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# A NEW HOMOGENEOUS RHODIUM CATALYST FOR FORMATION OF ETHYLENE GLYCOL FROM SYNTHESIS GAS: NOVEL EFFECT OF IMIDAZOLE PROMOTERS

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## Summary

A homogeneous rhodium catalyst, when treated with large excess of an imidazole compound has been found to show high activity for formation of ethylene glycol from synthesis gas. Solvent effect and IR analyses suggest that $HRh(CO)_3$(imidazole) plays an important role in formation of ethylene glycol.

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Homogeneous rhodium catalysts have been known to be effective for direct formation of ethylene glycol (EG) from synthesis gas [1–8], and several promoters, such as alkylamines, pyridine derivatives, and certain salts have been described [2,4,6]. Rhodium catalysts were shown to have high activity in polar aprotic solvents such as sulfolane, but these had low activity in nonpolar solvents such as toluene [3,4,6,8]. These results suggest that ionic rhodium species play important roles in catalysis. Vidal et al. analyzed these rhodium catalysts by IR spectroscopy, and suggested anionic rhodium carbonyl clusters as the active species for EG formation [9]. Promoters such as amines are thought to act as the counter cation ($R_3NH^+$) for rhodium anionic species [4]. Recently Wada et al. demonstrated the possibility of mononuclear rhodium complexes were the active species [10,11]. Previously, we discovered a novel ruthenium-imidazole catalyst for this reaction [12], furthermore we found that the activity of the rhodium catalyst for EG formation is also promoted by imidazole compounds. The solvent effect of this catalyst was found to be clearly different from that of the rhodium catalysts previously described. This catalyst showed high activity in relatively weak polar solvents. Here we report the characteristics and structural analysis of rhodium-imidazole catalysts.

Table 1 summarizes the results of synthesis gas reaction in the presence of rhodium-imidazole catalysts, the main products were EG and methanol (MeOH) (eq. 1).

$$CO + H_2 \xrightarrow[\text{catalyst}]{\text{Rh-imidazole}} HOCH_2CH_2OH + CH_3OH \qquad (1)$$

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TABLE 1

EFFECTS OF IMIDAZOLE COMPOUNDS AND OTHER N-CONTAINING BASES ON RHODIUM CATALYST IN THE REACTION OF SYNTHESIS GAS [a]

| Run | Additive (mol/Rh g-atom) | | Solvent | mol/Rh g-atom/h | |
|---|---|---|---|---|---|
| | | | | $HOCH_2CH_2OH$ | $CH_3OH$ |
| 1 | none | | TGM | 0.1 | 1.2 |
| 2 | *N*-methylimidazole | (100) | TGM | 5.4 | 4.0 |
| 3 | *N*-methylimidazole | (500) | TGM | 24.3 | 19.7 |
| 4 | *N*-methylimidazole | (500) | n-hexane | 15.2 | 21.1 |
| 5 | *N*-methylimidazole | (500) | toluene | 27.1 | 22.9 |
| 6 | *N*-methylimidazole | (500) | THF | 31.6 | 25.4 |
| 7 | *N*-methylimidazole | (500) | DMI | 0.8 | 1.0 |
| 8 | *N*-methylimidazole | (500) | sulfolane | 0.2 | 0.7 |
| 9 | *N*-ethylimidazole | (500) | TGM | 27.2 | 17.7 |
| 10 | *N*-n-propylimidazole | (500) | TGM | 29.8 | 19.8 |
| 11 | *N*-methylbenzimidazle | (500) | TGM | 17.3 | 16.4 |
| 12 | *N*-methylmorpholine | (100) | TGM | 0.3 | 3.4 |
| 13 | *N*-methylpiperidine | (100) | TGM | 0.3 | 9.1 |
| 14 | pyridine | (100) | TGM | 0 | 0 |
| 15 | 2-hydroxypyridine | (100) | TGM | 0 | 5.1 |
| 16 [b] | *N*-methylimidazole | (100) | THF | 1.2 | 2.8 |
| 17 [b] | *N*-methylmorpholine | (100) | THF | 0 | 0.4 |
| 18 [b] | *N*-methylpiperidine | (100) | THF | 0 | 0.6 |

[a] Charge: $Rh(CO)_2$(acetylacetonato) 0.1 mg-atom, solvent 10 ml, run conditions: $CO/H_2$ (1:1) 50 MPa, 240°C, 2 h. [b] Charge: $Rh(CO)_2$(acetylacetonato) 0.4 mg-atom, THF 20 ml, run conditions: $CO/H_2$ (1:1) 30 MPa, 200°C, 2 h.

High activities for EG formation were observed in the catalystic systems which contained a large excess of imidazole compounds in tetraglyme (TGM) as solvent. The activity increased with increasing basicity of imidazole compound (*N*-methylbenzimidazole < *N*-methylimidazole (NMI) < *N*-ethylimidazole < *N*-n-propylimidazole). Although the rhodium-NMI catalyst showed high activity in relatively weak polar solvents (n-hexane, toluene, tetrahydrofuran (THF)), it showed only low activity in highly polar solvents (sulfolane and 1,3-dimethyl-2-imidazolidinone (DMI)). This tendency is in contrast to that previously described for rhodium catalysts (see above). Conventional *N*-bases such as *N*-methylmorpholine, *N*-methylpiperidine, pyridine and 2-hydroxypyridine scarcely promoted EG formation by the catalyst in THF or TGM solutions as shown in Table 1.

Results of the reactions show the novel effect imidazole promoters have on the rate of EG formation, and the solvent effect suggests that non-ionic rhodium species play important roles in rhodium-imidazole catalysis. In order to throw some light on the active species in these catalysts, we investigated the reaction mixtures by IR spectroscopy under a $CO/H_2$ (1:1) pressure of 30 MPa at 200°C using a specially designed optical cell, and examined the correlation between the rhodium species and activities under the same conditions. Three rhodium-carbonyl species, $[Rh(CO)_4]^-$ (I) ($\nu$(CO) 1895 $cm^{-1}$) [13], $HRh(CO)_4$ (II) ($\nu$(CO) 2036 $cm^{-1}$) [14], and an unknown rhodium complex (III) ($\nu$(CO) 1996 $cm^{-1}$) were observed in the reaction mixtures using the rhodium-NMI catalyst (THF solvent). The relative intensities of these IR bands and activities of catalyst are plotted in Fig. 1 as a function of the

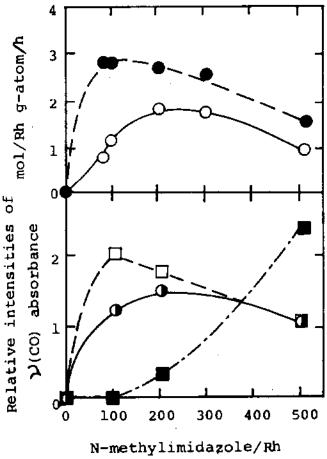

Fig. 1. Effect of molar ratio of NMI/Rh on activity and rhodium carbonyl species. Reaction conditions were the same as these in Table 1 run 16, except for the amount of NMI. The IR spectra of reaction mixtures were analyzed under constant $CO/H_2$ pressure at 200°C. (I): ■·—·—■, (II): □- - - - - -□, (III): ◑———◑, $HOCH_2CH_2OH$ mol/Rh g-atom/h: ○———○, $CH_3OH$ mol/Rh g-atom/h: ●- - - - - -●.

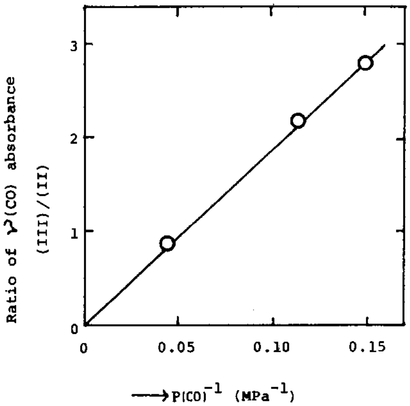

Fig. 2. Influence of CO pressure on the distribution of rhodium species. Reaction conditions and IR analysis conditions were the same as for those in Fig. 1 (NMI = 80 mmol), except for the pressure of CO and $H_2$ ($H_2$ = 14 MPa).

molar ratio (NMI/Rh) of catalyst. Rhodium complex III is thought to have the structure $HRh(CO)_3(NMI)$ and the equilibria shown in Scheme 1 may exist during the catalysis, deduced from the following observations and from the literature *.

(i) When the reaction mixture was cooled, at a $CO/H_2$ pressure of 30 MPa, both the concentrations of II and III decreased and that of I increased. Only I was

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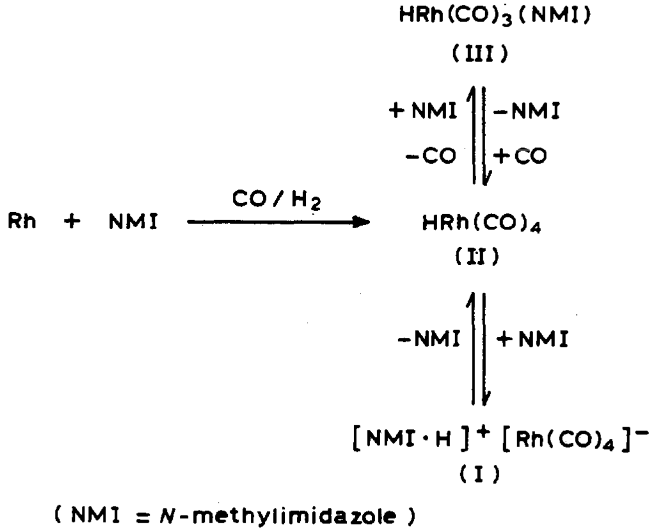
* Vidal et al. [14] reported that $HRh(CO)_4$ ($\nu(CO)$ 2038 $cm^{-1}$) is formed from the reaction of $Rh_4(CO)_{12}$ with synthesis gas in dodecane. They suggested that $HRh(CO)_4$ is converted to $[Rh(CO)_4]^-$ by reaction with an amine.

observed at room temperature. When this reaction mixture was heated to 200°C again, II and III were regenerated. These phenomena indicate that the conversion of II and III to I is reversible, and that II and III are more stable at high temperatures (eq. 2).

$$\mathrm{I} \xrightleftharpoons[\text{cool}]{\Delta} \mathrm{II} + \mathrm{III} \qquad (2)$$

(ii) The ratios of intensities of the $\nu$(CO) bands (III/II) were found to be inversely proportional to the partial pressure of CO (Fig. 2), and were found to be constant under various partial pressures of $H_2$. These results indicate III to be $HRh(CO)_3(NMI)$, which is formed by the coordination of NMI to II by ligand exchange.



SCHEME 1

Fig. 1 shows that activities for EG and MeOH were changed, depending on the amounts of rhodium species III and II present, respectively. This result suggests that rhodium species III and II play important roles in formation of ethylene glycol and methanol, respectively, and rhodium species I shows little or no activity. IR analysis of the rhodium-NMI catalyst in a polar solvent (DMI) showed I to be the main species, and II and III as the minor species. This catalyst showed only low activity as shown above. Since I is an ionic species, it is stabilized in polar solvents. This may be the reason for its low activity in polar solvents. IR spectra of the reaction mixtures using a rhodium catalyst with *N*-methylmorpholine (Table 1 run 17) or *N*-methylpiperidine (Table 1 run 18) showed only a broad peak around 1985 $cm^{-1}$ or 1970 $cm^{-1}$. These catalysts did not show any activity for EG formation.

Analysis of the rhodium-imidazole catalyst show that imidazole acts as ligand and counter cation to the rhodium species in catalysis, and these suggest that $HRh(CO)_3$(imidazole) plays an important role in the formation of ethylene glycol.

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