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COMMUNICATION

Syngas reactions XII.* The selective preparation of acetaldehyde, alkanols, esters and acetic acid from synthesis gas

John F Knifton and J J Lin
Texaco Chemical Company, PO Box 15730, Austin, Texas 78761, USA

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Several classes of commercially important oxygenates, including acetaldehyde, ethanol, methyl acetate, ethyl acetate and acetic acid as well as C_1-C_3 alcohol/acetate ester mixtures, may each be selectively generated from synthesis gas through the application of novel classes of ruthenium-containing bimetallic catalysts particularly those of ruthenium and cobalt (Ru–Co). A particular feature of these versatile catalysts is that all precursors are iodide-free. Products are formed through a combination of carbon monoxide hydrogenation, methanol homologation, methyl acetate homologation and methanol carbonylation reaction sequences.

Keywords: aliphatic organic oxygenates, synthesis gas, syngas, catalysis, ruthenium

INTRODUCTION

The utilization of homogeneous catalysis in organic syntheses is one of the most important research areas in chemistry today.[1] As part of our ongoing development of new technology for manufacturing specialty and commodity chemical from synthesis gas, novel, highly versatile classes of transition-metal bimetallic catalyst have been discovered in our laboratories that show great promise for the selective and facile hydrogenation of carbon monoxide and its C_1-derivatives. A wide range of specific aliphatic oxygenates may be prepared; the scope of the catalysis (Scheme 1 and Eqns [1]–[6]) includes:

(a) acetaldehyde and ethanol production via methanol homologation;
(b) methyl acetate synthesis via methanol carbonylation;
(c) ethyl acetate and acetic acid preparations from methanol;
(d) methyl acetate homologation to ethyl acetate;
(e) production of C_1-C_3 alcohols and their acetate esters directly from synthesis gas.

Ruthenium-containing bimetallic catalysts are necessary in each of these syntheses (a)–(e), particularly ruthenium–cobalt combinations in the presence of quaternary phosphonium salts. A particular feature of all these catalyst systems is that, in contrast to most prior studies, the ruthenium–cobalt combinations are iodide-free and no iodide component is necessary for the preparations of Scheme 1.

Each aliphatic oxygenate (Eqns [1]–[6]) is produced via a sequence of two fundamental steps in organometallic chemistry involving metal–alkyl and metal–acyl intermediates, viz. carbonylation and carbonylation followed by hydrogenation, that are well established in the science of homogeneous catalysis. The degree and order of these steps will determine the ultimate structure of the product. Syntheses are complicated, however, by competing and parallel reactions, and by the exceedingly reactive nature of certain intermediate species.

$$CH_3OH+CO+2H_2 \rightarrow C_2H_5OH+H_2O \quad [1]$$

$$CH_3OH+CO+H_2 \rightarrow CH_3CHO+H_2O \quad [2]$$

$$2CH_3OH+CO \rightarrow CH_3COOCH_3+H_2O \quad [3]$$

$$2CH_3OH+2CO+2H_2 \rightarrow CH_3COOC_2H_5+2H_2O \quad [4]$$

$$CH_3COOCH_3+CO+2H_2 \rightarrow CH_3COOC_2H_5+H_2O \quad [5]$$

$$CH_3OH+CO \rightarrow CH_3COOH \quad [6]$$

Acetaldehyde and ethanol are, of course, well

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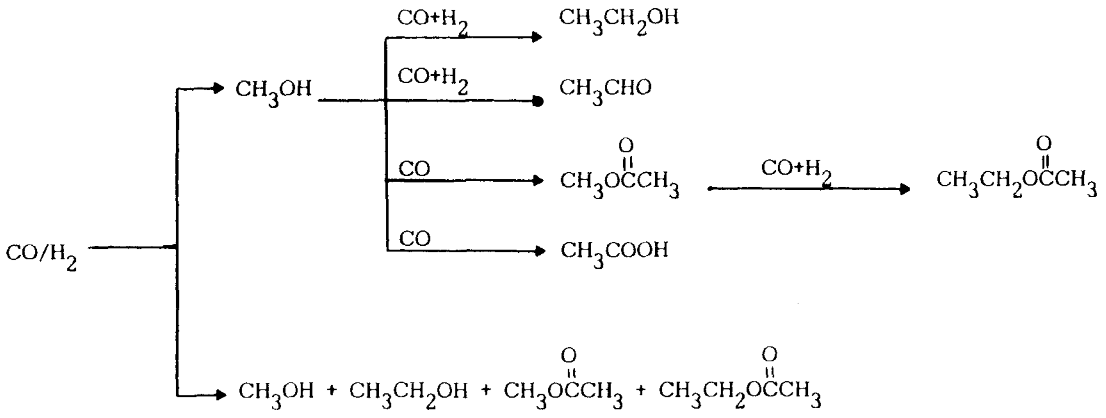
*For Paper XI, see *J. Mol. Catal.*, 1987, 43: 65.



Scheme 1 Synthesis of C–2 oxygenates using iodide-free homogeneous Ru–Co catalysts and synthesis gas.

established, large-volume, commodity chemicals.[2] They are currently manufactured in the US for the most part from petroleum-derived ethylene. Methyl and ethyl acetate esters enjoy combined markets of *ca* 300 × 10^6 lb yr^{-1} as solvents for coatings, plastics, etc.[3] Acetic acid is already a syngas-derived chemical. Both the BASF[4] and highly successful Monsanto[5] processes have been practiced commercially for some time now. C_1–C_3 alcohols and their acetate esters could see vastly expanded markets as high-octane blending agents for unleaded gasoline.[6]

RESULTS AND DISCUSSION

Ethanol and acetaldehyde syntheses

Methanol homologation is likely to become an important industrial route to ethanol.[7] Furthermore, it provides an excellent model for screening new homogeneous catalyst systems. The recurring problems in methanol homologation chemistry are difficulties in achieving a selective synthesis of ethanol versus acetaldehyde (Eqns [1], [2]), and the need for a stable, recyclable catalyst system, as well as the necessity for economically attractive rates of carbon monoxide hydrogenation. We have discovered that the iodide-free, homogeneous Co–Ru/Bu_4PBr catalyst precursor (Table 1) is an excellent candidate for rapid methanol homologation, giving an unusual 76–84% ethanol selectivity at high conversion levels (see Table 1, expts 1 and 2).[8] Furthermore, the same catalyst combinations are stable, homogeneous and easily recyclable. There is no obvious appearance of metal plating.

Additional modification of the catalyst, substituting ruthenium metal for ruthenium(IV) dioxide hydrate (RuO_2) substantially alters the overall reducing power of the system, such that acetaldehyde is now the major product fraction (Table 1, expt 3). All three catalyst components – the ruthenium metal (Ru), dicobalt octacarbonyl [$Co_2(CO)_8$] and tetrabutylphosphonium bromide (Bu_4PBr) – are critical to acetaldehyde production.[9] Cobalt is required to ensure the formation of C_2-oxygenates, while both the ruthenium metal and Bu_4PBr are necessary for acetaldehyde to be the ultimate product in preference to ethanol, methyl acetate and ethyl acetate (see expts 3–6).

Methyl acetate, ethyl acetate and acetic acid

The same ruthenium–cobalt–quaternary phosphonium salt combination is also effective for methanol carbonylation and the synthesis of methyl acetate (Eqn [3]).[10] Under the chosen conditions of Table 2, expt 7, 90% selectivity to methyl acetate can be achieved with this iodide-free catalyst at conversion levels of *ca* 56%. As the level of methanol conversion is raised to near-quantitative (in this case by raising the operating temperature), ethyl acetate becomes a significant by-product.

A further modification of the gas composition, using synthesis gas (CO/H_2 ratios of 4:1 to 12:1 Table 2, expts 10–13) rather than carbon monoxide alone, allows ethyl acetate to be the major product and

Table 1 Methanol homologation – synthesis of ethanol and acetaldehyde

Expt	Catalyst precursor[a]	Ru/Co/P molar ratio	Operating[b] pressure (atm/kPa)	MeOH conversion (%)	Product selectivity (%)				
					CH_3CHO	C_2H_5OH	C_3H_7OH	CH_3OAc	C_2H_5OAc
1	RuO_2–$Co_2(CO)_8$–Bu_4PBr	1:2:10	272/27.5	45	–[c]	76	4	–	–
2	RuO_2–$Co_2(CO)_8$–Bu_4PBr	1:2:10	408/41.3	66	–	84	4	–	–
3	Ru–$Co_2(CO)_8$–Bu_4PBr	1:1:10	429/43.3	88	48	19	–	10	8
4	Ru–$Co_2(CO)_8$–Bu_4PBr	1:0:10	429/43.3	5	–	–	–	–	–
5	Ru–$Co_2(CO)_8$–Bu_4PBr	0:1:10	429/43.3	30	24	–	–	38	16
6	Ru–$Co_2(CO)_8$–Bu_4PBr	0.5:1:0	429/43.3	87	4	62	–	6	–

[a] Typical reactor charge: 2 mmol RuO_2, 2 mmol $Co_2(Co)_8$, 20 mmol Bu_4PBr, 20 cm^3 MeOH, 20 cm^3 *p*-dioxane. [b] Operating conditions: CO/H_2 (1:2); 200°C, run in *p*-dioxane solvent. [c] –, Not observed.

Table 2 Methanol carbonylation – synthesis of methyl acetate, ethyl acetate and acetic acid

Expt	Catalyst precursor[a]	Promoter	Operating temp. (°C)	Gas composition	MeOH conversion (%)	Product selectivity (%)				
						MeOAc	EtOAc	PrOAc	BuOAc	HOAc
7	RuO_2–$Co_2(CO)_8$–Bu_4PBr	None	170[b]	CO	56	90	5	–	–	–
8	RuO_2–$Co_2(CO)_8$–Bu_4PBr	None	180[b]	CO	94	83	9	–	–	–
9	RuO_2–$Co_2(CO)_8$–Bu_4PBr	None	200[b]	CO	99	58	23	–	–	–
10	RuO_2–$Co_2(CO)_8$–Bu_4PBr	None	220[c]	CO/H_2 (12:1)	>98	32	25	11	4	–
11	RuO_2–$Co_2(CO)_8$–Bu_4PBr	None	200[c]	CO/H_2 (5:1)	>98	13	52	16	3	–
12	RuO_2–$Co_2(CO)_8$–Bu_4PBr	None	220[c]	CO/H_2 (4:1)	>98	8	43	18	5	–
13	RuO_2–$Co_2(CO)_8$–Bu_4PBr	None	240[c]	CO/H_2 (4:1)	>98	1	44	22	3	–
14	RuO_2–$Co_2(CO)_8$–Bu_4PBr	H_2SO_4	200[c]	CO	>98	3	18	–	–	75
15	RuO_2–$Co_2(CO)_8$–Bu_4PBr	Nafion®	200[c]	CO	>98	3	25	–	–	64
16	RuO_2–$Co_2(CO)_8$–Bu_4PBr	CH_3SO_3H	200[d]	CO	>98	33	9	–	–	57
17	RuO_2–$Co_2(CO)_8$–Bu_4PBr	CH_3SO_3H	200[e]	CO	>98	8	9	–	–	83

[a] Typical reactor charge: 0.5 mmol RuO_2, 0.5 mmol $Co_2(Co)_8$, 10 mmol Bu_4PBr, 20 cm^3 MeOH. Operating pressure: [b] 238 atm (24.0 kPa); [c] 400–410 atm (40.4–41.4 kPa); [d] 330 atm (33.3 kPa); [e] 450 atm (45.5 kPa).

provides a novel route to ethyl acetate from methanol (Eqn [4]).[11]

To our knowledge these are the first examples of selective methyl and ethyl acetate syntheses from methanol in the absence of an iodide promoter.[16]

A second route to ethyl acetate formation is methyl acetate homologation (Eqn [5]), again using the ruthenium–cobalt–quaternary phosphonium salt homogeneous catalyst system.[12] Modest selectivity to ethyl acetate (73%, at 100% MeOAc conversion) is achieved here with acetic acid the only detectable by-product in the liquid phase (22% selectivity).

Acetic acid may revert to the major product (Eqn [6]) when the Ru–Co–Bu_4PBr catalyst is coupled with a strong Brønsted acid such as sulfuric acid, Nafion® (a perfluorinated ion-exchange polymer) and methanesulfonic acid. Selectivities of 75–87% are possible at the higher pressures (see Table 2, expts 14–17).[13]

C_1–C_3 alcohols/acetate esters

C_1–C_3 alcohols and their acetate ester mixtures of varying composition can be generated directly from synthesis gas also using a ruthenium–cobalt–quaternary phosphonium salt homogeneous catalyst system. The actual composition of the product liquid is determined to a large degree by: (a) the choice of solvent, (b) the Ru/Co ratio, (c) the choice of quaternary salt and (d) the reaction time.

The use of a ruthenium(IV) dioxide/dicobalt octacarbonyl/tetrabutylphosphonium bromide mix (1:0.25:10), in ether solvents such as *p*-dioxane and tetraglyme, is highly effective for C_1–C_3 alcohol/acetate ester syntheses in 85% selectivity (Table 3, expt 18).[14] The reaction rate is $0.04\,g\,cm^{-3}\,h^{-1}$. Both aliphatic and aromatic hydrocarbon solvents lead to considerably lower productivities and amine solvents such as *N*-methylmorpholine tend to deactivate the

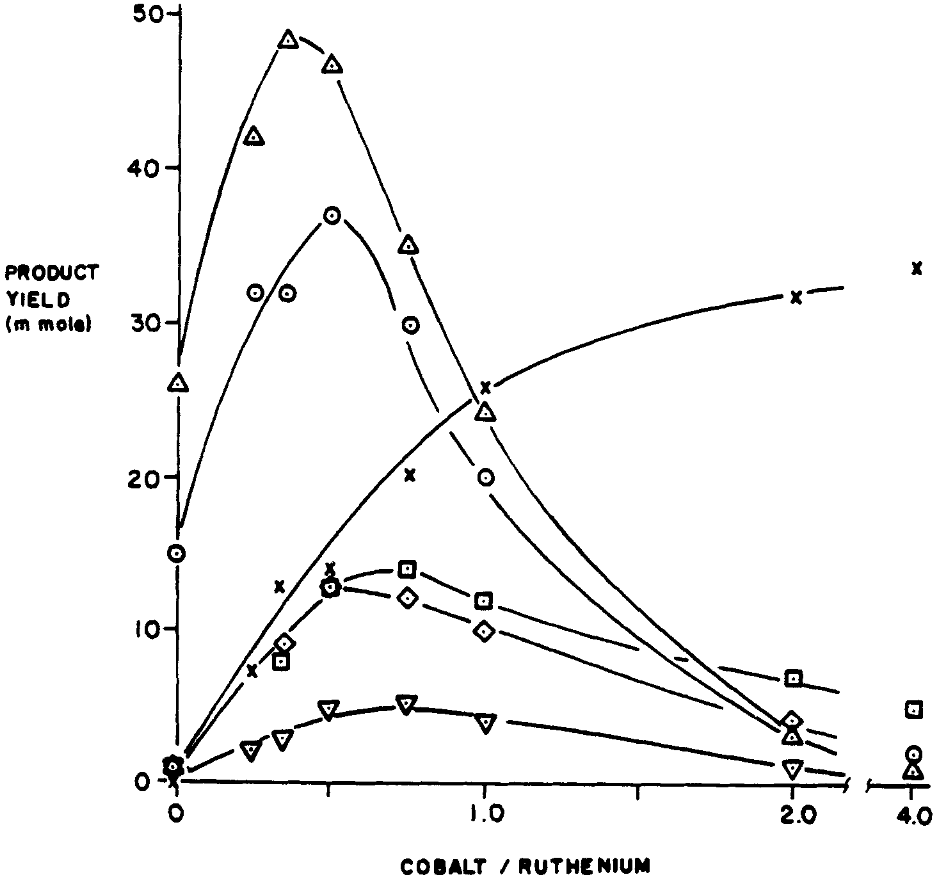


Figure 1 Alcohols and esters from synthesis gas. Effect of cobalt catalyst charge: Ru, 1·0 mmol; Co, 0–4·0 mmol; Bu_4PBr, 10·0 g. Product profile: methanol, Δ; ethanol, O; propanol, ∇; methyl acetate ◇; ethyl acetate, □; acetic acid, ×.

Table 3 C_1–C_3 alcohol/acetate ester syntheses from carbon monoxide/hydrogen

Expt	Catalyst precursor[a]	Solvent[b]	Product selectivity (%)						Productivity [g(g atom Ru)$^{-1}$ h^{-1}]
			CH_3OH	C_2H_5OH	C_3H_7OH	CH_3OAc	EtOAc	PrOAc	
18	RuO_2–$Co_2(CO)_8$–Bu_4PBr	*p*-Dioxane	20	35	6	19	15	–	670
19	RuO_2–$Co_2(CO)_8$–Bu_4PBr	Tetraglyme	21	29	10	–	3	–	620
20	RuO_2–$Co_2(CO)_8$–Bu_4PBr	Heptane	22	30	8	15	14	–	410
21	RuO_2–$Co_2(CO)_8$–Bu_4PBr	Toluene	24	21	9	20	12	–	510
22	RuO_2–$Co_2(CO)_8$–Bu_4PBr	*N*-Methylmorpholine	43	19	–	19	2	–	320
23	RuO_2–$Co_2(CO)_8$–$MePh_3PBr$	*p*-Dioxane	–	8	7	20	43	10	580
24	RuO_2–$Co_2(CO)_8$–$BuPh_3PBr$	*p*-Dioxane	–	4	16	8	60	–	470
25	RuO_2–$Co_2(CO)_8$–$C_7H_{15}Ph_3PBr$	*p*-Dioxane	–	4	20	7	54	6	440
26	RuO_2–$Co_2(CO)_8$–Ph_4PBr	*p*-Dioxane	–	5	28	14	38	–	240

[a] Typical reactor charge: 2 mmol RuO_2, 0.25 mmol $Co_2(Co)_8$, 20 mmol R_4PBr, 20 cm^3 solvent. [b] Operating conditions: 544 atm (54.9 kPa); 220°C; CO/H_2 (1:1); 16–18 h.

system further. The choice of phosphonium salt also has some bearing on the product composition, with tetrabutylphosphonium salt favoring the formation of methanol and ethanol and alkyltriphenylphosphonium bromides increasing the carbonylation capability and affording 60% selectivity to ethyl acetate directly from CO/H_2 (Table 3, expt 24).

The importance of the cobalt-to-ruthenium atomic ratio is illustrated in Fig. 1. Although C_1-C_3 alcohols are generated in substantial yields in the absence of cobalt, both methanol and ethanol content are maximized at Co/Ru ratios of *ca* 0.5. A further increase in cobalt content, on the other hand, leads to substantial enhancement in carbonylation activity and acetic acid is the major product fraction (up to 68% selectivities) at Co/Ru > 1 (Eqn [7]).[15]

$$2CO + 2H_2 \rightarrow CH_3COOH \qquad [7]$$

A typical synthesis profile for the $Ru_3(CO)_{12}/Co_2(CO)_8/Bu_4PBr$ catalyst shows that while the predominant initial reaction is methanol formation, homologation to C_2-C_3 alkanols becomes increasingly important so that ethanol is eventually the major fraction in the later stages – where methanol concentrations actually decline.[15] A similar sequence is evident for the methyl and ethyl acetate ester fractions.

CONCLUSIONS

Bimetallic, ruthenium–cobalt–quaternary phosphonium salt catalyst systems provide a new generation of catalyst systems for the generation of a variety of different aliphatic oxygenates from synthises gas.

Particular applications include:

acetaldehyde and ethanol production via methanol homologation;

methyl acetate synthesis via methanol carbonylation;

ethyl acetate and acetic acid preparations from methanol;

methyl acetate homologation to ethyl acetate;

production of C_1-C_3 alcohols and their acetate esters directly from carbon monoxide/hydrogen mixtures.

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