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A NOVEL RHODIUM-TRI-N-ALKYLPHOSPHINE CATALYST SYSTEM FOR THE HYDROGENATION OF CARBON MONOXIDE, FORMALDEHYDE, AND GLYCOLALDEHYDE

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Syngas treatment of a mixture from rhodium compound, a large equimolar tri-n-alkylphosphine, or tri(α-nonsubstituted alkyl)phosphine, and a solvent gives rise to an orange yellow solution, which is a highly active catalyst for hydrogenation of carbon monoxide to ethylene glycol and methanol. Similarly, under syngas condition, formaldehyde and glycolaldehyde are effectively hydrogenated to methanol and ethylene glycol, respectively, by the same orange yellow catalyst solution.

Previously, we have reported an unique catalyst system, $Rh_4(CO)_{12}$-1-methyl-2-pyrrolidinone (NMP), suggesting the participation of mono-nuclear rhodium complex in syngas conversion to ethylene glycol.[1] During a programed study to ensure the rhodium catalyst to be unequivocally mono- or di-nuclear state, we have found a highly effective phosphine modified rhodium catalyst for hydrogenation of carbon monoxide to ethylene glycol and methanol. Although the low valent rhodium-phosphine complexes are known to catalyze a variety of organometallic reactions, including hydrogenation and hydroformylation of olefinic compounds, no precedent seems to exist of the catalytic hydrogenation of carbon monoxide by rhodium-phosphine complex. Only the reaction catalyzed by the far less reactive phosphide cluster complex, $Rh_9P(CO)_{21}{}^{2-}$, was reported.[2]

The reaction of $Rh(CO)_2acac$ (0.1 mmol) in 1,3-dimethyl-2-imidazolidinone (DMI) (10 ml) under 47.0 MPa syngas ($H_2/CO = 1/1$) pressure at 240 °C produces ethylene glycol and methanol, in turnover frequencies (T.O.F.) of 12.3 and 8.5 h^{-1}, respectively. An addition of equi-molar tri-n-propylphosphine to the system, however, spoils the catalytic activity and the formation of ethylene glycol and methanol is suppressed completely. Surprisingly, it was found that more than fourty equi-molar addition of tri-n-propylphosphine regenerates a remarkable catalytic activity. Thus, the addition of the phosphine, to an extent as $P^nPr_3/Rh = 160$, results in the highest hydrogenation rate: 17.5 h^{-1}, ethylene glycol; 111 h^{-1}, methanol. The analogous results were obtained with the other solvents, such as 1-methyl-2-pyrrolidinone and 1,1-dimethylformamide. Tetraglyme (TGM) and γ-butyrolactone as solvents, however, lead to the lower yields in ethylene glycol and methanol. The use of tri-n-butylphosphine, instead of tri-n-propylphosphine, affords the similar result. However, quitely reduced yields of ethylene glycol and methanol were obtained, with tri-i-propylphosphine and triphenylphosphine as promoters. (Table 1)

The ir spectra of the orange yellow solution, under syngas atmosphere at ambient temperature, have shown interesting features of the catalytic system. (Fig. 1) Absorption at 2000 cm^{-1}, assigned to $[Rh_6(CO)_{15}]^{2-}$, disappears as P^nPr_3/Rh exceeds 2. The activity of the hydrogenation of carbon monoxide correlates with the intensity of the bands at 1990 and 1960 cm^{-1}. Although the information about exact nature of the species, correspond to 1990 and 1960 cm^{-1}, is scarce at present, we suppose that the absorption at 1960 cm^{-1} is related to the dimeric rhodium complex $[Rh(CO)_m(PR_3)_n]_2$, **1**, on the basis of ir data of known rhodium and cobalt complexes.$^{3)}$ The ir spectra, at 200 °C under 20.0 MPa, of the catalyst solution at P^nPr_3/Rh = 100 indicate the presence of a broad absorption at around 1920-1980 cm^{-1}. The visible spectra, on the other hand, demonstrate that the orange yellow color persists even at 200 °C under 20.0 MPa, thus excluding the participation of the rhodium carbonyl anion cluster complex.$^{4)}$ Therefore, the 1960 cm^{-1} species, or the non-cluster complex **1**, is likely to be a crucial species in the catalytic hydrogenation of carbon monoxide to ethylene glycol and methanol.

The potential ability of the catalyst is exemplified also by the hydrogenation of the aldehyde moiety. Only a scarce information is available about the homogeneous rhodium catalyzed hydrogenation of aldehyde.$^{5-9)}$ We now find that the rhodium-tri-n-alkylphosphine catalyst also catalyzes quite efficiently the hydrogenation of formaldehyde and glycolaldehyde.$^{11)}$

A tetraglyme (10 ml) solution of paraformaldehyde (10.0 mmol), $Rh(CO)_2acac$ (0.05 mmol), and tri-n-butylphosphine (0.5 mmol) are treated with syngas (H_2/CO = 1/1) at 80 °C under 9.8 MPa for 1 h. GC-MS analysis of the resultant reaction solution confirmed the presence of methanol, in 73.9% yield.

The results of the similar reactions of glycolaldehyde (GLA) are collected in Table 2. The catalytic hydrogenation of glycolaldehyde (10.0 mmol) in the presence of $Rh(CO)_2acac$ (0.05 mmol) and tri-n-propylphosphine (0.5 mmol) in TGM (10 ml) at

Table 1. Hydrogenation of carbon monoxide by rhodium catalysts

Run No.	$Rh(CO)_2acac$	Promoter		Solvent		Pressure H_2/CO	Temp	Time	T.O.F. MeOH	T.O.F. EG
	mmol		mmol		ml	MPa/MPa	°C	h	h^{-1}	h^{-1}
1	0.1		-	DMI	10	24/24	240	2	8.5	12.3
2	0.1	P^nPr_3	0.1	DMI	10	24/24	240	2	2.7	0.1
3	0.1	P^nPr_3	0.2	DMI	10	24/24	240	2	3.5	0.1
4	0.1	P^nPr_3	0.5	DMI	10	23/23	240	2	20.2	0.1
5	0.1	P^nPr_3	4.0	DMI	10	23/23	240	2	58.2	6.2
6	0.1	P^nPr_3	8.0	DMI	10	22/22	240	2	78.2	10.9
7	0.1	P^nPr_3	16.0	DMI	10	22/22	240	2	111	17.5
8	0.1	P^nPr_3	25.0	DMI	10	22/22	240	2	116	13.5
9	0.1	P^nBu_3	4.0	DMI	10	22/22	240	2	89.9	11.0
10	0.1	P^nBu_3	4.0	TGM	10	22/22	230	2	63.6	0.0
11	0.05	P^nBu_3	4.0	DMI	10	23/23	260	1	266	23.0
12	0.05	P^iPr_3	8.0	DMI	10	24/24	240	2	12.7	4.6
13	0.1	PPh_3	4.0	DMI	10	25/25	240	2	0.0	0.0

80 °C for 1 h, produces ethylene glycol in 90.2 molar % yield. This seems to be the first example of the effective hydrogenation of glycolaldehyde by the homogeneous rhodium catalyst. Other aliphatic and aromatic aldehydes, although the less readily, are also hydrogenated using the same catalyst.[12)] The analogous results are observed also in the other solvents as dioxane and m-xylene. As contrast to the hydrogenation of carbon monoxide, solvents of the larger dielectric constant, such as 1-methylpyrrolidinone 1,3-dimethyl-2-imidazolidinone, reduce slightly the hydrogenation activity.

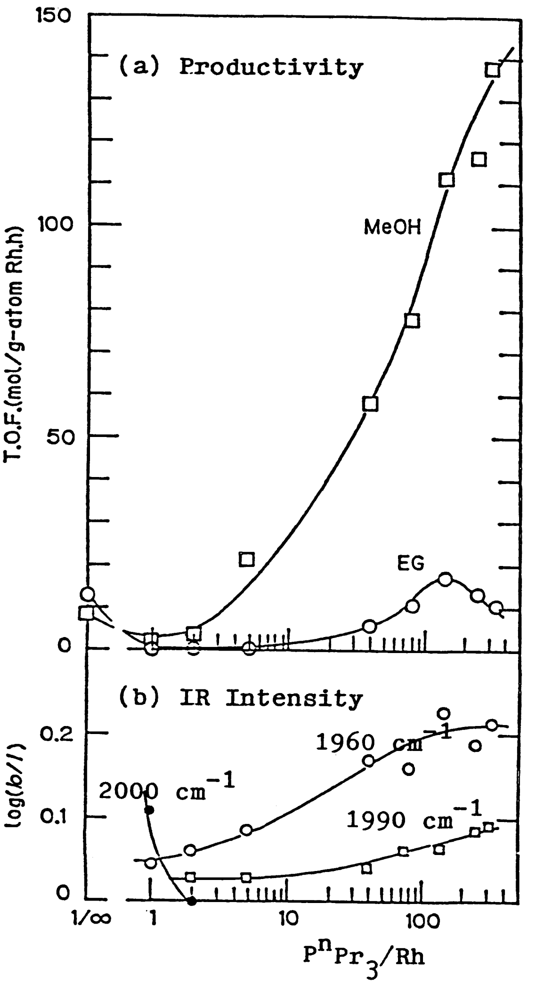

Fig. 1. Dependencies of productivity and ir intensity on phosphine/rhodium ratio in hydrogenation of carbon monoxide. (a) Reaction conditions: Rh 0.1 mg-atom, P^nPr_3 variable, DMI 10 ml, H_2/CO (1/1) 44.1 MPa, 240 °C, 1 h. (b) The catalyst solution from (a) is measured under syngas atmosphere at ambient temperature.

Table 2. Hydrogenation of glycolaldehyde by rhodium catalysts[a)]

Run No.	Rhodium Compound		Promoter		Solvent		Pressure H_2/CO	Conv. GLA	Yield EG	Select. EG	T.O.F. EG
		mmol		mmol		ml	MPa/MPa	%	%	%	h^{-1}
1	$Rh(CO)_2acac$	0.05	-		TGM	10	5/5	4.3	0.0	0.0	0
2	$Rh(CO)_2acac$	0.05	P^nBu_3	0.15	TGM	10	5/5	48.7	10.0	20.5	20
3	$Rh(CO)_2acac$	0.05	P^nBu_3	0.25	TGM	10	5/5	84.8	71.0	83.7	142
4	$Rh(CO)_2acac$	0.05	P^nBu_3	0.50	TGM	10	5/5	95.6	90.2	94.4	180
5	$Rh(CO)_2acac$	0.05	P^nBu_3	2.00	TGM	10	5/5	95.3	97.0	91.3	174
6	$Rh(CO)_2acac$	0.05	P^nBu_3	0.50	DMI	10	5/5	49.2	29.7	60.4	59
7[b]	$Rh(CO)_2acac$	0.01	P^nBu_3	0.10	TGM	10	5/5	57.6	60.3	95.5	288
8[b]	$Rh(CO)_2acac$	0.01	P^nPr_3	0.10	TGM	10	5/5	77.5	74.1	95.6	371
9	$Rh(CO)_2acac$	0.05	P^iPr_3	0.50	TGM	10	5/5	10.5	1.4	13.0	3
10	$Rh(CO)_2acac$	0.05	PPh_3	0.50	TGM	10	5/5	3.1	0.8	25.8	2
11[b,c]	$RhCl_3 \cdot 3H_2O$	0.01	NEt_3	1.53	TGM	10	5/5	42.1	12.8	30.4	64
12[b,d]	$[Rh(COD)Cl]_2$	0.005	P^nBu_3	0.022	TGM	10	5/5	4.0	0.4	10.0	2
13[b,d]	$[Rh(COD)Cl]_2$	0.005	P^nBu_3	0.022	TGM	10	5/0	38.4	27.2	70.8	136

a) glycolaldehyde 10.0 mmol, 80 °C for 1 h, b) 2 h. 3) the same catalyst as that used in ref. 7. d) the same catalyst as that used in ref. 6.

The rate of hydrogenation reaction is critically dependent on both nature and quantity of the phosphine promoter employed. Thus, while an equi-molar mixture of $Rh(CO)_2acac$ and tri-n-butylphosphine has only a feeble catalytic activity, incremental addition of tri-n-butylphosphine to the mixture increases the reaction rate markedly, reaching a maximum at $P^nBu_3/Rh = 10\text{-}40$. The use of the other tri-n-alkylphosphine, instead of tri-n-butylphosphine, shows analogous catalytic performances. The use of tri-s-alkylphosphine, tri-t-alkylphosphine or triarylphosphine, however, causes the considerable reduction in the rate of hydrogenation. The most striking feature of this catalytic process is in its high efficiency in the hydrogenation of aldehydes to the corresponding alcohols. As shown in Table 2, the present rhodium-tri-n-alkylphosphine mixture exerts catalytic behaviors superior, in both activity and selectivity, to any other known homogeneous rhodium catalysts, e.g. the cationic rhodium-phosphine complexes,5,6) the rhodium-amine combinations,7,8) and the rhodium oxo-catalysts, $HRh(CO)(PPh_3)_3$.10) Only exception is the Tani´s catalyst, $[Rh(^iPr_2P(CH_2)_3P^iPr_2)NBD]ClO_4$, which exhibits an excellent activity for aldehyde hydrogenation at ambient temperature.9) Studies, to elucidate the more precise nature of the active catalytic species, are currently undertaken.

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