Catalysis and Chemical Processes

Editors

R. PEARCE
B.Sc., D.Phil.
Senior Research Chemist
I.C.I. Petrochemicals and Plastics Division

W. R. PATTERSON
B.Sc., Ph.D.
Senior Research Chemist
I.C.I. Corporate Laboratory

Leonard Hill

Contributors

D. G. Bew	I.C.I. Petrochemicals and Plastics Division, Wilton, Middlesbrough
Dr J. P. Candlin	I.C.I. Petrochemicals and Plastics Division, Bessemer Road, Welwyn Garden City, Herts.
Dr T. Edmonds	B.P. Research Centre, Sunbury-on-Thames, Middlesex
Dr C. R. Harrison	I.C.I. Petrochemicals and Plastics Division, Wilton, Middlesbrough
Dr W. R. Patterson	I.C.I. Corporate Laboratory, Runcorn, Cheshire
Dr R. Pearce	I.C.I. Petrochemicals and Plastics Division, Wilton, Middlesbrough
Dr P. E. Starkey	I.C.I. Petrochemicals and Plastics Division, Wilton, Middlesbrough
Dr D. J. Thompson	I.C.I. Organics Division, Blackley, Manchester
Dr D. T. Thompson	Johnson Matthey Research Centre, Sonning Common, Reading
Dr M. V. Twigg	I.C.I. Agricultural Division, Billingham, Cleveland
Dr J. M. Winterbottom	Department of Chemical Engineering, University of Birmingham

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CHAPTER ONE

INTRODUCTION

W. R. PATTERSON

1.1 The catalytic property and what it means

The discovery of catalytic action in the early part of the nineteenth century coincides with the emergence of chemistry as a rational science. True, applied chemistry of a kind existed before this period, but it flourished in the absence of any rational theory and could almost be regarded as a craft based on the traditions of the alchemists of the previous century.

By 1770, there were 15 known and recognised elements. In the 60-year period which followed, an additional 33 were isolated and a further 3 recognised as their oxides. This is a measure of the intense experimental activity following Boyle's recognition that chemistry was properly the study of matter. It was during this fruitful period that catalytic action was noted for the first time in a number of isolated and diverse observations. These included the following:

(a) the ability of heated platinum wires or foils to cause oxygen to combine with coal-gas, alcohol and ether (Davy, 1817) and to promote the union of hydrogen and chlorine (Turner, 1834);
(b) the oxidation of hydrogen (to water) at room temperature, caused by the presence of platinum sponge (Dobereiner, 1822);
(c) the decomposition of hydrogen peroxide by platinum, gold and silver (Thenard, 1818);
(d) the conversion of starch to sugar on the addition of mineral acid (Kirchoff, 1812);
(e) sulphuric acid remained unchanged when it caused the dehydrogenation of alcohol to ether—a reaction known since medieval times (Mitscherlich, 1834).

It was left to Berzelius to recognise the common theme. He concluded that a new phenomenon had been discovered and, in 1835, applied the Greek word *catalysis* (meaning decomposition or dissolution) to describe it. Erroneously, he believed that a catalytic "force" was responsible since the catalyst was unchanged by the reaction it precipitated.

During the latter half of the nineteenth century, the theory of chemistry

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progressed considerably, and by the end of the century the kinetic theory of gases and basic chemical kinetics had been formulated. This paved the way for a more rigorous view of catalysis, and Ostwald in 1911 redefined catalysts as substances which changed the *velocity* of a chemical reaction, thus dispelling the intangible "catalytic force" of Berzelius.

Ostwald's view has stood the test of time, so that the following is now accepted as a fairly complete definition: *a catalyst augments the rate of a chemical reaction without itself becoming consumed or altering the position of final thermodynamic equilibrium for that reaction.*

It should be realised that, adequate though the definition is, it applies to the ideal situation. In practice, catalysts are observed to change while acting upon chemical species. This is particularly so for heterogeneous catalysts whose surfaces are very sensitive to their environment and undergo changes due to sintering, coking, structural reorganisation of the surface, etc. In many cases these changes come about via processes not directly related to the main chemical reaction. Furthermore, in polymerisation reactions the catalyst is not recovered from the polymer produced. The catalytic cycle ends with the catalyst molecule or particle becoming trapped or deactivated in the polymer matrix. In the chapters that follow, the reader will become aware of catalyst deactivation, regeneration, lifetime, etc. as important features in the operation of chemical plant and he should realise that catalysts can be rather metastable materials susceptible to change. There is no such thing as a universal catalyst. Catalysts are merely chemicals which induce other chemicals to combine or fragment.

Specificity is an important issue in catalytic chemistry. In a situation where a number of chemical reactions are possible, a catalyst may affect the rate of all or just some of them. Different catalysts will have different relative effects on these rates. Nevertheless, for each of these separate reactions the final equilibrium position will be determined by the thermodynamics of the overall reaction and cannot be influenced by presence of the catalyst. This ability to direct reactions along certain paths is a property of catalysts which is as valuable as their ability to enhance rates of reaction.

An example of this is provided by some reactions of cyclohexene under different conditions:

$$\xrightarrow[\text{Pd catalyst}]{\ll 300^\circ C,\ O_2}$$

$$+ \quad 2H_2O$$

$$\xrightarrow[\text{quartz tube}]{400^\circ C,\ O_2}$$

complex mixture of degradative oxidation products
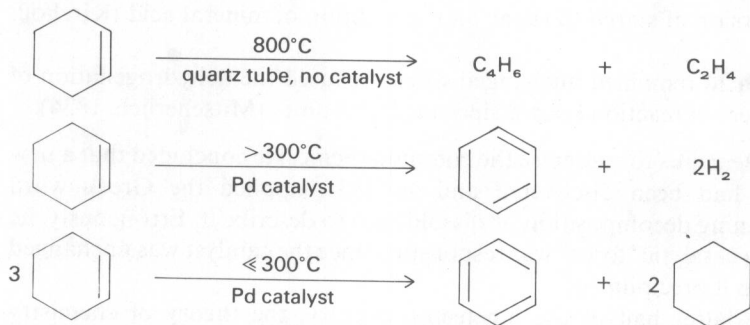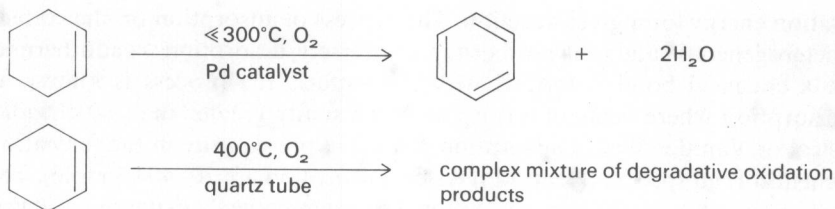
1.2 Catalytic reactions

Space allows only the briefest sketch of the basic features of the catalytic act. However, the reader is referred to the many good text books which exist, and suitable general books on catalysis which are listed at the end of the chapter.

Catalysts fall into two classes—homogeneous and heterogeneous. The former are present in the same phase as the reactants. Normally, this is the liquid phase, although gas-phase homogeneous catalysis is not unknown. Heterogeneous catalysis applies to reactions where the catalyst is in a separate phase—these reactions may be gas/solid, liquid/solid and gas/liquid.

In either case the catalytic act may be represented by five essential steps:

(1) Diffusion to the catalytic site (reactant)
(2) Bond formation at the catalytic site (reactant)
(3) Reaction of the catalyst–reactant complex
(4) Bond rupture at the catalytic site (product)
(5) Diffusion away from the catalytic site (product).

In the case of homogeneous catalysis, steps 2–4 represent the formation and decay of the reactive intermediate; in heterogeneous catalysis they represent surface-adsorption and desorption with reaction of the surface intermediates.

In some cases of homogeneous catalysis, the general mechanisms are now well established—perhaps the simplest case is that of acid-catalysed rearrangements involving carbonium ions. In others, the identity of the reactive, intermediate complex is subject to debate; nevertheless, the fact that such a complex is a molecular entity often reduces the number of possibilities. This is not so with heterogeneous catalysts where the true nature of any surface species is still a matter of conjecture. Moreover, the surface of a heterogeneous catalyst is energetically non-uniform: that is to say, surface atoms are exposed with varying degrees of coordinative unsaturation. Therefore, it is possible that adsorbed reactants may be too strongly bonded to undergo further reaction. Equally, adsorption may be too weak to allow a reactive enough intermediate to form. This argument can be extended to compare the activity of different catalysts for the same reaction. There are, therefore, optimum conditions for adsorption/desorption in relation to any particular reaction. These conditions can affect not only the rates of the catalytic reaction, but also the nature of that reaction.

This can be more clearly seen by examining the effect of a catalyst on the

activation energy for a given reaction. The process of adsorption on the surface of a heterogeneous catalyst is exothermic: conversely, desorption is endothermic. Since a chemical bond is formed with the surface, the process is known as chemisorption where heats of adsorption are usually greater than 80 kJ/mole. Physical or Van der Waal's adsorption is a usual prerequisite in the formation of a chemisorbed species. (Heats of physical adsorption are 20–40 kJ/mole). The formation of a chemisorbed species is shown diagrammatically in figure 1.1. If this chemisorbed species undergoes a reaction with activation energy E, the activated complex will have a potential energy which is decreased by the heat of chemisorption, ΔH_c (figure 1.2). In other words, chemisorption supplies some of the energy required to form the activated complex, energy which would otherwise only be available by raising the temperature of the system. Transformation of the activated complex gives the chemisorbed product which then absorbs energy from the system on desorption. Thus, it can be seen how in one way a catalytic surface lowers the activation energy of a chemical reaction. If the same reaction had taken place in the gas phase it would have energy of activation of E. On the catalyst surface, this has been lowered by an amount equal to the heat of chemisorption. Thus, in the appropriate rate equation, the
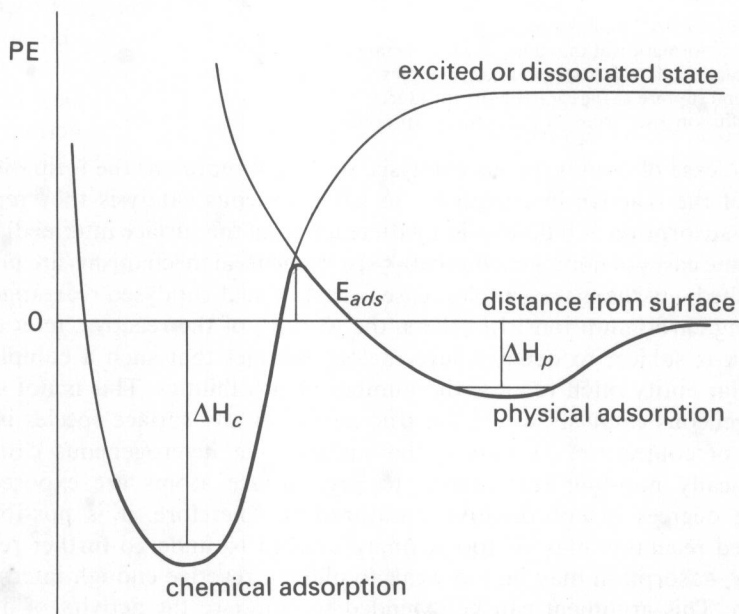
Figure 1.1 Formation of a chemisorbed species represented by the overlap of two potential energy curves. As an adsorbing molecule approaches the surface (thick line) it is initially physically adsorbed forming a species lying at a distance equal to the sum of the covalent radii plus the Van der Waal's envelopes ($\sim$0.3–0.4 nm). On closer approach to the surface, a chemisorbed species is formed at a distance approximating to that of a chemical bond ($\sim$0.1 nm). The energy of activation for the transition of a physisorbed to a chemisorbed species is usually low or negative.
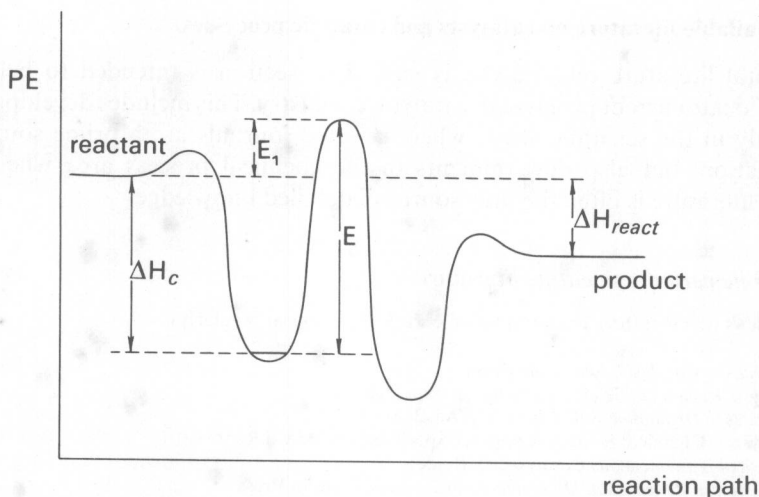
Figure 1.2 The energy profile for a typical catalytic reaction. Note that the activation energy for the same reaction in the gas phase is decreased by the heat of chemisorption, ΔH_c, of the reactant.

exponential term and hence the rate will have a higher value for the catalytic reaction than for the corresponding gas-phase reaction. Therein lies a simple explanation of catalytic *activity*.

The origin of catalytic *selectivity* is more complex. In the simplest case, the heat of desorption of product can determine how selective the reaction will be for that product. If the heat of desorption is low, the product can leave the surface easily and escape further reaction, which may be possible if the heat of desorption is high. More important, however, is the nature of the interaction between reactant and the active centres of the catalyst and, for that matter, the nature of the active centres. The type of activated complex which is formed will clearly be reflected in the products into which it decomposes.

It is not possible to calculate surface energetics of even the simplest catalytic reactions. It is not surprising, therefore, that catalysts are discovered by the experimental screening (often of large numbers) of candidates, rather than by calculated design. Many of the catalytic reactions and processes that are described in the following chapters have been discovered by this method, and it will become obvious to the reader that the implementation of a catalyst discovery by the chemical industry can occur long before any real scientific understanding of its mode of operation emerges. However, lest it should be felt that scientific endeavour in this area has little practical value, it should be emphasised that knowledge gained about the behaviour of a catalyst in a particular reaction can lead to improved (i.e. more selective or more active) catalysts for that reaction. In today's world of diminishing petrochemical feed-stocks, and the resulting need to generate an alternative base for the industry, selectivity is the all-important requirement for future catalytic processes.

1.3 Available literature on catalysts and catalytic processes

The total literature on catalysis is vast. This section is intended to help the reader locate current progress in catalytic chemistry. This includes developments not only in the scientific sense, where selected journals are a prime source of information, but also developments in the chemical process area where the patent literature is often the only source of detailed knowledge.

1.3.1 *The periodic scientific literature*

(a) **Reviews** (the first three are multi-volume works that appear regularly)

Advances in Catalysis, Academic Press
Catalysis Reviews in Science and Engineering, Dekker
Advances in Organometallic Chemistry, Academic Press
Catalysis—Chemical Society (London), Specialist Periodical Reports
Aspects of Homogeneous Catalysis, D. Reidel
Fundamental Research in Homogeneous Catalysis, Plenum Press

(b) **Journals of prime interest—scientific**
Journal of Catalysis
Applied Catalysis
Journal of Molecular Catalysis
Kinetika i Katalitika (Academy of Sciences, USSR)—English translation, *Kinetics and Catalysis*, Consultants Bureau, New York
Reaction Kinetics and Catalysis Letters
Journal of Organometallic Chemistry
Journal of the American Chemical Society
Journal of the Chemical Society, Faraday Transactions I
Surface Science

(c) **Journals of prime interest—technical**
Chemtech
Chemical and Engineering News
Chemical Engineering
Chemical Engineer
Chemical Engineering Progress
Hydrocarbon Processing
Oil and Gas Journal
In addition, *European Chemical News*, *Chemical Age*, and *Chemical Week* provide topical items on new processes.

1.3.2 *The patent literature*

A patent document contains a description of the catalyst or catalytic process for which the inventor has been granted the protection to operate free from interference from competitors. It must contain exemplification of the invention which must be in sufficient detail to enable the reader to reproduce the basic chemistry of the invention claimed in the patent.

Patents therefore contain a considerable amount of experimental information in substantial detail. Details of catalyst preparation and the manner of conducting the reaction are, and indeed are required to be, given in full. The