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Reverse Water-Gas Shift Reaction Catalyzed by Ruthenium Cluster Anions

Ken-ichi TOMINAGA, Yoshiyuki SASAKI,[*] Kohnosuke HAGIHARA,[†]
Taiki WATANABE,[†] and Masahiro SAITO
National Institute for Resources and Environment(NIRE), 16-3 Onogawa, Tsukuba 305
[†]Research Institute of Innovative Technology for the Earth(RITE), CO_2 Fixation Project Section,
16-3 Onogawa, Tsukuba 305

Reverse water-gas shift reaction ($H_2+CO_2 \rightarrow CO+H_2O$) was homogeneously catalyzed by anionic Ru cluster in the presence of bis(triphenylphosphine)imminium chloride ([PPN]Cl). The catalytic reaction was estimated to proceed via dehydrogenation of hydride cluster, followed by coordination of CO_2 and electrophilic attack of proton on its oxygen atom in the presence of chloride anion.

There are great interests in the recycling use of CO_2 as fuels or chemicals by the aid of hydrogen derive, for example, from photo-induced decomposition of water. The reverse water-gas shift reaction (RWGSR) will be a key step of this hydrogen-assisted utilization of CO_2, because its product, CO can be readily transformed to various useful compounds. Although a number of heterogeneous catalysts are known to be effective for RWGSR at high reaction temperature, there have been only a few homogeneous ones reported so far. Koinuma et al. found that $RhCl(PPh_3)_3$ was converted to $RhCl(CO)(PPh_3)_2$ when heated in polar aprotic solvents under CO_2/H_2 pressure.1) The presence of CO was confirmed in the resulted gas mixture. Khan et al. reported that K[Ru(EDTA-H)Cl] catalyzed the CO_2 hydrogenation to CO via formic acid and formaldehyde in aqueous solution.2)

In the course of our investigations on the CO_2 hydrogenation catalyzed by transition metal complexes,3) we have found that RWGSR was effectively catalyzed by anionic Ru clusters under relatively mild reaction conditions. $Ru_3(CO)_{12}$ was used as catalyst precursor in the presence of bis(triphenylphosphine)imminium chloride ([PPN]Cl) as shown in eq. 1.

$$CO_2 + H_2 \xrightarrow{Ru_3(CO)_{12}\text{-}[PPN]Cl} CO + H_2O \qquad (1)$$

In a typical experiment, an N-methyl-2-pyrrolidone (NMP) solution (20 ml) of $Ru_3(CO)_{12}$ (0.2 mmol) and [PPN]Cl (1 mmol) was stirred in 100 ml-autoclave for over 1 h and CO_2-H_2 (1:3) mixture gas was introduced under 80 kg/cm^2 at 30-32 °C. The autoclave was then heated at 160 °C for 5 h. GLC analyses of the resulted gas mixture and solution revealed the formations of CO (15.1 mmol), methanol (0.8 mmol) and water (21.6 mmol). No formic acid was detected in the reaction solution.

Table 1. Effects of Salt and Reaction Temperature[a)]

entry	salt	temp / °C	Products / mmol			CO_2 recovered
			CO	MeOH	CH_4	/ mmol
1	none	160	0.2	0.0	1.4	72.7
2	[PPN]Cl	160	15.1	0.8	0.3	54.2
3	[PPN]Br	160	9.7	0.2	0.0	58.4
4	[PPN]I	160	3.7	0.2	0.2	72.6
5	KCl	160	14.2	0.0	0.1	63.8
6	NaCl	160	14.8	0.2	0.2	62.2
7	LiCl	160	15.2	0.7	0.1	59.7
8	[PPN]Cl	140	9.6	0.2	0.0	64.0
9	[PPN]Cl	180	16.0	1.9	0.1	62.9
10	[PPN]Cl	200	13.6	3.2	0.9	55.8
11	[PPN]OCHO	160	0.4	0.0	0.0	73.5
12[b)]	none	160	0.6	0.0	0.0	43.2

a) $Ru_3(CO)_{12}$ (0.2 mmol), Salt (1 mmol), N-methyl-2-pyrrolidone (20 ml), 80 kg/cm^2 (at 30-32 °C) of CO_2-H_2 (1:3), 5 h. b)Formic acid (50 mmol) was added instead of CO_2-H_2 gas and reacted under nitrogen atmosphere (30 kg/cm^2). The autoclave was cooled down immediately after reaching 160 °C. H_2 was formed in the yield of 49.9 mmol.

Some representative results are shown in Table 1. All the reaction solutions resulted from these experiments were homogeneous and no significant amount of methane was formed, except for the reaction without salt, in which no homogeneous hydrogenation of CO_2 was occurred, and a slight plating of Ru metal was observed on the autoclave wall causing some methanation of CO_2 (entry 1). About 15 mmol of CO formation and turnover numbers up to 25 based on Ru atom were achieved in the reactions with chloride salts, however, bromide and iodide salts were less effective (entries 2-4). On the other hand, the reaction was insensitive to the nature of the cation species (entries 5-7). When the reaction temperature was increased from 140 to 200 °C (entries 2, 8-10), the yield of CO increased from 9.6 to 16.0 mmol and then slightly decreased while that of methanol gradually increased. Deposition of Ru metal was observed at higher reaction temperatures than 200 °C.

The FT-IR analyses of the resulted solutions indicated the presence of some Ru cluster anion species which were identified by the following IR bands observed in comparison with those reported in the literature:[4-6)]

$[H_3Ru_4(CO)_{12}]^-$ (**1**); 2072, 2038, 2030, 2018, 2000, 1974, 1949, 1929 cm^{-1}.
$[H_2Ru_4(CO)_{12}]^{2-}$ (**2**); 2028, 1988, 1953, 1945, 1904, 1886 cm^{-1}.
$[HRu_3(CO)_{11}]^-$ (**3**); 2073, 2014 cm^{-1}.

The trihydride tetranuclear cluster mono-anion **1** was the only Ru species observed in the reaction solution without salt (entry 1), while the dihydride tetranuclear cluster dianion **2** was also formed in a small amount in the reaction solution with [PPN]Cl (entry 2). **1** was mostly replaced by **2** when the reaction was carried out either at 180 °C (entry 9) or with [PPN]OCHO (entry 11). A slight formation of hydride trinuclear cluster mono-anion **3** was also observed at 180 °C.

There are two possible mechanisms for RWGSR catalyzed by transition metal complexes; one based on a direct hydrogenation of CO_2 coordinated to the metal center into CO and the other on an intermediary formation of formic acid followed by its decomposition into CO and H_2O. This mechanism assumed in the earlier reports1,2) seems impossible for the present RWGSR, because [PPN]OCHO which is expected to give a Ru formate complex7) and formic acid in the presence of dihydrogen8) gave only a small amount of CO (entry 8). Moreover, a Ru catalyzed decomposition of formic acid under nitrogen atmosphere resulted in the predominant formation of CO_2 and H_2 (entry 12).

$$CO_2 + H_2 \xrightleftharpoons{[Ru]} HCO_2H \not\longrightarrow CO + H_2O \qquad (2)$$

On the other hand, the first mechanism may be related to the direct conversion of the CO_2 complexes of Fe,9) Mo10) or Ni,11) with a metal-carbon bond, into the corresponding carbonyl complexes. This reaction was considered to take place via electrophilic attack by protons on an oxygen atom of CO_2 coordinated metallocarboxylate complexes as indicated in eq. 3.

$$M(CO_2) \xrightarrow{H^+} M(CO_2H)^+ \xrightarrow{H^+} M(CO)^{2+} + H_2O \qquad (3)$$

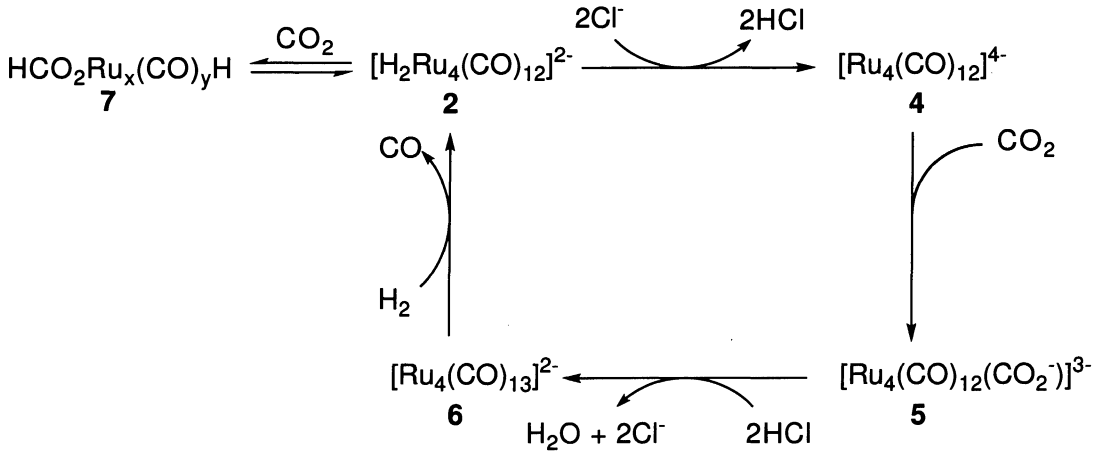
As for the interactions of CO_2 with Ru cluster anions, Chang12) reported that CO_2 was reduced to CO with hydrogen-free tetranuclear cluster tetra-anion, $K_4[Ru_4(CO)_{12}]$ according to eq. 4, while dihydride tetranuclear cluster dianion, $K_2[H_2Ru_4(CO)_{12}]$ was unchanged under CO_2 atmosphere.

$$K_4[Ru_4(CO)_{12}] \xrightarrow{CO_2} \left\{K_3[Ru_4(CO)_{12}(CO_2K)]\right\} \xrightarrow{CO_2} K_2[Ru_4(CO)_{13}] + K_2CO_3 \qquad (4)$$

Taking account of these significant facts, we propose the mechanism shown in Scheme 1 for the present RWGSR. Successive eliminations of the coordinated hydrogens from **2** may be caused by chloride anion to form hydrogen-free Ru cluster tetra-anion **4**. Similar deprotonation of hydride complexes by halide salt have been reported with $H_4Ru_4(CO)_{12}$13) and $HCoRu_2(\mu_3\text{-}NPh)(CO)_9$,14) showing that halide anions are sufficiently strong bases in non-aqueous solvents to deprotonate metal hydride complexes. The metallocarboxylate complex **5** formed by the coordination of CO_2 to **4** may be attacked by protons on an oxygen atom of CO_2 to give **6** with liberation of H_2O. Finally, a rapid oxidative addition of H_2 to **6** must regenerate **2** with liberation of CO.

Thus, hydride clusters (**1** and **2**) alone do not lead to any catalytic CO formation (entries 1 and 11), but a probable reverse formation of formic acid. Besides, the proton elimination necessary for the CO formation is expected to reflect the order of proton affinity of halide anion ($Cl^- > Br^- > I^-$),15) with which the order of catalytic activity is consistent (entry 2-4). The proton elimination or at least the loosening of Ru-H bond by the halide anion must cause the enhanced electron density at Ru nuclei to enable CO_2 to coordinate and form metallocarboxylate intermediate. The rate determining step is considered to be the deprotonation of hydride clusters, because of the presence of these clusters observed in the resulted reaction solutions.

A trinuclear complex **3** may be formed from **2** according to the accumulation of CO and play an important role in further hydrogenations of CO to methanol, methane and so forth.3,16)



Scheme 1.

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