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# Pressure Effect in Syngas Conversion to Ethylene Glycol. A Behavior of Rhodium-Tributylphosphine-*N*-Methylpyrrolidone System under 1000 atm

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**Synopsis.** In syngas ($CO+H_2$) conversion to ethylene glycol (EG), rhodium catalyst modified by tributylphosphine ($P^nBu_3$) was found to be ca. 20 times more active under 1000 atm at 210 °C than under 500 atm. This unusual pressure effect was discussed on the basis of IR spectral data.

A pressure effect has been observed in syngas conversion to ethylene glycol (EG), where *N*-methylpyrrolidone (NMP) solution of rhodium compound was used as catalyst system.[1] Also, rhodium systems modified by phosphine have been found to be more effective than Rh alone under the syngas pressure below 500 atm.[2] We have reported the effectiveness of the addition of some phosphines for the glycol synthesis using Co–Ru mixed system in toluene or dioxane solvent under 1000 atm.[3] These findings led us to examine briefly the behavior of Rh-phosphine-NMP catalyst system under 1000 atm, in comparison with that under 500 atm.

## Results and Discussion

NMP was employed as solvent, since it is one of the solvents suitable for Rh-catalyzed syngas conversion.[1] The reaction was carried out at 210 °C. The equimolar addition of some phosphines raised the catalytic activity. The effectiveness of phosphines when employed under the conditions of 1000 atm was in the order. $PCy_3(15.5)>P^iPr_3(14.6)>Cy_2PCH_2CH_2PCy_2(8.8)^{4)}>P^nBu_3(8.2)>$none$(5.8)>OPPh_3(4.4)>Me_2OPCH_2CH_2POMe_2(3.9)>P^nBu_3(2.7)>P^tBu_3(2.1)>P^sBu_3(1.8)>PPh_3(0)=P(OPh)_3(0)=P(O^nBu)_3(0)=P(O^iPr)_3(0)=PPh_2Me(0)=Ph_2PCH_2CH_2PPh_2(0)$. (Numerical values refer to turnover frequencies of ethylene glycol ($N_{EG}$ (mol (Rh mol)$^{-1}$ h$^{-1}$). Here Cy denotes cyclohexyl, Pr propyl, Bu butyl, Ph phenyl, and Me methyl; the superscripts *i*, *n*, and *t* are for iso-, normal, tertiary, respectively.)

The effect of P/Rh ratio on the activity is illustrated

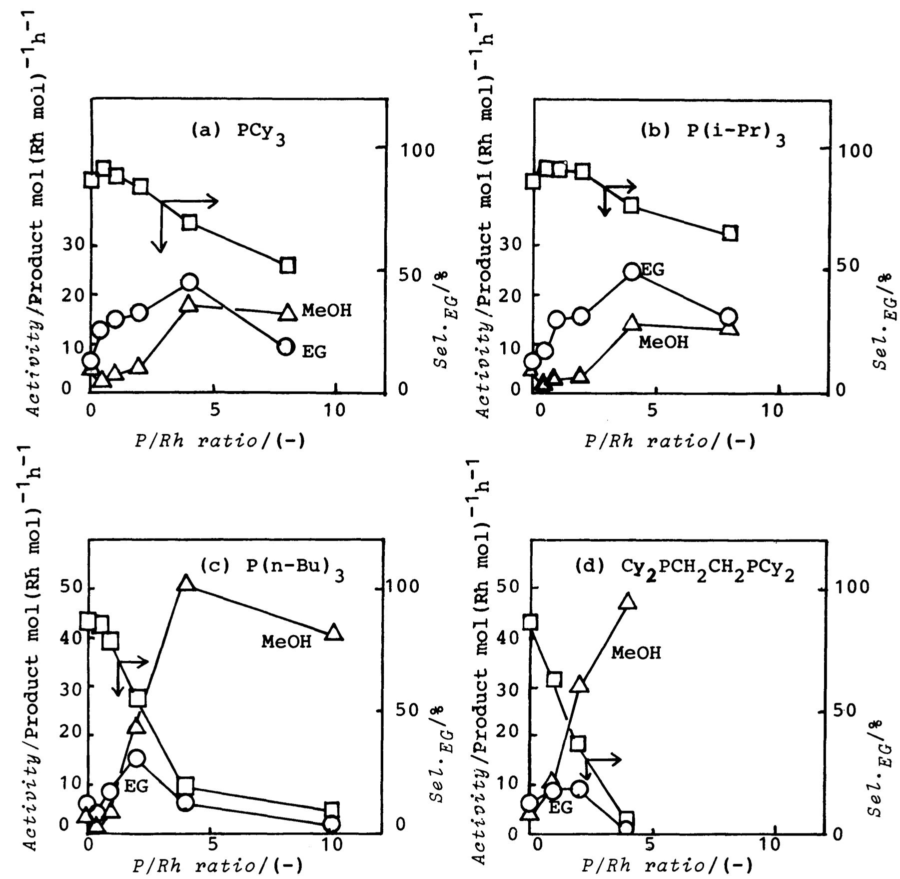

Fig. 1. Effect of P/Rh atomic ratio on catalytic activity and selectivity(Sel.$_{EG}$). Conditions: $Rh_4(CO)_{12}$ 0.05 mmol, NMP 20 ml, 210 °C, 3 h, 1000 atm($CO/H_2=1$).

in Fig. 1. In the cases of $PCy_3$ and $P^iPr_3$, the maximum activity was achieved at P/Rh ratio of 4,[2b] whereas, in the cases of $P^nBu_3$[2b] and $Cy_2PCH_2CH_2PCy_2$, the optimum ratio was found to be 2. However, the methanol formation was remarkably accelerated by these catalyst systems including $P^nBu_3$ or $Cy_2PCH_2CH_2PCy_2$ at the P/Rh ratio above 2 and, consequently, the selectivity to the glycol decreased (Fig. 1c, d).

The activity depends on the total pressure (Fig. 2). The rate of glycol formation for the catalyst systems containing $PCy_3$ or $P^iPr_3$ under 1000 atm was 3—4 times higher than that under 500 atm. These trends were similar to that of Rh alone (▽). However, the rate for Rh–$P^nBu_3$ system under 1000 atm was ca. 20 times higher than that under 500 atm (Fig. 2, ○).

In order to explain this unusual improvement of the activity in Rh–$P^nBu_3$ system, IR spectra of catalyst solution were measured at ambient temperature under 20 atm ($CO/H_2=1$). The catalyst solution pretreated at 210 °C under 1000 atm exhibited IR absorption at 1952 $cm^{-1}$, characteristic of a dimeric rhodium such as $[Rh(CO)_3(P^nBu_3)]_2$, **A**,[2b,5] and at 1895 $cm^{-1}$, assigned to $[Rh(CO)_4]^-$, **B**,[2b,6] with weak shoulder bands near 2000 $cm^{-1}$. These spectral patterns were analogous to those[7] of Rh–$PCy_3$ system after the reaction under 500 atm as well as under 1000 atm. On the other hand, the solution of Rh–$P^nBu_3$, pretreated under 500 atm, showed weak IR absorptions of both **A** and **B** and additional broad bands at 2050—1940 $cm^{-1}$ with 1849 $cm^{-1}$ band, characteristic of rhodium clusters.[8] Thus, in the case of Rh–$P^nBu_3$ under 1000 atm conditions, two rhodium species, **A** and **B**, which seem to be responsible for the catalysis,[1b,2b] are predominantly formed at a P/Rh ratio of 2,[9] whereas cluster species, the activity of which are low,[8a] predominates under 500 atm (Scheme 1).[2,8] In conclusion, the unusual pressure effect is considered to be due to the increase in the concentration of more active Rh species than clusters: This result supports the possibility of non-cluster Rh complex as active species, as suggested previously.[1b,2]

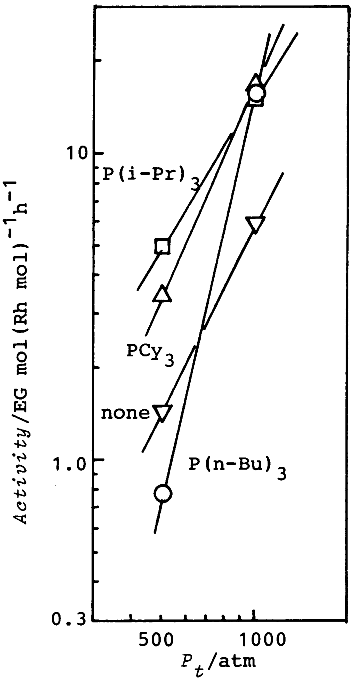

Fig. 2. Effect of total pressue. Conditions: $Rh_4(CO)_{12}$ 0.05 mmol, NMP 20 ml, phosphine 0.4 mmol, 210° C, 3 h.

## Experimental

**Materials.** NMP and phosphines were obtained commercially and used with no further purification. $Rh_4(CO)_{12}$ was purchased from Nippon Engelhard Co.

**Reaction Procedure.** A catalyst solution containing $Rh_4(CO)_{12}$ (0.05 mmol) and phosphine in NMP solvent (20 ml) was placed in a Hastelloy C-autoclave (100 ml), which was subsequently charged with syngas ($CO/H_2=1$, 650 atm at room temp). After the reaction at 210 °C for 3 h under 1000 atm, the reaction vessel was cooled to room temperature and the solution was analyzed by GLC. The high pressure IR spectra were recorded on a JEOL A302-type spectrometer.

Product selectivity is defined by

$$\mathrm{Sel.}_{EG} = \frac{2EG \times 100}{MeOH + MF + 2(EG + EtOH)}$$

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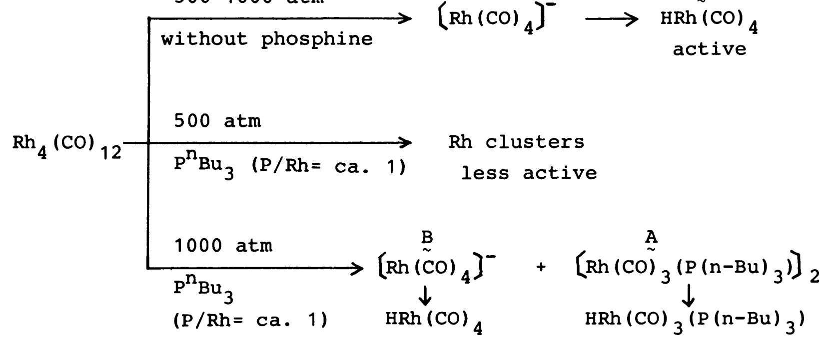

Scheme 1.

## References

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4) For the first time, the effectiveness of diphosphine was demonstrated for the Rh-catalyzed syngas conversion; for $MePCH_2CH_2PMe_2$ and $^tBu_2P(CH_2)_5P^tBu_2$, the reactions were found to be inhibited under 500 atm of syngas. H. Murakami, E. Watanabe, K. Wada, and T. Onoda, unpublished results.

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6) The catalyst solution of Rh–NMP system without phosphine showed the only IR band at 1895 cm$^{-1}$. P. Chini and S. Martinengo, *Inorg. Chim. Acta*, **3**, 21 (1969).

7) These exhibited the IR absorption at 1950(m) and 1895(m) cm$^{-1}$.

8) The formation of $[Rh_9P(CO)_{21}]^{2-}$ and $[Rh_6(CO)_{15}]^{2-}$ is likely.2) a) J. L. Vidal and W. E. Walker, *Inorg. Chem.*, **19**, 896 (1980); b) J. L. Vidal, W. E. Walker, R. L. Pruett, and R. C. Shoening, *ibid.*, **18**, 129 (1979); c) S. Martinengo, A. Fumagalli, P. Chini, V. G. Albano, and G. Ciani, *J. Organomet. Chem.*, **116**, 333 (1976).

$[Rh_9P(CO)_{21}]^{2-}$ : $\nu$(CO) 2010(s), 1840 cm$^{-1}$

$[Rh_6(CO)_{15}]^{2-}$ : $\nu$(CO) 2050, 1990, 1984(s), 1960, 1790, 1767 cm$^{-1}$.

9) Under the 1000 atm-conditions, where non-cluster species are predominantly present, the dependence of reactivity on the $P^nBu_3$/Rh atomic ratio (Fig. 1c) could be explained by the equilibria (a), as is the case for Rh–$P^iPr_3$ system under 500 atm.2)

$$\begin{aligned} &HRh(CO)_4 \xrightleftharpoons{\text{L, -CO}} HRh(CO)_3L \xrightleftharpoons{\text{L, -CO}} HRh(CO)_2L_2 \\ &\xrightleftharpoons{\text{L, -CO}} HRh(CO)L_3 \xrightleftharpoons{\text{L, -CO}} HRhL_4 \qquad \text{(a)} \end{aligned}$$