Selective synthesis of acetic acid from hydrogen and carbon monoxide by homogeneous bimetallic catalysts

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Abstract

Alcohols which are the main products of the reaction of hydrogen and carbon monoxide in onium halide promoted ruthenium systems, are changed to acetic acid with the addition of cobalt carbonyl as the second catalyst component. Among Group VIa–VIIIa transition metal complexes, cobalt carbonyl is the only compound which promoted acetic acid formation when combined with ruthenium carbonyl under the conditions studied. The selectivity to acetic acid varied appreciably with the combinations of solvents and promoters, and exceeded 80% with optimal catalyst composition. The effects of solvents and promoters were investigated together with ^{13}C tracer experiments from which the roles of halide anions of onium salts were determined.

Introduction

As the future availability of petroleum becomes uncertain, synthesis gas is expected to play an increasingly important role as an alternative source of various organic chemicals in the petrochemical industry. Because of the catalytic potentiality and higher selectivity to desired products, the application of homogeneous catalysis to the hydrogenation of carbon monoxide to oxygenated compounds is quite attractive. A number of carbonyl complexes of Group VIIIa metals have been reported to be effective in the formation of methanol, ethylene glycol, ethanol and several minor products, such as methyl formate, from synthesis gas conversion [1–4]. However, as the yield of, and selectivity to the desired products C-2 oxygenates, were poor, many attempts were made to improve catalysis. Application of bimetallic catalysts in this reaction is promising, and unexpected synergistic effects were sometimes observed with combinations of two transition metal complexes.

Homogeneous ruthenium catalysts dispersed in molten salts of onium halides effect syngas reaction to form ethylene glycol and primary alcohols [5]. Production of primary alcohols is greatly improved when the reaction is carried out in non-polar solvents with smaller amounts of onium halidees as promoters [6].

Catalytic behavior of ruthenium carbonyl complexes was considerably improved by the addition of a small amount of rhodium compounds. The main product, methanol in this ruthenium system, was converted into C-2 oxygenates, especially ethylene glycol [7–10].

Several articles have been published on bimetallic catalysts (other than ruthenium-rhodium catalyst systems) in synthesis gas reactions, but the synergistic effects of the combinations are not significant [3,7,11].

Among them, we found that cobalt had an interesting effect on the ruthenium catalyst system, which favors direct synthesis of acetic acid from hydrogen and carbon monoxide in non-polar solvents such as toluene [12]. At almost the same time, Knifton and co-workers also found that cobalt had an effect on the ruthenium catalyst in special melt systems [13]. They subsequently described in detail their catalyst system in the conversion of synthesis gas to acetic acid [14]. But, in their case, the reaction was carried out in the presence of a large excess of onium halides used as the solvent, further studies on the effects of solvents and promoters, which usually play important roles in catalysis, have not been carried out.

We report here our independent discovery and study on the selective synthesis of acetic acid from synthesis gas by homogeneous ruthenium-cobalt bimetallic catalyst systems.

Experimental

All high pressure experiments were performed in 50-ml SUS-316L stainless steel autoclaves equipped with agitators and Pyrex glass liners. Materials, dodeca-carbonyltriruthenium, octacarbonyldicobalt, PPNCl [bis(triphenylphosphine)iminium chloride] and HpPh$_3$PBr (n-heptyltriphenylphosphonium bromide) were purchased from Nippon Engelhard, Strem Chem. Inc., K.I. Chemical Industry Co. Ltd. and Tokyo Kasei, respectively. Other PPN salts and HpPh$_3$P salts were prepared by anion exchange from PPNCl and HpPh$_3$PBr. Products were determined by GLC on a Shimadzu GC-7A gas chromatograph using a flame ionization detector. Separations were achieved with a 3 m × 3 mm (i.d.) column, packed with Gaskuropack-55, a programmed temperature increase from 80 to 240 °C, at 4 °C/min, with nitrogen flow rate of 20 ml/min. Gaseous products were analyzed by a Gasukuro Kogyo Model-373-FG Fuel Gas Analyzer. Products were identified by GC-MS and GC-IR analysis.

In tracer experiments, ^{13}C distributions in each product were determined with a JEOL DX-300 GC Mass spectrometer (GC-MS).

Results and discussion

The main products in these reactions were methanol, ethanol, acetic acid, their esters and methane, and the selectivities were usually determined from the yields of these products. The sum of the selectivities to other products such as propanol, propionic acid, ethylene glycol and ethane was usually lower than 5%.

Table 1

Syngas reaction with Ru-Co bimetallic catalysts (catalyst: $Ru_3(CO)_{12}/Co_2(CO)_8/HpPh_3PBr\,^g$/Base, solvent: toluene (19 ml), $HpPh_3PBr$: 7 mmol. 220°C, 3 h. $CO/H_2 = 1$, 290 kg/cm² (at r.t.))

Exp. No.	Catalyst (mg-atom)		Base	(mmol)	Yield (mmol)					
	Ru	Co			MeOH	EtOH	AcOH	AcOMe	AcOEt	CH₄
1	0.7	–	–	(–)	4.25	2.35	0	0.40	0.11	5.13
2	0.7	0.23	–	(–)	0.11	0.46	0.70	0.28	0.62	0.53
3	0.7	0.23	Ph₃P	(0.23)	0.93	1.39	4.04	2.03	0.96	1.02
4 ^{a}	0.7	0.23	Ph₃P	(0.23)	1.64	2.22	4.94	3.08	1.41	0.30
5 ^{b}	0.7	0.23	Ph₃P	(0.23)	1.24	1.85	2.45	1.71	0.91	1.95
6 ^{c}	0.7	0.23	Ph₃P	(0.23)	15.96	1.79	1.08	0.42	0.02	0.80
7	0.7	0.23	Bu₃P	(0.23)	0.73	1.06	2.60	1.87	0.70	0.89
8	0.7	0.23	Ph₃As	(0.23)	1.52	1.74	3.25	0.28	1.60	1.38
9	0.7	0.23	PyOH ^{d}	(3.5)	0.01	0.23	0.61	0.05	0.49	0.37
10	0.7	0.7	Pyridine	(3.5)	9.65	3.29	2.01	2.89	0.75	0.67
11 ^{e}	0.47	0.16	(PhO)₃P	(0.16)	0.08	0.24	6.84	0.08	0.72	0.92
12 ^{f}	–	0.7	–	(–)	0	0	0	tr.	0	0

^{a} MeOH (12.4 mmol) was added before catalysis. ^{b} Solvent: n-heptane (19 ml). ^{c} Solvent: N-ethylpyrrolidone (19 ml). ^{d} 2-Hydroxypyridine. ^{e} HpPh₃PBr 22.7 mmol.
^{f} HpPh₃PBr 21 mmol. ^{g} n-Heptyltriphenylphosphonium bromide.

Addition of cobalt carbonyl complex to ruthenium-onium halide catalyzed synthesis gas reaction

Table 1 shows the effect of the concentration of cobalt carbonyl and added triphenylphosphine. The addition of cobalt carbonyl rather retarded the rate (Exp. No. 2), which was enhanced by the addition of an equimolar amount of triphenylphosphine (Exp. No. 3), where the main product changed dramatically from alcohol to acetic acid. Control experiments confirmed that the ruthenium complex catalyzed alcohol formation, whereas cobalt carbonyl was inactive for carbon monoxide hydrogenation under the same conditions (Exp. No. 1, 12).

It is remarkable that the rate of methane formation was decreased significantly by the addition of cobalt carbonyl. The yield and selectivity of the reaction were affected considerably by the concentration of cobalt carbonyl, and the rate maximum was observed at $Co/Ru = 3/5$ (Fig. 1).

Further studies showed that an optimum ratio of Co/Ru ratio was far from unique in these catalyst systems, and depended on the nature of solvents and promoters. The role of triphenylphosphine, which usually retarded the rate of syngas conversion with homogeneous ruthenium catalysts [15], has not been elucidated in this case, but it is likely that it neutralizes the high acidity of the reaction media. In fact, the use of other bases such as pyridine or triphenylarsine also led to similar results (Exp. No. 7–11). As the C-2 oxygenates (ethanol, acetic acid and their esters) are supposed to be derived from methanol (the intermediate) in this reaction (vide infra), the sum of the yields of methanol and C-2 oxygenates represents the total amount of methanol initially formed during the reaction. Figure 2 is a replot of Fig. 1 where the rate of this hypothetical methanol (defined as H-MeOH) formation is plotted as the ordinate. The rate of H-MeOH formation was almost constant when the value of the Co/Ru ratio was between 0 and 1. As cobalt exhibits no activity in the conversion of synthesis gas to methanol, the formation of this reaction intermediate can be concluded to be catalyzed mainly by ruthenium.
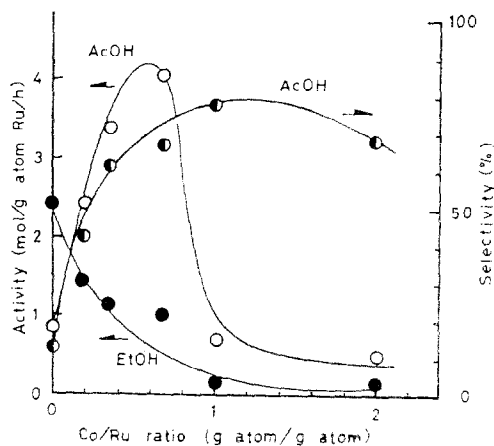

Fig. 1. Effect of concentration of cobalt carbonyl on activity and selectivity of ruthenium carbonyl catalyst. $Ru_3(CO)_{12}$: 0.7 mg-atom, $HpPh_3PBr$: 7 mmol, $Co_2(CO)_8/PPh_3 = 1$, solvent: toluene (19 ml), reaction conditions: $CO/H_2 = 1$, 290 kg/cm^2 (at r.t.), 220 °C, 3 h.
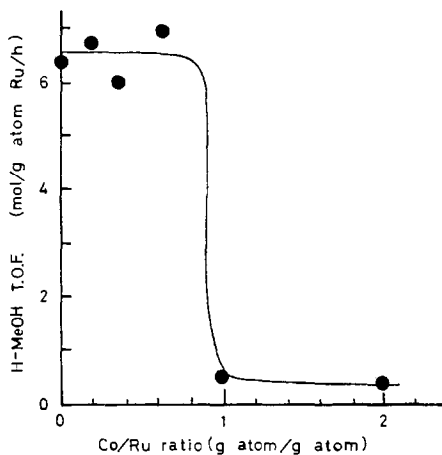
Fig. 2. Effect of concentration of cobalt carbonyl on H-MeOH (see text). For catalyst and reaction conditions: see Fig. 1. T.O.F. = Turnover frequency.

The addition of a certain amount of methanol to this catalyst gave a similar distribution of products, but the rate of net H-MeOH * production decreased significantly (Table 1, Exp. No. 4).

Further addition of cobalt carbonyl decreased the rate of methanol synthesis (Fig. 2). Figure 3 shows the effect of the triphenylphosphine concentration on the reactivity of ruthenium when Co/Ru = 1/3. Excess triphenylphosphine retarded the rate, and the steep decrease in yield of H-MeOH (Fig. 2) is probably due to the combined inhibition effect of triphenylphosphine and cobalt carbonyl.
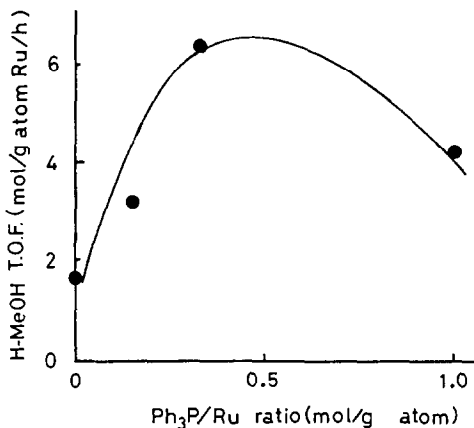

Fig. 3. Effect of concentration of triphenylphosphine on H-MeOH. $Ru_3(CO)_{12}$: 0.7 mg-atom, $Co_2(CO)_8$: 0.23 mg-atom, $HpPh_3PBr$: 7 mmol, solvent: toluene (19 ml), reaction conditions: $CO/H_2 = 1$, 290 kg/cm^2 (at r.t.), 220 °C, 3 h.

* Calculated by subtracting the amount of added methanol from the value of H-MeOH found in reaction mixture after catalysis.

Table 2

Effect of various n-heptyltriphenylphosphonium halide promoters in Ru-Co catalyzed syngas reactions ($Ru_3(CO)_{12}$: 0.7 mg-atom. $Co_2(CO)_8$: 0.23 mg-atom. Ph_3P: 0.23 mmol, promoter: 2 mmol, solvent: toluene (19 ml), 220 °C, $CO/H_2 = 1$, 340 kg/cm^2 (at r.t.))

Exp. No.	Promoter	Yield (mmol/h)						T-AcOH [a] selectivity (%)
		MeOH	EtOH	AcOH	AcOMe	AcOEt	CH$_4$	
1	HpPh$_3$PCl	5.73	0.02	1.23	1.78	0.22	1.18	38.0
2	HpPh$_3$PBr	0.31	0.46	1.35	0.68	0.32	0.34	59.8
3	HpPh$_3$PI	0.44	0.31	0.26	0.26	0.06	0.05	42.6

[a] Total AcOH including AcO in esters.

The effect of several solvents were also examined (Table 1. Exp. No. 5,6). In N-ethylpyrrolidone, the rate of carbon monoxide conversion was higher, but the main product was methanol. Higher selectivity to acetic acid was attained in less polar n-heptane or toluene but the rate was relatively low.

Of these catalytic reactions, the highest selectivity (82%) to acetic acid was attained with Ru/Co/HpPh$_3$PBr/(PhO)$_3$P (molar ratio = 3/1/48/1) catalyst in toluene solvent (Table 1, Exp. No. 11).

Effect of promoter

The yield of, and selectivity to the products were significantly affected by the nature of promoters. Table 2 shows the promotion effect of heptyltriphenylphosphonium (HpPh$_3$P) halides on Ru-Co catalyzed acetic acid synthesis. The proper selection of anion partner for HpPh$_3$P$^+$ is quite important, and the use of chloride resulted in higher yield but lower selectivity compared with bromide and iodide. The order of the promotion effect of halides was as follows: Reactivity: $Cl^- > Br^- > I^-$; Selectivity: $Br^- > I^- > Cl^-$.

Since iodide exhibits an excellent effect in carbonylation reactions with a homogeneous ruthenium catalyst [16], high efficiency was also expected in our case. However, rate enhancement in synthesis gas conversion with this promoter was far lower than that of bromide or chloride.

The effects of other promoters on this reaction are shown in Table 3. When a phosphonium chloride or a bis(triphenylphosphine)iminium (PPN) halide was used in place of HpPh$_3$PBr, the Ru-Co catalysts exhibited higher activity even without

Table 3

Effect of various promoters in Ru-Co catalyzed syngas reactions ($Ru_3(CO)_{12}$: 0.2 mg-atom. $Co_2(CO)_8$: 0.1 mg-atom, promoter 2 mmol; solvent: toluene (19 ml): 240 °C, 1 h. $CO/H_2 = 1$, 340 kg/cm^2 (at r.t.))

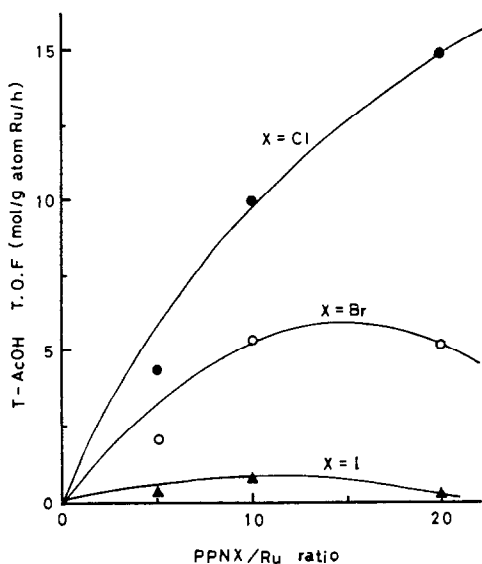| Exp. No.	Promoter	Yield (mmol)					
		MeOH	EtOH	AcOH	AcOMe	AcOEt	CH$_4$
1	Bu$_4$NCl	0.40	0	1.10	0	0	0.59
2	Bu$_4$PCl	4.05	1.00	0	0.70	0.04	0.97
3	PPNCl	7.85	1.73	0.64	1.04	0.04	1.29
4	PPNBr	4.06	1.21	1.72	0.78	0.33	4.25
5	PPNI	6.23	0.21	0	0.09	0.05	0.86

Fig. 4. Effect of concentration of various PPN-halides on the yield of acetic acid. $Ru_3(CO)_{12}$: 0.2 mg-atom, $Co_2(CO)_8$: 0.1 mg-atom, solvent: diphenyl ether (20 ml), reaction conditions: $CO/H_2 = 1$, 340 kg/cm^2 (at r.t.), 240 °C, 3 h. T-AcOH = total AcOH including AcO in esters.

the addition of base. Among salts used, PPN halides showed an excellent promotion effect on this reaction.

To attain higher yield of acetic acid, further studies on these PPN halide promoters were carried out. Figure 4 shows that the use of a larger amount of PPNCl is favorable to obtaining high yields of acetic acid. But selectivity with this promoter was lower than with HpPh$_3$PBr, and this could not be improved by the addition of base (unpublished results). The addition of other transition metal complexes was also examined under the same conditions, and it was found that cobalt was the sole metal which promoted acetic acid synthesis when combined with ruthenium under the conditions studied.

Mechanistic studies

For a better understanding of this catalysis, some mechanistic studies including ^{13}C tracer experiments were carried out. ^{13}C-labeled methanol was added in a Ru-Co catalyzed syngas reaction. Distributions of ^{13}C in each product were determined by GC-MS, and the results are shown in simplified form in Scheme 1. Thus it was found that 47.5% and 13.7% of the added methanol was converted to acetic acid and ethanol, respectively. These values are almost the same as those for acetic acid and ethanol produced from the synthesis gas reaction (48.5% and 13.7%, respectively).

Taking into account the results in Scheme 1 together with the data in Table 1, it can be concluded that the ruthenium carbonyl catalyzes the syngas reaction to form the intermediate methanol, while cobalt carbonyl converts it to acetic acid. At the same time, some of this (intermediate) methanol is converted to ethanol and methane by ruthenium. Thus, the product distributions of the reaction depend on the ratio of ruthenium and cobalt present in the system (Scheme 2).
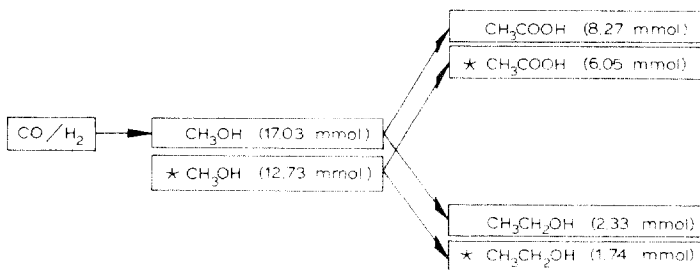
Scheme 1. Product distribution from syngas and ^{13}C-labelled methanol. ^{13}C MeOH 420 mg was added before catalysis. Ethyl or acetyl groups in esters were added to ethanol or acetic acid respectively. ★C = ^{13}C. Ru$_3$(CO)$_{12}$: 0.7 mg-atom, Co$_2$(CO)$_8$: 0.23 mg-atom, HpPh$_3$PBr: 7 mmol, Ph$_3$P: 0.23 mmol, solvent: toluene (19 ml), reaction conditions: CO/H$_2$ = 1, 340 kg/cm^2 (at r.t.), 220 °C, 3 h.
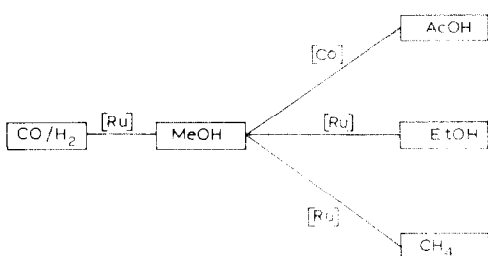
Scheme 2. Possible reaction route to each product.

The effect of various halide promoters and solvents can be interpreted as follows: (1) Syngas conversion to methanol with ruthenium catalyst, chloride and a polar, aprotic solvent enhances the rate more than bromide with non-polar solvent. Rate enhancement by iodide is quite small.

(2) Bromide or iodide and non-polar solvent promote the conversion of methanol to acetic acid with cobalt catalyst, where chloride and a polar, aprotic solvent are less favorable.

The present catalyst system is sensitive to the concentration of onium salts. Similar results have been encountered in the ruthenium-onium salt system. There was an optimum point at which the ratio of onium salt to ruthenium leads to maximum yield, and the addition of an excess of onium salt usually retarded the rate [17]. On the other hand, in the case of the carbonylation reaction of methanol in cobalt-halide systems, higher yields were attained with a higher ratio of halide to cobalt [18].

It is not necessary to consider the formation of ruthenium-cobalt bimetallic cluster [19] in the present reactions as all the experimental results are well explained by the independent functions of ruthenium and cobalt. Furthermore, IR spectra recorded under ambient conditions immediately after catalysis * confirmed the existence of [HRu$_3$(CO)$_{11}$]$^-$, [Ru(CO)$_3$Cl$_3$]$^-$ and [Co(CO)$_4$]$^-$, which also suggests

* IR spectra were recorded for a Ru-Co/PPNCl/toluene system after 3 h reaction at 220 °C, 450 kg/cm^2.

that there was no interaction between carbonyl complexes of ruthenium and cobalt after catalysis. Another route to acetic acid formation in syngas reaction has been proposed. Kaplan reported that acetic acid was formed by the coupling of carbon monoxide in aqueous solution of HI under 350 kg/cm^2 of synthesis gas pressure at 250°C [20], however, the yield was far smaller than that in our ruthenium-cobalt system, and the contribution by such a route will not be of importance.

Acknowledgement

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