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Temperature Effect on the Rhodium-Catalyzed Direct Synthesis of Ethylene Glycol from Carbon Monoxide and Hydrogen in Several Solvents

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Synopsis. The $Rh_4(CO)_{12}$/*N*-methyl-2-pyrrolidone system is featured in that the rate of ethylene glycol (EG) formation is significantly accelerated with increasing reaction temperature. The turnover frequency of EG at 300 °C and 2000 kg/cm^2 (H_2/CO=1) is about 2000 h^{-1}. The $Rh_4(CO)_{12}$/tributylamine system also has a high catalytic activity at a high temperature.

The direct synthesis of ethylene glycol (EG) from carbon monoxide and hydrogen is interesting from the fundamental and industrial points of view. Much attention has been paid on this direct synthesis and a number of patents have appeared.[1)] Clusters and complexes of group VIII elements of the periodic table such as Co,[2a)] Rh, Ru, and Ir[2b)] are used as catalysts. Most noteworthy is the work of Union Carbide Corporation which describes the direct synthesis of EG with rhodium catalysts. Union Carbide workers also carried out bench-scale experiments in a continuous flow unit capable of catalyst recycle.[3)] Fahey[4)] has reported of a Rh-catalyzed direct synthesis in tetraglyme solvent with promoters at about 2000 atm of synthesis gas. The highest turnover frequency of EG including ethylene glycol monoformate in his results was 248 h^{-1}, which is, to our knowledge, the highest rate to EG in the literature.[1—4)] However, little is known about the influence of temperature on the glycol producing activity of rhodium catalyst. In the present paper, we report of remarkable temperature effects on the Rh-catalyzed formation of EG from carbon monoxide and hydrogen in nitrogen-containing solvents.

Experimental

All reagents were commercially available. All experiments were carried out in a 20 ml rocking batch reactor made of Inconel Alloy under a constant pressure. Oxygenated compounds such as methyl alcohol (MeOH), ethylene glycol (EG), methyl formate (MF), ethyl alcohol (EtOH), and ethylene glycol monoformate (EGMOF) were formed as products. The products were analyzed by gas chromatography using a Chromosorb 102 column. Sulfolane was used as an internal standard. Rates to products were given in terms of turnover frequency, defined as the number of moles of the product formed per gram-atom of metal per hour. The turnover frequency of EG, N(EG), is obtained by

$$\mathrm{N(EG)} = \mathrm{mol(EG+EGMOF)/(g\text{-}atom\ Rh)h}$$

Product selectivity is defined as the carbon efficiency on the basis of reduced carbon monoxide in a product obtained. The selectivity value of EG, Sel.(EG), is obtained by

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

Results and Discussion

The results are summarized in Table 1. The $Rh_4(CO)_{12}$/tributylamine system has a high catalytic activity at 290 °C (Run 1). In intial patents, a number of amines have been used as promoters. Optimum EG productivities have generally been achieved at relatively low amine/rhodium ratios of 0.1—2.3.[1b)] However, there have been no precedents

Table 1. Influence of Temperature on the Direct Synthesis of Ethylene Glycol[a)]

Run No.	Solvent (7 ml)	Temp °C	Press. kg/cm^2	$Rh_4(CO)_{12}$ mg-atom	Products/mmol MeOH	MF	EtOH	EG	EGMOF	N (EG)	Sel. (EG)	Color[b)]
1	Tributylamine[c)]	290	1800	0.025	8.56	1.06	0.77	10.06	—[e)]	402	64.3	Colorless
2	NMP	230	1800	0.1	1.26	0.03	0.04	4.00	0.18	41.8	85.9	Colorless
3	NMP	250	1800	0.1	2.85	0.17	0.20	10.17	1.01	111.8	86.7	Colorless
4	NMP	290	1800	0.01	8.37	1.38	0.31	10.81	1.66	1247	70.6	Colorless
5	NMP	300	2000	0.01	11.06	2.24	2.43	17.40	3.29	2069	69.5	Colorless
6	Toluene[d)]	230	1800	0.1	7.55	3.15	0	0.14	—[e)]	1.4	2.6	Yellowish brown
7	Tetraglyme	230	1800	0.1	6.40	1.14	0.09	0.91	0	9.1	19.1	Wine red
8	Tetraglyme	250	1800	0.1	4.79	0.32	0.30	0.14	0	1.4	4.7	Purplish brown
9	γ-Butyrolactone	230	1800	0.1	1.83	0.17	0.07	0.24	0	2.4	18.3	Wine red
10	γ-Butyrolactone	250	1800	0.1	7.37	0.97	0.13	0.40	0	4.0	8.5	Wine red
11	γ-Butyrolactone	290	1800	0.01	9.82	1.78	0.06	0.03	0	3.0	1.0	Pale purple

a) Reaction conditions: $P_{H_2}/P_{CO}=1$; Reaction time 1 h. b) The color of product solution at ambient temperature and pressure. c) The reaction mixture (tributylamine+products) was homogenized by adding pyridine before analysis. d) The reaction mixture (toluene+products) was homogenized by adding tetrahydrofuran before analysis. e) Not determined.

in which reactions in amine solvents give as high a catalytic activity as the N(EG) of Run 1.

The $Rh_4(CO)_{12}$/*N*-methyl-2-pyrrolidone (NMP) system shows a remarkable temperature effect on the formation of EG. Keim et al.[5] reported that the $Rh(CO)_2acac$/NMP system yielded EG in the hydrogenation of carbon monoxide, but without giving no rates to EG. As can be seen from Runs 2—5, the rate of EG formation is significantly accelerated by increase in reaction temperature. The N(EG) at 300 °C and 2000 kg/cm^2 of synthesis gas is about 2000 h^{-1} (Run 5). The Sel.(EG) of Run 5 is about 70%. This value of N(EG) is the highest that has ever been found with rhodium catalysts. This value is interesting from the standpoint of the cost and availability of rhodium.

The result obtained for the $Rh_4(CO)_{12}$/toluene solvent system is given in Run 6. The rate of EG formation is significantly lower than that of the $Rh_4(CO)_{12}$/NMP system (Run 2), though the rate of MeOH formation is higher than that of Run 2. This reaction in toluene at 230 °C caused precipitation of rhodium metal, which suggests that the catalyst stability in toluene is low.

Although tetraglyme and γ-butyrolactone have been used as effective solvents in the presence of promoters in the literature,[1,4] little is known about their catalytic effectiveness in the absence of promoters. The results obtained for the $Rh_4(CO)_{12}$/tetraglyme solvent system are given in Runs 7 and 8. This catalyst system also gives lower rates to EG than the $Rh_4(CO)_{12}$/NMP system (Runs 2 and 3). The reaction in tetraglyme at 250 °C gives rise to precipitates of rhodium metal.

The results obtained for the $Rh_4(CO)_{12}/\gamma$-butyrolactone solvent system are shown in Runs 9—11. In contrast to the results of the nitrogen-containing solvents (Runs 1—5), increase in temperature has only a small effect on the rate of EG formation, though there was no visible evidence for the formation of rhodium metal at the end of the reaction.

For γ-butyrolactone, tetraglyme, and toluene, the effectiveness order for catalyst stability is γ-butyrolactone>tetraglyme>toluene. It appears that solvents having high dielectric constants enhance the stability of the rhodium catalyst. On the other hand, a comparison of Run 1 with Runs 6 and 7 shows that tributylamine improves the catalyst stability, though the dielectric constant of tributylamine is low (2.33 at 20 °C).[6] The nitrogen atom in NMP seems to contribute to the enhancement of the catalyst activity for the EG formation, as is evident from a comparison of Run 4 with Run 11.

As shown in Table 1, the reactions in toluene, tetraglyme, and γ-butyrolactone which show low turnover frequencies of EG give colored solutions at the end of reaction. On the other hand, the reactions in nitrogen-containing solvents which show high turnover frequencies of EG give colorless solution. Watanabe et al.[7] reported that the reaction with the $Rh(CO)_2acac$/NMP system under about 500 kg/cm^2 of synthesis gas gives a colorless solution. These results are interesting in connection with the active species and the role of solvent.

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