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Effect of $Ru_3(CO)_{12}$ and Triisopropylphosphine on the Catalytic Activity of CO Hydrogenation by $Co_2(CO)_8$

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Synopsis. A catalyst system, containing $Co_2(CO)_8$ coupled with Ru_3 $(CO)_{12}$ and triisopropylphosphine((i-Pr)$_3$P), was found to be effective for the ethylene glycol formation by homogeneous hydrogenation of CO: The most active catalyst, the activity of glycol formation of which was ca. 3 times higher than that of $Co_2(CO)_8$ alone, was obtained at phosphorus:Co:Ru ratio of 2:1:1.

Many efforts have been made to prepare ethylene glycol directly from syngas (CO+H_2) using homogeneous catalyst of Group 8 metals.[1] Rhodium,[1b,c] ruthenium,[1a,b,c] and cobalt[1b,c] metals are particularly favorable. Recently, it has been reported that the use of mixed metals, Rh and Ru, as catalyst precursors results in an improved catalytic activity.[2]

We have reported a direct synthesis of the glycol from syngas, where $Co_2(CO)_8$ in toluene solvent is employed under the standard conditions of 1800 atm (180 MPa) and 230 °C.[3] Also, we have found that, in the cobalt-catalyzed glycol production from formaldehyde and syngas, the addition of $Ru_3(CO)_{12}$ is effective for enhancing the glycol productivity.[4] The addition of phosphines has proved to be effective in the case of Rh-amide catalyst.[5] These findings prompt us to try Co–Ru or Co–Ru–P mixed catalysts for the hydrogenation of CO to give ethylene glycol under high pressure and high temperature. Now we describe here some of our results.

Results and Discussion

Some typical examples are shown in Fig. 1, where total amount of metals is held constant at 0.4 (Co+Ru) mmol. In our system involving cobalt coupled with ruthenium and triisopropylphosphine-((i-Pr)$_3$P), ethylene glycol (EG), methanol (MeOH), and methyl formate (MF) are mainly produced with a small amount of ethanol (EtOH) (See Table 1). The results are summarized as follows:

i) A small but clear synergism was observed in the absence of (i-Pr)$_3$P(●).

ii) The addition of (i-Pr)$_3$P resulted in enhancing the CO hydrogenation activity of Co–Ru system (○): The most active catalyst, the cativity of glycol formation of which was ca. 3 times higher than that of $Co_2(CO)_8$ alone, was obtained at phosphorus:Co:Ru ratio of 2:1:1. Further addition of the phosphine reduced the glycol formation. The effectiveness of other phosphines was in the order: (i-Pr)$_3$P(1.59)>(n-Bu)$_3$P(1.14)>Cy$_3$P(0.93)(Cy:cyclohexyl)>none(0.55)>

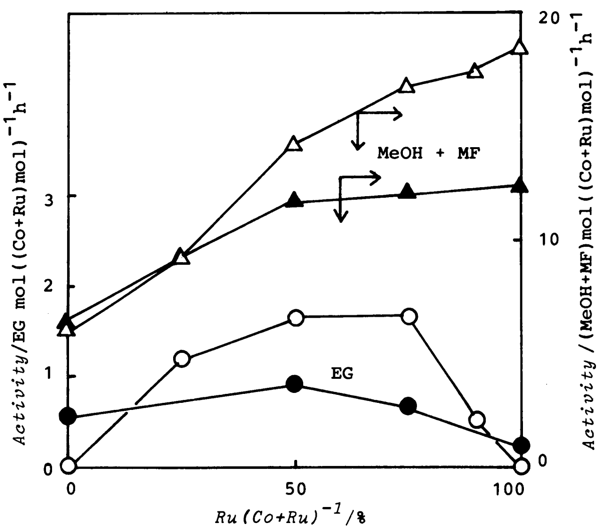

Fig. 1. CO hydrogenation activity vs. ruthenium mole fraction. Co+Ru=0.4 mmol, (i-Pr)$_3$P 0.4 mmol, dioxane 20 ml, 270 °C, 5 h, 1000 atm, H_2/CO=1. ○△ with (i-Pr)$_3$P, ●▲ without (i-Pr)$_3$P.

Table 1. Effect of H_2/CO Ratio under 2000 atm[a)]

H_2/CO Ratio	T/°C	Product/mmol				N_{EG}[b)]	Sel.$_{EG}$[c)]	N_{C_1}[d)]
		MeOH	MF	EtOH	EG	mol/g-atom. h	%	mol/g-atom. h
1	270	3.95	4.4	0.01	3.03	22.8	42	62.8
2	270	8.78	4.46	0.09	4.23	31.8	39	99.5
3	270	11.2	3.49	0.01	2.49	18.7	25	111
1	250	0.79	1.53	0.01	1.27	9.5	52	17.4
3	250	3.18	2.05	0.01	1.96	14.7	43	39.3

a) Conditions: $Co_2(CO)_8$ 0.0335 mmol, $Ru_3(CO)_{12}$ 0.0223 mmol, (i-Pr)$_3$P 0.133 mmol, toluene 7 ml, 2000 atm, 1 h. b) Turnover frequency relative to the total amounts of Co and Ru. c) Sel.$_{EG}$=2EG×100/(MeOH+MF+2(EG+EtOH)). d) MeOH+MF.

$(PhO)_3P(0.25) > Ph_3P(0.07) > Cy_2P(CH_2)_2PCy_2(0.012)$(Cy: cyclohexyl)(numerical values refer to turnover frequency of the glycol (N_{EG})). It was found for the first time that the addition of ruthenium-phosphine was effective for the cobalt-catalyzed CO hydrogenation.6)

iii) After the reaction, the data of which is shown in Fig. 1, each catalyst solution, which is pale red-brown color, is truly homogeneous. Isotope-labelling studies using dioxane-*d*$_8$ conclusively demonstrated that the glycol was primary product and not solvent-derived by hydrogenation of dioxane.

iv) Replacement of $Ru_3(CO)_{12}$ by other metal carbonyls such as $Re_2(CO)_{10}$, $Mo(CO)_6$, $Fe(CO)_5$, and $Cr(CO)_6$ resulted in negative effects on the activity, whereas $Rh_4(CO)_{12}$ promoted the reaction, but the extent was less than $Ru_3(CO)_{12}$. Catalytic behaviors of Co–Ru–P system were examined, in comparison with $Co_2(CO)_8$ alone. For Co–Ru–P (1:1:2) system, the pressure dependence of the glycol formation was greater than fourth-order, while that for C_1-(MeOH+MF) formation process was in the vicinity of first- to second-order, as shown in Fig. 2 (○,△). Analogous dependences were observed in the cobalt catalyst (Fig. 2, ●, ▲). The glycol formation increased with either increases in partial pressure of H_2 or CO; the C_1 formation increased with the increase in P_{H2} and decreased with the increase in P_{CO}. Similar trends were obtained for $Co_2(CO)_8$. The activity of Co–Ru–P system was affected by the initial H_2/CO ratio (Table 1): The maximum activity was achieved at the ratio of 2 at 270 °C. The activation energy for the glycol formation was 105 kJ mol^{-1} and that for C_1 products was 142 kJ mol^{-1}, in the case of Co–Ru–P in toluene solvent under 2000 atm.7) For $Co_2(CO)_8$ alone in the same solvent, the energies for glycol and C_1 have been found to be 100 and 138 kJ mol^{-1}, respectively.3)

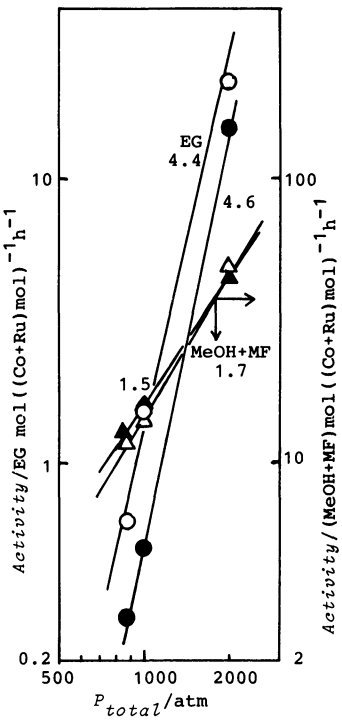

Fig. 2. Effect of total pressure.
toluene 7 ml, 270 °C, 5 h, $H_2/CO=1$.
○△ $Co_2(CO)_8$ 0.1 mmol, $Ru_3(CO)_{12}$ 0.0667 mmol, (*i*-Pr)$_3$P 0.4 mmol, ●▲ $Co_2(CO)_8$ 0.2 mmol.

The IR spectroscopic measurements were undertaken under the conditions of 20 atm at room temperature.8) The hexane solution of Co–Ru–P system exhibited IR absorptions characteristic of $Co_2(CO)_8$(2075 m, 2045 m, 2025 s, 1857 m cm^{-1})9), $Ru(CO)_5$(2040 s, 2002 s cm^{-1}),10) and $Ru(CO)_4[(i\text{-}Pr)_3P]$ (1982 m, 1940 vs cm^{-1}).11,12) Mixed cobalt-ruthenium carbonyl cluster species13) were not detected. For comparison, the Ru–P system, the spectra of which showed $Ru(CO)_5$ and $Ru(CO)_4[(i\text{-}Pr)_3P]$14), possessed high productivity of C_1 compounds but not glycol (Fig. 1) and, on the other hand, the Co–Ru system, exhibiting $Co_2(CO)_8$ and $Ru(CO)_5$ carbonyl bands,14) was favorable in the glycol formation but a little inferior to the Co–Ru–P system (Fig. 1). There findings demonstrate that the presence of $Co_2(CO)_8$ species seems to be essential for the glycol formation and that the presences of both $Ru(CO)_5$ and $Ru(CO)_4[(i\text{-}Pr)_3P]$ contribute to the enhancement of total catalytic activity.

Experimental

Materials. Phosphines, solvents, and $Ru_3(CO)_{12}$ were obtained commercially and used with no further purification. $Co_2(CO)_8$ was prepared according to an usual procedure.

Reaction Procedure. A catalyst solution containing $Co_2(CO)_8$, $Ru_3(CO)_{12}$, and phosphine in solvent was placed in a Hastelloy C(100 ml)- or Inconnel(20 ml)-autoclave, which was subsequently charged with syngas ($H_2/CO=1$). After the reaction, the reaction vessel was cooled to room temperature and the solution was analyzed by GLC. IR spectra were measured with a JEOL A-302 type spectrometer.

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8) A standard catalyst solution which is subjected to the IR analysis was prepared as follows; a hexane solution (20 ml) containing $Co_2(CO)_8$(0.2 mg-atom), $Ru_3(CO)_{12}$(0.2 mg-atom), and (i-Pr)$_3$P(0.4 mmol) was treated under the conditions of 1000 atm of syngas and 270 °C for 5 h. After the autoclave was cooled to room temp. and depressurized up to 20 atm, an aliquot sample was withdrawn from the vessel to a high pressure IR cell.

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12) UV spectra of the solution at atmospheric pressure were also consistent with the presence of $Co_2(CO)_8$(350 nm) and the absence of cluster $Ru_3(CO)_{12}$(390 nm). We also observed a weak IR band of $Co_2(CO)_7[(i\text{-Pr})_3P]$(1994 cm^{-1}).10) But little glycol is generated in $Co_2(CO)_8/(i\text{-Pr})_3P$ system under the conditions (Fig. 1).

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14) In the Ru/(i-Pr)$_3$P system, $Ru_3(CO)_{12}$ species was not present and, on the contrary, the cluster was present in Co–Ru system (UV spectra).