

CHAPTER III

THEORETICAL

3.1 Introduction

In the study of a reacting chemical system, two considerations are of importance. The first is, will the reaction proceed, and if so how far? All reaction must stop short of absolute completion: at what particular equilibrium position will the system come to rest? The answers to these and related questions are the province of chemical thermodynamics. The second consideration is, how fast does the reaction go? How quickly is the equilibrium situation attained? The answers to these and related questions are the concern of chemical kinetics. In the design of a chemical process, both considerations matter. The thermodynamics of the system determines the maximum attainable yield is low, if the equilibrium constant is small, a variable process cannot result. On the other hand, it is of no value to have a system with a large equilibrium constant, where a high yield of product is potentially attainable, if that equilibrium constant, where a high yield of product is potentially attainable, if that equilibrium can be attained only very slowly. In almost every case, economic factors require both favourable yields and rates.

Chemical thermodynamics is a well-established branch of science. Much information is available on very many chemical systems, from which the position of equilibrium may be estimated as

a function of temperature, pressures or concentrations, and other variables. Even when accurate information is lacking, the corpus of thermodynamic knowledge may be used to make an intelligent guess at the answer; it constitutes our chemical intuition, and the use of approximate estimates can be of great value.

It is a fundamental principle of thermodynamics that changes in Gibbs free energy G , enthalpy H and entropy S depend only upon the initial and final states of the system, and not upon the path taken to move from one to the other. The situation is however quite different with chemical kinetics. Here the kinetic parameters (rate coefficient k , activation energy E , order of reaction) depend sensitively on the path followed, and the introduction of a catalysed pathway changes not only the value of these parameters, but also their significance.

3.1.1 Mechanisms of contact catalysis [22]

The chemical reactions of heterogeneous catalysis occur between compounds adsorbed on the surface of the solid catalyst. The entire cycle comprises five consecutive steps, each of which can have more or less influence on the overall reaction rate, depending on its relation to the others. The steps are:

1. Diffusion of the reacting substances over the catalyst particle.
2. Adsorption of the reacting substances on the catalyst.
3. Interaction of the reacting substances on the surface of the catalyst.

4. Desorption of the reaction products from the catalyst particle.
5. Diffusion of the reaction products into the surrounding medium.

Steps 1 and 5 correspond to the physical processes of mass transfer to and from the catalyst particle and into and out of its pores, catalyst particles have internal pores that are accessible to the reactant molecules, so that diffusion proceeds in two steps, external and internal, as illustrated in Fig. 3.1

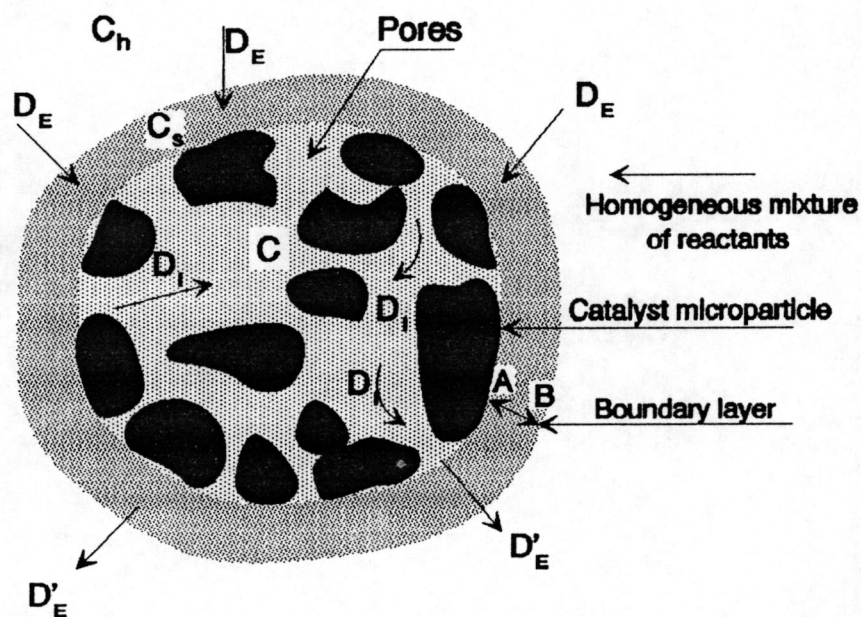


Fig. 3.1 Features of the diffusion process that occurs during heterogeneous catalysis

External diffusion (D_E): Particles of catalyst can be thought of as surrounded by a stationary layer of mixed molecules of reactants, products and diluents; the molecules of reactant must pass through this layer to reach the external surface of the particle. Since the stationary layer (or film) offers resistance to flow, a concentration gradient is set up between the fluid and the surface of the particle; and according to Fick's law, the flow of reactant through the layer is proportional to this concentration gradient, i.e., $D_E \sim (C_h - C_s)$, where D_E is the external diffusion, C_h is the concentration in the homogeneous fluid, and C_s is the concentration on the external surface of the catalyst particle.

Internal diffusion (D_I): Assuming that an excess of reactant molecules reach the external surface of the catalyst particle, a second concentration develops between that surface and any point in the interior pores; and the internal diffusion across this gradient is expressed by $D_I \sim (C_s - C)$, where D_I is the internal diffusion and C is the concentration at the point within the pores. However, the internal diffusion is more complex with respect to the important internal catalytic surface, S , following one or more of several possible mechanisms depending on the internal geometry of the catalyst particle. In addition to resistance to flow imposed by the medium in the catalyst pores, there is molecular (Knudsen) diffusion when the average diameter of the pores is of the same order to magnitude as the average free path of the molecules, as well as adsorbed-phase diffusion when gases condense inside the pores.

Step 2, 3 and 4 involve chemical phenomena that comprise the chemical transformation as shown in Fig. 3.2

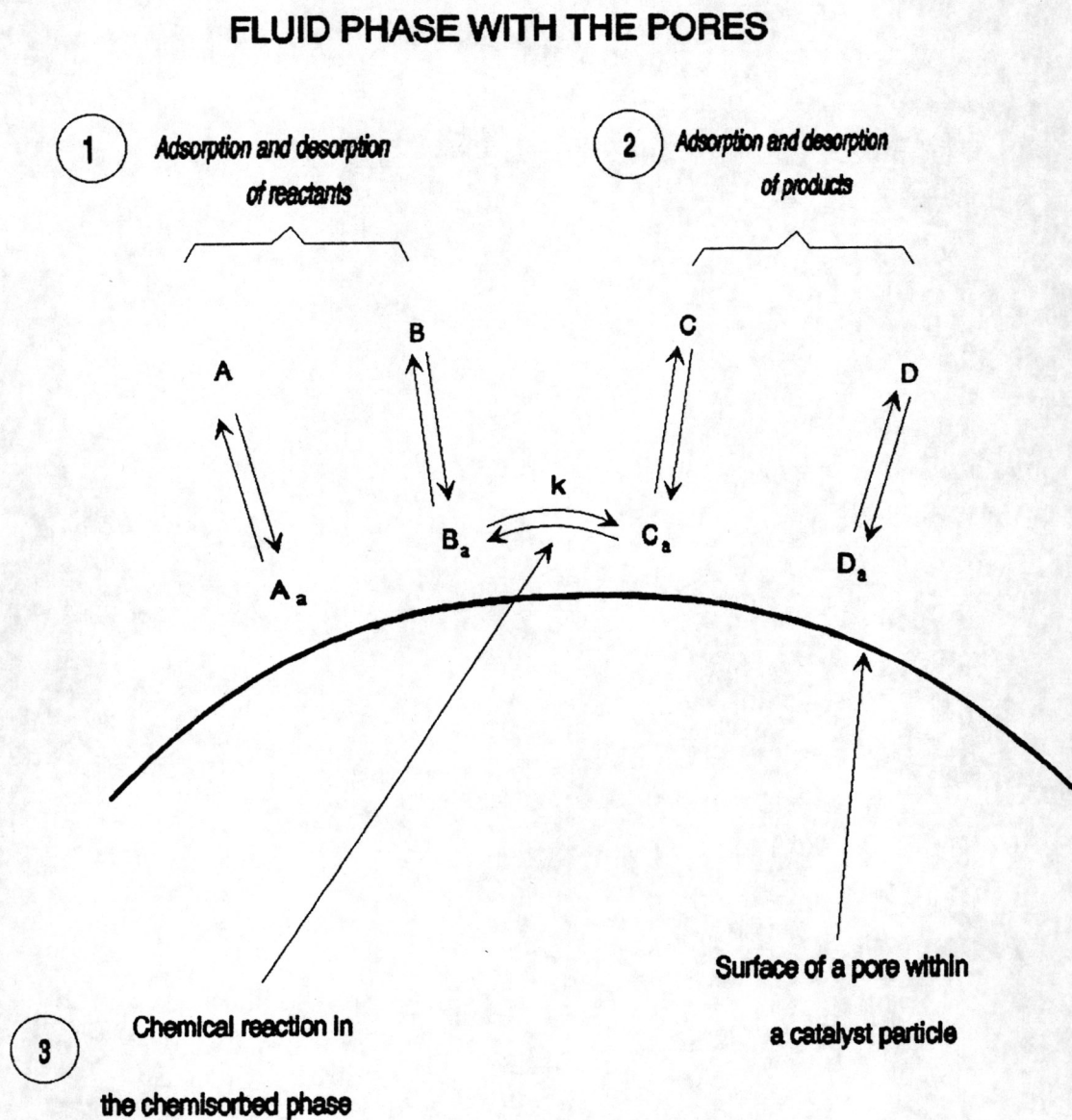


Fig. 3.2 Features of the chemical reactions occurring within the adsorbed fluid phase during heterogeneous catalysis.

3.1.2 Classification of catalytic systems [23]

They are of universal validity wherever catalysis occurs. In fact it is possible to divide catalytic systems into two distinct categories. When the catalyst is of the same phase as the reactants and no phase boundary exists, we speak of **homogeneous catalysis**. This may take place either:

- (i) in the gas phase, as for example, when nitrogen oxide catalyses the oxidation of sulphur dioxide; or
- (ii) in the liquid phase, as when acids and bases catalyse the mutarotation of glucose.

When a phase boundary separates the catalyst from the reactants, we speak of **heterogeneous catalysis**. A number of phase combinations can then occur, as shown in Table 3.1. Other possible phase combinations rarely arise in catalysis.

Table 3.1 Phase combinations for heterogeneous catalysis

Catalyst	Reactant	Example
Liquid	Gas	Polymerization of alkenes catalysed by phosphoric acid
Solid	Liquid	Decomposition of hydrogen peroxide catalysed by gold
Solid	Gas	Ammonia synthesis catalysed by iron
Solid	Liquid+Gas	Hydrogenation of nitrobenzene to aniline by palladium

3.1.3 Classification of solid catalysts [23]

Table 3.2 shows that transition metals are especially good catalysts for reactions involving hydrogen and hydrocarbons. This is because these substances readily adsorb at the surfaces of metals, in a manner to be described in more detail below, and except in a few cases the reaction does not proceed below the surface. Base metals are useless as catalysts for oxidation because at the necessary temperature they are rapidly oxidized throughout their bulk. Only those 'noble' metals (such as palladium, platinum and silver) that are resistant to oxidation at the relevant temperature may be used as oxidation catalysts. Many oxides on the other hand are excellent oxidation catalysts because they interact with oxygen and other molecules, but with some important exceptions, i.e. copper chromium oxide $\text{Cu}^{\text{II}}\text{Cr}_2^{\text{III}}\text{O}_4$ ('copper chromite') they are not well suited for hydrogenation because of the likelihood of reduction to metal. Those oxides which may be used for hydrogenation or dehydrogenation are of course immune to reduction by hydrogen at the temperature at which they are active. Similarly metal sulphides catalyse reactions of molecules containing sulphur: if oxides are used, they rapidly become sulphided. Those oxides such as alumina, silica, and magnesia which do not interact much with oxygen are poor oxidation catalysts, but they easily adsorb water and thus may be used to catalyse dehydration. The concept emerges that we must first understand the adsorption of molecules at solid surfaces before we can proceed to a deeper knowledge of catalysis.

Table 3.2 Classification of heterogeneous catalysts (less important functions in parentheses)

Class	Function	Examples
Metals	hydrogenation	
	dehydrogenation	Fe, Ni, Pd, Pt, Ag
	hydrogenolysis	
	(oxidation)	
Semiconducting oxide and Sulphides	oxidation	
	dehydrogenation	NiO, ZnO, MnO ₂ ,
	desulphurization	Cr ₂ O ₃ , Bi ₂ O ₃ -MoO ₃
	(hydrogenation)	WS ₂
Insulator oxides	dehydration	Al ₂ O ₃ , SiO ₂ , MgO
Acids	polymerization	
	isomerization	H ₃ PO ₄ , H ₂ SO ₄ ,
	cracking	SiO ₂ -Al ₂ O ₃ , zeolites
	alkylation	

3.2 Benzene and Its Chemistry [23]

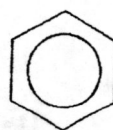
Benzene, C_6H_6 , is a volatile, colorless, and flammable liquid aromatic hydrocarbon which possesses a characteristic odor. It is used primarily as a chemical raw material in the synthesis of styrene (polystyrene plastics and synthetic rubber), phenol (phenolic resins), cyclohexane (nylon), aniline, maleic anhydride (polyester resins), alkylbenzenes (detergents), chlorobenzenes, and other products used in the production of drugs, dyes insecticides, and plastics. Benzene is also used as a solvent, but it has been replaced by safer solvents in most applications.

3.2.1 Structure

The representation of the benzene molecule has evolved from the Kekule ring formula (1), often abbreviated to a more realistic structure described by (2), in which all six carbon-to-carbon bonds are indential [24].



(1)

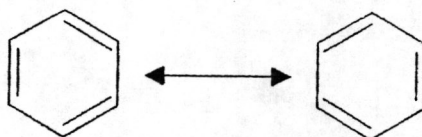


(2)

All of the carbon and hydrogen atoms in the benzene molecule are coplanar. The six carbon atoms form a regular hexagon in which each carbon atom is 0.139 nm from each of the two adjacent carbon atoms. Each hydrogen atom is 0.108 nm from the carbon atom to which it is bonded.

3.2.2 Resonance (Mesomerism)

Benzene has great thermal stability. It has lower energy (heat of formation from the elements) than the compound corresponding to formula (1) with three double bonds. When benzene is decomposed into carbon and hydrogen, it absorbs more energy than is predicted by the Kekule formula. Less heat is taken up during the dehydrogenation of cyclohexane to benzene than corresponds to the formation of three double bonds. This difference, 150.7 kJ/mol, (36.0 kcal/mol), between the energy expected to be taken up during the formation of three double bonds and that obtained experimentally for benzene formation from cyclohexane is the resonance energy of benzene. A more accurate term would be stabilization energy because the formation of benzene requires less energy than either of the two Kekule structures and hence is more stable by 150.7 kJ/mol. The carbon-to-carbon bond lengths are known accurately, all identical in benzene : they are intermediate between the bond lengths of normal single and double carbon-to-carbon bonds. The bonding electrons in the benzene molecule, based on quantum mechanics, occupy three sp^2 hybrid orbitals and one $2p_x$ orbital per carbon atom and one $1s$ electron per hydrogen atom. One sp^2 electron of each carbon forms a σ (sigma) bond with a $1s$ hydrogen electron, and the other two form bonds with adjacent carbon atoms. The remaining six $2p_x$ electrons combine to produce a π (pi) bond with a donut shaped probability distribution on each side of the ring [25]. These electrons are delocalized over the entire ring. Chemically, benzene reacts as if it had either of the two Kekule structures (see below). For benzene these two are identical, although there are a number of aromatic compounds for which this is not the case. These two structures are the principal resonance structures of benzene.



(1)

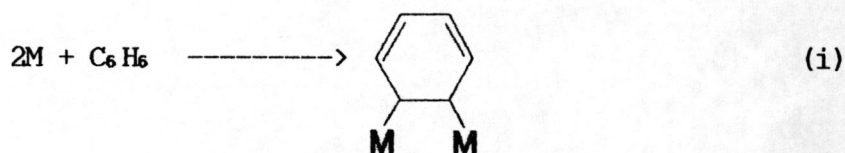
3.2.3 Hydrogenation of Benzene

Benzene can be reduced to cyclohexane [26,27]. At room temperature and ordinary pressure, benzene, either alone or in hexane or cyclohexane solution, is quantitatively reduced with hydrogen using a nickel catalyst. The speed of hydrogenation is tripled by increasing the temperature from 20 to 50 °C. Catalytic vapor-phase hydrogenation of benzene to cyclohexane is readily accomplished at elevated temperature (ca 200 °C) with a nickel catalyst. Nickel is cumulatively fouled by sulfur-containing impurities in the benzene, so nickel catalysts should be used only with thiophene-free benzene. Platinum catalysts are also used when the sulfur level is low. Less sulfur-sensitive catalysts, such as molybdenum oxide or sulfide, can be used when benzene has sulfur-containing impurities.

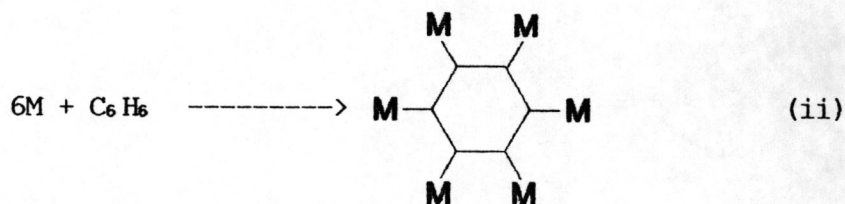
3.2.3.1 Adsorption of Benzene [28]

It appears that, on adsorption, benzene loses its resonance energy. The heat of adsorption of benzene is fairly low (~30 kcal mole⁻¹ on nickel powder and 12 kcal mole⁻¹ on copper powder at low coverage [29] and it would be expected to be

much higher than this if some or all of resonance energy were retained. Of some relevance is the difference between the heats of adsorption of thiophene (33 kcal mole⁻¹) and ethyl sulphide (65 kcal mole⁻¹) on platinum [30]. Similarly, the conversion of benzene to a cyclic diene is endothermic (5.6 kcal mole⁻¹) [31] and this compares with the activation energy for the hydrogenation of benzene ~7.4 kcal mole⁻¹. Selwood [32] has shown that when benzene is chemisorbed, at 150 °C, on supported nickel the relative magnetization of the catalyst decreases to an extent which is accounted for by benzene being attached to the surface by six bonds. Other important facts which are relevant to and interpretation are (i) when benzene is chemisorbed hydrogen is liberated and appears in the gas phase [33], and (ii) cyclohexene is the primary product in the hydrogenation of benzene [34]. The evidence therefore seems to favour adsorption processes such as



and



It would seem, because cyclohexene is the major product during benzene dehydrogenation, that the first mode of

adsorption exists under hydrogenation conditions. Benzene could, however, be chemisorbed in the form of a distorted hexane like molecule, as in (ii), and the interatomic metal distances are conveniently disposed for such a structure on the {111} planes of face-centred cubic metals and the {110} planes of body-centred cubic metals. The presence of benzene on a surface does not appear to inhibit para-hydrogen conversion and so it must be supposed that packing of the adsorbed molecules leaves vacant surface sites at which there is no overlap of molecular orbitals. From the published work it can only be concluded that benzene is chemisorbed strongly and probably exists at the surface either as phenyl radicals or as the diadsorbed state as in (i). The structure represented in (ii) may exist in the absence of hydrogen.

3.2.3.2 Thermodynamic of Benzene hydrogenation [22]

The exothermic hydrogenation of benzene occurs with a reduction in the number of molecules and is therefore thermodynamically favored by lower temperatures and higher pressures. Figure 3.3 shows the percentage of benzene remaining at equilibrium as a function of the temperature and pressure of hydrogen. The heat liberated at 200 °C is 51.2 Kcal/mol of hydrogenated benzene.

In practice, The hydrogenation is accompanied by secondary reactions that must be avoided to attain the required purity of cyclohexane and not reduce the yields. The various reaction that occur in the presence of benzene and hydrogen under conditions of the reaction are as follows:

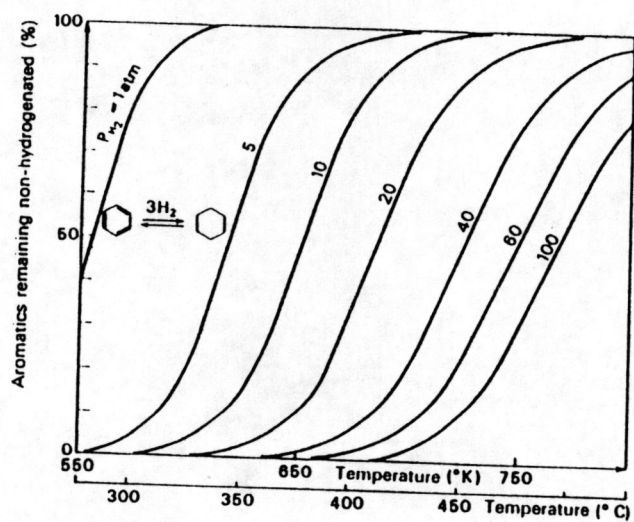
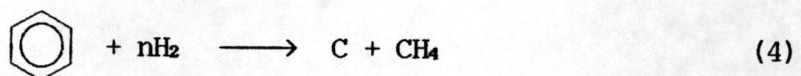
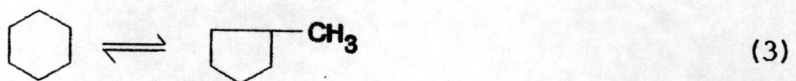
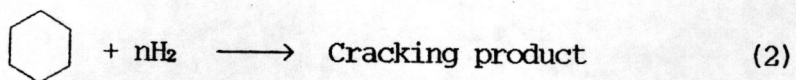
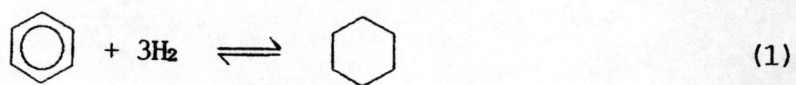


Fig. 3.3 Effect of hydrogen pressure and temperature on the equilibrium concentration of benzene in cyclohexane

Reaction (2) is of little importance up to temperatures of about 250 °C; it can be produced either by a hydrogenolysis-type reaction catalyzed by metals of group VIII, or by a hydrocracking-type reaction catalyzed by bifunctional catalysts of a hydrogenating metal deposited on an acid support (alumina or silica-alumina). This hydrocracking can be avoided by choosing a non-acid support.

Reaction (3) is thermodynamically favored by a rise in temperature (Fig. 3.4); it is catalyzed by acidity of the catalyst or of the support.

Reaction (4) occurs particularly in vapor phase. Catalyzed by metals of group VIII, it is relatively enhanced by a rise in temperature and a reduction in pressure.

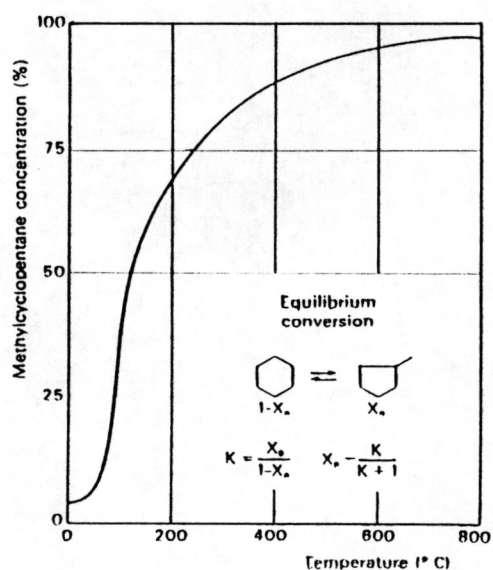


Fig. 3.4 Effect of temperature on the equilibrium concentration of methylcyclopentane in cyclohexane

3.3 Chemisorption of Carbon monoxide and Hydrogen on Platinum and Nickel surface [35]

Chemisorption can be thought of as resulting from solid-surface atoms that have free valences, so that the driving force is the tendency of these valences to saturate themselves selectively by reacting with certain molecules from the surrounding medium. For example, each of the points of a crystalline face-centered-cubic space-lattice is by geometry surrounded with 12 other such points when the lattices are joined in the mass of a crystal such as metallic nickel or platinum (Fig. 3.5). However, this crystal can also have external faces corresponding to one of the three possible lattice planes identified as 100, 110 and 111 in Fig. 3.5; the atoms in those face planes will have instead of 12 either 8, 7 or 9 neighbors depending on the respective plane; and they will have a corresponding tendency to chemisorb molecules from outside the crystal.

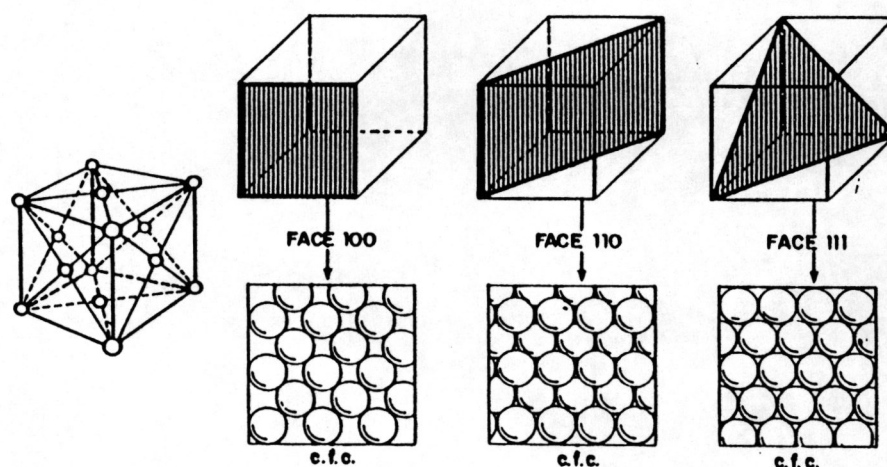


Fig. 3.5 Free valences on metal surface, as illustrated by nickel crystals.

3.3.1 Chemisorption of Carbon monoxide

The bonding of CO to transition metal surface (nickel and platinum at (100), (110) and (111) planes) is thought to be similar to the bonding in metal carbonyls. In carbonyls the bond is formed by transfer of electrons from the CO 5σ orbital to the metal, and transfer of charge from the metal atom into the $2\pi^*$ molecular orbital, more electrons can be donated from the 5σ level of CO to the metal. this is called a synergic process. But the donation and back-donation of electrons have opposite effects on the strength of the C-O bond. In general, as the CO coordination increases from one (terminally bonded CO) to two or three (bridge-bonded CO), the C-O frequency falls in both the ligands in carbonyls and in CO species Chemisorbed on single crystal surfaces.

3.3.2 Chemisorption of hydrogen

Hydrogen molecule is adsorbed in the dissociative manner, with the molecules cleaving into radicals or ions that have free valence to attach to the free valences of the adsorbing surface. Dissociative adsorption of hydrogen on platinum as shown in Figure 3.6. Two types of adsorbed hydrogen atom on nickel is shown in Figure 3.7.

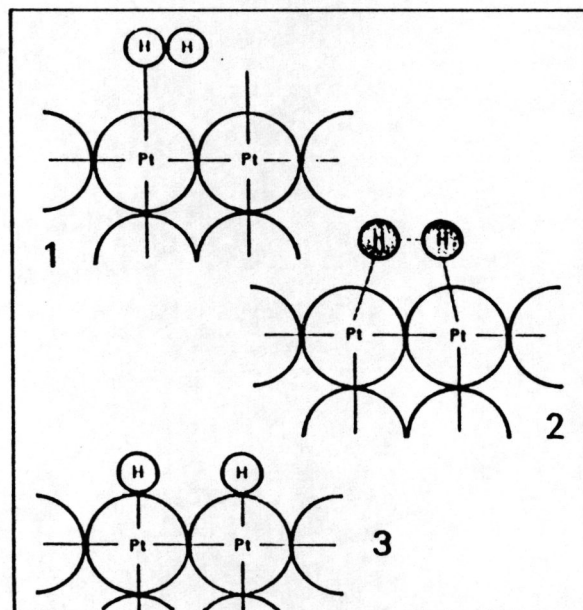
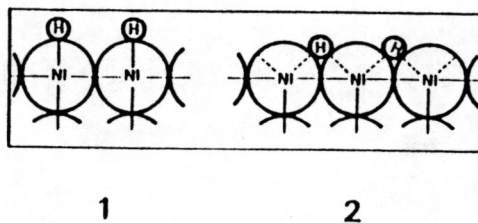


Fig. 3.6 Dissociative adsorption of hydrogen on platinum

(1) physical adsorption (2) transition state

(3) chemisorption



1

2

Fig. 3.7 Different type of hydrogen chemisorption

3.4 Possible Origins of Synergy in Reactions Involving Hydrogen [36]

In this section we consider how synergy may develop in various catalytic systems including : (a) classical bifunctional catalysis; (b) synergy through the formation of compounds between two phases acting synergistically; (c) through contamination of the surface of one phase by elements from another; (d) reaction of spill-over hydrogen, produced on one phase, with a reactant adsorbed on another phase; (e) the "remote control" concept, i.e.; creation or regeneration of active centres on one phase by spill-over hydrogen emitted by the other phase.

3.4.1 Classical bifunctional catalysis

Catalytic reforming involves the restructuring of hydrocarbon molecules without changing their carbon number, with the aim of increasing the octane number of the treated mixtures. Typical catalysts for the process are Pt/Al₂O₃ and Pt-Re/Al₂O₃ and are composed of at least two phases, i.e., supported metals and an acidic support. The metal loading rarely exceeds 0.6 wt % [37]. A complex series of reactions occur during reforming, including isomerization, hydrogenation, dehydrogenation and dehydrocyclization. The last three reactions are catalysed on the metal, whereas isomerization as well as some hydrocracking occurs on support. Each of the components of these catalysts, metal and acidic support, are necessary in producing a high octane number fuel. Synergy is normally observed if the activities and selectivities of the two-phase catalyst are compared to those of the separate metal and support.

Synergy in this system can readily be explained in terms of Figure 3.8 which envisages partial transformation of a reactant on the metal followed by further reaction on the support. An example is the hydrogenation of 1-heptene followed by its isomerization to form 2-methylhexene. In appropriate cases the reverse sequence may be envisaged, i.e., the partial reaction occurring on the support, followed by transfer of the primary reaction product to the metal for further reaction.

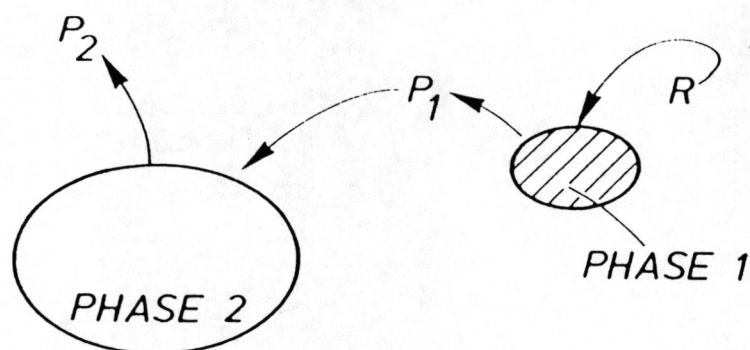


Fig. 3.8 Simple representation of bifunctional catalysis. The reactant (R) is transformed into the intermediate product (P_1) on phase 1; P_1 readsorbs on phase 2 to be transformed into the final product (P_2).

3.4.2 Formation of Compounds Between Two Phases

Most promoted and alloy catalysts may be included in this category. These are catalysts in which the second component changes the surface geometry or the electronic environment and many examples have been reported where a distinct new phase forms.

Addition of iridium to a Ni/SiO₂ catalyst increases its resistance to sulphur poisoning and its methanation activity at

282 °C. Wentrcek and coworkers [38] postulated that the added iridium changed the surface structure of the nickel particles. A synergistic effect was observed when an optimum surface concentration of iridium reduced the density of four- and three-fold coordinate sites, preferred for sulphur adsorption, and increased the number of sites (two-fold) available for CO adsorption.

The presence of some potassium metal in iron catalysts used for methanation and Fischer-Tropsch reactions increases the rate of former and shifts the selectivity of the latter in favour of longer chain hydrocarbons [39]. The effect appears to be electronic, with the alkali metal donating electron density to the iron. When CO adsorbs on this structure, the Fe-C bond stronger and C-O bond weaker than the unpromoted catalyst. It has been argued that carbon, activated in this way, is more prone to attack by hydrogen [40]. If the K:Fe ratio exceeds a critical value these effects are lost, presumably due to the presence of excessive amounts of inactive potassium on the iron surface.

Poels and coworkers [41] studied Pd-Mg/SiO₂ for hydrogenation of CO to methanol. Optimum activity was observed for Pd:Mg = 1:1. Scanning electron microscopy indicated that Pd, Mg and Cl occurred simultaneously in many locations in the catalysts. The synergistic behaviour followed exactly the trend in the concentration of unreduced Pd present during catalysis. It was postulated that Mg²⁺ stabilized Pdⁿ⁺, the active centres of these reactions.

Daage and Bonnelle [42] studied the hydrogenation of isoprene and 1,3 pentadiene over a series of Cu-Cr-O spinel bronzes

which also contained small amounts of supported metallic copper. The Cu:Cr ratios were in the range 0.5-1.4:1, but optimum activity was observed with the 1:1 composition. NMR studies pointed to the presence of a special hydrogen species in the bulk of the spinel phase after treatment in hydrogen at 150 ° C. This hydrogen diffused from the bulk and participated in hydrogenation, even when gaseous hydrogen was present. Some unusual selectivities were observed : the less substituted double bond in isoprene was hydrogenated preferentially, but in 1,3-pentadiene the more substituted double bond was the most reactive. These effects were attributed to copper ions in octahedral environments which acted as active sites when combined with hydride ions.

3.4.3 Contamination of the Surface of One Phase by Elements From the Other Phase

It is often difficult to prove whether a synergistic effect arises because of the interaction of two clearly defined phases or whether small amounts of one phase become detached and contaminate the second phase, hence acting like a classical promoter. For Cu-Zn-O catalysts, often used for the conversion $\text{CO} + \text{H}_2$ or $\text{CO}_2 + \text{H}_2$ into methanol, the weight of the evidence to date would favour the model in which small amounts of Cu^+ , mixed with ZnO, act as a promoter. The optimum Cu:Zn ratio is usually 1:1. However, a doubt remains because mechanical mixtures of CuO and ZnO can catalyse these reactions nearly as efficiently as coprecipitated catalysts [43].

Other systems of interest in this category are those which exhibit the so-called "strong metal-support interaction". This

term is applied to many metals supported on reducible oxides, such as TiO_2 , which, when treated in hydrogen at 500°C , lose the capacity to adsorb hydrogen and catalyse hydrogenation and dehydrogenolysis reactions. Originally this effect was thought to be due to electron transfer from the reduced oxide to the metal [44], but evidence has been accumulated which suggests that the metal particles become contaminated by the support [45].

3.4.4 Reaction of Spill-over Hydrogen Produced on One Phase with a Reactant Adsorbed on Another Phase

The phenomenon of interest here is described in Figure 3.9. Essentially a hydrogen species is formed on one phase (usually a metal) and spills over to react on the other phase. From the many examples of this type we will consider the following in detail : (i) the reactions of ethylene and acetylene over $\text{Pd}/\text{Al}_2\text{O}_3$; (ii) the role of spill-over hydrogen in the prevention of coke formation; (iii) the influence of spill-over hydrogen in controlling the selectivity of catalysed reaction.

Sarkany and coworkers [46] studied the hydrogenation of a mixture of 0.29 mole % C_2H_2 , 0.44 mole % H_2 and C_2H_4 up to 100 %, a so-called tail-end mixture, on palladium black and several $\text{Pd}/\text{Al}_2\text{O}_3$ catalysts. Hydrogenation of C_2H_4 increased with the time on stream for all the Al_2O_3 -supported catalysts; the opposite behaviour was noted with palladium black. Polymer formation was noted for all catalysts studied and also increased with time. It was recognized that a small number of C_2H_4 hydrogenation sites were located on the metal but the majority were on the polymer-covered support. The authors proposed that C_2H_4 adsorbed on the support and

was hydrogenated there. Spill-over hydrogen was tentatively identified as the source of hydrogen. Because of the parallelism between polymer formation and ethylene hydrogenation, it was proposed that the surface polymer served as a hydrogen pool or facilitated diffusion of hydrogen from Pd to the support.

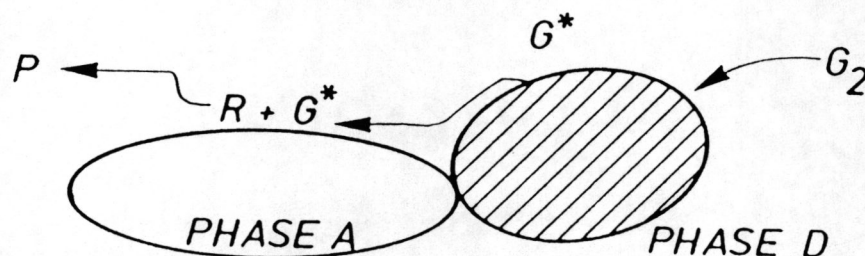


Fig. 3.9 Reaction between a species (G^*), formed on phase D, then transferred to phase A by spill-over and surface diffusion, where it reacts with an adsorbed molecule R.

Most reforming catalysts contain small amounts of chlorine located on the support. This influences the activity and selectivity : if too little Cl is present activity is lost; if too much is present selectivity, (i.e., high octane number) is lost. The optimum is usually ca. 0.9 wt % Cl [37] (Fig. 3.10). Parera and coworkers [47] observed a parallelism between chloride content and the build-up of carbonaceous deposits on these catalysts. Minimum coke build-up occurred when the chlorine concentration was such that half of the surface hydroxyl groups were replaced by chlorine. Maximum hydrogen spill-over was also observed at this concentration. A further publication [48] by the same group indicated that spill-over hydrogen from Pt could completely eliminate slightly polymerized coke on Al_2O_3 , by hydrogenation. In the absence of Pt,

decontamination of Al_2O_3 by hydrogen was incomplete. With more highly polymerized coke, hydrogenation with and without Pt succeeded in removing only a small fraction of the coke. However, this fraction was always higher with Pt than without. The proposed mechanism is outlined in Figure 3.11. The implication of this work is that with an optimum chlorine concentration the rate of coke formation is lower because spill-over hydrogen keeps the support clean by removing coke precursors.

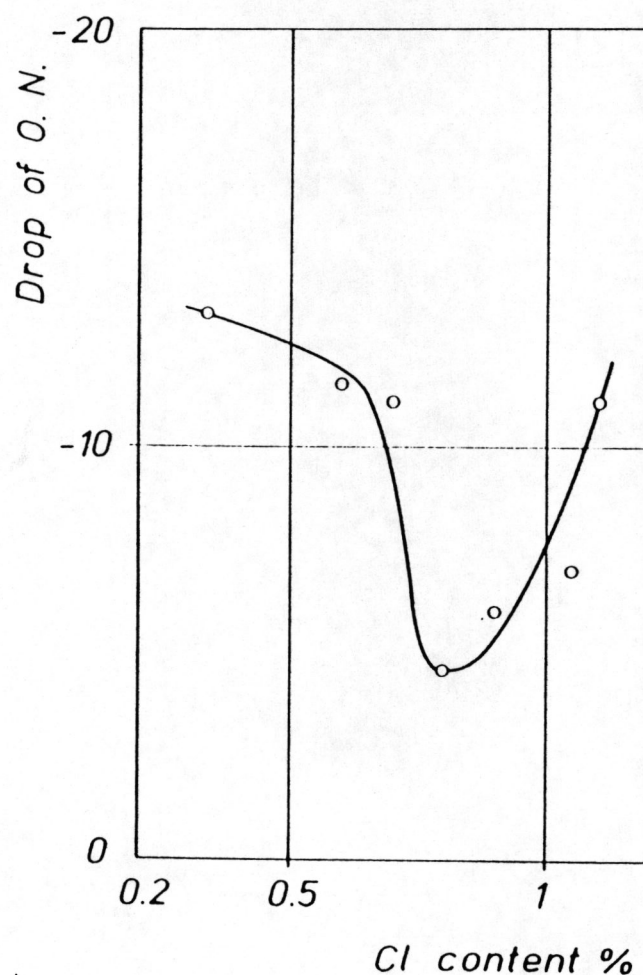


Fig. 3.10 Influence of chlorine content on the deactivation of $\text{Pt}/\text{Al}_2\text{O}_3$ reforming catalysts, measured by the decrease in octane number (O.N.) of the product.

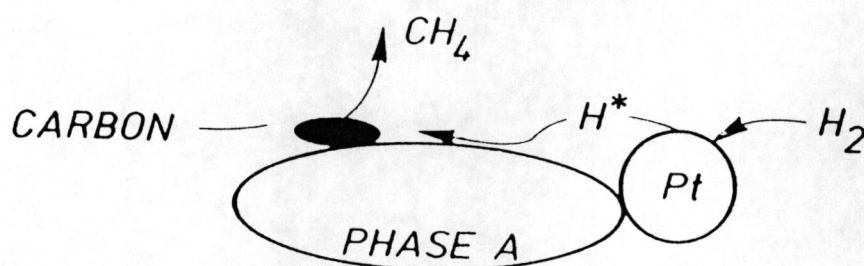


Fig. 3.11 Removal of carbonaceous deposits, more generally, of fouling materials or poisons, by reaction of spill-over hydrogen, leading to restoration of the catalytic site.

Gnep and coworkers [49] studied the reaction of *o*-xylene over a series of mordenite catalysts. Isomerization, disproportionation and coke formation occurred. These catalysts were more resistant to deactivation in hydrogen when Ni/SiO₂ was added. The greatest resistance was observed for mordenite which was treated in spill-over hydrogen which originated from Ni/SiO₂ (the latter was removed before exposure of the mordenite to *o*-xylene). Carbon deposition and disproportionation were both inhibited under these conditions by comparison with untreated mordenite. These workers postulated that spill-over hydrogen was capable of generating new catalytic sites on mordenite; These catalytic sites were believed to be capable of activating hydrogen for reaction with carbocations, which were intermediates in the disproportionation and coke formation reactions. The isomerization of *o*-xylene did not involve carbocations, but it benefited by not being inhibited by coke deposition.

3.4.5 Creation or Regeneration of Catalytic Centres on One Phase by Spill-over Hydrogen Emitted by the Other Phase: the "remote control" Concept

The creation of catalytic centres on phase A by reaction of spill-over hydrogen emitted by phase D is depicted in Figure 3.12

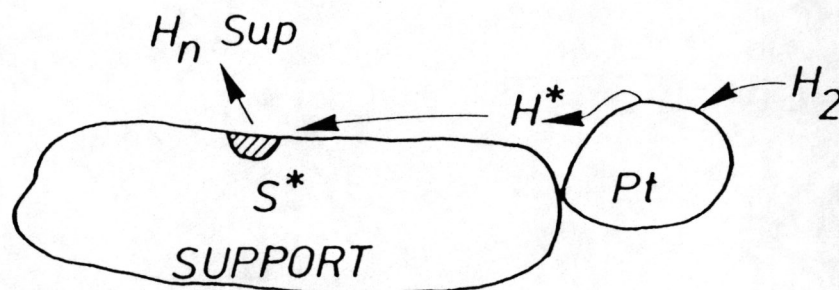


Fig. 3.12 Creation of an active site on phase A by reaction of its surface with spill-over hydrogen (with possible formation of a product H_n sup.).

Some of the most unambiguous evidence for the creation of catalytic centres by spill-over hydrogen comes from the work of Teichner and coworkers [50,51]. In the early 1970s these works developed an experimental device whereby an oxide, usually Al_2O_3 , could be activated by spill-over hydrogen produced on Pt/Al_2O_3 ; immediately after activation the donor, i.e., Pt/Al_2O_3 , could be removed. This system had the advantage that the oxide alone could be tested for catalytic activity in a number of hydrogenation and isomerization reactions. For our purposes it suffices to recall the principal conclusions:

- (1) Al_2O_3 could be activated for hydrogenation by heating in spill-over hydrogen at $430^\circ C$;
- (2) The sites which formed were catalytic, i.e., they were used more than once in hydrogenating feed molecules;

- (3) An induction period was often observed, which was ascribed to the need to desorb spill-over hydrogen before the sites were free for catalytic reactions.

In addition, for the temperature range within which synergetic effects of interest in catalysis occur, transport of the metal has been excluded.

For catalysts composed of two clearly defined phases, such as Co_9S_8 and MoS_2 , the "remote control" model has been developed by Delmon and coworkers. This model postulates that hydrogen is activated on the Co_9S_8 phase and spills over to create or regenerate two types of site on the MoS_2 phase, i.e., a slightly reduced region responsible for hydrogenation, and a more deeply reduced region responsible for hydrodesulphuration. The concept is shown in Figure 3.13, which is a detailed representation for hydrodesulphuration catalysts of the process suggested in Figure 3.12.

Two synergistic effects are observed with these catalysts (see Figure 3.14). The first is for hydrogenation: its maximum usually occurs at fairly low Co:Mo ratios. Under these conditions little spill-over hydrogen becomes available because little of phase D is present and the MoS_2 only becomes mildly reduced. The second synergistic effect is observed for hydrodesulphuration, and its maximum occurs at higher Co:Mo ratios. Under these conditions more spill-over hydrogen should be available from the higher Co_9S_8 content, hence the MoS_2 phase can become more deeply reduced.

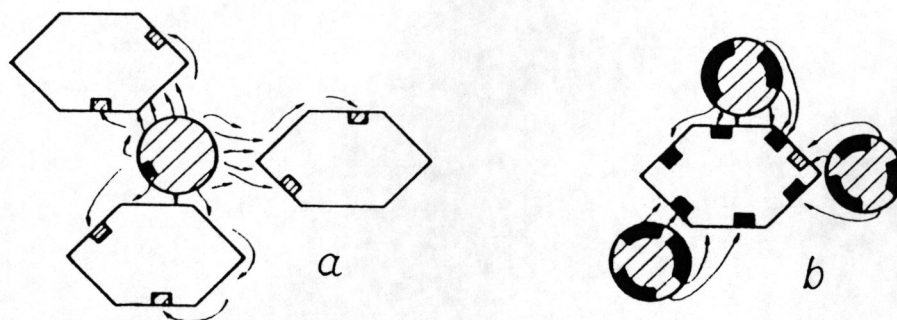


Fig. 3.13 Formation of active sites for hydrogenation and hydrodesulphuration by hydrogen spill-over : (a) low proportion of Co_9S_8 , hence small amounts of spill-over hydrogen with limited reduction of the MoS_2 phase; (b) high proportion of Co_9S_8 giving deeper reduction of MoS_2 .

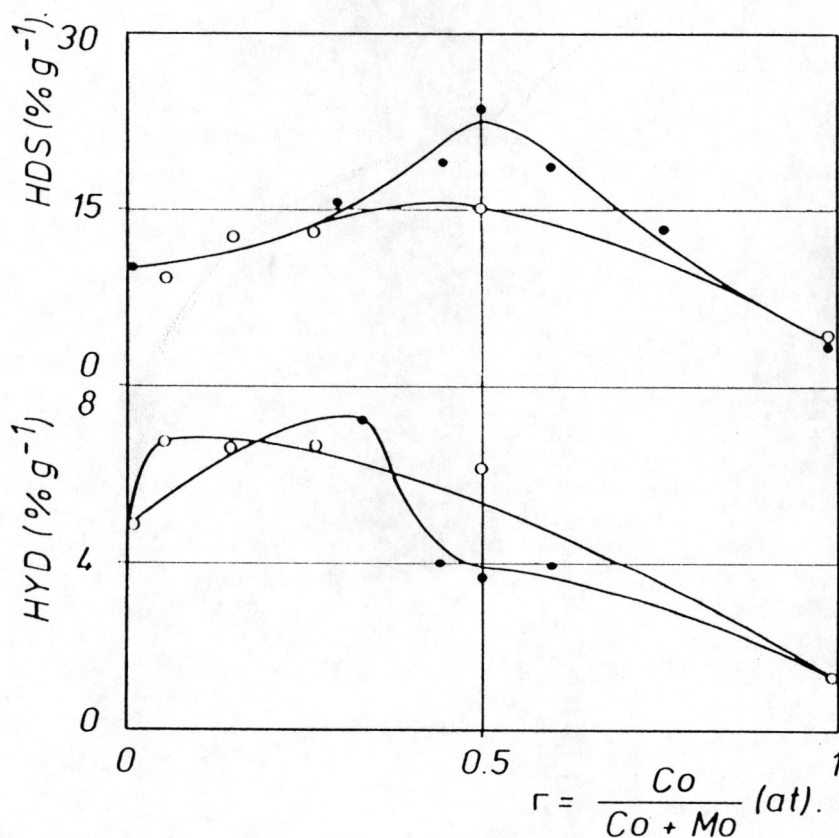


Fig. 3.14 Catalytic activity in hydrodesulphuration (HDS) and hydrogenation (HYD) of catalysts prepared by mechanically mixing MoS_2 with one of two samples of Co_9S_8 which had different specific surface areas ($\text{g m}^2 \cdot \text{g}^{-1}$; $27 \text{ m}^2 \cdot \text{g}^{-1}$).

The "remote control" hypothesis implies that sites responsible for hydrogenation may be converted into hydrodesulphuration sites by appropriate manipulation of the experimental conditions.