

HYDROGENATION OF CARBON MONOXIDE IN THE PRESENCE OF HOMOGENEOUS RUTHENIUM CATALYSTS: EFFECTS OF ONIUM HALIDES AS PROMOTERS

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Summary

The direct formation of ethylene glycol and ethanol from synthesis gas in the presence of a homogeneous ruthenium carbonyl catalyst is promoted by onium halides, such as ammonium, phosphonium and iminium halides. The catalytic activities for ethylene glycol and ethanol formation are dependent on the nature of the halides, and increase in the order $I^- < Br^- < Cl^-$ and $Cl^- < I^- \leq Br^-$, respectively. The ruthenium catalyst in conjunction with $(Ph_3P)_2NCl$ shows the highest activity for ethylene glycol formation. The catalytic activities are dependent on the electron-accepting abilities of the solvents. A moderate electron-accepting ability of the solvent is important for oxygenate formation.

Introduction

Recently, some homogeneous ruthenium catalysts have been reported to be active in the direct formation of ethylene glycol and ethanol from synthesis gas [1-3]. Dombek reported alkali metal halide-promoted ruthenium catalysts [1], and Knifton reported ruthenium catalysts dispersed in molten quaternary phosphonium halides [3]. More recently, we have found that imidazole compounds enhance extremely the catalytic activity of a ruthenium complex for ethylene glycol formation [4]. Although halide promoters have been studied in detail by Dombek [1], research has been confined to alkali metal iodides, and only a few studies concerning onium halide promoters, especially onium chlorides, have been reported. Furthermore, few solvents for the catalyst have been examined, since the very poor solubility of alkali metal iodides in organic compounds prevents the use of common solvents. A study of the solvent effects on the catalytic activity can be carried out in a ruthenium-onium halide catalyst because of the good solubility of onium halides in various organic compounds.

We report here the direct formation of ethylene glycol and ethanol from synthesis gas in the presence of ruthenium catalysts promoted by onium halides, such as ammonium, phosphonium and iminium halides, and discuss the effects of halides and solvents.

Results and discussion

Effects of onium halides

Synthesis gas reactions catalyzed by $\text{Ru}_3(\text{CO})_{12}$ and onium halides in *N*-methylpyrrolidone (NMP) were examined; the results are summarized in Table 1. The catalytic activities are dependent on the nature of the halide ions and onium ions.

The ruthenium catalysts promoted by chlorides show the highest activities for ethylene glycol formation. Thus, the activities for ethylene glycol formation increase in the order: $\text{I}^- < \text{Br}^- < \text{Cl}^-$. On the contrary, the activities for ethanol formation increase in the order: $\text{Cl}^- < \text{I}^- \lesssim \text{Br}^-$.

The observed order for ethylene glycol formation is noteworthy since Dombek has reported that the activation effects of iodide promoters are superior to those of chloride promoters in ruthenium-alkali metal halide catalysts [1]. Furthermore, ruthenium-onium halide catalysts have been found to be superior to Dombek's catalysts (ruthenium-cesium iodide) under the same conditions, as shown in Table 1.

The catalytic activities are also influenced by the nature of the onium ions of the onium halides. The activities for ethylene glycol formation increase in the order: $n\text{-Bu}_4\text{N}^+ < \text{Et}_4\text{N}^+ < \text{Me}_3\text{NH}^+ \sim \text{Ph}_4\text{P}^+ \sim \text{H}_4\text{N}^+ < \text{Me}_4\text{N}^+ < \text{PPN}^+ (= (\text{Ph}_3\text{P})_2\text{N}^+)$, while those for ethanol formation increase in the order: $n\text{-Bu}_4\text{N}^+ < \text{PPN}^+ \sim \text{Et}_4\text{N}^+ < \text{Ph}_4\text{P}^+ \sim \text{Me}_3\text{NH}^+ \sim \text{H}_4\text{N}^+ < \text{Me}_4\text{N}^+$.

TABLE 1

SYNTHESIS GAS REACTION USING RUTHENIUM-ONIUM HALIDE CATALYSTS ^a

Onium halide	mol/Ru (g-atom·h)			
	CH ₃ OH	HOCH ₂ CH ₂ OH	C ₂ H ₅ OH	n-C ₃ H ₇ OH
None	7.03	0	0	0
NH ₄ Cl	116.76	7.47	7.48	1.00
Me ₃ NHCl	143.81	6.92	6.84	1.12
Me ₄ NCl	115.29	9.11	9.50	1.16
Me ₄ NBr	83.84	5.20	21.99	2.29
Me ₄ NI	25.09	0.96	19.39	2.22
Et ₄ NCl	87.20	3.56	2.38	0.50
Et ₄ NI	24.15	0.53	15.37	4.56
n-Bu ₄ NCl	73.47	2.50	0.39	0
(Ph ₃ P) ₂ NCl	134.90	11.97	1.80	0.29
Ph ₄ PCl	73.93	7.12	6.40	1.35
Ph ₄ PBr	57.71	4.35	13.12	1.20
Ph ₄ PI	37.09	1.69	7.71	0.60
Reference				
CsI	35.02	1.26	0.47	0

^a Charge: $\text{Ru}_3(\text{CO})_{12}$ 0.1 mg-atom, halide 1 mmol, NMP 10 ml; run conditions: CO/H_2 (1/1) 500 kg/cm², 240 °C, 2 h.

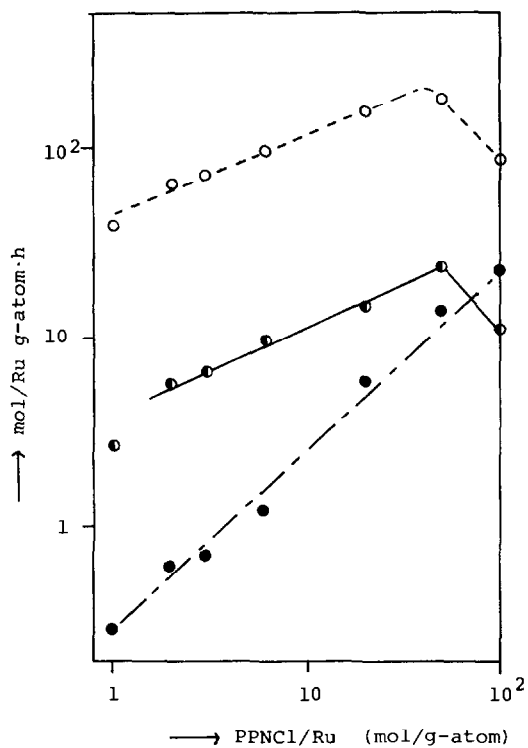


Fig. 1. Effect of the concentration of PPNCI on the catalytic activities. Charge: $\text{Ru}_3(\text{CO})_{12}$ 0.1 mg-atom, DMI 10 ml; run conditions: CO/H_2 (1/3) 500 kg/cm², 240°C, 2 h. ○-----○, CH_3OH ; ●——●, $\text{HOCH}_2\text{CH}_2\text{OH}$; ●- - - -●, $\text{C}_2\text{H}_5\text{OH}$.

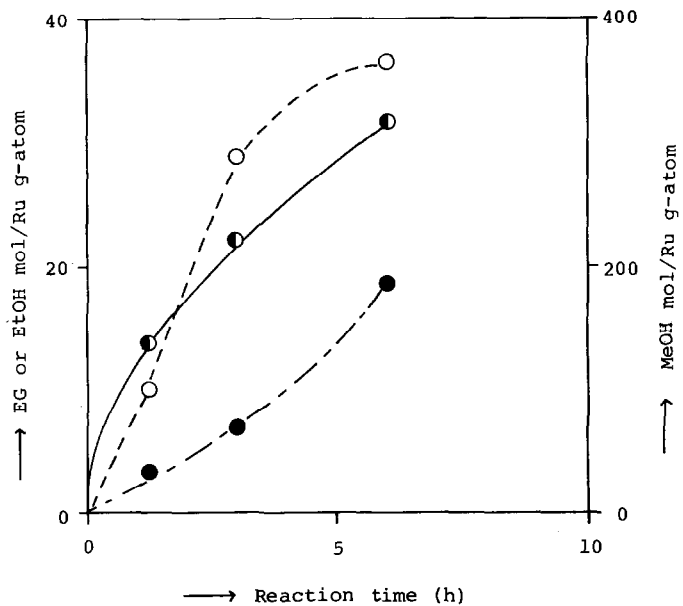


Fig. 2. Product distribution vs. reaction time. Charge: $\text{Ru}_3(\text{CO})_{12}$ 0.09 mg-atom, PPNCI 0.54 mmol, NMP 7.5 ml; run conditions: CO/H_2 (1/1) 500 kg/cm², 230°C. ○-----○, CH_3OH ; ●——●, $\text{HOCH}_2\text{CH}_2\text{OH}$; ●- - - -●, $\text{C}_2\text{H}_5\text{OH}$.

There is no relation between the cation radii of the onium ions and the catalytic activities. Generally, the order of onium ions for the activities of ethylene glycol formation and that for ethanol formation are the same, except for PPN⁺ which exhibits a very high activity for ethylene glycol formation, but a low activity for ethanol formation. A larger amount of 1-propanol was formed in the catalysis when tetraethylammonium iodide was used than when the other ammonium iodides were used. The ethyl group of tetraethylammonium iodide is thought to react with synthesis gas to form 1-propanol.

The effects of the concentration of the PPnCl promoter on the reaction are shown in Fig. 1. The catalytic activities for methanol, ethylene glycol and ethanol formation increase in the 0.4th, 0.4th and 1st order of PPnCl concentration, respectively.

The amount of products as a function of the reaction time is plotted in Fig. 2. Although the apparent rates of methanol and ethylene glycol formation decrease with time, the rate of ethanol formation increases with time. Ethanol is thought to be formed from methanol as shown in previous reports [1,3].

Effects of solvents.

The good solubilities of onium chlorides in various organic solvents enable the effects of the solvent on the catalytic activities to be examined. Reactions with the ruthenium-PPnCl catalyst in various solvents were examined, and the results are summarized in Table 2. High activities for ethylene glycol and methanol formation are obtained in solvents such as 1,3-dimethyl-2-imidazolidone (DMI), NMP and γ -butyrolactone. On the contrary, high activities for ethanol formation are obtained in solvents such as chlorobenzene, 1,2-dimethoxyethane and tetrahydrofuran.

For analysis of the solvent effects, we used the acceptor number (AN) and donor number (DN) of the solvent [5], which indicate the electron-accepting ability and electron-donating ability of the solvent, respectively.

TABLE 2

EFFECT OF THE SOLVENT ON THE CATALYTIC ACTIVITIES OF Ru-PPnCl IN THE SYNTHESIS GAS REACTION ^a

Solvent	AN ^b	DN ^b	mol/Ru (g-atom · h)		
			CH ₃ OH	HOCH ₂ CH ₂ OH	C ₂ H ₅ OH
DMI	13.9 ^c	—	155.28	14.87	5.84
γ -Butyrolactone	17.4 ^c	16	113.11	14.35	2.91
NMP	13.3	27.3	135.43	14.15	1.72
Tetrahydrofuran	8.0	20.0	50.35	4.55	8.40
Acetonitrile	19.3	14.1	79.92	4.19	—
Chlorobenzene	12.3 ^c	—	70.80	4.15	11.20
1,2-Dimethoxyethane	10.2	24	34.23	3.58	9.42
Benzene	8.2	0.1	21.72	1.03	4.89
Ethanol	37.1	20.0	43.83	0.81	—
Dimethylaniline	—	—	13.58	0.52	3.60
Sulfolane	19.0	14.8	10.68	0.41	0.61

^a Charge; Ru₃(CO)₁₂ 0.1 mg-atom, PPnCl 2 mmol, solvent 10 ml; run conditions: CO/H₂ (1/3) 500 kg/cm², 240°C, 2 h. ^b See ref. 5. ^c This work.

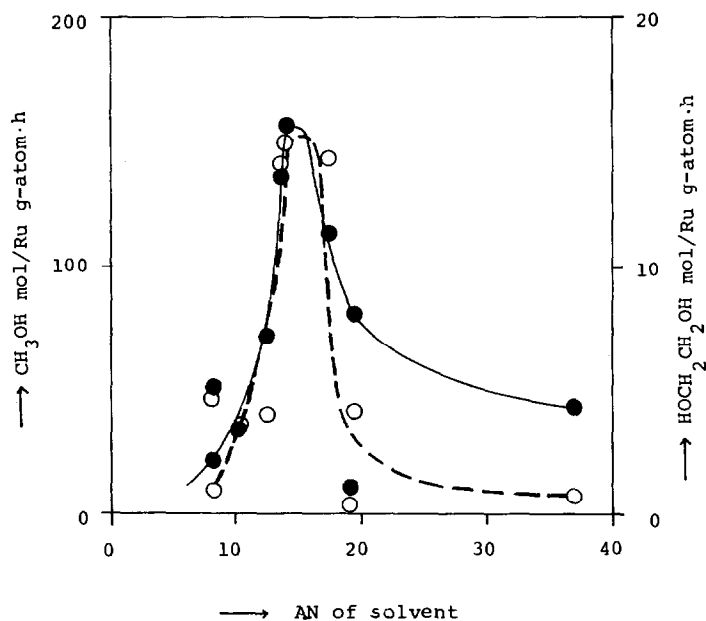


Fig. 3. Relation between the catalytic activities for the formation of methanol and ethylene glycol and the AN of solvents. For conditions, see Table 2. ●—●, CH₃OH; ○—○, HOCH₂CH₂OH.

- (i) The activities for methanol formation and ethylene glycol formation are maximal in a solvent having similar AN values (13–14 and 13–17, respectively) (Fig. 3).
- (ii) The activities for ethanol formation are maximal in a solvent having AN values of 10–12 which are lower than the most suitable values of AN in (i) (Fig. 4).
- (iii) There is no good relation between the activities and the DN of the solvent.

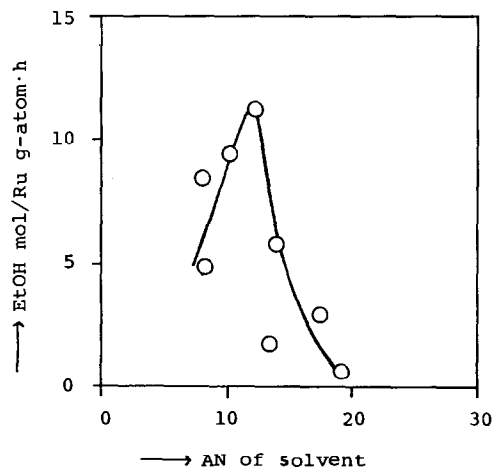


Fig. 4. Relation between the catalytic activities for the formation of ethanol and the AN of solvents. For conditions, see Table 2.

These results show that the catalytic activity is influenced by the electron-accepting ability of the solvent. Analysis of the catalysts indicates the formation of ruthenium anion species as mentioned later. The stabilizing effect of the solvent on the catalytically active species of the ruthenium anion is thought to be important.

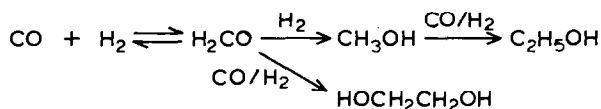
Analysis of the catalytic species

The reaction mixtures using the ruthenium-PPNCl catalyst in NMP solvent were analyzed by IR, Raman and visible spectrometry at room temperature, under an Ar atmosphere. These analyses show the formation of $[\text{HRu}_3(\text{CO})_{11}]^-$ (I) as the main species which was identical with $\text{PPN}^+[\text{HRu}_3(\text{CO})_{11}]^-$ prepared by the literature method [6] (IR: $\nu(\text{CO})$ 2060w, 2015s, 1986s, 1951m cm^{-1} ; Raman: $\nu(\text{Ru}-\text{Ru})$ 210, 160 cm^{-1} ; visible: 385 nm). Besides I, $[\text{Ru}(\text{CO})_3\text{Cl}_3]^-$ is thought to be formed, as inferred from the IR spectra (2100w and 2060w cm^{-1}) [7]. Dombek reported the formation of I and $[\text{Ru}(\text{CO})_3\text{I}_3]^-$ in a similar catalyst system (ruthenium-KI) [1].

The solvent effects on the ruthenium species were examined by IR and UV spectrometry. I was observed as the main species in the catalysts using NMP, DMI, γ -butyrolactone and acetonitrile as the solvents. These catalysts show high activities for ethylene glycol formation. The structures of the ruthenium species are not clear in the other systems, which show a low activity for ethylene glycol formation, using sulfolane, tetrahydrofuran, chlorobenzene and 1,2-dimethoxyethane as the solvents. From these analyses, I is thought to be an important species for ethylene glycol formation. The function of solvents such as NMP and DMI is thought to be stabilization of I.

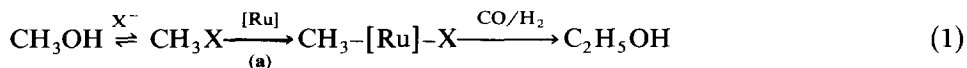
Mechanism

Concerning the reaction mechanism for methanol, ethylene glycol and ethanol formation from synthesis gas, several studies have been reported. One of the most reasonable mechanisms is shown in Scheme 1, in which methanol and ethylene glycol are formed from the common intermediate, H_2CO , and ethanol is formed from methanol [1,3b,8]. The synthesis gas reaction catalyzed by ruthenium-onium halides is thought to proceed according to this scheme.



SCHEME 1

In ethanol formation, the probable rate-determining step is oxidative addition of a methyl halide to the metal active species **a**, as shown with a cobalt catalyst (eq. 1) [9].



This mechanism is consistent with the fact that, in ruthenium-onium halide catalysts, the formation of ethanol is promoted in the order $\text{Cl}^- < \text{I}^- \leq \text{Br}^-$, and increases with 1st order in halide concentration.

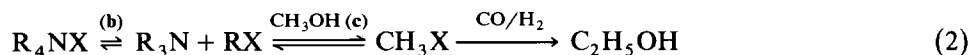
TABLE 3

³¹P CHEMICAL SHIFTS OF Et₃PO IN VARIOUS SOLVENTS AT DIFFERENT CONCENTRATIONS AND ACCEPTOR NUMBERS OF THE SOLVENTS

P Compound	Solvent	<i>c</i> (mol/l)/ δ (ppm)			δ_{∞} (ppm)	δ_{corr} (ppm) ^a	AN ^b
		1	2	3			
Et ₃ PO	n-Hexane	0.0626	0.1009	0.2082	16.98	0	0
		17.492	17.838	18.655			
Et ₃ PO·SbCl ₅	1,2-Dichloroethane	0.0649	0.1277	0.1681	60.23	43.25	100.0
		60.397	60.579	60.669			
Et ₃ PO	<i>N</i> -Methylpyrrolidone	0.0738	0.1369	0.2360	22.99	6.01	13.9
		22.979	22.978	22.960			
Et ₃ PO	<i>N,N'</i> -Dimethylimidazolidone	0.0785	0.1163	0.1988	23.00	6.02	13.9
		22.996	22.996	22.962			
Et ₃ PO	γ -Butyrolactone	0.0765	0.1158	0.1670	24.50	7.52	17.4
		24.468	24.431	24.431			
Et ₃ PO	Chlorobenzene	0.0666	0.1610	0.2062	22.29	5.31	12.3
		22.215	22.106	22.215			

^a $\delta_{\text{corr}} = \delta_{\infty} - \delta_{\infty(\text{n-hexane})}$. ^b AN = $100 \times \delta_{\text{corr}} / \delta_{\text{corr}}(\text{Et}_3\text{PO} \cdot \text{SbCl}_5 \text{ in } 1,2\text{-dichloroethane})$.

The ruthenium catalyst in conjunction with onium halides such as R₄NX and R₄PX shows higher activities for ethanol than the ruthenium catalyst using PPNCl. The reason may be the existence of an equilibrium of **b** and **c** in R₄NX or R₄PX, as shown in eq. 2. The formation of CH₃X from eq. 2 may promote the formation of ethanol. On the contrary, PPN⁺ is stable because of no equilibrium such as **b**, and this may be the reason for the low activity for ethanol formation and the high activity for ethylene glycol formation.



Experimental

Catalytic experiments were carried out in a 60 ml autoclave made of Hastelloy C-276 stainless steel. The reactor was charged with Ru₃(CO)₁₂, halide and solvent, pressurized with CO/H₂ gas, and heated under stirring with a magnetic stirrer. Analysis of the products was done by gas chromatography.

Infrared spectra were recorded with a Shimadzu IR-435 spectrometer. Laser Raman spectra were recorded with a JEOL JRS-400 spectrometer (Ar⁺ laser, 514.5 nm). Ultraviolet spectra were recorded with a Shimadzu UV-250 spectrometer.

The AN values of the solvents were measured according to the literature method [5]. The chemical shift values of ³¹P were determined against (C₆H₅)₃PO as external reference, and were not corrected for volume susceptibility differences. The results are summarized in Table 3. Good agreement between the reported AN value [5] and our measurement was found in the case of NMP (literature 13.3, this work 13.9).

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