



Commentary review

Metal catalysed CO hydrogenation: hetero- or homo-, what is the difference?

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With very best wishes to Renato Ugo on his 65th birthday

Abstract

The hydrogenation of CO is *heterogeneously* catalysed by ruthenium, rhodium, cobalt or iron (on silica); all four metals give largely *n*-1-alkenes as *primary* products, only small amounts of oxygenates are produced. The reactions already occur at temperatures $\geq 150^\circ\text{C}$ and pressures of syngas ≥ 1 atm, and mechanisms have been analysed [J. Am. Chem. Soc. 124 (2002) 10456]. In complete contrast, workers have shown that the hydrogenation of CO *in solution* by soluble cobalt, rhodium or ruthenium complexes, is much more demanding (temperatures $\geq 230^\circ\text{C}$ and pressures of syngas ≥ 400 atm) and leads to oxygenates (methanol, ethanol, ethylene glycol, and formates) and virtually no hydrocarbons. A few promoted systems give both, probably formed by independent paths. Reasons for this diversity are discussed.

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1. Introduction

The increasing importance of syngas (CO + H₂; derived from natural gas, methane) as a feedstock for the chemical industry makes the development of new, more efficient, and greener catalytic processes involving syngas very important. This paper offers an up-to-date commentary on the chemistry underlying carbon monoxide hydrogenation, with the aim of explaining some of the apparent anomalies in order to facilitate the development of new strategies. Major early rationalisations of complex metal catalysed organic reactions that occur heterogeneously on metal surfaces

came from the seminal reviews by Ugo [1] and also by Muetterties [2].

One of the most fascinating processes remains the catalytic hydrogenation of CO. Methane is almost invariably produced, but the reactions to higher value products are of greater interest. They include (Table 1) the Fischer–Tropsch reaction [3], leading to linear hydrocarbons over supported Fe, Co, Ru, or Rh [4]; the formation of mixed C₁ and C₂ oxygenates homogeneously catalysed by Co, Ru, or Rh in solution [5–7]; and the industrial synthesis of methanol using a Cu–ZnO–alumina catalyst [8].¹ Some selectivity (to ethanol, acetic acid or *iso*-butanol)

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¹ These reactions probably involve the hydrogenation of CO₂ (formed in a water-gas shift reaction) rather than CO, and proceed via surface formate which is then reduced to methanol.

Table 1
Summary of main conditions for CO hydrogenation over various catalysts

Major products	Catalyst support/solvent	Temperature/pressure	References
<i>n</i> -Alkenes + <i>n</i> -alkanes	Ru, Co, Rh, Fe on solid oxide (silica, alumina, etc.)	≥150 °C; ≥1 atm	[4]
Oxygenates (methanol, formate, ethanol, ethylene glycol)	Ru, Co, Rh in oxy-solvent plus I ⁻ ; or ionic liquids, e.g. (Bu ₄ P)Br	≥230 °C; ≥400 atm	[37–39,51]
Methanol	Cu-ZnO-alumina	250–300 °C; 50–100 atm; CO ₂ is involved	[8]

has also been reported over mixed oxides (such as ZrO₂/ZnO/MnO/K₂O/Pd) or promoted copper catalysts, but these may not be primary products [9,10]; thus, although interesting commercially, they offer little new mechanistic insight.

Our main concerns here are the CO hydrogenation reactions involving Co, Ru, or Rh catalysts, since they give largely linear hydrocarbons over heterogeneous catalysts, but C₁ and C₂ oxygenates in homogeneous solutions, and under very different conditions.

The Fischer–Tropsch hydrocarbons have long been used as liquid fuels but are currently being applied as olefin feedstocks to make long chain oxy-compounds that are the basis of surfactants, detergents, or soaps [11].

2. Thermodynamics

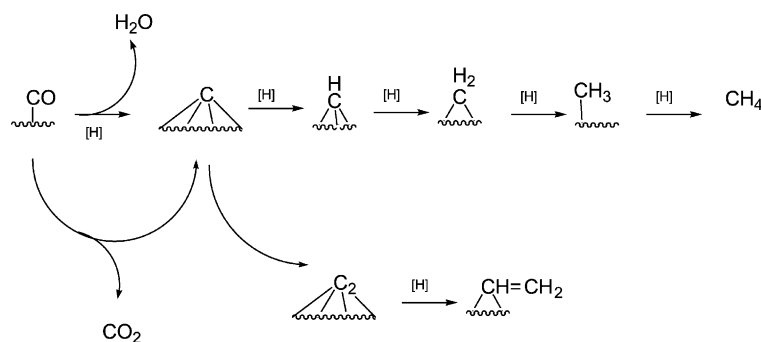
The thermodynamics shed useful light on the various transformations [3]. Thus, the free energy changes *leading to hydrocarbons* are favourable (e.g. for propene, 2H₂ + 1CO = H₂O + 1/3(C₃H₆) Δ*G*_(227 °C)[°] – 96 kJ/mol), and the numbers become more negative—more favourable—for longer chains. The driving force is the formation of water, or of CO₂ (the two are equivalent as they are related by the water-gas shift reaction, H₂ + CO₂ = H₂O + CO) as those are strongly exothermic processes. By contrast the syntheses of lower oxygenates are thermodynamically unfavourable, e.g. for methanol, 2H₂ + 1CO = CH₃OH, Δ*G*_(227 °C)[°] + 27 kJ/mol; for formaldehyde, H₂ + CO = HCHO, Δ*G*_(227 °C)[°] + 51 kJ/mol; and for ethylene glycol, 3H₂ + 2CO = HOCH₂CH₂OH, Δ*G*_(227 °C)[°] + 66 kJ/mol. The situation improves for the longer chain alcohols, the formation of which becomes more exothermic (ethanol Δ*G*_(227 °C)[°] – 28 kJ/mol; propanol Δ*G*_(227 °C)[°] – 67 kJ/mol). There water is

again a by-product that can drive the overall reaction, for example, 6H₂ + 3CO = C₃H₇OH + 2H₂O.

3. Heterogeneous CO hydrogenation

Interestingly, the thermodynamics are also reflected in the rates (kinetics) of the various CO hydrogenations; thus hydrocarbons are formed relatively easily. The Fischer–Tropsch synthesis of linear alkenes and alkanes by reaction of syngas over supported metals, first reported in 1926, has been much studied [3,6]. An in-depth mechanistic investigation of CO hydrogenation over ruthenium, iron, cobalt or rhodium catalysts supported on silica using ¹³C labelling and ¹³C NMR spectroscopy, has recently been published [4], which the reader is invited to consult for details. To minimise complications arising from by-product formation, the reactions were carried out under mild conditions (Ru, 150 °C; Co, 180 °C; Fe, 220 °C; or Rh, 190 °C; CO:H₂, 1:1; 1 atm), and although there are differences between their activities, all four metals give similar product distributions. The primary (kinetically determined) products consist chiefly of *n*-1-alkenes. *n*-Alkanes and internal alkenes are also formed, but the data suggest that these arise largely in secondary reactions from the 1-alkenes. Ruthenium is generally the most active catalyst, while rhodium and iron have lower activity towards hydrocarbon formation. Cobalt also has good activity but as it is a good hydrogenation catalyst *n*-alkanes are major products.

The mechanistic details were probed using a labelled C₂ probe (usually ¹³C₂H₄) introduced into a stream of ¹²CO plus H₂. Our key findings for reactions under relatively *mild conditions* are that: (i) the primary products are largely linear 1-alkenes; (ii) different metal catalysts give similar mixtures of hydrocarbons; (iii) although it influences the amounts



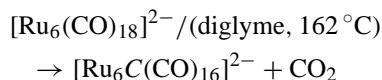
Scheme 1. Diagrammatic representation of the activation of CO on a metal surface giving surface carbide (leading to methylidyne, methylene, methyl and eventually methane) or to surface dicarbide, vinyl, etc.

of individual products formed, the ethene initiator does not substantially modify the course of the CO hydrogenation; (iv) when the reaction is initiated by a $^{13}\text{C}_2\text{H}_4$ probe, the *n*-alkene and *n*-alkane products² are generally of the type, $^{13}\text{CH}_3^{13}\text{CH}_2(\text{CH}_2)_n\text{CH}=\text{CH}_2$, $^{13}\text{CH}_3^{13}\text{CH}_2(\text{CH}_2)_n\text{CH}_3$, and $^{13}\text{CH}_3^{13}\text{CH}_2(\text{CH}_2)_n\text{CH}=\text{CH}_2(\text{CH}_2)_m\text{CH}_3$ (where undesignated C is ^{12}C), with the two labelled carbons of the ethene probe now adjacent at the alkyl ends of the hydrocarbons.³ The types of product and the amounts formed are consistent with their formation by a process involving the polymerisation of a C_1 monomer, and initiated by a C_2 species. While there has long been agreement on the first point, and the second is also not disputed, there is still some debate on the natures of the C_1 and C_2 species involved and of the polymerisation and termination steps. Very similar results and conclusions have been drawn by other researchers in respect of their results from isotope transient studies, not involving added C_2 probes [12–16], and it appears that our conclusions are fully applicable to Fischer–Tropsch reactions even without initiators.

Our data are in agreement with a molecular mechanism in which CO is adsorbed at a surface site and

is deoxygenated to give a surface carbide ($\text{C}_{(\text{ad})}$), which then undergoes hydrogenation to give sequentially, methylidyne ($\text{CH}_{(\text{ad})}$), methylene ($\text{CH}_{2(\text{ad})}$), and methyl ($\text{CH}_{3(\text{ad})}$) (Scheme 1). If the formation of the surface carbide ($\text{C}_{(\text{ad})}$) from adsorbed CO proceeds as indicated with the participation of surface hydrogen, the initial step of the Fischer–Tropsch synthesis is favoured, as once again the formation of water can provide the driving force. The hydrogenation can continue to give methane (CH_4). Alternatively, carbon–carbon bond formation leading to polymerisation may occur; the $\text{C}_{1(\text{ad})}$ monomer may be either a surface methylene, $>\text{CH}_{2(\text{ad})}$, or a surface methylidyne $\equiv\text{CH}_{(\text{ad})}$: we suggest that the $\text{C}_{2(\text{ad})}$ initiator is a surface vinyl, $\text{C}_2\text{H}_{3(\text{ad})}$.

Possible molecular models for the formation of $\text{C}_{1(\text{ad})}$ and $\text{C}_{2(\text{ad})}$ stem from Shapley's synthesis of ruthenium carbonyl carbide and dicarbide clusters from carbonyls simply on heating in a glyme solvent [17]; the formation of the carbide is effectively a disproportionation of CO to carbide and carbon dioxide, and should be thermodynamically favoured,

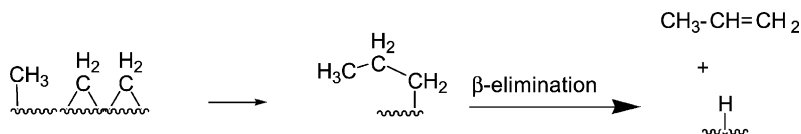


The temperatures at which such reactions occur are in the range of the Fischer–Tropsch synthesis and related conversions of carbonyls to carbides may be expected on metal particles.

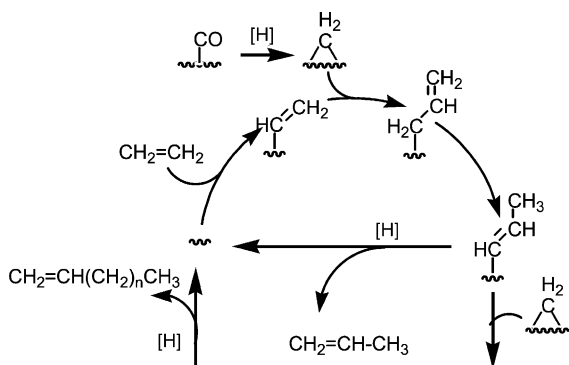
Two main cycles have been proposed involving $\text{CH}_{2(\text{ad})}$ as the repeating unit. The alkyl + $\{\text{CH}_{2(\text{ad})}\}$ cycle, devised by Brady and Pettit (Scheme 2) [18a], in which surface alkyls ($m\text{-CH}_2\text{-R}$) are the chain

² Over these catalysts and under these conditions only very small amounts of C_1 or C_2 oxygenates were formed; no ^{13}C from the probe was incorporated into these oxygenates which must thus arise by quite different paths [4].

³ However, reactions under more severe conditions, at the higher temperatures, where industrial Fischer–Tropsch processes are usually run, gave more complex products, involving C–C cleavage as well as C–C formation [4]. Thus, mono-, di-, tri- and even poly- ^{13}C -labelled products were found in such reactions initiated by $^{13}\text{C}_2\text{H}_4$.



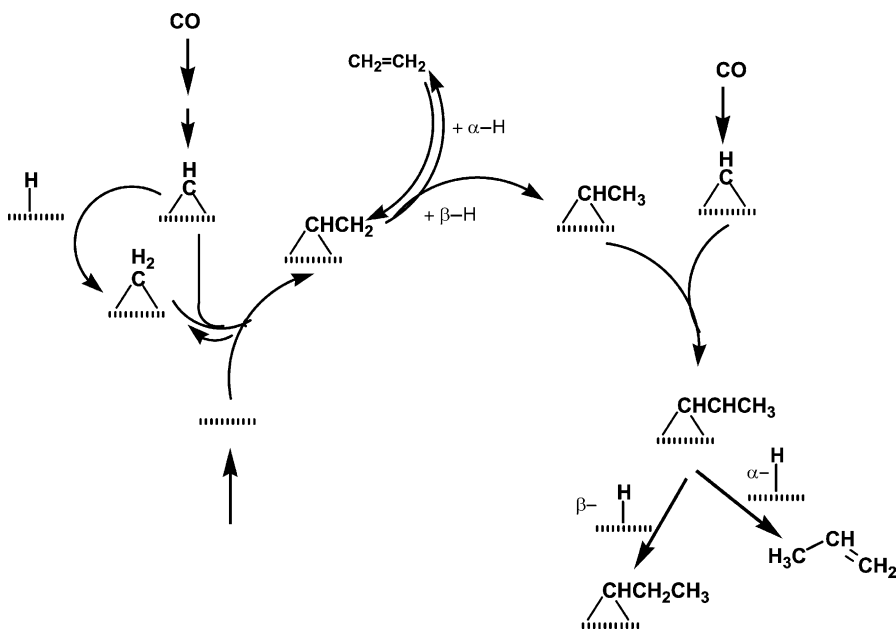
Scheme 2. Diagrammatic representation of the alkyl mechanism in which surface CH_2 and CH_3 couple to give surface n -propyl which then β -eliminates to give surface hydride and propene.



Scheme 3. Diagrammatic representation of the alkenyl + CH_2 mechanism in which surface vinyl, propenyl, etc. react with surface methylene in the chain propagation steps. 1-Alkenes arise by reductive elimination (adapted from [4]).

carriers, is appealing in its straightforward simplicity; unfortunately, it does not account for all the key observations [18b]. The alkenyl + $\{\text{CH}_2(\text{ad})\}$ cycle (Scheme 3), put forward by the Sheffield group, where the chain carriers are surface alkenyls ($m\text{-CH=CHR}$) [4,19,20], together with a σ -allylic to σ -propenyl rearrangement step, offers more satisfactory explanations.

An alternative, the van Santen and Ciobica alkylidene + $\{\text{CH}(\text{ad}) + \text{H}(\text{ad})\}$ polymerisation mechanism (Scheme 4) in which the chain carriers are alkylidene species which add $\equiv\text{CH}(\text{ad})$ and then $\text{H}(\text{ad})$ sequentially [21–23], fits the observations better than the alkyl + $\{\text{CH}_2(\text{ad})\}$ mechanism. However to explain the formation of the propene isotopomers ($^{13}\text{CH}_3\text{-}^{13}\text{CH=CH}_2$ and $\text{CH}_3\text{-}^{13}\text{CH=}^{13}\text{CH}_2$), found in

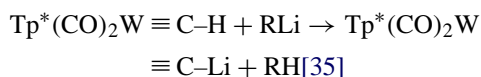
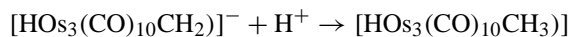
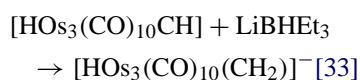
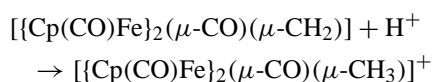
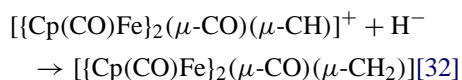


Scheme 4. Diagrammatic representation of the alkylidene + $\text{CH} + \text{H}$ in which surface CH and H react sequentially for chain propagation; 1-alkenes are released by α -elimination (adapted from [4,23]).

products from reactions of $^{13}\text{C}_2\text{H}_4 + \text{CO} + \text{H}_2$ over Fe and Rh, requires an isomerisation of a σ -allyl- to a σ -propenyl- species, which is only present in the alkenyl + $\{\text{CH}_2(\text{ad})\}$ mechanism [4].

Surface spectroscopic studies used in attempts to define catalytic species, showed that $>\text{CH}_2(\text{ad})$ forms easily from a variety of precursors on various metal surfaces [24–31]. However, *in high vacuum* $>\text{CH}_2(\text{ad})$ was not thermally stable but decomposed, initially to hydrogen and methylidyne, $\equiv\text{CH}(\text{ad})$, and then to other species. Models and computations also showed that the arrangement, where the tri-coordinate $\equiv\text{CH}(\text{ad})$ sits in a three-fold site on a metal surface is a particularly low energy favourable situation [21–23].

Since both $\equiv\text{CH}(\text{ad})$ and $>\text{CH}_2(\text{ad})$ can exist on metal surfaces, the question arises, which is the *active* monomer in the polymerisation? The chemistry of appropriate organometallic model systems shows that interconversions readily occur between carbide, methylidyne, methylene and methyl ligands, for example,



(Cp = $\eta^5\text{-C}_5\text{H}_5$; Tp* = hydridotris (3,5-dimethylpyrazolylborate).

By analogy to these organometallic reactions, ready equilibria, $>\text{CH}_2(\text{ad}) \rightleftharpoons \equiv\text{CH}(\text{ad}) + \text{H}(\text{ad})$, between surface species would be expected in which case the nature of $\text{C}_{1(\text{ad})}$ will depend on the equilibrium constant and the concentration of surface hydrogen, which will itself be a function of the hydrogen pressure and the nature of the surface. Methylene ($=\text{CH}_2(\text{ad})$) could, therefore, exist in significant amounts during the hydrogenation of CO since considerable surface hydrogen will be present. One would also expect that, if $>\text{CH}_2(\text{ad})$ was a more labile species than $\equiv\text{CH}(\text{ad})$, it should participate more readily in reactions. On both counts, therefore, the formation of *n*-alkenes by polymerisation of $>\text{CH}_2(\text{ad})$ monomers is not excluded.

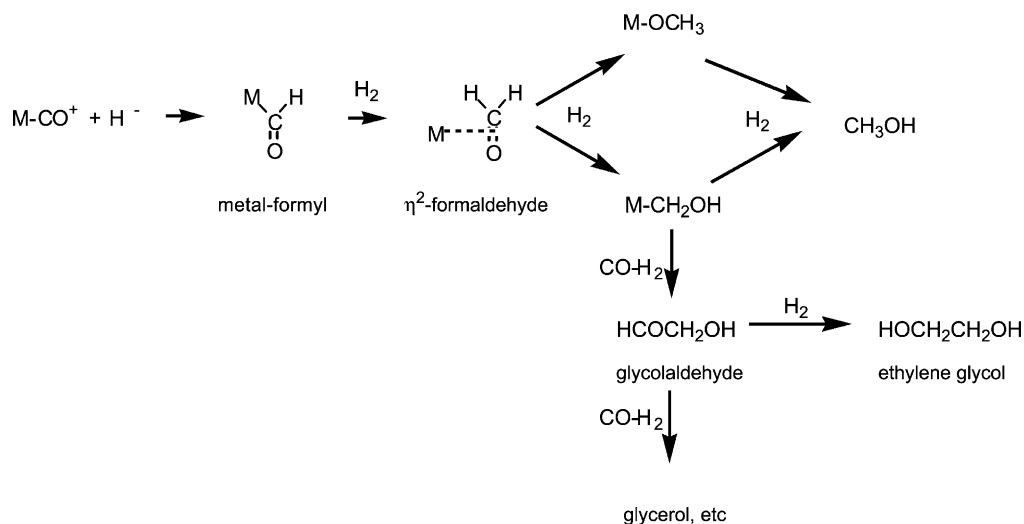
To summarise, therefore, in the present state of our knowledge, if in a hydrogen-rich system, the reactive monomer species is $>\text{CH}_2(\text{ad})$, then the evidence favours the alkenyl + $\text{CH}_2(\text{ad})$ polymerisation mechanism, whereas if it is $\equiv\text{CH}(\text{ad})$, an alkylidene + $\text{CH}(\text{ad}) + \text{H}(\text{ad})$ mechanism may be preferred.

4. Homogeneous CO hydrogenation

Even though it proceeds over the same metals (Co, Ru, and Rh), CO hydrogenation homogeneously catalysed in solution is quite different in all respects from the heterogeneously catalysed reactions [7,36–39]. While the latter give largely linear hydrocarbons, the homogeneous reactions give mainly C_1 and C_2 oxygenates (Table 2). The solution reactions also require higher temperatures ($>230^\circ\text{C}$) and higher syngas pressures than the heterogeneous ones (Table 1); certain oxy-solvents (glymes, *N*-methylpyrrolidone,

Table 2
Conditions for oxygenate formation from syngas over various homogeneous catalysts

Products	Catalyst	Temperature ($^\circ\text{C}$)	Pressure (atm)	Reference
MeOH	RuI ⁻	230	850	[37]
HCOOMe + MeOH + HOCH ₂ CH ₂ OH	Co	230	375–2000	[37]
EtOH	RuI/ <i>i</i> -Pr ₃ PO	230	850	[52]
HOCH ₂ CH ₂ OH	Rh/ <i>i</i> -Pr ₃ P/Me ₂ Im ⁺ I ⁻	220	500	[53]
AcOCH ₂ CH ₂ OAc + MeOAc	Ru/Rh/Cs ⁺ (2:0.2:2)/HOAc	230	1000	[51]
HOCH ₂ CH ₂ OH + ROCH ₂ CH ₂ OH + MeOH + EtOH	Ru/(<i>n</i> -Bu ₄ P)Br/Me ₂ Im ⁺ I ⁻	220	430	[38]



Scheme 5. Diagrammatic representation of possible homogeneous routes to methanol and ethylene glycol (adapted from [5,48]).

sulfolane, acetic acid, etc.), iodide [36,39], or ionic liquids, Bu₄PBr [38], are useful co-promoters.

The trinuclear anion [HRu₃(CO)₁₁][−] that has been detected during the ruthenium catalysed reactions may act as a hydride transfer agent.⁴ Thus, it is suggested that the steps in oxygenate formation are: (i) generation of a metal formyl (M(CHO)), possibly by intermolecular hydride transfer to a carbonyl, followed by (ii) hydrogenation to a formaldehyde complex (M(H₂C=O)), which is then (iii) further hydrogenated to a hydroxymethylene (M-CH₂OH), or a methoxy (M-OCH₃) complex, which is in turn (iv) hydrogenated to methanol (Scheme 5) [5,40]. Alternatively, the hydroxymethylene can be carbonylated to glycolaldehyde and reduced to ethylene glycol, both are known reactions, M-CH₂OH + CO → M-CO-CH₂OH → HCO-CH₂OH → HOCH₂-CH₂OH.

An intermediate formaldehyde complex could also explain why the needed conditions for the catalysis are so severe. The formation of formaldehyde from syngas is thermodynamically strongly disfavoured, and high pressures and high temperatures are needed in order to drive the equilibrium, CO + H₂ ⇌ HCHO, forwards to any extent. The reaction is unfavourable as there

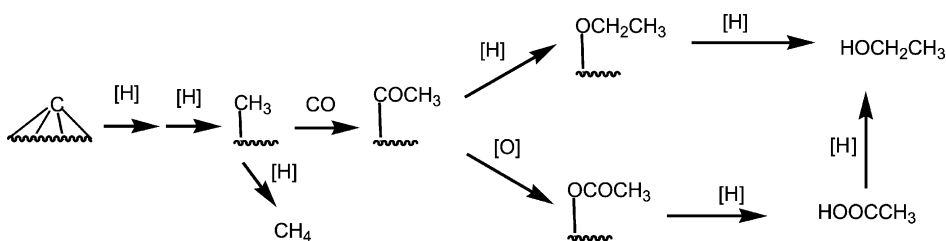
is no compensation from an exothermic formation of water, such as occurs when a carbide intermediate is formed in the initial stages of the Fischer–Tropsch process (CO + H₂ ⇌ C_(ad) + H₂O).

There are stoichiometric organometallic model systems for some of these steps, for example, the generation of formyl complexes [5,41,42], but further corroboration, and the development of effective cycles are needed.

5. Homogeneous and heterogeneous CO hydrogenation compared

CO hydrogenation is extremely complex and includes many secondary processes occurring either on the catalyst or involving the support and/or the promoters. In order to give a worthwhile analysis, some simplification is needed; thus, we may say that Co, Ru, or Rh catalysts under heterogeneous conditions on neutral supports give hydrocarbons, primarily *n*-1-alkenes, while in homogeneous solution the products are C₁ and C₂ oxygenates. The alkenes are thermodynamically preferred and quite drastic conditions are needed for the solution reactions. Virtually no hydrocarbons are formed in solution and, correspondingly, oxygenate formation is small over those heterogeneous catalysts.

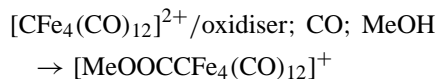
⁴ However, this is not certain and [HRu₃(CO)₁₁][−] may be a catalyst resting state.



Scheme 6. Diagrammatic representation of possible homogeneous routes to ethanol and acetate (adapted from [50]).

Surprisingly, the creation of the $C_{1(ad)}$ monomer (methylene or methylidyne) from CO does not appear to be rate limiting in the heterogeneously catalysed CO hydrogenation to 1-alkenes. A number of workers have shown that over metal surfaces these steps occur with apparent ease and it has been argued that in the Fischer–Tropsch reaction a reservoir of the needed $C_{1(ad)}$ monomer is available. The suggestion has been made that the rate determining step in the heterogeneously catalysed 1-alkene formation is rather the generation of a $C_{2(ad)}$ initiator [13–16], and our data are in agreement with this [4].

It, therefore, appears that in order to produce alkenes *in solution*, a CO cleavage step will also be needed. Although some homogeneous CO cleavage reactions are known, they mainly involve complexes of the earlier and more oxophilic metals such as Zr, Hf, Nb, or Mo [43–47] and have been difficult to develop into cycles. However, ruthenium carbonyl carbide clusters are readily formed on heating carbonyls [17]. Bradley [48] have also functionalised an iron carbonyl carbide cluster with methanol after oxidation,

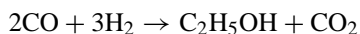
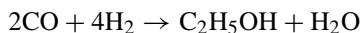


Some heterogeneous catalysts based on complex mixtures of oxides can convert syngas into ethanol and higher oxygenates [49]. At least part of the oxygenates are secondary products arising from a first formed methanol via carbonylation or Aldol-type condensation processes [9,10], but part may be formed directly, as is illustrated in Scheme 6, where one step, involving CO cleavage, surface carbide and water formation, is favourable, while in the other, a C–O bond is retained. The formation of both types of product has been reported over some promoted heterogeneous Rh, Co–Mn, Rh–Co–Mo and other mixed systems, but they

seem to arise from independent cycles, one leading to alkenes, the other to oxygenates [4,49,50].

6. Questions and future directions

Syngas from natural gas is, and will remain for the foreseeable future, a plentiful source of chemical feedstocks as well as of energy. Thus, its direct and efficient conversion into chemicals remains a desirable objective. The various reactions of syngas that have already been demonstrated show that this system is very versatile. One desirable objective is to couple oxygenate formation with a reaction giving water or carbon dioxide to allow the thermodynamic driver to operate more effectively, as for example, in



Such a process may indeed underlie the known heterogeneous rhodium catalysed ethanol formation [50]. The formation of long chain alcohols is thermodynamically favourable, but as a reaction in which syngas is converted into a long-chain alcohol in a single step is not easily realised, a more feasible approach would be to carry out the conversion in two stages, benefiting from the favourable thermodynamics of forming the hydrocarbon chain and then coupling it to an oxygenation.

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