A Novel Catalyst for the Low Pressure, Low Temperature Homologation of Methanol

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Methanol is homologated to ethanol with high selectivity (80 mol%) at low pressure and temperature (1000 lb in^{-2}; 140 °C) with a novel rhodium–ruthenium–diphosphine–methyl iodide catalyst.

The synthesis gas-based homologation of methanol [equation (1)] has received much attention.[1] To date, cobalt–ruthenium–methyl iodide catalysts show the best performance in terms of selectivity (60—90 mol%) and rate (2—6 mol l^{-1} h^{-1}). In order to achieve acceptable rates and selectivities these catalysts must be operated at high pressures (3000—8000 lb in^{-2}) and temperatures (≥175 °C); thus their industrial application is limited. Because rhodium is typically more

$$CH_3OH + 2H_2 + CO \rightarrow CH_3CH_2OH + H_2O \quad (1)$$

active than cobalt in synthesis gas catalysis, we considered that the use of this metal as a methanol homologation catalyst might allow operation at lower extremes of temperature and pressure without sacrificing rate or selectivity. Indeed, this approach has been investigated by others.[1,2] However, rhodium-based catalysts lead to essentially exclusive formation of acetic acid *via* methanol carbonylation; little or no homologation occurs except at very high (40:1) H_2:CO ratios. We felt that it would be possible to employ a rhodium catalyst modified by an appropriate ligand to produce ethanol selectively, as has been accomplished with cobalt catalysts.[3] We have found that diphosphine-modified rhodium catalysts can indeed homologate methanol at significantly lower pressures and temperatures than previously reported for other catalysts.

In a typical procedure, a 100 ml autoclave is charged with methanol, $Rh(CO)_2(acac)$, and the diphosphine ligand (Table 1). When gas evolution ceases (displacement of CO by the diphosphine) the reactor is charged with $RuCl_3 \cdot 3H_2O$ and methyl iodide. The autoclave is then heated and pressurized to 140 °C and 1000 lb in^{-2} (H_2 : CO 2 : 1). After 2—3 h the reactor is cooled and vented, and the products are analysed by gas chromatography. As shown in Table 1, methanol is homologated to ethanol under relatively mild conditions, with selectivities as high as 80 mol%. The remainder of the liquid product is acetic acid.† Depending on the particular diphosphine employed, the methanol conversion may approach 100% within 5—6 h. For $Ph_2P[CH_2]_3PPh_2$ the rate of conversion into ethanol is 4—6 mol l^{-1} h^{-1}, which rivals that obtained under more forcing conditions with a conventional cobalt catalyst.

Further inspection of Table 1 shows that the ethanol selectivity varies considerably with the diphosphine ligand employed. To date, the best catalyst performance has been obtained with $Ph_2P[CH_2]_3PPh_2$. Increasing or decreasing the chelate ring size, or alkyl substitution of the phenyl groups, generally results in a lower selectivity. Likewise, the use of 2 equiv. of PPh_3 in place of a chelating diphosphine yields poor results.

Our postulated pathway for the homologation reaction is summarized in equation (2), and is consistent with the following observations. Addition of ^{13}C-labelled acetic acid to an autoclave charge, followed by analysis (g.l.c.–mass spectrometry) of the liquid products at the end of the reaction, demonstrates that hydrogenation of acetic acid or its esters is not a pathway to ethanol. A similar experiment employing ^{13}C-labelled acetaldehyde shows that this label is incorporated into ethanol only.‡ Thus, acetaldehyde, an observable product during the homologation catalysis, is almost certainly an intermediate in the formation of ethanol.

$$CH_3OH \xrightarrow{HI} CH_3I \begin{cases} \xrightarrow{CO,\,H_2} CH_3CHO \xrightarrow{H_2} CH_3CH_2OH \\ \xrightarrow[CO]{} CH_3CO_2H \end{cases} \quad (2)$$

† Small amounts of acetaldehyde and methane are also formed.

‡ No label is found in methane, carbon monoxide, or acetic acid, demonstrating that acetaldehyde is formed irreversibly.

Table 1. Methanol homologation with rhodium–ruthenium–diphosphine–methyl iodide catalysts.[a]

Diphosphine	Ethanol selectivity (mol %)
$Ph_2P[CH_2]_3PPh_2$	80
$Ph_2PCH_2CMe_2CH_2PPh_2$	71
$Ph_2PCH_2CH_2CHMePPh_2$	65
$Ph_2P[CH_2]_2PPh_2$	43
$Ph_2PCH_2PPh_2$	12
$Ph_2P[CH_2]_4PPh_2$	7
$Me_2P[CH_2]_3PMe_2$	35
$Et_2P[CH_2]_3PPh_2$	17
$2\,PPh_3$	6

[a] Conditions: 1—2 mmol $Rh(CO)_2(acac)$, 4 mmol $RuCl_3 \cdot 3H_2O$, 1—4 mmol diphosphine, 40 mmol MeI, 40 ml MeOH, 140 °C, 1000 lb in^{-2} 2 : 1 H_2 : CO. Ethanol selectivity is based on the total amount of ethyl groups (*e.g.* ethanol, diethyl ether, and ethyl acetate) plus acetaldehyde produced. The remaining products are acetic acid and its methyl and ethyl esters.

We have also isolated and identified the catalyst components present at the end of the homologation reaction. Spectroscopic and analytical data show that rhodium and diphosphine are recovered as the acetyl complex Rh(diphosphine)$(COMe)I_2$. I.r. analysis shows that ruthenium is present as the well known anion $[Ru(CO)_3I_3]^-$.[4] Spectroscopic measurements (^{31}P n.m.r. and i.r.) show that the complexes account for >95% of the catalyst components originally present in the autoclave. Presumably a rhodium–diphosphine complex (and possibly the acetyl complex) is responsible for the high acetaldehyde/ethanol selectivities obtained with this novel catalyst. We have verified independently that the ruthenium complex is responsible for the hydrogenation of acetaldehyde to ethanol. Consistent with these ideas, these complexes can be reused for homologation catalysis with no loss in rate or selectivity. Both complexes are again isolable at the end of the reaction. Further studies of this novel homologation catalyst are in progress.

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