibration value. The temperature of the catalyst was then raised to 100°C. During this time the eluant gas was monitored on the chromatograph and counter. The process was repeated at 100°C, 200°C and 350°C and the results are shown in Table 4.16.

From the calibration runs (see Section 3.4) it was shown that the total count was proportional to the volume for a sample of ^{14}C-ethylene. The specific activity of calibration samples of ^{14}C-ethylene was known. From these figures any counts observed in 'inactive' samples could thus be converted into the volume of active ethylene and hence the extent of molecular exchange could be calculated. The exchange figures expressed as the percentage of retained ^{14}C-ethylene are shown in Table 4.17.

TABLE 4.16(a)

ETHYLENE EXCHANGE WITH ETHYLENE RESIDUES ON 1% Pt/Al_2O_3

Temp.(°C)	Injection	Retention (mls.)	Methane mls.	Methane $c/ml \times 10^{-5}$	Ethane mls.	Ethane $c/ml \times 10^{-5}$	Ethylene mls.	Ethylene $c/ml \times 10^{-5}$
20	$^{14}C_2H_4$	0·12	-	-	0·01	0·12	0·37	0·12
	C_2H_4	-	-	-	-	-	0·50	0·01
100	$^{14}C_2H_4$	0·08	-	-	0·04	0·08	0·38	0·11
	C_2H_4	-	-	-	-	-	0·50	<0·01
200	$^{14}C_2H_4$	0·15	-	-	0·12	0·08	0·27	0·10
	C_2H_4	-	-	-	0·03	0·01	0·47	-
350	$^{14}C_2H_4$	0·16	0·18	0·08	0·12	0·09	0·10	0·10
	C_2H_4	0·02	0·12	0·02	0·15	0·01	0·21	0·01

TABLE 4.16(b)

ETHYLENE EXCHANGE WITH ETHYLENE RESIDUES ON 1% Pt/SiO_2

Temp.(°C)	Injection	Retention (mls.)	Methane mls.	Methane $c/ml\times10^{-5}$	Ethane mls.	Ethane $c/ml\times10^{-5}$	Ethylene mls.	Ethylene $c/ml\times10^{-5}$
20	$^{14}C_2H_4$	0·04	–	–	0·03	0·17	0·43	0·17
	C_2H_4	–	–	–	–	–	0·50	>0
100	$^{14}C_2H_4$	0·04	–	–	0·01	0·15	0·45	0·17
	C_2H_4	–	–	–	–	–	0·50	~0·0
200	$^{14}C_2H_4$	0·24	–	–	0·03	0·12	0·23	0·16
	C_2H_4	–	–	–	<0·01	0·04	0·50	>0·0
300	$^{14}C_2H_4$	0·25	0·02	–	0·08	0·09	0·21	0·14
	C_2H_4	0·03	0·01	0·04	0·06	–	0·40	–

TABLE 4.17

EXCHANGE OF RETAINED ETHYLENE

		20°C		100°C		200°C		350°C	
		mls.	%	mls.	%	mls.	%	mls.	%
1% Pt/Al_2O_3	IN	0·01	8·3	<0·001	0·5	<0·001	0·3	0·05	10
	TOTAL	0·02	16·6	<0·001	0·5	<0·001	0·3	0·05	10
1% Pt/SiO_2	IN	0·005	4	–	–	<0·001	0·03	<0·001	0·2
	TOTAL	0·005	4	–	–	<0·001	0·3	<0·001	0·2

The fraction of retained ethylene undergoing molecular exchange, though low on both catalysts, was greater on 1% Pt/Al_2O_3 at every temperature and was usually complete after the first injection of inactive ethylene. At 200°C the exchange appeared mostly in the ethane product and at 350°C in the methane. A maximum of 20% of the retained ethylene is in a form on the surface capable of undergoing molecular exchange with gaseous ethylene; the majority of the exchanged material appeared as ethane.

Varying total counts, converted into volumes (mls.), recorded for each temperature rise showed that some of the ethylene residues were removed as the temperature was raised. Larger volumes of carbon containing species were removed from 1% Pt/Al_2O_3 than from 1% Pt/SiO_2 (Table 4.18).

There is a correlation between the experiments involving the use of tritium and those in which ^{14}C-ethylene was used in the sense that in both cases more of the radioactive species was removed from the alumina catalysts than from the silica catalysts.

There is, therefore, ethylene retained on the catalyst surface in a form which will not undergo molecular exchange but which can be removed by raising the catalyst temperature. The ethylene removed is readily replaced by further

TABLE 4.18

EFFECT OF TEMPERATURE UPON THE COUNT RATE OF THE REACTOR ELUANT.

	20°C → 100°C			100°C → 200°C			200°C → 350°C		
Catalyst	$cx10^{-4}$	mls.	%	$cx10^{-4}$	mls.	%	$cx10^{-4}$	mls.	%
1% Pt/Al_2O_3	0·03	0·02	16	0·04	0·04	25	0·22	0·20	74
1% Pt/SiO_2	(0·007)	(<0·005	(13)	0·02	0·01	13	0·02	0·02	6

adsorption at the higher tempetature. Despite the lower retention on 1% Pt/SiO_2 the retained species appears to be less reactive than that on 1% Pt/Al_2O_3. There still exists, however, a large percentage of retained ethylene which appears inert under the conditions used.

Section 4.4 Hydrogen on Tritiated Platinum Catalysts.

To study further the reactivity of the tritium retained on the catalyst, hydrogen was used under identical conditions to those described for ethylene (Section 4.2). Injections of hydrogen (0·5 ml.) were used in a series of experiments on 1% Pt/Al_2O_3, 0·1% Pt/Al_2O_3, Al_2O_3, 1% Pt/SiO_2, 0·1% Pt/SiO_2 and SiO_2 over the temperature range 20°C to 350°C. The results from these experiments are shown in Table 4.19.

In this section the term 'tritium' will be used to refer to the hydrogen retained on the catalyst and the term 'hydrogen' to refer to the gaseous hydrogen injected at various temperatures.

As described above (see Section 3.5(ii)), the chromatograph detector had a low sensitivity towards hydrogen when helium was used as the carrier gas. It was decided, how-

TABLE 4.19

HYDROGEN ON TRITIATED PLATINUM CATALYSTS

Catalyst Temp.(°C)	1% Pt/Al_2O_3	0·1% Pt/Al_2O_3	Al_2O_3	1% Pt/SiO_2	0·1% Pt/SiO_2	SiO_2
Retention						
20	X	X		X		
50						
100						
200	X	X	X	X	X	X
350			X			
Exchange (initial countsx10^{-5})						
20	0·45	0·63	0·16	0·40	0·45	0·11
50	0·48	0·88	0·26	0·47	0·35	0·09
100	0·64	1·17	0·41	0·41	0·18	0·07
200	0·72	1·46	0·54	0·42	0·35	0·30
350	0·91	1·64	0·84	0·54	0·75	0·45
Exchange (c/ml.x10^{-5} estimated)						
20	1·0	1·4	0·3	0·9	0·9	0·2
50	1·1	1·7	0·6	1·1	0·7	0·2
100	1·4	2·4	0·9	0·9	0·4	0·1
200	1·5	2·9	1·1	0·8	0·7	0·7
350	1·9	3·4	1·8	1·1	1·5	0·9
Temperature Increase (countsx10^{-5})						
20 → 50	0·01	-	-	0·01	-	-
50 → 100	0·11	-	-	0·01	-	-
100 → 200	0·10	-	-	0·01	0·02	-
200 → 350	0·03	0·01	-	0·01	0·01	-

ever, to keep helium as the carrier gas in order to be able to compare the hydrogen results with those obtained using ethylene. Since the carrier gas passed through the catalyst bed the use of a different carrier, for example, nitrogen, would preclude any comparison of results.

Since the volume of hydrogen eluted could not be accurately determined, no values for the hydrogen retention could be obtained. In Table 4.19 the retention of hydrogen is shown to occur only when the radioactivity of a second or subsequent injection at a particular temperature was greater than that recorded for the first injection. When retention was inferred, the specific activity of the product hydrogen was taken as twice the greatest count observed at a particular temperature. In other cases the specific activity was taken to be slightly greater than twice the count observed for the first injection.

Hydrogen exchange with retained tritium occurred on all the catalysts at every temperature. For a given platinum concentration, it tended to be greater on the alumina-supported catalysts than on the silica-supported catalysts.

The thermal desorption of a tritiated species was only significant on the 1% Pt catalysts. On the supports themselves, no tritiated species were removed by increasing the catalyst temperature. The results are quite similar to those obtained on heating catalysts which had been exposed to ethylene. For example, the total number of counts recorded on heating 1% Pt/Al_2O_3 was greater than in the case of 1% Pt/SiO_2 for both the hydrogen and ethylene experiments.

Section 4.5 Ethylene and Hydrogen on Tritiated Catalysts.

Certain similarities and certain differences in the behaviour of ethylene and hydrogen on the various catalysts have been mentioned. It was decided to study how the reactivity of the catalysts towards one component would be affected by the presence of the other component.

In all previous experiments any hydrogen that would easily desorb from the catalyst surface had been removed by the 'helium cleaning'. To study the reactivity of ethylene when a fresh 'store' of hydrogen was available, hydrogen (0·5 ml.) was injected onto the catalyst immediately prior to an injection of ethylene (0·5 ml.) at each temperature.

The reactivity of each component observed under these conditions was compared to that found in a second series of experiments in which 1 ml. of an equimolar mixture of ethylene and hydrogen was injected onto the catalysts.

The catalysts studied in both sets of experiments were 1% Pt/Al_2O_3, 0·1% Pt/Al_2O_3, Al_2O_3, 1% Pt/SiO_2, 0·1% Pt/SiO_2 and SiO_2 at temperatures of 20°C, 100°C, 200°C and 350°C.

The results from these experiments are shown in Table 4.20 for the hydrogen followed by ethylene injections, and in Table 4.21 for the ethylene-hydrogen mixture. The retention of ethylene on the alumina catalysts appeared to be almost unaffected by the pre-injection of hydrogen, although it was substantially lowered by the presence of gaseous hydrogen in the mixture. A marked reduction was found under both conditions on the silica catalysts which gave virtually no ethylene retention from the mixture until 350°C. The low retention values can be related to the high conversion of ethylene to ethane.

All the platinum catalysts showed increased hydrogenation activity under both conditions compared to previous experiments. Alumina, previously inert, displayed some hydrogenation activity at 100°C and above although silica remained inert at every temperature.

TABLE 4.20

HYDROGEN, ETHYLENE MIXTURES ON TRITIATED Pt CATALYSTS

Catalyst Temp.(^{o}C)	1% Pt/Al_2O_3	0·1% Pt/Al_2O_3	Al_2O_3	1% Pt/SiO_2	0·1% Pt/SiO_2	SiO_2
Ethylene Retention (ml.)						
20	0·02	0·01	-	-	-	-
50	0·02	-	-	-	-	-
100	-	0·05	-	-	-	-
200	0·03	0·04	0·05	-	0·04	-
350	0·02	0·02	0·01	0·02	0·01	-
Methane (ml.)						
350	0·33	0·03	-	0·06	0·04	-
Methane (c/ml.x10^{-5})						
350	(4·3)	(7·0)	-	(4·0)	(4·0)	-
Ethane (initial ml.)						
20	0·41	0·33	-	0·48	0·47	-
50	0·43	0·32	-	0·48	0·47	-
100	0·40	0·30	-	0·48	0·48	-
200	0·46	0·33	0·09	0·48	0·46	-
350	0·16	0·35	0·04	0·42	0·45	-
Ethane (maximum ml.)						
20	0·41	0·33	-	0·49	0·49	-
50	0·43	0·33	-	0·49	0·48	-
100	0·40	0·33	-	0·50	0·50	-
200	0·49	0·36	0·09	0·50	0·50	-
350	0·26	0·36	0·04	0·42	0·50	-
Ethane (c/ml.x10^{-5})						
20	0·83	0·41	-	0·42	0·87	-
50	1·14	0·86	-	0·55	1·18	-
100	0·66	1·03	-	0·41	1·18	-
200	0·53	0·85	0·53	0·94	1·59	-
350	4·68	3·06	1·62	4·31	2·53	-
Ethylene (c/ml.x10^{-5})						
20	0·71	0·08	-	-	(1·4)	-
50	1·68	0·21	-	-	(1·3)	-
100	2·13	0·73	-	-	(1·3)	-
200	-	3·26	0·10	-	(2·9)	-
350	-	5·71	0·16	-	-	-

cont'd.

TABLE 4.20 (cont'd.)

Catalyst Temp.(^{o}C)	1% Pt/Al_2O_3	0·1% Pt/Al_2O_3	Al_2O_3	1% Pt/SiO_2	0·1% Pt/SiO_2	SiO_2
Hydrogen (initial count)						
20	-	-	-	-	-	-
50	0·01	-	-	0·02	0·01	-
100	0·01	0·01	0·01	0·06	0·01	-
200	0·10	0·01	0·10	0·14	0·02	0·01
350	(0·30)	(0·2)	0·2	(0·3)	0·2	0·04
Hydrogen (c/ml.x10^{-5} estimated)						
20	-	-	-	-	-	-
50	1·0	-	-	0·6	0·3	-
100	1·0	(0·1)	(0·01)	0·8	0·5	-
200	1·2	0·1	2·4	0·9	1·0	(0·02)
350	(1·5)	3·3	4·8	1·2	(1·0)	0·1
Temperature Increase (count x 10^{-5})						
20 → 50	0·05	-	-	-	-	-
50 → 100	0·35	-	-	0·04	0·04	-
100 → 200	1·84	0·12	-	0·01	0·20	-
200 → 350	0·90	0·09	0·13	0·14	0·28	-

TABLE 4.21

HYDROGEN; ETHYLENE ON TRITIATED Pt CATALYSTS.

Catalyst Temp.(°C)	1% Pt/Al_2O_3	0·1% Pt/Al_2O_3	Al_2O_3	1% Pt/SiO_2	0·1% Pt/SiO_2	SiO_2
Ethylene Retention (ml.)						
20	0·11	0·04	0·02	0·03	0·03	-
50	0·02	0·04	0·03	0·01	0·01	-
100	0·03	0·06	-	-	0·02	-
200	0·07	0·08	-	0·01	0·01	-
350	0·11	0·10	0·02	0·03	0·02	-
Methane (ml.)						
350	0·09	0·03	-	0·01	-	-
Methane ($c/ml.x10^{-5}$)						
350	3·5	-	-	-	-	-
Ethane ml. (initial yield)						
20	0·37	0·08	-	0·09	0·13	-
50	0·48	0·18	-	0·06	0·11	-
100	0·37	0·12	0·03	0·06	0·10	-
200	0·30	0·07	0·09	0·05	0·08	-
350	0·29	0·12	0·01	0·10	0·13	-
Ethane ml. (maximum yield)						
20	0·48	0·20	-	0·09	0·13	-
50	0·48	0·20	-	0·06	0·12	-
100	0·38	0·15	0·03	0·07	0·10	-
200	0·30	0·09	0·09	0·06	0·08	-
350	0·31	0·12	0·01	0·10	0·13	-
Ethane ($c/ml.x10^{-5}$)						
20	1·08	1·41	-	2·39	2·35	-
50	1·22	0·96	-	4·80	2·31	-
100	4·02	3·53	0·30	4·48	2·64	-
200	5·66	3·51	0·41	5·80	2·01	-
350	4·31	5·80	1·12	4·80	4·00	-
Ethylene ($c/ml.x10^{-5}$)						
20	0·90	0·05	-	0·47	0·22	-
50	(1·4)	0·14	-	0·43	0·29	-
100	1·88	1·00	-	0·44	0·45	-
200	2·83	2·03	0·04	0·96	0·69	(<0·01)
350	3·78	4·99	0·05	2·34	1·78	(<0·01)

cont'd.

TABLE 4.21 (cont'd.)

Catalyst Temp.(^{o}C)	1% Pt/Al_2O_3	0·1% Pt/Al_2O_3	Al_2O_3	1% Pt/SiO_2	0·1% Pt/SiO_2	SiO_2
Hydrogen (count x 10^{-5})						
20	0·20	0·37	-	1·02	0·64	-
50	0·09	0·42	0·01	1·03	0·70	-
100	0·14	0·82	0·08	0·84	0·75	(0·01)
200	0·55	0·87	0·26	1·60	0·94	0·01
350	0·51	0·79	0·50	2·24	1·76	0·03
Hydrogen (c/ml.x10^{-5} estimated)						
20	1·5	0·9	-	2·6	1·7	-
50	4·0	1·4	0·02	2·3	1·8	-
100	2·3	2·2	0·16	1·9	1·9	(0·01)
200	2·8	2·1	0·55	3·6	2·2	(0·02)
350	4·0	2·6	1·00	5·6	4·6	(0·06)
Temperature Increase (count x 10^{-5})						
20 → 50	0·02	0·01	-	-	-	-
50 → 100	0·32	0·06	-	0·02	0·01	-
100 → 200	0·15	0·33	-	0·23	0·14	-
200 → 350	0·46	0·16	(0·01)	0·22	0·17	-

Both the initial yield and maximum yield of ethane at each temperature are shown. The former values were often less than the maximum yield due to the retention of ethylene which usually occurred with the first injection. A second factor may also be important, especially in the case of the silica-supported catalysts for the first series of experiments in which a broadening of the ethane peak in the second and subsequent injections implied the possibility of the removal of retained ethylene as ethane by the hydrogen injection.

In contrast to previous experiments in which the hydrogenation activity increased with increasing temperature, the yields of ethane on a particular catalyst under these conditions appeared relatively independent of temperature.

In the first series of experiments the ethane yield on the various catalysts decreased in the order:

$1\%\ Pt/Al_2O_3 > 0{\cdot}1\%\ Pt/Al_2O_3 > 0{\cdot}1\%\ Pt/SiO_2 \gtrsim 1\%\ Pt/SiO_2 \gg Al_2O_3 > SiO_2$

whereas in the second series the order changed to

$0{\cdot}1\%\ Pt/SiO_2 \sim 1\%\ Pt/SiO_2 \gtrsim 1\%\ Pt/Al_2O_3 > 0{\cdot}1\%\ Pt/Al_2O_3 \gg Al_2O_3 > SiO_2$.

Comparison of the specific activities of ethane and ethylene observed during these experiments with values obtained for ethylene alone on the same catalysts are difficult due to the difference in accuracy in each case. In the former, the low yields of ethylene obtained led to lower accuracy in the determination of the specific activities since both the counts and volumes were small compared to the latter experiments. For ethane, where the yields were greater in former experiments, the situation was reversed.

The specific activity of ethane appeared to be greater in the case of preadsorbed hydrogen than for the ethylene-hydrogen mixtures. Both results were, however, greater than in the case of ethylene alone. A sharp increase in the ethane specific activity at 350°C was observed for the ethylene-hydrogen mixtures.

The incorporation of tritium could occur in at least two ways. Firstly, gaseous hydrogen could react with adsorbed ethylene which has undergone exchange, or secondly by the reaction of hydrogen, which has exchanged, with adsorbed ethylene. These effects are probably combined.

There appears to be little difference in the ethylene exchange for the first and second series of experiments except using Al_2O_3 and 0·1% Pt/SiO_2 where the apparent exchange activity was greater in the second series. The presence of hydrogen in both forms appears to enhance the low temperature exchange although at 200°C and at 350°C the specific activity of ethylene appears to be similar for ethylene alone or in the presence of hydrogen.

Methane was, as before, only observed at 350°C. The similar retention times of hydrogen and methane under the conditions used led to a poor resolution of the two peaks. Although the effect was not critical for the volume determinations the counter peaks tended to merge. The yield of methane, compared to that from ethylene alone, was reduced by the pre-injection of hydrogen and enhanced by the presence of gas phase hydrogen. This effect was most noticeable with 1% Pt/Al_2O_3 where the yields, although always greater than on any other catalyst, were reduced from 0·25 ml. in the absence of hydrogen to 0·09 ml. by the pre-injection of hydrogen and increased to 0·33 ml. for the ethylene-hydrogen mixture.

The volume of hydrogen eluted was calculated to be small on most occasions due to the high conversion of ethylene to ethane. The volume was determined to be equal to, or less than, the difference between the volume injected and the volume of ethane produced. From these values the specific activities of hydrogen were calculated.

The hydrogen exchange on the supports alone was lowered at every temperature by the subsequent injection of ethylene and further lowered by the presence of gaseous ethylene in the mixture. For the platinum catalysts, however, the hydrogen exchange was enhanced by the following injection of ethylene although in the mixtures it was restored to the original values for hydrogen alone except at 20°C where no hydrogen exchange was observed.

The removal of a tritiated species was observed under certain conditions for each set of experiments. The supports alone were inert, except Al_2O_3 between 200°C and 350°C. In the case of the ethylene-hydrogen mixture, low values were obtained on all the other catalysts except 1% Pt/Al_2O_3. The highest values were obtained for 1% Pt/Al_2O_3 which also showed the greatest ethylene retention under these conditions.

Section 4.6 Effect of Hydrogen on Retained Ethylene.

It has been established that a small fraction of the retained ethylene will undergo molecular exchange and a small fraction can be removed by heating the catalyst. A large percentage of the retained ethylene, however, appears to be unreactive with respect to either process.

From the high conversion of ethylene, in the hydrogen-ethylene mixtures, to ethane it could be concluded that most of the ethylene was reversibly adsorbed onto the catalyst surface under these conditions. When hydrogen was injected immediately before ethylene the appearance of broad or doublet peaks for the product ethane could imply the removal of adsorbed ethylene as ethane by the hydrogen. It was thus decided to study the reactivity of the retained ethylene towards hydrogen. 1% Pt/Al_2O_3 and 1% Pt/SiO_2 were chosen as typical examples of each type of catalyst.

Ethylene (0·5 ml.) was injected as before onto the tritiated catalysts at 20°C until no further retention was observed. The products from these injections are denoted by prefix (1) in the tables of results. Hydrogen (0·5 ml.) was subsequently injected at the same temperature. The nature of the products was determined from their retention times on the chromatograph.

Except for 1% Pt/Al_2O_3 when a trace of methane was observed, the only product from the hydrogen injections, apart from exchanged hydrogen, was ethane. The removal of any retained hydrocarbon was usually complete after the first injection of hydrogen. In each case, however, three injections of hydrogen were made at each temperature to ensure the complete removal of any reactive retained material. Further injections of ethylene were made at this point until the readsorption of ethylene was complete. The products from these injections are denoted by prefix (2) in the tables of results.

The temperature was then raised to 50°C, and the procedure was repeated at this temperature and subsequently at 100°C, 200°C and 350°C. The results for 1% Pt/Al_2O_3 are shown in Table 4.22 and for 1% Pt/SiO_2 in Table 4.23.

On 1% Pt/Al_2O_3 at 20°C over 90% of the retained ethylene was removed as ethane by the addition of hydrogen. A slightly greater volume of ethylene was subsequently re-adsorbed onto the catalyst.

The hydrogen exchange was lower than that observed previously on the same catalyst for hydrogen alone. The hydrogen effected an increase in the ethane yield from 0·01 mls. to 0·23 mls. and a rise in the specific activities of both ethane and ethylene.

Similar effects were observed on 1% Pt/SiO_2 at 20°C although less ethane, approximately 30%, was removed by the hydrogen despite the similar initial retention value. The subsequent readsorption of ethylene was lower and the increase in ethane yield and specific activities were not so marked as on 1% Pt/Al_2O_3. The hydrogen activity, though lower, was nearer the original values for hydrogen alone.

A similar pattern was found at 50°C and 100°C. Above 100°C, no ethane was removed by hydrogen using 1% Pt/SiO_2 and was lower using 1% Pt/Al_2O_3. No enhancement of the exchange or hydrogenation activity was observed at 200°C or at 350°C.

TABLE 4.22

ETHYLENE, HYDROGEN, ETHYLENE on 1% Pt/Al_2O_2

Temperature (^oC)	20	50	100	200	350
(1) Retention	0·14	0·05	0·04	0·09	0·21
(1) Methane (mls)	-	-	-	(0·01)	0·03
Methane (c/mlx10^{-5})	-	-	-	(4·0)	(1·2)
(1) Ethane (mls)	0·02	-	0·02	0·09	0·33
Ethane c/mlx10^{-5})	0·08	-	1·65	1·87	1·40
(1) Ethylene (c/mlx10^{-5})	0·01	0·09	0·53	1.86	
Hydrogen Count	0·24	0·25	0·35	0·30	0·19
Hydrogen (c/mlx10^{-5})	0·49	0·51	0·70	0·65	0·40
Ethane Removed (mls)	0·13	0·16	0·08	0·01	0·03
Ethane Removed (c/mlx10^{-5})	1·20	1·61	4·58	4·50	
(2) Retention (mls)	0·15	0·15	0·13	0·07	0·16
(2) Methane (mls)	-	-	-	-	0·02
Methane (c/mlx10^{-5})	-	-	-	-	0·87
(2) Ethane (mls)	0·23	0·20	0·09	0·05	0·36
Ethane (c/mlx10^{-5})	1·01	0·45	3·33	1·83	0·68
(2) Ethylene (mls)	0·34	0·14	2·91	1·43	
Temperature Increase (c/mlx10^{-5})		0·01	0·13	0·29	0·10

TABLE 4.23

ETHYLENE, HYDROGEN, ETHYLENE on TRITIATED 1% Pt/SiO_2

Temperature (^oC)	20	50	100	200	350
(1) Retention C_2H_4(mls)	0·15	0·04	0·04	0·03	0·05
(1) Methane (mls)	-	-	-	-	(0·01)
Methane (c/mlx10^{-5})	-	-	-	-	-
(1) Methane (mls)	0·03	-	(0·01)	0·06	0·10
Methane (c/mlx10^{-5})	0·96	-	2·22	2·17	2·21
(1) Ethylene (c/mlx10^{-5})	0·15	0·31	0·41	0·74	1·31
Hydrogen (max. countx10^{-5})	0·31	0·30	0·24	0·32	0·41
Hydrogen (est. c/ml.x10^{-5})	0·62	0·60	0·49	0·64	0·84
Ethane Removed (mls)	0·05	0·06	0·04	-	-
Ethane Removed (c/ml.x10^{-5})	0·56	(6·0)	6·58	-	-
(2) Retention C_2H_4 (mls)	0·09	0·05	0·04	0·01	-
(2) Methane (mls)	-	-	-	-	(0·01)
Methane (c/mlx10^{-5})	-	-	-	-	(2·00)
(2) Ethane (mls)	0·08	0·06	0·05	0·05	0·07
Ethane (c/mlx10^{-5})	1·55	2·20	2·22	1·11	1·54
(2) Ethylene (c/mlx10^{-5})	0·62	0·69	0·48	0·67	0·83
Temperature Increase (counts x 10^{-5})		0·05	0·08	0·15	0·03

The hydrogen treatment suppressed the removal of a tritiated species on 1% Pt/Al_2O_3. It may be that a similar volume was removed but due to the available inactive hydrogen the desorbed species was less highly tritiated.

Section 4.7 Propylene on Tritiated Catalysts.

It has been shown (see Section 4.2) that the reactivity of ethylene is different on various Pt/Al_2O_3 and Pt/SiO_2 catalysts. To investigate if similar effects were common to other hydrocarbons, the reactivity of propylene on the same catalysts was studied using identical conditions.

Propylene (0·5 ml.) was injected onto the catalysts at 20°C until no retention or hydrogenation of propylene was observed. The catalyst temperature was raised to 100°C, during which the reactor eluent was monitored as before. The process was repeated at 100°C, 200°C and 350°C until both the exchange and hydrogenation (i.e. formation of propane) had decreased considerably. The complete results for a typical run using 1% Pt/Al_2O_3, are shown in Table 4.24. The experiment was then repeated using 1% Pt/SiO_2 and at 20°C, 50°C, 100°C, 200°C and 350°C using 0·1% Pt/Al_2O_3, 0·1% Pt/SiO_2, Al_2O_3 and SiO_2. The lower catalytic activity

TABLE 4.24

PROPYLENE ON TRITIATED 1% Pt/Al_2O_3

Temp. (°C)	Injection No.	Retention (mls.)	PROPANE			PROPYLENE		
			mls.	counts	c/ml $x10^{-5}$	mls.	counts	c/ml $x10^{-5}$
20	1	0·07	0·02	330	0·17	0·41	800	0·02
	2	0·07	0·0	-	-	0·43	600	0·01
	3	0·01	-	-	-	0·49	-	-
	4	-	-	-	-	0·50	-	-
100	1	0·07	0·03	23000	7·50	0·40	170400	4·25
	2	-	0·02	6300	3·88	0·48	134000	2·69
	3	-	0·01	2100	2·10	0·49	104500	2·22
	4	-	0·01	1700	1·82	0·49	91050	2·82
	5	-	0·01	950	1·76	0·50	69600	1·39
	6	-	0·01	650	1·31	0·50	55000	1·11
	7	-	0·01	(520)	1·30	0·50	51050	1·02
	8	-	-	(320)	-	0·50	45600	0·91
	9	-	-	(300)	-	0·50	47560	0·96
	10	-	-	(200)	-	0·50	42450	0·85
200	1	0·08	0·18	98000	5·57	0·24	107000	4·44
	2	0·03	0·11	39500	3·76	0·36	107600	3·07
	3	0·01	0·09	20300	2·48	0·41	94700	2·31
	4	-	0·06	10000	1·77	0·44	78300	1·78
	5	-	0·05	7800	1·59	0·45	67050	1·49
	6	-	0·05	6500	1·30	0·45	58050	1·29
	7	-	0·04	3250	0·81	0·46	46450	1·01
	8	-	0·03	2500	0·80	0·46	38650	0·84
	9	-	0·03	2700	0·67	0·47	31500	0·67
	10	-	0·03	1250	0·43	0·48	26880	0·56
350(a)	1	0·02	0·18	54200	3·01	0·02	3050	1·51
	2	-	0·19	38750	2·04	0·13	18600	1·43
	3	-	0·18	23250	1·29	0·20	20900	1·02
	4	-	0·17	15300	0·90	0·23	17700	0·77
	5	-	0·15	9150	0·61	0·26	14050	0·54
	6	-	0·13	5050	0·39	0·31	11450	0·37
	7	-	0·12	3360	0·28	0·32	8650	0·27
	8	-	0·10	1900	0·19	0·35	7000	0·20
	9	-	0·08	1200	0·15	0·38	5500	0·14
	10	-	0·08	900	0·11	0·39	4700	0·12

cont'd.

TABLE 4.24 (cont'd)

Temp. (°C)	Injection No.	METHANE mls.	METHANE counts	METHANE c/ml $\times 10^{-5}$	ETHANE mls.	ETHANE counts	ETHANE c/ml $\times 10^{-5}$
350(b)	1	0·18	28600	1·59	0·11	37850	3·44
	2	0·11	11800	1·07	0·07	16450	2·35
	3	0·07	4500	0·64	0·05	6300	1·26
	4	0·06	2200	0·37	0·04	3200	0·79
	5	0·05	1500	0·30	0·04	1800	0·44
	6	0·03	550	0·16	0·03	850	0·27
	7	0·03	400	0·11	0·03	550	0·19
	8	0·03	(250)	0·09	0·02	300	0·15
	9	0·02	(150)	0·06	0·02	(200)	0·08
	10	0·02	(100)	0·05	0·01	(100)	0·09

of the latter four catalysts meant that both the hydrogenation activity and retention was virtually complete after three injections at each temperature. A summary of the results for the first injection at each temperature is shown in Table 4.25.

At 350°C cracking products were observed with some catalysts. Below this temperature, however, the only products were propane and propylene.

The specific activities of propane and propylene were of a similar order of magnitude to the values found for ethane and ethylene. In the propylene experiments, however, the hydrogenation activity, though similar, tended to decrease more slowly than in the case of the ethylene experiments.

At a particular platinum concentration, similar values were obtained for the retention and hydrogenation of propylene. Further retention and an increase in the hydrogenation activity were observed for each increase in temperature.

A less definite pattern was discernible for the exchange of propylene with catalyst 'hydrogen' (exchange activity). On heating 1% Pt/Al_2O_3 and 1% Pt/SiO_2 from 20°C to 100°C a sharp increase in the exchange activity was observed. At higher temperatures, the activity remained fairly constant whereas a steady increase with temperature was found for

TABLE 4.25

PROPYLENE ON TRITIATED PLATINUM CATALYSTS

Catalyst Temp.(°C)	1% Pt/Al_2O_3	0·1% Pt/Al_2O_3	Al_2O_3	1% Pt/SiO_2	0·1% Pt/SiO_3	SiO_2
Retention (mls.)						
20	0·12	0·06	–	0·13	0·07	–
50		0·01	–		0·01	–
100	0·07	0·05	(0·01)	0·08	0·01	–
200	0·10	0·07	–	0·10	0·03	–
350	0·02	0·02	–	0·05	0·02	–
Methane mls.						
350	0·18	(0·01)	–	0·03	(0·01)	–
Methane (c/mlx10^{-5})						
350	1·59	(0·9)	–	(7·0)	(11)	–
Ethane mls.						
350	0·11	(0·01)	–	0·02	–	–
Ethane (c/mlx10^{-5})						
350	3·44	(7)	–	(6·6)	–	–
Propane (mls.)						
20	0·02	–	–	0·03	–	–
50		–	–		–	–
100	0·03	(0·01)	–	0·04	(>0)	–
200	0·18	0·01	–	0·05	0·01	–
350	0·18	0·07	–	0·10	0·04	–
Propane (c/mlx10^{-5})						
20	0·17	–	–	2·83	–	–
50		–	–		–	–
100	7·50	(0·11)	–	3·85	–	–
200	5·56	0·43	–	4·70	2·48	–
350	3·01	5·07	–	3·90	7·18	–
Propylene (c/mlx10^{-5})						
20	0·02	0·01	–	0·06	0·05	–
50		0·01	–		0·13	–
100	4·25	0·05	–	1·71	0·21	–
200	4·44	1·20	(0·01)	3·30	0·61	–
350	1·61	2·45	0·41	3·05	1·68	0·04
Temperature Increase (countx10^{-5})						
20 → 50	0·08	–	–	0·05	0·02	–
50 → 100		–	–		–	–
100 → 200	0·04	0·01	(0·01)	0·06	0·01	–
200 → 350	0·09	0·20	–	0·16	0·04	–

0·1% Pt/Al_2O_3 and 0·1% Pt/SiO_2. The specific activity of propane tended to be greater than that of propylene except at 200°C with 0·1% Pt/Al_2O_3.

Apart from slight propylene exchange at 350°C, the supports remained virtually inert. In this respect Al_2O_3 appeared to be more active than SiO_2.

On heating, tritiated species were usually removed from the catalysts during each temperature increase. The supports again appeared inert except for Al_2O_3 which gave a small peak on the counter when heated from 100°C to 200°C. Higher values were usually found for the catalyst with the greater concentration of platinum.

Section 4.8 Propylene-Hydrogen Mixtures on Platinum Catalysts.

The reaction of propylene-hydrogen mixtures with 1% Pt/Al_2O_3, 1% Pt/SiO_2, 0·1% Pt/Al_2O_3, 0·1% Pt/SiO_2, Al_2O_3 and SiO_2 were studied in a similar manner to that described for ethylene-hydrogen mixtures (see Section 4.5). Several considerations mentioned there, such as the lower accuracy in determining the specific activities of hydrogen and the olefin also apply to this set of experiments.

TABLE 4.26

PROPYLENE-HYDROGEN MIXTURES ON TRITIATED CATALYSTS

Catalyst Temp.(°C)	1% Pt/Al_2O_3	0·1% Pt/Al_2O_3	Al_2O_3	1% Pt/SiO_2	0·1% Pt/SiO_2	SiO_2
Retention (mls.)						
20	0·03	-	-	0·10	0·02	-
50	-	-	-	0·02	0·02	-
100	-	-	-	-	-	-
200	-	-	-	-	0·06	-
350	0·01	-	-	0·01	0·01	-
Methane (mls.)						
200	0·08	-	-	-	-	-
350	0·26	0·04	-	0·04	0·14	-
Methane (c/ml$\times10^{-5}$)						
200	5·06	-	-	-	-	-
350	2·90	(7)	-	(10)	(7)	-
Ethane (mls.)						
200	0·10	-	-	-	-	-
350	0·09	0·02	-	0·03	0·07	-
Ethane (c/ml$\times10^{-5}$)						
200	7·00	-	-	-	-	-
350	4·83	(9)	-	(11)	(9)	-
Propane (initial mls.)						
20	0·49	0·50	-	0·36	0·48	-
50	0·50	0·50	-	0·35	0·48	-
100	0·50	0·50	-	0·42	0·50	-
200	0·32	0·50	0·03	0·44	0·44	-
350	0·13	0·44	>0·0	0·40	0·28	-
Propane (maximum mls.)						
20	0·50	0·50	-	0·44	0·48	-
50	0·50	0·50	-	0·45	0·50	-
100	0·50	0·50	-	0·44	0·50	-
200	0·45	0·50	0·03	0·44	0·49	-
350	0·40	0·45	>0·0	0·40	0·40	-
Propane (c/ml$\times10^{-5}$)						
20	1·55	0·41	-	1·87	0·76	-
50	2·24	1·33	-	1·40	1·23	-
100	2·67	2·13	-	1·38	0·96	-
200	5·10	4·52	0·33	1·67	2·45	-
350	6·02	3·09	-	3·09	3·42	-

cont'd.

TABLE 4.26 (cont'd)

Catalyst Temp.(^{o}C)	1% Pt/Al_2O_3	0·1% Pt/Al_2O_3	Al_2O_3	1% Pt/SiO_2	0·1% Pt/SiO_2	SiO_2
Propylene (c/mlx10^{-5})						
20			-	3·12		-
50			-	1·89		-
100			-	3·19	3·33	-
200			0·05	5·25		-
350			0·68	9·5		0·05
Hydrogen (initial count x 10^{-5})						
20	-	0·01	-	-	0·01	-
50	-	0·03	-	-	-	-
100	-	0·03	-	-	-	-
200	-	-	0·03	-	0·40	0·01
350	-	-	0·32	-	-	0·01
Hydrogen (c/mlx10^{-5})						
20	-	-	-	-	0·25	-
50	-	-	-	-	0·20	-
100	-		-	-	-	-
200	-	-	0·07	-	3·5	0·02
350	-	-	0·65	-	-	0·02
Temperature Increase (countsx10^{-5})						
20 → 50	0·10	-	-	-	-	-
50 → 100	0·15	-	-	0·05	-	-
100 → 200	0·05	-	-	0·07	0·30	-
200 → 350	0·21	0·05	-	0·20	2·52	-

Injections (1 ml.) of an equimolar mixture of propylene and hydrogen were made over the catalysts at 20°C, 50°C, 100°C, 200°C and 350°C. The reactor eluant was monitored during the heating of the catalyst from one temperature to the next higher one. The results, shown in Table 4.26, apply to the first injection at each temperature apart from the figures given for the maximum yield of propane at each temperature.

The retention of propylene was much lower than in the experiments with propylene alone. This fact could be related to the high yield of hydrogenation products from the propylene-hydrogen mixtures, the conversion propylene to propane being complete in some cases.

The maximum yield of propane on each catalyst tended to be independent of temperature. For the alumina-supported catalysts a steady increase in the specific activity of the propane with increasing temperature was found whereas it was more variable in the case of the silica-supported catalysts. There appears to be no direct correlation between these values and the specific activities of the propane produced from propylene in the absence of hydrogen although the values tended to be higher for the propylene-hydrogen mixtures.

The low yields of hydrogen and propylene precluded any accurate comparison being made between the specific activities found for them in these experiments and previous values obtained for each component separately. Propylene, when observed, tended to have a higher specific activity when propylene-hydrogen mixtures were used than when propylene alone was used.

The presence of hydrogen did appear to enhance the cracking activity of all the platinum catalysts. On 1% Pt/Al_2O_3 both methane and ethane were produced at 200°C and were observed on all the platinum catalysts at 350°C. The yield of methane was always greater than the yield of ethane.

The supports themselves remained inert up to 200°C. At this temperature slight hydrogenation and propylene exchange occurred with Al_2O_3. At 350°C propylene exchange was greater over Al_2O_3 than SiO_2. The presence of propylene seemed to suppress the hydrogen exchange.

Despite the low retention values for propylene, the thermal desorption of a tritiated species was observed in several cases. Apart from 0·1% Pt/Al_2O_3, the values observed in the temperature range 200°C to 350°C were greater than for propylene alone. The particularly high value for 0·1% Pt/SiO_2 may be related to the relatively high retention of propylene at 200°C.

Section 4.9

(i) C^{14}-Propylene on Platinum Catalysts.

To determine the reactivity of retained propylene towards gaseous propylene and to find out if any hydrocarbon residues were thermally desorbed on heating the catalysts, 1% Pt/Al_2O_3 and 1% Pt/SiO_2 were studied using ^{14}C-propylene. The reaction conditions were identical to those used for the ^{14}C-ethylene experiments (see Section 4.3).

With the catalysts at 20°C, ^{14}C-propylene (0·5 ml.) was injected onto the catalyst until no further retention was observed. Injections of inactive propylene were then made until no radio-activity was recorded in any of the products. The exchange was usually complete after two injections. A further couple of ^{14}C-propylene injections were made at this temperature after which the temperature was slowly raised to 100°C. The process was repeated at 100°C, 200°C and 350°C.

The results in Tables 4.27A and 4.27B show the products from the first injection of ^{14}C-propylene and the first injection of inactive propylene at each temperature. The counts recorded have been converted into specific activities. The total ^{14}carbon content for the initial injection of inactive propylene and the sum of the values from each injection at every temperature have been converted into volumes and expressed in Table 4.28 as a percentage of the retained ^{14}C-propylene.

TABLE 4.27A

PROPYLENE EXCHANGE WITH PROPYLENE RESIDUES 1% Pt/Al_2O_3

Catalyst		Retention	Cracking Products		Propane		Propylene	
Temp.(°C)	Injection	(mls.)	(mls.)	(c/mlx10^{-5})	(mls.)	(c/mlx10^{-5})	(mls.)	(c/mlx10^{-5})
20	$^{14}C_2H_6$	0·12	–	–	0·05	0·62	0·39	0·59
	C_3H_6	–	–	–	–	–	0·50	0·05
100	$^{14}C_3H_6$	0·06	–	–	0·05	0·59	0·39	0·59
	C_3H_6	–	–	–	–	–	0·50	0·02
200	$^{14}C_3H_6$	0·08	<0·01	(0·6)	0·15	0·61	0·26	0·62
	C_3H_6	–	–	–	0·05	0·15	0·45	0·03
350	$^{14}C_3H_6$	0·08	0·06	0·62	0·25	0·55	0·11	0·64
	C_3H_6	–	0·03	0·18	0·15	0·02	0·29	0·03

TABLE 4.27B

PROPYLENE EXCHANGE WITH PROPYLENE RESIDUES 1% Pt/SiO_2

Catalyst Temp.(^{o}C)	Injection	Retention (mls.)	Cracking Products (mls.)	Cracking Products ($c/ml\times10^{-5}$)	Propane (mls.)	Propane ($c/ml\times10^{-5}$)	Propylene (mls.)	Propylene ($c/ml\times10^{-5}$)
20	$^{14}C_3H_6$	0·12	–	–	0·03	0·61	0·38	0·61
	C_3H_6	–	–	–	–	–	0·50	(0·01)
100	$^{14}C_3H_6$	0·06	–	–	0·04	0·60	0·48	0·60
	C_3H_6	–	–	–	~0	(0·06)	0·49	0·04
200	$^{14}C_3H_6$	0·12	–	–	0·05	0·60	0·33	0·60
	C_3H_6	–	–	–	0·02	0·06	0·48	0·10
350	$^{14}C_3H_6$	0·07	0·06	0·58	0·12	0·61	0·25	0·61
	C_3H_6	–	0·03	0·10	0·06	0·02	0·41	0·01

TABLE 4.28

EXCHANGE OF RETAINED PROPYLENE

		20°C		100°C		200°C		350°C	
		mls.	%	mls.	%	mls.	%	mls.	%
1% Pt/Al_2O_3	Initial	0·04	33	0·02	18	0·02	12	0·02	10
	Total	0·07	58	0·03	27	0·03	18	0·04	20
1% Pt/SiO_2	Initial	(0·005)	4	0·01	7	0·01	4	(0·02)	7
	Total	(0·007)	6	0·03	20	0·02	8	0·02	8

As the temperature was raised, the fraction of retained propylene undergoing molecular exchange on 1% Pt/Al_2O_3 appeared to decrease although the volume exchanging remained relatively constant. These values were usually higher than those observed with 1% Pt/SiO_2.

The specific activity of propane from inactive propylene tended to be greater than that of propylene itself. At 350°C the cracking products had the highest specific activity. The cracking products, methane, ethane and ethylene have been included together since their resolution was poor and a joint specific activity was more accurately determined than that of the individual components.

At each temperature increase the counts recorded implied the removal of ^{14}carbon residues from the catalyst. The counts were converted into volumes and expressed as a percentage of the retained ^{14}C-propylene in Table 4.29.

A larger volume was removed from the 1% Pt/Al_2O_3 than the 1% Pt/SiO_2 catalyst. This is in agreement with the results obtained for propylene on tritiated catalysts, where the same phenomenon was found.

In a similar manner to retained ethylene, some of the retained propylene not undergoing molecular exchange could be removed from the catalyst by increasing the temperature.

TABLE 4.29

THERMAL DESORPTION OF ^{14}C SPECIES

	$20^\circ C \rightarrow 100^\circ C$			$100^\circ C \rightarrow 200^\circ C$			$200^\circ C \rightarrow 350^\circ C$		
	Count$\times 10^{-5}$	mls.	%	Count$\times 10^{-5}$	mls.	%	Count$\times 10^{-5}$	mls.	%
1% Pt/Al_2O_3	0·01	0·02	33	0·02	0·03	50	0·03	0·04	50
1% Pt/SiO_2	(0·01)	0·01	10	0·01	0·02	12	0·01	0·02	10

However, a higher percentage of the retained propylene was found to be reactive in molecular exchange than was observed for retained ethylene on the same catalysts, under identical conditions.

(ii) The Reaction of Propylene Residues with Ethylene.

The reaction of retained propylene towards gaseous ethylene on 1% Pt/Al_2O_3 has been investigated. The experimental conditions and procedure were the same as those described in the previous section except that ethylene was used instead of inactive propylene. The results are shown in Table 4.30.

After the retention of propylene was complete, further retention of ethylene occurred at every temperature. Above 20°C, the volume of propylene retained on the catalyst was less than that observed during the experiments in which only propylene was studied. The retention of ethylene, though still present after the surface was saturated with propylene, was less than for ethylene alone.

The initial hydrogenation of propylene to propane was similar at every temperature, except 200°C, to that found when no preadsorbed ethylene was present (see Section 4.7). No ethylene hydrogenation was observed

TABLE 4.30

REACTION ON PROPYLENE RESIDUES WITH ETHYLENE

	20		100		200		350	
	$^{14}C_3H_6$	C_2H_4	$^{14}C_3H_6$	C_2H_4	$^{14}C_3H_4$	C_2H_4	$^{14}C_3H_6$	C_2H_4
Retention (mls.)	0·10	0·05	0·06	0·02	0·01	0·02	0·07	-
Methane (mls.)	-	-	-	-	-	-	0·04	0·02
(c/mlx10^{-5})	-	-	-	-	-	-	0·20	0·01
Ethane (mls.)	-	-	-	-	-	0·05	0·03	0·29
(c/mlx10^{-5})	-	-	-	-	-	-	0·20	-
Ethylene (mls.)	-	0·45	-	0·48	-	0·42	-	0·19
(c/mlx10^{-5})	-	-	-	-	-	-	-	-
Propane (mls.)	0·02	-	0·02	-	0·07	-	0·19	-
(c/mlx10^{-5})	0·39	-	0·40	-	0·38	-	0·39	-
Propylene (mls.)	0·38	-	0·38	-	0·42	-	0·17	>0
(c/mlx10^{-5})	0·36	>0	0·40	>0	0·35	-	0·39	>0
mls. $^{14}C_3H_6$ removed								
(i) by C_2H_4		0·01		(0·01)		-		0·02
(ii) by temperature increase		0·02		0·01		0·01		

below 200°C. This is not unexpected as little or no hydrogenation activity was originally observed after the third injection of either propylene or ethylene. The yield of ethane at 200°C and the total yield of methane and ethane at 350°C were less than when ethylene alone was used.

The cracking of propylene at 350°C appeared to be suppressed by the presence of adsorbed ethylene.

No evidence of propylene removal was found on the chromatograph recorder although small peaks were observed on the counter recorder. The counts from the latter were converted into volumes and are shown in the table of results.

The counts recorded for each increase in temperature were lower than in the previous experiments when no ethylene was present.

Section 4.10 Effect of Preadsorbed Oxygen.

Oxygen is known to adsorb very strongly on most metal catalyst surfaces and therefore to act as a poison for the reaction of hydrocarbons. The effect of preadsorbed oxygen upon the activity of 1% Pt/Al_2O_3 and 0·1% Pt/Al_2O_3 towards the adsorption and reactivity of propylene was investigated.

The catalysts were treated with oxygen (2 ml.) immediately after the tritium exchange period. This volume was chosen since it was far in excess of the value required to give a monolayer coverage of oxygen atoms on the metal surface of either catalyst. Except for the oxygen pretreatment, the experimental procedure was exactly the same as described previously for propylene (see Section 4.7).

From the results shown in Table 4.31, a comparison of the reactivity of propylene on the oxygenated and oxygen-free catalysts can be drawn. The retention at 20°C was enhanced by the presence of oxygen with 1% Pt/Al_2O_3 although no effect was observed with 0·1% Pt/Al_2O_3. At the higher temperatures, especially 200°C, however, the retention was lower on the oxygenated catalysts. The presence of oxygen suppressed both the hydrogenation and cracking activity for 1% Pt/Al_2O_3 whereas only the cracking activity was affected for 0·1% Pt/Al_2O_3. The exchange activity appeared to be similar or slightly enhanced by the presence of preadsorbed oxygen.

The total counts observed in the reactor eluant on heating the catalyst were similar with 0·1% Pt/Al_2O_3 to those found previously (see Section 4.7) in the absence of oxygen. With 1% Pt/Al_2O_3, however, they were lower than the previous values up to 100°C, and greater than the previous values at temperatures above 100°C.

TABLE 4.31

PROPYLENE ON OXYGEN TREATED PLATINUM CATALYSTS

	Catalyst Temperature (^{o}C)	1% Pt/Al_2O_3	0·1% Pt/Al_2O_3
Retention (mls.)	20	0·28	0·06
	50	-	-
	100	0·08	0·07
	200	-	0·04
	350	0·08	0·08
Propane (mls.)	20	>0	-
	50	>0	>0
	100	>0	0·01
	200	0·15	0·02
	350	0·27	0·08
Propane ($c/ml x 10^{-5}$)	20	-	-
	50	-	-
	100	-	0·12
	200	4·80	6·04
	350	4·92	7·44
Propylene ($c/ml x 10^{-5}$)	20	0·02	0·02
	50	-	-
	100	0·52	0·15
	200	0·57	2·45
	350	5·52	3·33
Methane (mls.)	350	0·08	>0
($c/ml x 10^{-5}$)	350	2·25	(5)
Ethane (mls.)	200	(0·01)	-
	350	0·06	>0
($c/ml x 10^{-5}$)	200	(7·5)	-
	350	5·42	(10)
Temperature Increase ($count x 10^{-5}$)	20 50	-	-
	50 100	0·01	0·01
	100 200	0·53	0·01
	200 350	0·82	0·11

Section 4.11 Acetylene on Tritiated Platinum Catalysts.

The reactions of acetylene on tritiated 5% Pt/Al_2O_3, 1% Pt/Al_2O_3, 0·1% Pt/Al_2O_3, Al_2O_3, 1% Pt/SiO_2, 0·1% Pt/SiO_2 and SiO_2 catalysts have been studied using similar conditions to those described for propylene (see Section 4.7).

At 20°C, samples of acetylene (0·5 ml.) were injected onto the catalysts until no further retention was observed. The catalyst temperature was then increased to 50°C during which time the reactor eluant was monitored. The process was repeated at 50°C, 100°C, 200°C and 350°C for all the catalysts except 5% Pt/Al_2O_3 which was only studied at 20°C, 100°C and 350°C. The results are shown in Table 4.32.

The most striking feature of these results is the high volume of acetylene retained compared to the values observed for ethylene and propylene under similar conditions. For example, using 1% Pt/Al_2O_3, 0·74 ml. of acetylene were retained at 20°C compared with only 0·12 ml. of ethylene and 0·15 ml. of propylene. Since the retention was often not complete until the third injection, both the initial and the total retention volumes at each temperature are shown in the table of results.

TABLE 4.32

ACETYLENE ON TRITIATED CATALYSTS

Catalyst Temp(°C)	5% Pt/Al_2O_3	1% Pt/Al_2O_3	0·1% Pt/Al_2O_3	Al_2O_3	1% Pt/SiO_2	0·1% Pt/SiO_2	SiO_2
Initial Retention (mls.)							
20	0·49	0·39	0·15	0·06	0·17	0·02	0·12
50		0·17	-	-	-	0·04	-
100	0·41	0·11	-	-	0·03	0·03	-
200		0·37	0·07	0·01	0·03	0·03	-
350	0·16	0·35	0·16	0·18	0·18	0·12	-
Total Retention (mls.)							
20	0·95	0·74	0·21	0·06	0·19	0·03	0·12
50		0·34	-	-	-	0·05	-
100	0·54	0·11	-	-	0·04	0·04	-
200		0·65	0·07	0·01	0·03	0·04	-
350	1·36	0·95	0·48	0·34	0·19	0·17	-
Acetylene (c/mlx10^{-5})							
20	0·07	0·40	0·33	0·04	0·02	0·03	-
50		0·24	0·26	-	0·01	0·06	-
100	0·52	0·48	0·29	-	0·27	0·12	-
200		1·57	0·49	-	0·25	0·05	-
350	0·65	(6·0)	(2·0)	0·12	0·63	0·33	-
Methane (mls.)							
200	-	>0	-	-	-	-	-
350	0·19	>0	>0	>0	>0	-	-
Methane (c/mlx10^{-5})							
200	-	>B	-	-	-	-	-
350	3·52	>B	-	-	-	-	-
Ethane (mls.)							
20	0·02	>0	-	-	-	-	-
50		-	-	-	-	-	-
100	0·02	>0	-	-	>0	-	0·01
200		0·02	0·01	-	0·01	0	-
350	0·04	0·03	0·02	-	0·02	0	-
Ethane (c/mlx10^{-5})							
20	0·23	>B	-	-	-	-	-
50		-	-	-	-	-	-
100	0·02	>B	-	-	-	-	-
200		0·45	(0·4)	-	(1·0)	>B	-
350	(6·0)	(6·4)	(12)	-	(8·0)	>B	-

cont'd.

TABLE 4.32 (cont'd)

Catalyst Temp(^{o}C)	5% Pt/Al_2O_3	1% Pt/Al_2O_3	0·1% Pt/Al_2O_3	Al_2O_3	1% Pt/SiO_2	0·1% Pt/SiO_2	SiO_2
Ethylene (mls.)							
20	0·01	>0	0·01	-	(0·01)	-	-
50		>0	-	-	-	0·01	-
100	0·04	0·01	-	-	-	-	-
200		0·04	(0·01)	-	0·02	-	-
350		0·07	0·06	>0	0·08	0·01	-
Ethylene (c/mlx10^{-5})							
20	0·42	-	>B	-	(0·01)	-	-
50		-	-	-	-	0·01	-
100	0·75	(4·5)	-	-	-	-	-
200		(10)	(12)	-	0·02	-	-
350	-	8·42	12·46	>0	0·08	0·01	-
X (mls.)							
200	-	>0	-	-	-	-	-
350	0·06	0·11	>0	-	-	-	-
X (c/mlx10^{-5})							
200	-	>B	-	-	-	-	-
350		6·45	B	-	-	-	-
Y(mls.)							
100	>0·04	0·03	-	-	-	-	-
200		-	-	-	-	-	-
350	0	-	0·13	-	-	-	-
Y(c/mlx10^{-5})							
100	>B	>B	-	-	-	-	-
200		-	-	-	-	-	-
350	>B	-	(4·0)	-	-	-	-
Temperature Increase (c x 10^{-5})							
20 → 50	1·01	-	-	-	-	0·01	0·04
50 → 100		-	-	-	-	-	-
100 → 200	2·52	0·56	0·09	-	0·14	-	-
200 → 350		3·24	1·04	-	0·65	0·05	-

For a given platinum concentration, the retention was generally greater on an alumina-supported catalyst than on a silica-supported catalyst. The supports alone, inert for both ethylene and propylene retention, showed some retention of acetylene. The value of silica at 20°C seems abnormally high in view of the values on the silica-supported catalysts. Acetylene exchange followed a similar pattern to that found for the retention of acetylene although silica was inert for acetylene exchange.

A variety of products were observed under certain conditions although their yield was low. This is probably due to the large extent of irreversible acetylene adsorption. Ethane and ethylene were observed although the yield of ethylene was usually greater than the yield of ethane when both products resulted from one injection of acetylene. The yields tended to be dependent on the platinum concentration of the catalysts. Except with 1% Pt/Al_2O_3 at 200°C, methane was only observed at 350°C.

The low yields of all these products preclude any accurate comparison between their specific activities and the specific activity of acetylene under similar conditions.

At the higher temperatures there was evidence of other species apart from methane, ethane, ethylene and acetylene being produced with the alumina-supported platinum catalysts. One peak, described as X in Table 4.32, appeared with a retention time of 1 min. 40 secs. intermediate between the retention times of ethane and ethylene (see Table 3.1). There were also diffuse peaks, described as Y in Table 4.32, which had retention times of approximately 4 to 5 minutes. Neither of these peaks had been observed previously, and they were not observed in any experiments with the silica-supported catalysts.

Despite the high retention of acetylene on the platinum catalysts at the lower temperatures, little or no tritiated species were removed below 100°C. The radioactive content of the reactor eluant was again greater for the alumina-supported catalysts. It is interesting to note that on heating silica from 20°C, where acetylene retention was observed, to 50°C a tritiated species was removed from the catalyst.

Section 4.12 Acetylene Exchange with Acetylene Residues.

The reactivity of retained acetylene towards gaseous acetylene was studied in an analogous manner to that described for propylene (see Section 4.9). The results of the experiments using 5% Pt/Al_2O_3, 1% Pt/Al_2O_3, 0·1% Pt/Al_2O_3 and 1% Pt/SiO_2 are shown in Table 4.33.

By the time the retention of ^{14}C-acetylene was complete, the hydrogenation of acetylene had diminished considerably from the initial value at each temperature. Thus no carbon-14 could usually be detected in any hydrogenation product for an injection of non-radioactive acetylene. The counts observed in all the products, apart from acetylene, are thus grouped together in the table of results. The counts observed for both the radioactive and non-radioactive acetylene have been converted into specific activities.

The extent of molecular exchange and the volume of acetylenic residues removed by heating the catalysts were calculated as before (see Section 4.3). The observed counts were converted into volumes and expressed as a percentage of the retained volume of acetylene. The volume undergoing molecular exchange appeared to be very low despite the high volume of acetylene retained.

TABLE 4.33

ACETYLENE EXCHANGE WITH ACETYLENE RESIDUES

	Catalyst Temp.(°C)	5% Pt/Al_2O_3	1% Pt/Al_2O_3	0·1% Pt/Al_2O_3	1% Pt/SiO_2
Retention (mls.)	20	1·01	0·72	0·26	0·16
	50	0·28	0·17	0·01	-
	100	0·54	0·14	0·01	0·05
	200	1·21	0·64	0·04	0·03
	350	1·48	0·99	0·52	0·15
C^{14}-Acetylene (c/mlx10^{-5})	20	2·85	2·54	2·68	2·12
Methane (mls.)	350	0·18	0·01	0·01	0·03
Ethane (mls.)	20	-	>0	-	-
	50	-	-	-	-
	100	0·02	-	-	>0
	200	0·02	0·01	0	>0
	350	0·09	0·02	0·02	0·02
Ethylene (mls.)	20	0·01	>0	0·01	0·02
	50	>0	>0	-	-
	100	0·04	0·01	-	-
	200	0·02	0·04	0·01	0·03
	350	-	0·08	0·03	0·09
Methane Ethane Ethylene (c/mlx10^{-5})	20	-	-	-	-
	50	0·01	-	-	-
	100	>B	>B	-	-
	200	0·01	-	-	0·02
	350	0·02	0·01	(0·01)	0·01
Acetylene (c/mlx10^{-5})	20	-	-	-	-
	50	0·02	-	0·06	0·02
	100	0·01	0·03	0·04	0·02
	200	(0·01)	-	0·03	-
	350	-	-	-	0·04
Exchange (mls.)	20	-	-	-	-
	50	0·006	-	0·011	0·005
	100	0·004	0·006	0·007	0·005
	200	0·003	-	0·007	0·009
	350	0·005	0·004	0·001	0·011
Exchange (%)	50	0·5	-	4·1	3·1
	100	0·2	0·5	2·5	3·1
	200	0·1	-	2·2	4·0
	350	0·1	0·1	0·02	2·8

cont'd.

TABLE 4.33 (cont'd)

	Catalyst Temp.(°C)	5% Pt/Al_2O_3	1% Pt/Al_2O_3	0·1% Pt/Al_2O_3	1% Pt/SiO_2
Temperature Increase ($c/ml x10^{-5}$)	20 → 50	-	-	-	-
	50 → 100	0·02	-	-	-
	100 → 200	0·04	0·56	0·01	>0
	200 → 350	0·35	0·09	0·01	0·01
Temperature Increase (mls.)	50 → 100	0·006	-	-	-
	100 → 200	0·01	0·25	0·01	0·002
	200 → 350	0·12	0·04	0·005	0·004
(%)	50 → 100	0·4	-	-	-
	100 → 200	0·7	24·2	3·5	0·9
	200 → 350	3·8	2·4	1·6	1·7

Below 100°C no acetylene residues were removed on heating the catalysts except with 5% Pt/Al_2O_3. Above this temperature some thermal desorption of ^{14}carbon residues was observed with every catalyst.

Section 4.13 Carbon Monoxide Retention Studies.

In order to correlate the retentions of the various hydrocarbons on the different catalysts a knowledge of the available metal area was required.

An estimate of this value for each of the catalysts, which had been previously studied, was made by determining the volume of carbon monoxide retained under identical conditions to those described for ethylene, propylene and acetylene (see Section 4.7). The same weight (0·45 gms.) of each catalyst 5% Pt/Al_2O_3, 1% Pt/Al_2O_3, 0·1% Pt/Al_2O_3, Al_2O_3, 5% Pt/SiO_2, 1% Pt/SiO_2, 0·1% Pt/SiO_2 and SiO_2 were used. Injections of carbon monoxide (0·5 ml.) were made over the catalysts at 20°C until no retention was observed, after which the catalyst temperature was raised to 50°C. The process was then repeated at this temperature and, at 100°C, 200°C and 350°C. The results are shown in Table 4.34 which also includes the ratio of the total number of carbon monoxide molecules retained at 20°C to the total number of platinum atoms present.

TABLE 4.34

CARBON MONOXIDE RETENTION (mls.)

Catalyst	20°C	50°C	100°C	200°C	350°C	Co/Pt 20°C
5% Pt/Al_2O_3	0·93	–	0·03	–	1·25	0·36
1% Pt/Al_2O_3	0·28	–	0·02	–	0·31	0·54
0·1% Pt/Al_2O_3	0·03	–	0·02	–	0·13	0·58
Al_2O_3	–	–	–	–	–	–
5% Pt/SiO_2	0·98	–	0·03	–	0·18	0·38
1% Pt/SiO_2	0·15	–	–	–	0·02	0·29
0·1% Pt/SiO_2	0·02	–	–	–	–	0·39
SiO_2	–	–	–	–	–	–

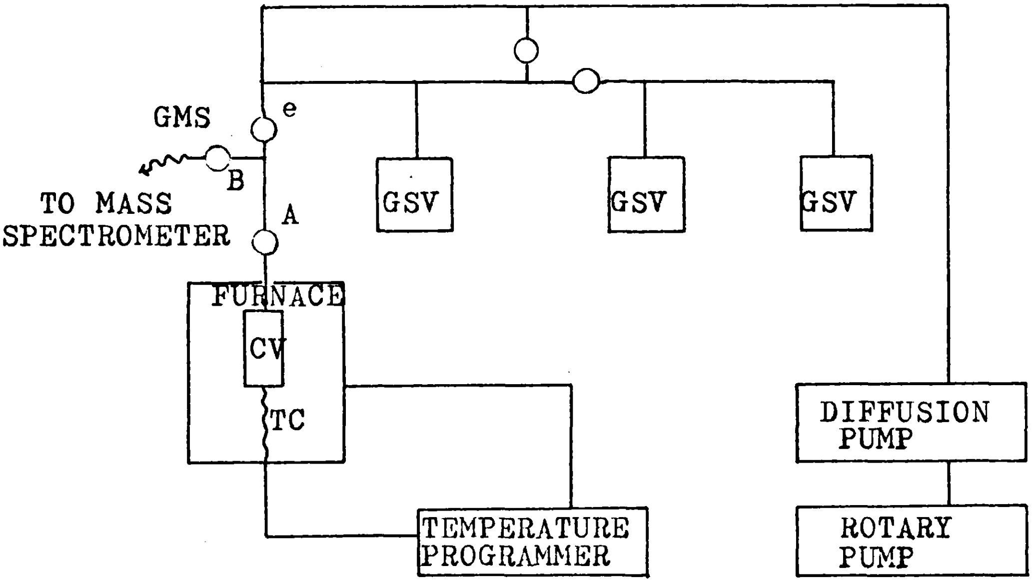
CHAPTER 5

Section 5.1 Experimental

In order to investigate the nature of the species removed by heating the catalysts a very sensitive technique was required. It was decided to attempt to analyse the products using a mass spectrometer (A.E.I. MS.10), which was the most sensitive technique which was readily available.

In order to obtain the best correlation between these results and those obtained using the flow system, the most desirable process would have been to pass the reactor eluant through a trap, kept at liquid nitrogen temperatures, attached to the end of the flow system. The products could then be collected for analysis by the mass spectrometer. This method, however, caused undesirable interruptions to the gas flow which could harm the operation of both the chromatograph and the counter. Unfortunately, the volumes desorbed from the maximum weight of catalyst that could be used (see Section 3.1) were too small to permit collection and subsequent mass spectrometric analysis.

An alternative method was developed whereby the products could be fed directly into the mass spectrometer. Different weights of catalysts (5% Pt/SiO_2) were treated with ethylene in a static system (Fig. 3.4). After



GMS .... Glass-Metal Seal

GSV .... Gass Storage Vessel

CV .... Catalyst Vessel

TC .... Thermocouple

O .... Tap

Figure 5.1 Diagram of Vacuum-Mass Spectrometer System.

evacuation to remove gas phase and weakly adsorbed ethylene, the catalyst vessel was connected to the sample inlet of the mass spectrometer and heated by means of a conventional furnace. When the required temperature was reached the tap was opened to allow any products to enter the mass spectrometer. The relatively large dead space, however, meant that only a very low pressure of gas was available for analysis unless very large samples of catalyst (>1·5 gm.) were used. A variety of products were, however, detected. Another disadvantage was the poor control over the catalyst temperatures.

Both these difficulties were overcome. A static system (Fig. 5.1) was constructed with a direct leak ($^1/4$" i.d. copper tubing) to the analyser tube of the mass spectrometer thus reducing the dead volume to a minimum.

The catalyst was heated by a silica furnace which was controlled by means of a temperature programmer (Weston Instrument Co.). By this method a very stringent control over the catalyst temperature (±2°C) was achieved, the required temperature being rapidly reached and maintained at a steady value for as long as necessary.

The conditions for the catalyst pretreatment in the flow system experiments were maintained as far as possible. Using the apparatus described in Section 3.1, the catalyst vessel was fitted with hydrogen and evacuated several times before the catalyst was reduced with hydrogen (200 mm.) for four hours at 350°C. At the end of the reduction period the vessel was evacuated (pressure $< 10^{-4}$ torr.) at the same temperature for one hour. When the temperature had reached 20°C, ethylene (80 mm.) was admitted and after five minutes gas phase or weakly adsorbed ethylene were removed by evacuation (pressure $< 10^{-4}$ torr.).

With tap A closed, the vessel (cv) was connected to the mass spectrometer system (Fig. 5.1) which was evacuated back to taps A and B by means of a mercury diffusion pump backed by a rotary oil pump (pressure $< 10^{-6}$ torr.).

The catalyst vessel was heated to the required temperature. During this time a background spectrum was run over the range m/e = 12 to m/e = 140. The pressure recorded on the ionization gauge of the mass spectrometer was approximately 1×10^{-7} torr. In order to reduce the complexity of the spectra, the mass spectrometer was operated with an electron beam voltage of 10 ev. At this low setting virtually no background was recorded. Peaks were usually only observed at m/e values of 18, 28 and 32.

When the required temperature was reached, tap C was closed and a sample of the gas removed from the surface of the catalyst was admitted to the mass spectrometer via taps A and B. The pressure was recorded and a spectrum was run over the same range.

After evacuation to a pressure of less than 10^{-6} torr., the catalyst vessel was isolated and heated to the next higher temperature. The background was again determined. This process was repeated for each temperature increase. In each case the background was subtracted from the spectra of the desorbed products.

The slow pumping of the products from the analyser tube during analysis meant that the spectra had to be run as quickly as possible to ensure reproducible results.

Although reasonable results could be obtained from 0·25 gm. of 5% Pt/SiO_2, a greater number of products were observed when 0·5 gm. were used. With weights of catalyst greater than 0·5 gm., peaks at $m/e = 36$ and $m/e = 38$ implied that the catalyst bed was too thick to allow complete reduction. The weight chosen for all experiments was thus 0·5 gm.

In the first experiments, samples were withdrawn for analysis at 50 degree intervals over the range 50°C to 350°C. However, only small quantities of products were removed at each temperature increase so that eventually samples were only withdrawn at 100°C, 200°C, 280°C and 350°C.

Several experiments were carried out using 5% Pt/Al_2O_3. The results from three experiments, shown in Table 5.1 have been chosen to show the widest variation observed throughout the series. Experiment (a) was the most typical although the experimental conditions were exactly the same as for experiment (b). The evacuation time, after exposure to ethylene, however, was ten minutes in the case of experiment (c).

In these experiments as in all the later ones, the heights of the peaks for the different m/e values have been related to an arbitrary value of 100 for the height of the maximum peak. In Table 5.1 only the major peaks have been shown although in each case many other m/e values (shown in Table 5.2) were observed at each temperature. The m/e values at which peaks were observed were constant from one experiment to another although their relative heights tended to vary.

The disparity in these results emphasises the importance of having stringently controlled conditions, if any comparative studies are to be made between various catalysts.

TABLE 5.1

MASS SPECTRAL ANALYSIS OF MAJOR PRODUCTS
DESORBED FROM 5% Pt/Al_2O_3

Temperature	(a)		(b)		(c)	
	m/e	Ht.	m/e	Ht.	m/e	Ht.
100°C	28	100	28	100	30	228
	30	66	30	67	28	100
	42	14	29	7	26	6
	26	7				
	43	6	42	7	29	4
	18	5	43	5	31	3
	29	3	50	4	42	2
	50	3	26	4	43	1
200°C	28	100	28	100	30	119
	30	60	30	58	28	100
	17	10	18	5	17	9
	18	5	29	5	26	4
	44	5	26	4	42	4
	26	3	17	4	29	3
	42	3	44	4	43	2
	29	3	43	3	44	2
280°C	18	100	18	100	30	100
	28	90	17	80	28	100
	17	88	30	38	26	50
	30	68	28	32	17	41
	26	30	26	23	18	30
	43	29	42	15	42	50
	42	19	43	13	43	41
	44	15	44	10	44	33
350°C	18	100	18	100	28	100
	28	33	28	54	17	21
	30	29	30	37	18	15
	43	12	42	18	30	13
	43	10	44	14	44	14
	26	10	43	12	42	9
	17	9	26	10	43	8
	42	8	32	7	26	6

TABLE 5.2

PRODUCTS DESORBED FROM 5% Pt/Al_2O_3

m/e	100°C	200°C	280°C	350°C
15	x	x	x	
16	x	x	x	x
17	x	x	x	x
18	x	x	x	x
19	x	x	x	x
27	x	x	x	x
29	x	x	x	x
31	x	x	x	x
32	x	x	x	x
39	x	x	x	
40	x	x	x	x
41	x	x	x	x
43	x	x	x	x
44	x	x	x	x
45	x	x	x	x
46	x	x	x	x
47	x	x		
50	x	x	x	x
52	x	x	x	
53	x	x		
54	x	x		
56	x	x	x	x
57	x	x	x	
58	x	x	x	x
59	x	x		
60	x	x		

Section 5.2 Results.

Using the conditions described in the previous section, a study has been made of the nature and quantity of products desorbed from ethylene pretreated catalysts. At leats two experiments were carried out using each catalyst, namely 5% Pt/Al_2O_3, 0·1% Pt/Al_2O_3, Al_2O_3, 5% Pt/SiO_2, 0·1% Pt/SiO_2 and SiO_2.

For a particular catalyst, a large number of m/e values were observed at each temperature and were constant from one experiment to the next. The relative abundance of the major peaks (i.e. those with a peak height greater than 2 units) were also constant although the heights of the minor peaks tended to be more variable. The average results for each catalyst are shown in Tables 5.3 - 5.8. The exact values for any m/e values with a relative peak height below 0·1 have been omitted from these tables. The height of the maximum peak and the pressure, which was observed at each temperature, are also shown.

From 5% Pt/SiO_2 and 5% Pt/Al_2O_3 the spectra were similar, peaks up to m/e = 60 being observed and also at m/e = 74 for 5% Pt/SiO_2. These results, however, differ considerably from those observed with all the other catalysts, where the range extended to m/e = 100. With 0·1% Pt/Al_2O_3 and Al_2O_3 additional peaks up to m/e = 124 were observed. Although the

TABLE 5.3

ETHYLENE ON 5% Pt/Al$_2$O$_3$

m/e	100°C	200°C	280°C	350°C
Pressure(torr.)	2·6x10^{-6}	4·3x10^{-6}	1·8x10^{-6}	1·6x10^{-6}
Ht. of max. peak	2500	1900	1200	1000
15	0·5	1·5	0·1	x
16	0·1	2	0·2	2
17	0·3	10	88	9
18	5	5	100	100
19	0·1	x	2	3
26	7	3	30	10
27	1	1	2	1
28	100	100	90	33
29	4	3	2	5
30	66	60	68	29
31	2	1	1	1
32	1	1	1	5
39	1	0·1	0·5	x
40	1	1	6	3
41	1·6	0·5	3	2
42	14	3	19	8
43	6	2	29	12
44	2	5	15	10
45	1·5	0·5	5	3
46	2	0·6	4	2
50	3	2	2	1
52	1	0·7	2	
53	0·3	0·2		
54	0·1	0·2		
55	x	x		
56	2	0·2	2	0·6
57	1·5	x	x	x
58	0·5	0·1	0·5	0·5
59	0·2	0·1		
60	0·5	0·2		

TABLE 5.4

ETHYLENE ON 0·1% Pt/Al_2O_3

m/e	100°C	200°C	280°C	350°C
Pressure(torr.)	$0{\cdot}4\times10^{-6}$	$1{\cdot}1\times10^{-6}$	$0{\cdot}2\times10^{-6}$	$0{\cdot}2\times10^{-6}$
Ht. of max. peak.	4500	1300	1800	1600
15	x	x	x	x
16	1	1	6	12
17	0·3			1
18	2		1	40
26	6	6	6	6
27	1	1	1	0·4
28	100	100	81	50
29	2	4	12	5
30	1	6	14	8
31	0·2	0·1	0·4	0·3
32	x	x	0·3	0·2
39	1	1	x	2
40	3	7	10	8
41	21	29	41	11
42	27	84	106	24
43	7	6	26	100
44	4	3	39	68
45	0·7	x	x	0·6
46	0·3			
50	x		0·2	0·2
52	x		0·2	0·2
53	x	x	x	
54	1	x	1	0·6
55	7	7	15	2
56	29	15	39	12
57	4	1	4	2·8
58	5	1	26	28
59	x		0·3	x
60	x			x
67		0·3	4	x
68	x	0·4	x	x
69	0·5		x	x
70	3	1	1	x
71	8	6	15	
72	2	0·6	0·1	x
78	2	0·8	12	28

cont'd.

TABLE 5.4 (cont'd)

m/e	100^oX	200^oC	280^oC	350^oC
Pressure(torr.)	$0{\cdot}4\times10^{-6}$	$1{\cdot}1\times10^{-6}$	$0{\cdot}2\times10^{-6}$	$0{\cdot}2\times10^{-6}$
Ht. of max. peak.	4500	1300	1800	1600
80				3
82	x	x		
85	3	1		
86	x	x	0·6	
93			3	
94	x	x	6	4
96	x	x	2	
100	x	x		
108	0·2	0·5	2	2
114	x	x		0·5
124		x	0·3	

TABLE 5.5

ETHYLENE ON ALUMINA

m/e	100°C	200°C	280°C	350°C
Pressure(torr)	$9{\cdot}8\mathrm{x}10^{-6}$	$1{\cdot}1\mathrm{x}10^{-6}$	$0{\cdot}4\mathrm{x}10^{-6}$	$0{\cdot}3\mathrm{x}10^{-6}$
Ht. of max. peak	66,000	9500	4500	8200
15	x	x	x	
16	x	x	0·6	
17	x			0·2
18	0·5	x		1
26	3	5	4	5
27	x	x	0·6	0·8
28	100	100	100	68
29	2	2	2	2
30	x	x	0·1	0·4
31	x	x	x	0·3
32			x	0·2
39	x	x	0·1	x
40	0·4	0·3	0·8	10
41	2	2	13	52
42	2	4	20	100
43	0·5	0·2	0·6	30
44	x	0·1	7	16
45	x		x	x
46	x			
50	x	x	0·3	x
52	x	x	x	
53	x	x	x	x
54	x	x	0·4	2
55	0·6	1	7	16
56	3	2	24	45
57		0·2		3
58		1		x
68	x	x	x	0·4
69	x	x	x	0·8
70	0·1	0·3	0·6	x
71	0·5	0·8	0·8	1
72	0·2	0·1	x	1

cont'd.

TABLE 5.5. (cont'd)

m/e	100°C	200°C	280°C	350°C
Pressure(torr)	$9\cdot8\text{x}10^{-6}$	$1\cdot1\text{x}10^{-6}$	$0\cdot4\text{x}10^{-6}$	$0\cdot3\text{x}10^{-6}$
Ht. of max. peak	66,000	9500	4500	8200
80	x	x	x	
83	x		x	
84	x	x	x	x
85	x	0·2	x	x
86	x	x	x	x
94	x	x		x
100	x	x		0·3
108		x	x	
112		x		
114	x	x		
124	x	x	x	
138			x	
144	x	x		

TABLE 5.6

ETHYLENE ON 5% Pt/SiO$_2$

m/e	100°C	200°C	280°C	350°C
Pressure(torr)	$9{\cdot}8\times10^{-6}$	$3{\cdot}8\times10^{-6}$	$0{\cdot}6\times10^{-6}$	$0{\cdot}4\times10^{-6}$
Ht. of max. peak.	3030	1360	400	350
15	3	5	x	x
16	0·5	4	x	0·3
17	31	41	50	80
18	10	13	12	100
19	x	1	2	2
26	13	10	4	12
27	2	3	1	1
28	100	100	100	63
29	6	4	3	2
30	25	43	30	21
31	1	1	1	1
32	2	0·5		x
39	x	x	x	x
40	5	7	2	4
41	2	3	1	2
42	20	18	6	15
43	20	13	5	9
44	9	14	3	11
45	5	x	x	0·5
46	4			x
50	1	x		0·3
52	0·1	0·5	1	0·2
53	x	0·4	x	x
54	x	x	x	x
55	1	1		x
56	1	0·5	0·3	0·5
57	2		x	0·2
58	2		0·4	0·4
59	1			
60	3			
74	0·5			

TABLE 5.7

ETHYLENE ON 0·1% Pt/SiO_2

m/e	100°C	200°C	280°C	350°C
Pressure(torr)	$0{\cdot}9\times10^{-6}$	$0{\cdot}3\times10^{-6}$	$0{\cdot}2\times10^{-6}$	$0{\cdot}3\times10^{-6}$
Ht. of max. peak	1620	1000	190	250
15	x	x	x	x
16	0·5	5	20	13
17	1		1	1
18	9	2		89
26	7	3	5	2
27	0·6	0·4	x	x
28	100	49	100	25
29	3	10	8	1
30	2	3	34	5
31	1	1	0·5	x
32	2	0·1	0·4	2
39	x	x		
40	4	10	2	2
41	23	26	2	4
42	30	100	8	13
43	11	7	12	24
44	2	4	16	100
45	9	8	0·9	4
46	10	7	0·8	x
50	0·3	9	5	x
52	0·2	3	8	x
53	x	x		
54	1	x		
55	8	0·4		2
56	40	3		5
57	6	0·5		x
58	1	2	6	20
59	x	x	1	3
60	2	3	x	
65		x		
66		2		
67	0·7			
68	0·7			
69	4	0·7		
70	7	x		
71	1·5	0·3		
72	0·4			
74		1		
78		2	8	3
85	0·3	0·5		
86	x			
100	x			

TABLE 5.8

ETHYLENE ON SILICA

m/e	100°C	200°C	280°C	350°C
Pressure(torr)	2·8x10^{-6}	0·6x10^{-6}	(0·1x10^{-6})	(0·1x10^{-6})
Ht. of max. peak	3300	620	40	110
15	x	x	x	
17	1	1	x	
18	3	2	x	5
26	2	1	4	4
27	1	0·8	2	1
28	100	35	100	100
29	2	3	9	3
30	2	5	1	4
31	4	35	3	1
32	5	x	x	0·5
39	0·2	0·3	x	x
40	1	0·6	x	x
41	14	8	3	8
42	10	5	5	13
43	3	3	3	2
44	1	6	6	3
45	32	89	12	1
46	30	35	6	x
47	1	1		
50	0·1			
52	0·1			
54	0·5	0·3		
55	4	2		x
56	15	9	3	9
57	3	1		x
58	0·6	1		2
59	25	40	20	
60	24	27	2	
61	1			
64	0·4	1	5	
67	0·3			
68	0·6			
69	3	2		
70	5	3		
71	1	1		
73	1	9		
74	15	100	21	
75		4		
85	5	0·1		
86	x	x		
100	x	x		
108	x			

major peaks observed with 0·1% Pt/Al_2O_3 and 0·1% Pt/SiO_2 were similar, the spectra for these catalysts tended to resemble the spectra of the support especially with respect to the peaks observed at high m/e (>70) values.

Except for 5% Pt/Al_2O_3 and 0·1% Pt/Al_2O_3, where the maximum pressure of desorbed products was observed at 200°C, the pressure was a maximum at 100°C and decreased with each temperature increase above 100°C. Up to 280°C, the maximum peak was at m/e = 28 with the exception of 0·1% Pt/SiO_2 and SiO_2 at 200°C and 5% Pt/Al_2O_3 and 0·1% Pt/Al_2O_3 at 280°C. At 350°C various maxima were observed.

From the results, it is evident that a large number of species are present on the catalyst in a form that is capable of being desorbed on heating. Many of the minor peaks may be formed by fragmentation and it is probable that many have contributions from several different parent peaks. However, since the limitation of the M.S.10 mass spectrometer leads to an increasingly poor resolution with increasing m/e ratios an unequivocal assignment of a particular peak at m/e > 80 is not possible.

In an attempt to assign some of the peaks observed below m/e = 80 to chemical species, calibration spectra of several pure compounds were run at the same electron beam voltage. These included saturated hydrocarbons ($C_1 \rightarrow C_8$), olefins ($C_2 \rightarrow C_8$), alkynes, dialkynes, diolefins and ketones ($C_2 \rightarrow C_4$) aldehydes, alcohols and acids ($C_1 \rightarrow C_4$) and water. Some of the results are shown in Tables 5.9 - 5.11 in which an arbitrary value of 10 was chosen to represent the height of the parent peak.

Cvetanovic[68] found that on heating an ethylene-pretreated catalyst to 100°C ethane and some ethylene were removed from the surface. In view of this there is a strong probability that ethane corresponds to the peak at $m/e = 30$ and that ethylene forms a high percentage of the peak, often the highest, observed at $m/e = 28$. Moreover, when no large peaks were observed at $m/e \geqslant 29$ as with alumina, the height of peak at $m/e = 29$ was $\sim 2\%$ of the peak at $m/e = 28$ which corresponded to the contribution from ^{13}C-ethylene ($2 \cdot 2\%$). In this case, a C_2 species rather than carbon monoxide or nitrogen gives rise to the peak at $m/e = 28$.

Since the spectra observed for the 5% platinum catalysts were the simplest in terms of the number of peaks, an attempt has been made to determine the chemical species which give rise to the peaks. From the calibration spectra, different species which could contribute to a particular peak can be deduced (Appendix 1). Certain peaks, for example $m/e = 16, 30, 32, 40, 50$ and 52 are unique or are

TABLE 5.9

m/e	Methane	Acetylene	Ethylene	Ethane	Propyne	Propylene	Propane
15	0·7						
16	10						
17	0·1						
26		10	1·0	0·3			
27		0·2	0·3	0·4			
28			10	7·5			
29			0·2	4·0			
30				10			
31				0·2			
39					1·0	1·0	
40					10	1·5	0·1
41					0·3	5·9	1·0
42						10	1·2
43						0·3	7·0
44							10
45							0·3

TABLE 5.10

m/e	Diacetylene	Butyne	1–3 Butadiene	Butenes	Butanes	Pentenes	Pentanes
15							
26					1·4		
27					2·3		0·6
28		1·8	1·6	0·2	2·0	1·4	5·1
29					14·9		2·5
30							
39		2·5	6·8	0·3	1·0	0·3	
40				0·6	1·2	0·5	0·7
41			1·6	10	15·4	0·2	8·6
42				0·4	18·8	18	84·5
43					107·1	0·9	102
44					4·1		3·6
49	2·3						
50	10						
52	0·4	1·0	2·5				
53		4·2	10				
54		10	1·0	0·3	0·2		
55		0·4	0·1	1·7	0·4	10·4	1·0
56				10	2·6	0·4	3·3
57				0·4	1·8		14·1
58					10		
59					0·4		
70						10	
71						0·4	
72							10

TABLE 5.11

m/e	Water	Formaldehyde	Acetaldehyde	Methanol	Ethanol	Propanol	n-butanol
17	2·0						
18	10						1·0
28		2·6	1·5	1·6		8·9	48·9
29		2·6	3·9	1·0		3·3	12·1
30		10		2·2		1·4	7·3
31				7·9		5·7	73·7
32				10		1·4	
33				0·1		0·7	
41						1·0	6·3
42			0·3		0·4	3·0	4·8
43			4·0		0·3	15·1	5·6
44			10		1·0	1·1	80·3
45					3·0	0·4	25·0
46					10	0·5	5·0
56						0·3	15·8
57						0·8	178·0
58						2·6	12·6
59						10	0·5
60						7·1	
73							1·0
74							10

composed of fragments from very few species. At the other extreme, peaks observed at m/e = 27, 29, 39, 41 and 43 appear in the spectra of many compounds and can only be used with reference to other peaks, sometimes to disprove the existence of certain possible products.

The maximum peak in most cases at m/e = 28 is most likely to be ethylene. There will, however, be a major contribution from ethane if it is present and minor contributions ($<10\%$) from fragment peaks of higher compounds. Only ethane and formaldehyde could account for the large peak at m/e = 30. At the low temperatures, at least, since the peak at m/e = 29 is small, ethane is a far more likely product than formaldehyde especially in consideration of Cvetanovic's results.[68] A higher percentage of ethane if usually produced over 5% Pt/Al_2O_3 than over 5% Pt/SiO_2.

The ratios of the peak heights at m/e = 15 and m/e = 16 are consistent with the formation of methane being responsible for the peak at m/e = 16 which seems to be unique. Apart from a possible contribution from various alcohols, the peaks at m/e = 17 and m/e = 18 are most likely to represent water formed by dehydration of the catalyst. The ratios of the water peaks are very sensitive to the electron beam voltage.

Five compounds give appreciable peaks at m/e = 26. Since n-butanol and propionic acid would have a lower height at this value than at m/e = 74 neither compound is important. Ethane and ethylene give peaks at m/e = 26 which are respectively, 3% and 10% of the parent peak. Thus a large fraction of the peak at m/e = 26 is probably due to acetylene. The peak at m/e = 32 may be caused by oxygen or methanol. It is unlikely that oxygen is formed or present as an impurity. Since evidence has been found for the formation of other alcohols, methanol is probably gives rise to the peak at m/e = 32. When the peak at m/e = 40 is larger than can be accounted for by fragmentation of propylene or other higher hydrocarbons, it may represent the formation of either propyne or allene. Although both these products are possible, propyne which gives a lower peak at m/e = 39 than allene seems more probable.

One of the most important peaks at m/e = 42, can probably be assigned, in part, to propylene. Although many other compounds give fragment peaks at this value, consideration of the other peaks heights indicates that they could contribute a maximum of 20% of the height of the peak at m/e = 42. The spectra are consistent with the formation of propane rather than acetaldehyde giving rise to the peak at m/e = 44. It is, however, not easy to determine the contribution of the possible species ethanol, formic acid or butanol to the peak at m/e = 46. Since the peak at m/e = 45 is relatively high as expected for ethanol, this compound is favoured although the peak at m/e = 31 seems too low.

Only the spectra of diacetylene and the isomeric compounds with the formula C_4H_6 have appreciable peaks at m/e = 50. Since in the latter case, the peaks are lower than either of the peaks at m/e = 53 and m/e = 54, the peak at m/e = 50 is probably due to diacetylene. Similar considerations lead to the assignment of the peak at m/e = 52 to vinylacetylene, m/e = 53 to 1:3 butadiene and m/e = 54 to one or more than one of the isomers of C_4H_6.

All the isomers of butene give similar spectra at 10 e.v. in which the major peaks are observed at m/e = 41 and m/e = 56. Since the peak at m/e = 41 is only important when a large peak is observed at m/e = 56, the latter is certainly due, at least in part, to butene formation. However, the peaks at m/e = 56 and m/e = 57 may result from the breakdown of higher hydrocarbons in the mass spectrometer. Many high molecular weight compounds have a base peak at low m/e ratios which may be up to 100 times larger than the parent peak. Since the sensitivity of the mass spectrometer might only allow detection of the fragment peaks it is not possible to refute the existence of compounds with a molecular weight greater than 74.

Since, however, Sheppard[66] observed the dimerisation of ethylene on silica-supported platinum catalysts the peaks at m/e = 56 and m/e = 58 are most likely to be caused by the formation of butene and butane, respectively. Butanol may give a peak at m/e = 58 with a height similar to height of the peak at m/e = 74. The peaks at m/e = 59 and m/e = 60 are ascribed to one or more than one of n-propanol, isopropanol, n-butanol, isobutanol or tert-butanol.

All the above assignments are tentative. A more rigorous calibration procedure with respect to the sensitivity of the mass spectrometer towards a given pressure of a compound, also to its partial pressure in known mixtures of compounds is necessary in order to make more precise deductions.

Comparing the cracking patterns of known compounds with the spectra of thermally desorbed products for 5% Pt/Al_2O_3 (A) and 5% Pt/SiO_2(B) it is possible to postulate the relative abundance of products at each temperature.

100°C A $C_2H_6 > C_2H_4 > C_3H_6 > C_2H_2 > H_2O > C_4H_2 > C_3H_8$

B $C_2H_4 > C_2H_6 > C_3H_6 > C_2H_2 > H_2O > C_3H_8 > C_3H_4$

200°C A $C_2H_6 \gtrsim C_2H_4 > H_2O > C_3H_8 > C_3H_6 > CH_4 > C_2H_2$

B $C_2H_6 \sim C_2H_4 > H_2O > C_3H_6 > C_3H_8 > C_2H_2 > C_3H_4$

280°C A $H_2O>C_2H_6>C_2H_4>C_2H_2>C_3H_6>C_3H_8>C_3H_4$
B $C_2H_4>H_2O>C_2H_6>C_3H_6>C_3H_8>C_3H_4\gtrsim C_2H_2$
350°C A $H_2O>C_2H_6>C_2H_4>C_3H_8\gtrsim C_2H_2\sim C_3H_6>C_3H_4$
B $H_2O>C_2H_4>C_2H_6>C_3H_6>C_2H_2\sim C_3H_8>C_3H_4$

Similar products are observed under all conditions although their relative abundance tends to vary with the form of the catalyst and the temperature. The saturated form of a product seems to be more favoured over 5% Pt/Al_2O_3 than over 5% Pt/SiO_2. Progressive dehydration with increasing temperature occurs for both catalysts whereas the products capable of being desorbed are more quickly removed from 5% Pt/SiO_2 than from 5% Pt/Al_2O_3.

The mode of interpretation of the results for 5% Pt/Al_2O_3 and 5% Pt/SiO_2 was also applied to the spectra observed with other catalysts, namely 0·1% Pt/Al_2O_3, Al_2O_3, 0·1% Pt/SiO_2 and SiO_2. The relative importance of the major products at each temperature are shown below.

0·1% Pt/Al_2O_3
100°C $C_2H_4>C_4H_8>C_3H_6>C_6/C_7/C_8>C_4H_{10}>C_3H_8$
200°C $C_2H_4>C_3H_6>C_4H_8>C_6/C_7/C_8>C_2H_6>C_3H_8$
280°C $C_3H_6>C_2H_4>C_3H_8>C_4H_8>C_4H_{10}>C_6/C_7/C_8$
350°C $C_3H_8>C_2H_4>H_2O>C_4H_{10}>C_3H_6>C_6H_6$

Al_2O_3
100°C $C_2H_4 > C_4H_8 > C_3H_6 > H_2O$
200°C $C_2H_4 > C_3H_6 > C_4H_8 > C_2H_2$
280°C $C_2H_4 > C_4H_8 > C_3H_6 > C_3H_8$
350°C $C_3H_6 > C_2H_4 > C_4H_8 > C_3H_8$
0·1% Pt/SiO_2
100°C $C_2H_4 > C_4H_8 > C_3H_6 > H_2O \sim C_2H_5OH > C_3H_7OH$
200°C $C_3H_6 > C_2H_4 > C_4H_2 > C_2H_5OH > C_3H_7OH > CH_4$
280°C $C_2H_4 > C_2H_6 > C_3H_8 \sim CH_4 > C_4H_4 > C_4H_8$
350°C $C_3H_8 > H_2O > C_2H_4 > C_4H_{10} > CH_4 > C_3H_6$
SiO_2
100°C $C_2H_4 > C_2H_5OH > C_3H_7OH > C_4H_9OH > C_4H_8$
200°C $C_4H_9OH > C_2H_5OH > C_3H_7OH > C_2H_4 > C_4H_8$
280°C $C_2H_4 > C_4H_9OH > C_3H_7OH > C_3H_5OH > C_3H_6$
350°C $C_2H_4 > C_3H_6 > C_4H_8 > H_2O > C_2H_6$

Although in this case peaks were observed at much higher m/e values than for the 5% platinum catalysts no additional peaks were observed below m/e = 60. Only with silica were relatively high peaks observed above this value. There was definite evidence for the formation of C_6 compounds and a peak sometimes found at m/e = 78 deduced to be C_6H_6 did not have a cracking pattern characteristic of benzene. It was not possible, however, to determine the exact nature of the other C_6 compounds or the C_7 and C_8 compounds although the spectra tended not to be characteristic of highly unsaturated compounds. The products from 0·1% Pt/Al_2O_3 and Al_2O_3 also included compounds with a higher carbon number.

In contrast to the results for the 5% platinum catalysts, the yield of ethane was low and butene was a major product under all conditions. For the products with a carbon number less than five, olefins were more important than the corresponding saturated compound except with 0·1% Pt/SiO_2 at 280°C and 350°C.

All the products which could be identified for a particular catalyst at each temperature are shown in Tables 5.12 - 5.15. in which X represents a major product and x represents other species which were observed.

TABLE 5.12

PRODUCTS DESORBED AT 100°C

Product	5% Pt/Al_2O_3	0·1% Pt/Al_2O_3	Al_2O_3	5% Pt/SiO_2	0·1% Pt/SiO_2	SiO_2
CH_4	x	x		x		
C_2H_2	X			X	X	
C_2H_4	X	X	X	X	X	X
C_2H_6	X	x	x	X	x	x
C_3H_4			x	x		
C_3H_6	X	X	X	X	X	x
C_3H_8	X	X		X	x	
C_4H_2	X	x	x	x	x	x
C_4H_4	x	x	x	x	x	x
C_4H_6	x	x	x	x	x	x
C_4H_8	x	X	X	x	X	X
C_4H_{10}	x	X		x	x	
C_5H_4						x
C_5H_8		x			x	
C_5H_{10}					X	
C_5H_{12}		X				
C_6H_6		x			x	
C_6		x	x		x	x
C_7					x	x
C_8			x			
$>C_8$			x			
H_2O	X		X	X	X	x
CH_3OH	x	x	x	x	x	x
C_2H_5OH	x	x		x	X	X
C_3H_7OH	x	x	x	x	X	X
C_4H_9OH				x		X

TABLE 5.13

PRODUCTS DESORBED AT 200°C

Product	5% Pt/Al_2O_3	0·1% Pt/Al_2O_3	Al_2O_3	5% Pt/SiO_2	0·1% Pt/SiO_2	SiO_2
CH_4	x	x		x	X	
C_2H_2	x		X	X	x	
C_2H_4	X	X	X	X	X	X
C_2H_6	X	X	x	X	x	X
C_3H_4			x	x		
C_3H_6	X	X	X	X	X	X
C_3H_8	X	X	x	X	x	X
C_4H_2	x		x	x	X	
C_4H_4	x		x	x	X	
C_4H_6	x	x	x	x	x	
C_4H_8	x	X	X	x	X	X
C_4H_{10}	x	X	X	x	x	
C_5H_4					X	x
C_5H_8		x			X	
C_5H_{10}		x				
C_5H_{12}		x				
C_6H_6					x	
C_6		x	x		x	x
C_7		x				x
C_8		x	x			
$>C_8$			x			
H_2O	X			X	x	x
CH_3OH	x	x		x	x	x
C_2H_5OH	x			x	X	x
C_3H_7OH	x	x		x	X	x
C_4H_9OH				x	x	X

TABLE 5.14

PRODUCTS DESORBED at 280°C

Product	5% Pt/Al_2O_3	0·1% Pt/Al_2O_3	Al_2O_3	5% Pt/SiO_2	0·1% Pt/SiO_2	SiO_2
CH_4		X			X	
C_2H_2	X		X	x		
C_2H_4	X	X	X	X	X	X
C_2H_6	X	X		X	X	
C_3H_4	x			x		
C_3H_6	X	X	X	X	X	X
C_3H_8	X	X	X	X		X
C_4H_2	x	x	x		X	
C_4H_4	x	x	x	x	X	
C_4H_6		x	x	x		
C_4H_8	x	X	X	x	X	x
C_4H_{10}	x	X	x	x	X	x
C_5H_4						X
C_5H_8		x	x			
C_5H_{10}		x	x			
C_5H_{12}						
C_6H_6		x			x	
C_6		X				
C_7		x				
C_8		x	x			
$>C_8$			x			
H_2O	X	x		X		
CH_3OH	x	x	x		x	x
C_2H_3OH	x				x	X
C_3H_7OH	x				x	X
C_4H_9OH						X

TABLE 5.15

PRODUCTS DESORBED AT 350°C

Products	5% Pt/Al_2O_3	0·1% Pt/Al_2O_3	Al_2O_3	5% Pt/SiO_2	0·1% Pt/SiO_2	SiO_2
CH_4	x	X		x		
C_2H_3	X	x	X	X		
C_2H_4	X	X	X	X	X	X
C_2H_6	X	X		X	X	X
C_3H_4	x	X		x		
C_3H_6	X	X	X	X	X	X
C_3H_8	X	X	X	X	X	X
C_4H_2	x	x	x	x	x	
C_4H_4		x		x	x	
C_4H_6		x	x	x		
C_4H_8	x	X	X	x	X	X
C_4H_{10}	x	X	x	x	X	x
C_5H_4						
C_5H_8		x				
C_5H_{10}		x				
C_5H_{12}						
C_6H_6		x			x	
C_6		x				
C_7		x				
C_8		x				
$>C_8$		x				
H_2O	X	X		X	X	X
CH_3OH	x			x	x	x
C_2H_5OH	x			x	x	x
C_3H_7OH						
C_4H_9OH						

CHAPTER 6. DISCUSSION

Section 6.1 The Reactions of Ethylene and Propylene.

(i) The effect of temperature upon the reactions of ethylene and propylene with tritiated platinum catalysts was studied as a function of (a) the metal concentration and (b) the support. With few exceptions, the results observed with both olefins were very similar and several observations were common for alumina and silica-supported catalysts. The tritium content of the products will be discussed in a later section.

The only products observed at temperatures below 350°C were the olefin and corresponding alkane. At 350°C, however, cracking occurred to give methane from ethylene, and methane and ethane from propylene. Olefin retention, hydrogenation and cracking appeared to be a function of the metal, since the extent of these processes decreased with decreasing metal concentration. Also, the supports themselves appeared virtually inert for these processes, except for a small amount of ethylene retention.

Alkanes were only produced from the corresponding olefin when retention was observed. Although the alkane yield was always less then the volume of olefin retained, a high retention was accompanied by a relatively high alkane yield. These results suggest that the alkane is formed by self-hydrogenation.

The alkane yield and retention from the first injection at each temperature was far greater than with subsequent injections. Rohrer et al[96] also observed a decrease in activity when hydrocarbons were contacted with a platinum catalyst in a flow system using helium as a carrier gas. Replacement of the helium by hydrogen, however, restored the catalytic activity.[96] He concluded that the decrease was due to the absence of hydrogen rather than the presence of helium. We have also observed that the catalytic activity remains relatively constant for a considerable time when mixtures of olefin and hydrogen are injected onto the catalyst (see Section 4.5). Furthermore, the olefin retention is negligible in the presence of hydrogen. In the absence of hydrogen, Kemball and co-workers[97,98] have shown that extensive decomposition, leading to the formation of hydrogen deficient residues, takes place during the reaction of hydrocarbons on various metals.

These results suggest that dissociation of the adsorbed olefin leads to retention and causes a decrease in the catalytic activity. The adsorbed species thus provide a source of hydrogen to yield alkane. The following reaction sequence can be written

$$C_2H_4(g) \longrightarrow C_2H_4\ (a) \tag{1}$$

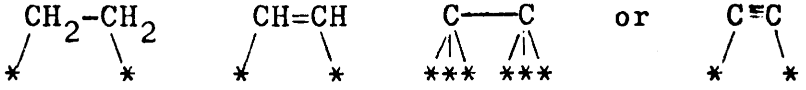
$$C_2H_4\ (a) \xrightarrow{-H} C_2H_3\ (a) \xrightarrow{-H} C_2H_2\ (a) \xrightarrow{-H} \text{etc.} \tag{2}$$

$$C_2H_4\ (a) + 2H\ (a) \longrightarrow C_2H_6 \tag{3}$$

$$C_2H_4\ (g) + 2H\ (a) \longrightarrow C_2H_6 \tag{4}$$

From the results, it is not possible to determine whether reaction (3) or reaction (4) leads to alkane production. It is also possible that some of the ethane may have resulted from reaction with hydrogen associated with the catalyst. The observation of tritiated alkanes in this context will be discussed later.

From ethylene, the above hypotheses are supported by the work of Sheppard.[61] He observed the formation of (A) and (B) during the chemisorption of ethylene on 16% Pt/SiO_2.



(A) (B) (C)

From the large spectral increase in intensity on treatment with hydrogen, he concluded that considerable initial dissociative adsorption must have occurred. Since the C-H intensity was initially very low, there may have been surface carbide formation (C). Polymer formation was absent until 95°C although even at this temperature the yield of C_4 hydrocarbons was very low.

The fact that at 20°C a high percentage of the retained ethylene was removed as ethane by injecting hydrogen onto 1% Pt/Al_2O_3 and 1% Pt/SiO_2 and that no other products were observed (Tables 4.22 and 4.23) is also in accord with the retained species being mainly in the form of C_2 units. However, the decrease in the amount of retained hydrocarbon removed with increasing temperature could imply that either (a) the extent of dissociation of the adsorbed species increases with increasing temperature, or (b) at different temperatures the modes of adsorption are different.

From the work of Sheppard et al[61] both of these possibilities appear to exist, since they observed the formation of surface $-CH_3$ groups and C_4 species during the initial adsorption of ethylene at 95°C and above. Furthermore, at 150°C the proportion of these species was greater than at 95°C.

Cormack et al[35] found that on 5% Pt/Al_2O_3 only 6·5% of the initially adsorbed ^{14}C-ethylene was retained after hydrogenation, in reasonable agreement with our results using 1% Pt/Al_2O_3 (Table 4.22). The results of these studies also suggest that the γ-alumina was virtually inert and it was concluded that the observed reactions were a property of the platinum, rather than of the support. As a possible explanation, they postulated that both associatively and dissociatively adsorbed species were present. The former were readily converted to ethane by reaction with hydrogen but the latter were inactive. However, infra-red studies[61] suggest that both species are readily hydrogenated to ethane.

For 0·1% Pt/Al_2O_3 and 0·1% Pt/SiO_2 the ratio of the total number of ethylene or propylene molecules retained to the number of platinum atoms present is greater than unity (see Table 6.1). It is, however, very unlikely that every platinum atom present is capable of adsorbing ethylene. This was substantiated by the fact that the ratio of carbon monoxide molecules retained per platinum atom was less than unity for every catalyst (Table 6.1). The platinum surface area, determined by carbon monoxide adsorption will be referred to as the available platinum in the discussion.

An associatively adsorbed ethylene molecule can be assumed to occupy at least two surface sites,[61] and in the case of dissociative adsorption may occupy more than two sites. Also, even when ethylene retention is complete, ethylene exchange is still observed, thus adsorption of exchangeable ethylene must still occur on vacant surface sites. Therefore, in view of carbon monoxide surface determination and the restriction on the number of sites

TABLE 6.1

	5% Pt/Al_2O_3	1% Pt/Al_2O_3	0·1% Pt/Al_2O_3	5% Pt/SiO_2	1% Pt/SiO_2	0·1% Pt/SiO_2
CO Adsorbed (mls.)	0·93	0·28	0·03	0·98	0·15	0·02
CO Adsorbed (molecules$\times 10^{-19}$)	2·50	0·75	0·08	2·63	0·40	0·05
C_2H_4 Adsorbed (mls.)	0·36	0·13	0·03	0·26	0·14	0·06
C_2H_4 Adsorbed (molecules$\times 10^{-19}$)	0·97	0·35	0·08	0·70	0·38	0·24
C_2H_4/Pt_A	0·40	0·47	1·00	0·27	0·95	4·80
$C_2H_4/(Pt_A/2)$	0·80	0·94	2·00	0·54	1·90	9·60
C_2H_4/Pt	0·12	0·25	0·58	0·10	0·27	1·74
C_3H_6 Adsorbed (molecules$\times 10^{-19}$)		0·40	0·16		0·35	0·19
C_3H_6/Pt_A		0·53	2·00		0·88	3·80
C_3H_6/Pt		0·29	1·16		0·25	0·35
C_2H_2 Adsorbed (molecules$\times 10^{-19}$)	2·28	1·98	0·70		0·51	0·08
C_2H_2/Pt_A	0·91	2·63	8·72		1·27	1·60
C_2H_2/Pt	0·32	1·43	5·03		0·36	0·58
C_2H_2/Pt_A + supp*	0·85	2·43	5·33		0·07	-

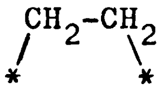
required for adsorption of one ethylene molecule, the ratio of ethylene to the available platinum (C_2H_4/Pt_A) and half the available platinum $(C_2H_4/Pt/2)_A$ is substantially in excess of unity (see Table 6.1).

One explanation for this high (C_2H_4/Pt) ratio is polymerisation of the retained ethylene on the surface. The observation that no products containing more than two carbon atoms were formed suggests that either polymer formation is negligible or that the polymeric species are very strongly adsorbed. However, below 95°C no polymeric species were observed with platinum-silica catalysts,[61] and although most of the adsorbed species were removed by hydrogen treatment, no polymers were removed. Thus if polymer formation is negligible, the question arises as to the location of the retained ethylene. At 20°C, both alumina and silica were inert for olefin retention and reaction, so that direct adsorption and retention on the support does not account for these observations.

The support may determine the particle size of the metal component and this influence the catalytic activity. However, although the retention of carbon monoxide was greater with 5% Pt/SiO_2 than with 5% Pt/Al_2O_3, the reverse situation was true for the retention of ethylene on these catalysts

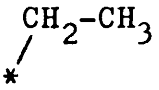
(Table 6.1). Moreover, the ethane yield at 20°C was similar on both, despite the higher metal area with 5% Pt/SiO_2. Thus the support may influence the catalytic activity as well as determining the metal surface area.

The fact that at 20°C, silica appeared inert for ethylene adsorption, exchange and hydrogenation is consistent with the lack of adsorption observed by infra-red spectroscopy (see Appendix II) and with results of other workers.[61,68] However, although the absence of retention on alumina at 20°C is in agreement with the work of Cormack et al,[35] other workers[72,99] have observed ethylene chemisorption on alumina. For example, Lucchesi et al[72] observed the formation of chemisorbed species when ethylene was in contact with η-alumina. On one type of η-alumina, species (A) was observed, whereas on another similar form of η-alumina the adsorption led to the slow formation of ethyl groups (D)



$$\underset{*}{CH_2}-\underset{*}{CH_2}$$

(A)



$$\underset{*}{CH_2}-CH_3$$

(D)

Thus our results, using γ-alumina cannot be directly compared with Lucchesi's work using η-alumina.[72]

With alumina it was shown that a slow increase in intensity in the spectra of chemisorbed ethylene occurred over eight days.[72] However, the same workers gave no comment about the change in intensity with time when platinum-alumina was used.[77] If it is assumed that the intensity does not change with time, it may be inferred that the presence of platinum enhances the adsorption of ethylene on alumina. In this context, the spectra of ethylene on platinum supported on silica at 20°C observed after five minutes, was the same after eighteen hours.[61] Adsorption on platinum at 20°C, thus appears to be much faster than on alumina at the same temperature.

These observations may help to rationalize results reported in this thesis for ethylene on alumina with those reported by other workers. Under flow system conditions, the time of contact of ethylene with alumina may not be long enough to allow adsorption to occur at 20°C. A second possibility is that the extent of adsorption is outwith the limits of the sensitivity of our detection system. The faster rate on platinum compared to alumina enables adsorption of ethylene to occur on platinum under flow system conditions. The adsorption of ethylene on alumina was observed in the thermal desorption work (see Chapter 5). Perhaps steady state conditions, as used in thermal desorption and infra-red studies are necessary to allow appreciable adsorption on alumina.

The fact that under flow system conditions, ethylene was retained on alumina at temperatures above 20°C may imply that adsorption on alumina is more highly activated than on platinum.

Lucchesi et al,[77] did find that although most of the ethylene was adsorbed on the alumina component of a 0·6% Pt/Al_2O_3 catalyst, the presence of platinum greatly increased the ease of removal of ethylene adsorbed on alumina by hydrogen treatment. It was shown that the adsorbed species could be completely removed at temperatures approximately 100° lower than those at which only a fraction of the adsorbed species could be removed from the alumina. There is thus the possibility that platinum, in addition to enhancing the removal of ethylene on alumina, also enhances the adsorption of ethylene on alumina.

Further retention and hydrogenation were observed at 100°C, 200°C and 350°C and occasionally at 50°C. It is possible that ethylene was adsorbed on sites left vacant by the thermal desorption of ethylene residues. Carbon-14 studies (discussed later) showed that ethylene residues were removed on heating the catalyst from one temperature to the next higher one, but that the volume removed was less than the subsequent retention of ethylene at the higher temperature. The nature of the products removed on heating will also be discussed later in conjunction with the thermal-desorption studies (Section 6.8).

The production of ethane at temperatures between 20°C and 200°C was always accompanied by a greater retention of ethylene. This is consistent with self-hydrogenation leading to ethane production and dissociation of ethylene residues, and with the increasing extent of dissociation with increasing temperature. However, the observation that the removal of ethylene with increasing temperature was always considerably less than the subsequent retention emphasises the problem of location of the retained ethylene since the ratio of C_2H_4/Pt increases with increasing temperature. Some of the ethylene is directly retained on the support above 20°C but the retention on the platinum catalysts is always greater than the retention observed with the support alone (Tables 4.15, 4.16).

At 200°C it seems that the processes which are occurring are similar to those thought to occur at 20°C, although the relative magnitude of the different reactions may vary with increasing temperature; the higher temperatures probably favour the more highly activated reactions. However, with 5% Pt/Al_2O_3 a trace of methane was observed and it became an important product with all platinum catalysts at 350°C. Evidence of methane formation was also found on the supports at 350°C. The presence and the amount of metal and the nature of the support all appear to influence the production of methane. It is not possible, however, to determine the role of the support. It is evident that alumina, unlike silica becomes catalytically active for ethylene exchange and hydrogenation at 350°C although the extent of both reactions is at least ten times lower than with platinum-alumina catalysts (Table 4.14). Thus the enhancement of adsorption on alumina by the presence of metal may also lead to enhancement of the catalytic activity of alumina at 350°C. Since a lower retention was observed with silica than with alumina it may be that enhancement also occurs for silica but to a much lower extent.

The observation that cracking is only appreciable at 350°C, and when the catalyst contains platinum, implies that high temperatures are necessary to break carbon-carbon bonds on platinum. In this context, it is interesting to quote Sheppard's[61] view that products on nickel at -78° are similar to those on platinum at +95°C and that the same chemical species occur on both metals but over a different range of temperature. At 150°C, he observed the formation of methane on hydrogenation of ethylene on nickel. From our results, we can predict that if it were possible to observe the spectra of ethylene on platinum at 350°C then this would show similar characteristics to that found with nickel at 150°C.

(ii) The results for the exchange of inactive ethylene with retained C^{14}-ethylene on 1% Pt/Al_2O_3 and 1% Pt/SiO_2 (Table 4.16) show that only a small percentage ($<$16%) is active in molecular exchange. Most of the retained species is thus in a form unable to react with ethylene from the gas phase, but which can be removed by treatment with hydrogen. These results again support the postulate that the retained species are hydrogen-deficient. Both catalysts show similar behaviour in that the percentage of retained ethylene removed in molecular exchange and by hydrogen decreases with increasing temperature. Since Sheppard[61] observed that dissociation also increases with increasing temperature, it is likely that the decreased reactivity in both processes is due to increased extent of dissociation of the retained species.

At 200°C and above, the exchanged fraction comprised both ethylene and ethane. This effect may have occurred at lower temperatures but was not observed, since the ethane yield decreased rapidly after the first injection of ethylene, several injections of C^{14}-ethylene being necessary to ensure complete surface coverage.

An argument against the exchanged fraction containing ethane is the observation that the formation of methyl groups in the absence of hydrogen was not found below 95°C. The surface ethyl groups, when formed would be expected to desorb more easily than diadsorbed species or acetylenic (hydrogen deficient) residues. However, the carbon-14 yield in the product ethanes, when observed was very much lower than the total yield of ethane. Also, with the exception of 1% Pt/Al_2O_3 at 20°C, the exchange was complete after the first injection of inactive ethylene. These results imply that ethane production does not involve the wholesale participation of preadsorbed ethylene. Therefore, ethane production must result from freshly adsorbed ethylene and the extent of hydrogenation must be determined

$$\left.\begin{array}{l} {}^{14}C_2H_4 \longrightarrow {}^{14}C_2H_{(4-x)} + xH\ (a) \\ C_2H_4\ (a) + 2H\ (a) \longrightarrow C_2H_6 \end{array}\right\}(5)$$

$$\left.\begin{array}{l} {}^{14}C_2H_4 \longrightarrow {}^{14}C_2H_5\ (a) \\ C_2H_4\ (a) + {}^{14}C_2H_5\ (a) \longrightarrow {}^{14}C_2H_6 + C_2H_3\ (a) \end{array}\right\}(6)$$

by the availability of surface hydrogen, reaction sequence (5), rather than by reaction (6). The surface hydrogen may arise from the dissociation of ethylene residues or from hydrogen used in the reduction of the catalyst and not removed during the higher temperature helium pretreatment. The role of hydrogen will be discussed at the same time as the tritium content of the products (Section 6.4).

The extent of molecular exchange and the volume of adsorbed hydrocarbon removed by heating was greater with 1% Pt/Al_2O_3 than with 1% Pt/SiO_2. Thus, the support does appear to influence the nature of the retained species or rather the ease of removal of the species. This observation is in agreement with the fact that a greater percentage of the retained species was removed by hydrogen from 1% Pt/Al_2O_3 than from 1% Pt/SiO_2 (Tables 4.22, 4.23).

If ethylene were retained solely on the platinum component of a supported catalyst this difference in reactivity is difficult to explain. If, however, ethylene is also retained on the support, as seems likely even at 20°C, the strength of adsorption and hence reactivity on alumina and silica would be expected to be different. Unfortunately, alumina appears to retain ethylene to a greater extent than silica.

Since the adsorption on silica is less than on alumina, it would appear that adsorption is more highly activated in the former case. However, if chemisorbed species were formed on silica they might have a higher heat of desorption and be less easily removed than from alumina.

(iii) The results for propylene (Table 4.25) and ethylene (Tables 4.14, 4.15) below 350°C are in most respects, remarkably similar. For example, on a particular platinum catalyst at a particular temperature:

(a) The extent of olefin retention and thus C_2H_4/Pt and C_3H_6/Pt are similar at 20°C and increase in a similar manner with increasing temperature (Table 6.1).

(b) The only products were the olefin and corresponding alkane and the alkane yield was similar.

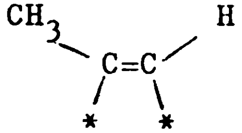
(c) No retention was observed on the support at 20°C and no products apart from untreated olefin were observed below 350°C.

It has also been shown[37] that the interaction of ethylene and propylene with deuterium over platinum-alumina gave similar kinetics and similar product distributions.

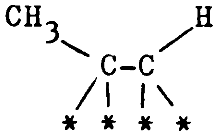
These results suggest that the same type of mechanism is operative for both ethylene and propylene and that the considerations described above for ethylene may perhaps be applied to propylene.

The adsorbed state of propylene on platinum-silica has been investigated by infra-red spectroscopy,[100] but only at room temperature. Propylene was considered to adsorb by a dissociative mechanism to yield species of the type (E) and

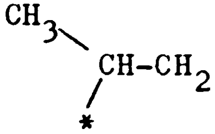
(F) rather than the associatively adsorbed species (G)



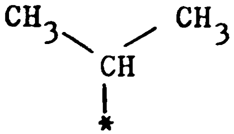
(E)



(F)



(G)



(J)

Hydrogenation produced a much more intense spectrum which was ascribed to (J). These observations are consistent with the retention of propylene, like ethylene being due to dissociation of adsorbed olefin and the production of alkane by self-hydrogenation.

$$C_3H_6\ (a) \longrightarrow C_3H_{6-x}\ (a) + xH\ (a) \qquad (7)$$

$$C_3H_6\ (a) + 2H\ (a) \longrightarrow C_3H_8\ (g) \qquad (8)$$

However, the results of propylene tend not to display the slight dependence upon the support observed with ethylene. This may be a consequence of the fact that propylene, unlike ethylene, was not retained on the support, apart from very slight retention on alumina at 100°C. Despite the lower retention of propylene relative to ethylene on alumina at 100°C, a tritiated species was removed on heating to 200°C which was not observed with ethylene. At 350°C, slight cracking and hydrogenation of ethylene were observed with the supports but not with propylene.

At 350°C, retention and the alkane yield was usually lower for propylene than for ethylene. However, the extent of cracking as indicated by the yields of methane and ethane from propylene and of methane from ethylene was similar for both olefins. Thus, for propylene cracking and perhaps retention and hydrogenation proceed through the same mechanism as ethylene. However, at 350°C, there appears to be an additional mode of retention and hydrogenation which is unique to ethylene.

The reactions discussed above appear to be determined primarily by the metal, but the support also plays a role which increases in importance relative to that of the metal with increasing temperature. It also seems likely that on the metal the reactions of ethylene and propylene are similar but the secondary influence of the support is more important for ethylene than for propylene. Furthermore, the higher the temperature the greater is the effect of the support. Thus in this respect reactions of ethylene and propylene differ.

One important difference between ethylene and propylene is in the extent of molecular exchange. Although the retention was similar for both olefins, except at 350°C, the fraction of propylene undergoing molecular exchange(Table 4.28) was greater than the corresponding value for ethylene (Table 4.17). The greater ease of molecular exchange may be explained by considering that a fraction of adsorbed propylene exists in a different form from ethylene.

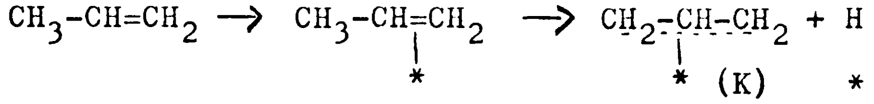
Further evidence for different type of adsorption comes from the observed effect of injecting inactive ethylene onto the surface of 1% Pt/Al_2O_3 precovered with ^{14}C-propylene (Table 4.30). The following interesting points emerge:

(i) Ethylene retention can still occur on surfaces effectively saturated with propylene although the extent of retention is less than on a 'clean' surface, i.e. some of the sites can adsorb both ethylene and propylene although some are active only for ethylene adsorption.

(ii) Except at 200°C, where propylene retention was low, the presence of ethylene does not greatly affect the retention of propylene. Thus there may be sites active only for propylene retention.

(iii) At 200°C and below, no radioactivity was displaced from the surface by the adsorption of ethylene and no C_3 species were displaced at any temperature. Only when cracking of propylene occurred to give C_2 products is displacement observed. Thus propylene must be adsorbed more strongly than ethylene and yet part of the retained propylene is in a form more reactive in molecular exchange than ethylene.

A species which could only be formed by propylene and not ethylene is a π-allyl surface complex (K).



$$CH_3-CH=CH_2 \rightarrow \underset{*}{\underset{|}{CH_3-CH=CH_2}} \rightarrow \underset{*\ (K)}{\underset{|}{CH_2\cdots CH\cdots CH_2}} + \underset{*}{H} \qquad (7)$$

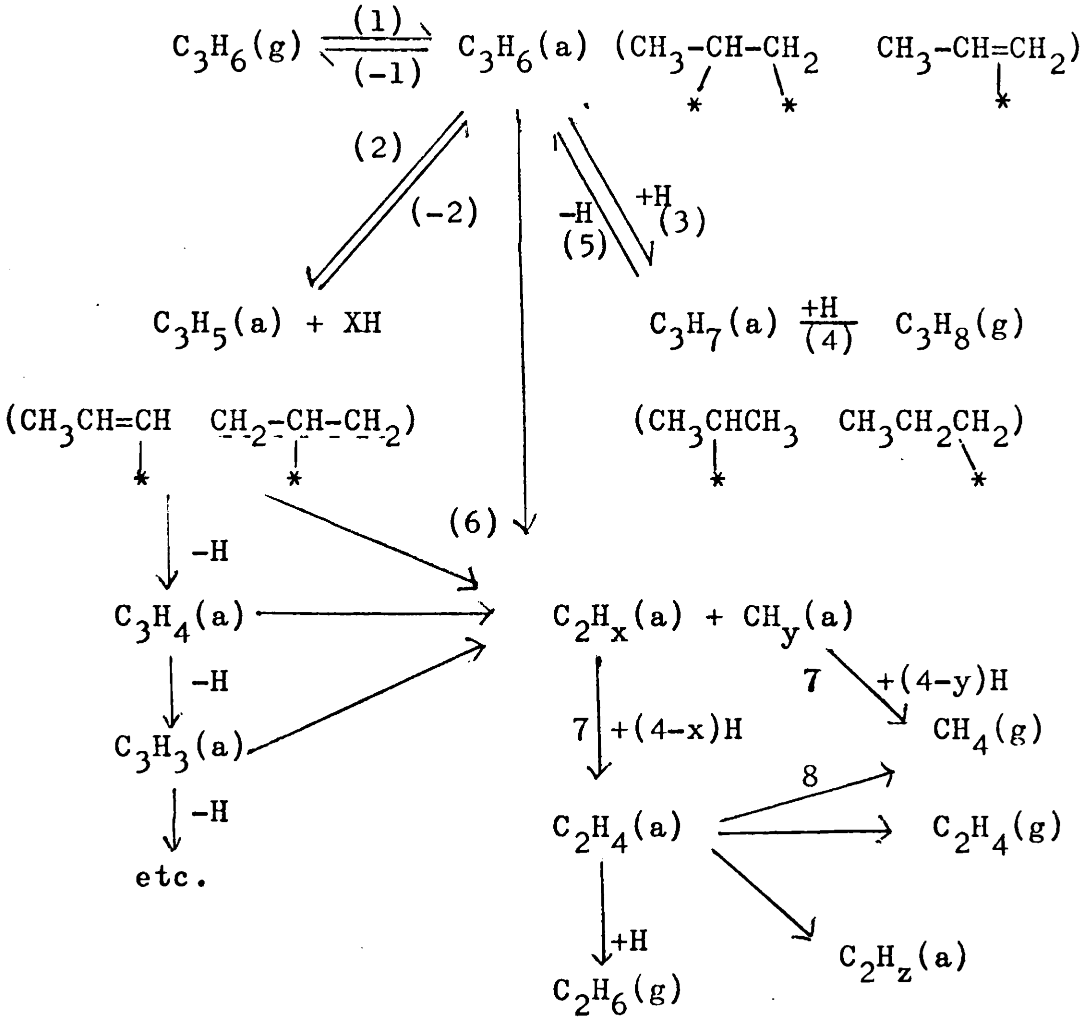
Although no evidence for a π-allyl species has been found from infra-red spectroscopy,[100] such species may nevertheless exist at surface concentrations too low to permit their detection. π-allylic intermediates have been postulated to explain the exchange of polymethylcyclopentanes over transition metals.[101, 102] The order of importance of π-allyl complexes on different metals appears to be in the reverse of the order of activity to produce products which are explained by π-allyl intermediates. Thus only when rather unstable complexes are formed, e.g. with platinum, would the products be influenced greatly by π-allyl formation.

At this stage a general scheme can be written to account for the products observed with propylene. Following associative adsorption on active sites (1) dissociation of adsorbed olefin proceeds by abstraction of hydrogen. (2) Dissociation, and hence the overall value of X_H increases with increasing temperature. The hydrogen, thus released, reacts with adsorbed olefin (3) since no hydrogen was observed in the products. The concentration of $C_3H_7(a)$

must be low, since none was observed in the infra-red work[100] and may either add hydrogen to yield propane (4) or lose hydrogen by alkyl reversal (5). Below 350°C these are the only processes for which we have evidence. At 350°C, methane, ethane and a trace of ethylene were produced as a result of breaking carbon-carbon bonds (6) followed by addition of hydrogen (7). The methane yield was usually greater than the yield of C_2 hydrocarbons. This is probably a result of reaction (8) since methane was also produced from ethylene at 350°C.

The lower yield of ethylene than of ethane may be explained by the fact that ethylene retention occurs on sites not active for propylene retention. Any product ethylene may readsorb on such sites and perhaps react to give methane or ethane whereas adsorbed ethane is more likely to be displaced by the excess propylene.

The reactions of ethylene can be easily fitted into this scheme which is similar to that proposed to account for the reaction of propylene on molybdenum oxide supported on alumina.[103] Because of the lower catalytic activity of metallic oxides relative to metals the reactions proceed at much higher temperatures. It is interesting to note that when alumina alone was used[103] the conversions were negligible in agreement with the work reported in this thesis.


C3H6(g)
(1)
(-1)
C3H6(a)
(CH3-CH-CH2
CH3-CH=CH2)
*
(2)
(-2)
-H
(5)
+H
(3)
C3H5(a) + XH
C3H7(a)
+H
(4)
C3H8(g)
(CH3CH=CH
CH2-CH-CH2)
(CH3CHCH3
CH3CH2CH2)
(6)
-H
C3H4(a)
C3H3(a)
etc.
C2Hx(a) + CHy(a)
7
+(4-y)H
CH4(g)
+(4-x)H
8
C2H4(a)
C2H4(g)
+H
C2H6(g)
C2Hz(a)

Section 6.2 The Reactions of Acetylene.

The reactions of acetylene, especially with respect to retention, were very different from ethylene and propylene on the same catalyst. For example at 20°C;

1% Pt/Al_2O_3	Ethylene	Retention	0·13 ml.
	Acetylene	"	0·72 ml.
1% Pt/SiO_2	Ethylene	"	0·14 ml.
	Acetylene	"	0·16 ml.

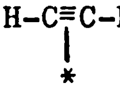
The marked difference between acetylene retention on platinum-alumina and platinum-silica catalysts was observed at other platinum concentrations and at higher temperatures (see Table 4.32).

In contrast to ethylene and propylene, retention of acetylene was observed with both alumina and silica at 20°C. In view of this, the volume retained on the support was subtracted from the total retention observed with the platinum catalysts at 20°C. The ratios for the number of acetylene molecules in the 'corrected volume', which are retained to the number of platinum atoms present are shown in Table 6.1. For 1% Pt/Al_2O_3 and 0·1% Pt/Al_2O_3 these ratios are greater than unity and the ratios for alumina-supported catalysts are greater than the value for the corresponding silica-supported catalysts. Thus even after correcting for the direct retention on the support, the overall retention on a supported-platinum catalyst is influenced by the support.

There are, however, some basic differences in the behaviour of silica and alumina towards acetylene. Further retention at higher temperatures, acetylene exchange and other products were observed with alumina. Silica, on the other hand, appeared virtually inert. Moreover, a tritiated species was removed on heating silica but not alumina from $20^{\circ}C$ to $50^{\circ}C$. Since this had not been observed in the absence of retained acetylene it can be assumed that the adsorbed acetylene was removed from the silica on heating. Silica thus appears to be inert whereas alumina is catalytically active but to a less extent than the platinum catalysts.

The infra-red spectra of acetylene adsorbed on silica and n-alumina at $20^{\circ}C$ has also demonstrated the difference between the supports.[73] On alumina two species were observed. These were postulated to be a strongly chemisorbed species (L) and a weakly chemisorbed species (M). Furthermore, the adsorbed

(L)



(M)

acetylene also exchanged with surface hydroxyl groups.[73] Since no tritiated species were removed by heating alumina it seems probable that, only the strongly adsorbed species is present on our catalyst or else both species are too strongly adsorbed to be removed. On silica, however, acetylene was only weakly adsorbed and was completely removed by evacuation,although a slight interaction with the surface hydroxyl groups was observed.[73] This is consistent with the observation that a tritiated species was removed from silica on heating to 50°C.

From the infra-red spectra of acetylene adsorbed on platinum supported on silica,evidence of polymeric species $C_n \geq 4$ was found.[66] Also, from the very great spectral intensity increase on hydrogenation, it was concluded that there was a high proportion of 'surface carbide' or hydrogen-deficient residues. Evidence for the polymerisation of acetylene has also been shown by Bond et al[104] who observed the formation of C_4 hydrocarbons during the hydrogenation of acetylene over 5% Pt/α-Al_2O_3.

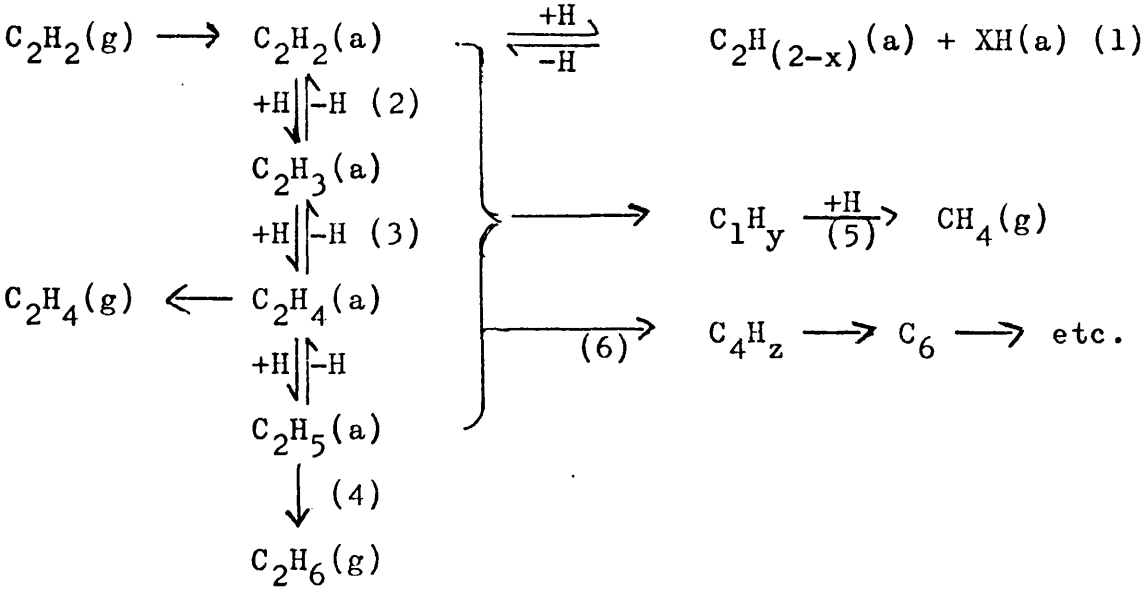
Thus polymerisation of acetylene could account for the very high retention values which are observed. Products were sometimes observed whose retention time on the chromatograph suggests that they were C_4 hydrocarbons. Occasionally higher hydrocarbons were also observed.

However, although such products were observed with all platinum-alumina catalysts none were produced with any platinum-silica catalyst or with alumina. These results suggest that the presence of both alumina and platinum are essential, not necessarily for the formation of polymers, but for the observation of polymer products.

Since no polymers were observed below 100°C the products may have been displaced by subsequent adsorption of acetylene. In fact, polymers were usually only observed with the first injection, when retention was high. Unfortunately, in studies of molecular exchange C^{14}-acetylene was injected until retention at each temperature was complete so that the possible removal of C^{14}-polymer by inactive acetylene could not be observed.

The molecular exchange studies do, however, emphasise the difference between 1% Pt/Al_2O_3 and 1% Pt/SiO_2. At every temperature the extent of exchange was slightly less with 1% Pt/Al_2O_3 than with 1% Pt/SiO_2 (Table 4.33) but the fraction of retained acetylene undergoing exchange was considerably less with 1% Pt/Al_2O_3 than with 1% Pt/SiO_2. This is probably a consequence of the greater retention with 1% Pt/Al_2O_3. However, on platinum-alumina catalysts the exchange tended to decrease with increasing platinum concentration.

The results for acetylene may be rationalised in the following manner. On the metal, adsorbed acetylene dissociates to give hydrogen-deficient residues (1) and the hydrogen thus liberated can react with adsorbed acetylene (2) leading to the formation of ethylene (3), and ethane (4) and at high temperatures methane (5).



Polymerisation of the residues (6) also occurs to give strongly adsorbed species thus giving a high C_2H_2/Pt ratio. A very low percentage of the adsorbed species which is similar for 1% Pt/Al_2O_3 and 1% Pt/SiO_2, may undergo molecular exchange. The yield of methane, ethane and ethylene decreases with decreasing metal concentration so that they are produced primarily by the metal. The fact that the yield of ethylene is greater than the yield of ethane may be rationalised by the fact that in acetylene hydrogenation over 5% Pt/Al_2O_3[104] the reaction is very selective for ethylene formation. Any ethylene produced in our reaction has a greater probability of being displaced by excess acetylene than reacting with adsorbed hydrogen to produce ethane. When inactive acetylene is injected onto a catalyst covered with ^{14}C-acetylene, product methane, ethane or ethylene, if observed, are radioactive. Thus molecular exchange on the metal involves the displacement of such products although direct displacement of acetylene also occurs.

However, the specific activity of product acetylene from inactive acetylene tends to increase with decreasing metal concentration. Thus molecular exchange may also be occurring directly on the support and the total exchange observed is composed of reaction on each component.

Even after correcting for the retention on the support the retention of acetylene on alumina-supported catalysts is greatly in excess of the retention of silica-supported catalysts. A possible explanation is that once all the available metal sites are filled, acetylene may still be weakly held to the metal component and may migrate to adjacent support sites when adsorption takes place. In some way the metal may activate the acetylene for adsorption on the support which would not normally occur directly under flow-system conditions. The fact that alumina adsorbs acetylene more strongly than silica would account for the higher retention with platinum-alumina than with platinum-silica catalysts.

Acetylene was not observed to polymerise on alumina but the increased concentration at the surface may perhaps lead to polymerisation in the presence of metal. This is a likely explanation in view of the observed desorption of butene from ethylene adsorbed on alumina during the thermal desorption studies (Chapter 5.). A second possibility is that acetylene on alumina may migrate to the metal and displace polymers. However, the observation that no species were removed on heating alumina on which acetylene was adsorbed and the fact that only high frequency hydroxyl groups exchange with acetylene[74] cast doubt on the mobility of acetylene on alumina.

Section 6.3 Reactivity of the Catalyst Hydrogen.

(i) The results presented in Table 6.2 show that after the desorbable tritium had been removed, considerable quantities of tritium remained on the catalyst. Although there is a slight decrease in the retention values with decreasing platinum concentration, the results for all the catalysts are remarkably similar. Consideration of the values of the total number of hydrogen atoms retained to the total number of platinum atoms present (Table 6.2), shows that this ratio is always in excess of unity.

Electron micrographs[105] of the catalysts show that the platinum is in the form of small crystallites (~ 50-150 Å) on the surface of the support. An estimate of the surface area of these crystallites was made by determining the volume of carbon monoxide retained on the catalysts. In contrast to the tritium retention, the ratios for the number of carbon monoxide molecules retained per platinum atom is less than unity and no retention was found with alumina or silica at 20°C. The difference between these results leads to the conclusion that most of the retained tritium is associated with the support rather than with the metal.

TABLE 6.2

Catalyst	Total Pt. (Atomsx10^{-19})	Tritium (mls. Removed)	Tritium (molecules retainedx10^{-19})	T/Pt	CO/Pt
5% Pt/Al_2O_3	6·90	0·22	4·8	1·4	0·36
1% Pt/Al_2O_3	1·38	0·29	4·6	6·6	0·54
0·1% Pt/Al_2O_3	0·14	0·37	4·4	64·0	0·58
Al_2O_3	-	0·32	4·5	∞	-
5% Pt/SiO_2	6·90	0·32	4·5	1·3	0·38
1% Pt/SiO_2	1·38	0·48	4·1	5·9	0·29
0·1% Pt/SiO_2	0·14	0·42	4·2	60·7	0·39
SiO_2	-	0·46	4·2	∞	-

Hydroxyl groups, located at the surfaces of alumina[106,107,108] and silica[109], have been found to exchange with gas-phase deuterium. We have also observed such exchange with our platinum-silica and silica catalysts (see Appendix II). Hall[108] has estimated the concentration of hydroxyl groups on the surface of alumina and silica to be $2\cdot8\mathrm{x}10^{14}$ $\mathrm{cm.}^{-1}$ and $2\mathrm{x}10^{14}$ $\mathrm{cm.}^{-2}$ respectively.

From the B.E.T. surface areas of alumina ($180\mathrm{m}^2/\mathrm{gm}$) and silica ($175\ \mathrm{m}^2/\mathrm{gm}$) respective values of $1\cdot1\mathrm{x}10^{14}$ and $1\cdot05\mathrm{x}10^{14}$ tritium atoms retained $\mathrm{cm.}^{-2}$ are obtained. These are in good agreement with those quoted by Hall and co-workers[108] and lead to the conclusion that the retained tritium is located at the hydroxyl groups at the surface of the support. Furthermore, he found[108] that the presence of platinum even in a highly dispersed form did not markedly affect the concentration of terminal hydroxyl groups. In view of this, the relatively constant retention values observed in the present work, for all the catalysts, substantiate the postulate that the tritium is in the form of surface hydroxyl groups.

(ii) Although the concentration of retained tritium was virtually constant for all the catalysts, the rate of exchange of the tritium with hydrogen tended to vary with the

$$OT + H \longrightarrow OH + T$$

different catalysts. The exchange was greater with platinum-alumina catalysts than with the corresponding platinum-silica catalysts and was greater with alumina than with silica. These observations may be accounted for by the greater acidity of alumina compared to silica leading more polar and hence more reactive hydroxyl groups in the former case.

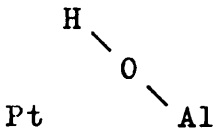
$$Al - \overset{\delta-}{O} \cdots \overset{\delta+}{H} \qquad Si - O - H$$

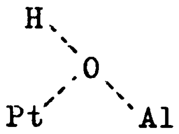
At every temperature, the specific activity of the product hydrogen decreased with each subsequent injection of hydrogen. Since this decrease was far greater than could be accounted for by dilution of the surface tritium with hydrogen and since the exchange increased with increasing temperature, the reactivity of the surface appeared to be non-uniform. This observation may be allied to the concept of 'active centres' in which only parts of the surface of a catalyst are thought to be active.

On γ-alumina[106] and η-alumina[107] the reactivity of the three different hydroxyl groups towards deuterium varied and the internal[109] and external hydroxyl groups on silica also had different reactivities towards deuterium. It is thus probable that the tritium retained on the support has different reactivities towards hydrogen. As Carter et al[107] point out hydrogen may dissociate at selected sites on the surface and then migrate to the most reactive hydroxyl groups to exchange.

The presence of platinum, however, increases the rate of exchange of hydrogen over alumina and silica. It was also found that, in the presence of gas phase deuterium, the rate of appearance of OD bands in the infra-red spectrum of silica was greatly enhanced by the presence of platinum (see Appendix II). The observed promoting effect of platinum upon the hydrogen exchange is in agreement with the works of Carter et al[107] and Hall.[108]

It thus appears that there is a co-operative effect of platinum and the support for the exchange of hydrogen, since the rate of exchange decreased with increasing platinum content. The mechanism of this effect is, however, uncertain. The metal may activate the support hydroxyl groups by increasing their acidity, for example the platinum may attract the oxygen atom of a neighbouring hydroxyl group thus weakening the hydroxyl bond.





This effect would be confined to hydroxyl groups close to platinum atoms and one would expect the greater the platinum content, the greater would be the exchange. If the enhanced exchange were due to exchange on the platinum, one would also expect the exchange to be greater with the greater platinum content.

$$H_2 \longrightarrow 2H(a)$$

$$Pt\text{-}T + H(a) \longrightarrow Pt\text{-}H + T(a)$$

$$T(a) + H(a) \longrightarrow HT$$

However, as mentioned above, the exchange increased from 1% to 0·1% platinum, despite the fact that the dispersion of the platinum was not greatly different at these concentrations. These effects do not appear to be of prime importance in accounting for the effect of the platinum unless as Hall[108] has postulated, the presence of halogen decreases the exchange activity. The decrease in rate with increasing platinum concentration may reflect a decrease in the concentration of reactive hydroxyl groups due to their replacement by chloride ions from the chloroplatinic acid used in catalyst preparation.

A second possibility is that the platinum activates the gas phase hydrogen to exchange with the hydroxyl groups. The increase in exchange with increasing temperature may imply that the exchange is an activated process. Perhaps the platinum reduces the activation energy of a reaction leading to exchange. Dissociation of hydrogen readily occurs on platinum and it is possible that the platinum may act as a source of dissociated hydrogen, which migrates to the support and exchanges with the hydroxyl groups.

The migration of hydrogen between the metal and support has been postulated by other workers[77,107] and is an example of the phenomenon termed 'spillover' and recently reviewed by Boudart.[110] Many examples exist in which the presence of traces of a noble metal, usually platinum, greatly enhances the total uptake, the rate of uptake or the reactivity of hydrogen of another 'inert' or less active component of the system. The most important criterion appears to be the degree to which the noble metal is in contact with the other component in that the greater the interface between the two, the greater is the acceleration of the process.

The following conclusions can be drawn regarding the exchange of hydrogen. Most of the exchanged hydrogen is produced by direct reaction on the support, the extent being determined both by the temperature and by the reactivity of the surface hydroxyl groups.

$$OT_{supp} + H \longrightarrow OH_{supp} + T$$

Dissociation of hydrogen also takes place on the platinum, when present, where it can exchange with tritium on the metal.

$$H_2 \longrightarrow 2H(a)$$

$$Pt\text{-}T + H(a) \longrightarrow Pt\text{-}H + T(a)$$

$$T(a) + H(a) \longrightarrow HT$$

However, some of the dissociated hydrogen may migrate to the support, exchange on the support and either desorb from the support or migrate back to the metal. The presence of metal

$$Pt\text{-}H \longrightarrow H\ supp.$$

$$H\ supp + OT \longrightarrow OH + T\ supp$$

$$T\ supp \longrightarrow Pt\text{-}T$$

$$T(a) + H(a) \longrightarrow HT$$

enhances the thermal desorption of retained tritium since the counts observed in the reactor eluant decreased with decreasing metal content and none was observed with the supports alone. Hence the platinum may enhance the exchange by increasing the desorption of hydrogen.

The effect of the platinum may be masked by other factors. For example, deposition of platinum may take place on active support sites and may lead to the replacement of hydroxyl groups by chloride.

An interesting feature of Boudart's work is that 'water has a profound and favourable effect' upon the reduction of WO_3, but only in the presence of platinum.[111] Water was thought to act at the interface by improving the 'contact' between the components although now it has been established that the water chemically aids the transport of hydrogen, presumably by forming H_3O intermediates.

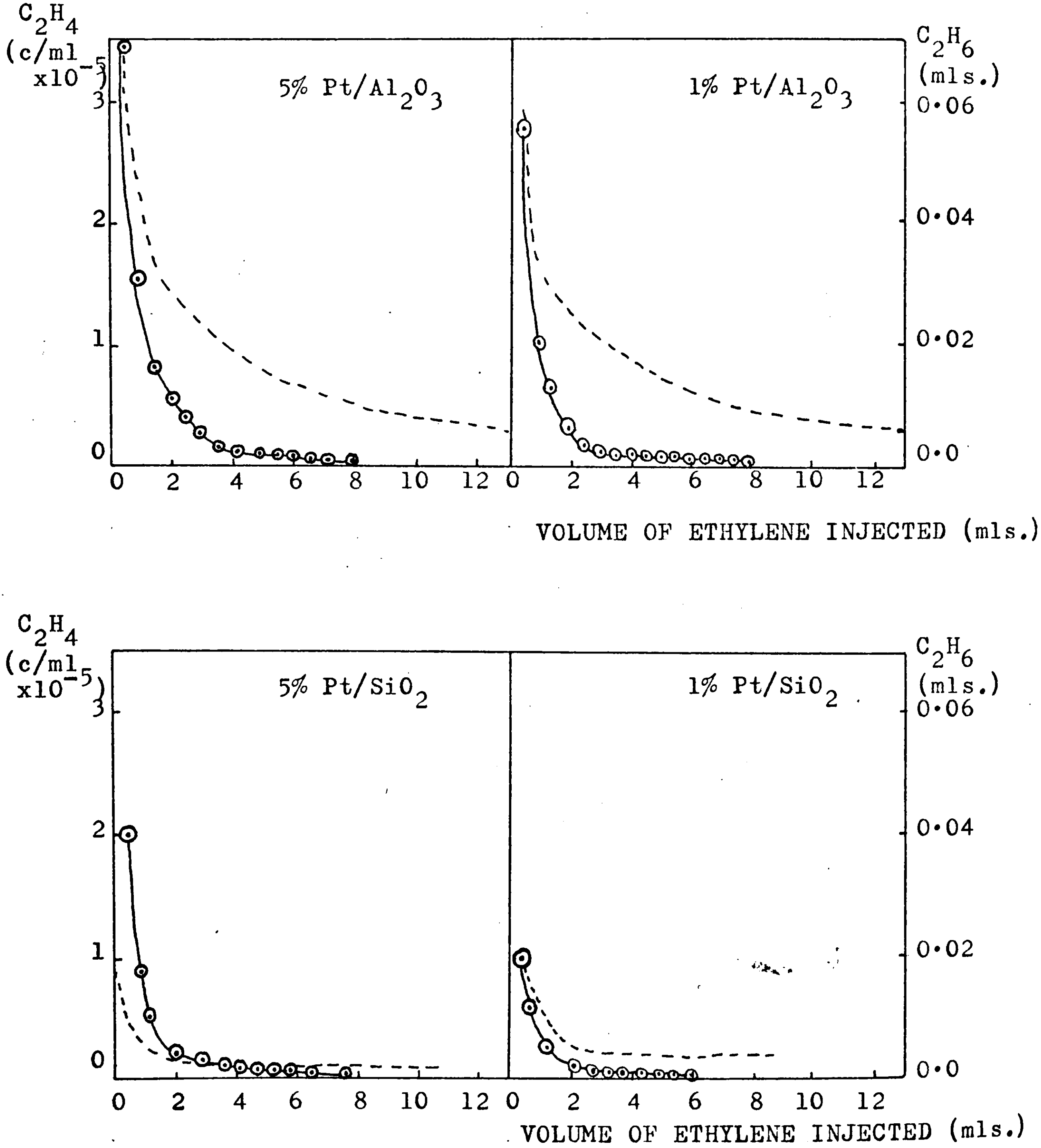


Figure 6.1

-⊙- Ethane Yield

---- Exchange

Section 6.4 The Tritium Content of the Hydrocarbons.

The results observed for the reaction of ethylene and propylene (Tables 4.14, 15, 25) with tritiated catalysts differ in several respects from those observed with hydrogen (Table 4.19). Whilst all the catalysts were active for hydrogen exchange, the presence of metal was essential for olefin exchange, except with alumina at 200°C and 350°C, where small amounts of olefin exchange were observed. The absence of ethylene exchange on alumina and silica at 20°C is in agreement with the work of Yates et al.[74]

In a series of experiments, successive injections of ethylene were made at constant temperature. From Fig. 6.1 showing typical results for the yield of ethane (ml) and the specific activity of the product ethylene(cpml) as a function of the volume injected onto the catalyst at 100°C, two important factors emerge. First, the hydrogenation activity decreased more rapidly than the exchange activity and second, when hydrogenation had ceased, the catalysts were still active for ethylene exchange. At this point, (point X) the specific activity of ethylene decreased very slowly with each subsequent injection, in fact, in a similar manner to that of the 0·1% platinum catalysts at the same temperature at which no hydrogenation was observed (see Fig. 6.2).

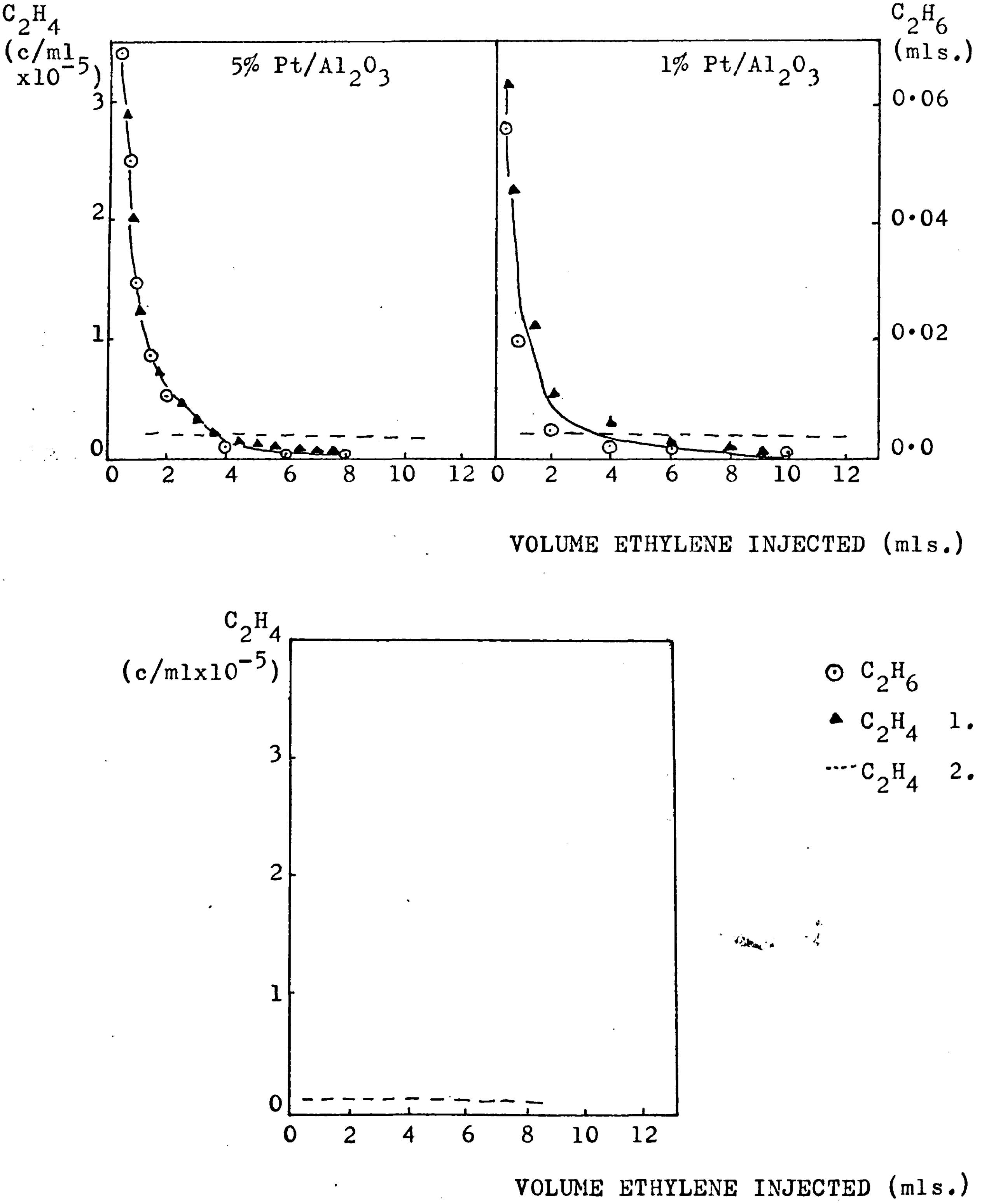

C_2H_4 (c/ml x10^{-5})
5% Pt/Al$_2$O$_3$
1% Pt/Al$_2$O$_3$
C_2H_6 (mls.)
0·06
0·04
0·02
0·0
3
2
1
0
0 2 4 6 8 10 12
VOLUME ETHYLENE INJECTED (mls.)
C_2H_4 (c/mlx10^{-5})
⊙ C_2H_6
▲ C_2H_4 1.
---- C_2H_4 2.

Figure 6.2

If the slope of the curve for exchange (~ linear) in the absence of hydrogenation is extrapolated back to zero and the values of the specific activity on this curve are subtracted from the total specific activity, the curves for hydrogenation and exchange virtually coincide (see Fig. 6.2 for 5% Pt/Al_2O_3 and 1% Pt/Al_2O_3). The same phenomenon was observed with 5% Pt/SiO_2 and 1% Pt/SiO_2. However, although the exchange at point X was similar with 5% Pt/Al_2O_3 ($3{\cdot}5 \times 10^4$ cpml) and 1% Pt/Al_2O_3 ($3{\cdot}8 \times 10^4$ cpml), these values were greater than for either of the corresponding silica-supported catalysts (4×10^3 cpml) and (1×10^3 cpml) respectively.

These results could imply that there are at least two processes resulting in ethylene exchange. One process, the first exchange process, closely related to hydrogenation and retention, decreases rapidly with each successive injection of ethylene and with decreasing metal concentration. It thus appears to be a process occurring on the metal.

The observation that the ethane was always radioactive shows that incorporation of catalyst 'hydrogen' occurs during the hydrogenation process and that the reaction does not simply proceed by the addition of hydrogen from adjacent olefin (1).

$$C_2H_4 + C_2H_4 \longrightarrow C_2H_6 + C_2H_2 \qquad (1)$$

A fraction of the ethane may be produced by this means but the extent of this reaction is obscured by the presence of tritiated alkane in the product. Hydrogen released in the dissociation (2) may exchange with the retained tritium (3) and subsequently react with adsorbed hydrocarbon (4), leading to

$$C_2H_4(a) \longrightarrow C_2H_{4-x}(a) + xH(a) \qquad (2)$$

$$H(a) + OT(a) \longrightarrow T(a) + OH(a) \qquad (3)$$

$$C_2H_4(a) + T(a) \rightleftharpoons C_2H_4T(a) \xrightarrow{T(a)} C_2H_4T_2 \qquad (4)$$

$$C_2H_{4-x} + T(a) \rightleftharpoons C_2H_{4-x}T(a) \qquad (5)$$

tritiated ethane or ethylene. The ethylene residues may also be exchanging with the tritium (5). The initial value of ethylene exchange tends to be high when the retention is high. If the hydrogen released in reaction (2) does enhance reaction (3), then the above mechanism would explain the initial rapid fall in ethylene exchange. Also, the increasing value of X H(a) with increasing temperature, would account for the increase in ethylene exchange with increasing temperature. It is not possible to determine whether the increase in the specific activity with increasing temperature is due to an increase in the total number of molecules exchanging or to an increase in the number of tritium atoms in the exchanged product, or a combination of both factors.

If olefin exchange and hydrogenation proceed through a common intermediate (adsorbed alkyl), the probability of alkyl reversal must be greatly in excess of the probability of addition of hydrogen to yield alkane. On the addition of ehtylene to 16% Pt/SiO_2,[61] gaseous ethane was produced although no ethyl groups were observed and hydrogenation of the adsorbed ethylene led to ethane production but no adsorbed ethyl groups. Also, the probability of alkyl reversal on platinum appears to be lower than with any other noble metal.[35] It thus appears that any adsorbed alkyl which is produced on platinum will rapidly react with hydrogen to yield alkane, rather than undergoing alkyl reversal to yield exchanged olefin.

It might be expected that the increasing retention with increasing temperature, would deplete the number of surface sites. Thus a decrease, rather than an increase, in olefin exchange with increasing temperature, would be observed, unless exchange occurred on sites inactive for olefin retention.

Since molecular exchange was observed in the absence of both hydrogenation and retention, tritiated olefin may result from molecular exchange (6).

$$C_2H_4(g) + C_2H_{(4-x)}T_{x(a)} \longrightarrow C_2H_4(a) + C_2H_{(4-x)}Tx(g) \quad (6)$$

It is possible, however, that the olefin reacts with adsorbed hydrocarbon species by a Rideal-type of mechanism, rather than displacing adsorbed olefin from the surface (7).

$$C_2H_4(g) + C_2H_xT_{y(a)} \longrightarrow C_2H_3T(g) + C_2H_{(x+1)}T_{(y-1)}(a) \quad (7)$$

The similarity in the results for propylene and ethylene, imply that similar mechanisms are involved in the reactions of both olefins. The slightly greater exchange of propylene, especially at high metal concentrations, may be related to the greater ease of molecular exchange of propylene than of ethylene. The formation of a π-allyl complex by propylene, may also lead to exchange by a different mechanism from ethylene,in addition to giving greater molecular exchange.

From the results discussed at the beginning of the section, it seems that there is another type of exchange process, the second exchange process. This reaction decreases more slowly, is less dependent upon the metal and more dependent upon the support than the first exchange process. The second exchange reaction also occurs in the absence of any observed retention or hydrogenation and it is possible, that it occurs by molecular exchange. This does not, however, explain why both olefin exchange and molecular exchange were greater over 1% Pt/Al_2O_3 than over 1% Pt/SiO_2.

From calibration injections of various volumes of tritium, the count observed in the products from one injection of ethylene could be approximately expressed as a volume of tritium. In a few cases, the volume of tritium removed during an injection of ethylene was a similar order to that which would give a monolayer coverage of the metal, as determined by carbon monoxide (Table 6.3). Thus the tritium retained on the support is directly involved in the reaction of ethylene. Since the supports themselves appear virtually inert for the reaction of ethylene the question arises as to the mechanism whereby the tritium associated with the support is incorporated into the olefin and the nature of the second exchange process.

From the previous discussion, it seems probable that the enhancement of the hydrogen exchange by the platinum is due to migration of hydrogen between the metal and the support. It is possible that ethylene adsorbed on the metal undergoes exchange, and the extent is controlled by the rate of migration of hydrogen between the metal and the support. The rate of hydrogen migration would have to be very fast in order to account for the high specific activity of ethylene. The enhancement of hydrogen exchange by the presence of platinum, as a result of hydrogen migration, does not appear

TABLE 6.3

Catalyst	Temp. (°C)	Vol. Tritium (1)	Vol. Tritium (2)	Vol. Tritium (3)
5% Pt/Al_2O_3	200	0·024	0·100	1·25
1% Pt/Al_2O_3	200	0·015	0·230	0·25
0·1% Pt/Al_2O_3	200	0·012	0·033	0·025
	350	0·025	0·066	0·025
5% Pt/SiO_2	200	0·009	0·046	1·25
1% Pt/SiO_2	200	0·001	0·007	0·25
0·1% Pt/SiO_2	200	0·007	0·017	0·025

(1) Counts in Ethylene from First Injection expressed as a Volume of Tritium.

(2) Total Counts in Products from Three Injections – Expressed as a Volume of Tritium.

(3) Volume of Tritium required to give Monolayer coverage of the Metal.

to be sufficiently high to account for a very high rate of migration of hydrogen. Unless, of course, the tendency of hydrogen to desorb from the metal before exchange, is greater than with ethylene.

The extent of exchange increases markedly with increasing temperature and the supports appear to be active for ethylene retention above 20°C. It is thus possible that ethylene adsorbed on the support undergoes exchange and the extent increases with increasing temperature. The reaction, however, only occurs in the presence of metal and perhaps only the hydrogen migrating between the metal and the support is active in exchange with ethylene on the support.

$$\mathrm{OTsupp} \rightleftharpoons \mathrm{Tm}$$

$$C_2H_4\mathrm{supp} + \mathrm{Tsupp} \longrightarrow C_2H_3T + \mathrm{Hsupp}$$

Such a mechanism would account for, (i) the greater amount of exchange over platinum-alumina than over platinum-silica due to greater reactivity of alumina than of silica and, (ii) the absence of exchange on the supports themselves. These considerations also apply to propylene.

With acetylene, (Table 4.32) the difference between platinum-alumina and platinum-silica catalysts is more striking than with ethylene and propylene. For example, at 50°C

	Acetylene retention (ml)	cpmlx10^{-5}
1% Pt/Al_2O_3	0·17	0·24
1% Pt/SiO_2	-	0·01
Al_2O_3	-	-
SiO_2	-	-

There is a definite co-operative effect of platinum and alumina for both acetylene exchange and retention. The observation of acetylene exchange and retention at 20°C and 350°C with alumina but not with silica at any temperature, is consistent with the work of Yates et al.[73] These workers observed two chemisorbed form of acetylene on η-alumina both of which exchanged with deuterated alumina. It is possible that the strongly bonded form corresponds to the retained species observed in the present work, whilst the weakly adsorbed form is the one leading to acetylene exchange. On silica,[73] only a weakly adsorbed form was observed which did not exchange with surface OD groups.

A small amount of acetylene exchange may occur directly on the metal. However, the 'spillover' of acetylene from the platinum to the support invoked in Section 6.1 to account for the reactions and retention of acetylene may also adequately account for the observed results for acetylene exchange. Once all the reactive metal sites are filled, acetylene may migrate to the support and either desorb unchanged or exchange with the support.

The hypothesis of migration of hydrocarbon as well as hydrogen would ratify many of the results obtained with ethylene and propylene. The lower activity of alumina with respect to these olefins, in comparison to acetylene, would explain the fact that differences between the various catalysts are not as marked with the olefins as with acetylene. In view of the acetylene results, it is probable that the 'second exchange process' observed for ethylene and also propylene proceeds on the support. The greater activity of alumina in comparison to silica would account for the greater exchange on alumina-supported catalysts than on silica-supported catalysts, in the absence of hydrogen.

There is the possibility, however, that the metal aids the desorption of hydrocarbons from the support, especially since Lucchesi[77] observed that platinum aided the removal by hydrogen, of ethylene on alumina. In the present work, with only two exceptions, both at high temperatures, no tritiated species were removed on heating alumina or silica, although tritiated species were observed to desorb from every platinum catalyst. In addition, the total count of the reactor eluant was greater for platinum-alumina than for platinum-silica. Thus if retained hydrocarbon is associated with the support, in addition to the metal, nevertheless the metal also aids the thermal desorption of the species associated with the support. The greater retention and exchange with alumina than with silica would explain the greater yield of tritiated species from platinum-alumina than from platinum-silica catalysts.

Section 6.5 The Effect of Hydrogen upon the Reaction of Ethylene.

(i) The effect of hydrogen upon the reaction of ethylene was investigated by (a) injecting hydrogen immediately before an injection of ethylene, and (b) by injecting equimolar mixtures of ethylene and hydrogen onto the catalysts. In the following discussion, these experiments will be referred to as experiment (a) and experiment (b) respectively, and hydrogen will be used to refer to reactant hydrogen and tritium to refer to the catalyst 'hydrogen'.

In both experiments (a) and (b) no retention of ethylene was observed on silica itself. For alumina, the retention of ethylene was reduced by the presence of hydrogen. Hydrogen must inhibit the retention of ethylene by either adsorbing on sites active for ethylene retention or by preventing the reaction leading to retention.

At 20°C, hydrogen was observed to react with alumina to form surface hydroxyl groups.[72] The newly created hydroxyl groups may act as sites for the retention of ethylene which was observed at 20°C in experiment (a) but not with ethylene alone or with the ethylene-hydrogen mixtures.

In both experiments, silica at every temperature and alumina below 200°C appeared virtually inert. At 100°C, ethane was observed with alumina only when hydrogen was injected immediately before ethylene. The nature of the ethane, however, suggested that the hydrogen may have been removing adsorbed ethylene as ethane. Since the ethane yield and the specific activities of ethane and ethylene were not significantly different for experiments (a) and (b), the reaction of hydrogen with alumina must be fast relative to that of ethylene with alumina. This is in agreement with the exchange of hydrogen, but not ethylene, observed with alumina below 200°C.

The slow self-hydrogenation of ethylene has been observed on η-alumina at 20°C.[72] The presence of hydrogen may favour the formation of adsorbed ethyl groups and ethane rather exchanged ethylene since the specific activity of the ethylene was lower in experiments (a) and (b) was less than with ethylene alone. Also, the greater 'store' of inactive hydrogen may result in a lower specific activity of ethylene.

(ii) The hydrogen exchange appears to be affected by the presence of ethylene. On alumina up to 200°C, and on silica, the decrease in specific activity of the hydrogen relative to the specific activity in the absence of ethylene, was greater in experiment (b) than is experiment (a). In view of this, it appears that adsorbed hydrogen is more likely to react with ethylene rather than adsorbing on sites active for ethylene retention.

With alumina above 200°C, the specific activity of the hydrogen in experiment (a) was less than and in experiment (b) greater than the specific activity of hydrogen in the absence of ethylene. In experiment (a) ethylene was retained on alumina so that it may be on the sites active for hydrogen exchange. In experiment (b), however, no ethylene was retained on alumina although hydrogenation was observed. A possible explanation is that usually ethylene inhibits hydrogen exchange when it adsorbs on sites active for hydrogen exchange. When hydrogen and ethylene are injected separately the ethylene retained at 200°C and 350°C still inhibits hydrogen exchange. When ethylene and hydrogen are simultaneously competing for the same sites, hydrogen can undergo exchange and also interact with the ethylene, which is in the process of exchanging.

(iii) The results with the supports themselves show that, with the exception of platinum-alumina above 100°C, results observed the platinum catalysts are determined by the metal. For the platinum catalysts, the decrease in retention and ethane yield observed in experiment (a) in comparison to ethylene alone, was even more marked with experiment (b). Since the same effects were observed with all catalysts, the different results must be due to the effect of hydrogen.

In both experiments (a) and (b), the retention of ethylene was greater with platinum-alumina than with platinum-silica catalysts. In experiment (a) this may be the result of the retention on alumina. With experiment (b), however, no retention was observed with alumina below 200°C and the retention was virtually the same with 1% Pt/Al_2O_3 and 0·1% Pt/Al_2O_3 although none was observed with 1% Pt/SiO_2 or 0·1% Pt/SiO_2. The higher yield of ethane in the latter case could be accounted for by the difference in retention. There thus appears to be a process leading to retention of ethylene from the mixture only when both platinum and alumina are present and not very dependent upon the amount of metal present. These results provide good evidence for the migration of adsorbed hydrocarbon between the metal and support.

In experiment (b) up to 200°C, no retention was observed with the supports. However, ethylene may adsorb on the platinum and either react with hydrogen to give ethane (1) or else may migrate to the support (2)

$$\text{Metal} \qquad C_2H_4 + H_2 \longrightarrow C_2H_6 \qquad (1)$$

$$C_2H_{4(metal)} \longrightarrow C_2H_{4(supp)} \qquad (2)$$

With silica, ethylene is only weakly adsorbed so that the ethylene may either desorb or migrate back to the metal where hydrogenation takes place. The hydrogenation reaction must be fast, since the conversion of ethylene to ethane was virtually complete with 1% Pt/SiO_2 and 0·1% Pt/SiO_2. In contrast, on alumina ethylene does adsorb quite strongly, and there is less possibility of migration back to the metal than with silica and thus the retention is similar with 1% Pt/Al_2O_3 and 0·1% Pt/Al_2O_3. There is, of course, the possibility that hydrogenation may also occur on the alumina. We cannot define the nature of the migrating species but it appears that hydrogen influences the extent of migration and hence the hydrogen content of the migrating species must be critical. In the absence of hydrogen, dissociation and self-hydrogenation are dominant so that by preventing dissociation of ethylene on the metal, hydrogen may enhance migration to the support.

The results of experiment (a) can also be rationalised in this manner. Retention does occur on the metal but to a lower extent than for ethylene alone. With the platinum-alumina catalysts the retention is greater than with the platinum-silica catalysts, due probably to a combined effect of direct adsorption on alumina and also migration from the platinum to the alumina. However, the ethane yields are also greater with platinum-alumina than with platinum-silica. Since alumina is observed to be active for hydrogenation at 100°C and above, some of the ethylene which migrates to the alumina may be hydrogenated.

One important feature of experiment (a) is the fact that a broadening of the ethane peak implied that the hydrogen was removing adsorbed ethylene as ethane. This fact may account for the differences in the ethane yields. However, at no time was the total volume of products greater than 0·5 ml. so that either the effect was minimal or else ethylene quickly adsorbed on sites left vacant by the removal of ethylene. This observation is consistent with the fact that hydrogen removed adsorbed ethylene as ethane (see Section 4.6).

One might expect that the relatively high concentration of inactive hydrogen would lead to lower specific activities of ethylene and ethane in comparison to the experiments using ethylene alone. The opposite effect was, however, observed with all platinum catalysts, although the difference tended to decrease with increasing temperature. Thus either, the rate of hydrogen exchange with the support must be fast relative to reaction with ethylene and/or the rate of migration of hydrogen is proportional to the concentration of hydrogen on the surface. The latter hypothesis is likely in view of the fact that the increasing dissociation of ethylene with temperature leads to an increased concentration of hydrogen and this is accompanied by an increase in the specific activity of ethylene (see Tables 4.14 and 4.15). The specific activities of ethane and ethylene are greater in experiment (a) than in (b) which probably reflects the great excess of inactive hydrogen present in experiment (b).

The methane yield from the ethylene hydrogen-mixtures and ethylene alone was very similar and much lower than the yield when hydrogen was injected before ethylene. These results imply that cracking is suppressed by hydrogen but when excess hydrogen is present in the gas phase it can react with C_1 species to yield methane. On the other hand, hydrogen adsorption may be slow relative to cracking. Thus only when hydrogen can adsorb before ethylene can it affect the extent of cracking.

(iv) From the lowering of the hydrogen exchange on alumina and silica by the presence of ethylene in experiment (a), one would expect the hydrogen exchange to be lowered with the platinum catalysts in experiment (a) since most of the hydrogen exchange, in the flow system, proceeds directly on the support. The hydrogen exchange on the platinum catalysts, however, was enhanced by the presence of ethylene and was greatest when the ethylene retention was appreciable. Also, the hydrogen exchange was less dependent upon the support than in the absence of ethylene. Thus the hydrogen exchange appears to be a function of the ethylene retained on the metal and perhaps exchanges with adsorbed ethylene by a Rideal-Eley mechanism.

$$C_2H_4(a) + \underset{\substack{\vdots \\ *}}{H_2} \longrightarrow C_2H_5(a) + H(a) \qquad (3)$$

$$C_2H_5(a) \longrightarrow C_2H_4(a) + H(a) \qquad (4)$$

$$2H(a) \longrightarrow H_2 \qquad (5)$$

(v) Since the results of propylene-hydrogen mixtures (Table 4.26) are similar to those observed with ethylene-hydrogen mixtures the considerations discussed for ethylene also appear to apply to propylene. The conversion of propylene to propane was complete in most cases and the retention was correspondingly very low. The retention of propylene was less than ethylene on the platinum-alumina catalysts. This observation together with the fact that the difference in reactivity of alumina- and silica-supported catalysts was less distinct than with ethylene may imply that migration of propylene from platinum to alumina is less important than with ethylene.

(vi) Hydrogen was injected onto ethylene covered 1% Pt/Al_2O_3 and 1% Pt/SiO_2 at temperatures up to 350°C. As mentioned above, the only products removed by the hydrogen were ethane, and at 350°C methane, although the fraction of the retained species removed decreased with increasing temperature. The specific activity of the products, however, increased with increasing temperature. These facts combined with the observation that the specific activity of the ethane removed was greatly in excess of the specific activity of ethane produced from ethylene and from ethylene-hydrogen mixtures, support the proposition that retention is due to extensive dissociation of the retained ethylene. The retained species must, however, also exchange tritium in the system by reactions such as (6) and (7)

$$C_2H_4(a) \longrightarrow C_2H_{4-x} \qquad (6)$$

$$C_2H_{4-x} \rightleftharpoons C_2H_{4-x}T_y \qquad (7)$$

The overall value of x and the ratio y/4-x increase with increasing temperature.

After the hydrogen treatment, the subsequent retention of ethylene was often greater than the volume of ethane removed by the hydrogen. This effect was more marked with 1% Pt/Al_2O_3 than with 1% Pt/SiO_2. Since the injection of hydrogen before ethylene was found to enhance the retention of ethylene on alumina but not silica, the hydrogen may be creating new sites for the adsorption of ethylene on the support component which would be greater for 1% Pt/Al_2O_3 than for 1% Pt/SiO_2.

Hydrogen exchange is reduced by the presence of adsorbed ethylene but not to the same extent as for the ethylene-hydrogen mixtures. It is interesting to note that in these experiments as, in experiment (a) the results for the hydrogen exchange on 1% Pt/Al_2O_3 and 1% Pt/SiO_2 are more similar than in the absence of ethylene. From the previous discussion, we can draw up the following sequence of reactivity of hydrogen on supported catalysts. (a) In the absence of ethylene (i) hydrogen exchange proceeds mainly on the support and the rate of exchange is greater on alumina than on silica. (ii) Exchange may also occur on the metal but the results (Table 4.19) show that this process is not appreciable. (iii) The presence of metal enhances the exchange with the support (see Appendix II), probably by acting as a source of 'reactive' hydrogen which can migrate to the support. (iv) The platinum enhances the desorption from the support. (b) In the presence of ethylene on the support the direct exchange with the support is inhibited. Ethylene thus appears to adsorb on the sites active for hydrogen exchange. However, when both ethylene and metal are present, the reaction of hydrogen with the ethylene adsorbed on the metal is faster than any other reaction of hydrogen, since the support effect is considerably reduced. The outcome of this interaction depends upon (i) the adsorbed state of the olefin, (ii) the time of adsorption, and (iii) the temperature. If the ethylene is weakly adsorbed, ethane is produced. However, if the ethylene is strongly adsorbed the interaction may lead only to hydrogen exchange. The tritium content of hydrogen thus depends on the available tritium from the ethylene, which will increase with increasing temperature.

Section 6.6 The Effect of Adsorbed Oxygen.

Treating 1% Pt/Al_2O_3 and 0·1% Pt/Al_2O_3 with sufficient oxygen to give more than a monolayer coverage of the metal, did not markedly change their catalytic activity towards propylene (Table 4.31). The yield of propane, below 200°C was lower and since at these temperatures hydrogenation appears to be only a metal process, oxygen appears to have poisoned the self-hydrogenation reaction. However, at 200°C and 350°C the propane yields were similar to those observed in the absence of oxygen. Alumina, itself appears to be reactive for the hydrogenation of propylene (Table 4.26) at 200°C and 350°C so that it is probable the observed yields at 200°C and 350°C are due largely to reaction on the support.

The retention and the specific activities of ethane and ethylene did not appear to be affected by the presence of oxygen although, in some cases, the retention was enhanced. These results suggest that either, (i) the oxygen is not adsorbed on metal sites which adsorb propylene, or (ii) propylene retention and exchange on the support are important. In view of the lower yield of propane and the fact that migration of hydrocarbon species could be important, the latter hypothesis appears to be more likely than the former.

Section 6.7 A Comparison of Platinum and Palladium.

The preliminary work with 5% Pd/Al_2O_3 and 5% Pd/SiO_2 suggest that the reaction of ethylene is similar to that with 5% Pt/Al_2O_3 and 5% Pt/SiO_2. The extent of ethane production was similar at each temperature although the methane yield was lower with palladium than with platinum. This observation is consistent with the ability of platinum to catalyze carbon-carbon bond fission more effectively than palladium.[84]

Differences in the behaviour of 5% Pd/Al_2O_3 and 5% Pd/SiO_2, especially with respect to ethylene exchange, suggests that support effects are to be found both with platinum-supported and palladium-supported catalysts. However, the extent of molecular exchange was greater with palladium than with the corresponding platinum catalyst, suggesting that the extent of dissociation is greater with platinum.

An important effect, observed with 5% Pd/SiO_2, was that after leaving the catalyst at a particular temperature for some time, the specific activity of the ethylene was greatly enhanced. This phenomenon suggests that there is a slow process leading to an increased concentration of 'reactive' tritium on the surface and may be due to diffusion of tritium from the bulk to the surface of palladium.

Section 6.8 The Thermal Desorption Studies.

From the above discussion (Section 6.1) it was proposed that retention of ethylene on platinum catalysts was due primarily to dissociation and that the retained species were in the form of C_2 units. Increasing the temperature of a tritiated platinum catalyst on which ethylene was retained led to the removal of tritiated species. The tritium content of these species (Tables 4.14 and 4.15), the volume of hydrocarbon removed and the percentage of the retained hydrocarbon removed (Table 4.18) decreased with decreasing metal concentration and was greater with alumina-supported than with silica-supported catalysts.

In order to attempt to determine the nature of these products and thereby obtain further information regarding the nature of the retained species, ethylene treated catalysts were heated in a static system and the thermally desorbed products were injected directly into a mass spectrometer (Chapter 5).

The nature and relative abundance of various products depended both on the metal concentration and on the support. A decrease in the pressure of the products was observed from 5% platinum to 0·1% platinum catalysts. Thus most of these products appear to be associated with the metal rather than the support. Since the yields of the products were shown relative to the height of the maximum peak, characteristics of the support may be obscured by the effect of the metal, especially in the case of 5% platinum catalysts. However, a greater pressure of desorbed products was observed with the supports themselves than with the 0·1% platinum catalysts, implying that the metal affects the adsorption and desorption on the support. The fact that products were thermally desorbed from both alumina and silica although no adsorption was observed at 20°C with either catalyst in the flow system tends to emphasise the difference between static and flow conditions mentioned in Section 6.1.

In view of the observations that, (i) at 20°C hydrogen removed over 90% of the retained species as ethane from 1% Pt/Al_2O_3; (ii) the percentage removed decreased with increasing temperature, and (iii) retention and self-hydrogenation increased with increasing temperature, it is likely that most of the desorbed products were formed during the heating of the catalyst. A similar conclusion was reached by Komers et al[68] from their thermal desorption studies of ethylene treated 4·6% Pt/SiO_2. They observed the removal of ethane, formed by self-hydrogenation and some ethylene at ~100°C and also some 'non-condensable' products at ~225°C and ~600°C which they considered to be methane.

The observation that ethane and ethylene were the major products using 5% Pt/Al_2O_3 and 5% Pt/SiO_2 is consistent with their work. The greater yield of ethylene relative to ethane, observed in our work, probably reflects the greater pressure of ethylene used in the pretreatment of our catalysts and in conjunction with the more sensitive analysis by mass spectrometry, probably accounts for the observation of more products.

The similarity in the results observed with 5% Pt/Al_2O_3 and 5% Pt/SiO_2 (Tables 5.3 and 5.6) implies that the products are characteristic of the metal. The only major difference between the alumina- and silica-supported catalysts was in the greater proportion of alcohols and the appearance of butanol from 5% Pt/SiO_2. Approximately 80% of the hydrocarbon products at each temperature were C_2 compounds which supports the hypothesis of the retained species, at least on platinum, being mainly in C_2 units. The slightly greater fraction of C_2 products removed from 5% Pt/Al_2O_3 than from 5% Pt/SiO_2 may be related to the fact that a greater fraction of the retained species were removed by hydrogen from 1% Pt/Al_2O_3 than from 1% Pt/SiO_2, since only ethane was observed.

It is likely that the ethylene was weakly adsorbed and desorbed without undergoing reaction. The ethane was most probably formed by self-hydrogenation. The much lower yield of acetylene relative to ethane and ethylene, especially at the lower temperatures, can be accounted for by the stronger adsorption of acetylene compound to ethylene and ethane.[104] Also, the process of self-hydrogenation leads the formation of surface carbide[61] in addition to acetylenic residues. The yield of acetylene and more markedly the yield of ethane decreased from a 5% platinum to a 0·1% platinum catalyst, indicating that these products are formed mainly on the metal. However, the yield of ethane decreased in the following order:
$5\%\ Pt/Al_2O_3 > 5\%\ Pt/SiO_2 \gg 0{\cdot}1\%\ Pt/Al_2O_3 > 0{\cdot}1\%\ Pt/SiO_2 \gg Al_2O_3 > SiO_2$
which is similar to the order of hydrogenation activity at 100°C and above in the flow system.

Alumina has been shown to be active for ethylene hydrogenation at relatively high temperatures (e.g., 350°C),[112] although self-hydrogenation has been observed on η-alumina at 20°C. These observations could account for the above sequence since silica appears to possess no hydrogenation activity, at least up to 350°C. Since, after correcting for the ethane formed directly on the supports and for differences in the available metal area, the yields are still greater on 5% Pt/Al_2O_3 than on 5% Pt/SiO_2, the support appears to influence the reaction.

The only other major products, other than water, observed with 5% Pt/Al_2O_3 and 5% Pt/SiO_2 were C_3 compounds. With 5% Pt/Al_2O_3, a greater proportion of saturated C_3 products relative to unsaturated C_3 compounds were observed than with 5% Pt/SiO_2. The question arises as to the mechanism whereby such compounds are formed. In view of the very low yield of methane and C_3 hydrocarbons and the absence of any higher hydrocarbons, cracking of polymers does not appear to be a likely route to the formation of C_3 products. Since adsorbed methyl groups have been observed on 16% Pt/SiO_2 at 95°C,[61] it is possible that the combination of C_1 and C_3 species leads to propylene etc., and would account for the low methane yield.

$$\left.\begin{array}{l} C_2H_x(a) \longrightarrow 2C_1H_y(a) \\ C_2H_x(a) + C_1H_y(a) \longrightarrow C_3H_{(x+y)} \end{array}\right\} \quad (1)$$

$$\left.\begin{array}{l} 2C_2H_x(a) \longrightarrow C_4H_{2x}(a) \\ C_4H_{2x} \longrightarrow C_3H_y + CH_z \end{array}\right\} \quad (2)$$

Both propylene and propane, were however, important products with every catalyst, including the supports, from which it could be inferred that reactions resulting in C_3 formation occur on the support. Polymers ($> C_4$) were observed with all catalysts except those with 5% platinum and their breakdown could lead to propylene etc.

The polymerisation of olefins has been observed on silica-alumina and alumina.[76,113] The greater activity of the former has been attributed to its greater acidity since acidic centres are generally accepted to be the sites active in polymerisation.[113] The initiation reaction is assumed to be by carbonium ion formation and the marked difference in reactivity between ethylene and propylene formation has been explained[76] by the greater ease of formation of propyl carbonium ions.

A characteristic of polymerisation on these catalysts is the formation of saturated compounds or mono-olefins, rather than highly unsaturated hydrocarbons.[76] The polymers thermally desorbed from alumina were almost always saturated or mono-olefinic compounds so that they resemble the products formed directly over acidic catalysts. The greater acidity of alumina, compared to silica, may explain both the greater volume and number of products in the former case. There is still much doubt about the mechanism of olefin polymerisation on acidic oxides although different workers using different systems have reached similar conclusions.[76,99,114]

Both ethylene on alumina[113] and propylene and butene on silica-alumina[114] resulted in the rapid formation of polymers at 20°C. Thus polymerisation appears to be a fast process which could be explained by an ionic mechanism, although it appears that the reaction of propylene also ceases quickly leading to an average of four molecules to each polymer.[114] Results for ethylene,[113] propylene[76,114] and butene[114] suggest that Brönsted sites are required for polymerisation. This conclusion is in agreement with the results of Holm et al[115] who showed that the polymerisation activity of a series of catalysts increased with increasing Brönstead acidity and not with the total acidity. Thus initiation is regarded to be of the type (3).

$$C_2H_4 + H^+S \longrightarrow (C_2H_5)^+S \qquad (3)$$

Since the presence of gaseous ethylene was found to be essential for polymerisation and the extent of reaction increased with increasing pressure, Amenomiya et al[113] proposed that a Rideal type mechanism was involved.

$$(C_2H_5)^+S \xrightarrow{C_2H_4(g)} (C_4H_9)^+S \xrightarrow{C_2H_4(g)} (C_6H_{13})^+S \longrightarrow \text{etc.} \qquad (4)$$

$$(C_4H_9)^+S \longrightarrow C_4H_8 + H^+S \qquad (5)$$

The dependence upon pressure for the extent of reaction (4) would explain the fact that higher polymers were observed in our work than by Amenomiya et al[113] since the pressure of ethylene was greater in the former work.

The products observed with alumina tended to decrease in the following order $C_4 > C_6 > C_8 > C_{10}$. This could imply that either the reactivity decreases with each addition of ethylene or that the heat of desorption increases with increasing molecular weight. It is, however, not possible to determine the 'shape' of the products, although the observation of relatively few peaks in the mass spectra, suggests that they were mostly linear.

The polymerisation of propylene[76] was accompanied by extensive cracking and isomerisation and it was shown that compounds e.g., C_5 were formed by the breakdown of higher polymers. It is thus probable that the C_3, C_5 and C_7 products observed were also produced in this manner. The yield of C_5 and C_7 products was very low at 100°C and tended to increase relative to other polymers ($>C_4$ with increasing temperature. The C_3 compounds, especially propylene, were important products at every temperature and at 350°C propylene was the major product. Thus the formation of C_3 compounds appears to be highly favoured process and perhaps C_3 species are the most stable species, since their yield increases with increasing temperature.

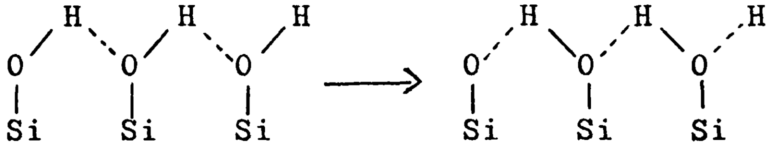
From the above discussion, it appears that on alumina polymerisation proceeds at low temperatures by a carbonium ion mechanism. At 100°C appreciable quantities of unreacted ethylene are desorbed along with saturated and mono-olefin polymers and some decomposition products (e.g., C_3H_6). As the temperature is raised, the more strongly held ethylene is desorbed and cracking of the polymers increases.

The yield of C_3, C_5, C_7 compounds, relative to $(C_2)_n$ products was greater with 0·1% Pt/Al_2O_3 than with alumina. Also, higher polymers e.g., C_{10} were observed with alumina than with 0·1% Pt/Al_2O_3. With 5% Pt/Al_2O_3 no compounds greater than C_4 were observed at any temperature. The metal must either inhibit polymerisation or else enhance the cracking of the polymers. It is also interesting to note that with increasing metal content the proportion of more highly unsaturated products increases. For example, C_3H_4 is an important product for 5% Pt/Al_2O_3 and 5% Pt/SiO_2 but was only observed at 350°C with 0·1% Pt/Al_2O_3 and only trace amounts were formed over alumina.

Enhancement of the cracking of polymers by the metal, could account for the high yield of C_3 products from the 5% platinum catalysts, when no high polymers were observed. It has been shown, however, that the products formed depend upon the supply of hydrogen.[76] Since, in the above discussion, the platinum was found to enhance hydrogen exchange with the support, it is possible that the platinum influences polymerisation by affecting the supply of hydrogen

One interesting effect is that the amount of water removed from the catalysts decreased in the order 5% Pt > 0·1% Pt > 0% Pt. The amount removed from the metal was so great that it seems improbable the water was associated with the metal. In the work of Boudart et al,[111] water was thought to act as an agent for the transport of hydrogen from the metal over the surface of WO_3. The hydrogen released in reactions such as (6) may be transported across the support via adsorbed water (7).

$$C_2H_4(a) \longrightarrow C_2H_{4-x}(a) + XH(a) \qquad (6)$$



(7)

The yield and number of products was lower with silica than with alumina, as would be expected, if the acid centres on alumina are the sites of reaction. Many products observed with alumina were, however, also observed with silica. The differences in the products observed with silica and alumina, are reflected in the differences in products observed with silica-supported and alumina-supported catalysts.

The most important difference between alumina and silica was the formation of alcoholic products, often the major products with silica, whereas with alumina, when observed, they were only minor products. No alcohol was, however, observed in the absence of the corresponding hydrocarbon. For example, butanol was only formed when butene was observed. This suggests that 'oxygen' is incorporated into the hydrocarbons after they were formed. One possible mode of formation is the addition of water, associated with the support, to adsorbed olefin; formed by polymerisation;

$$2C_2H_4(a) \longrightarrow C_4H_8(a)$$

$$C_4H_8(a) + H_2O(a) \longrightarrow C_4H_9OH$$

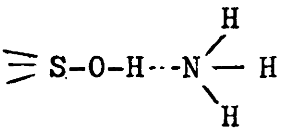
<u>or</u>

$$C_4H_9^+(a) + OH^- \longrightarrow C_4H_9OH.$$

From the infra-red results it appeared that the removal of water was easier from silica than from alumina. Also, even after extensive drying at 1000°C, γ-alumina continued to evolve traces of water.[106] The difference in the reactivity of the water may explain the different results with alumina and silica. The catalytic activity of alumina is generally attributed to its acidity[113] whereas silica is thought to be neutral.[28] Many products were, however, observed with both supports and unless silica is acidic their formation would presumably, have to be by a different mechanism on alumina than on silica.

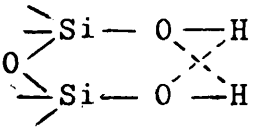
Hall et al[28,108] have collected much evidence showing that the hydroxyl groups on silica-alumina, alumina and silica are chemically similar and resemble more closely alcoholic hydrogen than the protons of a strong acid. It was concluded that these were the hydroxyl groups required to terminate the lattice and that any acidic hydrogen present could only amount to a small fraction of the total. Dehydrated alumina and silica-alumina, however, were thought to possess Lewis acid sites although no mention was made of the acidic nature of the hydrated oxides.

The catalytic activity of alumina appears to depend largely upon the extent to which it has been dried.[106] Water was also observed to have a profound effect upon the adsorption characteristics of aerosil silica,[116] from which the following model was proposed. After evacuation at high temperatures, up to 800°C, there are only 'free' hydroxyl groups on silica (A) which can act as strong adsorption sites, particularly for lone pair adsorbates.

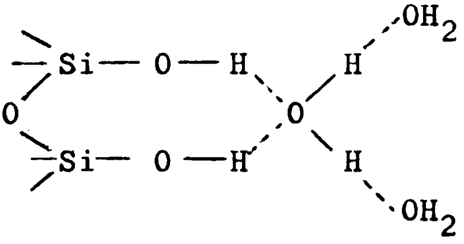


(A)

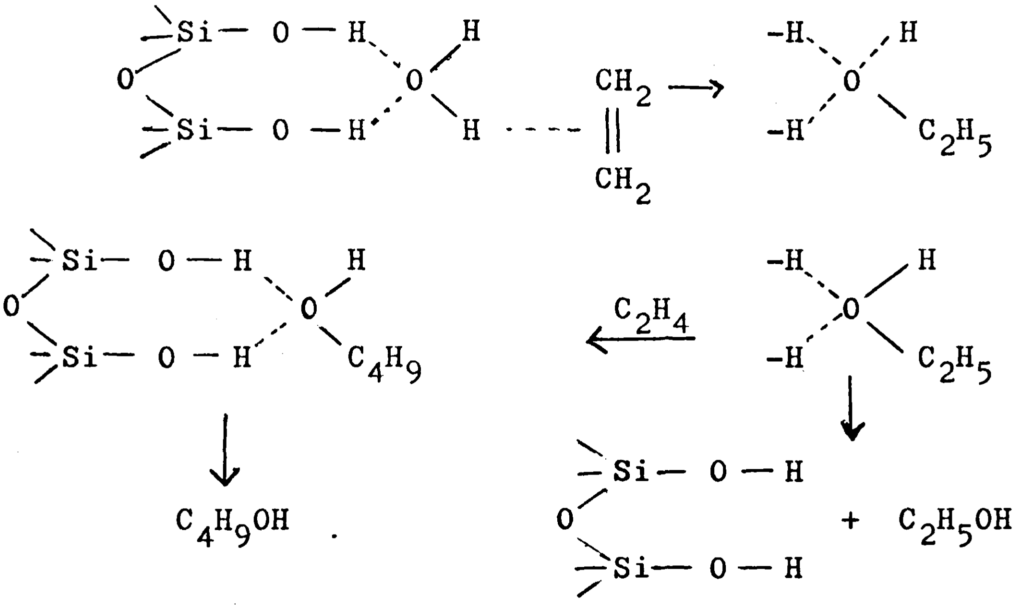
At lower evacuation temperatures and perhaps with untreated silica, hydroxyl groups are close together and interact together, thus adsorption is hindered (B).



If water is present, however, interaction occurs with groups (B) to give (C) which forms many new sites for adsorption.



These observations could help to rationalize the results observed with silica. Like other workers,[72] we observed no chemisorption of ethylene on silica by infra-red spectroscopy and Komers et al[68] observed no products from ethylene on silica. In all these experiments, no water was present and the catalyst was usually evacuated at quite high temperatures, thus only (B) and perhaps some (A) was present so that only weakly adsorbed species were formed. However, the silica used in the flow system experiments and thermal desorption studies was treated with water during the catalyst preparation and thus may be assumed to be in state (C). The interaction of ethylene with state (C) is perhaps too weak to allow reaction in the flow system but in static conditions, the interaction may lead to reaction.



Such mechanisms could account for the formation of ethanol, butanol and butene on silica. The activity is derived from the slightly polar nature of the C-O bond and the probability of ethylene desorbing is usually greater than the probability of reaction to give other products. The products formed on silica do appear to be weakly adsorbed, at least relative to alumina, since over 98% of the products removed up 350°C, were desorbed below 200°C.

It is also probable that species such as (C) are present on hydrated alumina since undried γ-alumina shows bands corresponding to the stretching and bending frequencies of liquid water.[106] Such bands were also observed on the alumina used in the present work (Appendix II). Evacuation at 1000°C was necessary to observe the bands of free hydroxyl groups (A).[106] The three hydroxyl groups of alumina show independent variations in intensity during reactions, e.g., with hydrocarbons. Thus both states (A) and (C) of alumina may have three different sites.

The products observed with both silica and alumina could be formed on sites of the type (C) and they constitute the only products from silica. Alumina, however, is catalytically active when silica appears inert so there must be other more reactive sites present on alumina, whose activity is dominant under most conditions.

At low temperatures polymerisation occurs and ethylene adsorbs on alumina.[72] Since in the latter case two crystallographically similar η-aluminas led to different forms of adsorbed ethylene, the adsorption characteristics must be controlled by minute differences on the surface, such as the degree of hydration or the degree of Brönsted acidity. Hall's work,[28,108] however, suggests that the degree of Brönsted acidity on alumina is very low.

There is the possibility that the precursor to polymerisation is an adsorbed ethyl radical (D) rather than a carbonium ion (E). The high yield of 2 butenes relative

$$\text{Al-O-C}_2\text{H}_5\ (\text{D}) \quad \text{Al-O}^- \quad (\text{C}_2\text{H}_5)^+ \quad (\text{E})$$

to isobutene during propylene polymerisation would tend to favour a non-carbonium ion mechanism.[76]

Ethylene was not observed to exchange with deuterated alumina at 20°C[72] although other workers[99] found that products thermally desorbed from alumina at ~300°C had exchanged with alumina. In the latter case, the exchange must have occurred during heating since alumina is inert for ethylene exchange at 20°C but active for exchange and hydrogenation at 300°C. The increasing activity of alumina with increasing temperature and dehydration must mean that the state (A) with isolated hydroxyl groups attached to aluminium is most active. Hall has indicated that Lewis acidity is important on dehydrated alumina and may involve donation of electrons to the aluminum. Water, when present on alumina, may thus screen these sites from the reactants.

Since platinum appears to enhance the removal of water from the supports, it is possible that the hydrogenation activity of alumina is thereby enhanced. Thus, in the presence of platinum, alumina may become active at temperatures below those at which it is normally active. The observation that, even after correcting for any direct reaction on the support, in both the flow system and thermal desorption studies, the yield of ethane was greater for a platinum-alumina than for the corresponding platinum-silica catalyst would be thus explained.

CONCLUSIONS

From the above discussion, the following conclusions can be drawn.

1. The retained tritium is associated with the support, in the form of surface hydroxyl groups, rather than with the metal.
2. Hydrogen exchange occurs directly with the support but the exchange is also enhanced by the presence of platinum on which hydrogen readily dissociates and migrates to the support. The presence of ethylene inhibits hydrogen exchange on the support, probably by adsorbing on sites active for hydrogen exchange. Ethylene adsorbed on the metal leads to a facile hydrogen exchange reaction, probably by a Rideal-Eley mechanism.
3. Hydrocarbon retention is due to dissociation of adsorbed species and leads to self-hydrogenation. Dissociation and self-hydrogenation increase with increasing temperature. The difference in reactivity of platinum-alumina and platinum-silica catalysts is due to the migration of hydrocarbon species to the support. The extent of reaction is greater on alumina than on silica.

4. Platinum may enhance the catalytic activity of alumina by enhancing the removal of water from alumina.
5. Under most conditions silica is inert, but reaction of hydrocarbons may occur with water adsorbed on silica.

APPENDIX I.

Compounds giving peaks at certain m/e values

(other peaks observed shown in brackets)

m/e	
15	CH_4 (16)
16	CH_4 (15)
17	H_2O (18) HCOOH (29, 44) C_4H_9OH (31, 44, 57, 74)
18	H_2O (17)
26	C_2H_2 (27, 28) C_2H_4 (27, 28) C_2H_6 (27, 28, 29, 30)
	C_4H_9OH C_7H_{16} C_8H_{18} CH_3CH_2COOH
27	C_2H_2 (26, 28) C_2H_4 (26, 28) C_2H_6 (26, 28, 29, 30)
	C_3H_6 (41, 42) C_3H_8 (28, 43, 44) C_4H_6 (53, 54)
	C_4H_8 (41, 58) C_5H_8 (39, 40, 41, 67, 68)
	C_6H_{10} (39, 41, 43, 67, 82) C_6H_{16} (29, 41, 43, 57, 86)
	C_7H_6 (28, 29, 42, 43, 56, 57, 71, 85, 100) C_8H_{16}
	C_8H_{18} (29, 41, 43, 85, 114)
28	C_2H_4 (26, 27) C_2H_6 (26, 27, 29, 30) C_3H_8 (29, 43, 44)
	C_5H_{10} (42, 55, 70) $CH_3CH_2CH_2OH$ (29, 31, 43, 60)
	C_4H_9OH (31, 44, 45, 57, 74) HCHO (29, 30)
	C_3H_4O (27, 29, 45, 46) HCOOH (29, 46)
	C_2H_5COOH (26, 27, 45, 74) C_4H_8O (27, 29, 41, 43, 44, 72)
	C_6H_{12} (41, 42, 43, 55, 56, 69, 84)
	C_7H_{16} (42; 43, 56, 57, 71, 85, 100)

m/e	
29	C_2H_4 (26, 27, 28) C_2H_6 (26, 27, 28, 30) C_3H_8 (43, 44) C_4H_8 (41, 58) C_4H_{10} (42, 43, 58) C_5H_{12} (27, 43, 57, 72) C_6H_{12} (28, 39, 41, 42, 55, 69, 84) C_6H_{14} (27, 41, 43, 57, 86) C_7H_{14} (27, 39, 41, 55, 56, 98) C_7H_{16} (27, 41, 43, 56, 57, 85, 100) C_8H_{16} (41, 43, 55, 57, 70, 97) C_8H_{18} (27, 41, 43, 71, 85, 114) CH_3CHO (43, 44) C_3H_7OH (28, 31, 43, 59, 60) C_4H_9OH (28, 31, 44, 45, 57, 58, 74)
30	C_2H_6 (26, 27, 28, 29) HCHO (28, 29)
31	C_2H_6 (26, 27, 28, 29, 30) CH_3OH (30, 32) C_2H_5OH (28, 45, 46) C_3H_7OH (28, 43, 59, 60) C_4H_9OH (28, 44, 45, 57, 58, 74) HCHO (28, 29, 30)
32	CH_3OH (30, 31
39	C_3H_4 (38, 40) C_4H_6 (28, 52, 53, 54) C_5H_8 (27, 40, 41, 42, 67, 68) C_5H_{10} (42, 55, 70) C_5H_{12} (27, 29, 43, 57, 72) C_6H_6 (77, 78) C_6H_{10} (27, 40, 41, 42, 53, 67, 82) C_6H_{12} (28, 29, 41, 42, 55, 69, 84) C_7H_{16} (27, 29, 41, 43, 85, 100) C_8H_{18} (27, 29, 41, 43, 71, 85, 114) C_4H_8O (27, 29, 41, 44, 57, 72)
40	C_3H_4 (39, 41) C_3H_6 (41, 42) C_5H_8 (27, 41, 42, 67, 68)

m/e

41 C_3H_6 (40, 42) C_4H_8 (56) C_4H_{10} (29, 42, 43, 58)
C_5H_8 (27, 39, 40, 42, 67, 68) C_5H_{10} (39, 42, 55, 70)
C_5H_{12} (27, 29, 39, 42, 43, 57, 72)
C_6H_{12} (28, 29, 42, 55, 69, 84)
C_6H_{14} (27, 29, 43, 56, 57, 86)
C_7H_{14} (27, 29, 39, 55, 56, 98)
C_7H_{16} (27, 28, 29, 42, 43, 56, 57, 71, 85, 100)
C_8H_{16} (29, 43, 55, 56, 70, 97, 112)
C_8H_{18} (27, 29, 43, 71, 85, 114)
C_4H_9OH (28, 31, 44, 45, 57, 58, 74)
C_4H_6O (27, 29, 39, 42, 57, 72)

42 C_3H_6 (41) C_3H_8 (43, 44) C_4H_8 (29, 41, 43, 58)
C_4H_{10} (29, 41,43, 58) C_5H_8 (26, 27, 39, 40, 67, 68)
C_5H_{10} (55, 70) C_5H_{12} (26, 28, 29, 41, 43, 57, 70)
C_6H_{10} (27, 39, 40, 41, 43, 67, 82)
C_6H_{12} (26, 28, 29, 39, 41, 43, 55, 56, 69, 84)
C_6H_{14} (27, 29, 41, 43, 57, 86)
C_7H_{16} (27, 28, 29, 41, 43, 56, 57, 71, 85, 100)

43 C_3H_6 (41, 42) C_3H_8 (42, 44) C_4H_8 (29, 41, 43, 56)
C_4H_{10} (29, 41, 42, 58) C_5H_{10} (42, 55, 70)
C_5H_{12} (26, 28, 29, 41, 42, 57, 72)
C_6H_{10} (27, 39, 40, 41, 42, 67, 82)

cont'd.

m/e	
43	C_6H_{14} (27, 29, 41, 42, 57, 86)
	C_7H_{16} (27, 28, 29, 41, 42, 56, 57, 71, 85, 100)
	C_8H_{18} (27, 29, 42, 57, 71, 85, 114)
	C_3H_7OH (28, 31, 59, 60) CH_3CO_2H (45, 60)
	CH_3CHO (29, 44) C_3H_6O (57) C_4H_8O (29, 44, 72)
	$C_5H_{10}O$ (27, 29, 57, 86)
44	C_3H_8 (43, 45) C_4H_{10} (29, 41, 42, 43, 58)
	nC_4H_9OH (28, 31, 45, 52, 74) C_2H_4O (29, 43)
	C_4H_8O (29, 43, 72) C_6H_{14} (57, 86) C_7H_{16} (57, 100)
45	C_2H_5OH (31, 46) C_3H_7OH (28, 31, 43, 59, 60)
	C_4H_9OH (28, 31, 41, 44, 57, 58, 74) CH_3CO_2H (42, 60)
	$C_2H_5CO_2H$ (28, 46, 74)
46	C_2H_5OH (31, 45) C_4H_9OH (28, 31, 41, 44, 45, 57, 58, 74)
	HCOOH (28, 29)
50	C_4H_2 (49, 51) C_4H_4 (52) C_4H_6 (39, 53, 54)
51	C_4H_6 (39, 53, 54) C_6H_6 (39, 50, 52, 77, 78)
52	C_4H_4 (50) C_4H_6 (39, 53, 54)
53	C_4H_6 (39, 54) C_5H_8 (27, 39, 40, 41, 42, 67, 68)
	C_6H_{10} (27, 39, 40, 41, 42, 67, 82)
54	C_4H_6 (39, 53)
55	C_4H_8 (41, 56) C_5H_{10} (39, 42, 70)
	C_6H_{12} (28, 29, 39, 41, 42, 69, 84)
	C_7H_{14} (27; 29, 39, 41, 56, 98) C_7H_{16} (57, 71, 85, 100)
	C_3H_4O (27, 28, 29, 56)

m/e	
56	C_4H_8 (41, 55) C_4H_{10} (29, 41, 42, 43, 58)
	C_6H_{12} (41, 42, 55, 69, 84) C_6H_{14} (41, 42, 43, 57, 71, 86)
	C_7H_{14} (27, 29, 39, 55, 98)
	C_7H_{16} (27, 28, 29, 41, 42, 43, 57, 71, 85, 100)
	C_4H_9OH (41, 44, 45, 57, 58, 74) C_3H_4O (27, 28, 29, 55)
57	C_4H_{10} (29, 41, 42, 43, 56, 58)
	C_5H_{12} (26, 28, 29, 41, 42, 43, 72)
	C_6H_{14} (41, 42, 43, 56, 71, 86)
	C_7H_{14} (29, 39, 55, 56, 70, 98)
	C_7H_{16} (27, 28, 29, 41, 42, 43, 56, 71, 85, 100)
	C_8H_{16} (29, 41, 43, 55, 70, 97, 112)
	C_8H_{18} (27, 29, 41, 43, 71, 85, 114)
	C_4H_9OH (28, 41, 44, 45, 56, 58, 74)
58	C_4H_{10} (29, 41, 42, 43, 56, 57)
	C_6H_{14} (41, 42, 43, 56, 57, 71, 86)
	iso-C_3H_6O (16, 43) n-C_3H_6O (29, 57)
59	C_3H_7OH (28, 31, 43, 60)
	t-C_4H_9OH (28, 31, 44, 45, 57, 58, 74)
60	C_3H_7OH (28, 31, 43, 59) CH_3CO_2H (42, 43, 45)
67	C_5H_8 (27, 39, 40, 41, 42, 68)
	C_6H_{10} (27, 39, 40, 41, 42, 53, 82)
68	C_5H_8 (27, 39, 40, 41, 42, 67)

m/e	
69	C_6H_{12} (28, 29, 39, 41, 42, 55, 84)
	C_7H_{16} (27, 29, 39, 41, 43, 57, 85, 100)
70	C_5H_{10} (39, 42, 55) C_6H_{14} (27, 29, 41, 43, 56, 57, 71, 86)
71	C_6H_{14} (43, 57, 86) C_7H_{16} (57, 85, 100
	C_8H_{18} (41, 85, 114) iso-$C_5H_{10}O$ (29, 39, 41, 44, 58, 86)
72	C_5H_{12} (27, 29, 39, 41, 42, 43, 57)
	C_4H_8O (29, 39, 41, 43, 44, 57)
74	C_4H_9OH (28, 31, 44, 45, 57, 58) $CH_3CH_2CO_2H$ (29, 45, 58)
78	C_6H_6 (39, 50, 51, 52, 77)
82	C_6H_{10} (27, 39, 40, 41, 42, 53, 67)
84	C_6H_{12} (28, 29, 39, 41, 42, 55, 69)
85	C_6H_{14} (27, 29, 41, 43, 56, 57, 71, 86)
	C_7H_{16} (57, 71, 100) C_8H_{18} (27, 29, 41, 43, 71, 114)
86	C_6H_{14} (27, 29, 41, 43, 56, 57, 71, 85)
	C_7H_{16} (57, 71, 85, 100)
100	C_7H_{16} (27, 28, 29, 42, 43, 56, 57, 71, 85, 100)
112	C_8H_{16} (29, 41, 43, 55, 57, 97)
114	C_8H_{18} (27, 29, 41, 43, 85)

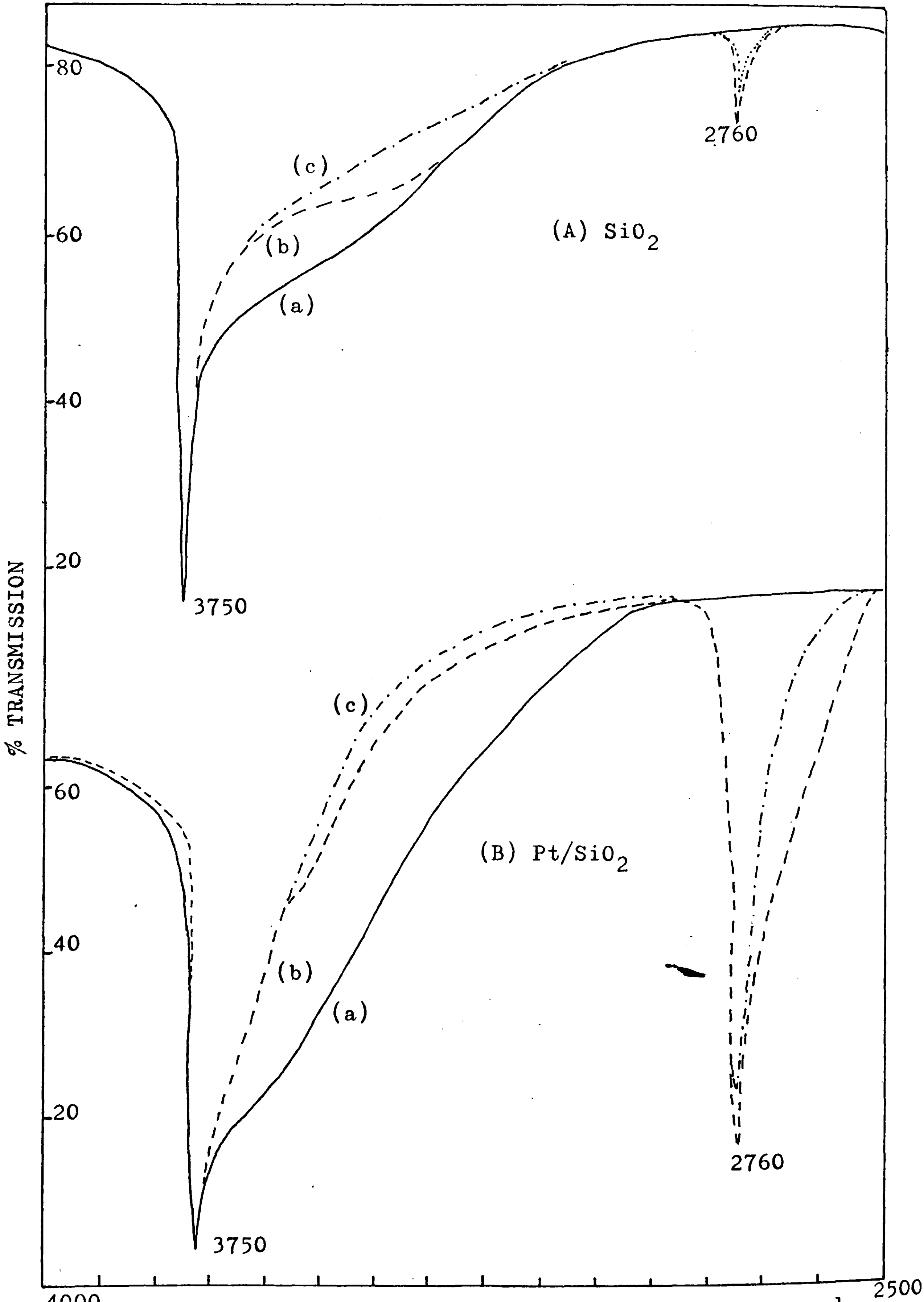
% TRANSMISSION
80
60
40
20
60
40
20
3750
2760
(A) SiO$_2$
(a)
(b)
(c)
(B) Pt/SiO$_2$
(a)
(b)
(c)
3750
2760
4000
2500
FREQUENCY cm^{-1}

Figure II.$_1$

APPENDIX II

INFRA-RED EXPERIMENTS AND RESULTS.

An attempt was made to determine the nature of the retained hydrogen and of the interaction of ethylene with various catalysts by looking at their infra-red spectra.

A single cell, of the type described by Little et al,[67] with sodium chloride windows was used together with a Perkin-Elmer double beam grating spectrometer (Type 257). Discs of SiO_2 (35 gm.) and 1% Pt/SiO_2 (35 and 60 gm.) were prepared using a pressure of 1½ tons/sq. inch for five minutes. In both cases a very broad band, corresponding in part, to adsorbed water was observed over the range 3750 cm.$^{-1}$ to 2800 cm.$^{-1}$. In order to obtain suitable spectra, the samples had to be outgassed for an hour at 550°C after which they were cooled under vacuum to 20°C. A spectrum was then recorded over the range 4000-600 cm.$^{-1}$, although only the range 4000-2500 cm.$^{-1}$ is shown. Fig.II. 1(a). (A) refers to silica and (B) refers to platinum-silica.

A band at 3750 cm.$^{-1}$ corresponding to the stretching vibrations of the free OH on the silica surface and a wide bank in the range 3750 to 3000 cm.$^{-1}$ corresponding to the vibrations of bound OH appear in the spectra of both samples.

The breadth of this band was greater with 1% Pt/SiO_2 than with SiO_2 although at lower frequencies the spectra were identical.

Deuterium (100 mm) was admitted to the cell and the spectra were again recorded. A peak was observed at 2760 cm.$^{-1}$, corresponding to the formation of free OD groups. On heating to 350°C for one hour the intensity of the 2760 cm.$^{-1}$ band increased (Fig. II. 1(b)). For 1% Pt/SiO_2, the intensity of the OD band was very much greater than with SiO_2 and was also accompanied by the formation of a wide band of bound OD groups in the range 2760-2500 cm.$^{-1}$. After evacuation for one hour at 350°C, the intensity of the OD bands of 1% Pt/SiO_2 were reduced to a greater extent than the OD bands of SiO_2.

Attempts to obtain satisfactory spectra with alumina and platinum-alumina from 3770-2800cm.$^{-1}$ tended to obscure this part of the spectrum, even after evacuation.

The samples of SiO_2 and Al_2O_3 were exposed to ethylene (10-100 mm); only physically adsorbed ethylene was observed.

Additional spectra of alumina were run using a double cell, designed and constructed by McCosh and Sheppard,[117] in conjunction with a Grubb-Parsons GS2 grating spectrometer. After evacuation at 350°C for one hour and six hours the

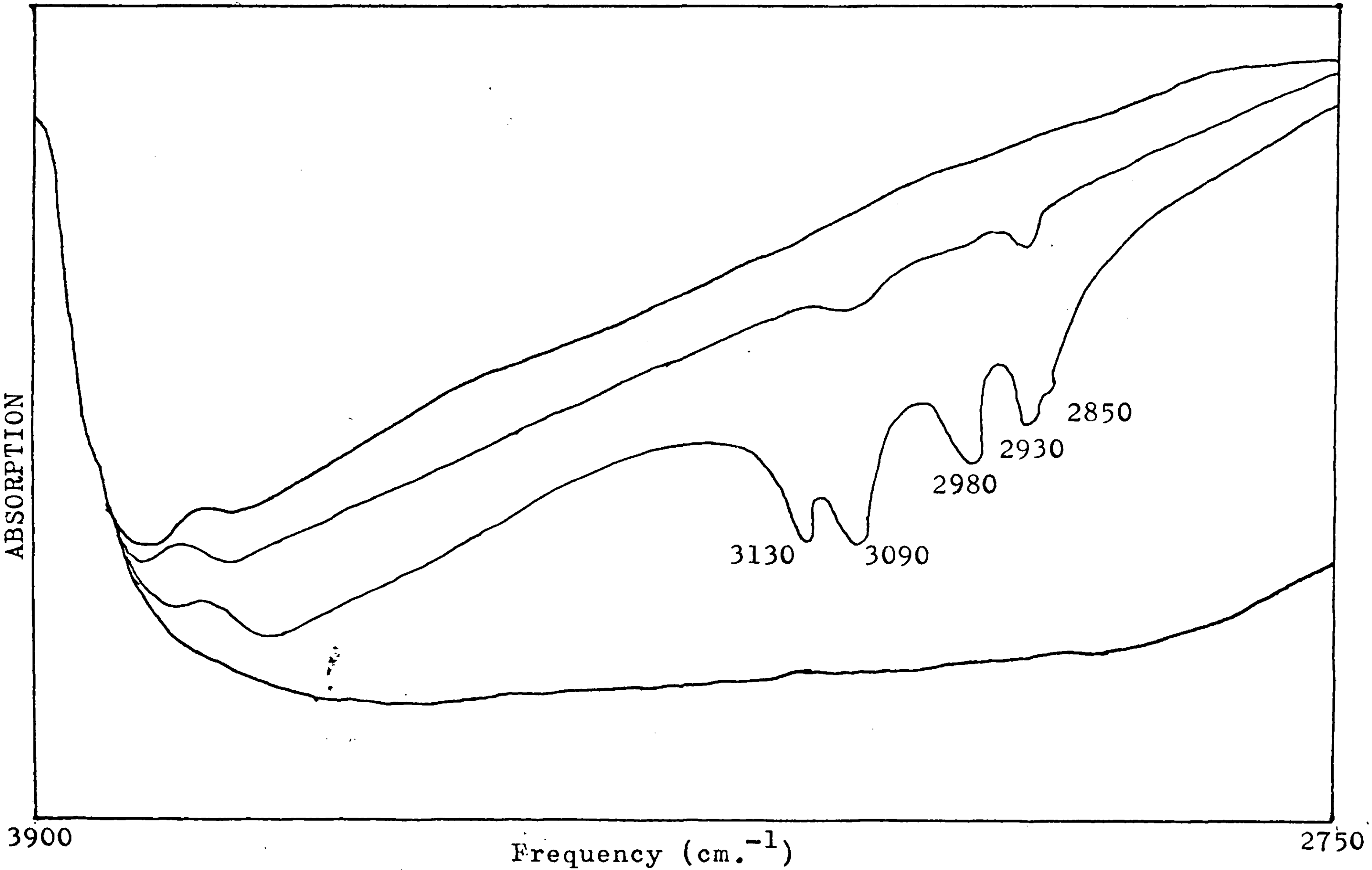


FIGURE II$_2$ SPECTRUM OF ALUMINA

spectra were similar (Fig. II. 1(a)). A group of bands were observed (3780-3650 cm.$^{-1}$) with a broad tail at lower frequencies and the former corresponded to hydroxyl groups and the latter tc bonded hydroxyl groups. Bands were also observed ~ 1600 cm.$^{-1}$ and ~ 1400 cm.$^{-1}$ which are probably Al-O bands. The addition of water generated the spectrum of alumina before evacuation Fig. II 2(b) in which the region 3780-2800 cm.$^{-1}$ was obscured. A band at 1650 cm.$^{-1}$ corresponding to the bending frequency of water was observed.

At 20°C, only physically adsorbed ethyelen was observed (Fig. II 2(c)) and after twelve hours, the spectrum was unchanged. On heating to 350°C, however, there was evidence of the formation of chemisorbed species Fig.II 2(d). Bands were observed at 3130, 3090, 2980, 2930 and 2850 cm.$^{-1}$, probably corresponding to CH stretching frequencies. The bands at 2850 cm.$^{-1}$ and 2930 cm.$^{-1}$ may be CH_3, symmetric CH stretching and CH_2 asymmetric CH stretching bands respectively.[72] The band at 3090 cm.$^{-1}$ and 2980 cm.$^{-1}$ may correspond to physically adsorbed ethylene,[57] although the latter could have a contribution from the 2970 cm.$^{-1}$ band of CH_3 asymmetric CH stretching. The frequency of the band at 3130 cm.$^{-1}$ is rather high for an olefinic CH stretching band and rather low for an acetylenic CH stretching band.

The spectra show that at 20°C, ethylene is physically adsorbed whereas at 350°C the mode of adsorption is very different.

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