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The water-gas shift deactivation studies

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CHAPTER ONE

INTRODUCTION

1.1 CATALYST DEACTIVATION

The nature of catalyst deactivation differs for individual processes, but it is true to say that most heterogeneous catalysts show an initial fast decline in activity, after which the activity stabilizes and declines more steadily with time (see Figure 1.1). Activity and the rate of deactivation between operating times t_1 and t_2 is of significant importance because the behaviour in this region can indicate whether or not the catalyst is suitable for industrial purposes.

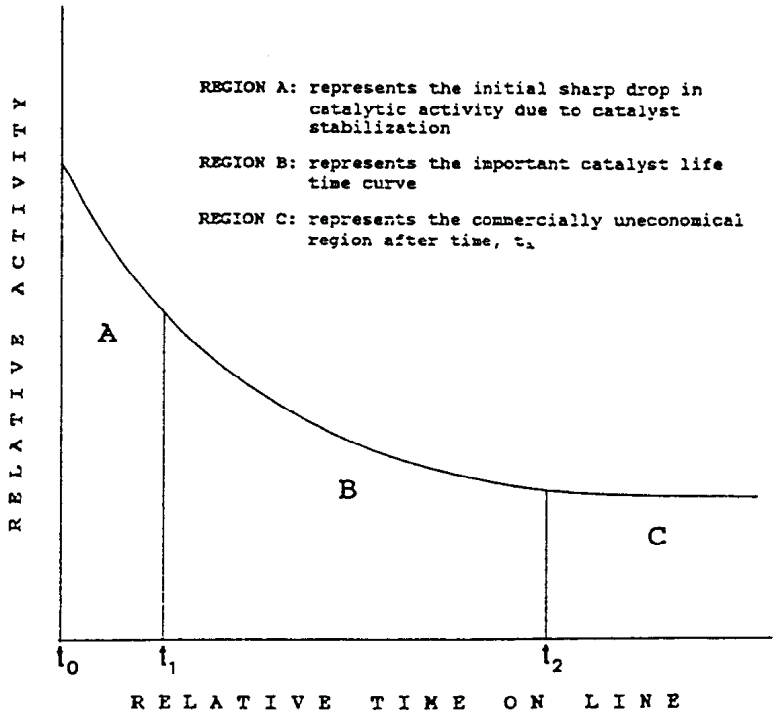

Figure 1.1 Catalyst deactivation profile (2)

Loss of catalytic activity makes it necessary to change catalyst reactor loads from time to time. As financial losses incurred during plant shut down are usually very high, it is highly desirable to develop catalysts with long, economically viable lifetimes. Lywood (1) described optimum catalyst lifetime as a function of catalyst

performance, catalyst manufacturing costs, catalyst reduction costs and catalyst vessel cost. A scheme has been suggested (Figure 1.2) by which the inter-related causes of catalyst deactivation may be linked (2).

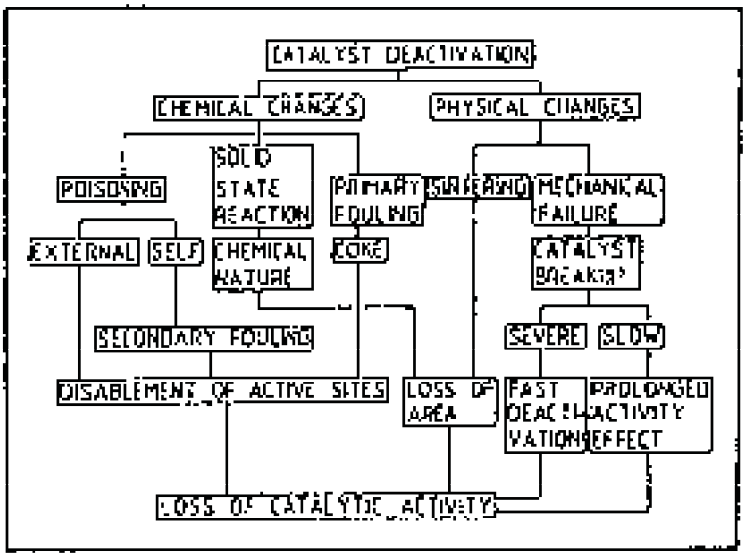

Figure 1.2 **A proposed scheme for the causes of deactivation (2)**

From Figure 1.2 it is evident that deactivation normally occurs either from poisoning, fouling, sintering, solid state transformations and mechanical defects or various combinations of the above, which leads to either a loss of surface area, blocking of active sites or breakup of the catalyst. Many attempts have been made to explain the phenomenon of catalyst deactivation. For instance, Spencer (1) has mentioned the usefulness of distinguishing between temporary and permanent loss of performance, and identified three different causes of catalyst decay: physical causes, poisoning by impurities, and poisoning by reactants or products. Trimm (3) described the fundamental causes for the decline of catalytic activity as the poisoning, coking and sintering of the catalyst, whilst Forzatti et al. (4) divided the causes for deactivation into four groups, namely: poisoning, fouling, sintering and solid state reactions.

Since poisoning, sintering and fouling are normally

considered the main causes of deactivation, they are discussed in more detail below.

1.1.1 Deactivation by poisoning

Poisoning may be defined as the irreversible (or reversible) chemisorption of an impurity on a catalyst surface which eliminates or alters the active sites used for product synthesis to such an extent that the activity or product selectivity of the catalytic species is negatively influenced (5, 6). For example, Oudar (7), as well as Hegedus and McCabe (8) distinguished between two main types of poisoning by impurities; competitive reversible adsorption of the impurity (also known as inhibition), and irreversible adsorption of the impurity, leading to permanent poisoning of a catalyst.

Irreversible poisoning may be explained by two different effects (7):-

i) **Catalytically active sites blocked by the impurity:** The active sites are blocked on a one-to-one basis by the poisoning substance. The catalytic activity decreases linearly as a function of the concentration of the impurity on the surface.

ii) **Electronic or ligand effects:**
In this case the reactivity of the catalytically active sites located at varying distances from the site covered by the poison may be influenced negatively to a greater or lesser extent through electronic or ligand effects.

Hegedus and McCabe (8) have suggested that the poisoning phenomenon can be decomposed into: (i) the nature of the interaction of the poison with the catalyst surface and (ii) the effect of the poison on the catalytic reaction. In their analysis four main categories of catalyst poisoning were mentioned: poison adsorption, poison

induction, surface reconstruction and compound formation between the poison and the catalyst.

Work by Maxted (9) and Butt (10) showed that the metals which are most susceptible to poisoning, are predominantly the Group 8 - 11 metals. These metals include iron, cobalt, nickel, copper, palladium, silver and gold. Three groups of *poisons* have been identified for these metals, namely molecules containing Group 15 (N, P, As and Sb) and 16 (O, S, Se and Te) elements, compounds which consist of toxic metals such as lead and mercury, and metallic ions and molecules with multiple bonds. The ability of the Group 15 or 16 elements to poison catalysts is related to their valence states. No toxicity is found for the elements which are coordinately saturated, but those having unshared electron pairs or empty valence orbitals can act as poisons. Thus, whenever strong chemisorption is possible between the elements with unshared electrons and a specific catalyst, this element may act as a poison preventing the catalyst from performing normally.

Uncertainty still exists with regard to a quantitative understanding of the intrinsic rates and mechanism of catalyst poisoning (11). Temperature, pressure and contact time between the active catalyst surface and poison are known to significantly influence the rate with which a poison slows down a catalytic reaction (12). Berkman *et al.* (13) linked several characteristic catalyst poisoning factors according to the relationship shown in Equation 1.1 below:

$$Kc = Ko(1-\beta c) \qquad - (1.1)$$

where: β = 'poisoning coefficient'

Kc and Ko = reaction velocity constants in the presence and absence of a poison respectively

c = the concentration of poison

The first characteristic factor, β, describes the 'susceptibility' of a defined quantity of catalyst to a poison. Kc, defines the absolute amount of poison needed to totally deactivate the catalyst and is a measure of the *extent* to which a poison acts. The factor, c, demonstrates the tendency with which a poison is retained on the catalyst surface and is also called the retention factor.

Bartholomew *et al.* (11) considered that both thermodynamic (i.e. bulk characteristics) and surface interactions (i.e. steric effects) may be involved in the mechanism by which metal catalysts are poisoned by sulphur.

From the list of free energies of formation of selected bulk metal sulphides at 300 and 600k presented in Table 1.1, it can be seen that metals more commonly used as catalysts, such as Co, Cu and Fe have lower free energies of formation of their bulk sulphides than the metals Cr, Mn and Zn which are often used in either alloy or oxide form as catalyst supports. This observation suggests that the sulphur poisoning of one metal may be reduced by combining it with another metal having a higher free energy of formation of the bulk sulphide. This forms the basis of the so called protection mechanism described by Bartholomew *et al.* (11).

Observations supporting this hypothesis have been reported. For example, Oudar (15) showed that the enthalpy of adsorption of sulphur containing compounds onto most catalytically active metals, (i.e. Ni, Cu, Fe, Cr and Pt) was directly related to the enthalpy of bulk sulphide formation. It was observed that for a 50% adsorption layer, the enthalpy of formation of a surface sulphide species was between 20 and 40% higher than the enthalpy of formation of the most stable bulk sulphide. It was thus demonstrated that sulphur may not only modify the bulk characteristics of a catalyst, but also the surface structure.

Table 1.1 Free energies of formation of various metal sulphides[a]

Element	Metal Sulphide	ΔG_f^θ (kJ/mol) 300K	600K
Co	CoS	-54.0	-47.7
	Co_3S_2	-69.8	-
	$Co_4S_{3.08}$	-39.3	-39.8
	Co_9S_8	-65.3	-55.3
Cr	CrS	-110	-108
Cu	CuS	-55.4	-62.3
	CuS_2	-44.4	-60.7
	Cu_2S	-46.5	-52.3
Fe	FeS	-58.2	-57.3
	FeS_2	-75.8	-
Mn	MnS	-185	-180
	MnS_2	-116	-128
Zn	ZnS	-168	-152

[a] Data computed from reference 11 and 14 and based on the following stoichiometry:
$(x/y)\ M + H_2S \rightarrow (1/y)\ M_xS_y + H_2$

1.1.2 Deactivation by sintering

The agglomeration of the crystallites of the active phase, leading to the loss of active surface and consequent decrease in activity is called sintering (16). Sintering occurs in order to decrease the free energy of the system (4). This process is therefore influenced by the interfacial free energies involved. Since the values of the free energies are affected by the physical and chemical interactions between crystallites, substrate, and atmosphere, these factors play a dominant role in the free energy of dispersion of small particles.

Lywood (1) has reported a number of factors which affect the rate and extent of sintering, including the metal concerned, the metal content, the initial crystallite size and size distribution, the dispersion of the metal across

the support, the nature of the support material and the operating conditions. As the activation energy of sintering is generally high, an increase in temperature can result in an increase in sintering rate. Thus, a metal with a low melting point may sinter more rapidly than one with a higher melting point (16). Often, catalyst aging may be described by the sintering process which increases with time. In most catalytic processes the temperature and size of the metal crystallites are such that extensive sintering would occur in seconds without the presence of a structural support. A major function of the support, then, is to act as a spacer, (7) preventing or minimizing the growth of, and movement by, metal crystallites to form clusters.

Two basic mechanisms for sintering have been suggested (17):

(i) migration of *crystallites* and their *coalescence* (18);

ii) emission of *single atoms* by the small crystallites and capture of single atoms by larger ones - *Ostwald ripening* (18, 20, 21, 22).

A brief summary of these models is given below:-

i) Crystallite migration and coalescence:

It has been hypothesized that the primary mechanism of sintering is the migration of metal particles on the support and the coalescence of the particles when they come into contact (23) with each other, thus minimizing the free energy of the system.

Two limiting situations have been considered by Ruckenstein (24): In one, the interactions are assumed to be so strong that two particles in contact form a single unit within a time which is short compared to the time of migration. The rate of sintering is then diffusion controlled. In the

second, the merging into a single unit is assumed to be slow compared to the crystallite diffusion process, and the process is "interface" controlled.

ii) The Ostwald Ripening Mechanism:

This model considers sintering to be a classical three-step process (emission, migration, and capture). Firstly, metal atoms escape from the metal crystallite to the support surface, these atoms then migrate along the support surface, to finally be captured by stationary metal crystallites upon colliding. A number of rate constants are involved with each of the mechanisms (24), making it difficult to evaluate them. In addition, the result predicted by the models, such as the decay of the exposed surface area, do not permit a clear discrimination between the various mechanisms. There are however, additional mechanisms of sintering based mostly on wetting and spreading. Ruckenstein (24) has stated that wetting determines the surface of contact between substrate (catalyst support) and crystallite, which affects the migration of the crystallites on the surface of the substrate. This mechanism shows that both the nature of the substrate and the metal play a major role in the sintering process.

1.1.1 Deactivation by fouling

Fouling may be defined as the loss of catalytic activity by either physical or chemical occurrences (25). These can originate from surface reactions in which carbonaceous deposits, or other impurities adsorb strongly onto the surface of the catalyst, physically blocking the active sites through which the principal reaction takes place. Most catalytic processes that use organic reactants form carbonaceous deposits on catalysts (1). These are usually described as "coke", even though the carbon may contain hydrogen. Other types of fouling are known. For example, methanol synthesis catalysts are carefully formulated (26)

to avoid the possibility of an iron impurity (e.g. iron carbonyls) which could promote Fischer-Tropsch reactions.

1.1.4 Conclusion

Catalyst deactivation is a complex phenomenon and its diagnosis and cure is often difficult. Solid state reactions (2) and mechanical failure (27) may also contribute to deactivation. Solid state reactions occur when a change in the chemical nature of the compounds within the catalyst matrix take place (2), which may result in a loss of total and active metal surface area, with a consequent loss of activity. Mechanical failure results from the loss of structural stability of a catalyst pellet. This has been regarded as a major reason for the deterioration of catalyst performance (5, 8, 27). Catalyst pellets are known to gradually loose their mechanical strength (6), crumble and break up, subsequently increasing the pressure drop over the catalyst bed (27). More fundamentally it can lead to overheating of the catalyst, loss of activity and a reduction of throughput (28). These effects may also be caused by coking.

1.2 THE WATER-GAS SHIFT REACTION

During the latter part of the nineteenth century, a process (1) was developed for the manufacture of *water-gas*, (an equimolar mixture of hydrogen and carbon monoxide), to supplement coal gas (used as a gaseous fuel). Water-gas is formed when steam is passed through incandescent coke at temperatures above 1000°C, according to Equation 1.2.

$$C + H_2O \rightarrow CO + H_2 \quad \Delta H = 131.2 kJ.mol^{-1} \qquad (1.2)$$

With the advent of the Haber process for ammonia synthesis in 1913, came the need for supplementary technology. Hydrogen needed to be produced on a large scale from coal,

and the process of removing excess carbon monoxide (an ammonia synthesis catalyst poison) by liquefaction and scrubbing with hot caustic solution was unsuitable for use on a large scale (29, 30). Before the turn of the century, it was known that if carbon monoxide and steam were passed over catalytic materials such as red hot refractories, hydrogen and carbon dioxide were obtained (31, 32). Thus a *catalytic* process was developed which converted carbon monoxide to carbon dioxide by reaction with steam according to Equation 1.3.

$$CO(g) + H_2O(g) \rightleftharpoons H_2(g) + CO_2(g) \quad \Delta H = -42.1\ kJ.mol^{-1} \qquad (1.3)$$

This reaction became known as the water-gas shift reaction (WGSR) or the CO shift reaction. The WGSR is moderately exothermic (1), controlled by a thermodynamic equilibrium, the kinetics of which can be accelerated by a catalyst.

1.2.1 Applications of the water-gas shift reaction

The most important use of the WGSR is in the production of ammonia. However, there are other areas where the reaction is utilised and these are described below:-

(i) In the 1930's commercial production of hydrogen (33) was effected by reacting waste gases rich in methane with steam over nickel based catalysts according to Equation 1.4.

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad (1.4)$$

The WGSR was then used to "shift" the unwanted carbon monoxide in the presence of more steam, to produce product gas rich in hydrogen. The carbon dioxide (from the WGSR) was removed by washing with water, compressed to 50 atm

pressure. Typically gas containing about 80% methane and 17% ethane could be transformed into a mixture of about 78% hydrogen, 20% carbon dioxide (before removal) and only 2% unconverted methane and carbon monoxide.

(ii) Synthesis gas derived from most coal gasification processes or steam reforming of hydrocarbons yields an approximately equimolar ratio of hydrogen to carbon monoxide. Fischer-Tropsch and methanol synthesis require a feed gas containing about two parts hydrogen and one part carbon monoxide, thus the WGSR is used to lower the CO content, producing more hydrogen, until the required H_2:CO ratio is achieved.

(iii) The WGSR has also been used in automotive emission control (34) to lower CO levels.

(iv) Newsome (35) has reported that some speculation and research has been aimed at employing the CO-shift reaction for hydrogenation reactions by using water as the hydrogenation agent instead of hydrogen. It is believed that under certain conditions this reaction proceeds more readily than when hydrogen is used alone. The hydrogenation of coal by the CO shift reaction could bring about a new means of hydrocarbon production (36).

(v) Recently Ogawa (37) has described a process utilising the WGSR to remove impurities and adjust the ratio of high temperature reducing gases. The clean gas product is useful as the fuel for a gas turbine in power generation.

With the demand for hydrogen becoming greater as new methods of its purification are perfected, the WGSR is certain to continue as an important industrial process.

1.2.2 Towards an industrial process

In 1912 Bosch and Wild (38) discovered that a catalyst consisting of iron oxide and chromium oxide could be used to oxidise carbon monoxide to approximately 98% CO_2 at 400 - 500°C. This finding led to the incorporation of the catalytic WGSR into the coal-based ammonia process in 1915.

This meant that carbon dioxide could be removed more easily than carbon monoxide by dissolving it in water, and there was the added advantage that the yield of hydrogen, from the given amount of coke, was significantly increased.

The WGSR has now been found to be catalysed heterogeneously by many metals and metal oxides. Grenoble and Estadt (39) found the activity of alumina supported metal catalysts (at 300°C) to decrease in the following order:

Cu > Re > Co > Ni > Pt > Os > Au > Fe > Pd > Rh > Ir

Since the late 1960's only two classes of catalysts have been used on an industrial scale, namely the iron based "high temperature" shift catalysts, and the copper based "low temperature" shift catalysts. During the last few years there has been some effort to develop homogeneous catalyst systems.

The extent of the forward WGSR depends on the proportion of CO, CO_2 and steam in the feed gas, as well as the temperature, the catalyst and the gas velocity through the catalyst bed (30).

Figure 1.3 shows that the equilibrium constant, Kp, decreases as temperature increases. Thus, for increased hydrogen production and reduced carbon monoxide content, it is desirable to conduct the reaction at low temperatures.

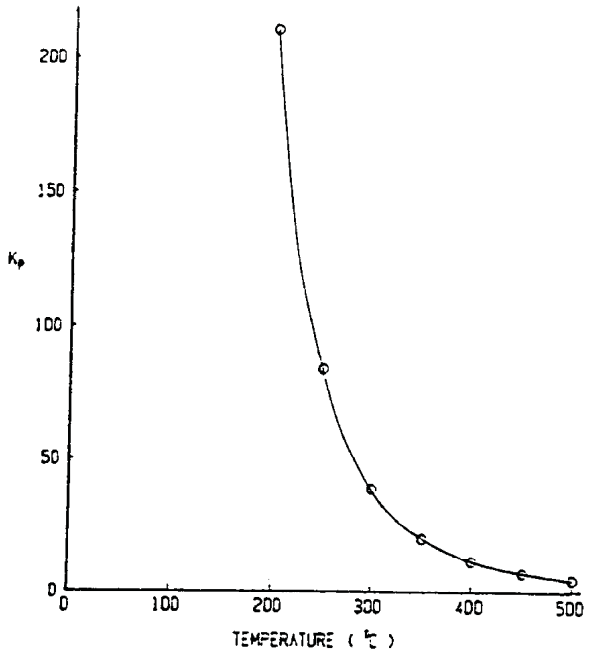

Figure 1.3 **Variation of equilibrium constant (Kp) for the water-gas shift reaction with temperature (1)**

Strelzoff (30) has reported that as the equilibrium degree of CO conversion approaches 100%, so the best steam economy is reached at low reaction temperatures. However, Newsome (35) has pointed out that it is often necessary to run the reaction at higher temperatures in order to achieve the necessary reaction rates. Thus a compromise between thermodynamics and kinetics is necessary. The amount of steam required for a single-stage reactor is large and uneconomical (30). Steam consumption in a two-stage CO conversion process is lower when the stages are operated with an equal change of heat content, than when operated with an equal degree of conversion. Consequently, the WGSR is often carried out in two or more stages (30). The use of a high temperature shift followed by a low temperature shift has improved the economics of ammonia production by reducing the amount of residual carbon oxide. With two stage systems, intermediate acid gas removal and desulphurisation tend to eliminate poisons to the second-stage catalysts (35). Industrial shift reactors are generally adiabatic with temperature increasing along the catalyst bed, since the reaction is slightly exothermic (35). If high purity hydrogen is not needed, only a single stage reactor is often required. An example of an adiabatic shift converter is given in Figure 1.4 below.

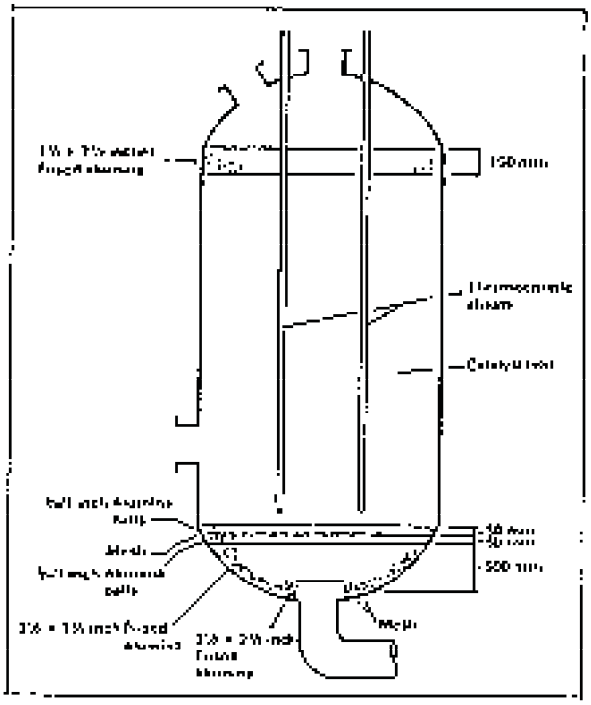

Figure 1.4 Adiabatic water-gas shift converter (1)

Figure 1.5 shows a typical commercial two-stage WGS operation.

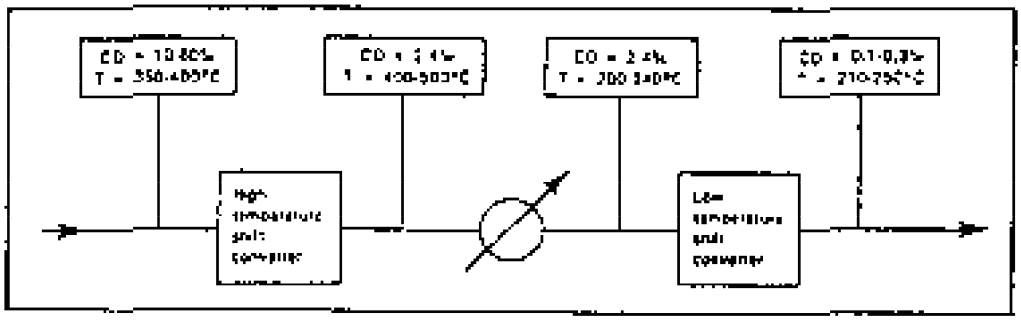

Figure 1.5 Typical CO conversion in two stages (49)

The carbon monoxide content of the effluent gas is lowered to 2.4 vol% at a temperature of 400 - 500°C, and to 0.1 - 0.3 vol% at temperatures of 200 to 250°C. (Figure 1.5).

Reaction pressure does not have any effect on the equilibrium of the WGSR since the number of moles does not change during the course of the reaction.

1.3 HIGH TEMPERATURE WATER-GAS SHIFT CATALYSTS

Ever since BASF claimed the use of an iron based WGS catalyst for the first commercial process in 1915, catalyst formulation improvements have been made (40). These improvements were necessary to provide the stability needed for more severe operating conditions of high pressures and temperatures encountered in modern plants. These catalysts were found to contain about 70 - 74% Fe_2O_3 and 8 - 10% Cr_2O_3 and other compounds (40) in their precursor stage. A typical example of the composition of a high temperature WGS catalyst is: 74.2% Fe_2O_3, 10.0% Cr_2O_3, 0.2% MgO, balance compounds (40). However, Markina et al. (41) later showed that the optimum chromium content appeared to be about 14% wt.

Before use, the high temperature water-gas shift catalysts

have to be activated by means of partial reduction of haematite, (Fe_2O_3) to magnetite (Fe_3O_4) (42). This step has to be carried out under controlled conditions as the formation of metallic Fe must be avoided. Metallic Fe catalyses both the highly exothermic methanation reaction (43), which can damage the catalyst, and the Boudouard reaction (1). The iron catalysts are usually prepared via precipitation. Structurally, the "ferrochrome" catalysts are solid solutions, where the lattice $\alpha - Fe_2O_3$ is substituted by Cr_2O_3. In the final reduced state of the catalyst, solid solutions of the spinel type $FeCr_2O_4$ have been reported (43).

1.3.1 Activity and Stability

Ferrochrome catalysts have very long lifetimes, and may last up to five years during "normal" operation (44). However, these catalysts do show deactivation with time-on-stream, and this problem has been the subject of many studies (45, 46, 47).

Bohlbro et al. (48) reported that iron shift catalysts should be used from about 320 to 450°C, whilst commercial operating temperatures of 400 to 500°C have been recommended (49). These relatively high operating ranges render the catalyst susceptible to sintering.

It is thought that Fe_3O_4 is the active component of the ferrochrome catalyst, whilst Cr_2O_3 acts as a stabilizer, to prevent deactivation due to high temperature sintering, and not as a catalyst promoter (35). Singh et al. (50) have supported this suggestion by showing that catalysts prepared without Cr_2O_3 lost catalytic activity much faster than Cr_2O_3 supported Fe_2O_3 catalysts. Newsome (35) however, has suggested that the Cr_2O_3 additive may increase the surface area of the catalyst, which results in an increased catalyst activity.

Despite the stabilizing influence of Cr_2O_3, some decline in catalytic activity with time is observed. Almed *et al.* (47) for example claimed that the deactivation was due to temperature and time-on-stream factors. Lloyd (1) reported that magnetite crystals are not completely stabilized by the chromium oxide. During the life of the catalyst, activity is thus lost as the surface area decreases due to thermal sintering, which is particularly apparent at temperatures in excess of 400°C. Recently Keiski and Salmi (47a) linked the decay of catalyst activity to a decrease of the surface area and to an increase of the mean pore size of the catalyst. Chinchen *et al.* (42) described two forms of catalyst decay - the initial fast decay to the stable steady-state activity, and the subsequent slow decay of that stable activity. They attributed the fast initial decay in activity to the rapid sintering of the unstabilized Fe_3O_4 crystallites formed in the reduction reaction which are in contact, or in near contact to the Cr_2O_3 crystallites. This process continues until all the Fe_3O_4 is separated by Cr_2O_3, after which slow decay may take place via "the appropriate transport of Fe_2O_3 or modification of the Cr_2O_3 crystallites".

Gonzalez *et al.* (43) discussed the influence of thermal pretreatment and reduction conditions on the activity of ferrochrome high temperature WGS catalysts. They concluded that process gas (a mixture consisting mainly of hydrogen, nitrogen, carbon monoxide, and carbon dioxide) and hydrogen gas are the best reducing agents to obtain a highly active WGS catalyst. Over-reduction was avoided as long as the temperatures were kept below 500°C. Their results showed that the presence of water vapour influenced the reduction of Fe_2O_3 to Fe_3O_4. When water vapour was added during hydrogen reduction, a less active catalyst resulted since a decrease of the specific surface area resulted from an increased pore size distribution. The equilibrium between Fe_2O_3 and Fe_3O_4 was proposed to be determined by the ratios of H_2O/H_2 and CO_2/CO (51). Lloyd (1) concluded a discussion on the reduction of the ferrochrome catalyst by

stating that steam must always be present during the reduction, and presented data to establish a thermodynamic minimum steam/hydrogen ratio necessary to prevent the reduction of Fe_3O_4 to FeO, and FeO to metallic Fe, at various temperatures. Bohlbro *et al.* (48) recommended a reduction temperature in the range of 250 to 400°C, and claimed that higher temperatures resulted in decreased catalytic activity due to sintering of the active phase.

Incentive exists however, to develop a catalytic material more active than iron, yet with similar advantages to the iron based catalysts.

Cobalt is known to be a highly active WGS catalyst (52) but unsupported, sinters rapidly, and produces significant by-product hydrocarbons. Hutchings *et al.* (53) and Gottschalk *et al.* (54) have recently reported that cobalt, modified with either manganese oxide or chromium oxide gives a catalyst with significantly improved activity when compared with current industrial formulations.

1.3.2 Poisoning and deactivation

Iron oxide based shift catalysts are not very susceptible to sulphur poisoning, thus, making them ideal choices for commercial plants operating on oil-based or coal-based feedstock (55). Small amounts of sulphur (i.e. < 50ppm) have a negligible effect on catalyst activity (48), but at sulphur levels higher than 100ppm activities decrease approximately in proportion to the square root of the sulphur concentration. As the total amount of sulphur in a coal based plant may be significant (56), the high-temperature shift catalyst may sulphide according to Equation 1.5.

$$Fe_3O_4 + 3H_2S + H_2 \rightarrow 3FeS + 4H_2O \qquad \Delta H = -75.0\,kJ.mol^{-1} \qquad (1.5)$$

The sulphided catalyst is reported (35) to have WGS activity, although its activity is much lower than that of a catalyst containing iron as magnetite (Fe_3O_4).

It has also been found that chlorine, in excess of 1ppm is an irreversible poison, whilst phosphorus and silicon compounds will cause deactivation by fouling (48). Arsenic compounds in small concentrations are also potential poisons (1).

1.4 LOW TEMPERATURE WATER-GAS SHIFT CATALYSTS

Copper based materials have been known to catalyse various reactions carried out on an industrial scale. These processes include carbon monoxide oxidation (57), methanol synthesis (58, 59) and nitrous oxide decomposition (60). Further, the ability of copper to catalyse the WGSR has long been known (1).

Catalysts prepared from mixed oxides of copper and zinc were tested commercially for the WGSR, in the late 1920's, but the problem of producing a catalyst with sufficiently long life to become an economical proposition was not resolved, due to the high level of poisons in the process streams at that time (1). The development of the "rectisol" process for synthesis gas purification and the advent of steam reforming in the nineteen sixties, meant that a much purer synthesis gas became available. Immediately, a renewed interest in low temperature copper based catalysts was stimulated. A standard copper oxide-zinc oxide (1:2 molar ratio) hydrogenation catalyst was used for the first low temperature shift process in the USA during 1963. It was soon realized that there were a large number of short-falls associated with the copper based catalyst. Non-optimum formulation, manufacturing procedures, sensitivity of the catalyst to operating conditions and residual traces of poisons were identified as reasons leading to an operating life as short as six months (1).

1.4.1 Activity and stability

Uncertainty still exists with regard to both the active copper phase of the low temperature WGS catalyst and the nature of the stabilizing role of additional catalyst components such as zinc oxide, alumina, and/or chromia. This section presents the findings of pertinent research studies aimed at resolving these questions.

In an attempt to stabilize activity, chromia (Cr_2O_3) was added to the copper oxide-zinc oxide formulation (35). However, it was found to be a poor support for the Cu catalysts and there was no significant improvement in catalyst operating life. Continued research has shown that alumina (Al_2O_3) together with zinc oxide (ZnO) could stabilize the copper crystallites against thermal sintering (61).

The nature of active sites on the surface of binary (Cu-Zn) and ternary (Cu-Zn-Al) systems used in low-temperature shift reactions is still a subject of discussion in the literature (62). Even today controversy still exists as to whether the reaction occurs primarily on metallic copper or on isolated Cu(I) cations dissolved in the ZnO lattice. Petrini *et al.* (63) used XPS to study the Cu-Zn and Cu-Zn-Al systems. In the unreduced copper-zinc system they found evidence for the existence of a non-equilibrium solid solution of Cu(II) in ZnO. The formation of a solid solution of Zn(II) in CuO was also suggested (64, 65). Petrini *et al.* (63) showed that if the copper-zinc system was not reduced prior to use, free Cu(I) ions are the active phase under reaction conditions. The role of aluminium (66) has been described as that of an anti-sintering agent with the ability to promote the dissolution of Cu(I) in ZnO (in co-precipitated catalysts). In an investigation on methanol synthesis by Cu-Zn-Al catalysts, Herman *et al.* (67) provided evidence for the formation of a solid solution of Cu(I) in ZnO. This solid solution was considered at the time to be active for the methanol

synthesis reaction.

Satterfield (68) had pointed out that it is difficult to establish the actual site on which the reaction occurs and that the existence of different oxidation states of copper can change the activity of copper based catalysts. Similar results were previously reported by Uchida and co-workers (69) who used XRD to show that metallic copper and ZnO were the major phases present after use of a CuO-ZnO catalyst.

A recent XPS investigation on the low temperature WGS Cu-Zn-Aℓ precipitated catalytic system was conducted by Stefanov *et al.* (62). On the basis of their results they concluded that on the surface of calcined catalysts, at least two types of copper species are formed: a crystalline CuO phase and Cu(II) ions dissolved substitutionally in a ZnO lattice. This observation is in agreement with a number of investigations on ternary Cu-Zn-Aℓ mixed oxides (64, 70, 71). In the case of a reduced catalyst, their findings support the conclusion that *metallic copper* is the active site, since catalytic activity was found to be proportional to the concentration of metallic copper on the surface. Campbell *et al.* (72) supported this theory by suggesting that the active phase consists of highly dispersed Cu metal supported on ZnO and alumina.

By use of an *in situ* XRD cell, Clausen *et al.* (73) were able to follow the phase transformations occurring in a co-precipitated ternary Cu-Zn-Aℓ WGS catalyst under activation and reaction conditions. Results showed that in the active catalysts, Cu metal is the only crystalline Cu phase observed, and the formation of this phase was seen to be closely related to the disappearance of CuO in the calcined catalyst. Many authors (1, 74, 75, 76) have shown that the copper surface area available for reaction is directly correlated to WGS activity. An example of this relationship was presented by Campbell (75) and is shown in Figure 1.6.

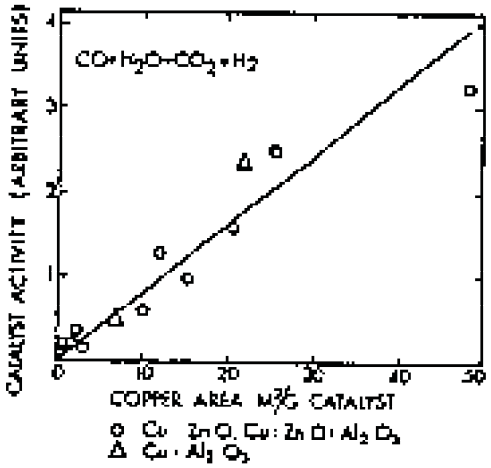

Figure 1.6 Relationship between copper area and water-gas shift activity (75)

From the curve it is apparent that support formulations do not *directly* influence catalytic activity. Thus, in order to achieve a high activity, it is necessary to have a high surface area of copper (76). Ray *et al.* (77) also found that for all catalysts tested, the copper surface area was linearly related to the catalyst activity. They also observed that by increasing the copper oxide percentage up to 46%, the copper metal area, as well as the low temperature shift activity increased (77).

Accordingly Ghorai *et al.* (74) found that the variation of copper metal area is due to the variation of ZnO area. As the ZnO area increased, so too did the dispersion of copper, which in turn led to a "generally proportional" increase in activity. Recently Chinchen *et al.* (78) have reported that the activity of Cu-ZnO-Al_2O_3 WGS catalysts are strongly dependent on catalyst parameters such as catalyst composition, size distribution of metal crystallites, nature of catalyst support, preparation parameters, impurities in the catalyst or reactants, but not copper metal area. In contrast to this result the relative activity in methanol synthesis has been shown to be a function of copper metal surface area. Uchida *et al.* (69) showed that an optimised copper oxide-zinc oxide

catalyst for the WGSR, had a Cu-Zn ratio of about 0.4. The authors found a proportionality between copper surface area and catalytic activity by ascribing increased activity at low Cu loading to finely divided, well dispersed copper crystals. At high Cu loadings, the surface concentration of copper obviously increased, but large copper crystals were observed, leading to a decline in specific activity.

The oxides of Cu, Zn, Al and Cr by themselves are not particularly stable, nor active catalysts for the WGSR, but mixtures of these oxides have been found to have excellent activity (35). Consequently, much research has been conducted to elucidate the effects of formulation and method of preparation on catalytic activity (68). To demonstrate this point, Campbell (75) has shown (Figure 1.7) the instability of a poorly formulated Cu-ZnO-Al_2O_3 catalyst as compared with the commercial ICI 52-1 catalyst, both with identical *bulk* chemical analyses.

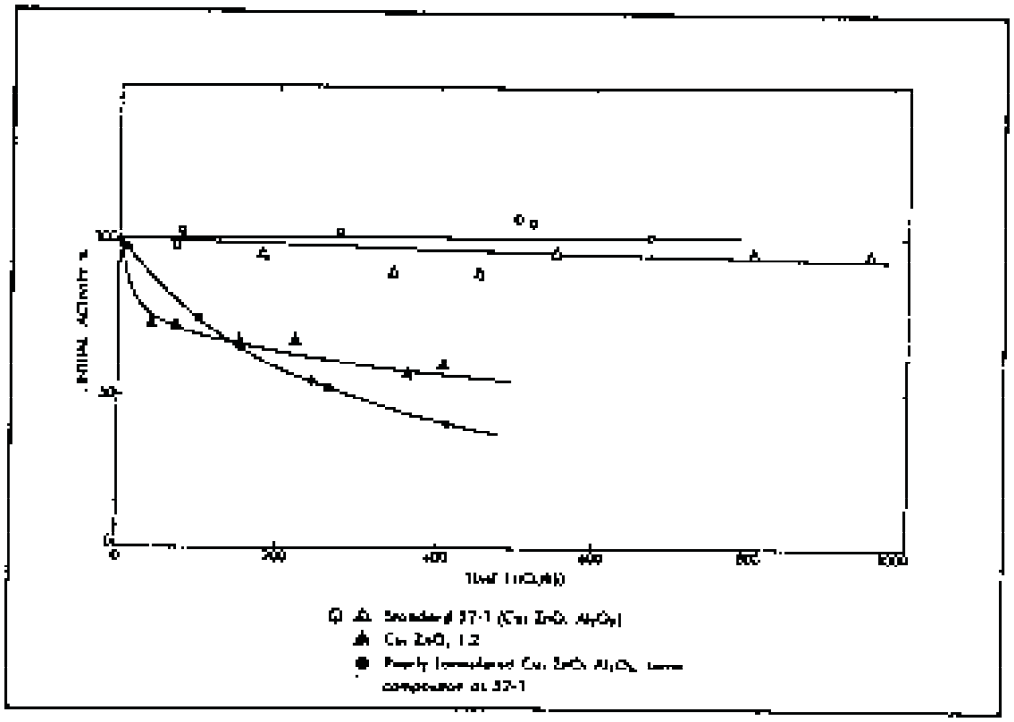

Figure 1.7 Thermal stability of different water-gas shift catalyst formulations (75)

The method of catalyst preparation and formulation

influences properties such as surface area and pore volume, which in turn affects the activity.

Uchida *et al.* (69) prepared a large number of catalysts using a variety of methods. These included kneading ZnO powder with copper hydroxide, and impregnation and coprecipitation to form CuO-ZnO catalysts. Only the kneaded catalysts were seen to be active. Lloyd *et al.* (79) established that the properties of particles precipitated under acid conditions were quite different with respect to both particle size and composition, from those formed when the solution was basic. Thus pH was shown to be a critical factor in the precipitation technique.

Copper-based catalysts are known to be sensitive to calcination temperature. Both Petrini (65) and Shchibrya (80) report that in certain preparations, high calcination temperatures cause a decrease in copper surface area. Reduction conditions are also crucial in establishing active and stable WGS catalysts (1). The hydrogen reduction reaction is highly exothermic (Equation 1.6) making it necessary to control the reaction carefully to prevent high catalyst surface temperatures.

$$CuO + H_2 \rightarrow Cu + H_2O \quad \Delta H = -80.8\,kJ.mol^{-1} \qquad (1.6)$$

Satterfield (68) has observed that reduction procedures are similar for a large variety of both laboratory and commercial scale catalysts. Reduction is performed in low concentrations of hydrogen. Steam may also be used but since it causes sintering of the copper crystallites, is usually avoided. The catalyst bed is heated at a controlled rate to prevent a temperature runaway, which will damage the catalyst. van Herwijnen and de Jong (81) observed the formation of α-brass in a Cu-ZnO WGS catalyst under reducing conditions. They noted that even low levels

of α-brass caused significant decreases in catalytic activity.

1.4.2 Promoters

"In heterogeneous catalysis by supported metals it has often been observed that the activity and the selectivity of the catalyst can be improved by the addition of a trace of another element called a promoter". (82).

Early efforts were made by Putanov *et al.* (83) to enhance the activity of a Cu-Zn-Cr catalyst by mechanically adding Mg, Al, Cu, Ti, and Mg plus Al separately, and Mg, Al, Cu and Ti together. No beneficial effects to either activity or temperature stability were noted. Amenomiya and Pleizer (84) investigated the WGSR on alkali-promoted alumina catalysts prepared by mixing alumina with various alkali metal salts. Results showed that the activity increased with the concentration of promoter until the surface was almost saturated by alkali metal ions. At the same concentration of metal ions, the efficiency of promotion was in the order:

$$Cs > K > Na > Li$$

Klier *et al.* (85) found that doping the surface of a binary Cu-ZnO catalyst with Cs, increased the forward WGS rate by 2.0 to 2.5 times when 0.1 to 0.8mol% Cs were added. Furthermore, it was predicted that alumina, chromia, and iron oxide based Cu-ZnO WGS catalysts may be expected to be promoted by alkali metals in the following descending order of efficiency:

$$Cs > Rb > K > Na > Li = \text{undoped catalyst}$$

In a recent patent (86) Klier has claimed that cesium, rubidium and potassium have a promotional affect on the activity of Cu-Zn-Cr, Cu-Zn-Al and Cu-Zn catalysts for the

WGSR.

1.4.3 Catalyst deactivation

The copper based low temperature shift catalysts are operated at much lower temperatures than the iron based high temperature shift catalysts. This arises from the low Hüttig temperature (68) for Cu (± 325°C) which reflects its relatively low melting point of 1063°C. Typical operating temperatures range from about 210 to 240°C (87). An operating temperature of higher than 280°C should be avoided in order to prevent catalyst deactivation by sintering (88). The tendency of a catalyst to sinter is largely dependent on its formulation. Young and Clark (61) reported that catalyst sintering results from high temperatures and poor catalyst formulations. In Figure 1.7 the authors showed that the loss of activity by sintering, is the result of a poorly formulated catalyst. In order to make a useful low temperature shift catalyst, the copper crystals must be both small, well dispersed and stable (87). Copper may be stabilized by both ZnO and alumina (61). The addition of a second component into the formulation such as ZnO, assists in the process of stabilization of copper crystals by acting as a spacer material. Alumina must be incorporated in the form of small crystals (± 40 Å), otherwise it will have a limited stabilizing effect.

Copper catalysts are very susceptible to poisoning, especially by sulphur and chlorine (87, 89, 89a). Newsome reported that copper-based catalysts are irreversibly poisoned by sulphur levels greater than 0.1 ppm (35). The copper sulphiding reaction (1) occurs as follows:-

$$2Cu + H_2S \rightarrow Cu_2S + H_2 \quad \Delta H = -59.4\,kJ.mol^{-1} \qquad - (1.7)$$

Young et al. (61) reported that the formation of cuprous

sulphide, at 230°C, requires an H_2S concentration of around 3 ppm, and as this value is usually much higher than is found in a commercial plant, poisoning by sulphur is probably due to a surface effect. Hawker (88) described a technique to minimize sulphur poisoning. As zinc sulphide can form from reaction of ZnO with H_2S in concentration of only $5x10^{-3}$ ppm, incorporation of a high surface area of *unbound* ZnO into the catalyst, would preferentially react with sulphur, according to Equation 1.8.

$$ZnO + H_2S \rightarrow ZnS + H_2O \quad \Delta H = -76.6\,kJ.mol^{-1} \qquad - (1.8)$$

Chlorine is regarded as the most serious poison for low temperature shift catalysts because it acts in concentrations as low as 0.1 ppm (44). It deactivates the catalyst by promoting the sintering process of both copper and zinc oxide crystallites causing a loss of surface area and hence activity (1). Thermodynamically, the reaction of chlorine with ZnO is more favourable than with Cu.

$$Cu + HCl \rightarrow CuCl + \tfrac{1}{2}H_2 \quad \Delta H = -43.5\,kJ.mol^{-1} \qquad - (1.9)$$

$$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O \quad \Delta H = -125.0\,kJ.mol^{-1} \qquad - (1.10)$$

Zinc chloride is known to melt under normal operating conditions. This has the effect of promoting sintering which leads to a decrease in copper surface area. Also, the sulphur tolerance of the catalyst is reduced as sulphur reacts preferentially with zinc (68).

Most modern plants make use of guard beds as a means of removing catalyst poison from the process gas stream. Extensive research (1) has shown that the use of a separate

guard vessel containing low-temperature shift catalyst is the best method of preventing all known poisons entering the main catalyst bed in high concentrations. As a result, several plants equipped with guard vessels have been able to operate the same catalyst load for a number of years.

1.5 SULPHUR TOLERANT WATER-GAS SHIFT CATALYSTS

Catalysts based on alumina supported Co-Mo and Ni-Mo are widely used as hydrogenation or hydrodesulphurisation catalysts (90). For these processes it is generally claimed that a mixture of Co_9S_8 and MoS_2 supported on γ-Al_2O_3 are the active phases of the Co-Mo-Al_2O_3 catalyst. Topsøe *et al.* (91) used *in situ* Mössbauer emission spectroscopy to provide evidence for the existence of a Co-Mo-S phase in catalysts with similar Co-Mo ratios. They proposed a possible reaction mechanism involving cobalt in the Co-Mo-S phase. Ni-Mo-S is believed to be an active phase of the Ni-Mo-Al_2O_3 formulation (90). However, due to the complexity of the sulphided catalyst, controversy still surrounds the precise structural features.

Formulations similar in composition to the hydrodesulphurisation catalysts have been shown to be active for the WGSR. Uniquely, these catalysts are only active in a sulphided form, which must be maintained by a *continuous* presence of ideally 10ppm to 3% H_2S in the feed stream (1). Typical unsulphided compositions may be 3.5% CoO and 12.5% MoO_3 (92) or 3.5% NiO and 10% MoO_3 (90), both supported on γ-Al_2O_3. Activation is generally carried out by pretreating the calcined precursor material with a gas mixture of H_2S and H_2 at an elevated temperature (93).

It has been shown that the addition of alkali to molybdenum-based catalysts promotes the WGSR. Potassium was found to be one of the best promoters giving the most active Co-Mo-Al_2O_3 WGS (92) catalyst. Kantschewa *et al.* (90) also showed that a potassium promoted Ni-Mo-Al_2O_3 catalyst gave enhanced activity for the WGSR.

Newsome (35) has used data to show that at 404°C and even at 300°C a Cs promoted Co-Mo-Al_2O_3 catalyst is superior in activity to both the Fe-based and the Cu-based catalyst systems. Lloyd *et al.* (1) have, however, pointed out that the unpromoted Co-Mo formulations are less active than the Cu-based catalyst operating with pure feed gas.

In recent years, the application of zeolite materials as supports for molybdenum has attracted much attention because of the unique and well defined parameters of the zeolites (94, 95). However, despite the scarcity of studies concerning molybdenum-loaded zeolites in the sulphided state, Laniecki *et al.* (95) have shown that $Mo(CO)_6$ loaded Y-zeolites which are subsequently sulphided display high activity in the WGSR. Although promising, these formulations show a tendency towards slow deactivation with time-on-stream. Sulphided Co-Mo-Al_2O_3 catalysts have in some cases shown no loss of activity or major deterioration of physical properties during life times of up to ten years (1).

Despite the potential versatility of Co-Ni-Mo-Al_2O_3 systems, drawbacks such as the fact that the level of sulphur compounds necessary to maintain catalytic activity are often higher than normally found in process gas, and the presence of sulphur being potentially harmful to other catalytic systems, have so far ensured few industrial applications.

1.6 HOMOGENEOUS WATER-GAS SHIFT CATALYSTS

"Impetus for the continuing exploration of homogeneous water-gas shift catalysts comes from the knowledge that homogeneous systems are in general, more active and more selective than their heterogeneous counterparts." (96).

Homogeneous catalysts have been considered as potential solutions to the high temperature necessary for iron based catalysts, and the sensitivity to poisoning of copper catalysts. The ability to simplify the technical process

from a strongly exothermic to a slightly endothermic reaction (97), has also added motivation to research in this area.

In 1953 Reppe *et al.* (98) were the first researchers to openly speculate on the possibility of using $Fe(CO)_5$ as a homogeneous WGS catalyst. Interest in the homogeneous catalysed WGSR was renewed in 1977 with the discovery of new catalyst systems. Cheng *et al.* (99) showed that a catalyst derived from $[Rh(CO)_2Cl]_2$, HCl and NaI in glacial acetic acid was an active homogeneous WGS catalyst, at a temperature as low as 80°C. Laine *et al.* (100) reported that aqueous alcoholic solutions of ruthenium carbonyl gave active catalysts. Kang *et al.* (101) demonstrated the activity of a number of Group 8 metals when dissolved in aqueous THF and made basic with trimethylamine. Since 1977, a number of reports have described the reactivity of a broad range of organometallic and co-ordination compounds for the WGSR. Cheng and Eisenberg (102) were the first to report a system based on platinum chloride-tin chloride. The use of numerous other catalysts based on metals such as platinum (103) and nickel (104) were soon reported. In general, metal carbonyl complexes have been found to exhibit WGS activity, and studies involving these complexes have subsequently dominated the literature. Laine and Wilson (96) have given a good review of the composition and mechanism of these complexes. Most homogeneous catalyst systems have been found to be active at temperatures of 100 - 200°C (105). For example, King *et al.* (106) showed that iron pentacarbonyl and other simple transition metal carbonyls were active within the temperature range 130 - 180°C, whilst Laine and Wilson (96) reported that an amine-promoted $Ru_3(CO)_{12}$ complex in an alkaline solvent showed outstanding WGS activity at a temperature of only 100°C.

As low temperature Cu-based WGS catalysts are not operated below 200°C, it is possible for homogeneous systems to take advantage of the favourable thermodynamic equilibrium conversion parameters at the lower temperatures.

Unfortunately, most homogeneous systems are susceptible to sulphur poisoning, and high costs of active transition metal components such as Ru and Rh, render these catalysts uneconomical on an industrial scale at this stage.

1.7 CATALYSIS BY ALLOYS

Research on alloys as potential catalysts received interest in the nineteen thirties after they were used to identify the role of the order-disorder phenomena (107). In the nineteen fifties alloys were widely used to determine the influence of the electronic structure on solids used for catalysis (107). This was a period of very rapid development in catalysis (107), and many ideas from theoretical and experimental physics were introduced into the field of catalysis in the form of "The Electronic Theory of Catalysis". This research was initiated by Dowden (108) and, measured by the response in the literature, has been ranked amongst the more important articles written on catalysis (109). As a direct consequence of these ideas, experimental studies on catalysis increased substantially. However, as more information became available, the basic principles on which "The Electronic Theory of Catalysis" was built, were disproved. These negative findings, coupled with the frequent use of inadequate techniques for alloy preparation and characterisation led to very controversial results which precipitated a crisis in alloy research. It was not until the early nineteen seventies that the following factors (108) signalled the beginning of a new period of very intensive work in this field:

(i) Considerable progress was achieved in the quantum theory of alloys and in the theory of predicting the surface composition of alloys. This helped to rationalise catalytic data and minimize inconsistent and contradictory results (109).

(ii) Fundamental investigations demonstrated that by alloying, dramatic changes in the selectivity of metal catalysts could be achieved, and very importantly: