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Ethylene Glycol from Synthesis Gas by Homogeneous Ruthenium and Ruthenium-Rhodium Catalysts

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In the formation of ethylene glycol from synthesis gas, amines (especially imidazole and its derivatives) enhanced the catalytic activity of a ruthenium carbonyl mixed with alkali metal halides. A rhodium carbonyl complex further promoted the activity and selectivity of a ruthenium-alkali metal halide-imidazole catalyst.

The direct formation of ethylene glycol from synthesis gas has been expected to be one of the most attractive new methods for ethylene glycol production on a commercial scale.[1,2] A number of homogeneous catalysts have been reported, such as rhodium, ruthenium, cobalt and iridium complexes.[3-10] Although some promoters, such as halides (alkali metal salt.[6] iminium salt[10] etc.) or carboxylic acids,[6,7] for ruthenium catalyst were reported, research concerning other types of promoters has scarcely been reported. In the course of our research regarding the formation of methanol and ethylene glycol from synthesis gas by ruthenium-alkali metal halide catalysts, we found that organic amines (especially imidazole compounds) promoted the activity of a ruthenium catalyst for ethylene glycol formation.[11] We also found that a rhodium carbonyl complex further enhanced the activity and selectivity of a ruthenium-halide-imidazole catalyst for ethylene glycol formation. In this paper, we report on the direct formation of ethylene glycol from synthesis gas by these ruthenium and ruthenium-rhodium bimetallic catalysts.

Results and Discussion

Ruthenium Catalyst Promoted by Halide and Amine. Dombek[6] reported that methanol and ethylene glycol are formed from synthesis gas when using a ruthenium-alkali metal halide catalyst. We examined the effect of organic amines on this ruthenium-halide catalyst (Eq. 1.).

$$CO + H_2 \xrightarrow{\text{Ru-halide-amine}} CH_3OH + HOCH_2CH_2OH \quad (1)$$

Table 1 summarizes the results for the synthesis of ethylene glycol and methanol in the presence of $[Ru_3(CO)_{12}]$, halide and amine. It was shown that *N*-methylmorpholine, pyridine, 2-pyridinol, benzimidazole, imidazole, and its methyl derivatives promoted the activity of a $[Ru_3(CO)_{12}]$-CsI catalyst for ethylene glycol formation. Of these amines, imidaozle derivatives and 2-pyridinol were especially effective. Furthermore, imidazole promoted the formation of ethylene glycol using a $[Ru_3(CO)_{12}]$ catalyst combined with several types of halide compounds (CsBr, CsCl, KI, Me_4NI, Ph_4NI). On the contrary, 2,2′-bipyridyl, pyrazole and triazole supressed the formation of ethylene glycol.

The activities for ethylene glycol and methanol formation were influenced by the molar ratio of amine to ruthenium. The molar ratio suitable for ethylene glycol formation increased in the following order; *N*-methylmorpholine<imidazole<pyridine≪2-pyridinol. This sequence shows that the more basic the amine, the lower the suitable molar ratio (pK_a at 25 °C: *N*-methylmorpholine 7.38, imidazole 6.95, pyridine 5.21, 2-pyridinol 1.25).[12] This result suggests that the amine acts as a base for the ruthenium catalyst. On the other hand, methanol formation increased with an increasing molar ratio of imidazole to ruthenium; however in the case of other amines, the activities did not greatly depend on the molar ratio of amine to ruthenium. We examined the IR spectra of a recovered reaction mixture started from $[Ru_3(CO)_{12}]$-CsI-imidazole catalyst system under a synthesis-gas atmosphere at room temperature. The spectra were similar to those started from a $[Ru_3(CO)_{12}]$-CsI catalyst system which result in the formation of $[HRu_3(CO)_{11}]^-$(ν(CO) 2020s, 1985s, 1950m cm^{-1}),[6]although the catalytic activities were different from each other. This result suggests that active species of both catalyst systems are similar; also, the ruthenium cluster anion is thought to play an important role in active species, as shown by Dombek in ruthenium-iodide catalyst system.[6] Probably, the amine is converted to an ammonium ion which acts as a cation against the ruthenium anion in the active species **1** (Eq. 2). A similar effect of amine as a cation has been proposed by Kaplan in ethylene glycol formation with a rhodium-amine catalyst:[6]

$$[HRu_x] + R_3N \rightleftharpoons \underset{\mathbf{1}}{[R_3NH]^+[Ru_x]^-}. \quad (2)$$

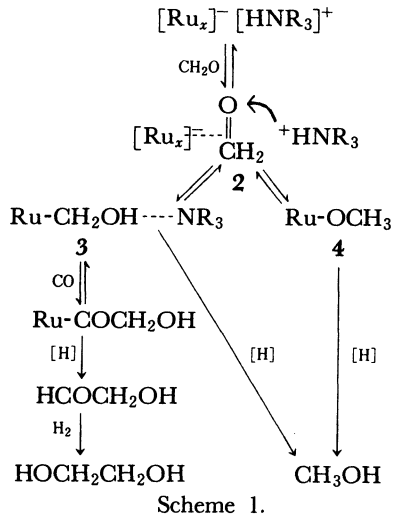
In ethylene glycol formation from synthesis gas, formaldehyde and glycolaldehyde are thought to be important intermediates; the formation of hydroxymethyl complex **3** from a formaldehyde complex **2** is an important step.[13] It is thought that amine promotes the formation of **3** by a proton transfer from the ammonium ion to **2** (Scheme 1). Without the aid of the ammonium ion, the formation of the methoxy complex **4** from **2** may be favored; this will produce methanol, not ethylene glycol.

Effect of Imidazole on Rhodium and Cobalt Catalysts. Rhodium carbonyls and cobalt carbonyls have

Table 1. Effect of Amine on $[Ru_3(CO)_{12}]$-Halide Catalyst for Synthesis Gas Reaction[a]

Halide	Amine	Amine concd[c]	mol (Ru mol·h)$^{-1}$		Selectivity[b]/%
			CH_3OH	$HOCH_2CH_2OH$	
CsI	None		1.34	0.13	9.1
CsI	*N*-Methylmorpholine	(1)	1.45	0.19	11.7
CsI	*N*-Methylmorpholine	(5)	1.61	0.17	9.5
CsI	*N*-Methylmorpholine	(50)	1.14	0.09	7.4
CsI	Pyridine	(5)	1.53	0.20	11.7
CsI	Pyridine	(20)	1.28	0.24	15.6
CsI	Pyridine	(50)	1.01	0.28	21.9
CsI	2-Pyridinol	(5)	1.43	0.21	12.8
CsI	2-Pyridinol	(50)	1.64	0.45	21.5
CsI	2,2′-Bipyridyl	(1)	0.22	0.01	3.7
CsI	Imidazole	(1)	1.98	0.36	15.2
CsI	Imidazole	(5)	2.17	0.64	22.9
CsI	Imidazole	(15)	2.32	0.62	20.9
CsI	Imidazole	(50)	5.82	0.44	7.0
CsI	1-Methylimidazole	(5)	1.61	0.43	21.3
CsI	2-Methylimidazole	(5)	2.74	0.30	9.9
CsI	4-Methylimidazole	(5)	2.24	0.46	17.0
CsI	Benzimidazole	(5)	2.19	0.37	14.6
CsI	Pyrazole	(5)	2.50	0.04	1.6
CsI	1,2,4-Triazole	(5)	0.48	0.02	3.3
CsBr	None		1.08	0.11	9.3
CsBr	Imidazole	(5)	2.21	0.48	17.9
CsCl	None		0.97	0.08	7.6
CsCl	Imidazole	(5)	1.90	0.27	12.6
KI	None		1.11	0.08	7.0
KI	Imidazole	(5)	2.00	0.48	18..9
Me_4NI	None		3.52	0.11	3.0
Me_4NI	Imidazole	(5)	1.69	0.27	13.8
Ph_4PI	None		2.01	0.17	7.7
Ph_4PI	Imidazole	(5)	2.10	0.47	18.4

a) Charge: $[Ru_3(CO)_{12}]$ 0.10 mmol, halide 1.80 mmol, sulfolane 7.5 cm^3; run conditions: CO/H_2 (1:1) 300 kg cm^{-2}, 200 °C, 4 h. b) $100\times(HOCH_2H_2OH)$ mol/$(CH_3OH+HOCH_2CH_2OH)$ mol. c) Molar ratio of amine against Ru atom.



Scheme 1.

been known to be active catalysts for ethylene glycol formation from synthesis gas.[6] Although the effect of amines on cobalt catalysts has scarcely been examined, amines such as alkylamines and pyridine derivatives have been reported to promote the activity of rhodium catalysts.[6] In our research of ruthenium catalysts, imidazole derivatives were found to be effective promoters. Since the effect of imidazole derivatives on other metal catalysts has not been reported, we examined the effect of imidazole on a rhodium catalyst ($[Rh(CO)_2(acac)]$ (acac=acetylacetonato) in sulfolane solvent) and a cobalt catalyst ($[Co_2(CO)_8]$ in toluene solvent), respectively (Table 2). These results showed that imidazole promoted the activity of a rhodium catalyst, though the level of activity was very low. On the contrary, a cobalt catalyst became deactivated upon adding imidazole.

Ruthenium-Rhodium Bimetallic Catalysts.[14] As shown for ruthenium catalysts, the activity for ethylene glycol formation was promoted by amines. However, the selectivity to ethylene glycol was still low for the formation of a large amount of methanol. In order to increase the selectivity of the ruthenium catalyst, we examined the effect of a small amount of $[Rh(CO)_2(acac)]$ on a ruthenium-CsI catalyst system, since several rhodium catalysts have been known to show a high selectivity to ethylene glycol. Table 3 summarizes the results of ruthenium-rhodium-CsI-imidazole catalyst. Although, rhodium itself did not show catalytic activity under the condition given in Table 3, it promoted the activity and selectivity of a ruthenium

Table 2. Effect of Imidazole on Rhodium or Cobalt Catalyst

Metal catalyst	Imidazole[c]	mol (metal mol·h)$^{-1}$	
		CH_3OH	$HOCH_2CH_2OH$
$[Rh(CO)_2(acac)]$[a]	0	0.11	<0.01
$[Rh(CO)_2(acac)]$[a]	5	0.25	0.08
$[Co_2(CO)_8]$[b]	0	0.62	0.02
$[Co_2(CO)_8]$	5	≈0	≈0

a) Charge: $[Rh(CO)_{12}(acac)]$ 0.3 mmol, sulfolane 7.5 cm^3; run conditions: CO/H_2 (1:1) 300 kg cm^{-2}, 240 °C, 4 h. b) Charge: $[Co_2(CO)_8]$ 1.0 mmol, toluene 10 cm^3; run conditions: CO/H_2 (1:1) 500—600 kg cm^{-2}, 240 °C, 4 h. c) Molar ratio of imidazole against Rh or Co atom.

Table 3. Synthesis Gas Reaction by Ruthenium-Rhodium Bimetallic Catalyst[a]

Ru	Rh	CsI	Imidazole	mmol h^{-1}	
mmol	mmol	mmol	mmol	CH_3OH	$HOCH_2CH_2OH$
0.3	0	1.8	1.5	1.005	0.230
0	0.1	1.8	1.5	0	0
0.3	0.1	1.8	1.5	0.618	0.465
0.3	0	1.8	0	0.678	0.085
0.3	0.1	1.8	0	0.372	0.212

a) Charge: $[Ru_3(CO)_{12}]$ $[Rh(CO)_2(acac)]$, CsI, Imidazole and *N*-methyl-2-pyrrolidone 7.5 cm^3; run conditions: CO/H_2 (1:1) 300 kg cm^{-2}, 200 °C, 2 h.

Table 4. Synthesis Gas Reaction in the Presence of $[Ru_3(CO)_{12}]$-$Rh(CO)_2(acac)]$ Catalyst Promoted by CsI and Imidazole[a]

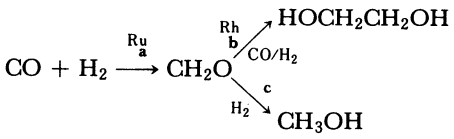
mol% of metal		mmol h^{-1}[b]	
Ru	Rh	CH_3OH	$HOCH_2CH_2OH$
100	0	6.51	0.97
86	14	4.07	2.18
75	25	2.65	2.16
50	50	1.84	1.86
0	100	0.05	0.11

a) Charge: Ru+Rh 0.4 mmol, CsI 2.4 mmol, Imidazole 2.0 mmol, *N*-methyl-2-pyrrolidone 10 cm^3; run conditions: CO/H_2 (1:1) 500 kg cm^{-2}, 200°C, 2 h. b) In addition to methanol and ethylene glycol, small amounts of other products were formed. For example in the case of catalyst Ru/Rh=75/25, methylformate 0.01 mmol h^{-1}, ethanol 0.08 mmol h^{-1} and 1,2-propanediol 0.22 mmol h^{-1} were formed.

catalyst for ethylene glycol formation. Furthermore, promotion by imidazole was also observed in ruthenium-rhodium-CsI catalysis.

In order to analyze the functions of ruthenium and rhodium metal centers, we examined the activity of ruthenium-rhodium bimetallic catalysts with various molar ratios of ruthenium/rhodium. Table 4 summarizes the results from synthesis gas reactions in the presence of $[Ru_3(CO)_{12}]$, $[Rh(CO)_2(acac)]$, CsI and imidazole. In these reactions, the total number of ruthenium and rhodium atoms were kept constant. Ethylene glycol and methanol were the main products, and small amounts of other products (methylformate, ethanol and 1,2-propanediol) were formed. The rate of ethylene glycol formation was maximum at a molar ratio of ruthenium to rhodium around 6:1—3:1.

As mentioned in the prior section, ethylene glycol and methanol are thought to be formed through the common intermediate, formaldehyde (Scheme 2).[15] Since little or no formaldehyde (or its derivatives) was detected by GC analyses, steps **b** and **c** may be faster than step **a**; therefore, the total rate of ethylene glycol and methanol formation may depend upon the rate of step **a**. This total rate (mol h^{-1}) was found to increase with increasing concentration of ruthenium (Fig. 1). This result suggests that step **a** is catalyzed mainly by ruthenium in ruthenium-rhodium bimetallic catalyst. The molar ratio of ethylene glycol to methanol, which depends upon the relative rate of step **b**/step **c**, increased upon increasing the concentration of rhodium (Fig. 1). Rhodium may promote the formation of ethylene glycol from formaldehyde. Thus, ruthenium and rhodium play important independent roles in bimetallic catalyst.



Scheme 2.

We analyzed the catalysts with IR spectra under a synthesis-gas atomsphere at room temperature. Rhodium anion species, $[Rh(CO)_4]^-$ (ν(CO) 1895s cm^{-1})[16] and minor $[Rh(CO)_2I_2]^-$ (ν(CO) 2010, 1975 cm^{-1})[17] were observed in the reaction mixture starting from rhodium-CsI-imidazole catalyst. An IR analysis of the reaction mixture starting from ruthenium-rhodium-CsI-imidazole catalyst showed the existance of $[HRu_3$-

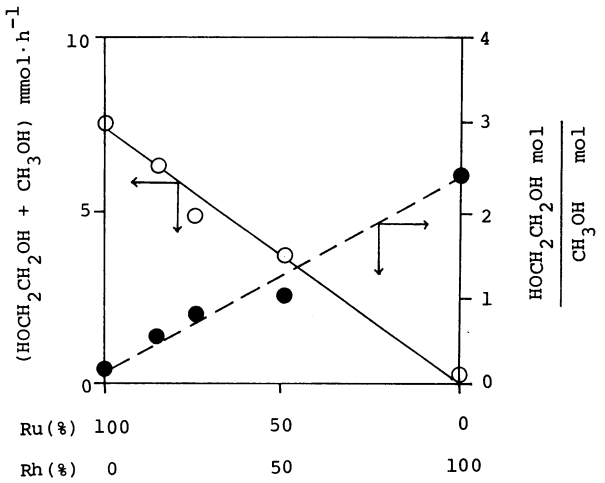


Fig. 1. Effect of molar ratio of ruthenium/rhodium on activities and selectivities of catalysts. —○—, ($HOCH_2CH_2OH+CH_3OH$) mmol h^{-1}; ——●——, molar ratio of $HOCH_2CH_2OH$ against CH_3OH. Conditions; see Table 4.

$(CO)_{11}]^-$, $[Rh(CO)_4]^-$, and $[Rh(CO)_2I_2]^-$. No other species (such as mixed metal clusters) were observed. These results support Scheme 2 in which ruthenium and rhodium act independently.

Experimental

Catalytic expreiments were carried out in a 60-ml autoclave made of Hastelloy C-276. The reactor was charged with metal carbonyl ($[Ru_3(CO)_{12}]$, $[Rh(CO)_2(acac)]$, $[Co_2(CO)_8]$), an additive (halide, amine) and a solvent and was pressurized with CO/H_2 (1 : 1) gas and heated under stirring with a magnetic stirrer (300—600 kg cm^{-2}, 200—240 °C, 2—4 h). An analysis of the products was performed by gas chromatography (column; 10% PEG20M TPA/Chromosorb 102). Infrared spectra were recorded with a Shimadzu IR-420 spectrometer under a synthesis-gas atomsphere at room temperature.

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