Selective Production of C_2-Oxygenate Esters from Synthesis Gas using Mixed Metal Homogeneous Catalysts

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C_2-Oxygenate esters, particularly ethylene glycol diacetate, may be prepared in high selectivity directly from synthesis gas in the presence of composite homogeneous catalysts which contain mixtures of ruthenium and rhodium, as major and minor components respectively, together with promoters in the form of nitrogen-containing bases or alkali metal cations, in acetic acid as solvent.

A feature which is a key to any wider utilisation of chemistry based on synthesis gas is an understanding of, and more particularly, an ability to control, those factors which determine the selectivity of the C_1 to C_2 transformation during the hydrogenation of carbon monoxide. With the exception of the rhodium catalysed conversion of carbon monoxide and hydrogen into ethylene glycol and methanol[1,2] other catalyst systems described to date exhibit only relatively poor selectivities to C_2 products.[3] We have discovered an unprecedented example of the effect of promoters particularly in the enhancement of C_2/C_1 selectivity and one which has led to the development of a composite mixed-metal homogeneous catalyst system for the conversion of CO/H_2 into C_2-oxygenate esters.[4]

Table 1. Promoter effect on catalytic activity and selectivity of Ru/Rh/HOAc system in carbon monoxide hydrogenation.[a]

			Products/mol l^{-1} h^{-1}				
Ru/mmol	Rh/mmol	Promoter/ mmol	MeOAc	EtOAc	CH_2OAc[d] | $CH_2OAc(H)$	Molar[b] selectivity	Activity[c]
2.0	—	—	0.180	0.008	0.017	0.09	0.23
—	0.2	—	0.175	0.009	0.011	0.06	0.22
2.0	0.2	—	0.419	0.013	0.038	0.09	0.52
2.0	0.2	2.0 Et_3N	0.211	0.065	0.276	1.31	0.89
2.0	0.2	4.0 Et_3N	0.182	0.098	0.262	1.44	0.90
2.0	0.2	2.0 Cs	0.226	0.044	0.365	1.62	1.04
2.0	0.2	4.0 Cs	0.219	0.060	0.335	1.53	1.01
2.0	0.2	2.0 Cs[e]	0.340	0.010	0.013	0.04	0.39

[a] Reaction conditions: 50 ml glacial acetic acid solvent, 1000 atm pressure, CO/H_2 (1 : 1), 230 °C, 2—4 h reaction time. [b] Selectivity defined as mol $CH_2(OAc)CH_2OAc(H)$/mol MeOAc. [c] Activity defined as CO consumed, mol l^{-1} h^{-1}. [d] Of the two possible esters of ethylene glycol the diacetate comprises *ca.* 90% of the product distribution. [e] Acetic acid solvent replaced by tetraglyme; products are methanol, ethanol, and ethylene glycol rather than acetate esters.

Our bimetallic catalyst system contains ruthenium in combination with rhodium,† the latter optimally as a *minor* component, in the presence of acetic acid as solvent/co-reactant and yields the products in the form of the acetate esters of methanol, ethanol, and ethylene glycol [equation (1)].

$$CO + H_2 \xrightarrow[HOAc]{Ru/Rh(10:1)} MeOAc + EtOAc$$
$$+ CH_2(OAc)CH_2OH + (CH_2OAc)_2 \qquad (1)$$

Some typical results are summarised in Table 1, from which four main points emerge. First, a small but experimentally significant synergism is observed on the addition of ruthenium to rhodium in the absence of any promoter. However, the selectivity to C_2 products is very poor and typical of those reported in other investigations, particularly those in which ruthenium is used as catalyst.[3] Secondly, the addition of approximately stoicheiometric amounts of triethylamine to the Ru/Rh catalyst combination has a very profound and totally unexpected effect on the course of the reaction—not only is the selectivity to ethylene glycol acetate dramatically enhanced, partially at the expense of methyl acetate production, but the overall catalytic activity, based on CO conversion, is almost doubled. The presence of triethylamine is therefore exerting a true promotional effect. Thirdly, replacement of triethylamine as promoter by an alkali metal cation such as caesium results in very similar effects on both reaction rate and selectivity although significantly lower rates of formation of ethyl acetate are observed. Finally, replacement of acetic acid by tetraglyme as solvent in the Ru/Rh/Cs system results in a dramatic reduction in the selectivity to C_2-oxygenate esters with catalyst productivities which are inferior to those observed with the unpromoted Ru/Rh/acetic acid catalyst. Clearly the combination of metals, promoters, and acetic acid solvent are all essential constituents of the composite catalyst for the selective production of C_2 esters.

These catalyst systems are truly homogeneous, thermally robust, and highly selective; methyl formate is the only other product formed in significant amounts under certain conditions. Radiolabelling studies‡ on the Ru/Rh/Et_3N/acetic acid catalyst system using ^{14}CO have conclusively demonstrated that methanol, ethanol, and ethylene glycol are all primary products and not solvent-derived by, for example, hydrogenation of acetic acid. No radiolabelled hydrocarbons are observed either in the gas phase or in solution and only traces of $^{14}CO_2$ are detected. As in much of the previous work[1,2] the formation of C_2 products shows a very strong pressure requirement whereas the rate of formation of methyl acetate is relatively independent of pressure in the range 250—1250 atm (see Figure 1).

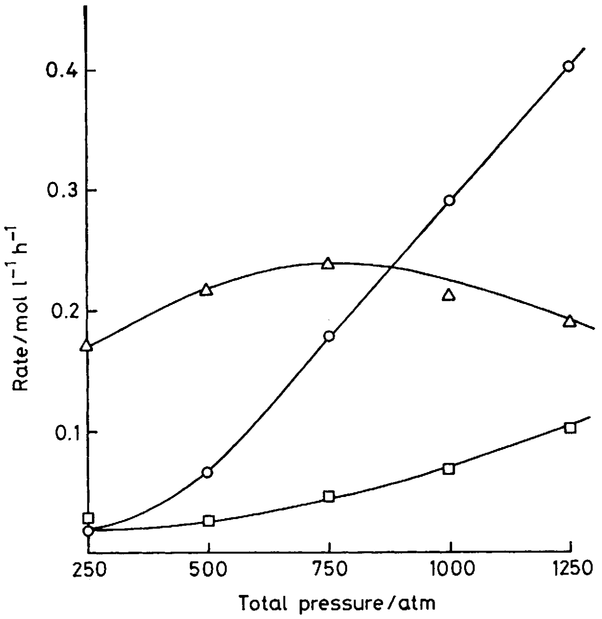

Figure 1. Product distribution as a function of pressure in the Ru/Rh/Et_3N/HOAc catalyst system. Reaction conditions: $Ru(acac)_3$ (2.0 mmol), $Rh(CO)_2acac$ (0.2 mmol), Et_3N (2.0 mmol), glacial acetic acid (50 ml), CO/H_2 (1 : 1), 230 °C. Key: △, MeOAc; □, EtOAc; ○, $CH_2(OAc)CH_2OAc(H)$.

These are clearly very complex catalyst systems and the origin and explanation of the effects of the promoters on

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† Introduced initially in the form of $Ru(acac)_3$ and $Rh(CO)_2$-acac, respectively (acac = MeCOCHCOMe).

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Table 2. Promoter effect on individual metal components of Ru/Rh/HOAc system in carbon monoxide hydrogenation.[a]

			Products/mol l^{-1} h^{-1}				
Ru/mmol	Rh/mmol	Promoter/ mmol	MeOAc	EtOAc	CH_2OAc $\vert$ $CH_2OAc(H)$	Molar[b] selectivity	Activity[c]
2.0	—	—	0.180	0.008	0.017	0.09	0.23
2.0	—	2.0 Et_3N	0.162	0.007	0.010	0.06	0.20
2.0	—	2.0 Cs	0.180	0.009	0.020	0.11	0.24
—	0.2	—	0.175	0.009	0.011	0.06	0.22
—	0.2	2.0 Et_3N	0.093	0.046	0.128	1.38	0.44
—	0.2	2.0 Cs	0.084	0.020	0.128	1.52	0.38

[a] Reaction conditions: 50 ml glacial acetic acid solvent, 1000 atm pressure CO/H_2 (1 : 1), 230 °C. [b] Selectivity defined as mol $CH_2(OAc)CH_2OAc(H)$/mol MeOAc. [c] Activity defined as CO consumed, mol l^{-1} h^{-1}.

catalytic activity and selectivity are not fully understood. An analysis of the behaviour of the separate metal components of the catalyst (see Table 2) shows that the major influence of the promoter in enhancing the selectivity to C_2 products is associated with rhodium. Thus the addition of, for example, triethylamine to rhodium is accompanied by a dramatic enhancement in selectivity to C_2-oxygenate esters, together with an increase in catalytic activity, whereas only minor effects are observed in corresponding experiments with ruthenium. The catalytic activity of rhodium, at the relatively low concentrations used, is indeed high in comparison with previously published data.[2] A comparison of the results in Table 2 with those of Table 1 demonstrates the absence of a simple additive effect when the two metal/promoter components are combined; instead *both* the total catalytic activity (based on CO consumed) and the selectivity to C_2 products are significantly enhanced. Truly synergistic effects are therefore occurring. It appears as if the minor component of the catalyst (Rh) is largely determining the product selectivity whereas the presence of the major component (Ru) is considerably enhancing the total catalytic activity. This behaviour contrasts markedly with that described recently by Knifton[5] in a report on a 'unique' homogeneous bimetallic ruthenium–rhodium melt catalyst composition for the production, directly from synthesis gas, of methanol, ethanol, and smaller amounts of ethylene glycol and its monoalkyl ethers. In the latter case the presence of ruthenium was considered essential for the formation of ethylene glycol whereas the presence of rhodium contributed to improved productivity.

In further contrast to the work of Knifton we have no evidence for the presence of mixed ruthenium–rhodium species in solution during or after reaction. Preliminary i.r. spectroscopic measurements taken under operating reaction conditions are consistent with the presence, in acetic acid solution, of $[Ru(CO)_3OAc]_2$, $Ru(CO)_5$, and $Ru_3(CO)_{12}$ for the $Ru/Et_3N/HOAc$ catalyst precursor, and $Rh_6(CO)_{16}$ and $[Rh_6(CO)_{15}X]^-$ where X = H or OAc, in the case of the $Rh/Et_3N/HOAc$ system. When the two components are combined in the appropriate concentrations most of the above species can be detected but in addition an absorption at 2040 cm^{-1} tends to dominate the spectrum. A band in this position may arise from a species such as $HRu(CO)_3OAc$.

In view of the lack of spectroscopic evidence for the presence of mixed-metal species and the fact that the preferred Ru : Rh catalyst ratio of 10 : 1 militates against catalysis involving a stoicheiometric Ru/Rh bimetallic complex it seems likely that other alternatives, namely the operation of intermolecular reaction pathways[6,7] appear most probable in these complex catalyst systems.

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