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Preliminary communication

ACTIVATION EFFECTS OF IMIDAZOLES ON HOMOGENEOUS RUTHENIUM CARBONYL-HALIDE CATALYSTS IN ETHYLENE GLYCOL FORMATION FROM SYNTHESIS GAS

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Summary

In the formation of ethylene glycol and methanol from synthesis gas, the catalytic activity of a ruthenium carbonyl mixed with halides is promoted by adding various amines, especially imidazole and its derivatives, in the direction of ethylene glycol formation with 23% selectivity.

Since the discovery of homogeneous rhodium catalysis by Pruett and Walker [1], the direct formation of ethylene glycol from synthesis gas has been the subject of much recent research [2,3]. Besides rhodium catalysts, now a number of other homogeneous transition metal catalysts, e.g. ruthenium [4—8], cobalt [5,9], and iridium [5,6,10] complexes have been found to be effective. However, these catalysts require rather severe operation conditions, and their catalytic activities remain low, especially in the case of catalysts which do not contain rhodium complexes. For the ruthenium catalysts, halides such as CsI [7] and Bu_4PBr [8] have been reported to promote catalytic activities. However, little research on other types of promoters has been reported. In the course of our research on homogeneous ruthenium-halide catalysts, we found that organic amines promote the catalytic activity and the selectivity of ruthenium for ethylene glycol formation in the reaction:

$$CO + H_2 \xrightarrow{\text{Ru-halide-amine}} CH_3OH + HOCH_2CH_2OH \qquad (1)$$

Table 1 summarizes the results for synthesis of ethylene glycol and methanol in the presence of $Ru_3(CO)_{12}$, halide and amine; it is shown that *N*-methylmorpholine, pyridine, 2-hydroxypyridine, imidazole and its methyl derivatives promote the activity of the $Ru_3(CO)_{12}$-halide catalyst system for ethylene

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TABLE 1

EFFECT OF AMINE ON THE Ru-HALIDE CATALYZED SYNTHESIS GAS REACTION [a]

Halide	Amine	mol/Ru g-atom·h		$\frac{100\times\mathrm{EG}}{\mathrm{EG}+\mathrm{MeOH}}$
		MeOH	EG [b]	
CsI	none	1.34	0.13	9.1
CsI	*N*-methylmorpholine	1.61	0.17	9.5
CsI	pyridine	1.53	0.20	11.7
CsI	2-hydroxypyridine	1.43	0.21	12.8
CsI	2,2′-dipyridyl [c]	0.21	0.01	3.7
CsI	imidazole	2.17	0.64	22.9
CsI	1-methylimidazole	1.61	0.43	21.3
CsI	2-methylimidazole	2.74	0.31	9.9
CsI	4-methylimidazole	2.24	0.46	17.0
CsI	pyrazole	2.50	0.04	1.6
CsI	triazole	0.48	0.02	3.3
CsBr	none	1.08	0.11	9.3
CsBr	imidazole	2.21	0.48	17.9
CsCl	none	0.97	0.08	7.6
CsCl	imidazole	1.90	0.27	12.6
KI	none	1.11	0.08	7.0
KI	imidazole	2.00	0.47	18.9

[a] Charge: $Ru_3(CO)_{12}$ 0.30 mg-atom, halide 1.80 mmol, amine 1.50 mmol, sulfolane 7.5 ml; conditions: CO/H_2 (1/1) 300 kg/cm², 200° C, 4 h. [b] EG = ethylene glycol. [c] 2,2′-Dipyridyl 0.30 mmol.

glycol formation. Of these amines, imidazole derivatives are especially effective, and the selectivity to ethylene glycol is appreciably enhanced in the case of imidazole, except for 2-methylimidazole. On the contrary, 2,2′-dipyridyl, pyrazole and triazole suppress the formation of ethylene glycol.

The activities for ethylene glycol and methanol formation are influenced by the molar ratios of amine to ruthenium (Fig. 1). The molar ratio suitable for

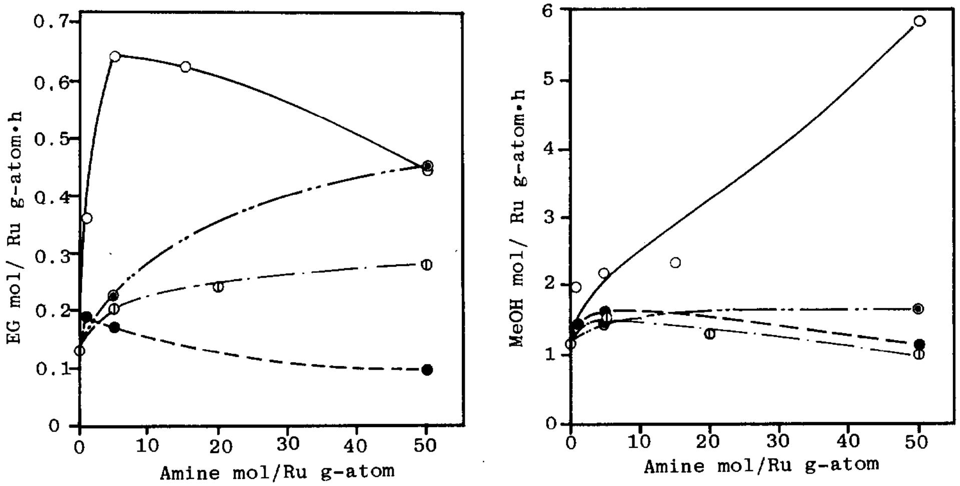
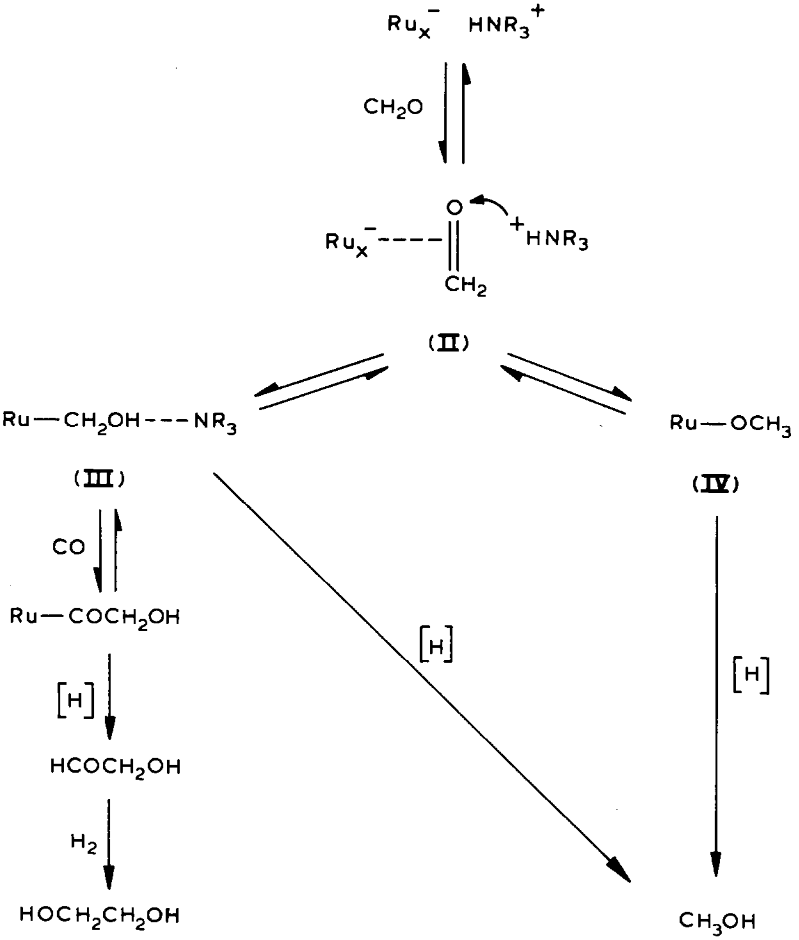


Fig. 1. Effect of the amine/Ru molar ratio on the activity for ethylene glycol and methanol formation: —○—, imidazole; — —●— —, *N*-methylmorpholine; —·—⦶—·—, pyridine; —··—◎—··—, 2-hydroxypyridine. Charge; $Ru_3(CO)_{12}$ 0.30 mg-atom, CsI 1.80 mmol, amine 0.30~ 15 mmol, sulfolane 7.5 ml; run conditions: CO/H_2 (1/1) 300 kg/cm², 200° C, 4 h.

ethylene glycol formation increases in the order: *N*-methylmorpholine < imidazole < pyridine $\lesssim$ 2-hydroxypyridine. This sequence exhibits that the more basic the amine, the lower the suitable molar ratio (pK_a^{25}: *N*-methylmorpholine 7.38, imidazole 6.95, pyridine 5.21, 2-hydroxypyridine 1.25) [11]. These results suggest that the amine acts as a base for the ruthenium catalyst. On the other hand, methanol formation increases extremely with increasing molar ratio of imidazole to ruthenium, whereas, in the case of other amines, the activities do not depend greatly on the molar ratio of amine to ruthenium.

We examined the IR spectra of a recovered reaction mixture using the $Ru_3(CO)_{12}$-CsI-imidazole catalyst system under synthesis gas atmosphere (1 atm, room temperature). The spectra were similar to those using a $Ru_3(CO)_{12}$-CsI catalyst system which show the formation of $[HRu_3(CO)_{11}]^-$ (ν(CO) 2020, 1985, 1950 cm^{-1}) [7], although the catalytic activities differ between these catalysts. These results suggest that active species of both catalysic systems are similar, and that the ruthenium cluster anion seems to play an important role in active species, as shown by Dombek



SCHEME 1

in the ruthenium-iodide catalytic systems [7]. Probably, the amine is converted to the ammonium ion, acting as a gegen cation for the ruthenium active species (I) (eq. 2) [12].

$$[HRu_x] + R_3N \rightleftharpoons \underset{(I)}{[R_3NH]^+ [Ru_x]^-} \tag{2}$$

In ethylene glycol formation from synthesis gas, formaldehyde and glycolaldehyde are assumed to be important intermediates, in which formation of methylol complex III from formaldehyde complex II is an important step [13]. As mentioned above one of the functions of the amine in promoting ethylene glycol formation is its basic character. Thus, presumbaly the amine promotes the formation of III by proton transfer to II from the ammonium ion (Scheme 1). Without the aid of the ammonium ion, formation of the methoxy complex IV from II may be favored, producing methanol, but no ethylene glycol.

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