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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)

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Abstract

The activity of the ruthenium-halide catalyst for ethylene glycol formation from CO/H_2 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_2. 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 $Ru_3(CO)_{12}$/bis(triphenylphosphine)iminium chloride (PPNCl), in which

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

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Table 1

Effect of a rhenium carbonyl complex on a ruthenium-PPNCl catalyst [a]

Re (mg-atom)	Activity		
	N(MeOH)	*N*(EG)	*N*(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 [c]	0.10 [c]	0 [c]	0 [c]

[a] Charge: $Ru_3(CO)_{12}$ 0.1 mg-atom, $Re_2(CO)_{10}$, PPNCl 0.6 mmol and *N*-methylpyrrolidone 7.5 ml; run conditions: CO/H_2 (1:1), 30 MPa, 230 °C, 2 h. [b] (MeOH) = methanol mol/Ru g-atom/h; *N*(EG) = ethylene glycol mol/Ru g-atom/h; *N*(EtOH) = ethanol mol/Ru g-atom/h. [c] Only $Re_2(CO)_{10}$, PPNCl and *N*-methylpyrrolidone were charged. Activity is based on rhenium.

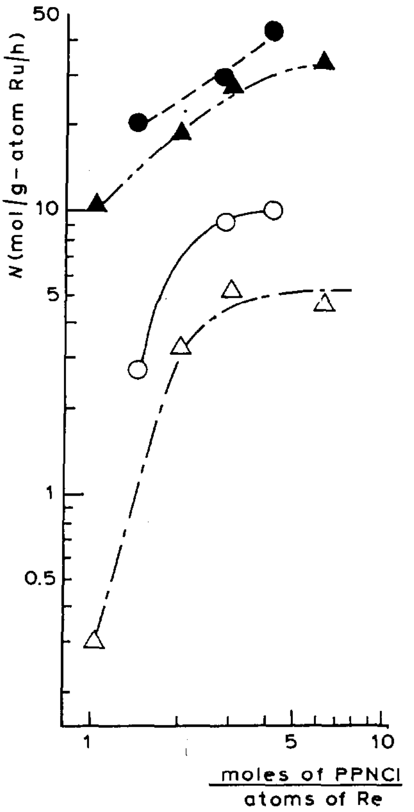

Fig. 1. Plots of activities as a function of the ratio of (moles of PPNCl)/(atoms of Re). Conditions: $Ru_3(CO)_{12}$ 0.1 mg-atom, $Re_2(CO)_{10}$ 0.10 mg-atom (△———△, ▲———▲) and 0.22 mg-atom (○———○, ●———●), PPNCl and *N*-methylpyrrolidone 7.5 ml; CO/H_2 (1:1) 30 MPa, 230 °C, 2 h. N(EG): ○———○ and △———△; *N*(MeOH): ●———● and ▲———▲.

methanol, ethylene glycol, and ethanol were formed [9]. We have now found that when this ruthenium catalyst is combined with $Re_2(CO)_{10}$, it promotes the formation of ethylene glycol. The results of the hydrogenation of carbon monoxide in the presence of $Ru_3(CO)_{12}$, $Re_2(CO)_{10}$, and PPNCl are listed in Table 1. Ethylene glycol formation (mol/g-atom Ru/h = *N*(EG)) increased with increasing amount of rhenium complex, and reached a maximum at an atomic ratio of about 2Re/Ru, whereas activities for methanol and ethanol formation (*N*(MeOH) and *N*(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 $Re_2(CO)_{10}$-PPNCl catalytic system [11*].

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

The effect of the total pressure of CO and H_2 on catalytic activity is shown in Fig. 2. The values of *N*(EG) of the Ru monometallic and the Ru-Re bimetallic

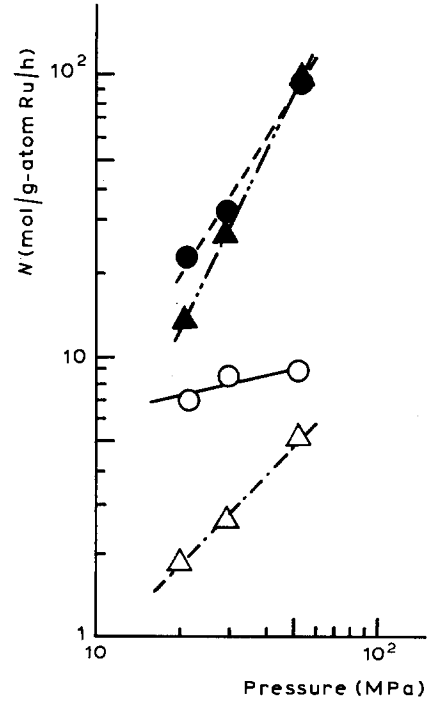

Fig. 2. Effect of pressure on the formation of methanol and ethylene glycol. Conditions: $Ru_3(CO)_{12}$ 0.1 mg-atom, $Re_2(CO)_{10}$ 0.23 mg-atom or none, PPNCl 0.6 mmol and *N*-methylpyrrolidone 7.5 ml; CO/H_2 (1 : 1) 230 °C, 2 h. Ruthenium-rhenium catalyst: *N*(EG): ○——○, *N*(MeOH): ●——●, ruthenium catalyst: *N*(EG): △——△, *N*(MeOH): ▲——▲.

catalysts, increased in first and 0.2th order of pressure respectively, whereas the *N*(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*(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 ~ forth 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*(MeOH) and *N*(EG) for the Ru monometallic catalyst and *N*(MeOH) for the Ru-Re bimetallic catalyst, *N*(EG) for the Ru-Re bimetallic catalyst increased with increasing ionic radius of the alkali metal ions (*N*(EG); $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$). An alkali metal ion has been reported to act as a counter-cation for active metal anionic species in

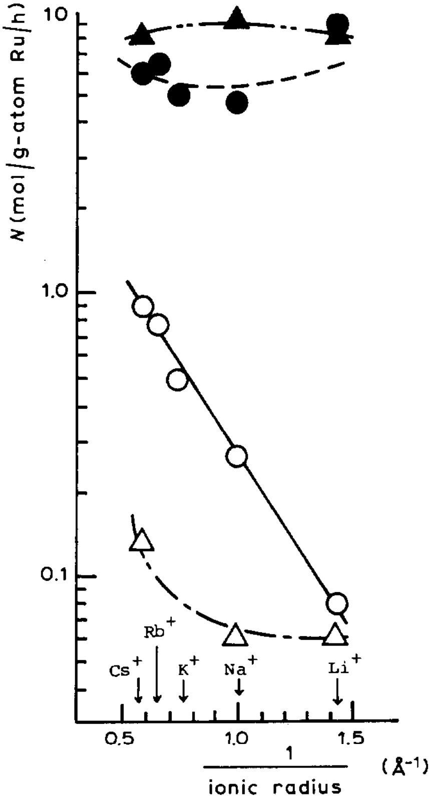

Fig. 3. Correlation between activity and ionic radius of alkali metal. Conditions: $Ru_3(CO)_{12}$ 0.3 mg-atom, $Re_2(CO)_{10}$ 0.3 mg-atom or none, alkali metal iodide 1.8 mmol and sulfolane 7.5 ml; CO/H_2 (1:1) 30 MPa, 230°C, 4 h. Ruthenium-rhenium-iodide catalyst; *N*(EG): ○———○, *N*(MeOH): ●———●, ruthenium-iodide catalyst; *N*(EG): △———△, *N*(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).

$$[\text{alkali metal}]^{+}\ [\text{M}]^{-} \rightleftharpoons [\text{alkali metal}]^{+} + [\text{M}]^{-} \qquad (1)$$

Analysis of catalysts

The effect of rhenium, on the Ru-Re catalysts, under a high pressure of CO/H_2 at high temperature (CO/H_2 (1:1) 30 MPa, 200 °C), was investigated by IR spectroscopy using a specially designed optical cell. The ruthenium anion species $[HRu_3(CO)_{11}]^-$ (I) (ν(CO) 2015s, 1986s 1951m cm^{-1}) was observed in the reaction mixture when the Ru-PPNCl catalytic system was used, and an unknown rhenium species (II) (ν(CO) 1993s, 1985s, 1903s cm^{-1}) 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 $[Re_x(CO)_yX_z]^{n-}$ (X = halogen), deduced from the effect of halide (see above).

Dombek has reported that I and $[Ru(CO)_3X_3]^-$ are important precursors of the active species for ethylene glycol formation from CO/H_2 [1]. In Ru-Re bimetallic catalysis, rhenium is the acceptor of the halide salt, and forms $[Re_x(CO)_yX_z]^{n-}$, 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 $[Rh(CO)_2I_4]^-$ 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 $Ru_3(CO)_{12}$, $Re_2(CO)_{10}$, halide salt and solvent, pressurized with CO/H_2 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_2. Catalytic reactions were carried out in an autoclave and reaction mixtures were placed in this optical cell under high pressure at high temperature.

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