Homogeneous Hydrogenation of Carbon Dioxide to Methanol Catalyzed by Ruthenium Cluster Anions in the Presence of Halide Anions

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(Received February 22, 1995)

Methanol, together with methane, is formed for the first time by homogeneous hydrogenation of CO_2 using a catalytic system consisting of $Ru_3(CO)_{12}$ and alkaline iodides in *N*-methylpyrrolidone (NMP) solution at 240 °C. The time course of the reaction indicates the successive formation of CO, methanol, and then methane. The FT-IR analysis of the resulting reaction solutions reveals the formation of several species of ruthenium carbonyl anion and their mutual interchanges during the reaction. A mechanism for the overall reaction is proposed, based on these results.

Several C1 compounds ranging in the oxidation state of carbon atom from formic acid (carbon monoxide is its dehydrated equivalent) to methane can be formed by the CO_2 hydrogenation. Among them, methanol is considered the most valuable product because it can be safely stored, readily used as a building block for the other useful chemicals and also simply burned as liquid fuel for the vehicles and the generation of electricity. Although some transition metal complexes were found to catalyze the hydrogenation of CO_2 to formate derivatives such as *N*,*N*-dialkyl-formamide, alkyl formate, or formic acid in the presence of dialkylamine, alcohol, or water respectively,[1—5] little has been known about the CO_2 hydrogenation to methanol with homogeneous catalysts. We recently reported the first example of the homogeneous hydrogenation of CO_2 to methanol which proceeds in the presence of $Ru_3(CO)_{12}$ and KI at a comparable rate with heterogeneous processes (Eq. 1).[6] We report here the results of the detailed catalytic and mechanistic studies on this novel catalysis.

$$H_2 + CO_2 \xrightarrow{Ru_3(CO)_{12}+KI} MeOH \qquad (1)$$

Results and Discussion

So far, the transition metal carbonyl clusters, though favorably used for the CO hydrogenation to produce various compounds such as methanol and ethylene glycol, have not been employed as a CO_2 hydrogenation catalyst except for the carbonyl clusters of Fe[4] and Ru,[5] which gave only small amounts of formate esters at relatively low temperatures. The main difficulty of using this kind of complex as the CO_2 hydrogenation catalyst lies in the fact that, as ligand, CO_2 is far less effective than CO in stabilizing the transition metal complexes at a high temperature such as is needed for methanol synthesis. In fact, when used as the CO_2 hydrogenation catalyst without any additives at 200 °C, $Ru_3(CO)_{12}$ is readily decomposed to ruthenium metal causing a vigorous methanation of CO_2 as shown in Table 1, Entry 1. On the contrary, the addition of salts such as potassium salts listed in Table 1 is very effective in preventing the decomposition of the complex and therefore the methanation of CO_2. Besides, significant amounts of CO are formed when chloride, bromide, or iodide is used as the additive, together with methanol: the yield increases in the order $Cl^- < Br^- < I^-$.

Table 1. Effects of Salts on CO_2 Hydrogenation at 200 °C [a)]

Entry	Salts	Product yield / mmol			CO_2 recovered
		CO	MeOH	CH_4	mmol
1	None[b)]	0.5	0.0	55.4	34.4
2	KI	11.0	6.9	0.4	52.4
3	KBr	15.2	2.1	2.0	56.5
4	KCl	15.9	0.7	1.1	56.5
5	KF	1.3	0.2	0.9	67.6
6	KOAc	3.1	0.1	0.1	56.9
7	K_2CO_3	1.4	0.2	2.3	56.0
8	K_2HPO_4	0.5	0.0	0.1	51.7

a) Conditions: $Ru_3(CO)_{12}$ (0.2 mmol), Salts (10 mmol), NMP (20 ml), $H_2/CO_2=3$ (80 atm at 30—32 °C), 5 h.
b) Metal deposit.

No significant formation of CO_2 hydrogenation products is observed when the transition metal carbonyl complexes other than ruthenium complex listed in Table 2 are used with KI at 200 °C, though the resulting solutions are homogeneous (except those of Fe and Co) under the reaction conditions.

The effect of reaction temperature was examined for the CO_2 hydrogenation catalyzed by $Ru_3(CO)_{12}$ in the presence of KI, as shown in Fig. 1. Practically no product is obtained below 160 °C, while CO is increasingly formed above this temperature and reaches its maximum at about 200 °C. The yield of methanol increases with increase in CO yield and reaches its maximum at about 240 °C. Then the formation of methane becomes significant from about this temperature upward. This result suggests that CO is the primary product of the CO_2 hydrogenation. Methanol is considered to be formed by its hydrogenation and methane through its further hydrogenation. This successive formation of CO, methanol, and methane, together with the constant decrease in the amount of CO_2 recovered, is also observed in the time course of the reaction at 240 °C, as shown in Fig. 2.

Figure 3 shows the effect of the amount of KI added on the product distribution. Even a slight addition of KI drastically suppresses the methanation caused by the deposited ruthenium metal at 240 °C. Its further addition enhances the yields of CO and methanol. The reaction solutions are clear red and no deposition of metal is observed for runs with over 5 mmol of KI. The yield of methanol reaches its maximum at 10 mmol of KI. More addition of KI causes a gradual increase in

Table 2. CO_2 Hydrogenation by Various Transition Metal Carbonyls[a)]

Entry	Complex	Product yield / mmol			CO_2 recovered
		CO	MeOH	CH_4	mmol
1	$Ru_3(CO)_{12}$	11.0	6.9	0.4	52.4
2	$Rh_4(CO)_{12}$	0.9	0.1	0.1	54.6
3	$Ir_4(CO)_{12}$	1.4	0.0	0.1	61.2
4	$W(CO)_6$	0.4	0.0	0.4	54.6
5	$Mo(CO)_6$	0.4	0.0	0.0	59.8
6	$Fe_2(CO)_9$[b)]	0.9	0.1	0.2	50.1
7	$Co_2(CO)_8$[b)]	1.0	0.0	0.0	63.8

a) Conditions: Complex (0.6 mg-atom), KI (10 mmol), NMP (20 ml), $H_2/CO_2=3$ (80 atm at 30—32 °C), 200 °C, 5 h. b) Metal deposit.

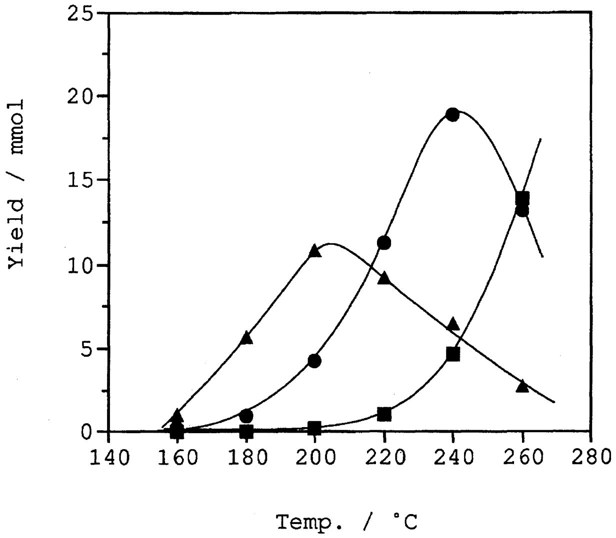


Fig. 1. Effect of the reaction temperature. Conditions: $Ru_3(CO)_{12}$ (0.2 mmol), KI (10 mmol), NMP (20 ml), $H_2/CO_2=3$ (80 atm at 30—32 °C), 3 h. ▲=CO, ●=MeOH, and ■=CH_4.

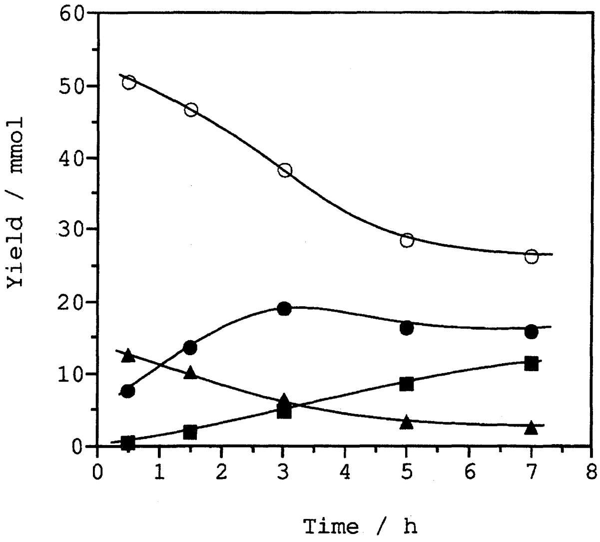


Fig. 2. Time course of the reaction. Conditions: $Ru_3(CO)_{12}$ (0.2 mmol), KI (10 mmol), NMP (20 ml), $H_2/CO_2=3$ (80 atm at 30—32 °C), 240 °C. ▲=CO, ●=MeOH, ■=CH_4, and ○=CO_2.

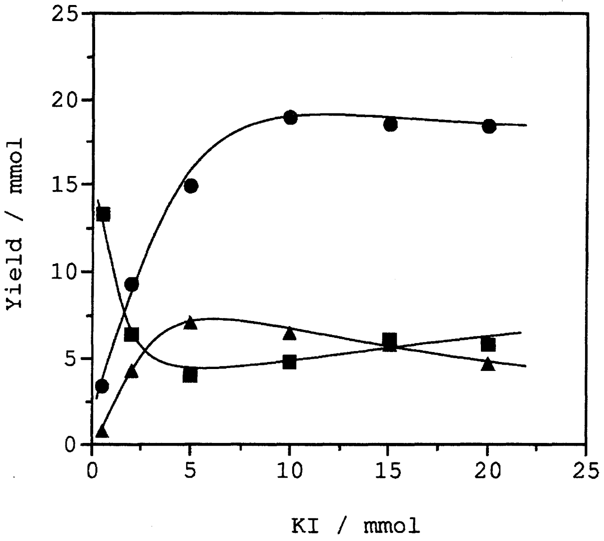


Fig. 3. Effect of the amount of KI. Conditions: $Ru_3(CO)_{12}$ (0.2 mmol), NMP (20 ml), $H_2/CO_2=3$ (80 atm at 30—32 °C), 240 °C, 3 h. ▲=CO, ●=MeOH, and ■=CH_4.

the yield of methane. A homogeneous hydrogenation of methanol mediated by iodide is considered responsible for this as described below.

Table 3 shows the effect of the cation species of iodide salt on the product distribution. Only when alkaline iodides are used as additive is methanol formed as main product in the yields of 15—19 mmol (or 25—32 turnover number based on the ruthenium atom) together with smaller amounts of CO and methane. The yields of these products are almost constant, regardless of the alkaline metal species, except that a considerable formation of methane is observed in the reaction with LiI. On the other hand, the iodine compounds other than alkaline metal salts tested are not effective for the formation of methanol. Instead, methane is mainly formed with [PPN]I, SrI_2, or I_2 which are expected to liberate HI in the presence of H_2 or H_2O. It is known that methanol reacts with HI to give CH_3I, which is readily hydrogenated in the presence of ruthenium complex to give methane. The occurrence of this process may be partly proved by the fact that methanol added prior to the reaction in which I_2 is used as additive is almost entirely converted to methane, as shown in Table 3, Entry 9. Thus the presence of alkaline metal cation is critical in order to prevent the excessive formation of HI which might otherwise take place, for example according to the equation: $SrI_2+CO_2+H_2O \rightarrow SrCO_3+2HI$, and which might cause the rapid hydrogenolysis of methanol to methane. Furthermore, when ZnI_2 is used as additive, CO is predominantly formed. This result indicates that some cation species may depress the hydrogenation of CO to methanol, probably preventing the iodide anion from assisting this reaction.

Thus, the CO_2 hydrogenation is efficiently promoted by iodide to give any of these products but only at high temperature (see Fig. 1). Our further investigation has revealed that chloride salts are much more effective in promoting the CO_2 hydrogenation to CO (the reverse water–gas shift reaction) than iodide at relatively low temperature (160 °C).[7] Even 1 mmol of chloride salts (1/10 of iodide salts used in the above experiments) is sufficient to promote this reaction; CO is formed in good yields (about 15 mmol) independent of the cation species of the salt (Table 4, Entries 2, 7—9).[7] The reactivity of bromide anion toward this reaction is just between those of chloride and iodide. No significant formation of CO_2 hydrogenation products is observed without salt nor with non-halide salts at this temperature.

Table 3. Effects of Iodide Salts on CO_2 Hydrogenation at 240 °C[a)]

Entry	Iodide salts	Product yield / mmol CO	MeOH	CH_4	CO_2 Recovered mmol
1	CsI	7.2	16.0	4.2	39.5
2	RbI	5.8	17.9	4.0	34.2
3	KI	6.5	18.9	4.7	38.1
4	NaI	6.1	17.3	5.6	39.0
5	LiI	4.1	15.1	11.0	36.1
6	[PPN]I [b)]	5.2	1.0	14.9	42.8
7	SrI_2	6.1	0.1	12.1	38.6
8	I_2	5.3	0.4	15.2	43.7
9	I_2[c)]	4.4	0.6	30.2	46.8
10	ZnI_2	14.5	0.8	0.7	55.3

a) Conditions: Complex (0.2 mmol), Salts (10 mmol), NMP (20 ml), $H_2/CO_2=3$ (80 atm at 30—32 °C), 3 h. b) [PPN] = bis(triphenylphosphine)iminium. c) Methanol (20 mmol) were initially added.

In order to elucidate the mechanism of this catalysis in terms of the ruthenium carbonyl species involved, FT-IR spectra were analyzed with the NMP solutions which resulted from the reactions with $Ru_3(CO)_{12}$ and KI under CO_2/H_2 pressure (80 atm) at various temperature for 0.5 h, as shown in Fig. 4. The original complex, $Ru_3(CO)_{12}$, is entirely converted to $[HRu_3(CO)_{11}]^-$ (**1**) and $[Ru(CO)_3I_3]^-$ (**2**) during the reaction at 60 °C. This is shown in spectrum (a) which is almost identical to the spectrum (b) of the authentic sample of **1** synthesized according to the published methods,[8] except for the band at 2100 cm^{-1} which corresponds to that of the authentic sample of **2**.[9] The trinuclear complex **1** is almost entirely changed into the tetranuclear species after being heated at 120 °C, as shown in spectrum (c). Trihydride monoanion, $[H_3Ru_4(CO)_{12}]^-$ (**3**) is the main ruthenium carbonyl species in this solution, as confirmed by reference to spectrum (d) of its authentic sample.[10] Then, the dihydride dianion, $[H_2Ru_4(CO)_{12}]^{2-}$ (**4**), the slight formation of which can be observed at lower temperatures, predominates at 240 °C, as shown in spectrum (e) which is almost identical to the spectrum (f) of the authentic sample[10] of **4**, except for the band at 2016 cm^{-1} which corresponds to that of **1**. The regeneration of **1** at this temperature can be confirmed by the subtraction of f from e, giving a spectrum almost identical to b. The mononuclear species **2** is gradually reduced at higher

Table 4. Effects of Salts on Reverse Water–Gas Shift Reaction at 160 °C[a)]

Entry	Salts	Product yield / mmol CO	MeOH	CH_4	CO_2 Recovered mmol
1	None	0.2	0.0	1.4	72.7
2	[PPN]Cl	15.1	0.8	0.3	54.2
3	[PPN]Br	9.7	0.4	0.0	58.4
4	[PPN]I	3.7	0.2	0.2	62.2
5	[PPN]OCHO	0.4	0.0	0.0	73.5
6	[PPN]OH	0.5	0.0	0.0	73.0
7	LiCl	15.2	0.7	0.1	59.7
8	NaCl	14.8	0.2	0.2	62.2
9	KCl	14.2	0.0	0.1	63.8

a) Conditions: $Ru_3(CO)_{12}$ (0.2 mmol), Salts (1 mmol), NMP (20 ml), $H_2/CO_2=3$ (80 atm at 30—32 °C), 5 h.

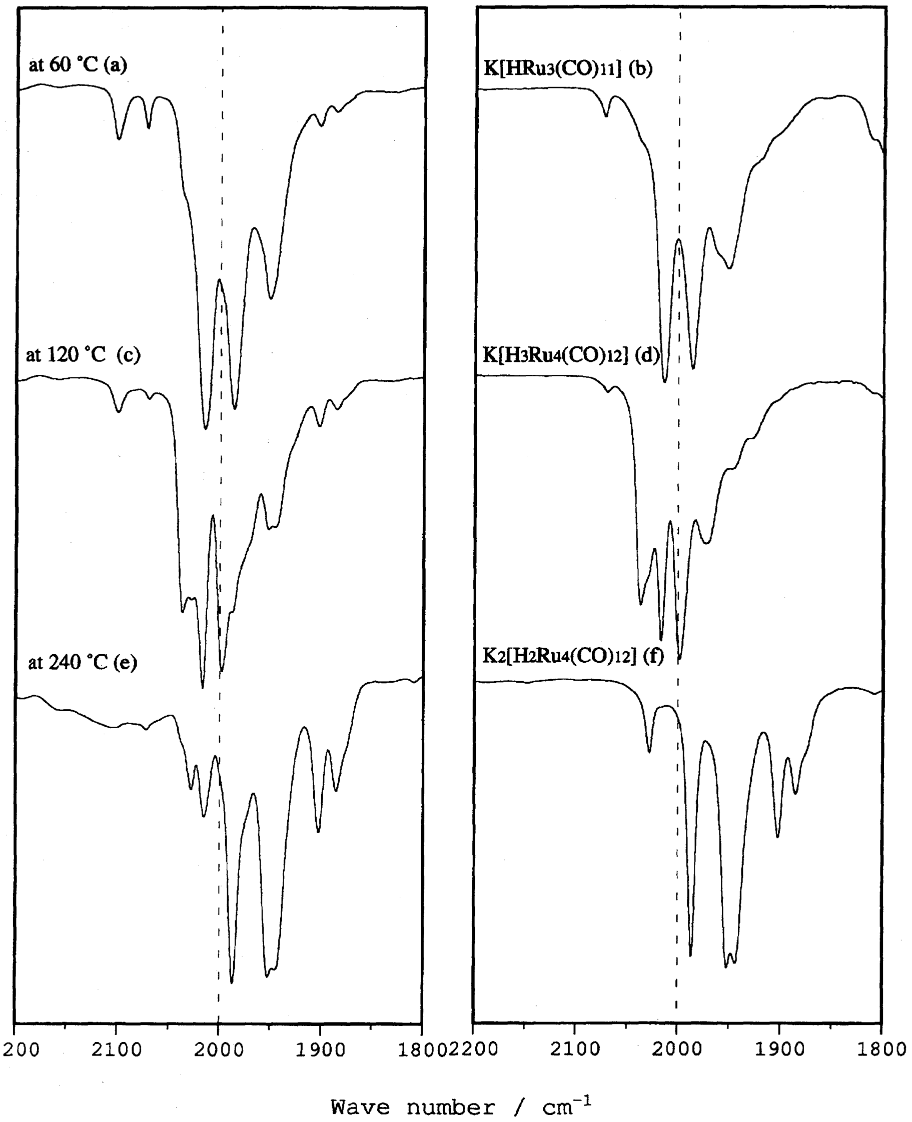


Fig. 4. Carbonyl region IR spectra of the reaction solution (left) and the synthesized complexes (right). Conditions: $Ru_3(CO)_{12}$ (0.2 mmol), NMP (20 ml), $H_2/CO_2=3$ (80 atm at 30—32 °C), 0.5 h.

temperature, but is still present to some extent at 240 °C.

As for the first step of the reaction (reverse water–gas shift reaction), we have proposed the following mechanism in which the dihydride tetranuclear species, $[H_2Ru_4(CO)_{12}]^{2-}$ (**4**), plays an important role together with halide anion.[7)]

(i) Halide anion (X^-) successively eliminates the coordinated hydrogens first from **3** then from **4**, to finally form hydrogen-free ruthenium cluster tetraanion $[Ru_4(CO)_{12}]^{4-}$ (Eq. 2), which must have high electron density on ruthenium atoms.

$$[H_2Ru_4(CO)_{12}]^{2-} + 2X^- \rightarrow [Ru_4(CO)_{12}]^{4-} + 2HX \qquad (2)$$

(ii) CO_2 coordinates to $[Ru_4(CO)_{12}]^{4-}$ to form a metallocarboxylate complex, $[Ru_4(CO)_{12}(CO_2^-)]^{3-}$, which is then attacked by protons on an oxygen atom of CO_2 to give $[Ru_4(CO)_{13}]^{2-}$ with liberation of H_2O (Eq. 3).

$$[Ru_4(CO)_{12}]^{4-}+CO_2 \rightarrow [Ru_4(CO)_{12}(CO_2{}^-)]^{3-}$$
$$[Ru_4(CO)_{12}(CO_2{}^-)]^{3-}+2H^+ \rightarrow [Ru_4(CO)_{13}]^{2-}+H_2O \qquad (3)$$

(iii) H_2 replaces one of the CO groups in $[Ru_4(CO)_{13}]^{2-}$ to regenerate **4** with liberation of CO (Eq. 4).

$$[Ru_4(CO)_{13}]^{2-}+H_2 \rightarrow [H_2Ru_4(CO)_{12}]^{2-}+CO \qquad (4)$$

The rate-determining step of this catalysis is considered to be that of the deprotonation of hydride clusters, because the catalytic activities of halide anions are exactly in the order of their proton affinity ($Cl^- > Br^- > I^-$) at relatively low temperatures (see Table 4), although they become almost comparable at 200 °C (see Table 1).

Once CO is thus formed, it is submitted to the methanol formation. A mechanism for the hydrogenation of CO in the presence of the ruthenium catalyst has been proposed by Dombec in which two ruthenium species, $[HRu_3(CO)_{11}]^-$ (**1**) and $[Ru(CO)_3I_3]^-$ (**2**), are involved as essential elements.[13] Since the formation of these two species is also observed in the present reaction, the second stage of this reaction (the formation of methanol) is considered to follow the same mechanism as that starting from CO. Complexes **1** and **2** are known to be simultaneously formed from $Ru_3(CO)_{12}$, iodide, and H_2 as indicated in Eq. 5.[13]

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

The dihydride tetranuclear complex **4** is in equilibrium with **1** under CO atmosphere (Eq. 6).[14]

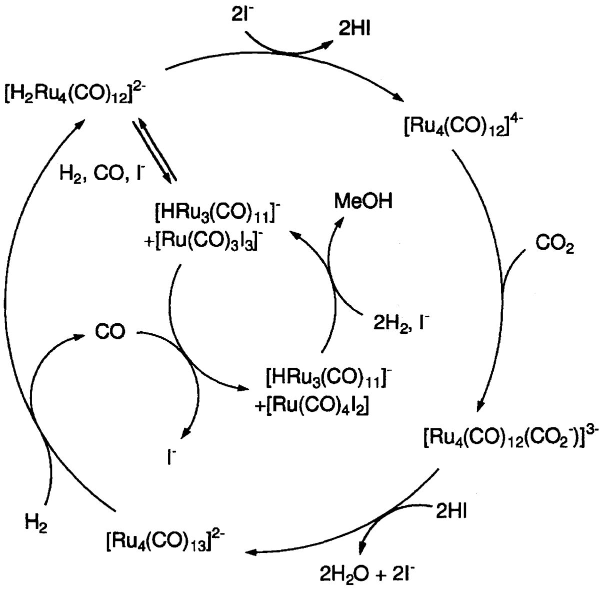
$$3[H_2Ru_4(CO)_{12}]^{2-} + 9CO \rightleftarrows 3[HRu_3(CO)_{11}]^- + Ru_3(CO)_{12} + 3/2H_2 \quad (6)$$

According to the mechanism proposed by Dombec, the complexes **1** and **2** undergo the intermolecular hydride transfer; one of the CO coordinated to the complex, $[Ru(CO)_4I_2]$, which is formed by the oxidation of **2** (Eq. 7) is hydrogenated by **1** to afford a formyl complex which is further hydrogenated to produce methanol.[13]

$$[Ru(CO)_3I_3]^- + CO \rightarrow [Ru(CO)_4I_2] + I^- \quad (7)$$

The formation of the mononuclear hydride species, $[HRu(CO)_4]^-$, though suggested in the mechanism of the CO hydrogenation as a hydride donor, is unlikely for the CO_2 hydrogenation, because this complex might be readily converted to $[HRu_3(CO)_{11}]^-$ (**1**) and H_2 in the presence of water, which is inevitably formed by the reverse water–gas shift reaction.[15]

Therefore, the hydrogenation of CO_2 to methanol by this catalytic system can be rationalized, as shown in Scheme 1. First, CO_2 is converted to CO by the hydrogenation catalysis of tetranuclear ruthenium clusters. CO is then hydrogenated to methanol by the interaction of $[HRu_3(CO)_{11}]^-$ (**1**) and $[Ru(CO)_3I_3]^-$ (**2**) derived from tetranuclear species in the presence of CO produced and iodide added.



Scheme 1.

Experimental

All chemicals were of reagent grade. *N*-Methyl-2-pyrrolidone (NMP) was dried over MS-5A. Bis(triphenylphosphine)iminium salts, [PPN]X, were prepared from purchased [PPN]Cl.[16] Complexes $K[HRu_3(CO)_{11}]$ (**1**),[8] $K[Ru(CO)_3I_3]$ (**2**),[9] $K[H_3Ru_4(CO)_{12}]$ (**3**), and $K_2[H_2Ru_4(CO)_{12}]$ (**4**)[10] were synthesized according to the procedures in the literature. Gas chromatographic analyses were performed on a Shimadzu GC-8A using Porapak T column for liquid products and on a GC-20B for gaseous products using MS-13X column (for H_2, CH_4, and CO) and Porapak Q column (for CO_2). IR spectra were recorded on a Shimadzu FT-IR 8100M spectrometer.

Catalytic experiments were carried out in a 100 ml-hastelloy autoclave (Nitto Koatsu). Typically, a solution of $Ru_3(CO)_{12}$ (0.2 mmol), salt (10 mmol), and NMP (20 ml) were stirred in the autoclave for over 1 h and CO_2/H_2 (1:3) mixed gas was introduced under 80 atm at 30—32 °C. The autoclave was then heated at the rate of 5 $°C\,min^{-1}$ and maintained at a nominal reaction temperature for a designated period. After the reaction, the autoclave was cooled to room temperature and the reaction gas was recovered with a sampling bag equipped with a accumulated flowmeter. Products were quantitatively analyzed by GC. Deposited ruthenium metal plate in the reactor was removed by washing with sodium hypochlorite solution, followed by careful polishing.

The present work was partly supported by the New Energy and Industrial Technology Development Organization (NEDO).

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