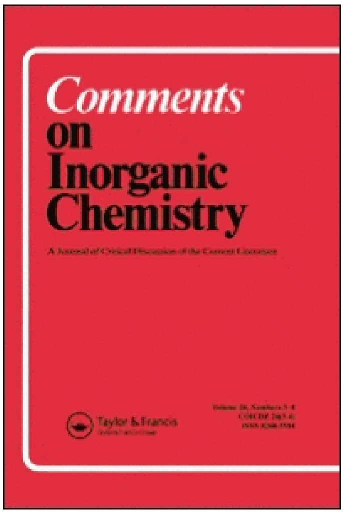

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On the Importance of Catalyst Oxidation State in Homogeneous Syngas Conversion

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On the Importance of Catalyst Oxidation State in Homogeneous Syngas Conversion

Homogeneous catalytic systems for CO hydrogenation often include promoters which improve the activity or selectivity for a certain product. A major function of these components is apparently to maintain the organometallic catalyst species in the appropriate oxidation state. This can be accomplished, for example, by coordination to the metal center or by a reductive deprotonation process. Amounts of promoter added are often critical because an excess can result in overreduction or overoxidation of the metal catalyst component.

INTRODUCTION

Certain additives or "promoters" are often found beneficial in homogeneously catalyzed reactions involving synthesis gas.[1] Some promoters actually function as co-catalysts and are involved in organic transformations independent of the metal catalyst. Other promoters are postulated to act as ligands, altering the reactivity of the catalyst by coordination to the metal center. In other reactions the promoters appear to be important because of a property less widely recognized—their ability to convert the catalytically important metal to a favorable oxidation state for the reaction of interest. Conversely, poisons or inhibitors for catalytic processes can also function by converting an active metal complex to an oxidation state unsuitable for catalysis. In addition to materials added in small amounts to catalytic reactions, solvents for these reactions can also serve as promoters or, indeed, as inhibitors.

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Reactions performed in the presence of hydrogen involve metals in low oxidation states because of the reducing character of this reagent. Nevertheless, for metal complexes with catalytic properties, more than one oxidation state is usually available under reaction conditions, and there is some flexibility in determining which oxidation state predominates. Consider the hypothetical reaction in Eq. (1) between molecular hydrogen and a divalent metal complex, L_nMX_2 (L = ligand).

$$L_nMX_2 + H_2 \rightleftharpoons L_mM + 2\,HX \tag{1}$$

The metal is shown as being reduced from the divalent to the zerovalent state in an equilibrium process. A related example is shown in Eq. (2), in which a metal hydride undergoes reductive deprotonation by a base, X^-.

$$L_nMH_2 + X^- \rightleftharpoons [L_mMH]^- + HX \tag{2}$$

The position of the equilibria in reversible reactions such as Eqs. (1) and (2) will be determined by a number of factors, including the identity of the metal and the ligands surrounding it, the acid strength of the "HX," and the concentrations of reactants, including hydrogen and the "HX" formed. It can be seen that the addition to Eqs. (1) or (2) of reagents such as HX or X^- (or additives which influence the concentrations of these species) will shift these equilibria. Since metal complexes in different oxidation states exhibit different catalytic activities and selectivities, it is to be expected that changing the concentrations of X^- or HX will alter the catalytic behavior of the system. By this mechanism, certain acids and bases can act as oxidizing or reducing agents in such systems, and can affect the catalytic properties of the system by influencing the concentrations of the active metal species. Several reactions involving syngas conversion will be considered here, and the probable roles of promoters and solvents in redox processes will be discussed.

COBALT CATALYSTS

Cobalt carbonyl complexes catalyze the conversion of synthesis gas to oxygenated hydrocarbons, including methanol, methyl formate, ethanol, and ethylene glycol.[1-10] The active catalytic species in the system has been shown to be the acidic hydride, $HCo(CO)_4$, which is normally the predominant species in solution.[2,11] The reaction is believed to be initiated by an intramolecular hydrogen atom migration from the metal atom to a carbonyl ligand, producing a reactive formyl intermediate, as shown in Eq. (3). Addition of further hydrogen to the metal center and to the reactive ligand will continue the reduction process leading to organic products.[1]

$$(CO)_4CoH \rightleftharpoons (CO)_3Co{-}CHO \qquad (3)$$

This reaction has been carried out in a variety of solvents, including heptane, benzene, 1,4-dioxane,2,2,2-trifluoroethanol, glymes, and N-methylpyrrolidone. It has been noted that the reaction rate is considerably enhanced in solvents with higher dielectric constants, suggests that these solvents more effectively stabilize a polar transition state or intermediate.[3] However, the solvent with the highest dielectric constant in the above list, N-methylpyrrolidone, provides a very low rate for the catalytic reaction.[6]

This amide solvent is also considerable more basic (pK_{BH^+} -0.9) that any of the other solvents listed. Since the active cobalt hydride is quite acidic ($pK_a \sim 1$), it is expected that a substantial amount of this hydride will be deprotonated by the basic solvent, as shown in Eq. (4).

$$(CO)_4CoH + B \rightleftharpoons [(CO)_4Co]^- + BH^+ \qquad (4)$$

The amide solvent can be considered an inhibitor in this case, since it retards the catalytic process by converting some of the active catalyst to an inactive form. In a formal sense, it does so by acting as a reducing agent. The cobalt hydride in Eq. (4) contains Co(I), whereas the anionic product contains Co(I^-). It is evident that one would wish to maintain the cobalt in this catalytic system mainly in the Co(I) oxidation state.

RHODIUM CATALYSTS

Catalytic systems based on rhodium also hydrogenate carbon monoxide to oxygenates, mainly methanol and ethylene glycol.[1,12-15] The characteristics of this system are quite different, however, from those of the cobalt system. When a neutral rhodium complex such as $Rh(CO)_2(acac)$ is employed as a catalyst precursor with no promoter in a nonbasic solvent, it exhibits very little catalytic activity. Such solutions monitored by high-pressure infrared spectroscopy exhibit an absorption characteristic of $Rh_6(CO)_{16}$. However, addition of any of several types of basic promoters causes much improved activity.[14] These promoters can be amines, salts with anions of varying basicity, or solvents with basic character. Thus, N-methylpyrrolidone as a solvent is an excellent promoter for this rhodium catalytic system, in contrast with the cobalt system.

The addition of weak bases or the proper amount of strong bases to the rhodium system apparently serves to reduce the predominant rhodium species in the system from Rh(0) (as in $Rh_6(CO)_{16}$) to a lower oxidation state, analogous to the cobalt reaction shown in Eq. (4). However, in this case it is the lower oxidation state which is the more active. Nevertheless, addition of an excess of base or reducing agent causes diminished activity. In such solutions the $Rh(I^-)$ species, $[Rh(CO)_4]^-$, is observed as the predominant species.[16] It therefore appears that the optimum average oxidation state for this system is between Rh(0) and $Rh(I^-)$. This effect of promoter concentration on the selectivity of a rhodium system is illustrated in Fig. 1.

Similar effects are observed for many amine promoters, including highly sterically hindered amines whose only plausible role is that of a proton base. Amines which have a pK_{BH^+} of 5 or greater appear to be essentially stoichiometrically protonated, since addition of amounts greater than an amine/Rh ratio of 0.1–0.5 either cause no further change or bring about a decline in catalytic activity. More weakly basic amines, however, require a higher amine/Rh ratio to effect optimum activity, and progressively weaker bases are required in greater amounts.[17]

Examination of rhodium catalytic solutions with good activity shows the presence of species such as $[Rh_5(CO)_{15}]^-$,$[Rh_{12}(CO)_{30}]^{2-}$, and $[Rh_{13}(CO)_{24}H_x]^{(5-x)-}$ $(x = 2,3)$.[18,19] The identity of the clusters present depends on conditions such as temperature and pressure, but it can be seen that these species contain rhodium in an average oxidation state between Rh(0) and $Rh(I^-)$, consistent with the observations discussed above. It is not known whether these species are themselves the catalysts for syngas conversion, or are simply the stable repositories of more active catalyst species.

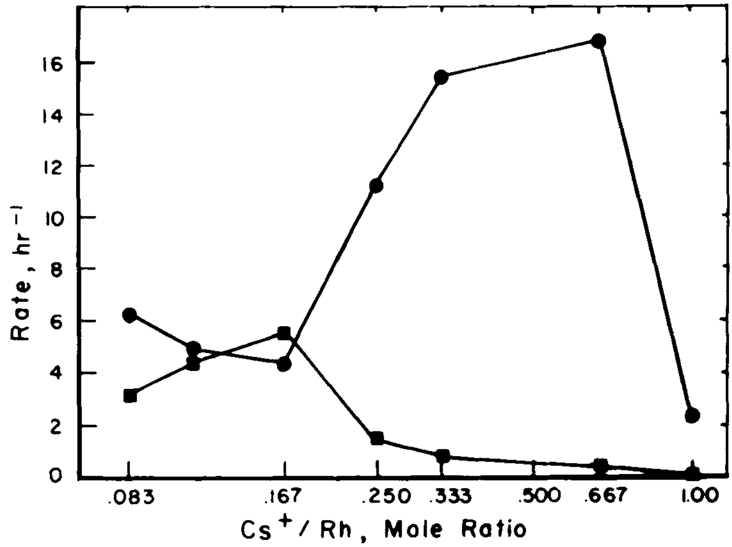

FIGURE 1 Effect of cesium formate promoter concentration on formation rate of methanol (●) and ethylene glycol (■) by a rhodium catalyst (Ref. 1).

HALIDE-PROMOTED RUTHENIUM CATALYSTS

In studies of ruthenium catalysts for conversion of H_2/CO to oxygenates, we observed that alkali metal halide salts, especially iodides, added to $Ru_3(CO)_{12}$ catalyst precursor caused enhanced catalytic activity.[1,20–22] These solutions were observed, by IR spectroscopy of the metal carbonyl region, to contain a reduced complex, $[HRu_3(CO)_{11}]^-$, both under reaction conditions and under ambient conditions after catalysis. The identity of the corresponding oxidized product was at first unknown. These batch reactions were often carried out in an inert, neutral solvent, sulfolane, and HI (a possible oxidation product) could not have escaped during reaction. It was also observed that salts of $[HRu_3(CO)_{11}]^-$ prepared in the laboratory did not possess the same activity as catalytic solutions obtained as above. Some understanding was gained when we found infrared spectroscopic evidence for a second ruthenium complex in these catalytic solutions in smaller amounts. This complex is an oxidized product, $[Ru(CO)_3I_3]^-$, and the balanced equation describing its formation in a catalytic reaction is given in Eq. (5).

$$7/3\ Ru_3(CO)_{12} + 3I^- + H_2 \rightarrow 2[HRu_3(CO)_{11}]^- + [Ru(CO)_3I_3]^- + 3\ CO \quad (5)$$

Since the number of CO ligands in the reduced product is more than seven times greater than that in the oxidized product, the initial difficulty in spectroscopically detecting the latter compound is understandable.

The reaction of Eq. (5) can be presented as a combination of two simpler redox reactions, based on further experimental results. It was found[22] that $Ru_3(CO)_{12}$ reacts with H_2 in the presence of a base such as an amine or phosphine oxide to form $[HRu_3(CO)_{11}]^-$ and a proton (which is stabilized by the added base) as shown in Eq. (6). It was also found[22] that $Ru_3(CO)_{12}$ reacts with HI and excess iodide ion to form the oxidized product, as shown in Eq. (7).

$$Ru_3(CO)_{12} + H_2 + B \rightarrow [HRu_3(CO)_{11}]^- + BH^+ + CO \quad (6)$$

$$1/3\ Ru_3(CO)_{12} + 2\ HI + I^- \rightarrow [Ru(CO)_3I_3]^- + H_2 + CO \quad (7)$$

One might then expect that addition of HI or a base, B, to a reaction mixture such as that shown in Eq. (5) would cause increased formation of $[Ru(CO)_3I_3]^-$ or $[HRu_3(CO)_{11}]^-$, respectively, and this is indeed observed. However, the optimum catalytic activity is observed with a ratio of these two complexes close to that seen in Eq. (5),[20] so the addition of acids or bases to this mixture usually inhibits rather than promotes catalysis.

The observation that both $[HRu_3(CO)_{11}]^-$ and $[Ru(CO)_3I_3]^-$ are found in the most active catalytic solutions indicates that both are involved in the catalytic process. Kinetic evidence supports the equilibrium conversion of these complexes to the more reactive species $[HRu(CO)_4]^-$ and $Ru(CO)_4I_2$, respectively, under catalytic conditions.[21] Reaction of these species by intermolecular hydride transfer from the reduced complex, $[HRu(CO)_4]^-$, to an electrophilic carbonyl ligand on the oxidized complex is proposed to be the first step in the hydrogenation process.[21,23] In this scheme, the reduced species is necessary to provide a nucleophilic hydride ligand, and the oxidized species is required for its highly electrophilic carbonyl ligands.

The necessity of having a certain proportion of oxidized and reduced ruthenium complexes in active catalytic solutions demonstrates the importance of balancing the oxidation state of the system. Fortuitously, the preparation of a catalytic solution in an inert, neutral solvent by the reaction of Eq. (5) yields a suitable mixture of these complexes. Strong acids or bases added to such a system act as inhibitors because they alter the oxidation state of the system and change the balance of oxidized and reduced complexes. However, if one uses a ruthenium complex in a higher oxidation state such as $[Ru(CO)_3I_3]^-$ as a catalyst precursor, one must add a reducing agent (or base) to obtain the desired mixture of reduced and oxidized complexes. Of course, addition of an excess of this reagent will lead to decreased activity. Likewise, a reduced ruthenium complex such as $[HRu_3(CO)_{11}]^-$ can be used as a catalyst precursor, but will have optimum activity only if an oxidizing agent (acid) is added in the proper amount to balance the oxidation state of the system.[24]

The complexes of Eq. (5) are catalytically active for reactions of synthesis gas other than CO hydrogenation. For example, $[HRu_3(CO)_{11}]^-$ will catalyze olefin hydroformylation,[25] and ruthenium halide complexes such as $[Ru(CO)_3I_3]^-$ are implicated in methanol homologation.[26] Of course, these catalytic reactions do not involve CO hydrogenation, and there is no need to have both types of complexes present. In these cases, one would prefer to maintain the oxidation state of the system so as to favor the existence of the appropriate complexes, either the reduced or the oxidized species.

HALIDE-PROMOTED RUTHENIUM CATALYTIC SYSTEMS IN BASIC SOLVENTS

The above discussion of ruthenium catalysts has been limited to the situation in which the solvent does not enter into the chemistry. When the solvent is sufficiently basic it can participate in the redox equilibria involved in determining the catalyst species present. Examples of two solvents we have studied which can be classified as basic relative to this system are tri-n-propylphosphine oxide (Pr_3PO, $pK_{BH^+} \sim -0.5$) and 1-methyl-2-pyrrolidininone (NMP, pK_{BH^+} -0.9). When catalytic solutions were prepared in these solvents according to Eq. (5), noticeably smaller amounts of $[Ru(CO)_3I_3]^-$ relative to $[HRu_3(CO)_{11}]^-$ were observed. This occurs because of the participation of the solvent as a base in the reaction of Eq. (6). A series of experiments with this system in Pr_3PO showed that optimum activity was obtained when a small amount of HI was added to the mixture.[22] This acid served to oxidize some of the excess reduced complex to $[Ru(CO)_3I_3]^-$, restoring the balance of these complexes in solution.

Studies in Pr_3PO showed that the reaction of Eq. (6) could be carried out in the laboratory, producing $[HRu_3(CO)_{11}]^-$ as the $[Pr_3POH]^+$ salt in Pr_3PO solution. These solutions have low activity for CO hydrogenation. Addition of HI to these solutions could be expected to convert some of this complex to $[Ru(CO)_3I_3]^-$ by an oxidation process similar to that of Eq. (7), and this is indeed observed. By this process, one can obtain a catalytic system with the proper balance of the oxidized and reduced complexes, and good catalytic activity is observed. Addition of further HI causes further oxidation and a decline in activity. These results are illustrated by Fig. 2.

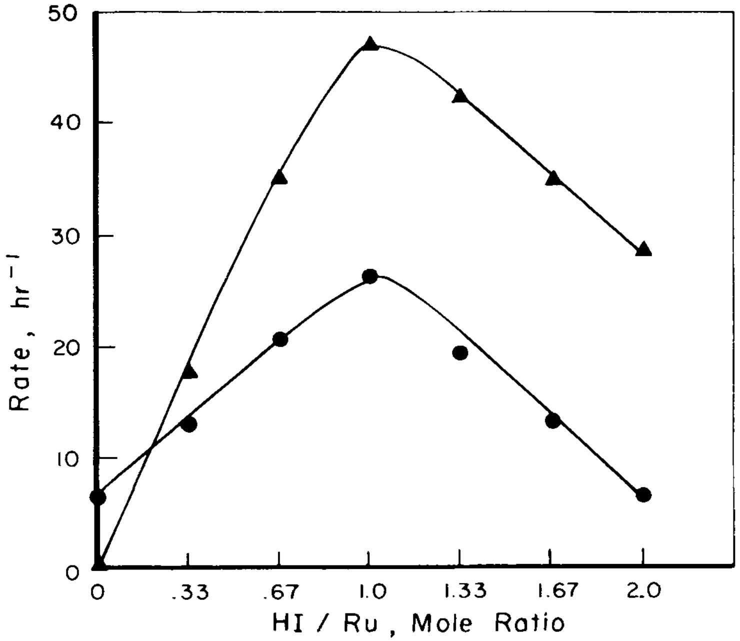

FIGURE 2 Effect of HI addition on catalytic activity to methanol (●) and ethanol (▲) with ruthenium catalyst in tri-n-propylphosphine oxide solvent (Ref. 22).

Catalytic solutions prepared from the appropriate proportions of $Ru_3(CO)_{12}$ and HI in Pr_3PO solutions thus can have good syngas conversion activity. However, these solutions exhibit unusual selectivity[22]; ethanol can be produced as the major product, as shown in Fig. 2. (The iodide salt-promoted systems described above produce mainly methanol and ethylene glycol.) The ethanol is apparently produced largely by an acid co-catalyzed homologation of methanol. Since all of the anionic ruthenium complexes are present in this system as their $[Pr_3POH]^+$ salts, there is an appreciable concentration of acid available for this purpose. (For comparison, catalytic solutions prepared according to Eq. (5), with an alkali metal iodide, produce only small amounts of ethanol.) The unique property of the Pr_3PO solvent which is responsible for this selectivity is apparently the acid strength of the $[Pr_3POH]^+$ cation. It is a sufficiently weak acid to allow the presence of anionic ruthenium hydrides necessary for the CO hydrogenation process, but is a sufficiently strong acid to enter into acid-catalyzed reactions involved in methanol homologation. Stronger acids, which would normally poison the CO hydrogenation process by oxidizing the ruthenium complexes, cannot exist in he Pr_3PO solvent.

Iodide promoters are commonly components of other catalytic systems for methanol carbonylation or homologation, apparently because HI can convert methanol to the more reactive methyl iodide intermediate. In these reactions, the iodide must be available in an acidic or "covalent" form, rather than an ionic form. It has been noted that an excess of this acidic promoter can be detrimental because of oxidation of the active catalyst species.[27]

A report that ruthenium(II) halide complexes or other ruthenium complexes in the presence of hydrogen halide promoters catalyze CO hydrogenation[28] is relevant to the above discussion. In the examples given, the preferred solvent is N-methylpyrrolidone, which will of course serve as a base to promote the reduction of the ruthenium species. Without such a basic additive, there would be no catalytic activity for CO hydrogenation.

SYNERGISTIC RUTHENIUM–RHODIUM CATALYSTS

Addition of small amounts of rhodium complexes to a halide-promoted ruthenium catalyst system produces a bimetallic catalyst system with significantly enhanced selectivity for the production of ethylene glycol.[29,30] Although the improved performance of a related Ru–Rh system has been attributed to the formation of a bimetallic cluster,[31] we and others[32] have not found evidence supporting this.

Our studies on the iodide-promoted ruthenium–rhodium catalyst system have shown that the ruthenium complexes present are the same as in the ruthenium systems described above and shown in Eq. (5). The rhodium is present, however, not as reduced clusters seen in the rhodium catalyst systems described above, but mainly in the form of a Rh(I) complex, $[Rh(CO)_2I_2]^-$. The mechanism by which this complex becomes involved in determining product selectivity appears to be closely tied to its oxidation state. This complex has been shown to be oxidized further by HI (or other oxidizing agents) to the Rh(III) state; several complexes are observed as products depending on conditions, as shown in Eq. (8).[33,34]

$$\begin{tikzcd}
 & {[Rh(CO)_2I_4]^-} \arrow[d, shift left] & \\
{[Rh(CO)_2I_2]^- + 2\,HI} \arrow[r, shift left] & {[Rh(CO)I_4]^- + H_2 + CO} \arrow[l, shift left] \arrow[u, shift left, "CO"] \arrow[d, shift left] & \\
 & {[Rh(CO)I_5]^{2-}} \arrow[u, shift left, "I^-"] &
\end{tikzcd} \qquad (8)$$

Since the catalytic system contains potential oxidizing agents, it is expected that equilibrium amounts of these Rh(III) complexes will be present under catalytic conditions, and their involvement in catalysis must be considered.

Examination of the metal cabonyl stretching frequencies (and force constants) of these complexes indicates that the $[Rh(CO)_2I_4]^-$ complex should contain particularly electrophilic carbonyl ligands, comparable in reactivity to those in $Ru(CO)_4I_2$.[30] It therefore seems very plausible that reaction of a ruthenium hydride donor, $[HRu(CO)_4]^-$, with this rhodium complex could lead to a rhodium formyl complex. Such an intermediate could undergo further hydrogenation or chain growth with a characteristic selectivity which should differ from that of a ruthenium-only system. In the absence of a reactive metal hydride complex, one would not expect these rhodium complexes to exhibit CO hydrogenation activity, and this is found to be so.

The key feature in this proposed mechanism is the availability of a reactive Rh(III) complex with electrophilic carbonyl ligands. Such a complex can be formed because of the presence of potential oxidizing agents in the system, particularly Ru(II) species which are generated by reaction such as Eq. (5). Addition of reducing agents to this system decreases the amount of these higher oxidation state complexes and thus lowers activity. Conversely, addition of oxidizing agents to increase the concentrations of the higher oxidation state components destroys the reduced complexes, such as the nucleophilic hydrides, which are presumably involved in the initial reduction step. A balance of oxidation states is required for optimum activity.

CONCLUDING REMARKS

In the reactions discussed here, promoters have in some cases served the role of ligand. In all of these reactions, however, the oxidation state of the catalyst species is determined by the promoters employed. Without these promoters (or if they are present in too large an amount), the catalytic activity can be greatly diminished. Recognition of this role of promoters can be very useful in the search to find or improve homogeneous catalytic systems.

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