

## SYNERGISTIC EFFECT OF HOMOGENEOUS RUTHENIUM-RHODIUM CATALYSTS FOR METHANOL HOMOLOGATION

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### Summary

Homogeneous solutions containing both ruthenium and rhodium complexes and methyl iodine are shown to exhibit a synergistic effect for the homologation of methanol to ethanol. Reactions were studied at pressures from 100 to 175 atm and at temperatures from 160 to 240°C. The highest selectivities were obtained with excess of ruthenium complexes present. Under these reaction conditions no evidence for cluster catalysis was found.

### Introduction

Methanol homologation (reaction 1) is catalysed by cobalt compounds, especially with ruthenium compounds as cocatalysts. Under similar conditions rhodium compounds are inactive for ethanol, except when very hydrogen-rich synthesis gas is used [1].



Under CO pressure rhodium compounds produce acetic acid very efficiently through methanol carbonylation [2]. Mixtures of ruthenium and rhodium complexes provide an effective bimetallic catalytic system for ethylene glycol by the hydrogenation of carbon monoxide [3]. In this study the bimetallic system containing both ruthenium and rhodium complexes is shown to catalyse methanol homologation.

### Experimental

#### Reagents

Carbon monoxide (99.997%) and hydrogen (99.9997%) were high purity grade.  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  and  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  were purchased from commercial sources and used without purification. Methanol and toluene were of 99.5% purity. Cluster compounds  $\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}$  [4],  $\text{HRuRh}_3(\text{CO})_{12}$  [5],  $\text{HRuRh}_3(\text{CO})_{10}(\text{PPh}_3)_2$  [5] and  $[(\text{Ph}_3\text{P})_2\text{N}][\text{RuRh}_5(\text{CO})_{16}]$  [6] were prepared according to published procedures.

### Homologation reactions

Catalytic experiments were performed in a Parr 4740 stainless steel autoclave of 71 ml nominal volume, stirred by a magnetic stirrer. Catalysts, methanol, methyl iodine and toluene (internal standard) were loaded in the autoclave under nitrogen atmosphere in VAC DRI-LAB glove box. The autoclave was pressurised by CO and H<sub>2</sub> to desired pressures at room temperature. The maximum pressure was (about 50% higher than the initial pressure) was achieved after about 0.5 h heating. After 3 h from the starting point of heating the autoclave was rapidly cooled first by water and then by isopropanol bath (about -50°C). Cold acetone (about -40°C) was added to the cold product mixture to prevent evaporation of dimethyl and ethyl methyl ethers (boiling points -23 and +11°C) by lowering the boiling point of the mixture. This was necessary for practical reasons. However, evaporation of dimethyl ether occurred to some extent in all experiments depending on the relative amounts of the products. Therefore the dimethyl ether amounts in the Tables are likely to contain some error. This did not interfere the quantitative analysis of the other products, which was made by <sup>13</sup>C NMR spectroscopy at +2°C. The samples were stored in a freezer before analysis.

The gas analyses were accomplished using a Carlo Erba 4240 multicolumn chromatograph equipped with a column switching valve, a thermal conduction detector and a Hewlett Packard integrator. H<sub>2</sub>, CO, CH<sub>4</sub> and N<sub>2</sub> (from the loading of the autoclave, internal standard) were separated on a molecular Sieve 5 Å column and CO<sub>2</sub> on a Chromosorb 102 column. 99.995% helium was used as carrier gas.

### Results

The synergistic effect of ruthenium and rhodium was observed at 100 atm synthesis gas pressure (Table 1), where ruthenium or rhodium chlorides alone were inactive for ethanol. The amount of rhodium was held constant and the Ru/Rh ratio was varied. Excess of ruthenium favours the ethanol (EtOH + EtOMe) production, giving the best results with 3/1 or 6/1 Ru/Rh ratios. With Ru/Rh = 6/1 ratio more ethanol than acetates (AcOH + AcOMe) were produced. In all experi-

TABLE 1  
THE EFFECT OF Ru/Rh RATIO ON METHANOL HOMOLOGATION <sup>a</sup>

Ru/Rh	Products (mmol)						Conversion (%)
	MeOH	EtOH	EtOMe	MeOMe	AcOH	AcOMe	
0/1	103	0.0	0.0	18	0.0	10.8	43
0.2/1	107	0.9	0.0	22	1.1	11.8	41
0.5/1	81	1.0	0.4	20	0.9	8.5	55
1/1	95	1.9	0.8	21	1.8	10.7	48
2/1	81	2.0	0.9	19	0.0	4.6	55
3/1	88	3.6	1.8	30	2.5	7.3	51
6/1	89	3.7	1.8	26	0.0	2.6	51
8/1	81	0.0	3.0	22	0.0	0.0	55
6/0	108	0.0	0.0	23	0.0	0.8	40

<sup>a</sup> Conditions: 200°C, 100 atm, CO/H<sub>2</sub> = 1/2, initially MeOH 180 mmol, CH<sub>3</sub>I 1.8 mmol, toluene 5.3 mmol, RhCl<sub>3</sub>·3H<sub>2</sub>O 0.084 mmol, Ru added as RuCl<sub>3</sub>·3H<sub>2</sub>O, conversion = [(180 - MeOH)/180] × 100%, reaction time 3 h.

TABLE 2  
THE EFFECT OF PRESSURE <sup>a</sup>

Pressure (atm)	Products (mmol)					Conversion (%)
	MeOH	EtOH	EtOMe	MeOMe	AcOMe	
100	89	3.7	1.8	26	2.6	51
120	110	3.7	1.7	21	1.5	39
140	101	4.1	2.2	19	1.6	44
160	139	4.6	2.1	21	2.1	23
175	104	6.0	3.1	20	1.9	42

<sup>a</sup> Conditions: Ru/Rh = 6/1, otherwise see Table 1.

ments the catalytic formation of ethers from the alcohols dominates. Some methane and carbon dioxide was also formed.

Increase in the ethanol production could be observed with increasing pressure in the range 100–175 atm (Table 2), while no change in the acetate production could be observed. In separate experiments with  $[(\text{Ph}_3\text{P})_2\text{N}][\text{RuRh}_5(\text{CO})_{16}]$  as the catalyst precursor some ethanol formation was observed even at 40 atm synthesis gas pressure.

The best results were obtained at 200°C (Table 3). The overall reaction rate increases with temperature, but high temperatures favour clearly the formation of ethers, carbon dioxide and methane. At 200 and 240°C experiments the dimethyl ether amounts were too high to be recovered by the usual procedure.

Hydrogen-rich synthesis gas favours ethanol production with pure rhodium catalysts. With the bimetallic ruthenium-rhodium system, the CO/H<sub>2</sub> ratio 1/2 gave the best results in the range 1/1–1/5 (Table 4).

Iodides are necessary for the reaction. Methyl iodide gave better results than NaI or I<sub>2</sub>.

When the metal chlorides were replaced by metal cluster compounds ( $\text{Ru}_3(\text{CO})_{12}$  +  $\text{Rh}_6(\text{CO})_{16}$ , 200°C, Ru/Rh = 6/1, 100 atm) slight decrease in the formation of both ethanol and acetates could be observed, possibly due to slower formation of the catalytically active species. No enhancement of ethanol production was also observed with mixed metal cluster compounds  $\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}$  [4],  $\text{HRuRh}_3(\text{CO})_{12}$  [5],  $\text{HRuRh}_3(\text{CO})_{10}(\text{PPh}_3)_2$  [5] and  $[(\text{Ph}_3\text{P})_2\text{N}][\text{RuRh}_5(\text{CO})_{16}]$  [6] as the catalyst precursors. This is reasonable since cluster decomposition was found

TABLE 3  
THE EFFECT OF TEMPERATURE <sup>a</sup>

Temperature (°C)	Products (mmol)							Conversion (%)
	MeOH	EtOH	EtOMe	MeOMe	AcOMe	CO <sub>2</sub>	CH <sub>4</sub>	
180	150	2.3	1.2	14	1.3	2.0	2.6	17
200	139	4.6	2.1	21	2.1	<sup>b</sup>	<sup>b</sup>	23
220	83	5.5	2.0	<sup>b</sup>	2.0	<sup>b</sup>	<sup>b</sup>	54
240	76	0.0	3.3	<sup>b</sup>	0.0	11	18	58

<sup>a</sup> Conditions: 160 atm, Ru/Rh = 6/1, otherwise see Table 1. <sup>b</sup> Not analysed.

TABLE 4  
THE EFFECT OF CO/H<sub>2</sub> RATIO <sup>a</sup>

CO/H <sub>2</sub>	Products (mmol)							Conversion (%)
	MeOH	EtOH	EtOMe	MeOMe	AcOMe	CO <sub>2</sub>	CH <sub>4</sub>	
1/5	120	1.8	1.8	28	1.3	1.2	6.8	33
1/3	124	2.3	1.9	26	2.4	2.4	4.6	31
1/2	96	3.8	2.1	20	2.5	3.4	6.7	47
1/1	135	2.8	1.3	15	2.1	4.0	2.9	25

<sup>a</sup> Conditions: 160 atm, Ru/Rh = 6/1, otherwise see Table 1.

to occur in all experiments. Similar catalytically active mononuclear species are probably formed from both metal chlorides and cluster compounds.

Rhodium complexes are active for the carbonylation of methanol, but not for the methanol homologation, where hydrogenation ability is needed. Therefore it is plausible that ruthenium compounds improve ethanol production by enhancing the hydrogenation of the carbonylated intermediates. The homologation reaction using ruthenium-cobalt catalysts can even be separated as two steps: cobalt-catalysed carbonylation of methanol to acetaldehyde and ruthenium-catalysed hydrogenation of acetaldehyde to ethanol [7].

The present systems do not exceed the activity of the well known ruthenium-cobalt catalysts for methanol homologation. However, the observed synergistic effect of ruthenium and rhodium encourages the search for new active bimetallic catalysts.

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