One and Two-Stage Synthesis of Ethanol by Hydrocarbonylation of Methanol in Chelating Solvents

In this Note we report an examination of the homologation of methanol to ethanol assuming that acetaldehyde is an intermediate. Two procedures to produce ethanol are proposed, both combining cobalt and ruthenium catalysts and using the chelating properties of glymes and cyclic ethers.
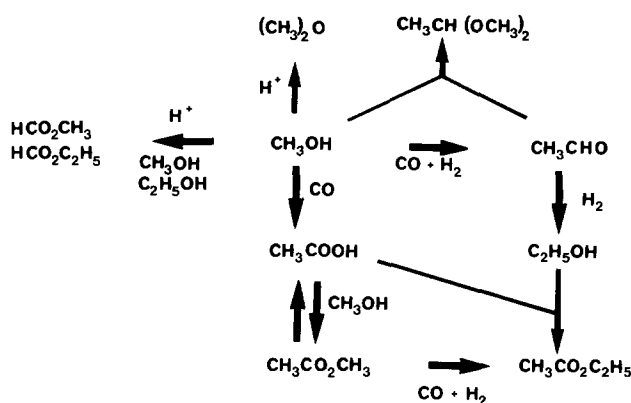
Since the pioneering work of Wender *et al.* (*1*) the homologation of methanol in presence of cobalt catalysts has been subject to a number of improvements and modifications of the catalytic system (*2*). One of the factors affecting the potential utility of the reaction is its lack of selectivity to a single product. Catalysts which possess high activity generally tend to give a broad spectrum of products and vice versa. The problem rests on the finding of a system combining high conversion and selectivity to ethanol or its precursors. Some recent results demonstrate substantial improvements in the conversion to ethanol via *direct* homologation of methanol at 190–220°C in the pressure range 20–30 MPa (*3–7*): conversion of methanol is 40–100% and selectivity to ethanol 50–90%.

Since acetaldehyde is presumed to be the primary product of the cobalt-catalyzed homologation reaction (*8*) and can be subsequently converted into ethanol with relative ease, we were prompted to search for processes leading to high conversion and selectivity for CH_3CHO. This immediately suggests the following method: one should aim to produce acetaldehyde under low temperature conditions, then hydrogenate it at a higher temperature in the same vessel. The procedure presupposes that some conditions are fulfilled before starting the reaction: especially, the carbonylation and the hydrogenation catalysts must be present. In the first stage, it is essential that CH_3CHO is produced in maximum yield, since according to Scheme 1, a number of parallel or inverse reactions may occur mainly due to the proton of the acidic intermediate $HCo(CO)_4$ (*9*). Formates are usually produced only in minute amounts. Dimethylacetal is a source of acetaldehyde; however, as it liberates again methanol, its formation should not be encouraged. Dimethyl ether is formed in minor amounts when operating at low temperatures. Formation of acetic acid and methyl acetate is difficult to avoid; the acetate must be kept at the lowest possible level, since in the further hydrogenation stage it is easily converted into ethyl acetate in the presence of ruthenium catalysts (*10*).

The synthesis of acetaldehyde has been examined in earlier work (*11, 12*). We have found, for example, that using the cheap typical catalytic system (cobalt compound-iodine), high pressures (100–140 MPa) (conversion up to 100%, selectivity to CH_3CHO up to 75%) (*11*), or chelating solvents (conversion up to 100%, selectivity to CH_3CHO up to 93%) (*12*) significantly promote the homologation reaction with selectivities quite comparable with or better than previously reported (*3–7*). Our best selectivity runs were achieved with cobalt acetate and iodine in the presence or not of tributylphosphine as catalytic system and glymes or cyclic ethers as solvents (conversion was 88–90% and selectivity to CH_3CHO 93%).

The hydrogenation procedures preferably involve catalysts employing ruthenium compounds in addition to cobalt acetate

$(CH_3)_2O$ $CH_3CH(OCH_3)_2$

H^+ ↑

HCO_2CH_3 H^+
$HCO_2C_2H_5$ ← CH_3OH → CH_3CHO
CH_3OH $CO + H_2$
C_2H_5OH ↓ CO ↓ H_2

CH_3COOH C_2H_5OH

↑↓ CH_3OH

$CH_3CO_2CH_3$ → $CH_3CO_2C_2H_5$
$CO + H_2$

SCHEME 1. Formation of products in the homologation of methanol.

due to their ability to readily hydrogenate CH_3CHO and thereby eliminate any of its undesired by-product derivatives (13, 14).

Thus the two-stage reaction was achieved by carrying out the reaction in a glyme or a cyclic ether in the presence of a mixture of cobalt acetate and ruthenium acetylacetonate with iodine as promoter, first at 140°C during 1.5 h to produce acetaldehyde, then by increasing the temperature to 200°C for another period of 1.5 h.

Table 1 lists the hydrocarbonylation results obtained by the sequential (two-stage) and the one-stage procedures. There is no definitive advantage of one method

TABLE 1

Hydrocarbonylation of Methanol in Chelating Solvents[a]

	Catalyst	Method[b]	$\Sigma(CH_3CHO)$[c]	$\Sigma(C_2H_5OH)$[c]	Rate[d]
A	Coac₂	Reference	87.1	0.1	—
A	Coac₂ + Ru(acac)₃	Reference	77.7	9.8	—
A	Coac₂ + Ru(acac)₃	One-stage	6.6	67.1	30
A	Coac₂ + Ru(acac)₃	Sequential	2.8	82.3	41
B	Coac₂	Reference	92.8	0	—
B	Coac₂ + Ru(acac)₃	Reference	51.3	42.0	—
B	Coac₂ + Ru(acac)₃	One-stage	0.5	85.7	25
B	Coac₂ + Ru(acac)₃	Sequential	1.5	85.8	27
C	Coac₂	Reference	81.6	0	—
C	Coac₂ + Ru(acac)₃	One-stage	0.5	75.5	23
C	Coac₂ + Ru(acac)₃	Sequential	0.1	84.7	30
D	Coac₂	Reference	89.8	0	—
D	Coac₂ + Ru(acac)₃	One-stage	1.3	83.0	30
D	Coac₂ + Ru(acac)₃	Sequential	10.2	78.0	28

Note. A, tetraglyme (5.0 ml), CH_3OH (1.0 ml); B, tetrahydrofuran (4.5 ml), CH_3OH (1.5 ml); C, dioxane (4.5 ml), CH_3OH (1.5 ml); D, dioxane (4.5 ml), CH_3OH (1.5 ml), $P(C_4H_9)_3$ (0.5 mmol).

[a] P (28–30 MPa), Coac₂, $4H_2O$ (0.15 mmol/ml of CH_3OH), Ru(acac)₃ (0.03 mmol/ml of CH_3OH), iodine (0.30 mmol/ml of CH_3OH), $CO:H_2$ (1:2).

[b] Reference: run at 140°C (3 h), one-stage: run at 200°C (3 h), sequential: run at 140°C (1.5 h), then at 200°C (1.5 h).
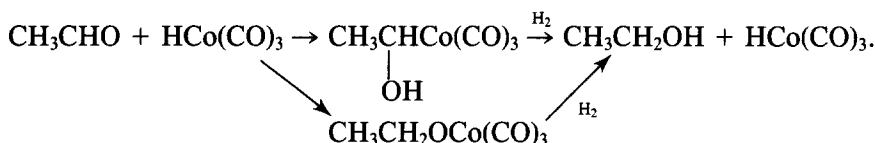
[c] $\Sigma(\%)$: molar selectivity.

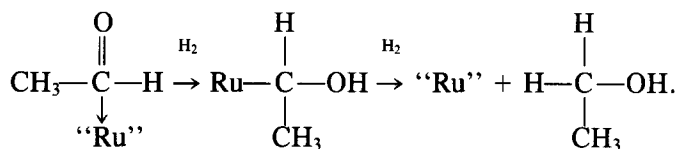[d] Turnover number: mol ethanol/mol Co/h.

over the other. For series A and C, the two-stage reaction affords higher rates and improved selectivity to C_2H_5OH; for reaction B the results are similar, while for the runs D, the advantage of the sequential method is not demonstrated, since CH_3CHO could not be completely hydrogenated under those conditions. This is quite surprising since a weakening of the hydrogenation properties of the catalyst due to the presence of the phosphine is hardly plausible. However, for all series the ruthenium catalyst is necessary, which is in conflict with a recent patent (4).

The actual mechanism of the passage from CH_3CHO to C_2H_5OH is not yet elucidated. Fahey proposed with Co catalysts (15):

$$CH_3CHO + HCo(CO)_3 \rightarrow CH_3\overset{\underset{\displaystyle OH}{|}}{\underset{\searrow}{C}}HCo(CO)_3 \overset{H_2}{\rightarrow} CH_3CH_2OH + HCo(CO)_3.$$

$$CH_3CH_2OCo(CO)_3 \nearrow H_2$$

In the presence of ruthenium we suggest a similar sequence (16)

$$CH_3\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle ``Ru"}{\downarrow}}{C}}H \overset{H_2}{\rightarrow} Ru\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}OH \overset{H_2}{\rightarrow} ``Ru" + H\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}OH.$$

To our knowledge, the present results are among the best reported in the literature up to now regarding the selectivity to acetaldehyde or to ethanol, especially at such high methanol conversions, although higher rates have been claimed in patents (17, 11).

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