(iii) A renewed industrial interest in the study of alloys as catalysts and more generally by bimetallic catalysts was noted. In particular, alloy catalysts derived from iron, cobalt or ruthenium and a rare earth metal for ammonia synthesis were discovered by Ozyagular (110) and Takeshita *et al.* (111). High specific activities were claimed and the active species were thought to be metal crystallites supported on the rare earth nitride. A wide range of compounds from first row transition metals and rare earth elements or actinides were found to be effective catalysts for the methanation of carbon monoxide (112, 113). Subsequent work by Ozyagcilar (114) suggested that methanol and ethanol could be produced from carbon dioxide and hydrogen at temperatures below 200°C using iron-titanium alloys. However, the most promising intermetallic catalysts for methanol synthesis are those derived from copper.

The first example of copper alloy-based catalysts dates back to 1927 when various brasses were activated by oxidation and subsequent reduction (115). Later work by Baglin *et al.* (116) showed that alloying copper with thorium-hafnium or zirconium resulted in active catalysts for the production of methanol from synthesis gas. The alloys themselves were not thought to be the actual catalysts, but rather *precursors* of the active catalyst which comprised of an oxidised Group 4 component. The copper-thorium system was studied in more detail (117) and the intermetallic compounds activated by exposure to air under ambient conditions were reported to exhibit activities greater than their co-precipitated analogues or the commercial catalyst, UCI C79-4. Owen *et al.* (118) showed that catalysts derived from intermetallic alloys of the lanthanide metals with copper were very active for methanol synthesis. Cerium-copper alloys in particular gave catalysts with activities comparable to the present commercial catalysts. An interesting variation to the co-precipitated copper-zinc oxide-alumina catalyst system was demonstrated by Marsden *et al.* (119) who leached a series

of copper-zinc-aluminium alloys of differing compositions in sodium hydroxide to give Raney copper catalysts containing zinc and aluminium. These catalysts were found to be both active and selective for methanol synthesis.

### 1.7.1 Raney catalysts

Raney catalysts are prepared by leaching extractable metal(s) from a composite alloy with aqueous sodium hydroxide or acid solutions to leave a higher surface area sponge metal with porous reaction product zones which act as catalysts (120).

Raney type catalysts were introduced in the nineteen twenties when Raney made a sponge nickel catalyst from a nickel-silicon alloy (121) which was observed to be pyrophoric if exposed to air. The catalyst was found to be very active for the hydrogenation of cotton seed oil. A short time later a sponge nickel catalyst was produced from a nickel-aluminium alloy (122) and formed the basis of the Raney technology as we know it today (123). Since their invention, Raney nickel catalysts have been of great practical importance in the production of substitute natural gas from coal (124) via the methanation reaction. It is also used as a reagent for the desulphurisation of organic sulphides, disulphides, sulphoxides and sulphones (125).

The first report of Raney copper based catalysts was by Fauconnau in 1937 (126). The catalysts were used for liquid phase selective hydrogenation reactions conducted in batch reactors using powdered catalysts (127). Recently, however, the catalysts have been shown to be active and selective for the vapour phase hydrogenolysis of esters (128) and ethyl formate (129) to produce alcohols, for the liquid-phase hydrolysis of nitrides to produce amides such as acrylamide (130) and for the vapour-phase dehydrogenation of methanol to produce methyl formate (131). A number of promoted Raney copper catalysts have been

investigated. For example, a cadmium promoted catalyst was used for the production of α, β-unsaturated carbonyl compounds (132). Copper promoted chromium alloy catalysts have been used to purify waste gas by removing NO (133) and for carbon monoxide oxidation (134). Nadirov and Savel'ev (135) investigated the preparation of 50 wt% Cu-Al-Fe alloys modified with Ca, In, Nb, No and W.

Reynolds and Mackenzie (136) described a process for the production of a partial acid extracted Raney copper-zinc catalyst for reactions such as the hydrogenation of furfural to furfural alcohol and the hydrogenation of acetone to isopropyl alcohol. Sultanov and Maslennikova (137) reported that Raney copper and Raney copper-zinc catalysts could catalyse the reduction of furfural to sylvan.

However, it was not until 1980 that Marsden et al. (119) demonstrated the activity of a zinc promoted Raney copper catalyst for methanol synthesis. Their research was promoted by a previous investigation by Wainwright and Anderson (138) who found that Raney copper had certain properties which are necessary for a methanol synthesis catalyst. These properties included a large pore size to eliminate pore diffusion problems, a sufficiently large surface area to permit high catalyst activity and the ability to selectively chemisorb carbon monoxide over hydrogen, making it an ideal mild hydrogenation catalyst.

Other Raney catalysts that have been prepared are promoted Raney nickel (139), Raney cobalt (140), Raney ruthenium (141) and Raney platinum (142). Recently, Imamura et al. (143) reported that high surface area, skeleton-like Raney nickel and cobalt could be prepared by leaching out rare earth components from rare earth - Ni or Co intermetallics, using solutions of 1,2-diiodoethane or 1,2-dibromoethane in methanol or tetrahydrofuran.

### 1.7.2 Raney copper catalysts for the water-gas shift reaction

During the initial evaluation of Raney copper as potential catalysts for methanol synthesis, Marsden *et al.* (119) suggested that to a certain extent, the system simultaneously promoted the WGSR. WGS activity was later reported by other researchers also testing Raney copper for methanol synthesis activity (144). In many cases, commercial low-temperature WGS and modern methanol synthesis catalysts contain the same oxides of copper, zinc and aluminium, albeit in different ratios. As recent developments (145) have revealed that the active composition of the Raney copper catalyst for methanol synthesis was $Cu-ZnO-A\ell_2O_3$, it appeared possible that this same catalyst system could be optimised for use in the WGSR.

## 1.8 MECHANISMS OF THE WATER-GAS SHIFT REACTION

The continued importance of the WGSR as a source of high purity hydrogen, and in the development of catalysis theory (146), has encouraged many researchers to improve process conditions and catalytic performance by elucidating the mechanism of the reaction. However, despite many theoretical and mechanistic studies (35, 96, 147, 148) there remains dispute over the exact mechanism operating in the WGSR. The merits and shortfalls of various aspects of the controversy will be discussed in brief.

### 1.8.1 The Redox mechanism

One of the earliest, and probably the first, mechanisms proposed for the WGSR was that made by Temkin *et al.* (149). In this mechanism the CO shift conversion involved an oxygen transfer reaction in which an oxygen atom is effectively transferred from a water molecule to a carbon monoxide molecule, the catalyst acting as the oxygen transfer agent. This type of transfer is known as the

regenerative or redox (reduction-oxidation) mechanism. The reaction is generally split into two half reactions in which the active surface sites S undergo successive oxidation and reduction cycles by water and carbon monoxide respectively, to form the corresponding hydrogen and carbon dioxide products of the WGSR.

**Reduction:**

$$H_2O(g) + S_{Red} \rightleftharpoons S_{Ox} + H_2 \qquad - (1.11)$$

**Oxidation:**

$$CO(g) + S_{Ox} \rightleftharpoons S_{Red} + CO_2(g) \qquad - (1.12)$$

This mechanism is characterised by two features (39): Firstly both reactions must be thermodynamically possible and secondly, the two reactions must, to a certain extent, proceed independently of each other.

Support for the regenerative mechanism came from Boreskov *et al.* (150) who showed that the required reduction of the active phase of the high temperature shift catalyst, $Fe_3O_4$, and the subsequent oxidation of the reduced species, was possible under normal conditions. They concluded that the Reactions 1.13 and 1.14 can proceed independently and at approximate equal rates, which correspond to the rate of the WGSR.

$$H_2O(g) + 3FeO \rightleftharpoons Fe_3O_4 + H_2(g) \qquad - (1.13)$$

$$CO(g) + Fe_3O_4 \rightleftharpoons 3FeO + CO_2(g) \qquad - (1.14)$$

Strong disagreement with regard to the involvement of the redox mechanism over Cu-based low temperature shift

catalysts is evident in the literature. van Herwijnen et al. (151) rejected the mechanism on the basis that neither CuO nor $Cu_2O$ could be formed from copper and steam under the reaction conditions. However, Chinchen et al. (152) demonstrated the possibility of a regenerative mechanism for the copper catalysed WGSR. More recently using $^{14}C$-isotopic labelling in an endeavour to elucidate the methanol synthesis mechanism, Chinchen and co-workers (153) showed the occurrence of two reactions needed for both the forward and reverse WGSR:

$$H_2O(g) + S \rightarrow O_{ads} + H_2(g) \qquad - (1.15)$$

$$CO(g) + O_{ads} \rightarrow S + CO_2(g) \qquad - (1.16)$$

where: S is a vacant surface site

In the light of some of these results, Lloyd (1) concluded that van Herwijnen's dismissal of the regenerative mechanism was invalid for adsorbed oxygen formation, because there is no equilibrium limitation to Reaction 1.15 for oxygen coverage of a half monolayer or less.

### 1.8.2 The Associative mechanism

Yur'eva et al. (154) proposed a mechanism on a copper chromite catalyst, where the reaction takes place through an activated complex or central intermediate of a prior unknown stoichiometry of reactants CO and $H_2O$:

$$\begin{aligned} CO(g) &\rightleftharpoons CO(ads) \\ H_2O(g) &\rightleftharpoons H_2O(ads) \\ CO(ads) + H_2O(ads) &\rightleftharpoons [\ ] \rightleftharpoons CO_2(ads) + H_2(ads) \\ CO_2(ads) &\rightleftharpoons CO_2(g) \\ H_2(ads) &\rightleftharpoons H_2(g) \end{aligned} \qquad - (1.17)$$

where: [ ] denotes the central intermediate of unknown concentration.

It is of relevance to mention studies conducted to determine the identity of this central intermediate.

### 1.8.3 Reagent adsorption onto the surface

Grenoble *et al.* (39) considered that it would be reasonable to expect a relationship between the activity of the metal catalyst and the strength of interaction of CO with the metal. Using heats of adsorption data as reported by Vannice *et al.* (155), they were able to draw a "volcano shaped" correlation between the heat of adsorption of CO, and metal activity at 300°C, as shown in Figure 1.8.

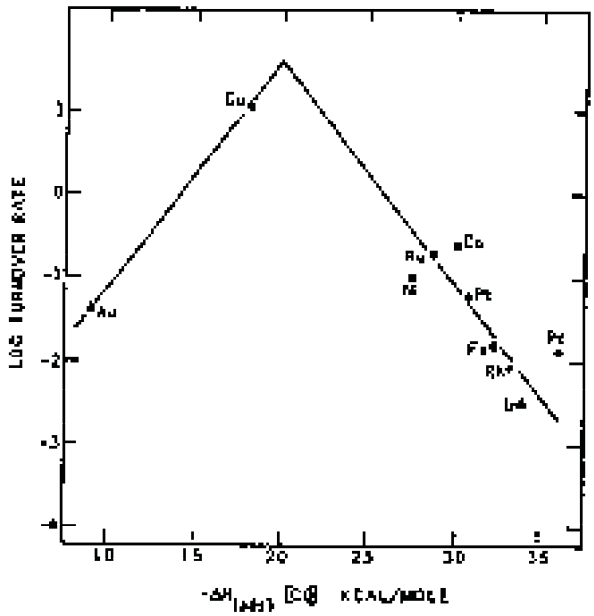



**Figure 1.8** Volcano-shaped relationship between metal turnover number at 300°C and heat of adsorption of carbon monoxide (155)

It was noted that the nature of the support may slightly alter the position of the metal. From the curve it is apparent that there should be an optimum strength of interaction between CO and the catalytic surface. It is argued that if this interaction is weak (as in the case of Au) the activity will be low because the surface concentration of CO will be low. However, if the interaction between CO and the metal is very strong (as in the case of Pd or Ir) then the CO-metal intermediate

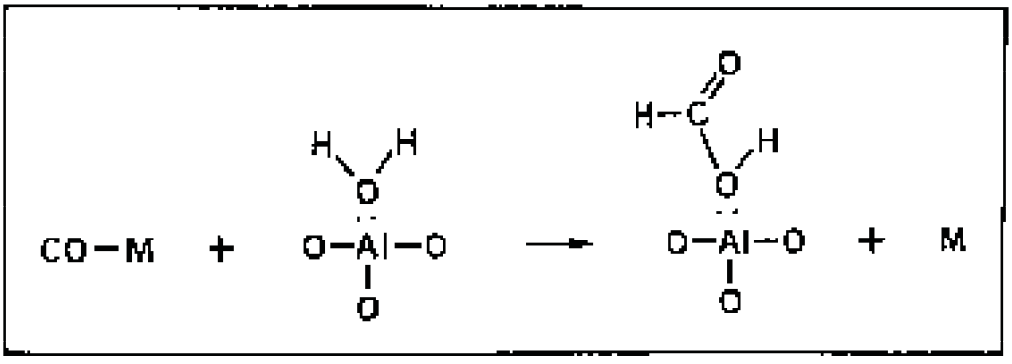
becomes so stable that subsequent reaction from a central intermediate slows down. For the WGSR the copper-carbon monoxide heat of adsorption at 300°C is about 18.3K.cal/mol (76.7KJ/mol) and may help to account for the metal's high activity at low temperatures. Based on their studies of support effects, Grenoble *et al.* (39) showed that $SiO_2$ and $Al_2O_3$ supports provided the principal sites for water activation. It was suggested that in the case of $Al_2O_3$, water could be activated via dissociative and non-dissociative adsorption.

In conclusion, they considered the WGSR to occur bifunctionally with the active metals activating CO, and the support activating $H_2O$.

### 1.8.4 The formation of the central intermediate

As early as 1920 Armstrong and Hilditch (156) suggested that formic acid was the central intermediate in the WGSR over a Cu-ZnO catalyst. They based their findings on the fact that copper became active for the reaction at a temperature corresponding to the onset of catalytic activity for the decomposition of formic acid.

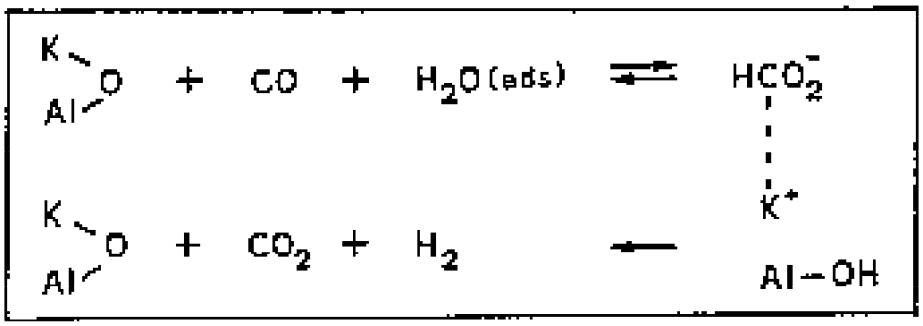
Grenoble *et al.* (39) proposed the following mechanism for the formation of a formic acid intermediate, over an alumina supported metal catalyst.




- (1.18)

where: M represents the metal surface

Formic acid must "shift" from the support to the active metal component of the catalyst, before decomposition to the products $H_2$ and $CO_2$ can take place. According to this proposal, the rate of reaction is governed by the accessibility of vacant surface sites on the metal, made available by the desorption of CO from the metal. Van Herwijnen *et al.* (151) also reported the existence of a central intermediate over a $Cu-SiO_2$ catalyst having the same stoichiometry as formic acid. They also suggested that copper was an active catalyst for the decomposition of formic acid. Amenomiya and Pleitzer (84) were able to identify the presence of formate ions on promoted alumina catalysts using infra-red spectroscopy, and proposed the reaction sequence shown below for the WGSR.




- (1.19)

Backing up their proposal, they also found that the reaction rate was proportional to the surface concentration of the formate ions.

Shido *et al.* examined the mechanism of the WGSR over MgO (157) and ZnO (158) using Fourier transform infra-red spectroscopy. In the case of MgO, they observed that hydroxyl groups reacted with CO to produce unidentate, bidentate and bridge type formate intermediates, whilst bidentate and bridge type formates occurred on ZnO. Very recently, Horvath and Siskin (159) used high pressure NMR spectroscopy to provide direct evidence for the formation of a formate ion intermediate on alkali metal catalysts present in coal. On the other hand Colbourn *et al.* (160) presented data to show that CO and $H_2O$ do not readily

generate formate-type adsorbates on unsupported and unpromoted copper catalysts. Instead, they considered the reaction to be occurring by the sequential oxidation and reduction of a small fraction of the Cu surface to produce the WGS products. Salmi and Hakkarainen (161) have reported the simultaneous operation of the regenerative and associative mechanism on copper based catalysts.

Shopov and Andreev (146) also demonstrated the *combined* mechanism over a cobalt oxide promoted iron-chromium catalyst, and extended it for all cases when the WGSR is carried out with the participation of transition metal ions. The mechanism assumes the participation of lattice oxygen and a change in the oxidation state of iron in accordance with the redox mechanism. Formation of the formate complex is associated with decomposition of surface hydroxide followed by the liberation of $CO_2$.

Hutchings *et al.* (162) investigated the reaction pathway over cobalt chromium oxide, cobalt manganese oxide and copper manganese oxide catalysts. Using kinetic and model reagent studies, they proposed mechanisms involving the formation of surface formate intermediates on both cobalt and copper containing catalyst systems. This work is discussed in more detail in Chapter 7.

### 1.8.5 Other mechanisms

Oki and co-workers used the stoichiometric number concept to conduct what Newsome (35) describes as "fundamental and exhaustive" mechanistic studies performed on the iron-chromium high temperature shift catalyst. The stoichiometric number concept is regarded as one of the most powerful techniques available for the determination of the rate-controlling step or steps for solid-catalysed gaseous reactions (35). Thermodynamic calculations, the assignment of stoichiometric numbers and the prediction of a rate-determining step were used to propose plausible elementary steps which constitute the overall reaction.

The value of the stoichiometric number procedure implied the number of times an elementary step had to be repeated in order to obtain the overall stoichiometric equation for the reaction. Using this concept, Oki concluded that the "Tempkin redox mechanism" (149) for the iron based catalysts was incompatible with his experimental data. He proposed the following two mechanisms:

**Mechanism 1:**

$$\begin{aligned} CO_{(g)} &\rightleftharpoons CO_{(a)} \\ H_2O_{(g)} &\rightleftharpoons 2H_{(a)} + O_{(a)} \\ CO_{(a)} + O_{(a)} &\rightleftharpoons CO_{2(a)} \\ CO_{2(a)} &\rightleftharpoons CO_{2(g)} \\ 2H_{(a)} &\rightleftharpoons H_{2(g)} \end{aligned} \qquad - (1.20)$$

**Mechanism 2:**

$$\begin{aligned} CO_{(g)} &\rightleftharpoons CO_{(a)} \\ H_2O_{(g)} &\rightleftharpoons OH_{(a)} + H_{(a)} \\ CO_{(a)} + OH_{(a)} &\rightleftharpoons COOH_{(a)} \\ COOH_{(a)} &\rightleftharpoons CO_{2(a)} + H_{(a)} \\ CO_{2(a)} &\rightleftharpoons CO_{2(g)} \\ 2H_{(a)} &\rightleftharpoons H_{2(g)} \end{aligned} \qquad - (1.21)$$

where: (a) represents species adsorbed on the active site.

Mechanism 1 modifies Temkin's redox mechanism (149) in that surface adsorbed oxygen (rather than lattice oxygen) is involved in the reaction pathway. Mechanism 2 is significant because Oki demonstrated that the idea of a central formate intermediate is consistent with predictions based on the stoichiometric number technique.

The mechanism of the homogeneous catalysed WGSR over simple transition metal carbonyls of general formula $M_x(CO)_y$ was considered by Ford (148). He proposed that the nucleophilic activation of CO by reaction with $H_2O$ or OH was a key process in the formation of a formate intermediate bonded to the catalytic surface via the carbon atom and *not* via the acidic oxygen as is often predicted.

Some researchers have reported that the formation of a formate intermediate does not necessarily ensure automatic decomposition to products. For example, Elliott *et al.* (163) showed that together with a formate intermediate, the presence of carbonate and hydroxide anions were necessary to complete the reaction. Also, Shido and Isasawa (158) noted that over a ZnO catalyst, water not only acted as a reactant to form a bidentate formate intermediate, but was also instrumental in activating its deactivation to hydrogen and unidentate carbonate, which desorbed as $CO_2$.

### 1.8.6 Summary of proposed mechanisms

Evidence has been presented in this review to clearly show that although controversy still surrounds the exact mechanism operative over WGS catalysts, two main mechanistic routes can be categorised. Firstly, the regenerative redox mechanism appears to be operational over iron based catalysts. Secondly, the discovery of a central formate intermediate especially on Cu based catalysts, provides evidence for an associative type of mechanism. Although overwhelming evidence must convince one that a formate species may play a pivotal role in the mechanism over copper containing catalysts, and even metal carbonyl homogeneous systems, it would be unwise to ignore significant experimental results showing the feasibility of having a modified redox mechanism in operation over similar catalysts.

Steps required to complete the reaction cycle appear to involve straight forward adsorption and desorption.

It is suggested that the mechanism of the WGSR is catalyst sensitive, and the simultaneous occurrence of both the redox and associative mechanisms, or variations thereof, may be possible for certain catalytic formulations and operational conditions.

## 1.9 THE KINETICS OF THE WATER-GAS SHIFT REACTION

A large number of kinetic expressions have been derived for both the iron based high temperature shift catalysts (164) and to a lesser extent the copper-based low temperature shift catalyst (151). As the kinetic rate expressions of catalytic processes are dependent on a number of factors such as catalyst preparation techniques, reagent gas impurities and operating conditions (35), it is not surprising that many researchers have obtained different mathematical rate expressions for similar WGS catalytic systems. A summary of some of the important expressions follows in this section.

For the high temperature Fe-Cr-O catalytic systems, Moe (165) presented an expression based on an equilibrium-limited, first-order dependence for all reactants in both the forward and reverse reactions. The expression has found wide application in industry, and has the form:

$$R_{WGS} = k[P_{H_2O} \cdot P_{CO} - P_{H_2} \cdot P_{CO_2} - k_p] \qquad - (1.22)$$

where: $R_{WGS}$ = WGS reaction rate
$k$ = rate constant
$k_p$ = equilibrium constant

Temkin *et al.* (166) derived a somewhat more complex *power expression* for the same catalytic system:

$$R_{WGS} = k\, P_{H_2O} \cdot P_{CO} - \frac{(K_{eq}^{-1} \cdot P_{CO_2} \cdot P_{H_2})}{A \cdot P_{H_2O} + P_{CO_2}} \qquad - (1.23)$$

where: $R_{WGS}$ = WGS reaction rate
$k$ = rate constant
$K_{eq}$ = equilibrium constant
$A$ = constant
$P_i$ = partial pressure of component i

Podolski and Kim (167) used statistical techniques to discriminate between rival models. Also, using their own and previously published data, they concluded that only the power law and a Langmiur-Hinshelwood model could best describe their results. However, Boudart (168) considered the form of the Langmiur Hinshelwood rate expression to be based largely on an overcorrelation of available data, but admitted that the model reasonably predicted the expected general order of adsorption strength of the species in the WGSR to be $CO > H_2O > CO_2 > H_2$. However, in a quest to move away from complex mathematical models, Chinchen *et al.* (42) successfully reported a modified rate equation based on a Langmiur-Hinshelwood model to describe the WGSR over an Fe-Cr-O catalyst. They managed to reduce the rate equation to the following expression:

$$R_{WGS} = \frac{KP_2}{(1+BP)^2} \qquad - (1.24)$$

where: $R_{WGS}$ = WGS reaction rate
K and B = constants
P = total operating pressure

Recent work by Hutchings *et al.* (162) showed that at low $P_{CO}$ the WGSR was also observed to obey Langmiur-Hinshelwood type behaviour over Co-MnO and Co-$Cr_2O_4$ high temperature shift catalysts.

For the copper-based low temperature WGS catalysts, the power expression derived by Temkin *et al.* (166) was also found to accurately describe the kinetics of the reaction over a Cu-ZnO catalyst (55). In addition, Lloyd *et al.* (1) have reported the pore-diffusion limited version of the Langmiur-Hinshelwood equation to be consistent with plant data and semi-technical scale results:

$$R_{WGS} = \frac{k[CO]\,[H_2O]^{1/2}(1-[CO_2]\,[H_2]-K[CO]\,[H_2O]}{P^{1/2}(1+C_1[CO]+C_2[H_2O]+\ldots)} \quad (1.25)$$

where: $R_{WGS}$ = WGS reaction rate
$k$ = rate constant
$C_1$ and $C_2$ = equilibrium constants

These findings might be difficult to explain if the iron catalysed WGSR is considered to proceed *only* via a regenerative redox mechanism and the copper catalysed reaction *only* via a formate type intermediate.

The kinetics over a sulphur tolerant Co-Mo oxide catalyst system was shown by Hou *et al.* (169) to be linked to the kinetics of the iron and copper based systems in terms of a Langmiur-Hinshelwood surface reaction.

The kinetic expression obtained by these researchers is shown in Equation 1.26.

$$R_{WGS} = \frac{k K_1 K_2 [CO] [H_2]}{(1 + K_1 [H_2O] + K_2 [CO])^2} \qquad (1.26)$$

where: $R_{WGS}$ = WGS reaction rate
$k$ = rate constant
$K_1$ and $K_2$ = equilibrium constants for $H_2O$ and CO adsorption respectively

Kinetic considerations of the WGSR have provided us with a means of analysing various reaction mechanisms and improving our understanding of the reaction system as a whole. Both the regenerative redox and the associative-intermediate type mechanisms have been shown by many authors to conform to various observed rate laws, substantiating their validity and importance in the WGSR.

## 1.10 AIMS OF THE THESIS

Whilst the WGSR is a very important catalytic and industrial process, catalyst development and operation is still not fully understood. At present there exists a need to develop a WGS catalyst that has high activity, structural stability and, sulphur poisoning insensitivity (55). Clearly, it follows that the achievement of a low concentration of carbon monoxide at the exit of the LT shift converter, as a result of a highly active, well stabilized catalyst, would be of considerable financial benefit to the plant operator. Lloyd and Twigg (79) stated that a perfect low temperature shift catalyst would operate continuously at the equilibrium outlet carbon monoxide content corresponding to the temperature determined by the inlet gas temperature and carbon monoxide content. Although in practise this is rarely possible, much research has given us criteria necessary to strive for this goal.

It may be concluded from this chapter that it is widely accepted that the activity of low temperature shift catalysts is to a greater or lesser extent dependent on the surface area of the copper metal content and thus, in general, the greater the copper area, the higher the activity. Therefore a catalyst containing 100% copper, in a sufficiently finely divided form should be the most active material for this duty (61). However, at low operating temperatures, small crystals grow by sintering, rapidly decreasing the copper surface area and hence activity. Thus a well formulated catalyst should be an optimised balance of dispersed, finely divided copper, with sufficient support incorporated to stabilize the copper crystals. The development of such a catalyst forms the basis of this thesis.

Initial investigations involved the identification, characterisation and preliminary optimisation of novel Raney copper catalysts for the WGSR (**Chapter 4 and Chapter 5**). The objective was to produce highly active and stable Raney catalysts by the caustic and acidic extraction of Cu-Zn-Al alloys. The continuous, sponge-like Raney copper rim suggested that a minimal amount of inactive zinc support may be required to provide catalyst stability. It was considered that the high copper surface area might be maintained by the unusual morphology of the catalyst system. Thus the effects, if any, of the zinc stabilizing promoter on WGS activity and long term catalyst stability was examined by the selective incorporation of the metal into the Raney catalyst, either during the extraction process from zincate added to the leach solution, or by ion implantation. Specific copper surface areas were determined using a nitrous oxide pulse chemisorption technique described in Chapter 3.

Statistically designed experiments (Chapter 6) were employed to assist in the formulation of an optimal Raney copper catalyst by simultaneously considering the large number of variables which may have contributed towards

catalytic activity and stability. This approach allowed for the identification of significant variable interactions on the desired responses which were important for accurately calculating the optimum catalyst composition. Raney copper catalyst performance was evaluated as a function of time-on-stream, operating temperature, GHSV and $CO:H_2O$ ratio.

Model reagent co-feed experiments were carried out in order to elucidate a possible WGS mechanism over the optimised Raney copper catalyst (Chapter 7). Also, the effects of the addition of alkali metal promoters on the WGS activity of the Raney copper catalysts were considered in Chapter 7. Alkali metals are well known to promote the activity of 'conventional' co-precipitated $Cu-ZnO-Al_2O_3$ WGS catalysts.

Earlier research work (55) showed that the high WGS activity and stability of chromium and manganese oxide supported cobalt catalysts could be sustained in gas containing up to at least 240ppm sulphur. This result suggested that these novel high temperature WGS catalysts could also be operated in coal-based plants which contain sulphur impurities in their feed gases. Chapter 8 expands on this research by analysing the performance of these catalysts in higher concentrations of sulphur.

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