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Direct Synthesis of Ethylene Glycol from Carbon Monoxide and Hydrogen by Use of Rhodium Catalyst. The Effect of Amine Promoters and Their Roles

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The influence of addition of amines on the direct synthesis of ethylene glycol (EG) has been investigated using a rhodium catalyst under a high pressure (1800 kg cm^{-2}). The addition of amines improved the catalyst activity and selectivity for the EG formation and the stability of the catalyst. The addition of amines further resulted in glycerol (GL) formation. Optimum amine/rhodium ratios for the EG formation were 50—100 in tetrahydrofuran solvent with a low polarity and 1—3 in γ-butyrolactone solvent with a high polarity. Optimum N/Rh ratios and IR spectra of reaction solutions suggested that amine promoters serve to accelerate the formation of mononuclear Rh species from the catalyst precursor. It was also suggested that amines promote formation of a Rh-CH_2OH complex and insertion of CO. Bulky amines such as triisobutylamine, N-ethylcarbazole, triisopropanolamine, and tribenzylamine were especially effective promoters for the formation of EG and GL. The effectiveness of bulky amines as the promoter is discussed.

Attention is focused on the direct synthesis of ethylene glycol (EG) as one of researches on the synthesis of useful chemicals from synthesis gas.[1] Researchers of Union Carbide discovered that rhodium compounds are useful as catalyst precursors for the EG direct synthesis. Further, they have so far made many proposals on promoters for improving the activity and selectivity of Rh catalysts for the EG formation.[1] Amine is one of such promoters. Amines promote the formation of anionic rhodium complex as proton bases.[1b] Rhodium cluster anion has been postulated to be the catalyst or its immediate precursor for the EG formation.[1b] Kaplan[2] has proposed that ion pairing between rhodium complex anions and counterions, R_3NH^+, has an adverse effect on the catalytic activity for the EG formation. However, details on the role of amine promoters are still left unclear. Deluzarche et al.[3] have reported that rhodium-2-hydroxypyridine catalyst system shows an effect on the GL formation. Keim et al.[4] have reported that the catalytic activity of iridium for hydrogenation of carbon monoxide is largely enhanced by addition of amines. And amines act as inhibitors in cobalt-catalyzed hydrogenation of carbon monoxide.[4]

In this study, the influence of addition of amines on the direct synthesis of EG was investigated at a high pressure (1800 kg cm^{-2}) to elucidate the behavior of amine promoters. We describe some roles of the amine promoter and effects of bulky amines on the EG formation.

Experimental

All reagents were commercially available. All experiments were carried out in a 20 ml rocking batch reactor made of Inconel Alloy at a constant pressure. Oxygenated compounds, i.e., methyl alcohol (MeOH), ethylene glycol (EG), methyl formate (MF), ethyl alcohol (EtOH), and glycerol (GL), were formed as products. The products were analyzed by gas chromatography using a Chromosorb 102 column. Sulfolane was used as an internal standard. Infrared spectra of catalytic reaction solutions were measured in a KRS cell under ambient conditions after reaction. Rates of formation of products were given in turnover frequency, defined as the number of moles of the product formed per gram-atom of metal per hour. The turnover frequency of EG, N(EG), is obtained by

$$N(\text{EG}) = \text{mol(EG)}/(\text{g-atom Rh})\text{h}.$$

Product selectivity is defined as the carbon efficiency on the basis of reduced carbon monoxide in a product obtained. The selectivity value of EG, Sel.(EG), is obtained by

$$\text{Sel. (EG)} = \frac{2\,\text{EG} \times 100}{\text{MeOH} + \text{MF} + 2(\text{EtOH} + \text{EG}) + 3\,\text{GL}}\,.$$

Results and Discussion

Influence of Some Solvents on the EG Formation. Table 1 shows the influence of solvents on the EG formation in the presence of triethylamine (Et_3N). An addition of Et_3N to a nonpolar solvent such as tetrahydrofuran (THF) or toluene in a molar ratio of Et_3N to Rh of 100 improved the activity and selectivity for the EG formation to a great extent (Nos. 2 and 4). When γ-butyrolactone (γ-BL) having a high polarity, on the other hand, is employed, an addition of Et_3N (N/Rh=100) remarkably decreased the catalytic activity (No. 6). From these results, it is suggested that the effect of addition of amines varies with the polarity of solvents to a considerable extent.

Influence of Amines on the $Rh_4(CO)_{12}$-THF System. Table 2 shows the influence of addition of some amines (N/Rh=100) on the $Rh_4(CO)_{12}$-THF system. Triisobutylamine ($(i\text{-Bu})_3N$) gave a remarkable effect on the activity and selectivity for the EG formation (No. 5) compared to straight-chain trialkylamines. (i-Bu)$_3$N showed a remarkable effect also on the GL formation.

Table 1. Influence of Some Solvents on the EG Formation[a)]

Expt. No.	Solvent (7ml)	Et_3N mmol	Product/mmol MeOH	MF	EtOH	EG	GL	N(EG)	Sel.(EG)
1	Toluene	—	7.55	3.15	0	0.14	0	1.4	2.6
2	Toluene	10	15.24	1.21	0.10	4.74	0	47.5	36.3
3	THF	—	9.32	3.55	0	1.28	0	12.8	16.6
4	THF	10	13.23	0.96	0.09	7.47	0.18	74.7	50.1
5	γ-BL	—	1.83	0.17	0.07	0.24	0	2.4	18.3
6	γ-BL	10	0.03	0	0	trace	0	0.04	21.1

a) Reaction conditions: 1800 kg cm^{-2}, $P_{H_2}/P_{CO}=1$, $Rh_4(CO)_{12}$ 0.1 mg-atom, 230 °C, 1 h.

Table 2. Effect of Amines on the $Rh_4(CO)_{12}$-THF System[a)]

Expt. No.	R_3N (10 mmol)	Product/mmol MeOH	MF	EtOH	EG	GL	N(EG)	Sel.(EG)	Sel.(GL)
1	—	9.32	3.55	0	1.28	0	12.8	16.6	0
2	Et_3N	13.23	0.96	0.09	7.47	0.18	74.7	50.1	1.8
3	$(n\text{-}Bu)_3N$	10.97	0.80	0.03	6.52	0.21	65.2	51.2	2.5
4	$(n\text{-}C_8H_{17})_3N$	9.99	0.73	0.05	6.09	0.31	60.9	50.9	3.9
5	$(i\text{-}Bu)_3N$	3.10	0.34	0	9.19	1.24	91.9	72.0	14.6

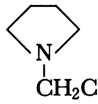
a) Reaction conditions: 1800 kg cm^{-2}, $P_{H_2}/P_{CO}=1$, solvent THF (7 ml), $Rh_4(CO)_{12}$ 0.1 mg-atom, 230 °C, 1 h.

Table 3. Effect of Branched-Chain Amines on the $Rh_4(CO)_{12}$-THF System[a)]

Expt. No.	R_3N (10 mmol)	Product/mmol MeOH	MF	EtOH	EG	GL	N(EG)	Sel.(EG)	Sel.(GL)
1	—	9.32	3.55	0	1.28	0	12.8	16.6	0
2	Et_3N	13.23	0.96	0.09	7.47	0.18	74.7	50.1	1.8
3	$(i\text{-}Pr)_2EtN$	10.16	0.63	0.08	7.01	0.36	70.1	53.8	4.2
4	$(i\text{-}Bu)_3N$	3.10	0.34	0	9.19	1.24	91.9	72.0	14.6
5	$(i\text{-}C_5H_{11})_3N$	10.42	0.83	0.04	6.69	0.65	66.9	50.2	7.3
6	Ph_3N	9.64	2.81	0	0.94	0	9.4	13.1	0
7	$(PhCH_2)_3N$	2.05	0.11	0	8.00	2.00	80.0	66.2	24.8
8	*N*-Ethylcarbazole	5.00	1.23	0	7.36	0.15	73.6	68.8	2.1

a) Reaction conditions: 1800 kg cm^{-2}, $P_{H_2}/P_{CO}=1$, solvent THF (7 ml), $Rh_4(CO)_{12}$ 0.1 mg-atom, 230 °C, 1 h.

Table 4. Effect of (Hydroxyalkyl)amines on the $Rh_4(CO)_{12}$-THF System[a)]

Expt. No.	R_3N (10 mmol)	Product/mmol MeOH	MF	EtOH	EG	GL	N(EG)	Sel.(EG)	Sel.(GL)
1	—	9.32	3.55	0	1.28	0	12.8	16.6	0
2	$(HOCH_2CH_2)_3N$	5.16	0.23	0.46	3.20	0.49	32.0	45.1	10.4
3	$[CH_3CH(OH)CH_2]_3N$	2.95	0.10	0.11	9.76	2.87	97.6	62.2	27.4
4	 $CH_2CH(OH)CH_2OH$	3.58	0.40	0.07	4.62	0.78	46.2	58.9	14.0

a) Reaction conditions: 1800 kg cm^{-2}, $P_{H_2}/P_{CO}=1$, solvent THF (7 ml), $Rh_4(CO)_{12}$ 0.1 mg-atom, 230 °C, 1 h.

Then, we have investigated the effect of addition of amines having branched alkyl groups. As shown in Table 3, an addition of amines having α- or β-branched alkyl group such as *N*,*N*-diisopropylethylamine (No. 3), *N*-ethylcarbazole (No. 8), or tribenzylamine (No. 7) gave an improving effect on the selectivity for the EG formation. Tribenzylamine showed a remarkable effect also on the GL formation. The sum of the selectivities to EG and GL exceeded 90%.

No effect was observed by addition of triphenylamine (No. 6). Triisopentylamine having γ-branched alkyl groups produced a relatively small effect on the selectivity to EG (No. 5). The selectivity to EG was almost the same as that attained by addition of the straight-chain alkylamines.

Table 4 shows the effect of (hydroxyalkyl)amines on the $Rh_4(CO)_{12}$-THF system. Triisopropanolamine (No. 3) and 3-(1-pyrrolidinyl)-1,2-propanediol (No. 4) which have a *β*-substituent gave an improving effect on the activity and selectivity for the EG formation, compared to triethanolamine (No. 2). Triisopropanolamine and 3-(1-pyrrolidinyl)-1,2-propanediol showed an effect also on the GL formation. The results of Tables 2 to 4 show that bulky amines are effective as the promoter for C-C bond formation.

We have further investigated the influence of amounts of Et_3N and $(i\text{-}Bu)_3N$ on the $Rh_4(CO)_{12}$-THF system. The addition of the amines increased the selectivity to EG and decreased the selectivities to MeOH and MF (Figs. 1 and 2). The rate of decrease in the selectivity to MF was larger than that of decrease in the selectivity to MeOH. The addition of Et_3N increased the yield of MeOH as well as EG up to the N/Rh ratio of about 100 (Fig. 1). Consequently, the EG selectivity was as much as 60% or lower. The addition of $(i\text{-}Bu)_3N$, on the other hand, suppressed the formation of MeOH and MF (Fig. 2). As a result, the EG selectivity exceeded 70%. $(i\text{-}Bu)_3N$ showed a remarkable effect also on the GL formation compared to Et_3N.

Influence of CO Partial Pressure on the $Rh_4(CO)_{12}$-THF System. Increase in CO partial pressure increased the selectivities to EG and MF as shown in Fig. 3. On the contrary, it decreased the selectivity to MeOH. Fahey[5] has reported that formaldehyde is trapped as its ethylene glycol acetal in a Rh-catalyzed direct synthesis of EG. Therefore, a reaction path con-

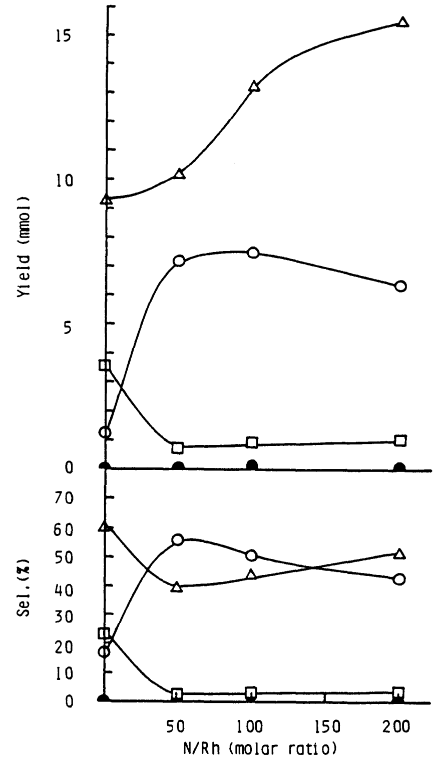


Fig. 1. Influence of Et_3N/Rh ratio. 1800 kg cm^{-2}, $P_{H_2}/P_{CO}=1$, THF (7 ml), 230 °C, $Rh_4(CO)_{12}$ 0.1 mg-atom, 1 h. ○: EG, △: MeOH, □: MF, ●: GL.

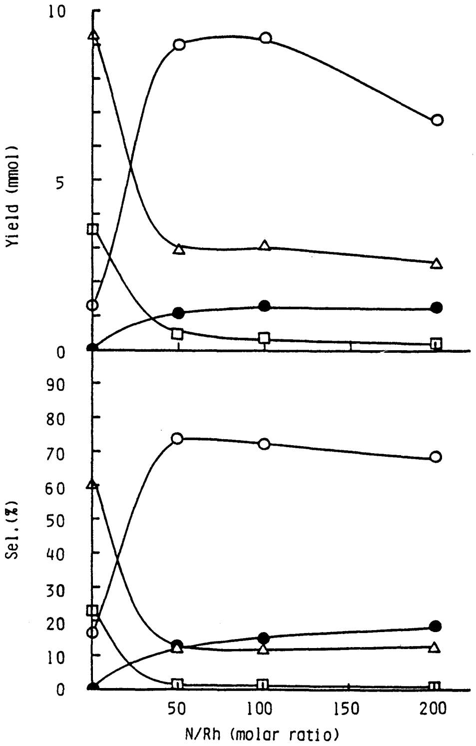


Fig. 2. Influence of $(i\text{-}Bu)_3N$/Rh ratio. 1800 kg cm^{-2}, $P_{H_2}/P_{CO}=1$, THF (7 ml), 230 °C, $Rh_4(CO)_{12}$ 0.1 mg-atom, 1 h. ○: EG, △: MeOH, □: MF, ●: GL.

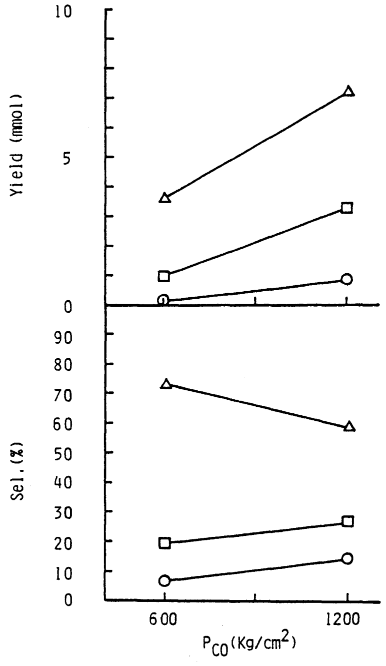
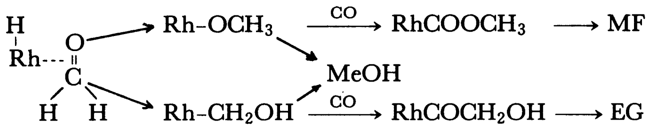


Fig. 3. Influence of CO partial pressure. THF (7 ml), $Rh_4(CO)_{12}$ 0.1 mg-atom, P_{H_2}=600 kg cm^{-2}, 230 °C, 1 h. ○: EG, △: MeOH, □: MF.

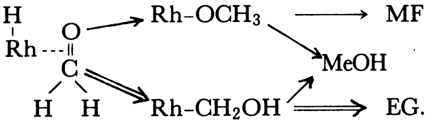


(1)

taining hydroxymethyl and methoxy intermediates, like that of the $Co_2(CO)_8$-toluene system already reported,[6] is suggested for the formation of EG, MF, and MeOH in the $Rh_4(CO)_{12}$-THF system. That is, the increase in CO partial pressure is considered to promote the insertion of CO and increase the selectivities to EG and MF.

In the $Co_2(CO)_8$-toluene system, the increase in CO partial pressure decreases the amount of MeOH and increases the amounts of EG and MF.[6] On the contrary, the increase in CO partial pressure increased the amount of MeOH as well as EG and MF in Fig. 3. This increase in the amount of MeOH can be explained by considering that the increase in CO partial pressure serves to improve the formation of the active species in the $Rh_4(CO)_{12}$-THF system.

As shown in Figs. 1 and 2, the addition of amines increases the selectivity to EG and decreases the selectivities to MeOH and MF. The rate of decrease in MF selectivity is larger than that in MeOH selectivity. This larger rate of decrease in MF selectivity and the improvement of EG selectivity by the addition of amines suggest that amines contribute advantageously to the formation of $Rh\text{-}CH_2OH$ intermediate compared to $Rh\text{-}OCH_3$ intermediate in the sequence



(2)

The decrease in MeOH selectivity and the increase in EG selectivity by the addition of amines in Figs. 1 and 2 suggest that the insertion of CO is promoted by the amines. The contribution of amines to the formation of $Rh\text{-}CH_2OH$ intermediate in Eq. 2 can be explained in terms of a nucleophilic attack on the carbonyl C atom of formaldehyde by Rh whose electron density is increased by amine coordination.

Amines show an effect also on the GL formation. The GL formation can be explained on the basis of the sequence

$$Rh\text{-}COCH_2OH \xrightarrow{H_2} Rh\text{-}CH(OH)CH_2OH \xrightarrow{CO} Rh\text{-}COCH(OH)CH_2OH,$$

$$Rh\text{-}COCH(OH)CH_2OH \xrightarrow{H_2} Rh\text{-}CH(OH)CH(OH)CH_2OH \xrightarrow{H_2} GL, \quad (3)$$

including $Rh\text{-}CH(OH)CH_2OH$ and $Rh\text{-}CH(OH)CH(OH)CH_2OH$ intermediates similar to $Rh\text{-}CH_2OH$ intermediate.

Influence of Catalyst Concentration. Figures 4 and 5 show the influence of catalyst concentrations on the $Rh_4(CO)_{12}$-Et_3N-THF and $Rh_4(CO)_{12}$-$(i\text{-}Bu)_3N$-THF systems, respectively. The $Rh_4(CO)_{12}$-Et_3N-THF system was affected by the catalyst concentration to a large extent. The selectivities to EG and GL were decreased and the MeOH selectivity was increased with increase in catalyst concentration. It is suggested that MeOH is formed advantageously at a high catalyst concentration by the diatomic reaction

$$Rh\text{-}CH_2OH + Rh\text{-}H \longrightarrow MeOH. \quad (4)$$

On the contrary, the influence of the catalyst concentration on the selectivities to EG, GL, and MeOH was small in the $Rh_4(CO)_{12}$-$(i\text{-}Bu)_3N$-THF system. It is suggested that the diatomic reaction mentioned above is relatively unlikely to proceed in the $Rh_4(CO)_{12}$-$(i\text{-}Bu)_3N$-THF system because of the bulkiness of $(i\text{-}Bu)_3N$ ligand. $(i\text{-}Bu)_3N$ which gives a

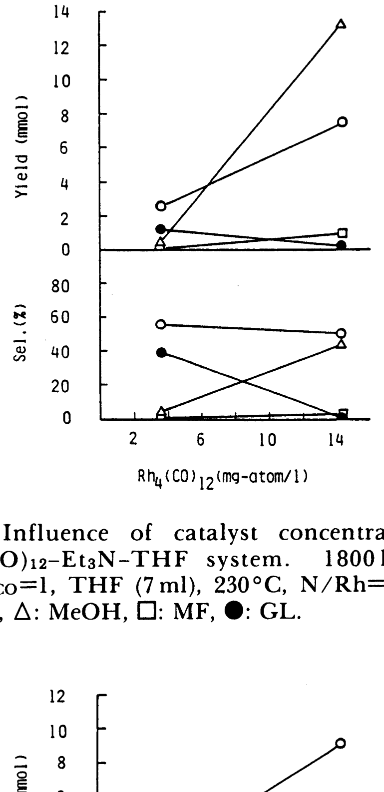


Fig. 4. Influence of catalyst concentration in $Rh_4(CO)_{12}$-Et_3N-THF system. 1800 kg cm^{-2}, $P_{H_2}/P_{CO}=1$, THF (7 ml), 230 °C, N/Rh=100, 1 h. ○: EG, △: MeOH, □: MF, ●: GL.

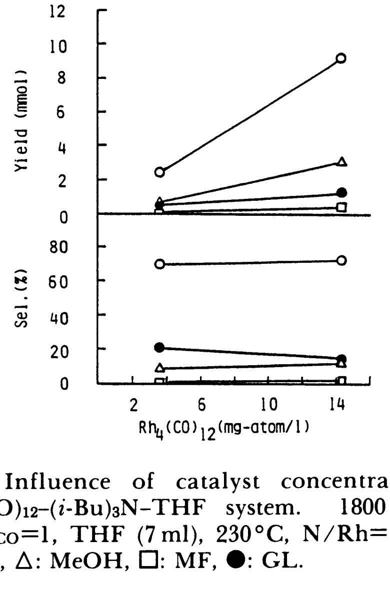


Fig. 5. Influence of catalyst concentration in $Rh_4(CO)_{12}$-$(i\text{-}Bu)_3N$-THF system. 1800 kg cm^{-2}, $P_{H_2}/P_{CO}=1$, THF (7 ml), 230 °C, N/Rh=100, 1 h. ○: EG, △: MeOH, □: MF, ●: GL.

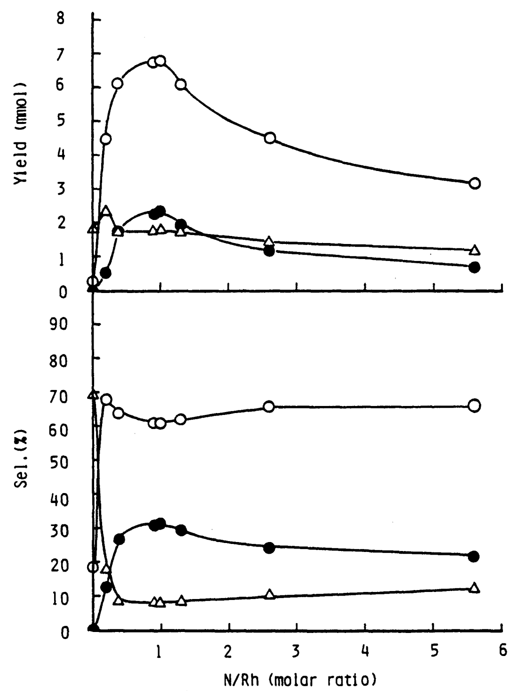


Fig. 6. Influence of $(n\text{-Bu})_3N/Rh$ ratio. 1800 kg cm^{-2}, $P_{H_2}/P_{CO}=1$, γ-BL (7 ml), 230 °C, $Rh_4(CO)_{12}$ 0.1 mg-atom, 1 h. ○: EG, △: MeOH, ●: GL.

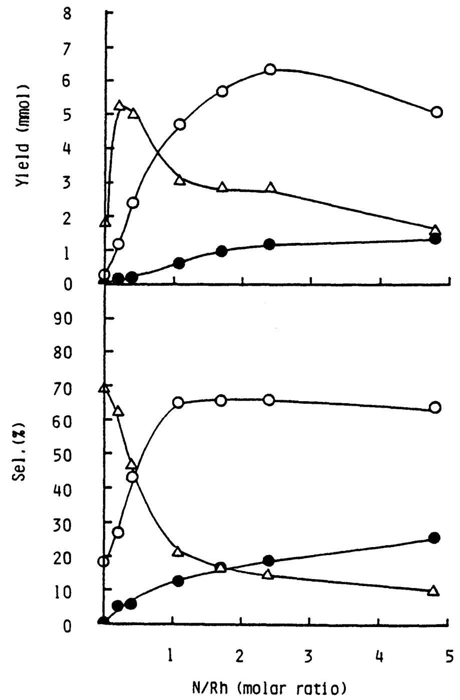


Fig. 8. Influence of $(i\text{-Bu})_3N/Rh$ ratio. 1800 kg cm^{-2}, $P_{H_2}/P_{CO}=1$, γ-BL (7 ml), 230 °C, $Rh_4(CO)_{12}$ 0.1 mg-atom, 1 h. ○: EG, △: MeOH, ●: GL.

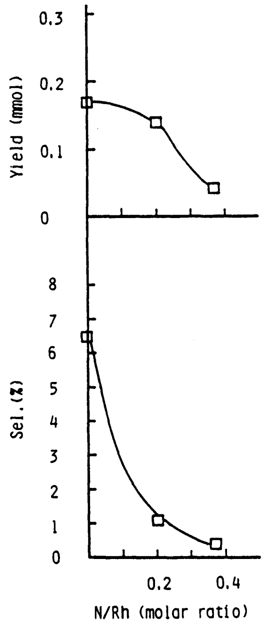


Fig. 7. Influence of $(n\text{-Bu})_3N/Rh$ ratio. 1800 kg cm^{-2}, $P_{H_2}/P_{CO}=1$, γ-BL (7 ml), 230 °C, $Rh_4(CO)_{12}$ 0.1 mg-atom, 1 h. □: MF.

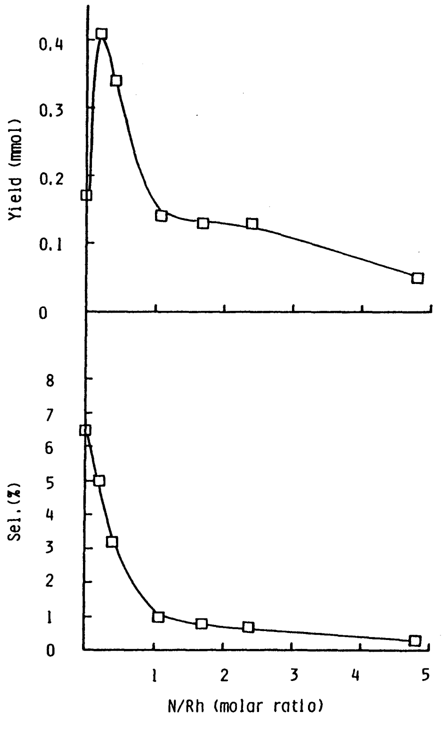


Fig. 9. Influence of $(i\text{-Bu})_3N/Rh$ ratio. 1800 kg cm^{-2}, $P_{H_2}/P_{CO}=1$, γ-BL (7 ml), 230 °C, $Rh_4(CO)_{12}$ 0.1 mg-atom, 1 h. □: MF.

higher EG selectivity at a high catalyst concentration can give a high space time yield (STY: g EG/l h) of EG. Amines that can provide a high STY are favorable as the promoter from the practical point of view. Tribenzylamine (No. 7, Table 3), *N*-ethylcarbazole (No. 8, Table 3), and triisopropanolamine (No. 3, Table 4) which give higher EG selectivities as compared with Et_3N, are also favorable promoters.

Influence of Amines on the $Rh_4(CO)_{12}$-γ-BL System. The influence of amounts of amines was also investigated using γ-BL with a high polarity as a solvent. Figures 6 and 7 illustrate the relationship of

Table 5. Effect of Et_3N on the $Rh_4(CO)_{12}$-TGM System[a)]

Expt. No.	Et_3N (mmol)	Temp °C	Product/mmol MeOH	MF	EtOH	EG	GL	N(EG)	Sel.(EG)
1	—	230	6.40	1.14	0.09	0.91	0	9.1	19.1
2	—	250	4.79	0.32	0.30	0.14	0	1.4	4.7
3	10	250	16.70	2.28	0.80	18.68	1.71	186.8	59.2

a) Reaction conditions: 1800 kg cm^{-2}, $P_{H_2}/P_{CO}=1$, solvent TGM (7 ml), $Rh_4(CO)_{12}$ 0.1 mg-atom, 1 h.

yields of MeOH, MF, EG, and GL and their selectivities with the amount of $(n\text{-Bu})_3N$ added. The yields of EG and GL increase with increase in N/Rh ratio (Fig. 6). The maximum value of the yields of EG and GL was obtained at the N/Rh ratio of 1. On the other hand, the yield of MeOH showed the maximum value at the N/Rh ratio of about 0.2. And the yield of MF decreased with increase in N/Rh ratio (Fig. 7). An increasing tendency of the MeOH selectivity was observed in Fig. 6 when the N/Rh ratio exceeded 1. A suppression of the coordination of an additional CO leading to the C_2 species may be caused by an excessive amount of $(n\text{-Bu})_3N$. This tendency of MeOH selectivity is similar to that of Fig. 1 at N/Rh ratios ranging from 100 to 200. The GL selectivity decreased with increasing amount of $(n\text{-Bu})_3N$ at N/Rh ratios above 1 (Fig. 6). This variation of GL selectivity will not contradict with the tendency of MeOH selectivity.

Figures 8 and 9 illustrate the relationship of yields of MeOH, MF, EG, and GL and their selectivities with the amount of $(i\text{-Bu})_3N$ added. The addition of $(i\text{-Bu})_3N$ also improved the selectivities to EG and GL and decreased the selectivities to MeOH and MF. The optimum N/Rh ratio for the EG formation was in the range from 2 to 3. This optimum N/Rh ratio for the EG formation in γ-BL solvent with a high polarity is remarkably smaller than that obtained in THF solvent with a low polarity (Fig. 2).

The addition of a small amount of $(n\text{-Bu})_3N$ increases the yield of MeOH (Fig. 6). This effect became more remarkable in the case of $(i\text{-Bu})_3N$ as shown in Fig. 8. The activity for the MeOH formation became maximum at N/Rh ratios ranging from 0.2 to 0.4. Simultaneously, the activity for the MF formation became maximum at the same N/Rh molar ratio (Fig. 9). The $Rh_4(CO)_{12}$-tribenzylamine-γ-BL system also showed the same effects. The maximum value for the yields of MeOH and MF was obtained at the N/Rh ratio of about 0.5.[7)]

The effectiveness order for the EG selectivity derived from the maximum activities for the EG formation in Figs. 6 and 8 is $(i\text{-Bu})_3N > (n\text{-Bu})_3N$. However, the difference in EG selectivity between $(i\text{-Bu})_3N$ and $(n\text{-Bu})_3N$ in γ-BL solvent is not so much as that obtained in THF solvent (Figs. 1 and 2 and Table 2). One possible explanation for this small difference in EG selectivity in γ-BL solvent is that the diatomic reaction (Eq. 4) is relatively unlikely to proceed in the $Rh_4(CO)_{12}$-$(n\text{-Bu})_3N$-γ-BL system because of the low concentration of the active species. The concentration of the active species in γ-BL solvent seems to be lower than that in THF, as will be described later.

Influence of Addition of Amine at a High Temperature. Table 5 shows the influence of addition of Et_3N on the $Rh_4(CO)_{12}$-tetraglyme (TGM) system at a high temperature. The $Rh_4(CO)_{12}$-TGM system produced Rh precipitates in the reaction solution after the reaction at 250 °C (No. 2). The catalytic activity in the reaction at 250 °C (No. 2) was lower than that at 230 °C (No. 1). However, an addition of Et_3N to the $Rh_4(CO)_{12}$-TGM system caused no Rh precipitation after the reaction at 250 °C and improved the activity for the EG formation remarkably (No. 3). The addition of Et_3N serves for a stabilization of the catalyst in addition to the improvement of the activity for the EG formation and of the EG selectivity.

IR Spectra of Reaction Solutions. As shown in Scheme 1 below, Vidal and Walker[8)] observed absorption bands of the cluster anion $[Rh_{13+x}(CO)_mH_y]^{n-}$ and the mononuclear species $[Rh(CO)_4]^-$ as a result of IR spectral measurement on a catalytic reaction solution of $Rh(CO)_2acac$-N-methylmorpholine-$CsPhCO_2$-sulfolane solvent system under condition (A) for the direct EG synthesis:

$$\begin{tikzcd}
 & \mathrm{Rh(CO)_2acac} \arrow[d, "\begin{array}{l}N\text{-methylmorpholine}\\ \mathrm{CsPhCO_2}\end{array}", "\begin{array}{r}\mathrm{CO,\ H_2}\\ \text{sulfolane}\end{array}"'] & \\
{[Rh_6(CO)_{15}]^{2-}+[Rh_7(CO)_{16}]^{3-}} & {[Rh_5(CO)_{15}]^{-}+[Rh(CO)_4]^{-}} \arrow[l] \arrow[r] & {[Rh_{13+x}(CO)_mH_y]^{n-}+[Rh(CO)_4]^{-}} \\
\text{(C): ambient conditions.} & \begin{array}{c}\text{(B): 100—180 °C,}\\ \text{500—1000 atm.}\end{array} & \begin{array}{c}\text{(A): 250—270 °C,}\\ \text{500—1000 atm.}\end{array}
\end{tikzcd}$$

Scheme 1.

Under condition (B) of low temperature, absorption bands of $[Rh_5(CO)_{15}]^-$ and $[Rh(CO)_4]^-$ anions were observed. Similar results are obtained when solutions of rhodium carbonyl clusters such as $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ are treated in the same way. They also observed absorption bands of Rh cluster anions, $[Rh_6(CO)_{15}]^{2-}$ and $[Rh_7(CO)_{16}]^{3-}$, under condition (C) of ambient temperature and pressure.

On the other hand, we observed that the IR spectrum of the catalyst system of Fig. 6 obtained at the N/Rh ratio of 1, where the activity for the EG formation became maximum, gave an absorption band (I) at 1900 cm^{-1} under ambient IR measurement conditions as shown in Fig. 10-a. This absorption band (I) at 1900 cm^{-1} seems to be due to the mononuclear Rh species $[Rh(CO)_4]^-$.[9] This IR spectrum gave also a broad absorption band (II) at about 1960 cm^{-1}. The absorption intensity of (I) decreased remarkably over a short period of time (5—30 min) as shown in Fig. 10-b. Simultaneously with the decrease in absorption intensity of (I), the absorption band (II) had its breadth widened and its intensity increased relative to (I). $[Rh_6(CO)_{15}]^{2-}$ has absorption bands at 1960 cm^{-1} and 1980 cm^{-1}.[9] Therefore, the above-mentioned variation of the absorption bands of (I) and (II) with time suggests a decrease in concentration of $[Rh(CO)_4]^-$ and an increase in concentration of $[Rh_6(CO)_{15}]^{2-}$.

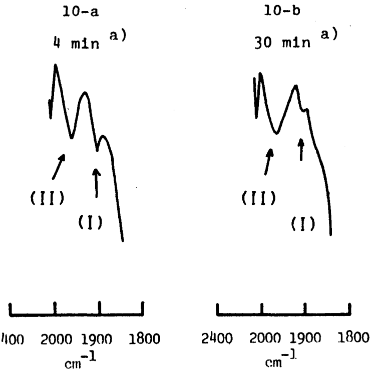


Fig. 10. IR spectra of the catalyst system of Fig. 6 obtained at the N/Rh ratio of 1. a) A time period from withdrawal of the reaction mixture from the autoclave to measurement for IR spectrum.

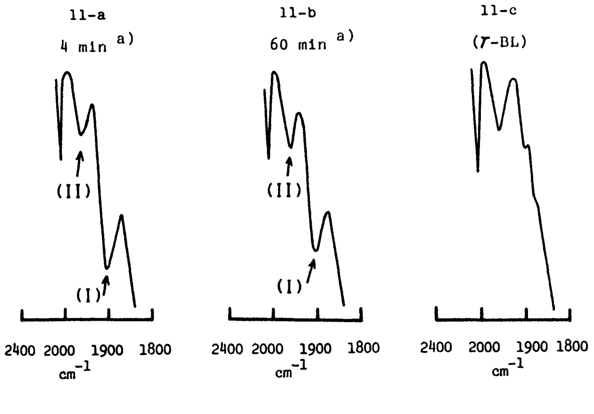


Fig. 11. IR spectra of the catalyst system of Fig. 6 obtained at the N/Rh ratio of 5.6. a) A time period from withdrawal of the reaction mixture from the autoclave to measurement for IR spectrum.

On the other hand, in the case of the catalyst system of Fig. 6 obtained at the N/Rh ratio of 5.6, the absorption band of (I) was relatively stable as shown in Figs. 11-a and 11-b. Since γ-BL solvent has a shoulder at 1900 cm^{-1} (Fig. 11-c), the shoulder was removed from the IR spectra of Figs. 11-a and 11-b by the compensation method. Consequently, it was confirmed that the IR spectra of the catalyst system of Fig. 6 obtained at the N/Rh ratio of 5.6 have a strong absorption band due to $[Rh(CO)_4]^-$ at 1900 cm^{-1} as shown in Figs. 12-a and 12-b.

The catalyst system of Vidal and Walker[8] composed of $Rh(CO)_2acac$, *N*-methylmorpholine, and cesium carboxylate contains $[Rh(CO)_4]^-$ anion under conditions of catalytic reaction such as elevated temperature (250—270 °C) and high pressure (500—1000 atm). And this $[Rh(CO)_4]^-$ anion changes into a cluster anion under ambient temperature and pressure as shown in Scheme 1. Therefore, in the case of the catalyst systems of Fig. 6 obtained at N/Rh=1—5.6 where the absorption band of $[Rh(CO)_4]^-$ anion is observed under ambient temperature and pressure, it is suggested that a mononuclear Rh species is present in the reaction solution under the reaction conditions of 230 °C and 1800 $kg\,cm^{-2}$. It seems that the formation of the mononuclear Rh species at 1800 $kg\,cm^{-2}$ of synthesis

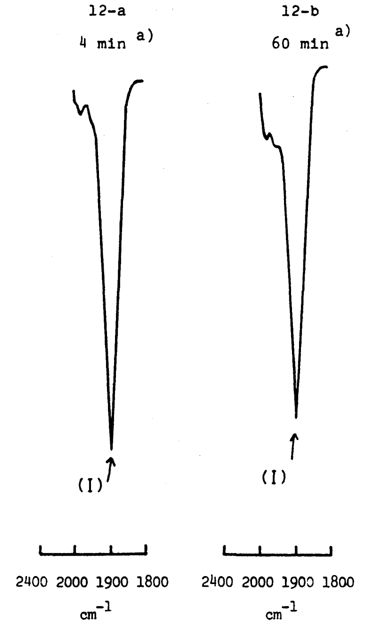


Fig. 12. IR spectra of the catalyst system of Fig. 6 obtained at the N/Rh ratio of 5.6. Absorption bands of γ-BL solvent were removed by compensation method. a) A time period from withdrawal of the reaction mixture from the autoclave to measurement for IR spectrum.

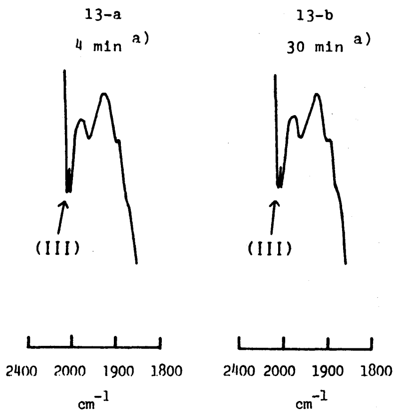


Fig. 13. IR spectra or the catalyst system of Fig. 6 obtained at the N/Rh ratio of zero. a) A time period from withdrawal of the reaction mixture from the autoclave to measurement for IR spectrum.

gas is easier than that at 500—1000 atm used by Vidal and Walker.[8)]

The IR spectrum of the catalyst system of Fig. 6 obtained at the N/Rh ratio of zero showed an absorption band (III) assignable to $[Rh_{12}(CO)_{30}]^{2-}$ anion[9)] at 2053 cm^{-1} (Fig. 13-a). The absorption band (III) is stable as shown in Figs. 13-a and 13-b. Further, it was confirmed by the compensation method that the shoulder[10)] at 1900 cm^{-1} in Fig. 13-a was due to γ-BL.

Active Species. The above results of the IR spectra in Figs. 10—13 suggest that $(n\text{-}Bu)_3N$ serves for the formation of mononuclear Rh species from the Rh catalyst precursor under the catalytic reaction conditions. Because the activity for the EG formation shows the maximum value at N/Rh=1 in Fig. 6, a mononuclear Rh species containing $(n\text{-}Bu)_3N$ is suggested to be a species for the catalytic activity at N/Rh=1. Further, the main product of the catalyst systems of Fig. 6 obtained at N/Rh ratios ranging from 1 to 5.6 was also EG. From the results of Figs. 11 and 12, a mononuclear species of Rh containing $(n\text{-}Bu)_3N$ is likewise suggested to be an active species of the catalyst systems of Fig. 6 obtained at N/Rh ratios ranging from 1 to 5.6.

The IR spectrum of the catalyst system of Fig. 8 obtained at N/Rh 2.5, where the yield of EG became maximum, showed also an absorption band of $[Rh(CO)_4]^-$ anion. A mononuclear Rh species containing $(i\text{-}Bu)_3N$ is likewise considered as an active species of the catalyst system of Fig. 8 obtained at N/Rh=2.5.

The optimum amine/Rh ratios for the EG formation are 50—100 in THF solvent with a low polarity (Figs. 1 and 2) and 1—3 in γ-BL solvent with a high polarity (Figs. 6 and 8). And the addition of excess Et_3N (N/Rh=100) decreases remarkably the catalytic activity in γ-BL solvent (No. 6, Table 1). Further, in our previous paper, we reported that a high catalyst activity for the EG formation is observed in $(n\text{-}Bu)_3N$ solvent with a low polarity at 1800 kg cm^{-2} of synthesis gas.[12)] Considering these results, in γ-BL solvent with a high polarity, factors diminishing the catalyst activity are suggested to include the formation of $[Rh(CO)_4]^-$ anion by an excessive amine. Therefore, a mononuclear species of neutral Rh complex containing amine, $HRh(CO)_3(R_3N)$ (**2**), is suggested as an active species.[13)] A possible reaction path for the formation of **2** may be written as the sequence

$$\begin{gathered} Rh_4(CO)_{12}+R_3N \xrightarrow{CO+H_2} [Rh(CO)_4]^- \, R_3NH^+, \\ [Rh(CO)_4]^- \, R_3NH^+ \rightleftharpoons \underset{\mathbf{1}}{HRh(CO)_4}+R_3N, \\ HRh(CO)_4+R_3N \rightleftharpoons \underset{\mathbf{2}}{HRh(CO)_3(R_3N)}+CO. \end{gathered} \tag{5}$$

The concentration of the neutral active species **2** in γ-BL solvent seems to be lower than that in THF because of the higher polarity of γ-BL. The effect of amine on the EG formation by Eq. 2 can be explained in terms of the nucleophilic attack on the carbonyl C atom of formaldehyde by Rh whose electron density is increased by amine coordination.

However, $Rh_4(CO)_{12}$-$(n\text{-}Bu)_3N$ catalyst system (Fig. 6) in γ-BL solvent with a high polarity seems to show high EG selectivities compared to those (Fig. 1 and Run Nos. 2—4, Table 2) in THF solvent with a low polarity. Therefore, there is a possibility that the proton of $[Rh(CO)_4]^- \, R_3NH^+$ contributes to the formation of $Rh\text{-}CH_2OH$ complex, an intermediate in the EG formation, by an electrophilic attack on the carbonyl O atom of the coordinated formaldehyde shown by Eq. 2. Another possible reason for the high EG selectivity of the $Rh_4(CO)_{12}$-$(n\text{-}Bu)_3N$-γ-BL system is that the diatomic reaction (Eq. 4) is relatively unlikely to proceed because of the low concentration of the active species.

The activity for the MeOH formation becomes maximum at N/Rh ratios ranging from 0.2 to 0.4 as shown in Fig. 8. Further, Tables 1 and 2 show that the catalyst systems without nitrogen-containing compounds form MeOH as the main product. $(i\text{-}Bu)_3N$ is considered to be weaker in coordination ability than $(n\text{-}Bu)_3N$ because of the bulkiness of $(i\text{-}Bu)_3N$. From this and the above results and a related result,[10)] a mononuclear Rh species, $HRh(CO)_4$ (**1**), shown in Eq. 5 is suggested as an active species for the MeOH formation of the catalyst system of Fig. 8 obtained at lower N/Rh ratios (0—0.5). $HRh(CO)_4$ is also suggested as an active species for the MF formation of the catalyst system of Fig. 9 obtained at lower N/Rh ratios (0—0.5).

The absorption band (I) of $[Rh(CO)_4]^-$ anion was observed also in the IR spectrum of the catalyst system of Fig. 1 obtained at Et_3N/Rh=100. But this catalyst system caused precipitaion of Rh species during the IR spectrum measurement at ambient conditions. This indicates that the stability of $[Rh(CO)_4]^-$ anion is low in THF solvent with a low polarity.

It is known[14)] that alkyl manganese pentacarbonyls react with amines producing amine acyl manganese tetracarbonyl complexes according to

$$\mathrm{RMn(CO)_5 + amine} \longrightarrow \mathrm{[amine \rightarrow Mn(R)(CO)_5]} \longrightarrow \mathrm{RCOMn(CO)_4(amine)}. \quad (6)$$

This study seems to provide a support for the C-C bond formation via a hydroxy acetyl Rh complex containing amine.

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