Homogeneous Catalysis of the Water Gas Shift Reaction Using Ruthenium Chloride in Aqueous Alkaline Solution

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The water gas shift reaction (WGSR) is of great industrial importance to increase the hydrogen content in synthesis gas.

$$CO + H_2O \rightleftarrows H_2 + CO_2 \qquad (1)$$

Commercial operation for the reaction has been carried out at elevated temperatures above 250 °C using heterogeneous metal oxide catalysts [1]. Recently several homogeneous catalyst systems, active at lower temperatures using metal carbonyl and metal phosphine complexes, have been reported [2–9]. However, all of the homogeneous WGSR reported are performed in the presence of organic solvents like alcohol, acetone and amine because metal complexes such as catalysts, are insoluble or unstable in pure water. In this communication, we wish to report a simple homogeneous catalyst system for the WGSR using $RuCl_3$ in KOH–water solution, which is more active than the system [2] based on KOH–water-alcohol solution of $Ru_3(CO)_{12}$.
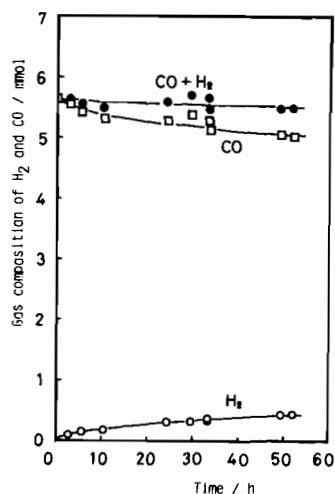

Fig. 1. Gas composition of H_2 and CO as a function of time. Catalyst solution: $RuCl_3$ = 0.1 mmol, KOH = 2.5 mmol, H_2O = 15 cm^3. Temperature = 90 °C, Initial CO pressure = 250 Torr.

The catalyst solution was prepared from $RuCl_3$ (0.1 mmol), KOH (2.5–25 mmol) and H_2O (15 cm^3) at room temperature in the reaction vessel of *ca.* 385 cm^3 with a Teflon-coated stirring bar. After the reactant CO (250 Torr) containing CH_4 (10 Torr) as an internal calibrant for GC analysis was introduced, the reaction vessel was immersed in an oil bath thermostatted at a reaction temperature. Samples of the gases above the reaction solution were withdrawn at intervals by a syringe through a side arm

TABLE I. Comparison of WGSR Activities between $RuCl_3$–KOH and $Ru_3(CO)_{12}$–KOH Catalyst Systems.[a]

Run	Catalyst system	Temp. (°C)	Solvent		KOH (mmol)	WGSR activity[b]
			H_2O (cm^3)	$C_2H_5OC_2H_4OH$ (cm^3)		
1	$RuCl_3$–KOH	90	15	0	2.5	3.0
2	$RuCl_3$–KOH	90	12	3	2.5	1.6
3[c]	$RuCl_3$–KOH	90	5	10	2.5	1.4
4[c]	$Ru_3(CO)_{12}$–KOH	90	15	0	2.5	0.3
5	$Ru_3(CO)_{12}$–KOH	90	5	10	2.5	0.2
6[d]	$Ru_3(CO)_{12}$–KOH	100	0.3	3	2.0	0.9
7	$RuCl_3$–KOH	90	15	0	5.0	2.1
8	$RuCl_3$–KOH	90	15	0	5.0	4.4
9[c]	$RuCl_3$–KOH	90	15	0	15.0	5.4
10[c]	$RuCl_3$–KOH	90	15	0	25.0	8.5

[a]Reaction conditions: $RuCl_3$ = 0.1 mmol, $Ru_3(CO)_{12}$ = 0.03 mmol, initial CO pressure = 250 Torr. [b]Normalized activity = number of H_2 produced per ruthenium atom in 24 h. [c]Runs 3, 4, 9 and 10 exhibited heterogenity in the catalyst solution. [d]From ref. 2(c). Reaction conditions: $Ru_3(CO)_{12}$ = 0.04 mmol, initial CO pressure = 680 Torr.

TABLE II. Results of Catalytic Decomposition of Sodium Formate by $RuCl_3$ at 90 °C.

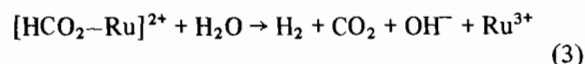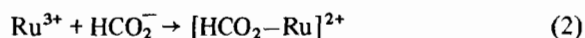| $RuCl_3$ (mmol)	NaO_2CH (mmol)	H_2O (cm^3)	Gaseous products[a]	
			H_2	CO_2[b]
0.1	2.5	15	4.5	1.8
0.1	5.0	15	11.6	2.3
0.1	15.0	15	30.8	3.5

[a]Number of H_2 or CO_2 produced per ruthenium atom in 24 h.   [b]The gas-phase concentration of CO_2 is less than that for H_2, which may be due to the reaction of OH^- with CO_2 to produce bicarbonate.

sealed with silicon rubber, and analyzed quantitatively by gas chromatography using a two-metre column of activated carbon.

Figure 1 shows the change in gas composition of H_2 and CO during the course of WGSR in a blood-red water solution containing $RuCl_3$ (0.1 mmol) and KOH (2.5 mmol) at 90 °C under an initial CO pressure of 250 Torr. Only trace amounts of CO_2 were detected in the gas phase during the reaction, but the addition of HCl at the end of reaction resulted in the formation of CO_2, indicative of the formation of bicarbonate from $CO_2 + OH^- \rightarrow HCO_3^-$ in the alkaline solution. Table I summarizes the amounts of H_2 produced in 24 h under different reaction conditions, together with the results (runs 4, 5 and 6) obtained using the catalyst system of $Ru_3(CO)_{12}$–KOH. The $RuCl_3$–KOH catalyst system exhibited much higher activity than the $Ru_3(CO)_{12}$–KOH system. An increase in the initial concentration of KOH resulted in the acceleration in the rate of H_2 formation for the WGSR using $RuCl_3$. However, higher initial concentrations of KOH over 1.0 M caused heterogenity of the catalyst solution.

In connection with the mechanism of the homogeneous WGSR in aqueous alkaline solution of $RuCl_3$, the decomposition of sodium formate by $RuCl_3$ has been examined at 90 °C under CH_4 pressure of 20 Torr. The result is given in Table II. It was found that $RuCl_3$ functions as a catalyst for the decomposition of formate ion to H_2 and CO_2. The rate of H_2 fomation was almost proportional to the initial concentration of sodium formate. This result can be interpreted in terms of the decomposition of an

intermediate $[HCO_2-Ru]^{2+}$ produced by the addition of formate ion to Ru^{3+}:

$$Ru^{3+} + HCO_2^- \rightarrow [HCO_2-Ru]^{2+} \qquad (2)$$

$$[HCO_2-Ru]^{2+} + H_2O \rightarrow H_2 + CO_2 + OH^- + Ru^{3+} \qquad (3)$$

In the WGSR using aqueous alkaline solution, formate ion appears to be formed by the reaction of OH^- with CO:

$$CO + OH^- \rightarrow HCO_2^- \qquad (4)$$

The identification of possible intermediates in the homogeneous WGSR is the focus of further investigation.

Acknowledgement

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