

Alternative pathways in the ruthenium catalysed hydrogenation of CO to alcohols†

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CO hydrogenation in $[\text{PBu}_4]\text{Br}$ in the presence of $[\text{Ru}_3(\text{CO})_{12}]$ gives predominantly methanol, ethanol and propanol with small amounts of 1,2-ethanediol. Using RuO_2 as the catalyst precursor, the same products are formed along with higher alcohols (1-butanol–1-heptanol). Reactions carried out using added $^{13}\text{CH}_3\text{OH}$ or ^{13}CO show that ethanol and propanol come from homologation reactions of methanol and ethanol respectively, but that the higher alcohols are not formed through the lower alcohols as intermediates.

Introduction

The hydrogenation of carbon monoxide using heterogeneous catalysts, the Fischer Tropsch (FT) process, has been well-developed and fine-tuned on a huge scale for the production of alkanes and alkenes from coal or natural gas.^{1–3} In these processes all of the oxygen is discarded as water so oxygen functionalised molecules are minor side-products. With the rising scarcity of oil, the production of oxygenates such as alcohols from coal, natural gas or CO_2 ^{4–7} (C_1 feedstocks) has become more attractive, but despite this, following a flurry of activity in the 70's and 80's the conversion of CO into higher alcohols is still underdeveloped. Homogeneous CO hydrogenation may potentially give better selectivity and control over product formation and especially selectivity towards oxygenates.⁸

Homogeneous carbon monoxide hydrogenation was pioneered by Gresham and Schweizer using cobalt based systems at high temperatures and pressures.⁹ Lower pressure operation was possible using rhodium^{10,11} or ruthenium, mainly $[\text{Ru}_3(\text{CO})_{12}]$,^{12–14} based catalysts with the major products being methanol and 1,2-ethanediol.

Improvements were obtained by adding halides to the ruthenium system and Knifton and co-workers introduced^{15–17} phosphonium bromides as the solvent as well as RuO_2 as an alternative catalyst precursor.¹⁵ In these cases, ethanol also became a significant product.

We have recently reported¹⁸ studies on $[\text{Ru}_3(\text{CO})_{12}]$ catalysed CO hydrogenation in $[\text{Bu}_4\text{P}]\text{Br}$, under milder conditions (250 bar, 200 °C), than those studied by Knifton

in which we discovered that $[\text{Bu}_3\text{PH}]\text{Br}$, sometimes present as an adventitious impurity in the solvent acts as a significant promoter of the reaction by releasing HBr into the system.

The main products were methanol, ethanol and propanol in declining amounts. Significant amounts of ethylene glycol were also formed. We now report that the product distribution obtained when using RuO_2 as the ruthenium precursor is significantly different from that obtained when using $[\text{Ru}_3(\text{CO})_{12}]$ and use ^{13}C labelling studies to examine the mechanisms of formation of the various products.

Experimental

Unless stated otherwise, all chemicals were obtained from Sigma Aldrich and used as received. Air-sensitive compounds were handled under N_2 using standard Schlenk techniques. NMR spectra were recorded on Varian 300 NMR or Bruker AM 300/400 NMR spectrometers. The chemical shifts were referenced to the solvent, which were in turn referenced to a TMS standard. IR spectra were recorded by pressing a sample of the liquid product between two KBr plates in a holder. The samples were recorded on a Thermo Nicolet Avatar FTIR spectrometer with a nitrogen cooled MCT detector. For quantitation Gas Chromatography analysis was performed using a Supelcowax-10 capillary column (60 m \times 0.32 mm \times 1.0 μm film thickness) using an Agilent 6890 N Network GC system equipped with a flame ionisation detector. For identification a HP 6890 series GC system equipped with a HP 5973 mass selective detector was used. Both machines used the same column using 1 ml min^{-1} helium carrier gas flow and 250 °C injector and detector temperatures. The temperature programmes was as follows: 50 °C, hold 3 minutes, ramp 20 °C min^{-1} , 150 °C, hold 5 min, ramp 20 °C min^{-1} , 220 °C, hold 13 minutes. Split ratio: 1 : 100.

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Full details of the methods used to analyse the positions and amounts of ^{13}C incorporated into the products are provided in the ESI.†

Catalytic experiments

General procedure. A mixture of the solvent and catalyst precursor was purged of air using syngas ($\text{CO}:\text{H}_2$ 1:1) by repeatedly pressurising up to 10 barg and venting. The system was then tested for leaks at 170 bar before being heated up to 200 °C with the vessel sealed and under continuous stirring. At 200 °C the pressure was adjusted to 250 bar and the reaction mixture was allowed to react for 4 h at constant pressure, with $\text{CO}:\text{H}_2$ (1:1) being fed from a ballast vessel. The heating was switched off and the reactor swiftly cooled to room temperature. The excess gas was vented and the liquid product was collected for analysis. When employing ^{13}CO the reactor was not kept at constant pressure (no feed from the ballast vessel) in order to prevent unnecessary dilution of the ^{13}C label.

For instance: in an unlabelled control experiment (used as a reference for GCMS analysis) $[\text{Ru}_3(\text{CO})_{12}]$ (0.5 g, 2.3 mmol Ru) and $[\text{PBu}_4]\text{Br}$ (15 g, 44.2 mmol) were added to the autoclave. The autoclave was screwed onto the holder and purged by pressuring to 11 bar and venting to ambient pressure 6 times using $\text{CO}:\text{H}_2$ 1:1 v/v before pressurising to over 170 bar. A leak test was performed and no pressure drop was observed overnight other than that resulting from cooling the autoclave. The following morning the heating jacket was mounted, and switched on, the stirrer was switched on. When the temperature reached 200 °C, the pressure was adjusted to 250 bar and the stirrer was set to a fixed power input. The temperature and pressure were held constant until the heating and stirring were switched off after 4 h. Taps to the autoclave were closed to prevent gas flowing into the reactor because of the cooling. When the autoclave temperature reached below 30 °C the autoclave was vented and opened. The product mixture was usually a red liquid of which a small sample was stored and was often analysed using NMR or IR. The remainder of the liquid was transferred to a flask and stripped of volatiles by vacuum distillation using temperatures up to 250 °C and a liquid N_2 cold trap. The volatiles that were collected were diluted using acetonitrile/NMP stock solution (2 mL of 5% (v/v)) and analysed using GC. The total product amounts were calculated using the NMP and acetonitrile peaks as internal references.

Reactions using ^{13}CO . $[\text{PBu}_4]\text{Br}$ (15 g, 44.2 mmol) and RuO_2 (0.3 g, 1.6 mmol Ru) were added to the autoclave. The system was purged using 1:1 syngas and brought to 185 bar to test for leaks. When the system did not leak the autoclave was vented to ambient pressure. Then the pressure was raised to approximately 13 bar using ^{13}C labelled CO and H_2 was added to approximately 24 bar total pressure. Then the pressure was increased to 180 bar using regular $\text{CO}:\text{H}_2$ (1:1). These pressures were measured using the Back Pressure Regulator (BPR) which is accurate at higher pressures but not

very accurate at low pressures. The autoclave was closed and subsequently heated to 200 °C under constant stirring. The work-up and analysis were as described above. In this case the distillate was analysed by GC–MS to assess the compound individual masses and fragmentation patterns.

A similar reaction and work-up procedure was carried out using $[\text{PBu}_4]\text{Br}$ (15 g, 44.2 mmol), $[\text{Ru}_3(\text{CO})_{12}]$ (0.5 g, 2.34 mmol), ^{13}CO (17 bar) and H_2 (pressure to 33 bar) before pressurising to 180 bar.

Reactions using $^{13}\text{CH}_3\text{OH}$. Reactions using $^{13}\text{CH}_3\text{OH}$ were carried out similarly except that $^{13}\text{CH}_3\text{OH}$ (1 cm³) was added to the autoclave with the $[\text{PBu}_4]\text{Br}$ and the Ru source and the autoclave was pressurised with $\text{CO}:\text{H}_2$ (1:1, 180 bar). $\text{CO}:\text{H}_2$ were fed continuously from a ballast vessel to maintain constant pressure and to make up for $\text{CO}:\text{H}_2$ used in the reaction: $[\text{PBu}_4]\text{Br}$ (15 g (44.2 mmol)), RuO_2 (0.3 g (1.6 mmol)), and methanol (99% ^{13}C , 12% ^{18}O , 0.5 ml, 12.35 mmol) were added to the autoclave. The system was purged using 1:1 syngas and then pressurised to 180 bar. The autoclave was closed, heated to 200 °C and stirred for 4 h. The autoclave was cooled to 30 °C and the work up was performed as described above.

A similar reaction and work-up procedure was carried out using $[\text{PBu}_4]\text{Br}$ (15 g, 44.2 mmol), $[\text{Ru}_3(\text{CO})_{12}]$ (0.5 g, 2.34 mmol) and methanol (99% ^{13}C , 12% ^{18}O , 0.5 ml).

Results

During the course of our studies on CO hydrogenation in melt systems, we discovered that the product distribution was different when using RuO_2 as the catalyst precursor from that obtained with $[\text{Ru}_3(\text{CO})_{12}]$. In both cases the major products were methanol, ethanol and propanol in declining amounts together with 1,2-ethandiol (Fig. 1). However, when using RuO_2 as the catalyst precursor, significant amounts of higher alcohols (1-butanol –1-heptanol, with an almost Gaussian distribution peaking at 1-pentanol) were observed as products (Fig. 2).

This unusual product distribution (the higher alcohols do not follow the expected Schulz–Flory distribution adopted by

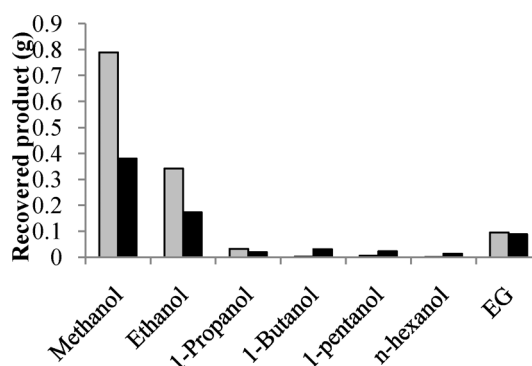


Fig. 1 Product distribution from the homogeneous hydrogenation of CO in $[\text{PBu}_4]\text{Br}$ using $[\text{Ru}_3(\text{CO})_{12}]$ (grey rectangles) or RuO_2 (black rectangles) as the catalyst precursor. $\text{CO}:\text{H}_2$ (1:1, 250 bar), 200 °C, 4 h.

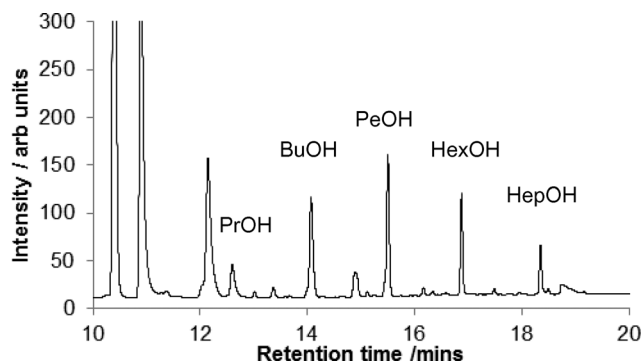


Fig. 2 Vertically expanded GC trace from CO hydrogenation in the presence of RuO_2 , showing higher alcohol products; conditions as in Fig. 1.

the lower alcohols) led us to believe that at least two different mechanisms may operate in the formation of C–C coupled products depending on the catalyst species present during the reaction. One possibility was that the tetrabutylphosphonium bromide solvent could act as a C_4 source in the synthesis of the higher alcohols, *via* solvent degradation. We were also interested to discover whether ethanol and propanol in the $[\text{Ru}_3(\text{CO})_{12}]$ and/or $\text{RuO}_2 \cdot \text{H}_2\text{O}$ catalysed reactions might be formed from intermediate methanol, as has previously been reported.^{19–23} Knifton has shown that, when $^{13}\text{CH}_3\text{OH}$ is added to a similar system ($[\text{Ru}_3(\text{CO})_{12}]$, $[\text{Bu}_4\text{P}]\text{Br}$, 220 °C, CO/H_2 , 276 bar) the ethanol produced contains significant ^{13}C in the methyl group,²¹ whilst Ono *et al.* have shown similar results when using $[\text{Ru}_3(\text{CO})_{12}]$ and $[\text{Co}_2(\text{CO})_8]$ in toluene containing $[\text{heptylPPh}_3]\text{Br}$ and PPh_3 ,²³ or when using $[(\text{Ph}_3\text{P})_2 \text{N}]\text{Cl}$.²⁰ Using heterogeneous catalysts and $^{13}\text{CH}_3\text{OH}$, ^{13}C can be incorporated into both the methylene and methyl groups of ethanol.²² When we added some methanol at the start of the reaction we found increased formation of ethanol.

Ethanol and propanol formation

To confirm that methanol homologation was occurring for the production of ethanol (and ethanol homologation for propanol), we carried out the CO hydrogenation with $^{13}\text{CH}_3\text{OH}$ added at the start of the reaction.

When 99% ^{13}C enriched methanol was added to reactions using either $[\text{Ru}_3(\text{CO})_{12}]$ or RuO_2 catalyst precursors. The ^1H NMR spectra of the product mixtures showed large ^{13}C coupled satellites for the ethanol beta protons.[‡] Interestingly, the protons from the α -position did not show increased ^{13}C labelling in either case. Due to the crowded nature of the ^1H NMR spectra only rough estimates of the isotopic abundances for some compounds found in the products can be made. Fortunately, the GC–MS data analysis (Table 1) showed that ethanol contained 40% and 34% of the ^{13}C isotope for the reactions using RuO_2 and $[\text{Ru}_3(\text{CO})_{12}]$, respectively.

‡ Unlabelled ethanol is also produced, presumably from methanol synthesised during the reaction from CO and H_2 . Unlabelled methanol is also present (86 and 78% from $[\text{Ru}_3(\text{CO})_{12}]$ and $\text{RuO}_2 \cdot 2\text{H}_2\text{O}$ respectively).

Table 1 The isotopic enrichment^a of the products when adding $^{13}\text{CH}_3\text{OH}$ at the start of the reaction

Precursor	Methanol	Ethanol	Propanol	Butanol	Pentanol
RuO_2	22	40	33	2	0
$\text{Ru}_3(\text{CO})_{12}$	14	34	34	22	7

^a The isotopic enrichment is calculated as $^{13}\text{C}/(^{12}\text{C} + ^{13}\text{C}) \times 100\%$ based on GC–MS isotopic patterns of the relevant peak groups.

The GC–MS pattern once again indicated exclusive labelling at the β -position. Thus, in combination with the evidence from NMR studies, we conclude that methanol carbonylation is the major pathway to ethanol.

Interestingly, for propanol, the isotopic enrichment does not occur exclusively at the γ -position. Instead, the label is also found with almost equal abundance in the β -position but not in the α -position (see Scheme 1). This indicates that the ethyl moiety has time to switch carbons on the metal centre, probably *via* reversible β -hydride elimination and H addition steps before the CO insertion takes place.

Similar conclusions have been drawn by other workers when adding $^{13}\text{CH}_3\text{OH}$ to CO hydrogenation systems (see above) but the position of the label in propanol has not previously been discussed.

Higher alcohol formation

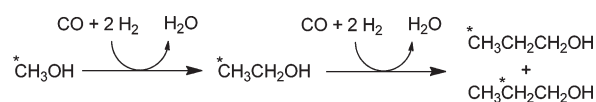
In order to understand the mechanisms of formation of the C_{4-6} alcohols in the two systems, we carried out studies using ^{13}C -labelled CO with no added methanol.

We considered four main mechanistic routes towards C–C coupled products:

1. Chain growth at the metal centre with irreversible release of the product alcohol
2. Chain growth through methanol and other alcohol carbonylation
3. C–C coupling *via* aldol condensation from free aldehyde intermediates
4. Alcohol synthesis *via* solvent degradation

These mechanisms and their expected outcomes when using RuO_2 as the catalyst precursor and partially labelled CO or added $^{13}\text{CH}_3\text{OH}$ are shown in Table 2.

GC–MS analysis of the higher alcohols produced when using RuO_2 as the catalyst and adding ^{13}C labelled methanol shows that no label is present in the higher alcohol products. Hence, all the C atoms come from the gas phase and the mechanism of formation of these longer chain alcohols is different from that of the formation of ethanol and propanol, thus ruling out mechanism 2.



Scheme 1 Ethanol and propanol synthesis *via* alcohol carbonylation. The * indicates the position of ^{13}C when starting with $^{13}\text{CH}_3\text{OH}$.

Table 2 Possible pathways to butanol from CO hydrogenation using RuO₂ as the catalyst precursor, the predicted labelling patterns and outcomes from CO hydrogenation using partially ¹³C labelled CO or ¹³CH₃OH are shown. Those in bold are observed, but those in italics are not

Mechanism	Expected labelling pattern for butanol using RuO ₂	
	Using ¹³ CO	Adding ¹³ MeOH
All C entirely from gas CO + H ₂ → BuOH	Up to 4 ¹³C in butanol	No ¹³C in butanol
Methanol reincorporation MeOH + CO + H ₂ → BuOH	Up to 4 ¹³C in butanol	<i>A single ¹³C in butanol</i>
Acetaldehyde and aldol MeOH + CO → CH ₃ CHO → BuOH	Up to 4 ¹³C in butanol	<i>Up to two ¹³CO in butanol in the β and δ positions</i>
Solvent degradation [Bu ₄ P]Br → BuOH	<i>No ¹³C in butanol</i>	No ¹³C in butanol

If the synthesis of higher alcohols occurs through the synthesis of methanol, which is then carbonylated to ethanal and undergoes subsequent aldol condensation we expect to find some product doubly labelled exclusively at the β and δ-position. Since there is no label in the higher products, mechanism 3 is also eliminated.

Using ¹³C enriched syngas and no added methanol we would expect that ¹³C incorporation should take place uniformly throughout the products, regardless of the mechanism except when product formation occurs through degradation of the solvent, [Bu₄P]Br.

It is possible to work out the average ¹³C percentage incorporation into each C position of the products using mass spectrometry (see ESI†). If all the C atoms come from the CO, the average % incorporation normalised for chain length should be the same for all the products. If, however, the C₄₊-alcohols display a lower ¹³C abundance than the C_{1–3} alcohols this would indicate that the higher alcohols were made from degradation of the solvent, [Bu₄P]Br.

Fig. 3 shows the % of ¹³CO incorporated into each product after reaction of ¹³C enriched syngas (H₂:CO, 1:1) with [Ru₃(CO)₁₂] or RuO₂ in tetrabutylphosphonium bromide at 200 °C and at a starting pressure of 260 bar (at 200 °C) in a closed batch system.

Fig. 3 clearly shows that a reaction using RuO₂ in ¹³C enriched syngas yields isotopically enriched products. The average ¹³CO incorporation found for this reaction was 8.5%.

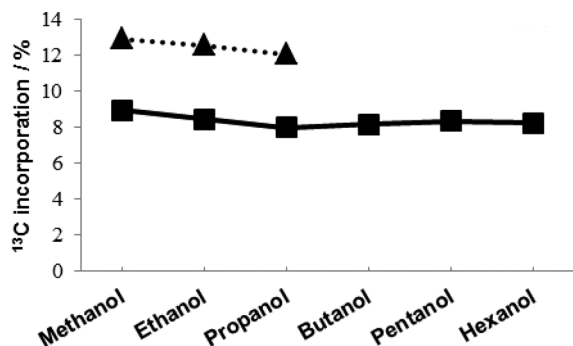


Fig. 3 The incorporation of ¹³CO into alcohol products during CO hydrogenation using ¹³CO enriched synthesis gas, based on the isotope pattern found in the GC-MS analysis for each product. The values given are ¹³C/¹²C + ¹³C × 100%, normalised for chain length. ▲ [Ru₃(CO)₁₂] as catalyst precursor; ■ RuO₂ as catalyst precursor.

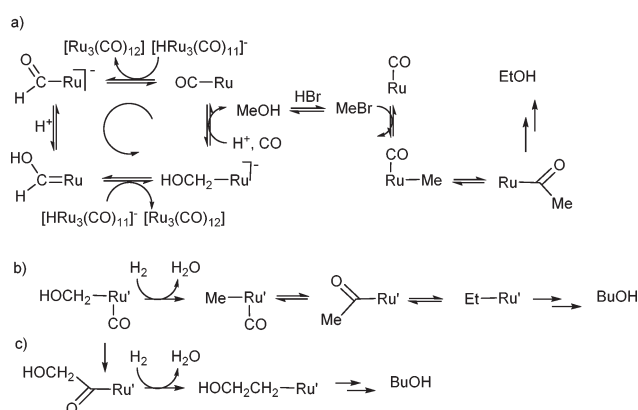
More interestingly, the average ¹³C incorporation for all compounds is of the same order, indicating that solvent degradation does not contribute significantly to the formation of the longer chain alcohols.

For the reaction using [Ru₃(CO)₁₂] the average level of ¹³C in the products was higher because the initial partial pressure of ¹³CO used for the ¹³CO – ¹²CO mixture was higher. § Again, the GC-MS of the methanol, ethanol and propanol show patterns consistent with extensive labelling in the products. The found % incorporations for the first three alcohols are more or less the same at 11.5–12%. The amount of higher alcohols formed when using [Ru₃(CO)₁₂] is not sufficient to obtain meaningful information.

We are not aware of any other studies that report labelling experiments for the production of higher alcohols from homogeneous CO hydrogenation.

Discussion

It has been proposed^{14,24–26} that methanol is formed on ruthenium catalysts by a series of intermolecular hydride transfers and protonations (Scheme 2a). The initial hydride transfer



Scheme 2 Possible mechanisms for the formation of a) methanol, ethanol and propanol; b), c) higher alcohols from the hydrogenation of CO using RuO₂ as the catalyst precursor.

§ Different pressures were used because the cylinder containing the ¹³CO depleted between the reactions.

is believed to occur from a species such as $[\text{Ru}_3\text{H}(\text{CO})_{11}]^-$ to CO bound to another ruthenium centre, probably derived from $[\text{Ru}(\text{CO})_3\text{Br}_3]^-$ in this system. The reaction is proposed to proceed *via* formyl and hydroxycarbene intermediates to a hydroxymethyl group which can be protonated to give methanol²⁴ (see left side of Scheme 2a). Since we have shown that ethanol is formed by homoligation of methanol, the mechanism probably involves reaction of methanol with HBr (HBr is a promoter for this reaction) to give methyl bromide which is attacked by the ruthenium centre to give a coordinated methyl group. Methyl migration onto coordinated CO then provides the C–C bond forming step (right side of Scheme 2a).

For the higher alcohols, a different mechanism clearly operates and it must involve a different ruthenium centre since it is only observed when using RuO_2 not when using $[\text{Ru}_3(\text{CO})_{12}]$ as the catalyst precursor. IR studies of post reaction mixtures do not show major differences between the two systems, so it is not possible to speculate on what the alternative ruthenium centre may be, although the production of water during the formation of active species from RuO_2 may make the systems different.

One possible chain growth mechanism is that the hydroxymethyl intermediate in this alternative catalytic complex is reduced to methyl and that a sequence of migrations and reductions occurs (Scheme 2b). If this is the case, the methyl complex formed on this catalytic centre by reduction of the hydroxymethyl complex cannot be available from a reaction of the related ruthenium centre with MeBr derived from methanol as this would allow homologation. A further alternative mechanistic possibility is that the hydroxymethyl ligand migrates onto CO and the acyl is then reduced to hydroxyethyl (Scheme 2c). Repeating this sequence leads to chain growth. Interestingly, these two mechanisms leave the hydroxide on opposite ends of the growing chain in the final alcohol product, but our labelling studies cannot distinguish between them.

We do note, however, that, when adding $^{13}\text{CH}_3\text{OH}$ to either system, NMR and GCMS give no evidence for ^{13}C incorporation into the 1,2-ethanediol formed, although ^{13}CO is incorporated from the gas phase. The most logical initial steps in the formation of 1,2-ethanediol are those shown in Scheme 2c, with reductive elimination of 2-hydroxyethanal (glycolaldehyde) from the hydroxyacetyl complex, followed by aldehyde hydrogenation. It may be that hydrodeoxygenation of the hydroxyacetyl complex competes with reductive elimination and thus that chain growth occurs by the mechanism of Scheme 2c.

Both mechanisms 2b and 2c require the reduction of acyl complexes to alkyl complexes. This is proposed as a key step in the Pichler–Schulz mechanism for chain growth in Fischer–Tropsch reactions,²⁷ but does not appear to have been demonstrated in model systems using molecular hydrogen as the reducing agent. Both silanes²⁸ and boranes^{29–31} can affect the reduction so it is plausible that a ruthenium hydride donor similar to that involved in the initial formation of the formyl complex could be one component of the reducing system.

Conclusions

CO hydrogenation using ruthenium based catalyst precursors in $[\text{PBU}_4]\text{Br}$ under relatively mild conditions (250 bar, 200 °C) gives mainly methanol ethanol and propanol together with small amounts of ethylene glycol. Studies, in which $^{13}\text{CH}_3\text{OH}$ is added at the start of the reaction, show that ethanol and propanol are formed by homologation of methanol and ethanol respectively. When using RuO_2 as the ruthenium source, higher alcohols (butanol–heptanol) are produced with a Gaussian distribution centred on pentanol. Studies using either added $^{13}\text{CH}_3\text{OH}$ or ^{13}CO and no added methanol show that these higher alcohols are not formed by homologation but rather by a chain growth mechanism occurring at the Ru centre.

Acknowledgements

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