Chemical Processes on Heterogeneous Catalysts

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1 Introduction

This review is based on an address given at the University of St. Andrews as part of the Irvine Review Lectures on 'Catalysis' in November 1982. The title was chosen deliberately to cover two rather different aspects of catalysis. The first of these is concerned with major industrial processes and selected examples will be briefly reviewed. The approach adopted will embrace the development of processes in the present century and not concentrate solely on current practice. The second, and more substantial part of the article is concerned with the scientific investigation of catalysts to establish the chemical mechanisms which occur thereon. The subject of heterogeneous catalysis is so enormous that it is necessary to be more than usually selective in deciding on the scope of this review and the choice of what to include or exclude presents a problem.

2 Major Industrial Processes

Catalysis is of the very greatest importance in the chemical industry. Most of the processes involve heterogeneous catalysis, usually of the gas/solid type, but some depend on homogeneous catalysis in a single phase. The history of the subject of industrial catalysis has been reviewed recently by Heinemann[1] in a valuable account which includes a list of major innovations in the period 1935—78. For the purposes of this article a decision was made to illustrate the role that catalysts play in practice by reference to a limited number of topics or themes. If experts in the field are asked for their own list of a dozen topics which they believe to be representative examples of industrial catalysis, there is generally good agreement about some that should be included but considerable variation in the others that appear. Consequently, there is an element of subjectivity about the dozen topics which will now be briefly reviewed.

A. Synthesis of Ammonia.—This reaction involving a decrease in the number of molecules and an exothermic process must be carried out under high pressures and at as low a temperature as possible to give a reasonable yield of ammonia. A catalyst is essential and the development of the first successful process was achieved by F. Haber and his associates, early in the present century. An account of this work has been given by Mittasch.[2] Most of the successful catalysts seem to involve metallic iron stabilized by the presence of some alumina to act as a structural

[1] H. Heinemann, in 'Catalysis, Science, and Technology', ed. J. R. Anderson and M. Boudart. Springer-Verlag, (Berlin, Heidelberg, New York), 1981, Vol. 1, p. 1.
[2] A. Mittasch, *Adv. Catal.*, 1950, 3, 81.

promoter and with some potash too. The latter is believed to enhance the rate of the difficult step, the dissociative chemisorption of the nitrogen gas, by some electron transfer through the iron to the anti-bonding orbitals of the diatomic molecules. A recent review by Ertl[3] discusses not only the role of potassium on the surface of the iron catalysts but also the substantial variation in rates associated with different crystal faces of which the (111) is normally the most active. The catalytic synthesis of ammonia is a vital process for the chemical industry and the main route by which atmospheric nitrogen can be converted into a great range of substances.

B. Catalytic Oxidation of Ammonia or Sulphur Dioxide.—These processes pre-date the synthesis of ammonia and, of course, provide a convenient source of nitric acid or sulphuric acid. A detailed account of them was given by Dixon and Longfield[4] in the latest volume of a useful series of books edited by P. H. Emmett. The oxidation of ammonia is carried out over gauze catalysts (10% rhodium–90% platinum) typically with about 9% ammonia in air at temperatures around 850 °C. Two main types of catalysts have been used for the oxidation of sulphur dioxide: platinum supported on one of a number of bases or vanadium pentoxide promoted with potassium sulphate or related compounds. The manufacture of sulphuric acid is often quoted as an indicator of the economic climate of the chemical industry and the level of consumption of sulphuric acid can be used as a measure of a country's technical development.[5]

C. Catalytic Hydrogenation.—The field of catalytic hydrogenation embraces a very wide range of reactions.[6] One of the older processes is the hydrogenation of double bonds in oils and fats—the so-called 'hardening of fats'. More recent applications include the selective hydrogenation of small quantities of acetylene in the presence of excess ethylene as part of the purification of the alkene for polymerization. Then there are numerous examples of hydrogenation of molecules containing atoms other than carbon or hydrogen such as the hydrogenation of adiponitrile to hexamethylenediamine. Raney nickel, prepared by the caustic leaching of aluminium from a Ni–Al alloy, is a well-known catalyst in this field. But a number of transition metals are used because they exhibit the desirable features of activity or selectivity for particular reactions—advantages which are sufficient to balance the higher cost of some of the metals.

The reverse process of dehydrogenation, *e.g.* of paraffins to olefins, is a related type of catalytic reaction. Because of thermodynamic limitations, higher temperatures are required and oxides such as chromia supported on alumina are more useful than metal catalysts which would give undesirable side reactions.

D. Catalytic Cracking of Hydrocarbons, including Fluidization and Use of Zeolites.—In terms of tonnage, the catalytic cracking of petroleum feed stocks must be near

[3] G. Ertl, *Catal. Rev.-Sci. Eng.*, 1980, **21**, 201.
[4] J. K. Dixon and J. E. Longfield, in 'Catalysis', ed. P. H. Emmett, Reinhold, (New York), 1960, Vol. 7, p. 281.
[5] B. G. Reuben and M. L. Burstall, 'The Chemical Economy', Longman, (London), 1973.
[6] See 'Catalysis', ed. P. H. Emmett, Reinhold, (New York), 1955, Vol. 3.

the top of the league. Both the nature of the catalysts and the technology used have developed significantly over the last 40 to 50 years. Nearly all the catalysts are some variation of 'acidic' oxides. In the early processes natural montmorillonite clays were used but soon replaced with synthetic silica-aluminas containing 10—13% alumina. The formation of 'coke' on the catalyst leading to deactivation and requiring an oxidizing treatment for its removal and regeneration of the catalyst was countered by the introduction of the new technology of fluidization in the early 1940s. The catalyst was prepared with a particle size such that it could be transported by the gas stream and cycled between a reactor in which the cracking reaction occurred and a second chamber in which the coke was burnt off before the catalyst was returned to the reactor. A further development in this field was the introduction of zeolite catalysts in 1964. In the early stages, inclusion of some zeolites in the catalysts gave improved performance with less undesirable side reactions and longer life. But the whole subject of zeolite catalysis has expanded enormously in recent years because of their shape-selective properties.[7] There are two main aspects of shape-selectivity. First, because of the sizes of the channels in the zeolites some classes of molecules have relatively easy access to the internal surfaces upon which the majority of the acidic sites are located—other larger molecules do not. Secondly, there can be steric control of the various possible reaction rates in that the volume of the cavities in the zeolites may enable reactions with a small transition state to occur more readily than others with a less compact activated complex.

E. Partial Oxidation.—In contrast to the more complete oxidations discussed in Section B above there are many important applications of catalysts in selective oxidation.[8,9] The formation of ethylene oxide from ethylene is a well-known reaction using silver catalysts. The manufacture of phthalic anhydride originally from naphthalene but also from *o*-xylene is frequently accomplished by a supported vanadium pentoxide catalyst. Likewise, the oxidation of *p*-xylene to terephthalic acid is a step on the route to the polyester 'Terylene'. Another chemical of value to the polymer industry, acrylonitrile, is produced by the ammoxidation of propene with ammonia and oxygen using tin–antimony oxides or other mixed-oxide catalysts such as bismuthphosphomolybdate.[10,11]

F. Ziegler–Natta Polymerization.—A great industrial development grew from the pioneering work of K. Ziegler and G. Natta who devised a remarkable class of catalysts. The combination of a transition metal (usually titanium) compound with a reactive organometallic compound, such as triethylaluminium, was shown to

[7] P. B. Weisz, 'Proceedings of the 7th Int. Congr. on Catalysis', ed. T. Seiyama and K. Tanabe, Elsevier. (Amsterdam, Oxford, New York), 1981, Vol. A, p. 3.

[8] J. K. Dixon and J. E. Longfield, in *ref.* 4, p. 183.

[9] R. Higgins and P. Hayden, in 'Catalysis', ed. C. Kemball (Specialist Periodical Reports). The Chemical Society, (London), 1977, Vol. 1, p. 168.

[10] G. W. Keulks, L. D. Krenzhe, and T. M. Notermann, *Adv. Catal.*, 1978, **27**, 183.

[11] B. C. Gates, J. R. Katzer, and G. C. A. Schuit, 'Chemistry of Catalytic Processes', McGraw-Hill, (New York), 1979, p. 325.

have the ability to polymerize alkenes and dienes with high activity and selectivity. Important commercial processes have been devised for the production of high-density polyethylene, isotactic polypropylene and other polymers based on dienes, or mixed alkenes. The great advance associated with the Ziegler–Natta catalysts was the high degree of stereospecificity associated with their function.[12,13]

G. Catalytic Reforming of Hydrocarbons.—While catalytic cracking of petroleum feed stocks provides products with the required range of molecular weights, further processing is necessary to satisfy the demand for (*a*) gasoline and (*b*) starting materials for the petrochemical industry. The types of reaction which must be catalysed are isomerization of alkanes to convert straight-chain to branched-chain molecules and dehydrocyclization to form aromatics—both of these reactions raise the octane rating of the products. Reactions which have to be avoided are the formation of coke on the catalysts and also the breakdown of the feed stock to smaller hydrocarbon molecules. The reforming reactions are normally accomplished on so-called 'dual function' catalysts,[14] which have both a hydrogenation/dehydrogenation capability associated with a supported metal like platinum or rhodium and an isomerizing function associated with acidic oxides such as halided alumina. An excellent account of the evolution of reforming catalysts was given by Sterba and Haensel[15] and the book[16] by Gates, Katzer, and Schuit contains a chapter which relates the practice of catalytic reforming to the scientific principles upon which it is based. In recent years, improved performance in reforming has been achieved by the use of bimetallic supported catalysts such as the platinum–iridium catalysts developed by Exxon[17] or platinum–rhenium by Chevron.[18]

H. Hydrodesulphurization.—Many catalysts, particularly metals, are poisoned by relatively small percentages of sulphur compounds. The removal of such impurities from feed stocks is frequently accomplished[19] by the conversion of sulphur-containing organic compounds into hydrogen sulphide by use of catalysts like cobalt molybdate (which under working conditions becomes a mixed sulphide). The hydrogen sulphide may be removed by reaction with a zinc oxide catalyst, although this second stage is not really a true catalytic process because the zinc oxide is converted into sulphide which is then discarded. In a wider sense hydrodesulphurization is typical of a number of processes including purification of feed stocks or removal of substances which would otherwise lead to environmental problems.

[12] M. N. Berger, G. Boocock, and R. N. Hayward, *Adv. Catal.*, 1969. **19**. 211.
[13] A. D. Caunt, in *ref.* 9, p. 234.
[14] P. B. Weisz, *Adv. Catal.*, 1962, **13**, 137.
[15] M. J. Sterba and V. Haensel, *Ind. Eng. Chem., Prod. Res. Dev.*. 1976. **15**, 2.
[16] *Ref.* 11, p. 184.
[17] J. H. Sinfelt, 'Bimetallic Catalysts,' John Wiley and Sons, (New York), 1983.
[18] R. L. Jacobson, H. E. Kluksdahl, C. S. McLoy, and R. W. Davis, *Proc. Am. Petroleum Inst., Div. of Refining*, 1969, **49**, 504.
[19] J. J. Phillipson, 'Catalyst Handbook', Wolfe Scientific Books. (London), 1970. p. 46.

I. Steam Reforming of Hydrocarbons.—The high-temperature reaction of hydrocarbons with an excess of steam, typically over a nickel-supported catalyst, has a number of uses.[20] These include the production of hydrogen for ammonia synthesis, the formation of carbon monoxide and hydrogen for methanol synthesis and, under circumstances where natural gas is not readily available, the formation of methane-rich mixtures from higher hydrocarbons for use as 'town gas'. The temperature operation and the steam ratio (moles of H_2O : moles of C) have to be chosen with regard to the desired products and the relevant thermodynamic equilibria. The water gas shift equilibrium

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

is also an important factor and carbon dioxide is a by-product of many steam reforming processes. Because of the rather vigorous conditions involving steam at the high pressures and temperatures under which the catalysts have to operate, various solid–solid and solid–gas reactions have to be taken into account in the design of catalysts with sufficient activity, strength, and life.

J. The Wacker Process.—The single-step oxidation of ethylene to acetaldehyde is an important example of the applications of homogeneous catalysis on a commercial scale. The process was developed by Smidt and Hafner and their associates.[21] The hydrocarbon is oxidized in aqueous solution by dissolved $PdCl_2$ as follows:

$$CH_2CH_2 + H_2O + PdCl_2 \longrightarrow CH_3CHO + Pd + 2HCl$$

Cupric chloride is also present and it brings about the reoxidation of the palladium by the reaction

$$Pd + 2CuCl_2 \longrightarrow PdCl_2 + 2CuCl$$
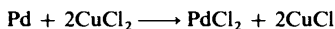
and the cycle is completed by the reoxidation of the cuprous chloride by dissolved oxygen

$$2CuCl + \tfrac{1}{2}O_2 + 2HCl \longrightarrow 2CuCl_2 + H_2O$$
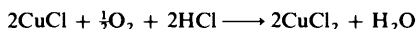
The amounts of palladium and copper salts required are relatively small and, of course, the overall reaction amounts merely to the desired oxidation of ethylene to acetaldehyde, *i.e.*

$$CH_2CH_2 + \tfrac{1}{2}O_2 \longrightarrow CH_3CHO$$
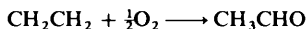
A full account of the process has been given by Stern.[22]

K. Synthesis of Methanol.—There are a variety[23] of catalytic processes which are operated with carbon monoxide and hydrogen as reactants, such as the Fischer–Tropsch synthesis,[24] which can be used to produce long-chain hydrocarbons or

[20] G. W. Bridger and G. C. Chinchen, *ref.* 19, p. 64.

[21] J. Smidt, W. Hafner, R. Jira, J. Sedlmeier, R. Sieber, and H. Kojer, *Angew. Chem.*, 1959, 71, 176.

[22] E. W. Stern, *Catal. Rev.*, 1967, 1, 73.

[23] P. J. Denny and D. A. Whan, 'Catalysis', ed. C. Kemball and D. A. Dowden (Specialist Periodical Reports), The Chemical Society, (London), 1978, Vol. 2. p. 46.

[24] H. H. Storch, N. Golumbic, and R. B. Anderson, 'The Fischer–Tropsch and Related Syntheses', Wiley. (New York), 1951.

oxygenated compounds. But the synthesis of methanol is undoubtedly one of the most important of present-day catalytic processes.

The reaction

$$CO + 2H_2 \rightleftharpoons CH_3OH$$
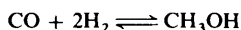
is exothermic with $\Delta H = -91$ kJ mol^{-1} and so there is advantage in carrying out the conversion at relatively low temperatures in order to achieve good yield. At one stage the synthesis used to be carried out at temperatures above 300 °C using a zinc oxide–chromia catalyst but this process has been superseded by the use of copper-containing catalysts operated at 220 and 300 °C under pressures of 50 to 100 atm. The selectivity is typically in excess of 99%.

L. Automotive Emission Control.—One of the greatest challenges in the catalytic field has been the requirement to control the amounts of carbon monoxide and oxide of nitrogen emitted in the exhaust gases from cars. The problem has been not only to achieve the specified low limits for these gases but also to design a catalysis system which could continue to operate successfully for long periods under the changing conditions associated with the normal use of a car. Accounts of work in this field have been given by Wei,[25] and by Shelef *et al.*[26] The main groups of catalysts which have been found to be effective can be classified as base metal, platinum, or promoted platinum catalysts. Prominent amongst the last group is a rhodium–platinum catalyst developed by G. J. K. Acres and others at Johnson Matthey.

3 Metals

Having completed the survey of selected major industrial applications of catalysis, we now consider some of the evidence about the nature of the chemical processes that actually take place on the surface of the catalysts. In this section some aspects of catalysis by metals are reviewed and in the following some recent work on mechanistic studies on oxides is discussed.

A. Catalytic Activity.—The essential property of any catalyst is that it provides a new and less energetic reaction path for passage from reactants to products. For effective catalysis, the strength of adsorption of the molecules must be in the right range. This aspect is illustrated by the diagram in Figure 1 for the decomposition of formic acid on metals to yield hydrogen and carbon dioxide. It is assumed that the reaction proceeds through an adsorbed intermediate which is essentially a surface metal formate.[27] Curve A in Figure 1 shows what happens when adsorption is too weak; the reaction involves passage through some activated complexes of rather high energy. Curve B is the case where adsorption is too strong; the intermediate is formed without difficulty but a substantial energy is then required to decompose it

[25] J. Wei, *Adv. Catal.*, 1975, **24**, 57.
[26] H. Shelef, K. Otto, and N. C. Otto, *Adv. Catal.*, 1978, **27**, 311.
[27] J. Fahrenfort, L. L. van Reijen, and W. M. H. Sachtler, 'The Mechanism of Heterogeneous Catalysis . ed. J. H. de Boer, Elsevier, (Amsterdam, London, New York), 1960, p. 23.

into products. Curve C represents the ideal situation; an intermediate strength of adsorption such that both the formation of the intermediate from reactants and its decomposition can occur without involving substantial energies of activation.
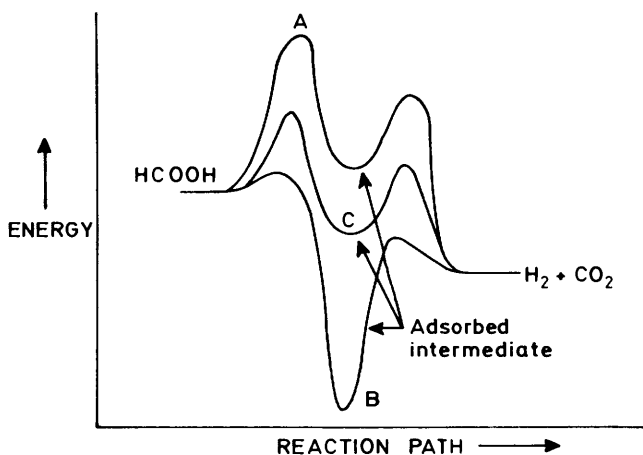

Figure 1 *Reaction paths for the decomposition of formic acid: formate species adsorbed—(A) too weakly, (B) too strongly, (C) with intermediate strength*

These ideas about the likely variation of rate with strength of adsorption can be tested by examining the relative activity of a series of metal catalysts for the decomposition of formic acid. The typical volcano-shaped curve shown in Figure 2 (based on Figure 8 of *ref.* 27) illustrates the variation observed. The vertical scale gives the temperature required to achieve a fixed catalytic activity for the reaction, the lower this temperature the more active is the metal. The heat of formation of bulk metal formate is plotted along the horizontal axis and it is assumed that there will be a correlation between the strength of adsorption of formic acid as a surface formate and the heat of formation of the bulk compound. Gold and silver are poor catalysts because the strength of adsorption is too small; iron, cobalt, and nickel are poor catalysts because the adsorption is too strong. The greatest activity is found for the various metals near the top of the volcano because they exhibit the appropriate strength of adsorption. This interpretation of the volcano-shape is substantiated by kinetic measurements which suggest that formation of the adsorbed intermediate is rate-determining on gold and desorption of product rate-determining on nickel, *i.e.* cases A and B respectively of Figure 1.

Another example illustrating the importance of strength of adsorption is the variation of activity of the first row transition metals for the synthesis of ammonia shown in Figure 3 (based on Figure 2.9 of the book by G. C. Bond[28]). Metals to the left react too strongly with nitrogen, those to the right too weakly and the appropriate strength of adsorption is found with iron which is widely used as an ammonia synthesis catalyst.

[28] G. C. Bond, 'Heterogeneous Catalysis—Principles and Applications,' Oxford University Press, 1974.
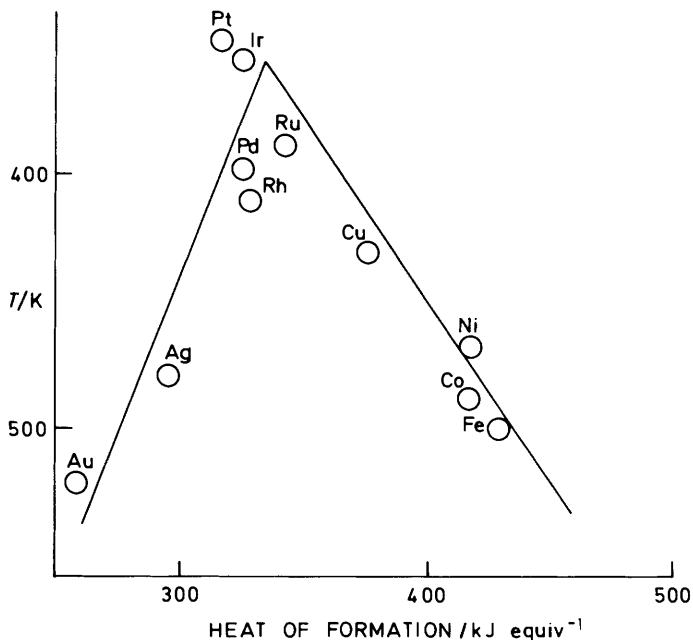
Figure 2   *Activity of metals for the decomposition of formic acid correlated with the heat of formation of bulk metal formates: T represents the temperature required to achieve the same fixed rate of reaction on each metal*
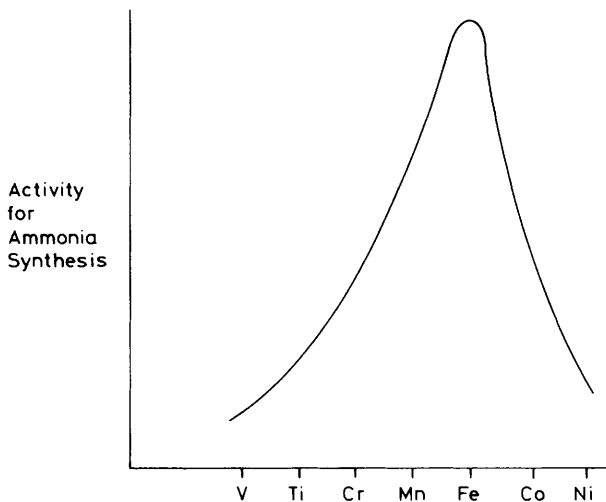

Figure 3   *The variation in the rate of ammonia synthesis across the transition metals in the first row of the periodic table*

B. Exchange Reactions of Hydrocarbons with Deuterium.—One of the most powerful methods of learning about the nature and reactivity of adsorbed intermediates on catalyst surfaces has been the study of exchange reactions, *e.g.* of hydrocarbons with deuterium. This technique has been a fruitful source of information about the types of dissociated species formed from saturated hydrocarbons on metals and the way in which these species are involved in the mechanism of hydrocarbon reactions.[29,30] In general, the main features associated with hydrocarbon exchange reactions with deuterium are the following:

(*a*) H atoms in the molecule are replaced with D atoms.

(*b*) This may involve dissociation of C–H followed by the formation of C–D.

(*c*) Alternatively, particularly with unsaturated molecules, formation of C–D is followed by dissociation of C–H.

(*d*) The mechanism may be stepwise, involving a single replacement of H by D during adsorption on the catalyst, or multiple, with two or more atoms being exchanged before products desorb.

(*e*) Adsorbed intermediates are formed reversibly.

(*f*) Adsorption of reactant and desorption of product occur at the same rate.

Frequently, on metal catalysts multiple exchange occurs and the study of suitably chosen reactants can be valuable for obtaining an indication about the types of adsorbed intermediates which are important. Some of these reactants with the reason for their study are listed in Table 1. The use of cyclopentane as an interesting test reactant has long been recognized—early work[31] using evaporated films of palladium as catalysts demonstrated two main types of multiple exchange for this molecule. At lower temperatures, the distribution of initial products showed a pronounced maximum at the compound with five deuterium atoms, $C_5H_5D_5$. The formation of this was attributed to the interconversion on the surface of adsorbed cyclopentyl radicals and adsorbed cyclopentene molecules leading to the replacement of all the H atoms on one 'side' of the ring. At high temperatures the initial distribution products gave a maximum for the perdeutero-compound, C_5D_{10}, and the formation of this is now believed to involve the 'turn-over' on the surface of an adsorbed cyclopentene species[30]—a process involving a rather higher activation energy than the mechanism responsible for the multiple exchange of one side of the ring. Recent work[32] using deuterium n.m.r. spectroscopy has confirmed that the D_5 product is indeed the compound with five equivalent deuterium atoms, one on each carbon atom. Figure 4 shows deuterium n.m.r. spectrum of the mixture of deuterocyclopentanes formed at an early stage in the exchange of cyclopentane over a supported platinum catalyst. The positions of the resonances are dependent not only on the nature of the deuterium atom being observed but also on isotopic shifts due to the neighbouring deuterium atoms. In favourable circumstances

[29] C. Kemball, *Adv. Catal.*, 1959, **11**, 223.
[30] R. L. Burwell, Jr., *Acc. Chem. Res.*, 1969, **2**, 289.
[31] J. R. Anderson and C. Kemball, *Proc. R. Soc. London, Ser. A*, 1954, **226**, 472.
[32] A. C. Faro, Jr., C. Kemball, R. Brown, and I. H. Sadler. *J. Chem. Res.*. 1982, (S) 342. (M) 3735.

various groupings of deuterium atoms can be recognized and estimated. The percentages of the various products in this sample, determined by mass spectrometry, were 2.3% D_1, 1.2% D_2, 0.6% of D_3 and D_4, 1.7% of D_5, and a total of 0.6% for D_6 to D_{10}. The products C_5H_9D, *cis*-1,2-D_2-cyclopentane, *cis*-1,2,3,4,5-D_5-cyclopentane and the perdeutero-compound, C_5D_{10}, are easily recognized in the spectrum as the peaks labelled A—D respectively.

Table 1 *Model reactants for multiple exchange*

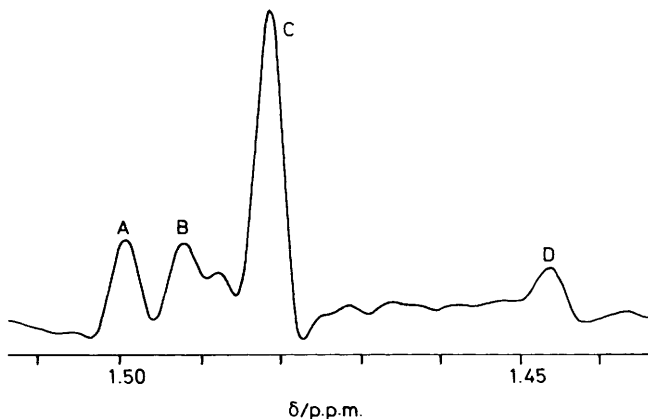| Reactant	Information gained
CH_4	Role of (CH_2) ads.
C_2H_6	Extent of alkyl-alkene interconversion on the surface
cyclo-C_5H_{10}	Extent of the propagation of the exchange beyond $C_5H_5D_5$
$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_3$	Extent of the propagation of the exchange beyond one methyl group

Figure 4 *Deuterium n.m.r. spectrum (line-narrowed) for cyclopentanes formed after 7% exchange with deuterium over a 0.51% Pt–alumina catalyst: peaks A to D correspond to C_5H_9D, cis-1,2-$C_5H_8D_2$, cis-1,2,3,4,5-$C_5H_5D_5$, and C_5D_{10} respectively*

The main intermediates which are important for exchange reactions of hydrocarbons on metals are shown in Figure 5 which also illustrates the system of labelling commonly used to describe the intermediates: this is based on the position

of the hydrogen atoms that have to be removed from the corresponding alkane to form each species.
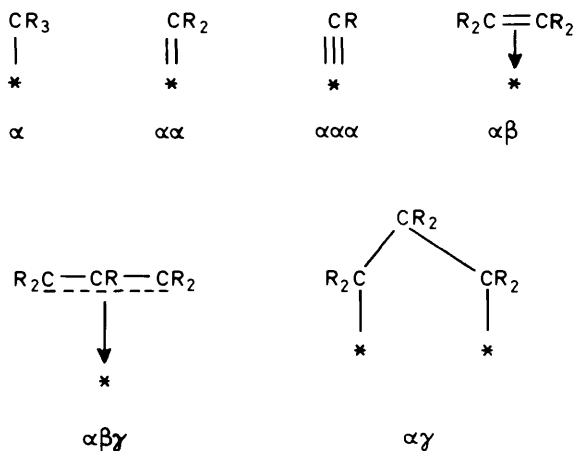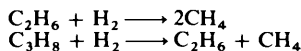
$$CR_3 \qquad CR_2 \qquad CR \qquad R_2C = CR_2$$

$$\alpha \qquad\qquad \alpha\alpha \qquad\qquad \alpha\alpha\alpha \qquad\qquad \alpha\beta$$

$$R_2C - CR - CR_2 \qquad\qquad R_2C \overset{CR_2}{\diagup \diagdown} CR_2$$

$$\alpha\beta\gamma \qquad\qquad\qquad \alpha\gamma$$

Figure 5 *The main adsorbed intermediates involved in the exchange of hydrocarbons on metals*

C. Hydrogenolysis Combined with Exchange.—Hydrogenolysis of hydrocarbons involves the breaking of C–C bonds with the formation of small saturated molecules. Reactions such as

$$C_2H_6 + H_2 \longrightarrow 2CH_4$$
$$C_3H_8 + H_2 \longrightarrow C_2H_6 + CH_4$$

are thermodynamically very favourable at moderate temperatures and so it is perhaps surprising that there are so many hydrocarbon/metal systems for which it is possible to observe the exchange of the hydrocarbon with deuterium without some accompanying hydrogenolysis or isomerization of the reactant. The key factor is that C–H bonds are 'activated' (broken and made) more easily on many transition metal catalysts than are C–C bonds, despite the higher bond dissociation energy of the C–H bonds. But on most transition metals increase of temperature will lead to both isomerization and hydrogenolysis, the onset of these reactions implies that the species shown in Figure 5 are no longer formed reversibly as the temperature is raised[33] and either give rise to alterations in the carbon skeleton of the molecules or dissociate to other species which do so. Naturally, the degree of reversibility varies from one intermediate to another and the last species shown, the αγ-diadsorbed entity, is often found to lead on to isomerization or hydrogenolysis.

Evidence from the initial products of reaction of 2,2-dimethylpropane with deuterium on evaporated metal films of iron[34] at 213 °C has shown clearly the differing degrees of reversibility of the intermediates on that metal. The main

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[33] C. Kemball, *Catal. Rev.*, 1971, **5**, 33.
[34] R. S. Dowie, C. Kemball, J. C. Kempling, and D. A. Whan, *Proc. R. Soc. London, Ser. A*, 1972, **327**, 491.

intermediates expected to be formed from 2,2-dimethylpropane are shown in Figure 6. The initial products and the consequential deductions are as follows:

   (*a*) Stepwise exchange gives $(CH_3)_3C(CH_2D)$. This implies that intermediate (I) is formed reversibly.

   (*b*) The only multiply-exchanged initial product is $(CH_3)_3C(CD_3)$. There must be efficient interconversion between intermediates (I) and (II). It is, of course, possible that the formation of an $\alpha\alpha\alpha$-triadsorbed species plays a part in the exchange reaction in addition to (I) and (II).

   (*c*) No initial products have deuterium in two methyl groups. It follows that the intermediate (III) is not formed reversibly at 213 °C on iron.

   (*d*) Hydrogenolysis gives the perdeuteromethane, CD_4, as the only significant product. This confirms that the route to the breaking of C–C bonds lies through intermediate (III).
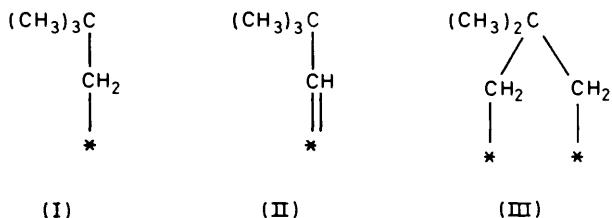

Figure 6 *Intermediates involved in reactions of 2,2-dimethylpropane*

On other metals, particularly platinum, species closely related to (III) are considered to be important for the isomerization of 2,2-dimethylpropane and it has been suggested that the formation of the intermediate may involve only one and not two or more surface atoms of the metal.[35]

4 Oxides

As mentioned above, many of the most important non-oxidative reactions of hydrocarbons on oxides involve the use of 'acidic' oxides and these lead to the formation of carbocations (carbenium ions) as surface intermediates which play a part in a wide range of processes. But the application of exchange studies over the last 20 years or so has revealed that a great variety of species can be formed by the interaction of hydrocarbons on different oxide catalysts. Some of the earlier work in this field has been reviewed[36] but interesting results continue to appear. Alkenes are frequently used as test reactants in studies of the catalytic properties of oxides and they can undergo exchange, isomerization, or hydrogenation depending on the nature of the catalyst.

A. Reactions of Ethylene.—With transition metal catalysts, the reaction of

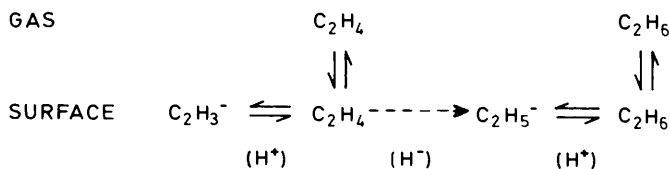[35] J. K. A. Clarke and J. J. Rooney, *Adv. Catal.*, 1976, **25**, 125.
[36] C. Kemball, *Ann. N.Y. Acad. Sci.*, 1973, **213**, 90.

ethylene with hydrogen on deuterium almost always gives rise to hydrogenation with the production of ethane, possibly accompanied by some alkene exchange as well. The situation is entirely different with oxides and the relative ratio of ethylene exchange:ethylene deuteration can vary by a factor of 10^6 depending on the oxide selected.[37] Magnesia gives exchange of the alkene without any trace of addition; conversely, with zinc oxide or chromia, ethane formation takes place without any observable exchange of the alkene and the sole product of the reaction is the ethane molecule, $C_2H_4D_2$, formed by the addition of a molecule of deuterium to the alkene (although not necessarily in a single step).

There is an interesting paradox to be explained when one considers a catalyst like γ-Al_2O_3 and the reactions of C_2 hydrocarbons. This oxide is an efficient catalyst for the exchange of H_2 and D_2 and the rates of various reactions of the hydrocarbons are given in Table 2. The problem is to explain why the alumina which can exchange relatively well both ethylene and ethane should be so comparatively inactive as a catalyst for the thermodynamically favoured reaction—the deuteration of ethylene; this reaction occurs 10^3 more slowly than the exchange of the alkene at 16 °C. A possible explanation is given in Scheme 1. There is considerable evidence in support of the idea that hydrocarbon exchange on alumina involves the formation of carbanionic intermediates with the hydrocarbon molecule essentially dissociating like an acid

$$RH \longrightarrow R^- + H^+$$
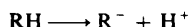
and the products of the dissociation being suitably bonded to the alumina surface. The relative reactivity for deuterium exchange of different hydrocarbons can be correlated with hydrocarbon acidity by means of typical Brönsted linear free energy relationships.[38] So the point illustrated in Scheme 1 is that the reversible

GAS C_2H_4 C_2H_6

SURFACE $C_2H_3^-$ $\rightleftharpoons$ $C_2H_4^-$ ----▶ $C_2H_5^-$ $\rightleftharpoons$ C_2H_6

              (H^+) (H^-) (H^+)

Scheme 1 *Possible mechanisms for the exchange of ethylene and ethane on alumina and for the slow hydrogenation*

Table 2 *Rates of reaction on alumina at 16 °C*

Reaction	*Rate/molecules s^{-1} m^{-2}*
C_2H_4 exchange	5×10^{14}
C_2H_6 exchange	6×10^{12}
Deuteration of C_2H_4	3×10^{11}

[37] C. Kemball, J. D. Nisbet, P. J. Robertson, and M. S. Scurrell, *Proc. R. Soc. London. Ser. A.* 1974. **338**. 299.
[38] P. J. Robertson, M. S. Scurrell, and C. Kemball, *J. Chem. Soc., Faraday Trans. 1.* 1975. **71**, 903.

dissociation of both hydrocarbons occurs in a similar manner and these reactions, involving a loss of H^+ or gain of D^+, give rise to exchange. The two exchange mechanisms are separate and the link between them is slow and difficult, requiring the acquisition of a H^- species by adsorbed ethylene. The suggestion is that oxides which tend to form charged hydrocarbon intermediates may be less efficient for alkene hydrogenation, whereas oxides upon which the hydrocarbon intermediates are less highly charged (or can be neutralized by electron transfer to or from the solid) behave more like metals and act as hydrogenation catalysts. Most of the hydrocarbon intermediates formed on metals are thought to be essentially uncharged—many of those on oxides, particularly polar oxides which are not semi-conducting, are likely to be charged.

B. Propene Intermediates.—Propene has proved to be a useful molecule for exploring the catalytic properties of oxide catalysts, partly because microwave spectroscopy[39] can be used to determine the position of deuterium atoms in the alkene molecule. The early products from the exchange of propene with deuterium, or with heavy water, can be analysed both by mass spectrometry and microwave spectroscopy to find out which hydrogen atom or atoms have been replaced and this in turn gives a clear indication of the nature of the adsorbed intermediates involved in the mechanism. Some of the results so obtained[40] are shown in Table 3 and a surprising variety of intermediates is involved. Additional information has come from the examination of the reactions of the labelled propene, $CD_2=CHCH_3$, on various oxides using both mass spectrometry and microwave spectroscopy.[41] With this molecule it is possible to follow double bond movement and at the same time to determine the extent of self-exchange (forming initially C_3H_5D and $C_3H_3D_3$). In this way, the relative importance of

Table 3 *Intermediates for propene exchange on oxide catalysts*

Intermediate		Catalysts
carbenium ion	$CH_3\text{–}\overset{+}{C}H\text{–}CH_3$	zeolites, ZrO_2
propen-1-yl	$\underset{\ast}{\overset{\displaystyle CH=CH\text{–}CH_3}{\shortmid}}$	Al_2O_3
propen-2-yl	$\underset{\ast}{\overset{\displaystyle CH_2=C\text{–}CH_3}{\shortmid}}$	Al_2O_3
π-allyl	$\underset{\ast}{\overset{\displaystyle CH_2\text{–}\text{–}CH\text{–}\text{–}CH_2}{\downarrow}}$	MgO, TiO_2
σ-allyl	$\underset{\ast}{\overset{\displaystyle CH_2\text{–}CH=CH_2}{\shortmid}}$	Ga_2O_3, Al_2O_3

[39] K. Hirota, 'Proc. 5th Int. Congr. Catalysis, ed. J. W. Hightower, North-Holland/Elsevier. 1973. p. C-37.

[40] B. T. Hughes, C. Kemball, and J. K. Tyler, *J. Chem. Soc., Faraday Trans. 1*, 1975, **71**, 1285.

[41] C. S. John, C. Kemball, R. Dickinson, and J. K. Tyler, *J. Chem. Soc., Faraday Trans. 1*, 1976, **72**, 1782.

intramolecular and intermolecular movement of hydrogen and deuterium atoms can be measured and analysis of the products will also reveal[42] whether the double bond movement occurs by a dissociative process (through allyl species) or by an associative mechanism (through propyl species)—a question which is not easily answered by other methods.

C. Reactions of Cyclopentene.—Like propene, this alkene has proved to be a useful model reactant for mechanistic studies on oxide catalysts. By appropriate techniques, which now include deuterium n.m.r. spectroscopy, it is possible to determine which of the hydrogen atoms are most readily exchanged, whether double bond movement occurs, and the extent of hydrogenation. One of the early exciting results was the discovery by Hightower and Hall[43] that exchange with deuterium over alumina at temperatures below 100 °C was limited to the replacement of the two olefinic hydrogen atoms without any double bond movement. The mechanism proposed was the reversible dissociation of the alkene to form cyclopentenyl species on the oxide surface and the existence of a kinetic isotope effect (dissociation of C–H being 2—3 times faster than dissociation of C–D) supported this conclusion. Recent results with cyclopentene as a reactant over zinc oxide as a catalyst[44] illustrate the type of information that can be obtained in favourable circumstances. As with alumina, the exchange reaction was limited almost entirely to replacement of the two olefinic hydrogen atoms in a stepwise process. The peaks in the deuterium n.m.r. spectrum of exchanged cyclopentene for olefinic D (δ = 5.78 p.p.m.) and allylic D (δ = 2.31 p.p.m.) had a ratio of intensity of 50:1. But in contrast to alumina, a slow addition reaction occurred over zinc oxide at about 1/10th of the rate of the exchange reaction. The initial product of this reaction was $C_5H_8D_2$ but subsequently products containing 1, 3, or 4 deuterium atoms were formed. Scheme 2 shows the main reactions involved. The exchange process leads to the replacement successively of both the olefinic hydrogen atoms but without double bond movement. The addition reaction takes place without further exchange so the initial product is 1,2-dideuterocyclopentane. Subsequently, as addition takes place to exchanged cyclopentenes and as the D_2 gas becomes diluted with some HD, the other products are formed but the presence of D atoms is limited to the two adjacent carbon atoms which were associated with the double bond in the alkene. The deuterium n.m.r. spectrum of the cyclopentanes observed after 13% of the cyclopentene had been saturated is shown in Figure 7. Table 4 indicates the main isotopic compounds which contribute to this spectrum and the expected position of the peaks based on subsequently determined isotope shifts[32] for the various groupings of deuterium atoms. The two prominent peaks in the spectrum correspond to the initial product, 1,2-dideuterocyclopentane which has two equivalent D atoms, and the most highly deuterated product, the 1,1,2,2-tetradeutero species which has four equivalent D atoms. Thus, the main reactions

[42] C. S. John, C. E. Marsden, and R. Dickinson, *J. Chem. Soc., Faraday Trans. 1*, 1976, **72**, 2923.
[43] J. W. Hightower and W. K. Hall, *Trans. Faraday Soc.*, 1970, **66**, 477.
[44] R. Brown, C. Kemball, and D. Taylor, *J. Chem. Res.*, 1982, (S) 223, (M) 2329.
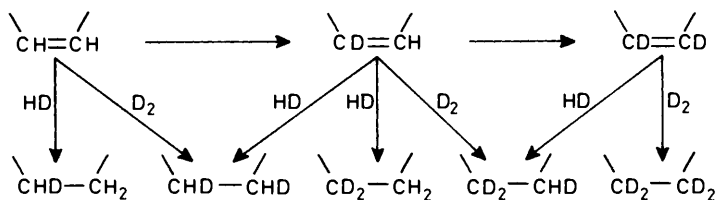
Scheme 2 *The main reactions of cyclopentene and deuterium on zinc oxide*
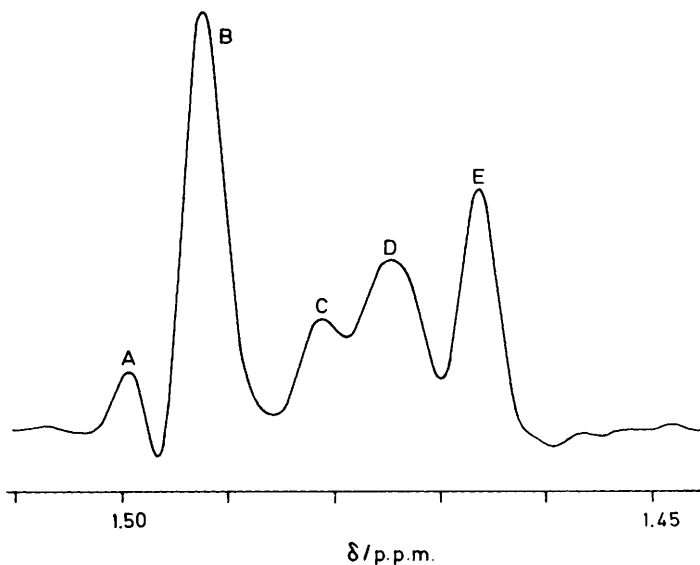

Figure 7 *Deuterium n.m.r. spectrum (line-narrowed) for the cyclopentanes formed after* 13% *conversion of cyclopentene into alkane over zinc oxide. Peak A corresponds to* C_5H_9D, *Peak* B *to* cis-1,2-dideuterocyclopentane *and Peak* E *to* 1,1,2,2-tetradeuterocyclopentane; *the remaining peaks correspond to the other compounds listed in Table* 4

Table 4 *Position of n.m.r. peaks for deuterocyclopentanes formed over* ZnO

Compound	Calculated δ/p.p.m.	Observed γ/p.p.m.
$\diagdown\diagup$ CHD–CH$_2$	—	1.501
$\diagdown\diagup$ CHD–CHD ^{a}	1.494	1.494
$\diagdown\diagup$ CD$_2$–CH$_2$	1.483	1.482 ⎫
$\diagdown\diagup$ CD$_2$–CHD	1.486, 1.476, 1.475	1.476 ⎬
$\diagdown\diagup$ CD$_2$–CD$_2$	1.468	1.468

^{a} this is the initial product

which occur with cyclopentene on zinc oxide on 80 °C are the reversible formation of the adsorbed cyclopentenyl species and, more slowly, the formation of adsorbed cyclopentyl species which are then rapidly desorbed as cyclopentane. The addition reaction of cyclopentene is similar to the corresponding reaction of ethylene with deuterium which also leads to a 1,2-dideuteroalkane as the sole product.[45]

D. Isomerization of Alkenes on Alumina.—Pretreatment has a very important influence on the activity of most oxide catalysts and also on the nature of the intermediates involved in the reactions. Increasing temperature of pretreatment reduces the surface population of hydroxy-groups and can lead to the formation of active sites by removal of some of the surface oxygen as water molecules. Surface acidity may be increased by suitable treatment such as the use of halides on alumina or even addition of hydrogen sulphide. The results quoted above for the exchange of propene on alumina have indicated that different types of catalytic processes occur on this oxide. The same complexity has been revealed in relation to the isomerization of alkenes and this topic can be used as an illustration of some of the different types of mechanism which can be found. Some of the earlier work was reviewed by John and Scurrell[46] in 1977 but the account here brings in results of more recent research.[47-51]

The catalytic properties of alumina are complex, but three main types of mechanism have been identified for alkene isomerization.

(a) The easiest type of reaction occurs with alkenes which can isomerize by formation of a tertiary carbenium ion, $R^1R^2R^3C^+$, and examples include:
(i) the conversion of 2,3-dimethylbut-1-ene into 2,3-dimethylbut-2-ene,
(ii) double bond shift in the labelled isobutene, $(CH_3)_2C=CD_2$,
(iii) the conversion of methylenecyclopentane into 1-methylcyclopentene.
These processes often take place readily at temperatures around 0 °C and little increase in rate occurs if the catalyst is pretreated with hydrogen sulphide.

(b) The next type of reaction occurs with alkenes which can isomerize by formation of an adsorbed π-allyl intermediate and examples are:
(i) the interconversion of but-1-ene and the but-2-enes,
(ii) the conversion of 3-methylcyclopentene into 1-methylcyclopentene.
Treatment of the catalysts with hydrogen sulphide, which is known to be a poison[52] for reactions on alumina involving π-allyl species, typically reduces these rates of isomerization by a factor of 10 or more.

[45] R. J. Kokes and A. L. Dent, *Adv. Catal.*, 1972, **22**, 1.
[46] C. S. John and M. S. Scurrell, 'Catalysis,' ed. C. Kemball, (Specialist Periodical Reports). The Chemical Society, (London), 1977, Vol. 1, p. 136.
[47] C. S. John and R. Dickinson, *J. Chem. Res.*, 1977, (S) 88, (M) 1020.
[48] C. S. John, A. Tada, and L. V. F. Kennedy, *J. Chem. Soc., Faraday Trans. 1*, 1978, **74**, 498.
[49] C. S. John, C. Kemball, and R. A. Rajadhyaksha, *J. Catal.*, 1979, **57**, 264.
[50] E. A. Irvine, C. S. John, C. Kemball, A. J. Pearman, M. A. Day, and R. J. Sampson, *J. Catal.*, 1980, **61**, 326.
[51] C. S. John, C. Kemball, R. C. Patterson, and R. A. Rajadhyaksha, *J. Chem. Soc., Chem. Commun.*, 1977, 894.
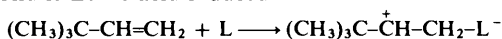[52] M. P. Rosynek and F. L. Strey, *J. Catal.*, 1976, **41**, 312.

(*c*) A more difficult and slower type of isomerization is exemplified by the reaction of 3,3-dimethylbut-1-ene to the 2,3-dimethylbutenes. For this process it is generally accepted that the mechanism must involve the formation of a secondary carbenium ion which rearranges by methyl shift to the more stable tertiary carbenium ion leading to the product alkenes, the presence of the quaternary carbon atom in the reactant eliminates the possibility of isomerization through a π-allyl species. Treatment of the alumina with hydrogen sulphide enhances the rate of reaction by a small factor of 2—3 but the presence of a small percentage of fluoride on the alumina increases the rate by factors of 10^2—10^3.

Increase of the pretreatment temperature of the alumina (up to 800 °C) gives rise to increased rates of reaction for all three kinds of alkene isomerization, although there are minor differences in the size of the effects. At first sight it is perhaps surprising that types (*a*) and (*c*) involving adsorbed carbenium ions do not show some evidence for a maximum as the surface becomes dehydroxylated because of the need to acquire a proton to convert the alkene into the corresponding carbocation. A possible explanation may be that there are two potential mechanisms for carbenium ion formation. The first involves the usual proton addition, *e.g.*

$$(CH_3)_3C\text{-}CH\text{=}CH_2 + H^+ \longrightarrow (CH_3)_3C\text{-}\overset{+}{C}H\text{-}CH_3$$
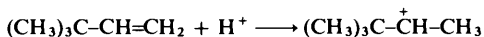
whereas the second is Lewis acid induced

$$(CH_3)_3C\text{-}CH\text{=}CH_2 + L \longrightarrow (CH_3)_3C\text{-}\overset{+}{C}H\text{-}CH_2\text{-}L^-$$

These examples of isomerization on alumina illustrate clearly the variety of ways in which the catalyst may operate through a range of different intermediates. The reaction path is influenced by a number of factors, not least of which is the nature of the reactant itself.

5 Conclusions

The catalytic processes which have been developed for the industrial applications in the present century are extensive, both in number and variety, and of the very greatest importance. The majority of these are examples of heterogeneous catalysis but homogeneous processes are becoming more significant as knowledge progresses. Selectivity is sometimes almost more important than activity and even marginal increases in efficiency of large scale processes can bring substantial economic advantages.

The review presented here has concentrated almost entirely on the chemical aspects of catalysis with emphasis on the increasing knowledge that is now available about the character and reactivity of the adsorbed intermediates on metals and oxides. The behaviour of these intermediates and the part that they contribute to the mechanisms is becoming much more clearly understood. But the nature of the catalytic sites and the way in which they are related to the surface composition and structure of catalysts continue to present some formidable problems for fundamental and applied research.