

### Preliminary communication

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## NOVEL EFFECT OF IMIDAZOLE COMPOUNDS ON A HOMOGENEOUS RUTHENIUM CARBONYL CATALYST IN HYDROGENATION OF CARBON MONOXIDE: A NEW CATALYST FOR ETHYLENE GLYCOL SYNTHESIS

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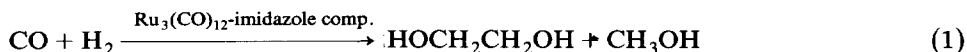
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### Summary

Direct formation of ethylene glycol from synthesis gas has been found to be catalyzed markedly by dodecacarbonyltriruthenium combined with a large excess of imidazole compounds, especially benzimidazole.

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Since the discovery of homogeneous rhodium catalysts for direct formation of ethylene glycol from synthesis gas by Pruett and Walker [1], this synthetic route has been expected to be one of the most attractive new methods for ethylene glycol production on a commercial scale. To date, several homogeneous catalysts containing rhodium, ruthenium, cobalt and iridium have been reported to be effective for this reaction [2–11]. Of these catalysts, rhodium complexes are the most effective for ethylene glycol formation [2,6a]. Although some ruthenium catalysts in conjunction with alkali metal halides or carboxylic acids as promoters have been reported to be effective for ethylene glycol formation, other types of promoters such as *N*-bases have been scarcely examined [3,5,6,7]. Recently, we have found that a ruthenium-halide catalyst is promoted by amines [8]. In the course of our research on activation of a homogeneous ruthenium carbonyl catalyst which does not contain halide promoters, we have found that conventional amines are not effective for activation of the ruthenium catalyst, but imidazole compounds enhance remarkably the catalytic activity for the formation of ethylene glycol and methanol (eq. 1).



In reactions of synthesis gas catalyzed by dodecacarbonyltriruthenium in *N*-methylpyrrolidone, only small amounts of methanol and methyl formate were formed under an atmosphere of CO/H<sub>2</sub> (1/1), 500 kg/cm<sup>2</sup> at 240°C. No ethylene glycol was detected in the reaction mixture. The catalytic activity of ruthenium for

TABLE 1

EFFECT OF *N*-BASES ON RUTHENIUM CATALYSTS IN ETHYLENE GLYCOL AND METHANOL FORMATION FROM SYNTHESIS GAS <sup>a</sup>

| Run No. | Ru<br>g-atom | <i>N</i> -Base<br>(mmol) | mol/Ru g-atom/h                      |                    | Selectivity <sup>b</sup><br>(%) |
|---------|--------------|--------------------------|--------------------------------------|--------------------|---------------------------------|
|         |              |                          | HOCH <sub>2</sub> CH <sub>2</sub> OH | CH <sub>3</sub> OH |                                 |
| 1       | 0.1          | none                     | 0                                    | 7.0                | 0                               |
| 2       | 0.1          | benzimidazole (2)        | 3.0                                  | 25.8               | 10.5                            |
| 3       | 0.1          | benzimidazole (10)       | 19.6                                 | 67.5               | 22.5                            |
| 4       | 0.1          | benzimidazole (50)       | 48.3                                 | 140.7              | 25.6                            |
| 5       | 0.05         | benzimidazole (25)       | 48.2                                 | 156.6              | 23.5                            |
| 6       | 0.05         | benzimidazole (50)       | 76.7                                 | 226.6              | 25.3                            |
| 7       | 0.1          | imidazole (10)           | 5.7                                  | 179.4              | 3.1                             |
| 8       | 0.1          | naphthoimidazole (10)    | 9.4                                  | 37.3               | 20.2                            |
| 9       | 0.1          | 4-azabenzimidazole (10)  | 1.4                                  | 159.9              | 0.9                             |
| 10      | 0.1          | pyrazole (10)            | 0.2                                  | 30.7               | 0.7                             |
| 11      | 0.1          | pyrazole (50)            | 0.3                                  | 53.2               | 0.5                             |
| 12      | 0.1          | indazole (10)            | 0.1                                  | 28.6               | 0.3                             |
| 13      | 0.1          | 7-azaindole (10)         | 0.4                                  | 25.3               | 1.5                             |
| 14      | 0.1          | 7-azaindole (50)         | 0.1                                  | 76.8               | 0.1                             |
| 15      | 0.1          | 1,2,4-triazole (10)      | 0.3                                  | 31.8               | 0.9                             |

<sup>a</sup> Charge: Ru<sub>3</sub>(CO)<sub>12</sub>, *N*-base, *N*-methylpyrrolidone 10 ml; run conditions: CO/H<sub>2</sub> (1/1), 500 kg/cm<sup>2</sup>, 240 °C, 2 h. <sup>b</sup> 100 × (HOCH<sub>2</sub>CH<sub>2</sub>OH)<sub>mol</sub> / (HOCH<sub>2</sub>CH<sub>2</sub>OH + CH<sub>3</sub>OH)<sub>mol</sub>.

ethylene glycol formation started when benzimidazole was used as a promoter for the catalyst. As shown in Table 1 (Run No. 1–6), activities for the formation of both ethylene glycol and methanol increased remarkably with increasing molar amounts of benzimidazole. These results show that activity based on the ruthenium is dependent of the molar ratio of benzimidazole to ruthenium. Some other imidazole compounds (unsubstituted imidazole, naphthoimidazole and 4-azabenzimidazole) were also effective. Among these, benzimidazole was the most effective for ethylene glycol formation, while imidazole itself and 4-azabenzimidazole were effective for methanol formation. The ruthenium catalyst combined with a large amount of benzimidazole showed very high catalytic activity for ethylene glycol formation (Run No. 6). Under similar reaction conditions, this catalyst is superior to the previously reported ruthenium catalysts \* and also to the rhodium catalysts \*\* in its activity for ethylene glycol formation.

Heterocyclic compounds containing N=C–N or N–N=C bonds such as pyrazole, indazole, 7-azaindole and 1,2,4-triazole promoted the methanol formation. The activity for methanol formation increased with increasing amounts of these *N*-heterocycles and this tendency is similar to that of imidazole compounds. However, the activity for ethylene glycol formation was very low. *N*-Bases such as 2-hydroxy-

\* One of the most active ruthenium catalysts, Ru<sub>3</sub>(CO)<sub>12</sub>,NaI in *N*-methylpyrrolidone, was reported to exhibit activity for 1–2 mol of ethylene glycol/g-atom of Ru/h under an atmosphere of CO/H<sub>2</sub> (1/1), 500–600 kg/cm<sup>2</sup> at 230 °C [6a].

\*\* One of the most active rhodium catalysts developed by Union Carbide Corp., Rh(CO)<sub>2</sub>(acac), *N*-methylmorpholine and trimethylphosphine oxide in 18-crown-6, was reported to exhibit activity for 30 mol of ethylene glycol/g-atom of rhodium/h under an atmosphere of CO/H<sub>2</sub> (1/1) 544 atm at 270 °C [6a].

pyridine, pyrrole, oxazole, triethylamine, *N*-methylmorpholine and tetramethylethylenediamine did not exert any influence on the activity of the ruthenium catalyst for methanol formation (5–12 mol/g-atom of Ru/h), without formation of ethylene glycol. Pyrimidine, pyridazine, pyrazine, 1,3,5-triazine and thiazole suppressed the activity of the ruthenium catalyst, giving only a small amount of methanol (0.02–0.6 mol of methanol/g-atom of Ru/h). These results apparently show that the effect of imidazole compounds on the catalytic activity of ruthenium for ethylene glycol formation is unique.

Although the precise mechanism for imidazole compounds to promote ethylene glycol formation is not clear at present, some speculations can be made. One of the most important functions of the imidazole compounds may be coordination as a ligand to the ruthenium metal center [12], since the activity increases with increasing molar ratios of imidazole to ruthenium. Furthermore, the imidazole compound may act as a gegen-cation ( $\text{imidazole} \cdot \text{H}^+$ ) to ruthenium carbonyl anion species, since  $[\text{HRu}_3(\text{CO})_{11}]^-$  has been observed as main species in the recovered reaction mixture (IR analysis at room temperature under 1 atm of synthesis gas) [13]. Some other functions such as solvation of the ruthenium active species by the imidazole compound might be important, since high catalytic activity is observed when a large amount of imidazole is used.

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