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Water–gas shift reaction: finding the mechanistic boundary

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Abstract

The mechanism of the water–gas shift reaction is discussed for both copper/zinc oxide/alumina and iron oxide/chromium oxide catalysts. The associative and regenerative mechanisms are presented and the evidence concerning each mechanism is critically reviewed. It is concluded that for the low temperature shift reaction over copper/zinc oxide/alumina catalysts considerable evidence exists to support both mechanisms and it is possible that either could proceed on the catalyst surface. For the iron oxide/chromium oxide catalysed high temperature shift reaction the experimental evidence supports a regenerative mechanism.

1. Introduction

Prior to the use of the water–gas shift (WGS) reaction, the production of hydrogen was achieved from the addition of metallic iron to strong acids or from the electrolysis of water [1]. Both processes were expensive to operate and neither could meet the growing demand for pure hydrogen. Consequently research was carried out to find alternative methods of hydrogen production.

The first report of the WGS reaction was published in 1888 [2] and described how the passage of carbon monoxide and water vapour over red-hot refractory material produced carbon dioxide and hydrogen (Eq. 1).

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \Delta H = -41.1\ \text{kJ/mol} \qquad (1)$$

Among others, researchers at BASF, [3,4] as part of the ammonia synthesis development programme, screened a series of metallic oxides for their ability to accelerate the attainment of the water–gas shift equilibrium. Investigations attempting to determine the most suitable catalytic material were extremely time consuming, taking many hundreds of hours, as possible catalytic materials were individually examined. The iron oxide/chromium oxide type catalyst discovered by BASF still forms the basis for today's high temperature WGS catalyst [5–10].

In accordance with Le Chateliers principle [11], when pressure is applied to a system at equilibrium the system will adjust to minimise this increase. For the WGS reaction, where the total number of moles of reactants and products in the gas-phase at any one instant is not determined by the relative position of the forward and reverse reactions, the equilibrium constant is independent of pressure.

In 1909 Haber [12] examined the value of the equilibrium constant (K) and the dependence of K upon temperature. He noted (Table 1) that with increasing temperature the forward reaction, favouring hydrogen production, became less dom-

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Table 1
Variation of the equilibrium constant with temperature, ref. [12]

Temperature (°C)	227	327	400	500	600
K, equil. constant	0.006	0.030	0.050	0.160	0.320

Note the equilibrium constant as described by Haber, $K = ([CO]\cdot[H_2O]/[CO_2]\cdot[H_2])$, is the inverse of what would normally be used today.

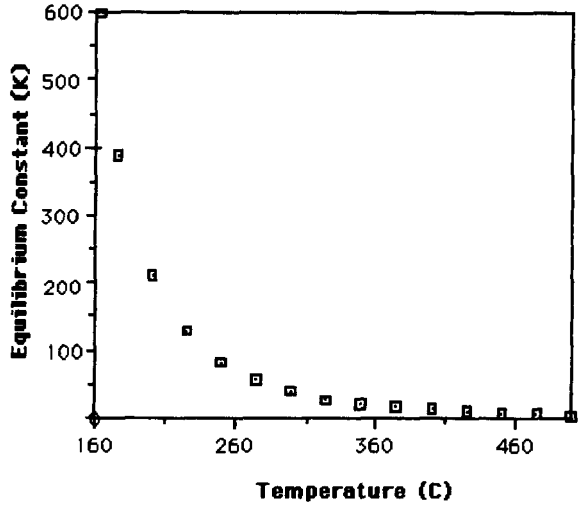


Fig. 1. Variation of equilibrium constant (K_p) for the water–gas shift reaction with temperature. Taken from ref. [13].

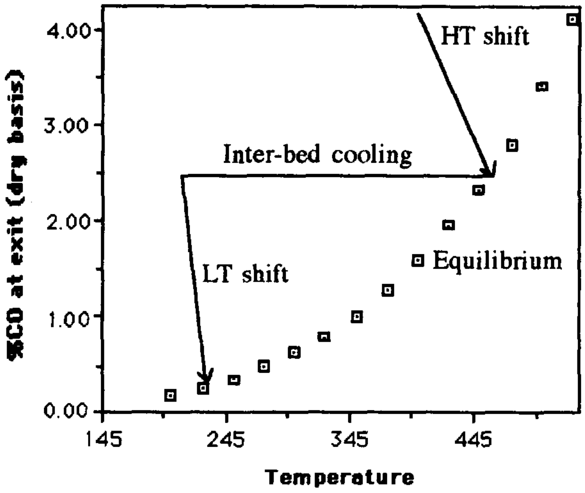


Fig. 2. Typical variations of carbon monoxide levels in high temperature and low temperature shift catalyst beds. Taken from ref. [13].

inant; higher carbon monoxide conversions are favoured by lower temperatures.

Being moderately exothermic ($\Delta H = -41.1$ kJ/mol) the equilibrium constant, $K_p = (p_{H_2}\cdot p_{CO_2}) / (p_{H_2O}\cdot p_{CO})$, for the WGS reaction decreases with increasing temperature (Fig. 1) [2,12]. Commercially, a balance is struck between temperature dependent factors: equilibrium position, and the rate of reaction.

As an integral part of ammonia synthesis [14] and hydrogen production [15], the water–gas shift reaction continues to maintain a position of importance in the modern chemical industry. At first sight it is a simple bimolecular process, converting a mixture of carbon monoxide and steam into carbon dioxide and hydrogen.

In modern ammonia synthesis plants the WGS reaction is a two-stage, high and low temperature, process. Prior to the 1960s the configuration of shift reactors was quite different to that of today and used coupled multiple beds of iron oxide/chromium oxide catalyst which, with the aid of interbed cooling, achieved exit carbon monoxide levels of ca. 1% (Fig. 2) [13]. The remaining carbon monoxide was then completely removed by absorption into a copper liquor (copper ammonium formate) [16] followed by methanation using a nickel catalyst. Methanation consumed a portion of the valuable hydrogen product but was necessary for the removal of the traces of carbon monoxide. It is essential that these trace levels of carbon oxides are removed as they are well known reversible poisons [17] for the ammonia synthesis catalyst.

Early in the 1960s the series of iron oxide/chromium oxide catalyst beds were replaced by two separate catalyst beds one containing an iron oxide/chromium oxide catalyst and the other a copper-containing catalyst [13]. This configuration achieved exit carbon monoxide levels that were much lower than previously possible, typically ca. 0.1%. This format is still most commonly used today.

1.1. Water–gas shift reaction over copper-based catalysts

The low-temperature shift catalyst functions 100–200°C below the temperature of the high temperature system and is operated between 210–

240°C. The catalysts used in this process are copper/zinc oxide/alumina materials capable of converting virtually all the CO remaining in the product of the high temperature shift reaction (typically 3%).

The composition and method of preparation of the copper-based precursors is crucial in determining the final properties of the catalyst. The typical composition of a commercial copper/zinc oxide/alumina catalyst may be: 33% CuO, 34% ZnO and 33% Al_2O_3.

Although the ability of copper/zinc oxides to catalyse the water–gas shift reaction was recognized in the late 1920's routine usage in commercial plants did not occur until 1963. Until that time the susceptibility of the catalyst to rapid thermal sintering and poisoning limited the effective life of the catalyst to approximately six months. To improve catalyst lifetime alumina was introduced into the catalyst formulation. Alumina reduced the likelihood of sintering, enhanced the strength of the catalyst pellet and minimized the pellet shrinkage that occurs during reduction.

The copper/zinc oxide/alumina catalyst is highly sensitive to sulphur poisoning and could only be used industrially in a routine manner when effective feedstock desulphurisation, capable of bringing process gas sulphur levels down to 10–100 ppb, was possible. Copper/zinc oxide/alumina catalysts can presently be expected to have lifetimes of ca. 2–4 years.

1.2. Water–gas shift reaction over iron oxide-based catalysts

The high temperature WGS reaction is typically carried out industrially at ca. 310–450°C, 25–35 bar (2.5–3.5 MPa) using an iron oxide catalyst structurally promoted with chromium oxide [18]. In the absence of chromium oxide the effective lifetime of the catalyst is severely restricted because of rapid thermal sintering. The extended activity of the iron oxide/chromium oxide catalyst results from the presence of Cr_2O_3 which prevents the sintering of neighbouring magnetite (Fe_3O_4) crystallites. During the initial stages of catalyst use, rapid catalyst deactivation occurs, but after ca. 1500 h [19] catalyst activity stabilises. The catalysts typically operate in plants for 2–5 years before relatively slow thermal sintering leads to a sufficiently large decrease in activity to warrant catalyst replacement.

The exact proportion of iron oxide and chromium oxide varies with the manufacturer as does the composition of other minor components. However, the simplest catalyst is usually composed of ca. 92% iron oxide ca. 8% chromium oxide. Compared to copper-based catalysts, the activity of the iron oxide system is moderate and the concentration of carbon monoxide exiting commercial HT shift reactors is ca. 3% which is close to equilibrium for the exit temperature of ca. 450°C.

In contrast to the copper-based catalysts the iron oxide/chromium oxide catalysts are not particularly sensitive to sulphur poisoning and can operate in the fully sulphided form albeit at reduced activity.

2. Studies of the water–gas shift reaction: setting the scene

To successfully understand the mechanism of any catalysed reaction it is necessary to: (a) gain an understanding of the structure of both the catalyst surface and bulk and, (b) use as many complementary investigative techniques as possible. Commonly the methods employed to observe the elemental processes occurring within an overall reaction scheme interfere with the nature of the processes being observed or proceed under conditions very different to those of the catalysed reaction. Data produced may, therefore, misrepresent the true nature of the reaction and make it difficult to identify the reaction pathways that are significant from those that are not. By collecting data from a diverse range of techniques the likelihood of proposing accurate mechanisms can be improved.

Research conducted on the WGS reaction has been very extensive, utilising almost every available technique: in situ infrared spectroscopy [20,21] (IR), X-ray photoelectron spectroscopy [22] (XPS), X-ray diffraction [23] (XRD), model reagent studies [20], radioactive labelling [24], chemical trapping [20] and temperature-programmed desorption [25] (TPD).

Uniform standard catalysts have, however, not been used. Compounding the problem further is the array of bed temperatures, reactor pressures and gas compositions selected by numerous researchers. Catalyst performance can be dramatically affected by very small changes in the catalyst composition, indeed, such is the sensitivity of the water–gas shift catalyst that catalysts of similar chemical composition, prepared by different manufacturing routes, often behave differently under identical reaction conditions. It has been noted [26,27] that twenty different kinetic equations have been proposed for the WGS reaction and that one of the most common topics of controversy among authors [5,27–30] is the effect of pressure on the WGS reaction rate. The range of pressures and temperatures over which data has been gathered over the last century is considerable. A typical UHV adsorption may, for instance, occur at 1×10^{-7} atm and −183°C, while typical laboratory scale reactors may operate at 30 atm and 400°C.

Until techniques are available, that can permit surface science phenomena and microreactor studies to be acquired in situ, where the experimental conditions mirror the operation of the commercial process, the question of whether data are relevant will persist.

It is our intention in this paper to overview the information gathered regarding the water–gas shift reaction and attempt to place the often contradictory pieces of evidence in perspective.

3. Catalyst structure of copper and iron oxide-based WGS reaction catalysts copper-based catalysts

3.1. Copper-based catalysts

The copper/zinc oxide/alumina catalyst precursor requires reduction before use. The copper in the precursor is present as an oxide supported on zinc oxide/alumina. The reduction of the copper-based shift catalyst is normally carried out using a dilute hydrogen stream ([H_2] ca. 3%, balance N_2). Care must be taken during the reduction of copper/zinc oxide/alumina catalysts since although 'over-reduction' is not a cause for concern, the exothermicity of the reduction (Eq. 2) of CuO to Cu metal and the relatively high copper loading in the catalysts can lead to excessive catalyst temperatures. This can result in severe thermal sintering of the active species (Cu metal). To avoid this the temperature and hydrogen concentration are carefully controlled during the reduction step.

Table 2
Composition of a $Cu/ZnO/Al_2O_3$ catalysts, fresh and used, ref. [37]

Concentration (atom %)				
Catalyst	Cu	Zn	O	Zn/Cu
Fresh	9.84	17.41	72.73	1.76
Used	7.13	23.54	69.31	3.29

$$CuO + H_2 \rightarrow Cu + H_2O$$
$$\Delta H = -80.8\ \text{kJ/mol} \qquad (2)$$

Despite copper shift catalysts being well characterised, uncertainties remain about the precise nature of the active site. Some researchers [31–35] consider that a synergy exists between copper and zinc whilst others consider zinc oxide acts only as a support for the dispersed copper [36]. The XPS work of Salmi and Hakkarainen [37] using a commercial $Cu/ZnO/Al_2O_3$ catalyst determined the surface Zn:Cu ratio to be 1.76 whilst the bulk composition has a ratio equal to 1.67. The used catalyst was found to be enriched with zinc at the surface (Table 2) perhaps due to the disproportionate thermal sintering of the supported copper metal particles under reaction conditions, with respect to zinc oxide.

The oxidation state of zinc in these studies remained unchanged and was +2. Also detected to be present upon the catalyst surface simultaneously with Cu^0 were Cu^I [36] and Cu^{II} species.

Measurement of the relative amounts of Cu^0 and Cu^I was hindered by the copper catalyst being exposed to air in the transfer from the reactor to the spectrometer. As the authors acknowledge, finely divided metallic copper would be expected to be readily oxidised to Cu^I and Cu^{II} under atmospheric conditions, and hence this casts some doubt on the validity of the oxidation states of copper detected in this work. Herman et al. [35] proposed that Cu^I is the catalytically active species in copper/zinc oxide/alumina catalysts and that a synergy exists between copper and the zinc oxide support. Near infrared visible absorption spectra have shown that Cu^I is dissolved in ZnO. The formation of a solid solution readily occurs since Cu^I is isoelectronic with Zn^{II} and furthermore Cu^I, in common with Zn^{II}, exhibits tetrahedral co-ordination in many inorganic compounds.

Campbell and Daube [38] investigated a clean Cu(111) single crystal using combined microreactor studies with AES, XPS and LEED to study the WGS reaction. The copper surface was found to be completely metallic post-reaction, even after being heavily pre-oxidised. Garbassi and Petrini [36] and Yurieva et al. [39] also confirm the presence of metallic copper in a reduced catalyst using XPS. Chinchen et al. [40] also suggest that metallic copper was the active species for both the water–gas shift reaction and methanol synthesis but that under reaction conditions, relevant to both processes, the copper surface has approximately one third monolayer coverage of adsorbed oxygen.

3.2. Iron oxide-based catalysts

The iron oxide water–gas shift catalyst, in common with the copper-based catalyst, requires careful reduction before use. Catalyst pretreatment involves the partial reduction of haematite (Fe_2O_3) to magnetite (Fe_3O_4) using process gas mixtures of hydrogen, nitrogen, carbon monoxide, carbon dioxide and water vapour [13,41,42] (Eqs. 3 and 4).

$$3Fe_2O_3 + H_2 \rightarrow 2Fe_3O_4 + H_2O \quad \Delta H = -16.3\ \text{kJ/mol} \tag{3}$$

$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2 \quad \Delta H = +24.8\ \text{kJ/mol} \tag{4}$$

During and subsequent to the reduction process it is important to avoid over-reduction of the magnetite active material to lower oxides, carbides, or metallic iron species. Metallic iron species are active catalysts for methanation and the Fischer–Tropsch processes (Eq. 5). The processes are particularly undesirable since: (a) hydrogen is consumed and (b) the exothermic nature of these reactions is such that hot spots can develop in the reactor. Furthermore even a relatively small degree of ‘over-reduction’ can cause weakening and physical damage to catalyst pellets. In industrial reactors,this could lead to pellet degradation which could result in a significant pressure drop across the reactor bed being incurred.

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad \Delta H = -206.2\ \text{kJ/mol} \tag{5}$$

To ensure reliable operation of the iron oxide/chromium oxide catalyst an empirical formula has been developed, based on plant experience, which indicates the gas composition required to avoid over-reduction of the catalyst (either during reduction or subsequent operation). The formula for the reduction factor (R) (Eq. 6) is as follows: [42].

$$R = [\{(CO) + (H_2)\}/\{(CO_2) + (H_2O)\}] \tag{6}$$

Plants operating with $R < 1.2$ can be expected to experience little difficulty associated with catalyst ‘over-reduction’. Plants operating with high reduction factors, $R > 1.6$, can be expected to suffer from severe ‘over-reduction’ related difficulties. It is important to note that a reactor feed with a relatively low concentration of steam can cause, even during short plant upsets, the catalyst to become ‘over-reduced’. The reduction factor (Eq. 6) therefore helps to predict the degree of reduc-

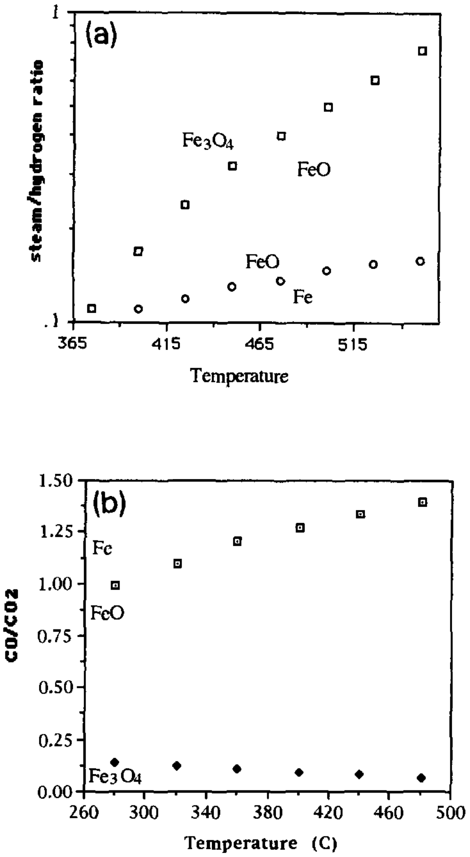


Fig. 3. (a) Minimum ratio of steam-to-hydrogen for reduction of iron oxide shift catalysts [13]. (b) Minimum ratio of carbon monoxide-to-carbon dioxide for reduction of iron oxide shift catalysts.

tion that could be expected for a catalyst for a given process gas composition.

The effects of the steam/hydrogen and CO/CO_2 ratios in relation to the phase changes between iron metal and the various iron illustrated below (Figs. 3a and 3b).

Few reliable thermodynamic data are available that allow conditions for carbide formation to be predicted accurately, it is probable however that under plant conditions carbides (e.g.: Fe_2C) may be produced during catalyst over-reduction [43].

For an iron oxide/chromium oxide catalyst that has undergone the required reduction from haematite to magnetite, the active catalyst comprises a crystalline inverse spinel structure [41,44] in which the octahedral lattice sites are occupied equally by Fe^{2+} and Fe^{3+} ions. Topsøe and Boudart [23] have demonstrated, using Mössbauer spectroscopy [45–47], that Fe^{2+} and Fe^{3+} ions are present in defined quantities. Above 119 K, fast electronic exchange (hopping) in the octahedral sites is detectable and an average value of $Fe^{2.5+}$is observed. The ratio of Fe^{3+}/Fe^{2+} is reported as being close to 2 as would be expected for stoichiometric magnetite. X-ray photoelectron spectroscopy [48–50] has also identified the coexistence of both di- and tri-valent iron on the catalyst surface.

3.3. Overview of the WGS catalyst structure

The evidence currently available concerning the structure of the copper-based water–gas shift catalysts appears to be as variable as the techniques used to study the catalyst. The copper-based water–gas shift catalyst, and the model materials used to represent it, are highly susceptible to oxidation when exposed to air and many of the investigations have required the removal of the catalyst from one apparatus into another.

However based on the evidence of the literature it appears the active species in the copper-based water–gas shift catalyst are metallic copper islands supported on a zinc oxide/alumina support.

The structure of the iron oxide water–gas shift catalyst is less controversial because the reduced catalyst can be removed from micro-reactor for surface characterization without suffering the problems associated with reduced copper/zinc oxide/alumina. Correct stabilization of the catalyst [51] allows direct exposure to air and prevents magnetite oxidation.

4. Mechanism of the water–gas shift reaction: associative or regenerative?

After more than one hundred years of research on the water–gas shift reaction the progress made in clarifying the mechanism(s) by which the reaction occurs has been limited. Two contrasting mechanistic pathways have been proposed based on either: (a) an associative mechanism or (b) a regenerative mechanism.

The associative mechanism was first proposed by Armstrong and Hilditch [52] in 1920 using data gathered from a copper chromite catalyst. This mechanistic proposal involves the adsorption of CO and H_2O onto a catalyst surface to form an intermediate of unspecified structure that subsequently decomposes into the reaction products (Eq. 7).

$$CO+H_2O \rightarrow (\text{intermediate}) \rightarrow CO_2+H_2 \qquad (7)$$

The regenerative mechanism was originally described by Armstrong and Hilditch [52]. This mechanistic proposal involves the reactants effecting a cyclic change in the oxidation state of a catalytic material. The regenerative mechanism can be most simply visualized as the lysis of water on the catalyst to produce hydrogen and subsequent oxidation of the catalyst surface. The catalyst surface is then reduced by carbon monoxide to produce carbon dioxide and the catalyst surface subsequently returns to its original, pre-reaction, state (Eq. 8).

$$\left.\begin{array}{l} H_2O+\text{Red} \rightarrow H_2+\text{Ox} \\ CO+\text{Ox} \rightarrow CO_2+\text{Red} \end{array}\right\} \qquad (8)$$

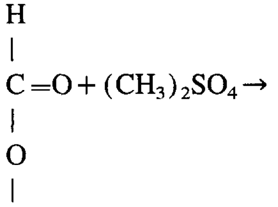
4.1. WGS reaction mechanism over copper-based catalyst. The associative mechanism

In 1969 Yurieva [53] set a general trend by describing an associative mechanism for copper chromite as a simple Langmuir–Hinshelwood process. (Eq. 9).

$$\left.\begin{array}{l} CO_{(g)} \rightarrow CO_{(ads)} \\ H_2O_{(g)} \rightarrow H_2O_{(ads)} \\ CO_{(ads)}+H_2O_{(ads)} \rightarrow [\,*\,] \\ \quad \rightarrow CO_{2(ads)}+H_{2(ads)} \\ CO_{2(ads)} \rightarrow CO_{2(g)} \\ H_{2(ads)} \rightarrow H_{2(g)} \end{array}\right\} \qquad (9)$$

Following the proposal of Armstrong and Hilditch [52] that a 'formic acid decomposition' mechanism occurs with copper catalysts, many researchers have attempted to confirm that this is indeed the case. Evidence for the existence of the formate species upon copper and other catalysts is extensive. Indeed, as early as 1920, Armstrong and Hilditch used ammonia as a chemical probe molecule to produce ammonium formate which was detected by the silver nitrate test.

Diagne et al. [20] produced methyl formate using dimethyl sulphate as the reagent for trapping formates, (Eq. 10).



$$\begin{array}{l} H \\ | \\ C{=}O+(CH_3)_2SO_4 \rightarrow \\ | \\ O \\ | \end{array}$$

$$HCOOCH_3+H(CH_3)SO_4 \qquad (10)$$

Trapping experiments of this kind are very sensitive and concentrations of 1×10^{11} ions cm^{-2} can be detected, one order of magnitude less than is possible with infrared spectroscopy.

Using dimethyl sulphate Deluzarche et al. [54], in 1985, studying a $PdO/MgO–SiO_2$ catalyst used for methanol synthesis quote Sneeden [55]; "One of the big problems in the field of the reduction of carbon monoxide concerns the identification and the evolution of the active adsorbed species under reaction conditions".

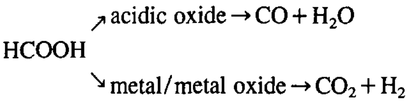
Most evidence for the surface adsorbed formate intermediate has been gathered from research using infrared spectroscopy [21,31,32,56,57], identifying the possible reaction intermediate species. Infrared spectroscopy is a technique well placed for observing the characteristic bond vibrations of formate species. Surface bound, as well as free formate species, are distinguishable and this technique has been widely used to investigate the associative type mechanism. As highlighted by Deluzarche et al. [54] however, caution must be used when drawing conclusions solely from infrared data since the formate observed may be spectator species and not an active intermediate. The presence of formate species upon a catalyst may result from a reaction between the products of the water–gas shift reaction, carbon dioxide and hydrogen.

However, using a combination of chemical trapping experiments, infrared spectroscopy, kinetic calculations, and reactor data it has been demonstrated that for catalysts operating under conditions capable of sustaining the WGS reaction there is firm evidence for the presence of formate species.

Amenomiya and Pleizer [57], in 1982, investigated the possibility of an associative mechanism on alkali-promoted alumina and unpromoted alumina and proposed that a formate type of intermediate existed on these catalysts. When a $CO + H_2O$ reaction feed was passed over a potassium-promoted catalyst heated between 200–300°C, four infrared bands, assignable to a potassium formate species, were observed. At higher temperatures formate species were less dominant on the surface and carbonate ions observed. The behaviour of the formate species was said to mirror the composition, pressure and temperature of the reactant gases and appeared to be in equilibrium with the conditions of reaction. Amenomiya and Pleizer [57] indicate that the reaction rate is proportional to the surface concentration of formate, suggesting that the $CO + H_2O$ reaction takes place via the formate ions on the surface. Promoted samples were considered to have greater catalytic activity because the electron donating properties of the catalyst caused surface formate to be less stable.

In 1980 van Herwijnen and de Jong [58] indicated that the coverage of formate species upon a $Cu/ZnO/Al_2O_3$ catalyst was approximately 75% under process gas at one bar. Two possible rate determining steps were proposed for the rate of the water–gas shift reaction: (i) the reaction between carbon monoxide and water, and (ii) the decomposition of the adsorbed complex. Since the calculated coverage of the intermediate was high it was suggested that step (ii) was more likely to be rate determining. An increase in pressure would be expected to increase the rate if the reaction between carbon monoxide and water vapour was rate determining. Experiments carried out at elevated pressures, however, highlighted that the reaction rate is pressure independent up to 6 bar.

For the water–gas shift reaction to proceed via a formate intermediate, formate decomposition must be possible. A commonly used experiment in testing this possibility involves the adsorption of formic acid directly onto the catalyst surface. Using the formic acid species to represent the formate group generated from the interaction between CO and H_2O formate decomposition can be monitored. This technique has been used by several researchers, Mailhe and Sabatier [72], Krylov [59] and Trillo et al. [60], who have been able to show that decomposition of surface adsorbed formic acid does give the reaction products expected from the water–gas shift reaction. The dehydration reaction is catalysed by acidic oxides (Al_2O_3), whereas the dehydrogenation reaction is more readily catalysed by metals and basic metal oxides (Eq. 11).



$$\mathrm{HCOOH}\begin{array}{l}\nearrow \text{acidic oxide} \rightarrow CO + H_2O \\ \searrow \text{metal/metal oxide} \rightarrow CO_2 + H_2\end{array} \qquad (11)$$

In contrast, the work of Noto et al. [21] using a variety of alumina catalysts provides evidence against a formate species being the route by which the water–gas shift reaction proceeds. Combined isotopic labelling and infrared spectroscopy studies were performed in which deuterated formic acid, DCOOD, was introduced onto a catalyst pretreated with unlabelled formic acid. The deuterated formic acid did not displace the pre-dosed HCOOH, but although not adsorbed on the catalyst surface, DCOOD was observed to decompose to appropriate WGS reaction products. Throughout the DCOOD decomposition the concentration of the unlabelled surface formate remained almost constant.

Grenoble et al. [61], considering that formic acid decomposition alone could not describe the mechanism of the WGS reaction suggested decomposition of the intermediate involves trans-

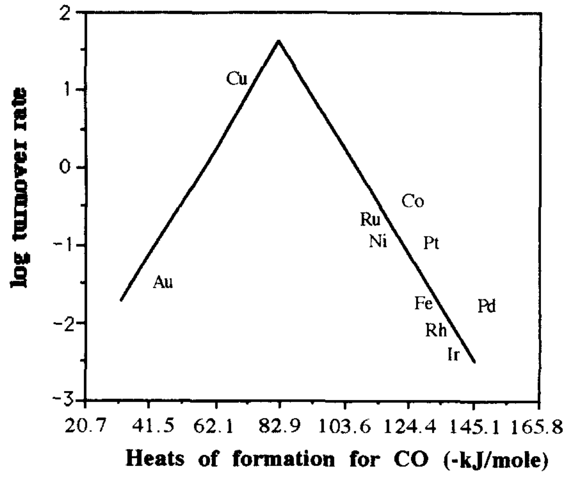


Fig. 4. Volcano-shaped relationship between metal turnover number at 300°C and heat of adsorption of carbon monoxide. Taken from ref. [61].

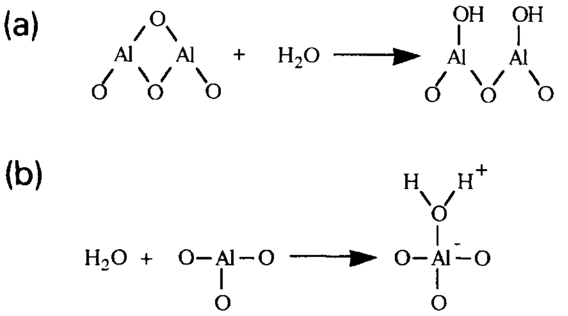


Fig. 5. (a) Dissociative type of adsorption of water. (b) Associative type of adsorption.

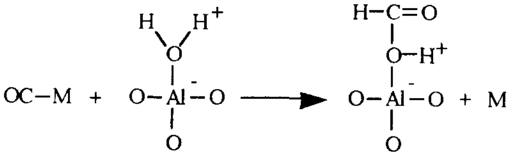


Fig. 6. Mechanism on Cu/Al2O3 by Grenoble et al.

fer from the support to a metal centre. An activity series for metallic species supported upon γ-alumina was constructed based on the heat of formation of the bulk metal CO compounds:

Cu > Re > Co > Ni > Pt > Os > Au

> Fe > Pd > Rh > Ir

Grenoble et al. [61] suggested that the heat of adsorption of CO on a bulk metal (assumed to be the same as that for alumina supported metals) determines it's overall catalytic reactivity for the WGS reaction. For a metal such as Au for which the heat of adsorption of CO is low it is predicted that CO coverage will also be low and correspondingly so will the formate coverage and catalytic activity. Similarly for high heats of adsorption of CO, e.g. Pd or Ir, it is proposed that the metal–CO interaction will be strong and the coverage of formate species will be low due to the inability of $CO_{(ads)}$ to insert into $OH_{(ads)}$. A strong substrate–metal interaction will also retard the rate of reaction as CO blocks metal sites required for formic acid decomposition. A heat of adsorption of ca. 84 kJ/mol has been predicted for maximum activity based on a plot of heat of adsorption against turnover rate (Fig. 4). Copper has the heat of adsorption (ca. 67 kJ/mol) closest to this value and this does indeed correlate well by being the most active in the series. Iron has a significantly higher heat of adsorption, ca. 136 kJ/mol. However, it should be noted that the heats of adsorption quoted here are those tabulated by Vannice [62,63] for the metallic species and not, as would be most relevant for the magnetite catalyst, for metallic oxides.

Campbell and co-workers [64] suggest that the strength of CO adsorption may not be the only reason why these metals are not as effective as copper in WGS. Instead it is proposed that upon oxide catalysts the surface hydroxyl species are more stable than on the metal and that the conversion of $OH_{(a)}$ to $O_{(a)}$ may be rate determining.

The mechanism proposed by Grenoble et al. [61] for metals supported on alumina is shown in Fig. 5. For the dissociative adsorption of water the scheme (Fig. 5a) is envisaged. However, the Lewis acid sites of the alumina support could facilitate the adsorption of H_2O and this possibility is shown in (Fig. 5b).

In this proposal adsorption it is suggested that adsorption of CO and H_2O both occur at the metal centre and that the adsorbed CO then inserts into one of the OH bonds to form the intermediates as illustrated (Fig. 6). For decomposition of the formate to occur, Grenoble et al. [61] envisaged a shift of the whole intermediate species from the support back to the metal centre. In stating that a shift from the support to the metal is necessary, the observation that water–gas shift catalyst activity is not related solely to the formic acid decomposition rate is accounted for. The controlling factor illustrated by this proposed mechanism is therefore the fraction of unoccupied metal sites where decomposition can occur. If bi-functionality of this type exists then a relationship between the number of metal–support interfaces and the catalyst activity could be expected: the greater the metal dispersion, the greater the activity of the catalyst.

Single crystal studies by Campbell and Daube [38] using Cu(111) doped with zinc from an aqueous solution showed an enhancement or change in activity compared to the clean Cu(111) for the WGS reaction at 350°C. Wachs and Madix [65], Sexton [66], and Iglesia and Boudart [98] have all studied formate decomposition kinetics upon a variety of copper systems: Cu(110), Cu(100), Cu powder and Cu/SiO_2. In each system the formate decomposition behaviour was found to be almost identical and hence it is concluded that formate decomposition kinetics appear to be structure insensitive.

4.2. Regenerative mechanism

In the last decade the proposal that the water–gas shift reaction proceeds by the redox mechanism over copper-based catalysts has become increasingly popular [20,52,48,67–70]. For the redox mechanism to be valid then cyclic reduction–oxidation reactions must be permissible on the catalyst surface. Whilst it is well documented [37,71,73–77] that the surface of a copper-based catalyst can be effectively reduced using carbon monoxide and hydrogen, doubts remain as to whether copper can be oxidised by water rapidly enough to account for the observed WGS reaction rate.

For the oxidation of a copper-based shift catalyst to proceed with process gas the dissociation of water must occur. The thermodynamics of this reaction are sufficiently endothermic to indicate that this is unlikely for a bulk material (Eq. 12). Van Herwijnen and de Jong [58] in discussing the half reactions necessary for copper redox note that although the reduction of copper is known to proceed smoothly at 200°C it is not until 800°C [78] that oxides of copper, Cu_2O or CuO, can be formed in the absence of oxygen although surface oxides could possibly form.

$$2Cu + H_2O \rightarrow Cu_2O + H_2 \quad \Delta H = +20.65\ \mathrm{kJ/mol} \tag{12}$$

The heats of chemisorption of small molecules, including oxygen, onto a variety of polycrystalline and single crystal transition metal surfaces have been studied [62] and it has been demonstrated that the heats of chemisorption are highest for the early transition elements, decreasing to the lowest values for Cu, Ag and Au. Chinchen et al. [40,70] have calculated, using the relationship between the relative partial pressures of carbon monoxide and carbon dioxide and adsorbed oxygen coverage, that the free energy of formation for adsorbed oxygen on copper at 340°C is −240 kJ/mol. Chinchen et al. [70] compare this to the free energy of formation of cuprous oxide at the same temperature and conclude that adsorbed oxygen on copper is some 110 kJ/mol more stable than cuprous oxide. Van Herwijnen and de Jong [58] quote the standard free energy of formation for the formation of cuprous oxide as being +80 kJ/mol.

Much debate surrounds the ability of copper materials to dissociatively adsorb water. Campbell and Daube [38], investigating the WGS reaction on clean Cu(111) single crystals, which display activity and kinetics comparable to Cu/ZnO, demonstrated in a series of adsorption experiments at 230–380°C involving water, that any attempt to oxidise or deposit surface oxygen was unsuccessful. Subsequently, however, Campbell and co-workers [79,80] comparing Cu(111) and Cs-promoted Cu(110) surfaces provide strong evidence for adsorbed oxygen upon copper using (AES). Clean Cu(110) displayed the ability to dissociate water and a small build up in the amount of adsorbed oxygen upon the surface was observed despite the probability of dissociation being very small. Caesium-promoted Cu(110) exhibited accelerated water dissociation. Spencer et al. [70,81] and Au and Roberts [82] confirmed that the above partial dissociation of water is possible and is favoured when adsorbed oxygen is present on the surface. Campbell et al. [38,83] also noted that oxygen adatoms, arising from partially oxidised surfaces, can aid the adsorption of water. Activation energies for the reverse water–gas shift reaction and carbon dioxide dissociation were calculated and found to be in good agreement with each other, supporting the proposition that the reverse water–gas shift reaction proceeds via a redox mechanism. It was accepted that the nature of the surface was heavily dependent on the gas composition over the crystal.

Spitzer and Luth [84], in 1982, using a Cu(110) single crystal studied the adsorption of water and found that water was bound to the surface via the oxygen through the interaction of a lone pair orbital. The bond angle of the adsorbed water was found to have increased with respect to the free water molecule and it was suggested that there were specific four-fold sites upon the crystal where bonding was favoured. Increasing the temperature of the crystal from -183°C to 23°C brought about changes in the species resident upon the surface. At -93°C hydroxyl species from the partial dissociation of water (Eq. 13) became observable. At -23°C UPS and LEED provided evidence for the existence of a (2×1) pattern of $O_{(a)}$. AES determined the coverage of $O_{(a)}$ to be approximately 8% of a monolayer.

$$H_2O_{(a)} \rightleftharpoons OH_{(a)} + H_{(a)} \qquad (13)$$

Recently Colbourn et al. [25] using polycrystalline copper followed the adsorption of water on the catalyst using mass spectrometry. At temperatures between 150–231°C hydrogen evolution was rapid and indicative of a 7–8% of a monolayer coverage of adsorbed oxygen being produced. Colbourn et al. [25] and Heras and Viscido [85,86] both recognise that the promotion of water decomposition is determined by the 'surface roughness' of the copper being investigated.

Salmi and Hakkarainen [37] preadsorbed water onto a commercial $Cu/ZnO/Al_2O_3$ catalyst but failed to detect any significant evolution of hydrogen that may suggest adsorption of oxygen upon the catalyst surface.

Clearly, much evidence exists for the dissociative adsorption of water on clean and promoted, single and polycrystalline copper surfaces, under ultra-high vacuum conditions and at one bar. Detection of hydroxyl groups and their decomposition to adsorbed oxygen, identifiable by LEED patterns, can be readily achieved. Although there is considerable evidence that H_2O can be dissociatively adsorbed on a copper surface it remains unclear whether this process can occur at an appreciable rate. Boreskov [59], using isotopic labelling, noted that the individual half reactions for the redox mechanism occur at rates much lower than the actual rate of the copper catalysed WGS reaction. Campbell and co-workers [79] also indicate that there appears to be little evidence that the rate of H_2O dissociation to produce $O_{(a)}$ can proceed rapidly enough to form part of a catalytic cycle.

It has been proposed [40,79,87], that the kinetics of the reverse water–gas shift reaction offers the best evidence for the redox process on copper. Nakamura et al. [64] have shown on clean Cu(110), dissociative adsorption of carbon dioxide can occur at a rate comparable to the rate of the reverse water–gas shift reaction on $Cu/ZnO/Al_2O_3$. The reaction of $O_{(a)} + H_2(g)$ is also known to occur relatively rapidly [88,89]. Campbell and co-workers [90] using kinetic data from single crystal studies have successfully modelled the water–gas shift reaction and found good agreement between the single crystal data and that obtained for a working catalyst.

4.3. WGS reaction mechanism over iron oxide-based catalysts. Associative mechanism

Armstrong and Hilditch [52] wrote "we have seen that copper decomposes formic acid from

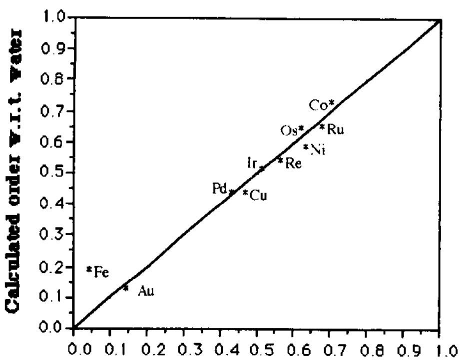


Fig. 7. Comparison of the calculated order of reaction w.r.t. water with experimentally determined orders of reaction w.r.t. water. Taken from ref. [61].

190°C; on the other hand, the iron oxide process is dependent upon the temperature ranges at which oxidation of carbon monoxide by iron oxide and decomposition of steam by iron or ferrous oxide occur at sufficiently rapid rates ... it is evident that the relative activity of: (a) copper and (b) iron oxide to carbon monoxide and steam at lower ranges of temperature are closely parallel to their respective powers of decomposing (a) formic acid and (b) steam''.

While it is possible that the activity of magnetite at lower temperatures may be limited by the dissociation of steam, as Armstrong and Hilditch [52] suggest, it could equally be true that at lower temperatures the associative mechanism is dominant over iron oxide. From the modelling of kinetic data, using Grenoble's associative mechanism, experimental and theoretical orders of reaction with respect to water have been established [61] (Fig. 7). With the exception of iron these data all correlate remarkably well, which perhaps indicates that the chemistry of the WGS reaction involving metallic iron differs from the other metallic catalysts studied.

In contrast to most of the materials used in the study of Grenoble et al. [61], iron is unusual because under the WGS reaction conditions the catalyst is iron oxide and not iron metal. It has been suggested [79], from hydroxyl decomposition data on nickel oxide, that the rate limiting step on oxides may be $OH_{(a)}$ conversion to $O_{(a)}$ and not CO desorption. Armstrong and Hilditch [52] indeed note that it was the "... respective powers of decomposing steam ..." which distinguished the activity of copper and iron oxide at lower temperatures. If this is indeed the case, it is interesting to draw comparisons between the results for cobalt, which agrees with the Grenoble theory, and those for iron which do not. Cobalt-based high temperature WGS catalysts, like iron-based catalysts, are stable oxides. Both materials, cobalt oxide and iron oxide, have almost identical atomic and ionic radii and both can exist with oxidation states of +2 or +3. From electrode potential data [90] it would appear that the +3 oxidation state of both metals is readily reduced and that this reduction is more favourable for Co^{3+} than for Fe^{3+}. Indeed, such is the oxidative power of the $[Co(H_2O)_6]^{3+}$ complex that it can oxidise water to evolve oxygen [91]. Whilst electrode potential data [90] can never be a satisfactory measure of the reductive/oxidative behaviour of any solid material it may help to correlate the differences between otherwise similar materials. It is reasonable to assume that parallels can be drawn between the hexa-aquo cationic species and the octahedral ions in a spinel. In both cases six oxygen atoms surround the positively charged centre. Indeed, modern spinel theory [92], predicting site preference energies, is based successfully upon ligand field theory which is derived from aqueous chemistry.

$$Co^{3+} + e^- \rightarrow Co^{2+} \quad E = 1.81 \text{ V} \qquad (14)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad E = 0.77 \text{ V} \qquad (15)$$

The problem with the description of cobalt oxide behaving as a redox catalyst is that the redox couple is heavily biased towards Co^{2+}. It appears that di-valent cobalt is unlikely to undergo oxidation by water and the data supplied by Grenoble et al. [61] could indicate that iron and its oxide is unique with respect to other WGS catalytic materials.

Using copper and cobalt oxide-based catalysts, Hutchings et al. [93] utilised model reagents to simulate the role that water might play. With

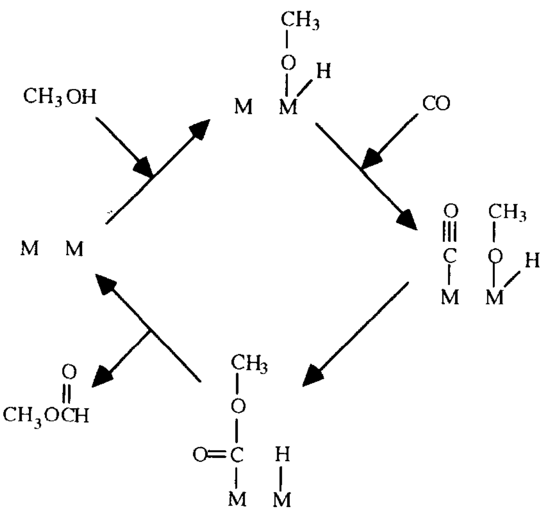


Fig. 8. The formation of methyl formate. Taken from ref. [93].

methanol replacing water in the shift reaction it was proposed that if the WGS reaction over cobalt oxide/manganese oxide, cobalt oxide/chromium oxide and copper/manganese oxide catalysts proceeded by an associative mechanism, oxidative addition of methanol to the catalyst surface would occur. The production of a surface methoxy group proceeded by CO insertion would lead to the production of CH_3OCOH (Fig. 8).

In confirming that CH_3OCOH was produced it is apparent that, under these experimental conditions, the WGS reaction over cobalt and copper systems may proceed by the formate mechanism. The concept that the associative mechanism does not predominate over iron but does with cobalt, its nearest neighbour, is supported by the work of Diagne et al. [20]. These studies suggest that for magnetite catalysts the formate species is not the intermediate for the water–gas shift reaction. These authors [20] found that formate coverage of a commercial magnetite catalyst, operated under WGS reaction conditions, decreased with temperature over the range 250–400°C (Fig. 9) whereas the rate of the WGS reaction was considerably enhanced.

4.4. Regenerative mechanism

Magnetite, as described previously, has octahedral sites that are occupied by Fe^{2+} and Fe^{3+} ions together with tetrahedral sites occupied by Fe^{3+} ions [94]. Topsøe and Boudart [23] using Mössbauer spectroscopy have clearly identified these species and the fact that rapid electron hopping can occur between two octahedral sites. The high electrical conductivity of magnetite, $\sigma = 200$ ohm^{-1} cm^{-1}, [16], indicates that a redox couple is present and highly facile. Reithwisch and Dumesic[45,47] have also studied a number of spinel structures, Fe_3O_4 (inverse), $ZnFe_2O_4$ (normal) and $MgFe_2O_4$ (mixed inverse), and have stated that of these structures only the magnetite can readily undergo rapid electron exchange between Fe^{2+} and Fe^{3+}.

Boreskov [96], based on a wide range of experiments demonstrated that the Fe^{2+} and Fe^{3+} ions located in octahedral sites in the magnetite-based structure can function as a redox couple, and that magnetite-based catalysts can be highly effective for the complete dissociation of water into hydrogen and adsorbed oxygen under reaction conditions. Water dissociation causes the oxidation of the octahedral Fe^{2+} centres to Fe^{3+} and liberates hydrogen. The oxidised iron centres may subsequently be reduced by carbon monoxide thereby producing carbon dioxide to complete the catalytic cycle.

Salmi et al. [48], using a commercial Fe_3O_4/Cr_2O_3 catalyst 290–365°C under one atmosphere of pressure, observed that pretreatment of the catalyst with water led to the liberation of a small amount of hydrogen. In conjunction with the liberation of H_2 the number of surface sites covered

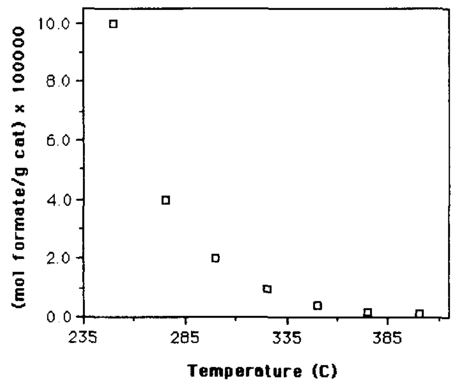


Fig. 9. Formate coverage.

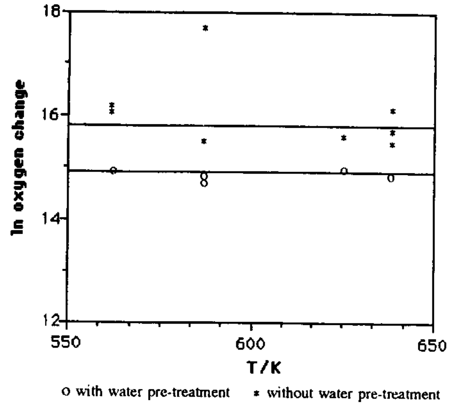


Fig. 10. The total surface oxygen coverage change determined from experiments with and without water pre-treatment.

by oxygen increased and the number of H_2O adsorption and dissociation sites decreased. Measurement of the differences between the carbon dioxide and hydrogen responses was used to acquire data that allowed the net change of surface oxygen, during the reaction, to be determined. Fig. 10.

It is clear that for the catalyst which has undergone pre-treatment with water that the overall change in the total surface oxygen, during reaction, is much less than that for the catalyst which was not pre-treated.

Lund and Dumesic [97] in 1982 investigated strong oxide–oxide interactions for silica supported magnetite. They outlined how the activity of the water gas shift catalyst decreased rapidly as the particle size of the iron oxide crystallites supported on silica decreased below 200 nm. Unsupported magnetite was not found to show this apparent dependence of rate on particle size for particles of similar size. It was concluded that the small islands of magnetite on silica were being influenced by the highly polarising Si^{4+}. In close proximity to Si^{4+}, Fe^{2+} was capable of being oxidised by the silicon species. This was shown to be energetically feasible and so the presence of Si^{4+} around magnetite might create an electron deficiency at the surface octahedral iron cations disrupting the redox couple. For larger magnetite particles the polarising effect of Si^{4+} is limited by the core magnetite helping to balance the affected redox couple.

Topsøe and Boudart [23] found that the presence of Pb^{4+} in chromia-promoted magnetite leads to increased activity of the catalyst. Pb^{4+} was reported to cause tetrahedral sites to expand and octahedral sites to contract leading to increased covalency in the system and improved electron hopping capabilities. Contraction of the distance between octahedral sites might be expected to facilitate more rapid electron transfer between neighbouring iron centres and help to enhance the already very high conductance of the magnetite solid. Boreskov [80] has also indicated that by improving the covalency of the catalyst, the activity is also improved.

5. Conclusions

From the initial discovery that the water–gas shift reaction could be catalysed over a variety of metallic oxides, investigations have been carried out attempting to trace the elementary steps involved in the process. Decades later, a wholly satisfactory and universally accepted mechanistic description of the WGS reaction fails to exist for either the magnetite or copper metal catalysed reaction. Although the reaction, at first sight, appears not to be complex, the catalysts are susceptible to small changes in operating conditions and this complicates the study of this process.

Currently, the structure of copper and iron oxide-based catalysts can be summarized as follows. Copper/zinc oxide/alumina appears to be constructed of islands of metallic copper supported upon zinc oxide alumina. The zinc oxide/alumina may exert some influence upon catalytic activity, but most of the evidence suggests that this contribution is small. The metallic copper islands can accommodate the dissociative adsorption of water required for a redox mechanism and the reactions needed to produce and decompose a formate species. Strong evidence exists supporting both reaction pathways and there is much debate as to which pathway the WGS reaction favours under reaction conditions. It is possible that either reaction mechanism could proceed and that the relative rates of the two pathways could be influenced by the experimental conditions. At present there are insufficient data to allow the dominant pathway to be ascertained under industrial conditions. Clearly, considerable further work is required to fully unravel this mechanistic problem.

The iron oxide water–gas shift catalyst mechanistic debate is less controversial. The catalyst has been well characterized and has an inverse spinel structure. Mössbauer spectroscopy and isotopic labelling evidence indicates that the redox couple (Fe^{2+}/Fe^{3+}) is highly labile and capable of dissociating water readily. Magnetite seems to be an unusual material with respect to other spinel structures, possessing properties that are unique and well suited to operation as a WGS redox catalyst.

Cobalt oxide, the closest neighbour of iron in the periodic table, and also a spinel under reaction conditions fails to match the properties of iron oxide. There is some indication, despite the close structural similarities between iron oxide and cobalt oxide, that different mechanistic pathways proceed over these catalysts and that the transition iron to cobalt may mark the mechanistic boundary for the water gas shift reaction.

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