

# Ethylene Glycol from Synthesis Gas *via* Bimetallic Catalysis

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Ethylene glycol and its monoalkyl ether derivatives have been prepared from synthesis gas through the application of a unique ruthenium–rhodium ‘melt’ catalyst system.

Ethylene glycol preparation directly from synthesis gas has been demonstrated now for a number of soluble, Group 8 metal catalysts.<sup>1–3</sup> Rhodium,<sup>1</sup> ruthenium,<sup>2</sup> and cobalt<sup>3</sup> metal centres are particularly favoured. These syntheses, however, still necessitate fairly vigorous operating conditions, while rates of CO hydrogenation remain slow. One possibility, that has not been extensively studied to date, is an improved glycol synthesis where mixed metal centres with bimetallic, poly-metallic, or bridged-metal carbonyl clusters are employed either as catalyst precursors, or generated *in situ*. In particular, the use of combinations of Group 8 metals, already known to be effective catalysts for CO-hydrogenation to aliphatic diols, would be a logical extension.

In this communication we describe the preparation of ethylene glycol and its monoalkyl ether derivatives [equation (1)] from synthesis gas using a mixed ruthenium–rhodium catalyst system dispersed in a low-melting point quaternary phosphonium salt<sup>4</sup> (see Table 1). Intrinsic preparative advantages for this mixed metal system are improved glycol productivity and the ability to operate under CO/H<sub>2</sub> pressures lower than those normally required for single metal centres. In particular, it may be noted that:

- i, The productivity of the Ru–Rh melt catalyst is high; liquid weight gains may exceed 200 wt % (see Table 1, expt. 2).
- ii, Glycol: alkanol weight ratios of 1:1.37 have been realized where ethylene glycol plus its monoalkyl ethers constitute >30 wt % of the total liquid organic products (Table 1, expt. 6).
- iii, Both alkanol and diol products may be readily isolated by fractional distillation of the crude liquid product and the solid residual Rh–Ru catalyst recycled several times.<sup>4</sup>

The data in Figure 1 illustrate how both the ruthenium and rhodium catalyst components are beneficial to the formation of ethylene glycol (expressed here in terms of total glycol plus glycol ether productivity) for a catalyst precursor comprising ruthenium(III) acetylacetonate [Ru(acac)<sub>3</sub>] coupled with

rhodium(III) acetylacetonate dispersed in tetrabutylphosphonium bromide. Methanol and ethanol are the major by-products (Table 1). Maximum glycol productivity is achieved, with increasing rhodium additions, at Ru:Rh ratios of 1:1. It is worth noting, however, that very little diol is generated in the absence either of the ruthenium catalyst component [Figure 1, Rh(acac)<sub>3</sub>–Bu<sub>4</sub>PBr alone], or of the quaternary

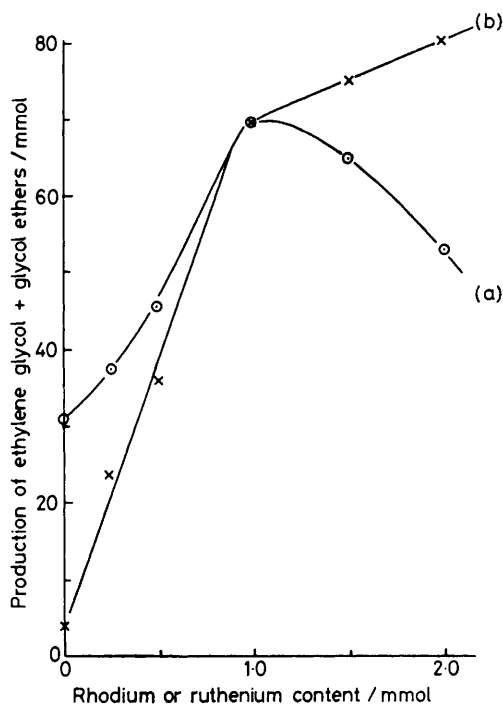


Figure 1. Ethylene glycol synthesis from CO/H<sub>2</sub>—effect of Ru:Rh catalyst molar ratio. (a) Effect of varying [Rh], added as Rh(acac)<sub>3</sub>, ○; Ru(acac)<sub>3</sub>, 1.0 mmol; Bu<sub>4</sub>PBr, 7.5 g. (b) Effect of varying [Ru], added as Ru(acac)<sub>3</sub>, ×; Rh(acac)<sub>3</sub>, 1.0 mmol; Bu<sub>4</sub>PBr, 7.5 g. Operating conditions: 220 °C; 430 atm constant pressure; CO/H<sub>2</sub> (1:1); 18 h.

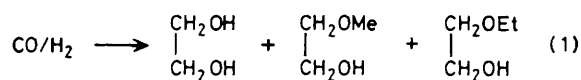
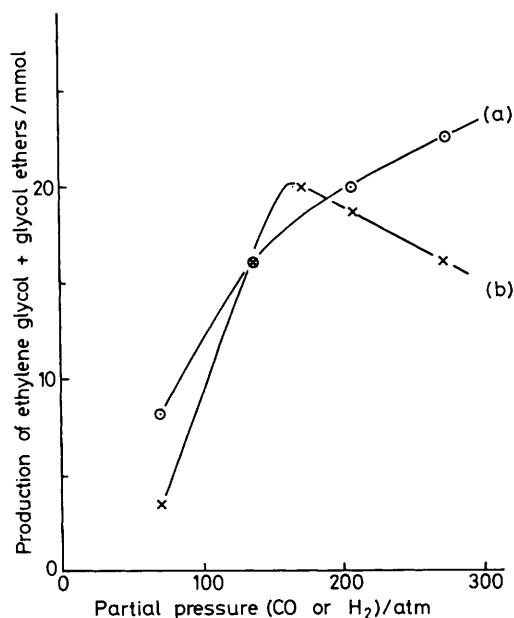


Table 1. Ethylene glycol from synthesis gas *via* ruthenium–rhodium ‘melt’ catalysis.<sup>a</sup>

Expt.	Ruthenium–rhodium source	Quaternary salt	M.p. <sup>c</sup> /°C	Product yield /mmol <sup>b</sup>				Total liquid yield, wt % <sup>e</sup>
				(CH <sub>2</sub> OH) <sub>2</sub>	HOCH <sub>2</sub> CH <sub>2</sub> OR <sup>d</sup>	MeOH	EtOH	
1	Ru(acac) <sub>3</sub> –Rh(acac) <sub>3</sub>	Bu <sub>4</sub> PBr	100	77.2	62.6	250	168	189
2	“	Bu <sub>4</sub> PI	96	80.4	41.6	312	237	214
3	“	C <sub>16</sub> H <sub>33</sub> Bu <sub>3</sub> PBr	54	11.4	42.8	295	228	176
4	“	C <sub>7</sub> H <sub>15</sub> Ph <sub>3</sub> PBr	179	0.5	0.4	0.1	0.7	<3
5	“	None	—	0.2	—	8.9	0.9	†
6	“	Bu <sub>4</sub> PBr	100 <sup>g</sup>	30.3	14.3	96	23	57

<sup>a</sup> Charge: Ru, 4.0 mmol; Rh, 2.0 mmol; R<sub>4</sub>PX, 15 g; run conditions: 220 °C, 430 atm constant pressure; CO/H<sub>2</sub> (1:1), 6–18 h. <sup>b</sup> Analysis of crude liquid product by g.l.c. using a modified porous polymer column, programmed from 125–250 °C, at 20 cm<sup>3</sup>/min He flow; smaller quantities of water, methyl acetate, ethyl acetate, propan-1-ol, acetaldehyde, and ethylene glycol monoacetate were also detected; carbon dioxide and methane are present in the product gas samples along with much larger quantities of unreacted CO/H<sub>2</sub>. <sup>c</sup> Melting point of quaternary salt must be substantially below the reaction temperature (220 °C). <sup>d</sup> R = Me, Et. <sup>e</sup> Liquid yield (wt %) calculated on the basis of the total weight of catalyst charged. <sup>†</sup> Product liquid is >90% water. <sup>g</sup> Run time, 2 h.



**Figure 2.** Ethylene glycol synthesis from CO/H<sub>2</sub>—effect of CO and hydrogen partial pressures. (a) Effect of varying H<sub>2</sub> partial pressure, ○; CO partial pressure, 136 atm; 220 °C. (b) Effect of varying CO partial pressure, ×; H<sub>2</sub> partial pressure, 136 atm; 220 °C. Catalyst composition: Ru(acac)<sub>3</sub>, 0.5 mmol; Rh(acac)<sub>3</sub>, 1.0 mmol; Bu<sub>4</sub>PBr, 5.0 g.

phosphonium salt (Table 1, expt. 5). A variety of low melting point (<150 °C), thermally stable, quaternary phosphonium salts are effective media for these syntheses (Table 1), and the Fourier transform i.r. spectra of their product solutions routinely exhibit distinct metal–carbonyl bands at *ca.* 2062m, 2038sh, 2015s, 1991m, and 1836w cm<sup>-1</sup>. Chromatographic separation of these crude product solutions (*e.g.*, Table 1, expt. 1, with Ru:Rh = 1:1) on silica allows isolation of a mixed ruthenium–rhodium carbonyl of the empirical formula RhRu<sub>2</sub>(CO)<sub>12</sub><sup>5</sup> as well as Ru<sub>3</sub>(CO)<sub>12</sub>.<sup>6</sup> Although the combined spectra of these two carbonyl complexes can account for most of the observed ν<sub>CO</sub> bands, chromatography also leads to the isolation of fractions containing [HRu<sub>3</sub>(CO)<sub>11</sub>]<sup>-</sup> (ref. 2) and [Ru(CO)<sub>2</sub>Br<sub>4</sub>]<sup>2-</sup> (ref. 7). No ruthenium-free rhodium carbonyl species were detected.

Glycol production with this type of Ru–Rh ‘melt’ catalysis is very sensitive to applied partial pressure of CO and hydrogen (see Figure 2). The near linear dependence upon hydrogen partial pressure, coupled with a preferred CO partial pressure of *ca.* 170 atm, ensures satisfactory yields of ethylene glycol from 1:1 CO/H<sub>2</sub> at *ca.* 300 atm. Syntheses are believed to be homogeneous, since hydrocarbons higher than methane are

rarely detected<sup>8</sup> and the product distribution remains essentially unchanged upon catalyst multicycling.<sup>4</sup>

Typical product distributions (ethylene glycol, glycol monoalkyl ethers, methanol, and ethanol), including the formation of smaller quantities of propylene glycol,<sup>4</sup> are in keeping with a chain-growth mechanism<sup>1</sup> for these syntheses (Table 1), possibly involving known<sup>9</sup> formyl- and hydroxymethyl-type intermediates. The presence of a ruthenium metal centre is necessary for glycol formation by melt catalysis (Figure 1). Mixed ruthenium–rhodium metal clusters, such as the isolated Ru<sub>2</sub>Rh(CO)<sub>12</sub>, point to the role of the second metal, rhodium, in ensuring improved glycol productivity. Although the participation of bimetallic bridged species (as in related cobalt catalysis<sup>10</sup>) cannot be discounted, the involvement of rhodium unimetallic species during the critical propagation steps is ruled out by the sensitivity of glycol yields to [Rh] (Figure 1, preferred Rh:Ru ratio 1:1) and the effect of CO pressure (Figure 2) that is in contrast to prior synthesis using either rhodium<sup>-1</sup> or ruthenium-based<sup>2</sup> catalysts alone.

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