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LOW TEMPERATURE, SULFUR TOLERANT HOMOGENEOUS CATALYSTS FOR THE WATER-GAS SHIFT REACTION

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INTRODUCTION

Objectives and Scope

The purpose of this report is to update and reorganize our recent review on homogeneous catalysis of the water-gas shift reaction (WGSR) based on recent literature publications and patents. This updated version will serve as means of selecting 10 candidate catalyst systems for use in developing effective, sulfur-tolerant, low temperature WGSR catalysts.

This report discusses the variations possible in the basic chemistry associated with WGSR catalytic cycles, including basic, acidic, and neutral conditions. Then individual mechanisms for specific WGSR catalyst systems are discussed. Finally, on the basis of the literature reports, a list is presented of candidate catalysts and basic systems we have chosen for study in Task 3.

The Water-Gas Shift Reaction

Water-gas, a primary source of the world's hydrogen supply, derives from steam reforming of methane and naphtha:

$$CH_4 + H_2O \longrightarrow CO + H_2 + CO_2 \qquad (1)$$

Stripping the water-gas mixture of CO_2 and any residual water gives syngas (CO/H2). Syngas can be converted to pure hydrogen via the WGSR:

$$H_2O + CO \longrightarrow H_2 + CO_2 \qquad (2)$$

ΔG = -6.82 kcal/mol, ΔH = -9.84, ΔS = -10.1 eu for $H_2O(g)$ at 298 K

ΔG = -4.76 kcal/mol, ΔH = 0.68, ΔS = +18.3 eu for $H_2O(l)$ at 298 K

In essence, the WGSR represents an additional source of the world's hydrogen.

The WGSR, as currently practiced industrially,[1-3] is an inefficient two-step, two-catalyst process. The inefficiency stems from the thermodynamics of reaction (2) and the susceptibility of the more efficient catalyst system, the low temperature (LT) shift catalyst (normally a mixture of zinc and copper oxides), to poisoning by sulfur compounds. The poisoning problem necessitates a prior catalytic step in which the product stream from reaction (1) is initially treated with a high temperature (HT) shift catalyst (generally a mixture of iron and chromium or molybdenum oxides) at temperatures above 350°C. This step converts all of the sulfur-containing contaminants to H_2S, which can then be removed before use of the LT catalyst. In addition, the HT catalyst shifts up to 85% of the CO to H_2. Figure 1 illustrates the overall relationship between shift temperature and conversion efficiency. In the second step, an LT catalyst is used to "complete" the conversion at temperatures of approximately 200°C; however, even at these temperatures, Figure 1 suggests that conversion is incomplete.

Thus, the current industrial WGSR processes suffer from being multi-step, thermodynamically inefficient and sensitive to poisoning. Because natural gas prices are projected to rise considerably over the next few decades, especially relative to coal prices (particularly in the United States), hydrogen derived from coal gasification could readily become an important alternative to hydrogen from steam reforming of methane or naphtha. The United States has impressive reserves of coal, compared with its reserves of methane; therefore, it is desirable to develop an economically viable process for hydrogen production from coal. One way to improve the overall efficiency of current "hydrogen from coal" processes is to improve the efficiency of industrial WGSR catalysis. In light of this, the development of a one-step, low temperature process that will maintain high activity in the presence of high sulfur and nitrogen contaminant levels typical of coal gas would be particularly attractive.

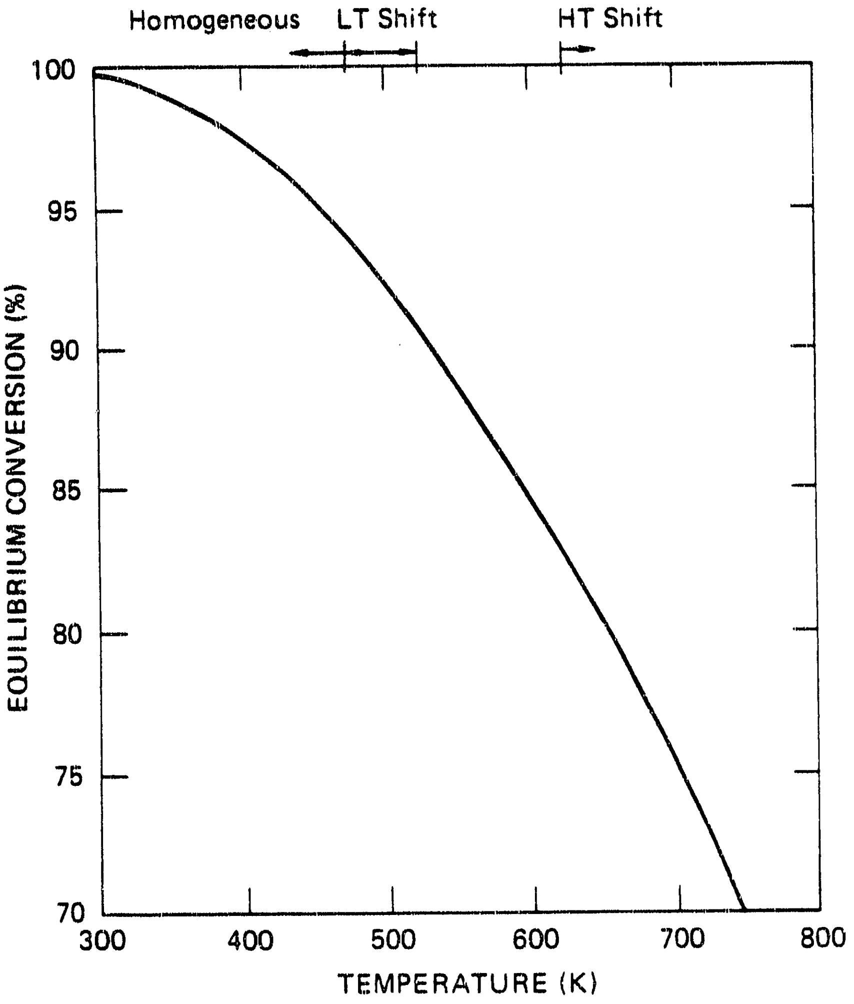

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FIGURE 1 EQUILIBRIUM CONVERSION OF CO AND H_2O TO CO_2 AND H_2 BY WGS REACTION AT DIFFERENT TEMPERATURES

The development of homogeneous WGSR catalysts would be one possible solution to the need for a one-step, low temperature process, providing that the catalyst system could be made sulfur and nitrogen tolerant. The impetus for research in this area is that homogeneous catalysts are known to be (in general) more active and more selective than their heterogeneous counterparts, and in some instances they have been shown to be resistant to sulfur poisoning. Thus, the potential exists to develop homogeneous catalysts that can operate in the most efficient temperature range defined in Figure 1--that is, 100°-200°C.

BACKGROUND

The first researcher on the possibility of homogeneous catalysis of the WGSR, was Reppe. Reppe's work with catalytic reactions of the general form shown in reaction (3) led

$$CO + H_2O + S \xrightarrow{\text{catalyst}} SH_2 + CO_2 \qquad (3)$$

S = substrate, catalyst = $Fe(CO)_5$ or $Ni(CO)_4$

him to postulate[4] that a process akin to WGSR catalysis was occuring. However, it was only in the early 1970s that the first examples of homogeneous catalysis of the WGSR appeared in the patent literature and then in the open literature. Fenton was the first to describe homogeneous catalysis of the WGSR, in three patents,[5-7] wherein catalysis was promoted by a variety of group 8 metals used in conjunction with phosphine, arsine, or stibine ligands and amine or inorganic bases.

In the same time period, the first reports on the homogeneous catalysis of the WGSR appeared in the open literature. Four different types of catalyst systems were identified initially. Laine et al. reported that aqueous alcoholic solutions of ruthenium carbonyl made basic with KOH gave active WGSR catalyst systems.[8] Kang et al. were able to show that the majority of the group 8 metals were active catalysts for the WGSR when dissolved in aqueous THF containing trimethylamine as base.[9] In contrast, Cheng et al. demonstrated that it was possible to catalyze the WGSR in acidic solution[10]. They were able to show that dissolution of rhodium carbonyl complexes in aqueous acetic acid containing iodide gave active WGSR catalysts. Likholobov et al. reported, at approximately the same time, the discovery of a palladium phosphine WGSR catalyst system that requires aqueous trifluoroacetic acid as the working medium.[11] The initial evidence suggested that the two base-promoted catalytic cycles were similar, but differed mechanistically from the acid-facilitated systems.

From these original reports, as well as the mechanistic evidence presented later by other research groups, it is evident that there are a variety of catalytic cycles possible for homogeneous catalysis of the WGSR (see, for example, the recent review by Ford[12]). In general, the various types of catalytic cycles proposed for the WGSR can be distinguished according to whether CO or H_2O activation occurs in the primary step and whether catalysis occurs under acidic, basic, or neutral conditions. Other distinguishing features include the presence or absence of ligands other than CO or H_2O and the use of group 6 or 8 metal complexes. Because so many mechanisms for catalysis of the WGSR have been proposed in the literature, we have organized our discussions in terms of the types of mechanisms described or proposed to date.

Before discussing the individual mechanisms for specific systems studied, we describe the variations possible in the basic chemistry associated with WGSR catalytic cycles. These discussions will allow the reader to compare and contrast the chemistry presented in the various catalytic cycles that follow.

BASIC STEPS IN WGSR CHEMISTRY

The majority of the WGSR systems described in the literature are initiated by activation of CO followed by its reaction with water, OH^-, or H_3O^+. The less well-studied systems commence with activation of H_2O followed by reaction with CO. We will begin our discussions by considering catalytic cycles that begin with CO activation and proceed to those that begin with H_2O activation.

Carbon monoxide activation normally starts with complexation of free CO to a coordinately unsaturated metal. Once bound, the carbonyl's reactivity towards water OH^-, or H^+ is determined by the extent to which it pi backbonds to the metal, the metal's oxidation state, the overall charge on the complex, and the extent to which the complex can stabilize the various possible intermediates that could form following reaction with water, base, or acid.

In the case where the metal is neutral and supports several good electron donor ligands or is negatively charged, it will backdonate considerable electron density to the coordinated CO group. Thus, only a strong nucleophile, such as OH^- or CH_3O^-, will be capable of reacting with the "activated" CO. In fact, high electron density at the metal can have a dramatic adverse effect on nucleophilic attack at CO. For example, Gross and Ford observe that the substitution of a single phosphite group onto $Ru_3(CO)_{12}$ reduces its reactivity towards CH_3O^- by approximately two orders of magnitude.[13]

When the nucleophile is OH^-, the product will be an anionic metallocarboxylic acid, reaction (4).

$$MCO + OH^- \longrightarrow M(CO_2H)^- \qquad (4)$$

In contrast, when the metal has little electron density to donate to the coordinated CO, as occurs when the metal is in a high oxidation state or the overall complex is positively charged, then even weak nucleophiles such as H_2O can react with the CO, reaction (5), to produce a metallocarboxylic acid.

$$MCO^{+} + H_2O \xrightarrow{\hspace{6em}} M(CO_2H) + H^{+} \qquad (5)$$

This reaction has been used by several researchers as a facile way of labeling carbonyl oxygens:[14-16]

$$Re(CO)_6^{+}\ S + H_2O \longrightarrow (CO)_5Re[C(=O)^{*}OH]^{+}$$

$$\longrightarrow (CO)_5Re[C(=^{*}O)OH]^{+} \longrightarrow (CO)_5Re(C^{*}O)^{+} + H^{O} \qquad (6)$$

An alternate reaction pathway is available for CO bound to a relatively electron-rich metal. It is quite reasonable that under acidic conditions the entire complex can be protonated. This reduces the electron density available for backbonding with the CO, making it sufficiently electron deficient that it can then react with water, as illustrated in reaction (7), to form a metallocarboxylic acid.

$$MCO + H^{+} \longrightarrow HMCO^{+} + H_2O \longrightarrow HM(CO_2H) + H^{+} \qquad (7)$$

For acidic reactions, the introduction of strong electron donor ligands should have the opposite effect to that observed with the nucleophilic reactions; it should promote the reaction of H^{+} with MCO. There is no evidence to support this idea at present.

An additional route to CO activation that does not rely on initial complexation with a coordinately unsaturated metal, begins with reaction of CO with OH^{-} to produce formate and with excess water, formic acid:

$$CO + OH^{-} \xrightarrow{\hspace{6em}} HCO_2^{-} \qquad (8)$$

$$HCO_2^- + H_2O \text{ -------------------> } HCO_2H + OH^- \qquad (9)$$

The formate anion or formic acid can then bind to a coordinately unsaturated metal to form a metalloformate rather than a metallocarboxylic acid:

$$M + HCO_2H \text{ --------------> } HM(\eta^1 \text{ or } \eta^2\ O_2CH) \qquad (10)$$

$$M + HCO_2^- \text{ ----------------> } [M(O_2CH)]^- \qquad (11)$$

Metal formates could also arise via rearrangement of a metallocarboxylic acid, as shown in reactions (12) or (13):

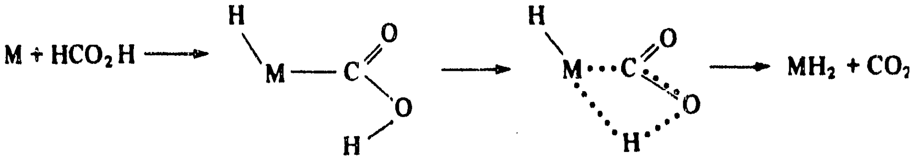
$$M(CO^2H) \text{ ------> } [HM(\eta 2\text{-}CO_2)] \text{ ------> } M(O_2CH) \qquad (12)$$

$$HM(CO_2H) \text{ ------> } M + HCO_2H \text{ -------> } HM(O_2CH) \qquad (13)$$

The existence of metallocarboxylic acids and evidence for their formation upon reaction of carbonyls with OH^- is now well established, beginning with the initial report by Deeming and Shaw[17] and continuing with the more recent work of Darensbourg et al.,[18,19] Ford et al.,[13] Lane et al.,[20] and others. The following complexes have been isolated and/or identified spectroscopically:

$IrCl_2(CO_2H)(CO)(PMe_2Ph)_2$[17], $CpFe(CO)(PPh_3)CO_2H$[21], $CpRu(CO)(PPh_3)CO_2H$[22], $(Et_3P)_2Pt(Cl)CO_2H$[23], trans-$PtH(CO_2K)[P(iPr_3)_3]_2$[24], $CpRe(NO)(CO)CO_2H$[25], $Mn(CO)_5CO_2H$[18], $Ru_3(CO)_{11}CO_2H$[13], and $Fe(CO)_4CO_2H^-$ (gas phase).[20]

Metallocarboxylic acids could also arise via the formate pathway, reaction (8) [and (9)], if the metal preferentially inserted into the formate (formic acid) C–H bond rather than forming a metalloformate:



Scheme 1

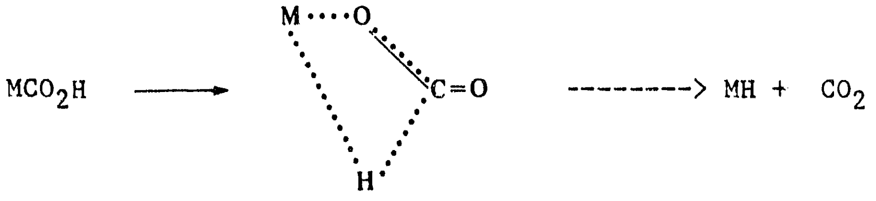
Support for the reactions shown in Scheme 1 comes from the work of Grey et al.,[26] who find that $H_2Ru(C_6H_4PPh_2)(PPh_3)_2$ reacts with formate esters to give decarbonylation reactions. Presumably these reactions are initiated by C-H insertion.

Although metalloformate complexes have been less well studied, the emphasis in those publications that are available has been with regard to the catalytic decomposition of formate and formic acid via metalloformate intermediates in WGSR catalysis. The formate or formic acid is assumed to be produced via reactions (8) and (9). For example, Darensbourg has described the preparation and characterization of a number of formate complexes including $CpFe(CO)_2(O_2CH)$,[27] and the group 6 complexes $(HCO_2)M(CO)_5$[19] (where M = Cr, Mo, W).

Once the activated CO has reacted with water to give either a metallocarboxylic acid or a metalloformate, the possibility now exists for eliminating CO_2--one of the products of the WGSR. Deeming and Shaw[17] were the first to observe that metallocarboxylic acids can decompose with loss of CO_2, reaction (14). In fact, the majority of the above cited metallocarboxylic acids and metalloformates decompose rather

$$IrCl_2(CO_2H)(CO)(PMe_2Ph)_2 \dashrightarrow IrHCl_2(CO)(PMe_2Ph)_2 + CO_2 \quad (14)$$

readily to produce CO_2 and a metal hydride; however, the exact mechanisms can vary. Originally, it was assumed that the decomposition process proceeds via beta elimination, as seen in reaction (15). More recently, a number of groups



(15)

have described decomposition processes wherein catalytic amounts of base are required to promote decomposition. This suggests that the metallocarboxylate anion, MCO_2^-, is a necessary intermediate in some decomposition processes:

$$MCO_2^- \dashrightarrow CO_2 + M^- + H_2O \dashrightarrow MH + OH^- \tag{16}$$

Three other bimolecular decomposition pathways have been proposed in the literature. Reactions (17) and (18) are suggested by the work of Darensbourg.[19,28]

$$MCO_2H + OH^- \xrightarrow{[MC(OH)_2O^-]} MH + HCO_3^- \tag{17}$$

$$MCO_2H + H_2O \xrightarrow{[MC(OH)_2O^-]} MH + H_2CO_3 \tag{18}$$

Reaction (19) is suggested by the work of Gibson and Ong:[22]

$$MCO_2H + MH \dashrightarrow H_2 + M_2 + CO_2 \tag{19}$$

Unfortunately, quantitative studies of the decomposition kinetics of metallocarboxylic acids are quite limited, and thus the mechanism(s) of decomposition must remain at least partly conjecture.

Reaction (20) is another decomposition pathway available to metallocarboxylic acids; however, the decomposition process is

$$MCO_2H \xrightarrow{[M(OH)CO)]} MOH + CO \tag{20}$$

counterproductive in a WGSR sense, because it leads back to reactants rather than to products. Grice et al. report[21] that in some solvents $CpFe(CO)^+$ reacts reversibly with OH^- as shown in (20), but can be coerced into undergoing decarboxylation by changing solvent and adding base. Therefore, some control over the dominant mechanism in metallocarboxylic acid decomposition is possible.

Metalloformate intermediates decarboxylate to give essentially the same products as obtained from decomposition of metallocarboxylic acids; consequently, it is likely that in some WGSR catalysis systems it will not be possible to distinguish between two similar catalytic cycles.

As noted above, metalloformates are proposed intermediates in the catalytic decomposition of formate and formic acid formed as per reactions (8) and (9). The general reactions for these decompositions can be written as in reactions (21) and (22).

$$M^+ \ O_2CH^- \xrightarrow{[M(O_2CH)]} MH^- + CO_2 \qquad (21)$$

$$M + HCO_2H \xrightarrow{[HM(O_2CH)]} M + H_2 + CO_2 \qquad (22)$$

The formation and decomposition of transition metal formate complexes have been discussed as part of a review by Eisenberg and Hendriksen.[29]

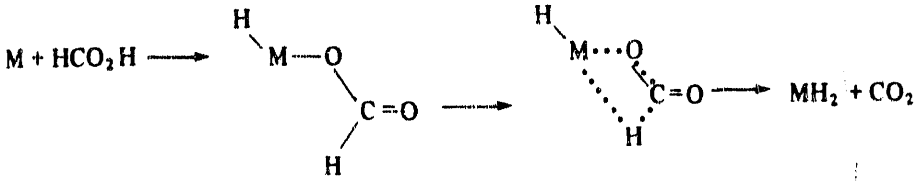
A number of metal complexes have been reported to promote reaction (22) catalytically. Shriver reports[30] that $Rh(C_6H_4PPh_2)(PPh_3)_2$ catalyzes (22) and compares the activity of this catalyst with the activities of $Pd(HCO_2)_2$, $PtCl_2(PBu_3)_2$, $IrH_2Cl(PPh_3)_3$, and $Pt[P(iPr)_3]_3$. The platinum isopropylphosphine complex appears to have the highest activity of the catalysts compared. Other compounds, including $Ru_3(CO)_{12}$[12] and $Ir_4(CO)_{12}$,[31] have also been found to be active catalysts for (22).

Metalloformates such as the intermediate shown in (22) can also be isolated in the reversible reaction between metal hydrides and CO_2 as exemplified by reaction (23):[32]

$$PtH_2(PEt_3)_2 + CO_2 \rightleftharpoons (HCO_2)PtH(PEt_3)_2 \qquad (23)$$

The reversible reaction of CO_2 with metal hydrides to form metalloformates is of importance to the current discussion because such a reaction, e.g. (23), is potentially counterproductive in a WGSR sense, because it ties up metal hydride and CO_2 as metalloformate, preventing release of both H_2 and CO_2. This potential problem is particularly important in WGSR catalysis by group 6 metal catalysts, as discussed below.

The mechanism of η-1 or η-2 formamato decomposition is generally assumed to be one that involves a Beta elimination process:



Scheme 2

One other organometallic source of CO_2 was described by Yoshida et al.,[33] who report that selected rhodium phosphine complexes (see below) undergo a reaction sequence wherein reaction (18) is followed by reactions (24) and (25).

$$MH + H_2CO_3 \text{ ------------> } H_2 + M(O_2COH) \qquad (24)$$

$$M(O_2COH) \text{ ------------> } M^{+} + OH^{-2} + CO_2 \qquad (25)$$

In the preceding paragraphs, we have discussed the potential organometallic intermediates that can activate CO and promote its reactions with H_2O; we have also examined the potential intermediates available for the evolution of the WGSR product, CO_2. The following discussions provide a similar treatment of how H_2 evolution, the other WGSR product, can result from organometallic complexes such as MH--the likely byproduct of CO_2 formation.

Unimolecular reductive elimination provides the simplest possible route for generation of H_2:

$$MH_2 \xrightarrow{\hspace{4em}} H_2 + \text{"M"} \tag{26}$$

Kinetic studies have shown that a number of complexes, including $H_2Fe(CO)_4$,[34] $H_2RhCl(PPh_3)_3$,[35] $H_2IrCl(CO)(PPH_3)_2$,[36] and $H_2Co[P(OR)_3]_4$,[37] eliminate H_2 by unimolecular reductive elimination. H_2 can also be formed through bimolecular elimination reactions [e.g., (27)] as shown by Marko for $HCo(CO)_4$[38] and by Norton for $H_2Os(CO)_4$:[39]

$$MH + MH \xrightarrow{\hspace{4em}} M_2 + H_2 \tag{27}$$

$$2HCo(CO)_4 \xrightarrow{\hspace{4em}} Co_2(CO)_8 + H_2 \tag{28}$$

$$2H_2Os(CO)_4 \xrightarrow{\hspace{4em}} H_2Os(CO)_8 + H_2 \tag{29}$$

In most instances, bimolecular loss of H_2 requires an initial dissociative step in which creation of a coordinately unsaturated species [e.g., $HCo(CO)_3$ in (28)] permits the formation of a bridging hydride intermediate, which then leads to H_2 and a dimeric species. In the case of $H_2Fe(CO)_4$ the process is further complicated by that competing multinuclear processes, which provide additional routes for reductive elimination of H_2, as demonstrated by Collman et al.[40]

$$H_2Fe(CO)_4 + Fe(CO)_4 \xrightarrow{\hspace{2em}} H_2Fe_2(CO)_8 \tag{30}$$

$$H_2Fe_2(CO)_8 + HFe_2(CO)_8^- \longrightarrow HFe_3(CO)_{11}^- + Fe(CO)_5 + H_2 \tag{31}$$

In the analogous ruthenium systems, it appears that multinuclear H_2 elimination processes are the only pathways available,[41] (32), but as described below, this may not be the case.

$$3[H_3Ru_4(CO)_{12}]^- + 9CO \longrightarrow 3[HRu_3(CO)_{11}]^- + Ru_3(CO)_{12} + 3H_2 \quad (32)$$

Reactions (26)-(32) illustrate only that portion of known organometallic chemistry where H_2 formation proceeds via reductive elimination from metal hydrides. Alternate mechanisms are available for H_2 production that do not proceed via reductive elimination. For example, metal hydrides are known to react with acids according to reaction (33):

$$MH + HX \longrightarrow MX + H_2 \quad (33)$$

Reactions (34)-(37) provide specific examples of reaction (33) wherein MH is an organometallic hydride:[42a]

$$CpFe(CO)_2H + HCl \longrightarrow CpFe(CO)_2Cl + H_2 \quad (34)$$

$$Cp_2ZrH_2 + HOAc \longrightarrow Cp_2Zr(OAc)_2 + H_2 \quad (35)$$

$$mer\text{-}HIrCl_2(PPh_3)_3 + HCl \longrightarrow mer\text{-}IrCl_3(PPh_3)_3 + H_2 \quad (36)$$

$$Pd[P(Ph)_3]_4 + 2HX + H_2O \longrightarrow Pd(H_2O)[P(Ph)_3]_3X_2 + P(Ph)_3 + H_2 \quad (37)^{42b}$$

As discussed below, it is likely that transition metal hydrides will undergo similar reactions when HX = H_2O.

Bricker et al.[41,43] have suggested another mechanistic process leading to H_2 evolution. Given that metal formyl complexes are very efficient hydride donors and, based on the rationale by Pearson et al.[34b] that metal formyls can form under mild conditions[34] (recently supported by the theoretical work of Blyholder et al.[44]), Shore proposes reaction (38) as a plausible source of H_2:

$$MC(=O)H + H_2O \text{ -------------->} M(CO)^+ + OH^- + H_2 \qquad (38)$$

Unfortunately, it may not be possible to distinguish between reaction (33), where HX = H_2O, and reaction (38).

In contrast to the work on WGSR processes wherein the first step is CO activation, there are very few examples where metal-promoted activation of water precedes reaction with CO. As seen in reactions (39)-(41), the overall WGSR mechanisms that begin with H_2O activation are quite similar to those beginning with CO activation. In reality, it appears that the specific factors that cause the differentiation between H_2O and CO activation apply only for the first step in the WGSR catalytic cycle.

$$M + H_2O \text{ -------------------->} HM(OH) \qquad (39)$$

$$HM(OH) + CO \text{ --------->} [HM(CO)(OH)] \text{ ---->} HM(CO_2H) \qquad (40)$$

$$HM(OH) + CO \text{ -------->} HMCO + OH- \text{ -------->} HM(CO_2H) \qquad (41)$$

The key features that appear to facilitate water activation rather than CO activation are simultaneous high coordinative unsaturation and high electron density at the metal as found in $Pt[P(iPr)_3]_3$,[45] $Rh[P(iPr)_3]_3$,[46] and $W((CO)_3(PCy_3)_2$.[47] These compounds react with water to give trans-$PtH(OH)[P(iPr)_3]$, $HRh(OH)[P(iPr)_3]_3$ and $HW(OH)(CO)_3(PCy_3)$. Under these circumstances, it seems reasonable to suggest that oxidative addition of H_2O is preferred to CO coordination because it significantly reduces both electron density and coordinative unsaturation compared to what can be attained with CO coordination. Only the platinum and iridium complexes have been shown to react with CO to form metallocarboxylic acids and catalyze the WGSR as discussed below.

The various possible WGSR reaction intermediates described above serve as the basis for the following detailed discussions on the reported examples of homogeneous catalysis of the WGSR. These examples are separated into two groups: catalysis of the WGSR under basic conditions and catalysis under acidic or neutral conditions.

CATALYSIS OF THE WGSR UNDER BASIC CONDITIONS

Iron Carbonyl Catalysis of the WGSR

Perhaps the simplest WGSR catalyst system studied to date is the system based on $Fe(CO)_5$. The first reports on a base-promoted catalyst system were made by Kang et al.[48] and King et al.[49] Kang et al. described studies using a $Fe(CO)_5$, $Me_3N/THF/H_2O$ WGSR system. King et al. studied WGSR catalysis using a system comprising of aqueous alcoholic solutions of $Fe(CO)_5$ made basic with alkali metal hydroxides.

King et al. have since continued their studies[50] on the hydroxide-promoted systems; based on high temperature IR data and Kang et al.'s work, they propose the mechanism shown in Scheme 3.

$$Fe(CO)_5 + OH- \longrightarrow Fe(CO)_4C(=O)OH^-$$

$$Fe(CO)_4C(=O)OH^- \longrightarrow HFe(CO)_4^- + CO_2$$

$$HFe(CO)_4^- + H_2O \longrightarrow H_2Fe(CO)_4 + OH^-$$

$$H_2Fe(CO)_4 \longrightarrow H_2 + Fe(CO)_4$$

$$Fe(CO)_4 + CO \longrightarrow Fe(CO)_5$$

Scheme 3

King et al. report that the rate determining step in the catalytic cycle is the reaction of base with $Fe(CO)_5$, which was confirmed by Pearson and Mauermann.[34] From kinetic studies of these same systems, Pearson and Mauermann show that loss of CO_2 proceeds via deprotonation of the metallocarboxylic acid rather than directly from the metallocarboxylic acid:

$$Fe(CO)_4CO_2H^- + OH^- \text{ -------> } [Fe(CO)_4(CO_2)]^{2-} \qquad (47)$$

$$[Fe(CO)_4(CO_2)]^{2-} + H_2O \text{ -------> } HFe(CO)_4^- + HCO_3^- \qquad (48)$$

In support of reactions (47) and (48), Lane et al.[20] report that $Fe(CO)_4CO_2H^-$ is stable to decarboxylation in the gas phase even in the presence of added water molecules or unsolvated secondary bases. However, they do find that the addition of the hydroxide/ammonia cluster ion $(OH)NH_3^-$ promotes decarboxylation of $Fe(CO)_4CO_2H^-$ as in (47). Lane et al. also calculate that the lower limit to the enthalpy of decarboxylation is approximately -17 kcal/mol. This points up a continuing problem in WGSR catalysis studies--namely, the extreme dearth of thermodynamic data needed both to differentiate between various possible mechanistic pathways and to calculate the potential efficiencies of new WGSR catalyst systems.

Contrary to the work of Pearson and Mauermann and of Lane et al., recent kinetic studies by Gross and Ford[13] on the $Fe(CO)_5/OH^-$ system in mixed $THF/MeOH/H_2$ solvent systems indicate that decarboxylation proceeds via the metallocarboxylic acid, $Fe(CO)_4C(=O)OH^-$, rather than the dianion as in reaction (47). The evidence suggests that protic media catalyze the decarboxylation step.[51]

Ruthenium Carbonyl Complexes

Since the original reports on ruthenium catalysis of the WGSR in 1977,[8] this system has been the subject of considerable study by the original discoverers as well as many other groups in the field. The currently proposed mechanism, shown in Scheme 4, can be derived from the work of Gross and Ford[13] and of Shore et al.[43]

$$Ru_3(CO)_{12} + OH^- \dashrightarrow HRu_3(CO)_{11}(CO_2H)R-$$

$$HRu_3(CO)_{11}(CO_2H)R- \dashrightarrow CO_2 + HRu_3(CO)_{11}^-$$

$$HRU_3(CO)_{11}^- + CO \longrightarrow [HRU_3(CO)_{12}^-]$$

$$[HRU_3(cO)_{12}^-] + H_2 \longrightarrow RU_3(CO)_{12} + H_2$$

$$HRu_3(CO)_{11}^- + H_2 \longrightarrow H_3Ru_4(CO)_{12}^-$$

$$H_3Ru_4(CO)_{12}^- + CO \rightleftharpoons HRu_4(CO)_{12}^- + H_2$$

$$HRu_4(CO)_{12}^- + CO \rightleftharpoons HRu_3(CO)_{11}^- + Ru_3(CO)_{12}$$

<u>Scheme 4</u>

Gross and Ford have presented concrete evidence for the intermediacy of the trinuclear cluster metallocarboxylic acid formed in Scheme 4. Moreover, the results of their kinetic studies indicate that $Ru_3(CO)_{11}(CO_2H)R-$ is the intermediate that undergoes decarboxylation rather than the dianion, $Ru_3(CO)_{11}(CO_2)R2-$. Bricker et al. provide convincing evidence that the reaction of $HRu_3(CO)_{11}^-$ with CO leads to hydrogen evolution by either of two pathways.

In the absence of water, $HRu_3(CO)_{11}^-$ reacts reversibly with CO as in reaction (42):

$$KHRu_3(CO)_{11}^- + CO \rightleftharpoons Ru_3(CO)_{12} + KH \qquad (42)$$

Based on reaction (42), Shore et al. suggest that hydrogen evolution results from the formation of the intermediate or transient species, $HRu_3(CO)_{12}^-$. This species can lose hydride and generate H_2 either as in reaction (42), with subsequent hydrolysis of KH, or through formation of a formyl intermediate, $(CHO)Ru_3(CO)_{11}^-$, coincident with reaction (38). Shore et al. also suggest that the two equilibria in Scheme 4, wherein tetranuclear species interconvert with trinuclear species, are side reactions that diminish the reactivity of the ruthenium WGSR catalyst system because they tie up metal in a nonproductive or less productive form.

Slegeir et al.[52] have briefly studied a number of aspects of ruthenium catalysis of the WGSR using amine as base. Their studies with the $(CH_3)_3N/THF/H_2O$ solvent system suggest the following mechanism for amine-promoted WGSR catalysis.

$$Ru_3(CO)_{12} + 3CO \rightleftharpoons 3Ru(CO)_5$$

$$Ru(CO)_5 + (CH_3)_3N \rightleftharpoons (CO)_4RuC(=O)N(CH_3)_3$$

$$(CO)_4RuC(=O)N(CH_3)_3 + H_2O \rightleftharpoons HRu(CO)_4^- + CO_2 + (CH_3)_3NH$$

$$HRu(CO)_4^- + H_2O \rightleftharpoons H_2Ru(CO)_4 + OH^-$$

$$H_2Ru(CO)_4 \rightleftharpoons H_2 + Ru(CO)_4$$

$$Ru(CO)_4 + CO \rightleftharpoons Ru(CO)_5$$

Scheme 5

The evidence in support of this mechanism is contrary. Slegeir et al. find that at higher $Ru_3(CO)_{12}$ concentrations, CO pressure dependence studies implicate clusters as the active catalyst species, and they isolate $H_4Ru_4(CO)_{12}$ by acidifying the reaction solution. At lower $Ru_3(CO)_{12}$ concentrations and CO pressures, they observe higher WGSR catalysis activity and conclude that mononuclear species are involved.

Two explanations for these observations are possible, both of which would discount the mechanism shown in Scheme 5. One is that the last two equilibria in Scheme 4 could readily account for the pressure/activity dependence data if trinuclear species are the true active WGSR catalyst species in amine-promoted ruthenium WGSR as they are in the hydroxide-promoted system. Then Scheme 4 rather than Scheme 5 provides the appropriate mechanism. The alternative, which we believe is more likely, is that strong amine cluster interactions change the nature of the catalyst entirely. This is evidenced by the disparity between the recorded amine- and OH^--promoted WGSR catalyst activities, especially for the Ru and Rh systems, as seen from a comparison of the data in Tables 1-3.

The work of Wilson et al.[53] provides a possible explanation of these differences. In an effort to explain the reversal in relative activities of the two catalysts, Wilson et al. have presented evidence that a majority of the second- and third-row group 8 metals interact strongly with tertiary amines through C-H activation, as evidenced by reaction (43) where the catalyst can be ruthenium, osmium, rhodium, or iridium carbonyl.

$$Et_3N + D_2O + CO \xrightarrow{\text{catalyst}} Et_2NCHDCD_3 + CO_2 + HDO \quad (43)$$

The fact that amine cluster complexes can be isolated from the catalyst solutions containing many types of amines suggests that the catalyst system is extremely complex. Thus, a simple explanation of the mechanisms of amine-promoted group 8 metal catalysis of the WGSR is not at present possible.

Despite a decade of effort, several key questions concerning ruthenium carbonyl WGSR catalysis under base-promoted conditions remain to be clarified. These include: (1) Do mononuclear or dinuclear species participate to any extent in WGSR catalysis and are these species involved in the equilibria between the active trimer, $HRu_3(CO)_{11}^-$ and the inactive or less active $H_3Ru_4(CO)_{12}^-$? (2) What species are responsible for H_2 elimination? and (3) Is the hydroxide-promoted ruthenium WGSR system analogous in nature to the amine promoted system?

Most recently, a new type of mononuclear/dinuclear ruthenium WGSR catalysis system was described by Shvo et al.[54] The system is based on the reaction of tetraphenylcyclone (CPD) ruthenium tricarbonyl, (η-4 CPD)Ru(CO)$_3$, with OH$^-$. The mechanism, as shown in Scheme 6, involves the formation of several extremely unusual intermediates. In reaction (44), or just prior, the tetrahapto-CPD complex is transformed into a

$$\mathrm{CPDRu(CO)_3 + OH^- \dashrightarrow [CPDRu(CO)_2CO_2H]^-}$$

$$\mathrm{[CPDRu(CO)_2CO_2H]^- \dashrightarrow CPDRu(CO)_2H^- + CO_2}$$

$$\mathrm{CPDRu(CO)_2H^- + H_2O \dashrightarrow CPDRu(CO)_2H_2 + OH^-} \qquad (44)$$

$$\mathrm{2CPDRu(CO)_2H_2 \dashrightarrow [CPDRu(CO)_2H]_2 + H_2} \qquad (45)$$

Scheme 6

complex containing a pentahapto hydroxycyclopentadienyl ligand and a ruthenium hydride, (HOCp)Ru(CO)$_2$H, rather than the expected dihydride. The (HOCp)Ru(CO)$_2$H complex can readily dimerize with loss of hydrogen to give a dimer, (CO)$_2$Ru(CpO-μ-H)(μ-H)-(O-Cp)Ru(CO)$_2$, whose x-ray structure indicates that it contains both a bridging hydride and a bridging proton. Reaction (45) represents an unusual form of reaction (33), wherein HX is the monomer (HOCp)Ru(CO)$_2$H. In addition, the unique structure of (HOCp)Ru(CO)$_2$H suggests that the metallocarboxylic acid intermediate may also have unusual bonding interactions.

The dimer is air stable and represents a useful precursor for the WGSR catalyst system. However, its most important feature may be its apparent stability in the presence of H_2S.

Doi and Tamura have briefly described[55] the use of a totally aqueous phase ruthenium WGSR catalyst system, RuCL$_3$/KOH/H$_2$O, which is more active in the absence of an ethoxyethanol co-solvent than in its presence (see Table 1). Only limited kinetic studies were performed and no attempt was made to identify any intermediates.

Group 6 Metal Complexes as Catalysts for the WGSR

King et al.[49,56] were the first group of researchers to report the use of group 6 metal carbonyls [$Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$] as catalyst precursors for catalysis of the WGSR in the presence of OH^-. Based on kinetic studies of WGSR catalyst solutions generated from these three carbonyl complexes, King et al. suggest the following general catalytic cycle:

$$CO + OH^- \longrightarrow HCO_2^-$$

$$M(CO)_6 \rightleftharpoons M(CO)_5 + CO$$

$$M(CO)_5 + HCO_2^- \longrightarrow M(CO)_5(O_2CH)^-$$

$$M(CO)_5(O_2CH)^- \longrightarrow HM(CO)_5^- + CO_2$$

$$HM(CO)_5^- + H_2O \longrightarrow H_2M(CO)_5 + OH_{-}$$

$$H_2M(CO)_5 \longrightarrow M(CO)_5 + H_2$$

Scheme 7

This type of mechanism is supported by the results of Slegeir et al.,[57] who show that thermally and photochemically activated group 6 metal carbonyls can catalyze the decomposition of formates to H_2 and CO_2. Weiller et al.[58] have also examined the photoinitiated decomposition of formate in the presence of $Cr(CO)_6$ and $W(CO)_6$. Their kinetic and mechanistic studies concur with the mechanism proposed by King et al. These studies, which are extremely detailed, lead to the conclusion that decarboxylation is the rate determining step; it occurs with activation enthalpies of 26.0 and 24.8 kcal/mol for Cr and W, respectively.

A contrasting argument has been presented by Darensbourg and Rokicki,[19,28] who find that the reaction that produces the anionic metal hydride and CO_2 is actually an equilibrium favoring the metalloformate, (46), and thus is not a particularly viable intermediate. In addition, from kinetic studies of the reaction of $M(CO)_6$ with base, they find

$$M(CO)_5(O_2CH)^- \rightleftharpoons HM(CO)_5^- + CO_2 \qquad (46)$$

that WGSR catalytic activity exhibits a second order dependence on OH^- and that the metallocarboxylic acid intermediate is, energetically, a more favorable intermediate than the metalloformate. Furthermore, they note that there is no evidence that the metallocarboxylic acid and the metalloformate complexes interconvert intramolecularly. The interconversion can take place, but only via the metal hydride intermediate, reaction (23). Finally, Darensbourg and Rokicki suggest that reaction (8) is much slower than reaction of hydroxide with $M(CO)_6$ although the kinetics of the reaction have not yet been evaluated.

These features cannot be reconciled with the mechanism proposed in Scheme 7. Thus, Darensbourg proposes an alternate mechanism that takes into account these differences and wherein (46) is a deadend side reaction:

$$M(CO)_6 + OH^- \longrightarrow M(CO)_5CO_2H^-$$

$$M(CO)_5CO_2H^- + OH^- \longrightarrow M(CO)_5H^- + CO_2$$

$$M(CO)_5H^- + H_2O \longrightarrow M(CO)_5H_2 + OH^-$$

$$M(CO)_5H_2 \longrightarrow M(CO)_5 + H_2$$

$$M(CO)_5 + CO \longrightarrow M(CO)_6$$

Scheme 8

It is important to note that because Weiller et al. and Darensbourg et al. performed their studies at much lower temperatures than King et al., it is not clear that their kinetic results are totally applicable to predicting the rate determining step under King's conditions.

Klingler et al.[59] provide the first thermodynamic data concerning equilibria such as shown in reaction (46). They find that nBu_3SnH will react reversibly with CO_2 to give nBu_3SnO_2CH, reaction (47). Over the temperature range of 115°-175°C, they find

$$nBu_3SnH + CO_2 \rightleftharpoons nBu_3SnO_2CH \qquad (47)$$

that for the forward reaction (formate formation), $\Delta H = -18.3$ kcal/mol and $\Delta S = -20.2$ kcal/mol. Whether these thermodynamics are applicable to reaction (46) or related reactions remains to be seen.

Rhodium WGSR Catalyst Systems

Laine et al.[60,61] have briefly explored the WGSR catalysis chemistry of $Rh_6(CO)_{16}$/KOH systems. Although the evidence is incomplete because of the extreme complexity of the cluster equilibria, a very simplified catalytic cycle can be written based on spectroscopically identified species and on the work of Chini et al:[62]

$$Rh_6(CO)_{16} + OH^- \dashrightarrow HRh_6(CO)_{15}^- + CO_2$$

$$2HRh_6(CO)_{15}^- \dashrightarrow H_2 + Rh_{12}(CO)_{30}^{2-}$$

$$Rh_{12}(CO)_{30}^{2-} + 2CO + 2H_2O \dashrightarrow Rh_6(CO)_{16} + H_2 + 2OH^-$$

Kaneda et al [63] have studied $Rh_6(CO)_{16}$/amine WGSR catalyst systems. They find that diamines such as ethylene diamine considerably enhance the activity of the catalyst (see Table 3). They conclude that amine configuration plays a more important role in determining catalyst activity than amine basicity, which suggests that the amines function both as base and as ligands in the WGSR catalytic cycle.

Two drawbacks to using primary or secondary amines as cocatalysts are the well-known formamidation reaction, (48), and reaction (49), both of which can lead to irreversible loss of amine:

$$R_2NH + CO \xrightarrow{\text{catalyst}} R_2NC(=O)H \qquad (48)$$

$$2RNH_2 + CO \xrightarrow{\text{catalyst}} RNH(C=O)HNR + H_2 \qquad (49)$$

Reaction (50), the transalkylation reaction,[53] can change the amine configuration considerably and may also diminish the effectiveness of WGSR catalyst systems that use primary or secondary amine promoters by disproportionating all of the amine into tertiary amine species.

$$2R_2NH \xrightarrow{\text{catalyst}} R_3N + RNH_2 \qquad (50)$$

No detailed studies have been reported to date on the kinetics or mechanisms of the $Rh_6(CO)_{16}$/amine WGSR system, again emphasizing the need for research in the area of amine promoters.

Iridium WGSR Catalyst Systems

Although iridium-catalyzed WGSR systems were described some time ago, detailed kinetic studies have only recently been reported by Vandenberg et al.[31] Their observations lead them to propose the following catalytic cycle:

$$Ir_4(CO)_{12} + OH^- \longrightarrow HIr_4(CO)_{11}^- + CO_2$$

$$HIr_4(CO)_{11}^- + OH^- \longrightarrow [HIr_4(CO)_{11}(CO_2H^{2-}]$$

$$[HIr_4(CO)_{11}(CO_2H^{2-}] \longrightarrow H_2Ir_4(CO)_{11}^{2-} + CO_2$$

$$H_2Ir_4(CO)_{11}^{2-} + H_2O \longrightarrow H_3Ir_4(CO)_{10}^- + OH^-$$

$$H_3Ir_4(CO)_{10}^- + CO \longrightarrow HIr_4(CO)_{11}^- + H_2$$

Scheme 9

At low CO pressures, an irreversible side reaction involving formation of the dimer [reaction (51)] is observed. The dimer exhibits only slight

$$2HIr_4(CO)_{11}^- \longrightarrow H_2 + 2CO + Ir_8(CO)_{20}^{2-} \qquad (51)$$

WGSR catalyst activity. The catalyst system was also found to be active for formate decomposition. Its formate decomposition activity is almost twice that of its WGSR activity under similar conditions. On the basis of this observation, Vandenberg et al. suggest that a viable alternative to the catalytic cycle proposed in Scheme 9 would be a catalytic cycle based on formate decomposition analogous to that shown in Scheme 7. No evidence is presented that permits differentiation between the two possibilities.

The rate-limiting step in iridium cluster catalysis of the WGSR is hydroxide attack on $HIr_4(CO)_{11}^-$, followed by decarboxylation to $H_2Ir_4(CO)_{10}^{2-}$. The apparent activation energy for the overall catalytic process, determined for the temperature range of 90-130°C, is 10.7 kcal/mol.

Mixed-Metal Catalysis of the WGSR

Only three examples of mixed-metal catalysis of the WGSR and the related Reppe reactions have been reported in the literature. One system, described by Ford et al.,[64] involves the use of iron/ruthenium mixtures to catalyze the WGSR. The other two reports concern the use of iron/ruthenium or iron/rhodium mixture for the hydroformylation.[65] As seen in Table 1, the use of mixtures of iron and ruthenium in place of the individual metals in conjunction with OH^- gives catalyst solutions that are more active then identical catalyst solutions made up with the individual metals. At present, there is no firm evidence to provide a rationale for these observations. However, the two most reasonable explanations are that a mixed-metal cluster forms during the reaction and it either undergoes more facile reductive elimination of H_2 than the single metal catalyst intermediates or is more susceptible to OH^- attack. Knox et al.[66] report that the cluster $H_4FeRu_3(CO)_{12}$ loses H_2 more readily than the all-ruthenium analog. In the related Reppe hydroformylations, mixed-metal rate enhancement is observed where essentially no H_2 is produced, thus making the first conclusion unlikely. Gross and Ford[13] find that the order of reactivity for the iron triad clusters, for nucleophilic attack by methoxide, is $Fe_3(CO)_{12} > Ru_3(CO)_{12} > Os_3(CO)_{12}$. They propose that the iron cluster is more reactive than the ruthenium or osmium clusters, because it alone, of the three, contains bridging carbonyl groups. Iron may also cause the formation of bridging carbonyls in the mixed-metal cluster, making it more susceptible to nucleophilic attack by OH^-. This explanation is also reasonable for the iron/ruthenium Reppe hydroformylation catalysts.

WGSR Systems in the Presence of Sulfur Species

In the Introduction, the need for LT sulfur-tolerant WGSR catalysts was emphasized. Very little is currently known about the H_2S tolerance for any of WGSR systems currently described in the literature. King et al.[67] have demonstrated that with the exception of iron, all of the group 8 metal catalysts listed in Table 4 are active catalysts for the

WGSR when Na_2S is substituted for OH^- as the base. Although the rates are low, this important contribution clearly demonstrates the considerable potential available for the use of homogeneous catalysts for industrially important processes.

Darensbourg et al.[68] have briefly studied the reactions of SH^- with $Mn(CO)_6^+$, reaction (52), and with the group 6 metal carbonyls, reaction (53). Although $Mn(CO)_6^+$ does react as expected to give COS and a metal hydride presumably via a metallothiocarboxylic acid, they were unable to observe a similar reaction with the group 6 metal carbonyls. However, their studies do suggest that a metallothiocarboxylic acid intermediate forms during the course of reaction (53). These results could be extremely valuable in developing an understanding of how group 6 metal WGSR catalysts will function in the presence of SH^- generated from H_2 in an OH^--promoted system. Furthermore, it suggests that in King et al.'s original studies it may have been necessary for the added Na_2S to react with water to generate OH^- before WGSR catalysis could proceed. Based on the directives outlined in the Introduction concerning the need for tolerant WGSR catalysts, it seems reasonable that these catalyst systems require further study.

$$Mn(CO)_6^+ + SH^- \longrightarrow HMn(CO)_5 + CO_2 \qquad (52)$$

$$M(CO)_6 + SH^- \longrightarrow M(CO)_5SH^- + CO \qquad (53)$$

$$M = Cr, Mo, W$$

Ford[12] briefly mentions that the iron-ruthenium mixed-metal system rapidly loses iron upon exposure to H_2S; however, extensive studies of the system have yet to be performed to establish whether or not poisoning occurs under industrial conditions.

Table 1. Hydroxide Promoted Catalysis of the WGSR

Catalyst	Solvent	Pressure CO (atm)	Temp. (°C)	Turnovers /24h	Ref.
$Fe(CO)_5$	n-BuOH	28.2	137	16	49
$Fe(CO)_5$	n-BuOH	28.2	181	72	49
$Ru_3(CO)_{12}$	$EtOCH_2CH_2OH$	1	100	2.2	64b
$Ru_3(CO)_{12}$	$EtOCH_2CH_2OH$	1	100	7.4	64b
$Fe_3(CO)_{12}$					
$RuCl_3$	H_2O	0.33	90	3	55
$RuCl_3$	$H_2O/EtOCH_2CH_2OH$	0.33	90	1.4	55
$Ru_3(CO)_{12}$	MeOH	75	135	53	64b
$Os_3(CO)_{12}$	MeOH	75	135	12	64b
$Rh_6(CO)_{16}$	MeOH	75	135	110	64b
$Ir_4(CO)_{12}$	MeOH	75	135	17	64b
$Ir_4(CO)_{12}$	EtOCH2CH2OH	0.9	100	15	31
$Cr(CO)_6$	MeOH	7.8	140	280	49
$Mo(CO)_6$	MeOH	11	145	130	49
$W(CO)_6$	MeOH	7.8	130	140	49

Table 2. Amine-Promoted Catalysis of the WGSR

Catalyst	Solvent /amine	Pressure CO (atm)	Temp. (°C)	Turnovers /10h	Ref.
$Fe(CO)_5$	$THF/(CH_3)_3N$	23.8	110	5	9
$Ru_3(CO)_{12}$	$THF/(CH_3)_3N$	23.8	100	3300	9
$Os_3(CO)_{12}$	$THF/(CH_3)_3N$	23.8	180	270	9
$Rh_6(CO)_{16}$	$THF/(CH_3)_3N$	23.8	125	1700	9
$Ir_4(CO)_{12}$	$THF/(CH_3)_3N$	23.8	125	300	9
$[Pt_3(CO)_6]_2^-$	$THF/(CH_3)_3N$	23.8	125	700	9
$Rh_6(CO)_{16}$	$EtOCH_2CH_2OH/$ $NH_2CH_2CH_2NH_2$	0.8	100	250	63
$Rh_6(CO)_{16}$	$EtOCH_2CH_2OH/$ $NH_2(CH_2)_3NH_2$	0.8	100	76	63
$Rh_6(CO)_{16}$	$EtOCH_2CH_2OH/$ $NH_2(CH_2)_4NH_2$	0.8	100	15	63

Table 3. Amine-Promoted Ruthenium Catalysis of the WGSR

Catalyst	Solvent /amine	Pressure CO (atm)	Temp. (°C)	Turnovers /10h	Ref.
$Ru_3(CO)_{12}$	diglyme/$(CH_3)_3N$	51	100	5740	52
$Ru_3(CO)_{12}$	diglyme/Et_3N	51	100	860	52
$Ru_3(CO)_{12}$	diglyme/Bu_3N	51	100	540	52
$Ru_3(CO)_{12}$	diglyme/pyridine	51	100	300	52
$Ru_3(CO)_{12}$	diglyme/$NH(CH_3)_2$	51	100	2200	52

Table 4. Sulfide-Promoted Catalysis of the WGSR

Catalyst	Solvent/ amine	Pressure CO (atm)	Temp. (°C)	Turnovers /24h	Ref.
$Fe(CO)5$	MeOH	27.2	140	0	67
$Ru_3(CO)_{12}$	MeOH	27.2	160	550	67
$Os_3(CO)_{12}$	MeOH	27.2	160	200	67
$Cr(CO)_6$	MeOH	27.2	160	60	67
$Mo(CO)_6$	MeOH	27.2	160	130	67
$W(CO)_6$	MeOH	27.2	160	180	67

CATALYSIS OF THE WGSR UNDER ACIDIC OR NEUTRAL CONDITIONS

In 1977, the first two examples of homogeneous catalysis of the WGSR using acidic media were reported. One WGSR system, described[10] and patented[69] by Cheng and Eisenberg, uses a rhodium catalyst in acetic acid/HI solution. The second system, reported by Zudin et al.[11] and essentially unnoticed in the literature, involves the use of palladium phosphine complexes in trifluoroacetic acid.

In continuing work on the rhodium system, Baker et al.[70] describe kinetic and mechanistic investigations that suggest the catalytic cycle shown in Scheme 10.

$$Rh(CO)_2I_3^- + HI \rightleftharpoons H_2 + Rh(CO)_2I_4^-$$

$$Rh(CO)_2I_4^- + CO \rightleftharpoons I^- + Rh(CO)_3I_3$$

$$Rh(CO)_3I_3 + H_2O \rightleftharpoons H^+ + Rh(CO)_2I_3(CO_2H)^-$$

$$Rh(CO)_2I_3(CO_2H)^- \dashrightarrow HI + Rh(CO)_2I_2^- + CO_2$$

$$Rh(CO)_2I_2^- + HI \rightleftharpoons HRh(CO)_2I_3^-$$

or

$$Rh(CO)_2I_3(CO_2H)^- \dashrightarrow HRh(CO)_2I_3^- + CO_2$$

and

$$Rh(CO)_2I_4^- + I^- \rightleftharpoons CO + Rh(CO)I_5^-$$

Scheme 10

Baker et al. have spectroscopically identified the species, $Rh(CO)_2I_2^-$, $Rh(CO)I_5^-$, $Rh(CO)I_4^-$, cis and trans $Rh(CO)_2I_4^-$ in solution and have isolated and characterized $Rh(CO)_2I_2^-$. An Arrhenius plot of the WGSR catalysis over the range of 55°-100°C reveals unusual behavior, giving an Ea of 25.8 kcal/mol between 55°-60°C and an Ea of 9.3 kcal/mol above this range. The authors argue that there is a change in the rate-limiting step at higher temperatures. Furthermore, they propose that at low temperatures the rate-limiting step is oxidation of Rh(I) by HI to Rh(III), and at high temperatures the rate-limiting step is reduction of a Rh(III) carbonyl species with concomitant release of CO_2.

These observations are similar, but not completely in accord with, the work of Singleton and Forster, who studied the same system but under more forcing conditions.[71,72] The major difference appears to be that at higher temperatures and pressures, WGSR is nearly independent of CO pressure at high acidity, but is inversely affected by changes in CO pressure at low acidities. These observations are the opposite of Cheng and Eisenberg, whose work was performed at subatmospheric pressures.

More recently, Marnot et al.[73,74] have identified another rhodium WGSR catalyst that operates under acidic conditions. These workers report that rhodium and iridium 2,2'-bipyridine (bipy) or related ligand complexes such as $Rh(bipy)_2(H_2O)^{3+}$, $Rh(L)_2(H_2O)^{3+}$, and $Ir(L)_2(H_2O)^{3+}$ where L = 4,7-diphenyl-1,10-phenanthroline disodium sulfonate(Phen-S), or L = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline disodium sulfonate (2,9-dmphen-S), are active WGSR catalysts under acidic conditions. Aside from the catalyst activities listed in Table 5, no mechanistic work has as yet been reported. However, the authors do suggest that in the case of iridium, the much higher activity of the 2,9-dimethylphen complexes as compared with the simple phen complexes can be ascribed to steric hindrance between the methyl groups that prevents the formation of stable square planar, inactive bis(dimethylphen) complexes.

In a somewhat related study, Alessio et al.[75] have examined the WGSR catalyst activity of mixtures of $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, and $Ir_4(CO)_{12}$ with the same types of 2,2'-bipyridyl (bipy) and phenanthroline (phen) ligands as Marnot et al.; however, they have examined these systems only in the presence of nitrobenzene. Their objective was to examine the activity of these systems for the catalytic reduction of nitrobenzene to aniline. In these studies only the ruthenium system was active, with the phen/Ru system exhibiting greater activity than the bipy/Ru system under the conditions studied. Unfortunately, no attempts appear to have been made to test these systems for WGSR activity.

Mahajan et al.[76] have reported studies of polypyridine rhodium complexes that provide some mechanistic explanations about the WGSR catalysis systems originally described by Marnot. In their studies of rhodium WGSR catalysis in the presence of phen, bipy, pyrazine, and 4,4'dimethyl-bipy, they were able to obtain spectroscopic and kinetic evidence suggesting that the active catalyst species under acidic conditions is likely to be $Rh(bipy)_2(CO)H^{2+}$. Scheme 11 is suggested as a reasonable catalytic cycle.

$$Rh(bipy)_2(CO)H^{2+} + H_2O \longrightarrow [Rh(bipy)_2(CO_2H)H^{2+}] + H^+$$

$$[Rh(bipy)_2(CO_2H)H^{2+}] \longrightarrow Rh(bipy)_2H_2^+ + CO_2$$

$$Rh(bipy)_2(CO)H_2^+ \longrightarrow Rh(bipy)_2^+ + H_2$$

$$Rh(bipy)_2^+ + CO \longrightarrow Rh(bipy)_2(CO)^+$$

$$Rh(bipy)_2(CO)^+ + H^+ \longrightarrow Rh(bipy)_2(CO)H^{2+}$$

Scheme 11

The system illustrated in Scheme 11 shows optimal activity at pH 3, leading the authors to suggest that metallocarboxylic acid formation or decarboxylation is the slow step in the reaction. They also conclude that the active catalyst species is a Rh^{3+} complex formed in the protonation step (see Scheme 11). Mahajan et al. also find that under CO, there are significant equilibria between the $Rh(bipy)_2^+$ species and free bipy. Interestingly, formation of free bipy is enhanced by increasing the pH, contrary to what might be expected. These results are extremely pertinent to those of Marnot et al., because the latter authors find that the ligand-to-metal ratios in their systems strongly affect the overall WGSR catalyst activities and that different ratios are preferable for optimal rhodium activity (2:1) and optimal iridium activity (1:1).

In the platinum metals group, both palladium and platinum complexes have been shown to be active WGSR catalysts in the presence of acid cocatalysts. Likholobov et al.[77] have followed up on the original report by Zudin et al.[11] and propose the catalytic cycle shown in Scheme 12 for Ph_3P-complexed palladium WGSR catalysis system run in 20% aqueous trifluoroacetic acid.

$$P_2PdX_2 + CO \rightleftharpoons [P_2Pd(X)CO]^+ + X^-$$

$$[P_2Pd(X)CO]^+ + H_2O \rightleftharpoons [P_2Pd(H_2O)CO]^{2+} + X^-$$

$$[P_2Pd(H_2O)CO]^{2+} + H^2O \rightleftharpoons [P_2Pd(OH)CO]^+ + H_3O^+$$

$$[P_2Pd(OH)CO]^+ + X^- \dashrightarrow P_2Pd(CO_2H)X$$

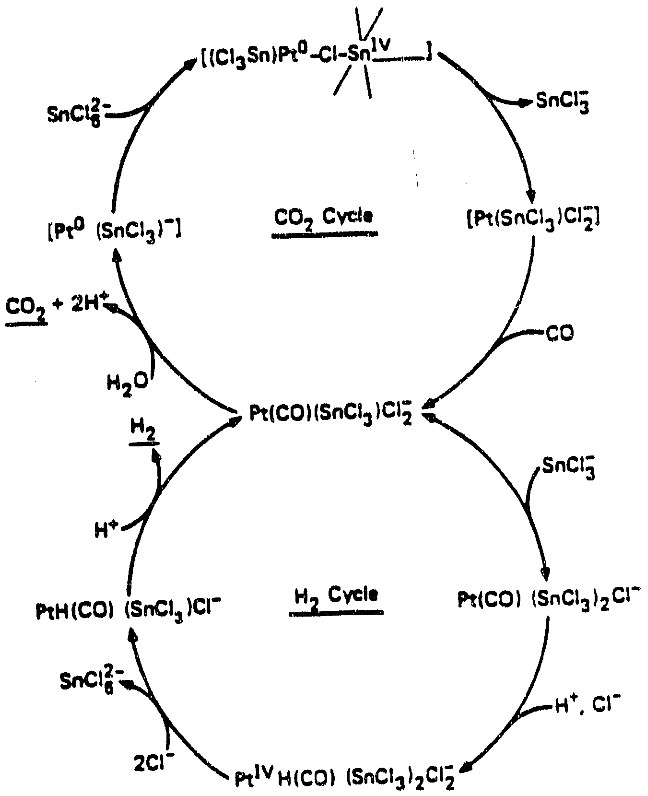
$$P_2Pd(CO_2H)X \dashrightarrow P_2PdHX + CO_2 \quad P_2PdHX + HX \dashrightarrow P2PdX_2 + H_2$$

$$P = Ph_3P,\ HX= CF_3CO_2H$$

Scheme 12

In view of the work of Cariati et al.,[42b] reaction (37), the mechanism proposed in Scheme 12 appears quite reasonable. More recently, Giannoccaro et al.[78] have reported the existence of nickel-based WGSR systems similar to those of Zudhin et al. The Giannoccaro work demonstrates that NiX_2P_2 complexes where X = Cl or Br and P = basic phosphines such as PR_3 (R = Me, Et, Bu, iPr) will catalyze the WGSR under 1 atm of CO at 90°-160°C in the presence of up to five equivalents of acid (see Table 5). The WGSR mechanism proposed is essentially that of Zudin et al., although in the nickel system it is possible to observe and/or isolate species such as $(CO)_2NiP_2$ and $(CO)X_2NiP_2$, which are not stable in the palladium system. The Giannoccaro systems are not very stable, giving metal and or inactive systems after only a few days of activity.

In addition to their studies on rhodium WGSR catalysis in acid media, Cheng and Eisenberg also report[79] that mixtures of platinum chloride and tin chloride are active WGSR catalysts in an acetic acid/HCl solvent system. They report that a spectroscopic analysis of the active catalyst solution shows the presence of both $PtCl(CO)(SnCl_3)^{2-}$ and $PtCl_2(CO)(SnCl_3)^-$. Preliminary kinetic and mechanistic studies allow them to suggest the catalytic cycles shown in Scheme 13.



Scheme 13

These researchers conclude that the Sn(II)/Sn(IV) redox couple is actively involved in the observed reaction chemistry. The H_2-forming catalytic cycle results in the oxidation of Sn(II) to Sn(IV), with coproduction of H_2, and CO is oxidized to CO_2 concurrent with the reduction of Sn(IV) to Sn(II).

Ford et al.[80,81] have reported that ruthenium carbonyl will also catalyze the WGSR under acidic conditions. Thus, mixtures of either $Ru_3(CO)_{12}$ or $H_4Ru_4(CO)_{12}$ in a solvent system of H_2SO_4 in diglyme or ethoxyethanol give the same active WGSR catalyst system that functions at 100°C, as shown in Table 5. The system is first- order-dependent on both ruthenium concentration and CO pressure (below 1 atm), but showed little or no dependence on acidity or water concentration over the ranges studied. Above 1 atmosphere of CO, there was a considerable decrease in reactivity that was at least partially due to the enhanced formation of $Ru_3(CO)_{12}$, which sublimed out of the reaction solution. The apparent activation energy for WGSR catalysis was 14 kcal/mol over the temperature range of 90°-140°C. From kinetic and spectroscopic studies Yarrow et al.[81] conclude that the reduced anionic species [e.g., $HRu_2(CO)_8^-$], previously proposed as the likely participants in the WGSR catalytic cycle, do not form. They now propose a catalytic cycle based on solvent-substituted ruthenium dimers, as seen in Scheme 14:

$$HRu_2(CO)_{9-x}(OR_2)_x{}^+ + CO \dashrightarrow HRu_2(CO)_{10-x}(OR_2)_{x-1}{}^+ + OR_2$$

$$HRu_2(CO)_{10-x}(OR_2)_{x-1}{}^+ + H_2O \dashrightarrow HRu_2(CO)_{9-x}(CO_2H)(OR_2)_{x-1} + H^+$$

$$HRu_2(CO)_{9-x}(CO_2H)(OR_2)_{x-1} \dashrightarrow H_2Ru_2(CO)_{9-x}(OR_2)_{x-1} + CO_2$$

$$H_2Ru_2(CO)_{9-x}(OR_2)_{x-1} + OR_2 \dashrightarrow Ru_2(CO)_{9-x}(OR_2)_x + H_2$$

$$Ru_2(CO)_{9-x}(OR_2)_x + H^+ \dashrightarrow HRu_2(CO)_{9-x}(OR_2)_x{}^+$$

Scheme 14

Yarrow et al. examined the possibility of enhancing the activity of the ruthenium system under acidic conditions through the addition of $Fe(CO)_5$, which significantly promotes ruthenium WGSR catalysis in alkaline solution. Unfortunately no effect was observed. In addition, they also find that $Ir_4(CO)_{12}$, which is active in alkaline solutions, shows no WGSR activity under acidic conditions.

Kaspar et al.[82] describe an active WGSR system based on rhodium/phosphine catalyst species that function in dioxane/water mixtures, both in base and in acid. The acid-promoted catalyst systems can be much more active than the base-promoted systems. The data for the catalyst deriving from the precursor complex $Rh(COD)(PPh_3S)_2^-$, where PPh_3S is meta-monosulfonated triphenylphosphine, are listed in Table 5. The authors are hesitant to propose a mechanism for their observations because of the unusual results and the limited amount of data. However, it seems reasonable to suggest that the electron-rich metal might promote reactions such as suggested above, in which CO binding is followed by protonation of the complex and subsequent nucleophilic attack of water on the protonated complex to give a metallocarboxylic acid, and so forth.

Only three WGSR catalyst systems have been described wherein it has not been necessary to activate and maintain the catalytic reactivity of the system through addition of either base or acid. One reaction system uses platinum phosphine catalysts and the other two systems use rhodium phosphine catalysts. The one platinum system and one of the rhodium systems were described by Otsuka et al.[24,33] These investigators report catalyst systems that function by H_2O activation rather than CO activation, which appears to be a requirement of all of the systems described above.

Yoshida et al.[24] reported in 1978 that platinum phosphine complexes of the type PtL_3, where L = $P(iPr)_3$, or PEt_3 could be used to catalyze the WGSR under mild conditions in a number of solvents. They proposed the catalytic cycle shown in Scheme 15 to account for their observations.

$$PtL_3 \rightleftharpoons PtL_2 + L$$

$$PtL_2 + H_2O \rightleftharpoons PtH(OH)L_2$$

$$PtH(OH)L_2 + S \rightleftharpoons [PtH(S)L_2]OH$$

$$[PtH(S)L_2]OH + CO \rightleftharpoons [PtH(CO)L_2]OH + S$$

$$PtH(CO)L_2]OH \rightleftharpoons [PtH(CO_2H)L_2]$$

$$[PtH(CO_2H)L_2] \rightleftharpoons PtH_2L_2 + CO_2$$

$$PtH_2L_2 + L \rightleftharpoons PtL_3 + H_2$$

Scheme 15

Complexes such as trans-$PtH(CO_2K)L_2$, trans-$PtH(CO_2CH_3)L_2$, and trans-PtH_2L_2 were prepared as examples of the proposed intermediate, and the latter complex was independently shown to catalyze the WGSR.

In the neutral rhodium system[33] the complex $RhHL_3$, where L = $P(iPr)_3$ or $P(c-C_6H_{11})_3$, was found to be an active WGSR catalyst in either acetone, THF, or pyridine, with the pyridine (py)-solvated reaction having the higher catalyst activity. The following reaction sequence is proposed for the catalytic cycle:

$$RhHL_3 + H_2O + py \rightleftharpoons [RhH_2(py)_2L_2]OH$$

$$[RhH_2(py)_2L_2]OH + CO \rightleftharpoons [Rh(CO)(py)_2L_2]OH + H_2$$

$$[R(CO)(py)_2L_2]OH + CO \rightleftharpoons [Rh(CO)_2(py)L_2]OH + py$$

$$[Rh(CO)_2(py)L_2]OH \dashrightarrow [Rh(CO)(CO_2H)(py)L_2]$$

$$Rh(CO)(CO_2H)(py)_2L_2 + CO \dashrightarrow RhH(CO)_2L_2 + CO_2 + py$$

$$RhH(CO)_2L_2 + H_2O \rightleftharpoons [RhH_2(CO)L_2]OH$$

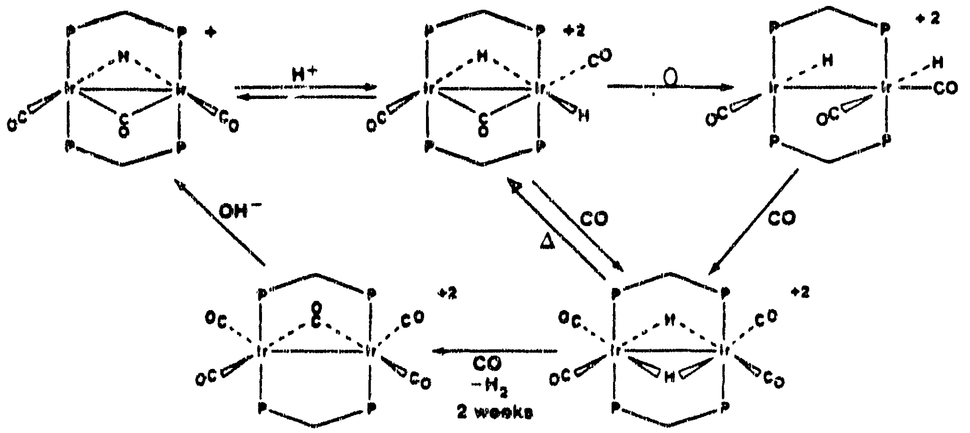
$$[RhH_2(CO)L_2]OH + py \rightleftharpoons [Rh(CO)(py)L_2]OH + H_2$$

Scheme 16

The complexes trans-$[Rh(CO)(py)L_2]^+$ and $[RhH_2(py)_2L_2]OH$ can be isolated when pyridine is used as solvent. When acetone is the solvent, $RhH(CO)_2L_2$ can be isolated from the reaction solutions, as can the complex $Rh_2(CO)_4L_2$. The majority of these complexes were shown spectroscopically or in separate reaction studies to react as depicted in Scheme 16.

A recent set of papers describe the use of DPM (bisdiphenylphosphinomethane) ligands to form cluster complexes of rhodium,[83,84] iridium,[85] and platinum[86,87] that all promote the WGSR under neutral conditions and that do not require the addition of acid or base. The earliest report was that of Kubiak and Eisenberg,[83] who mentioned that the complex, $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(DPM)_2]^+$ was an active WGSR catalyst under neutral conditions. In a later paper,[84] they report that in the presence of one equivalent of toluenesulfonic acid and two equivalents of a salt (e.g., LiX, X = Cl, Br), the catalyst system was most active at near neutral pH. The presence of carboxylate salts, including formate salts, diminished catalyst activity. Additionally, the catalyst system deactivated over time, under all conditions studied. The former observation suggests that formates do not participate in the catalytic cycle. The authors discuss a catalytic cycle based on formate decomposition but their data, specifically with regard to the inhibitory effect of formate, make this cycle suspect; however, their discussions do suggest another type of catalytic cycle akin to the one proposed later by Sutherland and Cowie[85] (Scheme 17).

Most recently, Sutherland and Cowie[85] have extended the work of Kubiak and Eisenberg through studies of both the original rhodium system and its iridium analog. Their work was initially based on the hypothesis that a bridging hydroxide would be a likely intermediate in the catalytic cycle; however, they disprove this hypothesis. Sutherland and Cowie suggest a potential catalytic cycle based on their iridium studies (Scheme 17) that could be applicable to the rhodium system; however, the step resulting in loss of H_2 from the iridium analog requires two weeks!



Scheme 17

Puddephatt et al.[86,87] report that $[Pt_2H_2(mu\text{-}H)(mu\text{-}DPM)_2]PF_6$ is a precursor to a quite active WGSR catalyst (see Table 5) whose activity is strongly dependent on CO pressure. They suggest the catalytic cycle shown in Scheme 18.

$$Pt_2H_2(\mu\text{-}DPM)_2^+ + CO \text{ ---------> } Pt_2HCO(\mu\text{-}DPM)_2^+ + H_2$$

$$Pt_2HCO(\mu\text{-}DPM)_2^+ + OH^- \text{ --------> } Pt_2H(CO_2H)(\mu\text{-}DPM)_2$$

$$Pt_2H(CO_2H)(\mu\text{-}DPM)_2 + H^+ \text{ ---------> } Pt_2H_2(\mu\text{-}H)(\mu\text{-}DPM)_2 + CO_2$$

Scheme 18

The proposed cycle in Scheme 18 raises some questions. For example, if the work is conducted in a neutral solution, then what is the source of hydroxide. Sutherland and Cowie's work suggests that an intermediate bridging hydroxide might form upon reaction of the starting complex with water. If not, then it is known that carbonyls bound to positively charged metal complexes can react directly with water to form metallo-carboxylic acids. These possible alternatives to the Scheme 18 cycle may have been overlooked.

CANDIDATE CATALYSTS FOR SULFER TOLERANT WGSR CATALYSIS

As shown by the revised review presented in this report, considerable new work has been done in the area of homogeneous catalysis of the WGSR. However, the most of the work is quite academic in nature and not particularly useful in providing directions for our choice of candidate sulfur-tolerant WGSR catalysts or for the reaction conditions to be studied after selection. For example, more than 20 different systems studied used WGSR catalysis conditions with CO pressures ranging from 500 torr to less than 10 atm. These do not in any way approach those required under industrial conditions and can often lead to incorrect assumptions when extrapolations are made. For example, References 10 and 69 deal with systems at below 0.9 atm of CO, and the mechanistic conclusions differ from those obtained in studies of the same system at much higher pressures as performed in References 71 and

Table 5. Catalysis of the WGSR Under Acid or Neutral Conditions

Catalyst	Solvent	Pressure CO (atm)	Temp. (°C)	Turnovers /24h	Ref.
$[Rh(CO)_2Cl]_2$	HI/HOAc	0.53	100	34	10
$RhCl_3.3H_2O$/ 2.2,9-dmphen-S	H_2O	1.0	100	550	73
$IrCl_3.3H_2O$/ 2.2,9-dmphen-S	H_2O	1.0	100	225	73
$IrCl_3.3H_2O$/ bipy-S	H_2O	1.0	100	9.6	73
$Pd(PPh_3)_4$	CF_3CO_2H	1.0	70	60	77
$NiCl_2(PMe_3)_2$	EtOH	1.0	130	0.016	78
$NiCl_2(PMe_3)_2$	EtOH	1.0	160	0.03	78
K_2PrCl_4/ $SnCl_4.5H_2O$	HCl/HOAc	0.53	88	25	79
$Ru_3(CO)_{12}$	H_2SO_4/diglyme	1.0	100	60	81
$Rh(COD)PPh_3S$	Dioxane/H_2O				
	pH =11	30	155	168	82
	pH = 8	30	155	144	82
	pH = 6	30	155	84	82
	pH = 4	30	155	432	82
	pH = 2	30	155	3050	82
$Pt[P(iPr)_3]_3$	acetone	19.3	100	125	24
$RhH[P(iPr)_3]_3$	acetone	19.3	100	672	33
$RhH[P(iPr)_3]_3$	pyridine	19.3	100	792	33
$Rh_2(H)(CO)_3(DPPM)$+ PrOH	1.0	90	60	84	
$Rh_2(\mu\text{-}CO)(CO)_2)(\mu\text{-}DPM)_2$	0.66	90	14	85	
$Pt_2H_2(\mu\text{-}H)(\mu\text{-}DPM)_2]PF_6$	3.0	100	90	86	

72. In the one paper (Reference 67) that attempts to evaluate the effects of sulfur on WGSR catalysis, the system is so overloaded with sulfide that it is not clear what activities are possible, especially in view of the recent paper by Darensbourg.[68] Other potential problems that have provided some guidelines that define unsuitable catalysts include the following:

- Cost of catalyst. This eliminates all of the third-row metals except tungsten and makes rhodium a borderline choice. This is especially true of the $Rh(iPr_3P)_3$ catalysts of Otsuka et al.[24,33]
- High acidity or acetic acid solvents (pH 2 or less). WGSR catalysis under these conditions is likely to be extremely corrosive and destructive toward reactor and analytical systems, in addition to being environmentally hazardous.
- High volatility solvents and promoters (e.g., low boiling alcohols and amines). If special care is not taken to choose the proper solvent system for an industrial process, there could be considerable loss of material through volatilization, making the process too costly.

On the basis of these guidelines as well as the results recorded in Tables 1 through 5, we have chosen the following catalysts and basic systems to study:

(1)-(3) Predicated on King et al.'s work[67] with group 6 metal carbonyls [$Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$] showing that they are active in alcoholic base containing considerable amounts of sulfide, all three metals should be evaluated under coal gas/industrial WGSR conditions.

(4) The simple $Ru_3(CO)_{12}$/alcohol/hydroxide system was also shown by King et al.[67] to be sulfur tolerant; because we have examined it in great detail over the past ten years, it represents a useful, relatively well understood standard for gauging the other catalyst systems.

(5) The mixed-metal $Fe(CO)_5/Ru_3(CO)_{12}$/alcohol/hydroxide catalyst system is another system that we have examined under many conditions over the past decade. It exhibits exceptional activity under a variety of conditions. One obvious negative aspect is that King et al.[67] found iron to deactivate in the presence of sulfur, and Ford[12] also

mentions that the mixed-metal system is susceptible to sulfur poisoning. However, King et al. used 26 equivalents of sulfide per equivalent of $Fe(CO)_5$ and Ford used 0.9 atm of CO. Consequently, neither has tried conditions that might prevent the formation of the iron carbonyl deactivation product, $Fe_3(CO)_9S_2$. These conditions would be "relatively low" sulfur and/or high pressures of CO (30 atm). It may be possible to alleviate the problem of formation of $Fe_3(CO)_9S_2$ because of the presence of ruthenium carbonyl species and/or higher CO pressure. If it is possible to prevent iron precipitation, then we will also try to evaluate the $Fe(CO)_5/Rh_6(CO)_{16}$/alcohol/hydroxide system, which is even more active than the ruthenium system, but more costly.

(6) We have observed that the ruthenium/amine systems are likely to suffer from degradation/and or volatility of the amine. In other studies we have observed that $(Me_2N)_2$ N,N,N'-dimethylpiperazine and tetramethylethylene diamine are rather unreactive in the presence of $Ru_3(CO)_{12}$ under CO; therefore, we will attempt to determine the efficacy of a ruthenium/amine system as one of our candidates.

(7) The work of Marnot et al.[73] indicates that sulfonated rhodium/phenanthroline WGSR systems are quite active. Therefore, we plan to test such a system as a candidate catalyst for a sulfur-tolerant WGSR catalyst.

(8) The work of Alessio et al. suggests that the related ruthenium/phenanthroline system could be an effective WGSR catalyst; we plan to examine such a system for sulfur tolerance.

(9) Marnot et al. also mention, without any details, that cobalt/phenanthroline complexes also catalyze the WGSR; we plan to test the efficacy of this system.

(10) The work of Kaspar et al.[82] with the meta-monosulfonated triphenyl phosphine complexes of rhodium gives a catalyst that is extremely active at pH = 2. Although the acidity is quite high, the activity is so high relative to other catalyst systems available that this system must be evaluated under proper conditions with the idea that selective modifications may reduce the acidity requirements.

As we begin to test these catalyst systems, there is a reasonable possibility that some will fail immediately. If this should happen, then we plan to substitute one or two new systems either from the list of systems in Tables 1 through 5 or based on new developments published in the literature.

Finally, we have not outlined the exact solvent systems nor the exact reaction conditions that we will use to evaluate these ten candidate catalyst systems. Such choices are planned as part of the Task 2 efforts, which we will begin shortly.

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