

## Hydrogenation of carbon monoxide by homogeneous ruthenium-rhenium bimetallic catalysts: effects of rhenium carbonyl as a promoter for ethylene glycol formation

Masahide Tanaka, Yoshihisa Kiso\* and Kenji Saeki

*Research Center, Mitsui Petrochemical Industries, Ltd., Waki-cho, Kuga-gun, Yamaguchi-ken, 740 (Japan)*

(Received January 8th, 1987)

### Abstract

The activity of the ruthenium-halide catalyst for ethylene glycol formation from CO/H<sub>2</sub> is enhanced by a rhenium carbonyl compound. The activity of the Ru-Re bimetallic catalyst is dependent upon the ratio of Re/Ru atoms and the ratio of moles of halide to atoms of Re. The activities of Ru-Re-alkali metal iodide catalysts increased with increasing ionic radius of alkali metal.

---

### Introduction

Formation of ethylene glycol (EG) from synthesis gas is catalyzed by a number of homogeneous transition metal catalysts, such as rhodium, ruthenium and cobalt complexes [1]. Although a bimetallic catalyst system is expected to show high activity, only two examples, ruthenium-rhodium and platinum-rhodium catalysts, have been reported [2–6]. Recently, we described the novel ruthenium catalyst combined with an imidazole or with an onium chloride for this reaction [7–9]. In the course of our studies of the ruthenium-halide salt catalysts, we have found that a rhenium carbonyl complex enhances the activity of the ruthenium catalyst in the formation of ethylene glycol from CO/H<sub>2</sub>. We wish to report here a novel ruthenium-rhenium bimetallic catalyst [10\*].

### Results and discussion

#### *Effect of rhenium on the ruthenium catalyst*

Recently, we have reported catalysis of the hydrogenation of carbon monoxide by Ru<sub>3</sub>(CO)<sub>12</sub>/bis(triphenylphosphine)iminium chloride (PPNCl), in which

---

\* Reference number with asterisk indicates a note in the list of references.

Table 1

Effect of a rhenium carbonyl complex on a ruthenium-PPNCl catalyst <sup>a</sup>

Re (mg-atom)	Activity		
	<i>N</i> (MeOH)	<i>N</i> (EG)	<i>N</i> (EtOH)
0	27.10	2.62	1.47
0.10	33.57	4.70	1.54
0.15	27.22	6.61	2.14
0.20	27.20	7.90	2.18
0.23	32.85	8.59	2.66
0.28	23.87	6.77	1.49
0.41	20.77	3.79	0.59
0.20 <sup>c</sup>	0.10 <sup>c</sup>	0 <sup>c</sup>	0 <sup>c</sup>

<sup>a</sup> Charge: Ru<sub>3</sub>(CO)<sub>12</sub> 0.1 mg-atom, Re<sub>2</sub>(CO)<sub>10</sub>, PPNCl 0.6 mmol and *N*-methylpyrrolidone 7.5 ml; run conditions: CO/H<sub>2</sub> (1:1), 30 MPa, 230 °C, 2 h. <sup>b</sup> (MeOH) = methanol mol/Ru g-atom/h; *N*(EG) = ethylene glycol mol/Ru g-atom/h; *N*(EtOH) = ethanol mol/Ru g-atom/h. <sup>c</sup> Only Re<sub>2</sub>(CO)<sub>10</sub>, PPNCl and *N*-methylpyrrolidone were charged. Activity is based on rhenium.

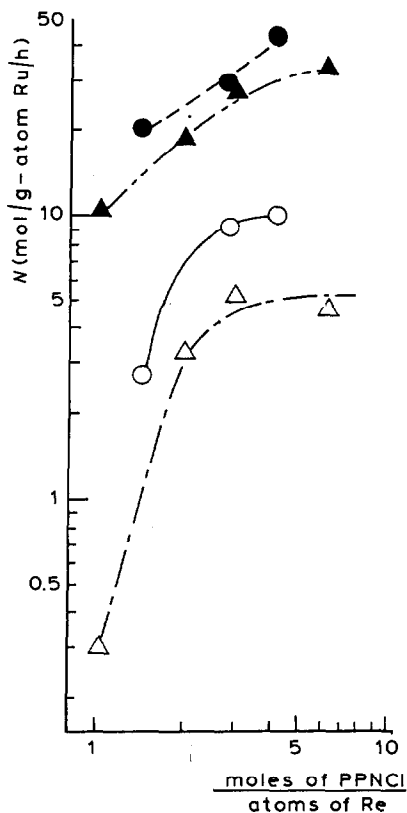


Fig. 1. Plots of activities as a function of the ratio of (moles of PPNCl)/(atoms of Re). Conditions: Ru<sub>3</sub>(CO)<sub>12</sub> 0.1 mg-atom, Re<sub>2</sub>(CO)<sub>10</sub> 0.10 mg-atom (Δ—Δ, ▲—▲) and 0.22 mg-atom (○—○, ●—●), PPNCl and *N*-methylpyrrolidone 7.5 ml; CO/H<sub>2</sub> (1:1) 30 MPa, 230 °C, 2 h. *N*(EG): ○—○ and Δ—Δ; *N*(MeOH): ●—● and ▲—▲.

methanol, ethylene glycol, and ethanol were formed [9]. We have now found that when this ruthenium catalyst is combined with  $\text{Re}_2(\text{CO})_{10}$ , it promotes the formation of ethylene glycol. The results of the hydrogenation of carbon monoxide in the presence of  $\text{Ru}_3(\text{CO})_{12}$ ,  $\text{Re}_2(\text{CO})_{10}$ , and PPNCI are listed in Table 1. Ethylene glycol formation ( $\text{mol/g-atom Ru/h} = N(\text{EG})$ ) increased with increasing amount of rhenium complex, and reached a maximum at an atomic ratio of about  $2\text{Re/Ru}$ , whereas activities for methanol and ethanol formation ( $N(\text{MeOH})$  and  $N(\text{EtOH})$ ) were not greatly changed by adding the rhenium complex. Furthermore, only a small amount of methanol was formed from synthesis gas in the presence of the  $\text{Re}_2(\text{CO})_{10}$ -PPNCI catalytic system [11\*].

We have showed in a previous report [9] that both  $N(\text{MeOH})$  and  $N(\text{EG})$  of the Ru monometallic catalyst increased by 0.4 orders magnitude in PPNCI concentration. This is in contrast with that observed for the Ru-Re bimetallic catalytic system (Fig. 1). Although  $N(\text{MeOH})$  increased with increasing amount of PPNCI,  $N(\text{EG})$  values levelled off in the presence of large amounts of PPNCI. This phenomenon was dependent upon the ratio of moles of PPNCI to atoms of Re ( $\geq 3$ ), but independent of the ratio of moles of PPNCI to atoms of Ru. This result shows that when the ratio (moles of PPNCI)/(atoms of Re) = 3 it becomes limiting for  $N(\text{EG})$ .

The effect of the total pressure of CO and  $\text{H}_2$  on catalytic activity is shown in Fig. 2. The values of  $N(\text{EG})$  of the Ru monometallic and the Ru-Re bimetallic

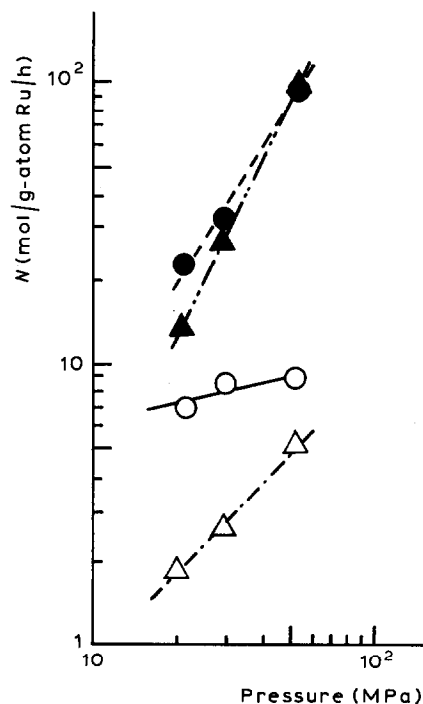


Fig. 2. Effect of pressure on the formation of methanol and ethylene glycol. Conditions:  $\text{Ru}_3(\text{CO})_{12}$  0.1 mg-atom,  $\text{Re}_2(\text{CO})_{10}$  0.23 mg-atom or none, PPNCI 0.6 mmol and *N*-methylpyrrolidone 7.5 ml;  $\text{CO}/\text{H}_2$  (1:1) 230 °C, 2 h. Ruthenium-rhenium catalyst:  $N(\text{EG})$ : ○—○,  $N(\text{MeOH})$ : ●—●, ruthenium catalyst:  $N(\text{EG})$ : △—△,  $N(\text{MeOH})$ : ▲—▲.

catalysts, increased in first and 0.2th order of pressure respectively, whereas the  $N(\text{MeOH})$  values of these two catalysts increased in about second order of pressure. The bimetallic catalyst showed a very low dependence on pressure for ethylene glycol formation. Dependence of  $N(\text{EG})$  on pressure in Ru-Re bimetallic catalysis is noticeable, since previous work on ethylene glycol formation in the presence of Rh or Ru catalysts have shown pressure dependence of rather high order (second ~ fourth order) [1].

#### *The effects of alkali-metal iodide*

The rhenium complex also enhanced the activity of a ruthenium-alkali metal iodide catalyst for ethylene glycol formation. Fig. 3 shows the effect of alkali metal ions on the Ru monometallic catalyst and the Ru-Re bimetallic catalyst. Although the nature of the alkali metal ions did not greatly affect  $N(\text{MeOH})$  and  $N(\text{EG})$  for the Ru monometallic catalyst and  $N(\text{MeOH})$  for the Ru-Re bimetallic catalyst,  $N(\text{EG})$  for the Ru-Re bimetallic catalyst increased with increasing ionic radius of the alkali metal ions ( $N(\text{EG}); \text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$ ). An alkali metal ion has been reported to act as a counter-cation for active metal anionic species in

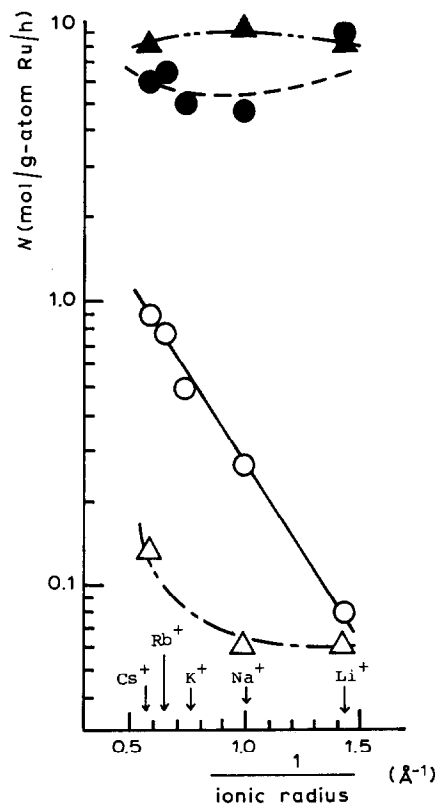
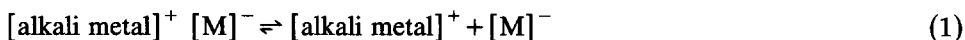


Fig. 3. Correlation between activity and ionic radius of alkali metal. Conditions:  $\text{Ru}_3(\text{CO})_{12}$  0.3 mg-atom,  $\text{Re}_2(\text{CO})_{10}$  0.3 mg-atom or none, alkali metal iodide 1.8 mmol and sulfolane 7.5 ml;  $\text{CO}/\text{H}_2$  (1:1) 30 MPa, 230 °C, 4 h. Ruthenium-rhenium-iodide catalyst;  $N(\text{EG})$ : ○—○,  $N(\text{MeOH})$ : ●—●, ruthenium-iodide catalyst;  $N(\text{EG})$ : △—△,  $N(\text{MeOH})$ : ▲—▲.

ethylene glycol formation by ruthenium or rhodium catalysts [1,4,7,9]. The alkali metal ions of the iodides are also thought to act as counter-cations for ruthenium or rhenium anionic species in Ru-Re bimetallic catalysis. The effect of the alkali metal ions suggests that naked anionic metal carbonyl species are effective for ethylene glycol formation by the Ru-Re bimetallic catalyst, since an alkali metal ion with large ionic radius is easily solvated to produce naked anionic metal species (eq. 1).



#### *Analysis of catalysts*

The effect of rhenium, on the Ru-Re catalysts, under a high pressure of CO/H<sub>2</sub> at high temperature (CO/H<sub>2</sub> (1:1) 30 MPa, 200 °C), was investigated by IR spectroscopy using a specially designed optical cell. The ruthenium anion species [HRu<sub>3</sub>(CO)<sub>11</sub>]<sup>-</sup> (I) ( $\nu(\text{CO})$  2015s, 1986s 1951m cm<sup>-1</sup>) was observed in the reaction mixture when the Ru-PPNCl catalytic system was used, and an unknown rhenium species (II) ( $\nu(\text{CO})$  1993s, 1985s, 1903s cm<sup>-1</sup>) was observed in the reaction mixture when the Re-PPNCl catalytic system was used. It was found that in the Ru-Re-PPNCl catalytic system both the ruthenium species (I) and the rhenium species (II) were present. No new species such as ruthenium-rhenium mixed clusters were observed. Although the precise structure of the rhenium species is not clear yet, II is thought to be a rhenium anion complexed with a few molecules of halide salt [Re<sub>x</sub>(CO)<sub>y</sub>X<sub>z</sub>]<sup>n-</sup> (X = halogen), deduced from the effect of halide (see above).

Dombek has reported that I and [Ru(CO)<sub>3</sub>X<sub>3</sub>]<sup>-</sup> are important precursors of the active species for ethylene glycol formation from CO/H<sub>2</sub> [1]. In Ru-Re bimetallic catalysis, rhenium is the acceptor of the halide salt, and forms [Re<sub>x</sub>(CO)<sub>y</sub>X<sub>z</sub>]<sup>n-</sup>, then an interaction between I and this rhenium species is thought to enhance the formation of ethylene glycol. Similar synergistic behavior has been reported in Ru-Rh bimetallic catalysts for ethylene glycol formation from synthesis gas, in which interaction between the ruthenium anion species and [Rh(CO)<sub>2</sub>I<sub>4</sub>]<sup>-</sup> promoted ethylene glycol formation [4].

#### **Experimental**

Experiments were carried out in a 60 ml vessel in a Hastelloy C-276 autoclave. The vessel was charged with Ru<sub>3</sub>(CO)<sub>12</sub>, Re<sub>2</sub>(CO)<sub>10</sub>, halide salt and solvent, pressurized with CO/H<sub>2</sub> gas, and heated with stirring. Analysis of products was carried out by gas chromatography (PEG 20M TPA/Chromosorb 102). Infrared spectra were recorded with a Shimadzu IR-435 spectrometer. High pressure IR spectra were obtained using a specially designed optical cell made of CaF<sub>2</sub>. Catalytic reactions were carried out in an autoclave and reaction mixtures were placed in this optical cell under high pressure at high temperature.

#### **Acknowledgement**

This work is a part of "C<sub>1</sub> Chemistry Project", a National Research and Development Program of the Agency of Industrial Science and Technology, Ministry of International Trade and Industry (M.I.T.I.), Japan. We wish to thank Messrs. Tetsuo Hayashi, Michio Sakamoto, Hideto Matsuoka and Hiroyoshi Tarumoto for

their technical assistance, and are grateful to the members of the Ethylene Glycol Group of the Project for valuable discussions.

## References

- 1 B.D. Dombek, *Adv. Catal.*, 32 (1983) 325.
- 2 Y. Kiso and K. Saeki, Japanese Patent. Kokai, (1982) 128644, (1983) 194827; *Bull. Chem. Soc. Jpn.*, 60 (1987) 617.
- 3 J.F. Knifton, *J. Chem. Soc., Chem. Commun.*, (1983) 729.
- 4 B.D. Dombek, *Organometallics*, 4 (1985) 1707.
- 5 R. Whyman, *J. Chem. Soc. Commun.*, (1983) 1439.
- 6 M. Roper, M. Schieren, and A. Fumagalli, *J. Mol. Catal.*, 34 (1986) 173.
- 7 Y. Kiso and K. Saeki, *J. Organomet. Chem.*, 303 (1986) C17.
- 8 Y. Kiso and K. Saeki, *J. Organomet. Chem.*, 309 (1986) C26.
- 9 Y. Kiso, M. Tanaka, H. Nakamura, T. Yamasaki, and K. Saeki, *J. Organomet. Chem.*, 312 (1986) 357.
- 10 Knifton reported a similar ruthenium-rhenium bimetallic catalyst for synthesis gas reaction. However main products were methanol and ethanol. Formation of ethylene glycol was not mentioned. J.F. Knifton, US Patent, (1982) 4332914.
- 11 Recently, Nakamura et al. reported that the  $\text{Re}_2(\text{CO})_{10}\text{-LiCl}$  catalyst was effective for the ethylene glycol formation under severe conditions. S. Nakamura, T. Deguchi, T. Takano, and M. Ishino, Japanese Patent, Kokai, (1983) 150525.