

Electrochemical promotion by potassium of Rh-catalysed Fischer–Tropsch synthesis at high pressure

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Rh-catalysed Fischer–Tropsch synthesis at high pressures exhibits reversible electrochemical promotion by potassium. At 473 K and 14 bar, 43 products were detected, comprising alkanes, alkenes and primary alcohols. Potassium increased selectivity towards alkenes and primary alcohols as a result of actual increases in the rates of formation of these products – an apparently unprecedented observation. Alkane formation was progressively suppressed by added alkali. These findings are discussed in terms of K-induced acceleration and retardation of possible rate limiting steps for alkene and alkane formation, respectively. Plausible mechanisms are discussed.

KEY WORDS: electrochemical promotion; Fischer–Tropsch synthesis; potassium

1. Introduction

Electrochemical Promotion (EP) is a non-faradaic phenomenon that brings together heterogeneous catalysis and solid-state electrochemistry [1,2]. The technique permits controlled and reversible alteration of the behaviour of thin film metal catalysts in contact with ionic conductors, which act as electro-active supports from which mobile promoter species may be pumped to or from the catalyst surface under reaction conditions. This *in situ* control of promoter concentrations provides a unique means for studying the mechanisms of heterogeneously catalysed reactions [3]. EP is implemented (figure 1a) by interfacing a thin film catalyst with a solid electrolyte (in the present case K β '' alumina, a K⁺ conductor) and by varying the overpotential of the catalyst, electrochemically pumping the promoter species from/to the solid electrolyte to/from the catalytically active surface [4,5].

Fischer–Tropsch synthesis (FTS) continues to attract attention for both academic and technical reasons. In this respect, the situation is not unlike that which prevails in regard to ammonia synthesis – an even older and simpler catalytic process for which increased fundamental understanding and consequent improvement in catalytic performance have recently been achieved [6,7]. FTS is catalysed by cobalt, iron, ruthenium, nickel and rhodium [8], but only iron and cobalt catalysts are used commercially at temperatures of 500–600 K and at 10–60 bars of pressure [9,10]. Fe, Co and Ru catalysts have been extensively studied, whereas in contrast Rh has been hardly studied at all. This is somewhat surprising,

given that Rh yields linear alcohols in addition to hydrocarbons [11].

We have already reported an EP study of Rh-catalysed FTS at atmospheric pressure [12], in which the reactor was coupled to an XPS spectrometer chamber. This work demonstrated the applicability of EP to FTS, allowed us to identify surface compounds formed under reaction conditions, and uncovered certain aspects of the reaction mechanism. However, the high pressure regime could not be explored due to hardware limitations. As a result, hydrocarbons only up to C₄ were detected, and no alcohols were found. Performing EP measurements at elevated temperatures and in the presence of high pressures of hydrogen is non-trivial due to the high thermal conductivity of H₂ and its rapid permeation through the insulating materials used in conventional electrical feedthroughs. Accordingly, a special purpose built reactor (figure 1b) was used for the present work, in which extensive measurements were carried out over the regime 1–14 bar. The most revealing data (obtained at 473 K and 14 bar) are presented here. It is found that K promotion results in a general decrease in rates and selectivities towards *alkane* formation, whereas the opposite is true for *alkene* and *primary alcohol* formation: alkali increases the yield of both – an apparently unprecedented observation.

2. Experimental

The Rh catalyst (working electrode) consisted of a porous thin film, deposited by DC sputtering in argon, on one face of a 50 mm × 15 mm × 1 mm wafer of a K β '' alumina solid electrolyte (Ionotec Ltd., 99.99%). Au

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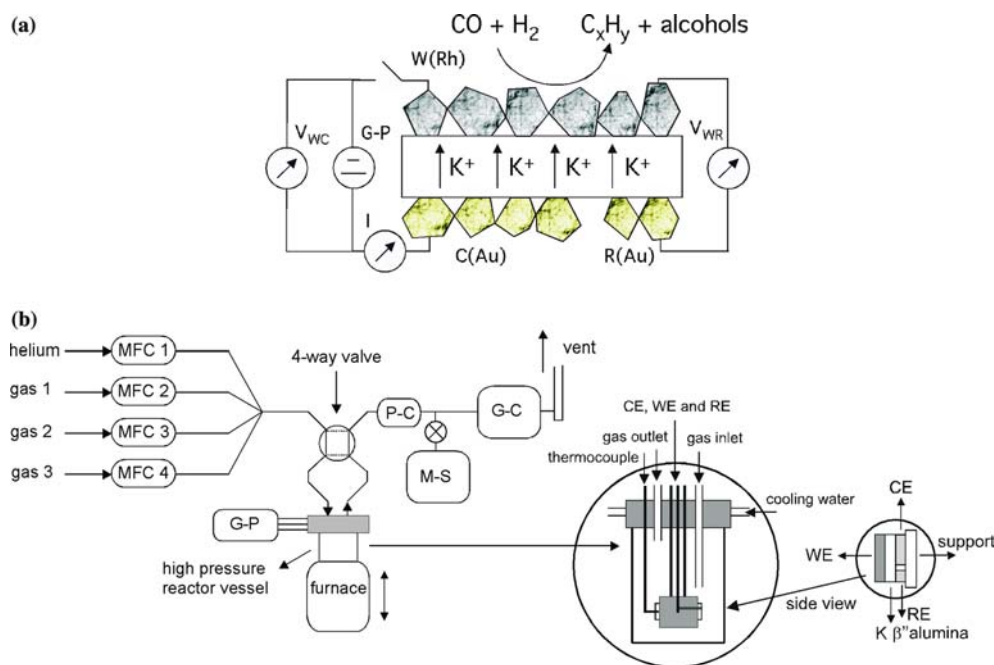


Figure 1. (a) Schematic diagram of the solid-state electrochemical cell. Working (W), counter (C) and reference (R) electrodes are interfaced with a K^+ conductor. A galvanostat-potentiostat (G-P) is used to control the driving voltage and catalyst overpotential (V_{WC} , V_{WR} , respectively) and current (I). (b) Schematic diagram of the high pressure microreactor. MFC: Mass flow controllers, PC: pressure controller, GC: gas chromatographer and MS: mass spectrometer.

reference (R) and counter (C) electrodes were deposited on the other face, again by DC sputtering in argon. The sample was suspended in a stainless steel reactor, whose internal walls were coated with Au and subsequently shown to be catalytically inactive. Thermocouple and electrode connections were made with Au wires using hydrogen-impermeable boron nitride sealed high-pressure electrical feedthroughs (MHC series, Conax Buffalo) mounted on the top flange of the reactor. Tests showed that the system behaved as a single pellet, well-mixed reactor.

Quantitative analysis of the reaction products was carried out by on-line gas chromatography (Shimadzu 14B; DB-1 capillary column (J & W Scientific); flame ionization detector). The detector was calibrated using standard gases of known concentration and the reactants consisted of pure CO (99.995% BOC gases) and pure H_2 (99.999% BOC gases) delivered to the reactor by high pressure mass flow controllers (Brooks 5850 S) with $CO:H_2 = 1:10$ and at a total flow rate of $50 \text{ cm}^3 \text{ min}^{-1}$ (STP). The total pressure (P) was maintained constant by an upstream pressure controller (Brooks 5866). Pressures greater than 14 bar were not accessible due to excessive heat losses resulting from the high thermal conductivity of high pressure hydrogen. A galvanostat-potentiostat (Ionic systems, PG1) was used to impose measured potential differences between the working and reference electrodes (potentiostatic mode). All experiments were carried out in potentiostatic mode by following the effect of catalyst potential (V_{WR} ,

measured with respect to the reference electrode) on the reaction rates and product selectivities.

3. Results

Carbon monoxide was hydrogenated to hydrocarbons and alcohols over the Rh thin film at 473 K and total pressures in the range 1–14 bar. An inlet gas composition of $CO:H_2$ (1:10) was used because deactivation due to carbon deposition was observed at lower hydrogen concentrations. Increasing the pressure resulted in an increase in the rate of hydrocarbon formation as well as in the number of products formed and maximum chain length obtained. For pressures ≤ 4 bar the maximum hydrocarbon chain length was 4. At higher pressures (5–14 bar) the maximum chain length increased to 12 and at 14 bar the largest number of products and greatest hydrocarbon chain length were observed. We have previously demonstrated by means of XPS that decreasing (increasing) V_{WR} results in a reversible increase (decrease) in K surface coverage [12]. In agreement with this, under all the conditions explored in the present study, the catalytic response of the system was reproducible and reversible with respect to the catalyst potential: returning V_{WR} to any given value restored the corresponding values of all reaction rates.

At 473 K and 14 bar a total of 43 products was detected, including linear alkenes and alkanes of carbon number up to 12 (C_1 – C_{12}); also methanol, ethanol and

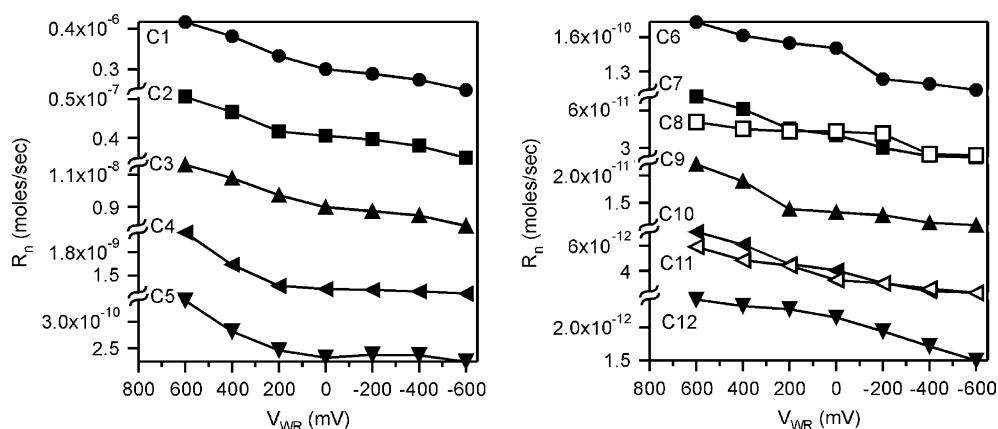


Figure 2. Effect of catalyst potential (V_{WR}) on the total rate of hydrocarbon formation (a) C₁–C₅ and (b) C₆–C₁₂. K coverage increases from left to right as V_{WR} decreases. Note the breaks in the scale on the vertical axes. Conditions: $T=473$ K, $P=14$ bar, $\text{CO:H}_2 = 1:10$.

propanol. Figure 2a, b shows the dependence on catalyst potential of the steady-state rates of linear hydrocarbon formation, R_n , under potentiostatic conditions; R_n is defined as the rate of formation of alkane + alkene for a given value of the carbon number n and is expressed as moles of product formed s^{-1} . It is apparent that decreasing V_{WR} (which electro-pumps potassium towards the Rh catalyst) resulted in a decrease in all R_n values ($n=1-12$). However, for a given n , alkali promotion affected the individual alkene and alkane formation rates in opposite senses.

Figure 3a, b shows steady-state rate data for individual C₄ and C₅ products as a function of catalyst potential. It is apparent that increasing potassium coverage (decreasing V_{WR}) inhibits the formation of linear alkanes (n -butane and n -pentane) whilst promoting the formation of unsaturated hydrocarbons (1-butene, *trans*-2-butene, *cis*-2-butene, 1-pentene, *trans*-2-pentene and *cis*-2-pentene). Thus, K increases selectivity towards the formation of alkenes while decreasing alkane selectivity. The same effect was observed for all higher

hydrocarbons, $n > 5$: K enhanced alkene production and reduced alkane production.

The K-induced increase in the overall selectivity towards formation of longer chain hydrocarbons is reflected by an increase in the chain growth probability, α , calculated from the Anderson-Flory-Schulz distribution [13]: specifically, an increase of 15% in the chain growth probability was observed at the highest K loading. As to the actual K loadings present in these experiments, the relevant parameters are absolute amount and spatial distribution. Our earlier [12] post-reaction XPS data showed that maximum K loading corresponded to 50 monolayers of K having been supplied to the Rh surface. This result, combined with SEM, and EDX analyses [12] showed that most of the alkali was present as crystallites of (catalytically inert) potassium carbonate with sub-monolayer amounts of K promoting the catalytically active Rh surface.

Figure 4a, b shows the steady-state rate and selectivity data for alcohol production as a function of catalyst potential. Selectivity towards formation of product

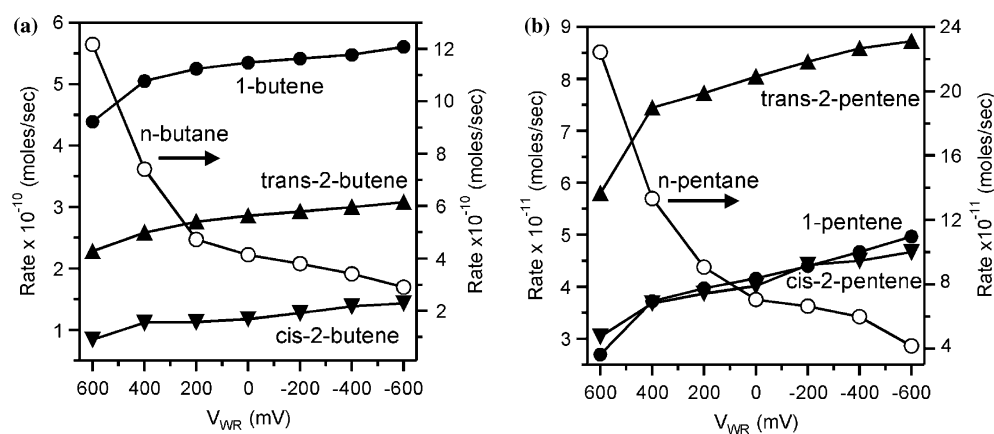


Figure 3. Effect of catalyst potential (V_{WR}) on (a) rates of formation of C₄ alkanes and alkenes and (b) C₅ alkanes and alkenes. Right hand axes refers to alkanes. K coverage increases from left to right as V_{WR} decreases. Conditions: $T=473$ K, $P=14$ bar, $\text{CO:H}_2 = 1:10$.

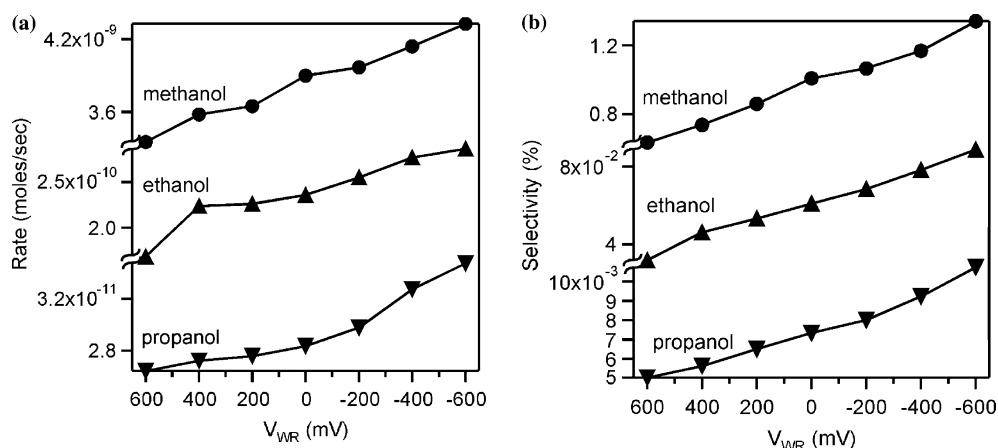


Figure 4. Effect of catalyst potential (V_{WR}) on (a) rates of formation and (b) selectivity towards the formation of C₁–C₃ linear alcohols. K coverage increases from left to right as V_{WR} decreases. Note the breaks in the scale on the vertical axes. Conditions: $T=473$ K, $P=14$ bar, $\text{CO:H}_2=1:10$.

i is defined as $S_i = R_i / \sum R_n$ where R_i is the rate of formation of product i . It is apparent that K markedly promotes methanol, ethanol and propanol formation, to about the same extent (factor of ~ 2).

4. Discussion

A concise review of mechanistic issues in FTS has been given by Davis [14]. As he says, “the description of a mechanism for a reaction as complex as the Fischer–Tropsch synthesis is fraught with pitfalls” an observation that we have tried to keep in mind in what follows.

It is apparent that under our conditions (14 bar, 473 K) methane is the principal product, with much smaller yields of higher hydrocarbons. This closely parallels, for example, the observations of Hedrick *et al.* [15] who found very similar behaviour at 10 bar and 545 K for a variety of metals dispersed on silica (Fe, Co, Ni, Ru, Rh, Os, Ir). The single most striking aspect of our data is the alkali-induced increase in rates for alkene and primary alcohol production: to our knowledge, this effect has not been reported before and we shall therefore focus on it. Our earlier work, at 1 bar on EP by K of FTS over ruthenium [16] showed that although alkali *did* increase alkene selectivity, this was the result of K decreasing the alkane rate more than it decreased the alkene rate – K never induced any actual increases in the alkene rate. This suggests that on Ru and Rh, at least some aspects of the reaction mechanism must be different.

It is well known that co-adsorbed alkalis act to weaken the C–O bond in carbon monoxide by increasing the population of the π^* molecular orbital [17]. And although it is generally agreed that FTS of hydrocarbons proceeds *via* CO dissociation [18], this process is not thought to be rate controlling [16,18]. We take this as the starting point for the discussion that follows.

Potassium, by promoting CO adsorption and dissociation to form C(a) + O(a), inhibits dissociative chemisorption of H₂. Hydrocarbon formation depends on hydrogenation of C(a) to CH₂(a) followed by chain growth that results in adsorbed alkyl species CH₃(CH₂) _{n} . Chain termination can occur by hydrogenation of CH₃(CH₂) _{n} to yield the corresponding gaseous alkane. Alternatively, H-elimination by CH₃(CH₂) _{n} yields the corresponding gaseous alkene – a process that corresponds formally to β -hydride elimination [19]. Our results show that K acts to inhibit alkane formation whilst actually *increasing* the rate of alkene formation. In the light of the above, we may propose that the alkali promotes β -hydride elimination, the driving force being formation of a transient surface species akin to an adsorbed potassium hydride. Recall that bulk KH is a stable compound [20] and that adsorbed alkalis are known to increase the strength of hydrogen chemisorption on the surfaces of platinum metals – an effect that was plausibly ascribed to the formation of adsorbed potassium hydride [21]. An additional or alternative mechanism by which co-adsorbed K may promote alkene formation is by lowering the adsorption enthalpy of the alkene by altering the nature of its bonding to the surface from σ -like to π -like. This effect has been well established by means of XPS [22] and HREELS [23] studies on single crystal surfaces.

The fact that K increases the rate of alkene formation whilst decreasing the rate of alkane formation provides a strong indication that the rate limiting step for the formation of alkenes and alkanes is different. That is, the rate limiting step for formation of both products must come *after* alkyl formation, assuming that the latter species is the precursor to both alkenes and alkanes. As argued above, we may rationalise this in terms of (i) K-induced promotion of β -hydrogen elimination and/or alkene desorption versus (ii) K-induced inhibition of alkyl \rightarrow alkane hydrogenation.

In their wide-ranging study of FTS catalysed by a range of classical dispersed catalysts [15], Hedrick *et al.* noted the formation of small amount of ethanol, accompanied by a much larger amount of acetaldehyde, but no methanol, propanal or propanol, when using Rh/silica as the catalyst. Our observation that primary alcohol formation over Rh catalysts is promoted by potassium appears to be without precedent. For C₂ and higher, it seems likely that oxygenate formation, including alcohol production, involves CO insertion as the key step [15]. Primary alcohols can be considered to arise as a result of CO insertion into an adsorbed alkyl species to form an adsorbed acyl that undergoes subsequent hydrogenation to the alcohol. The first step in this process bears a formal resemblance to hydroformylation and in this connection it is interesting to note that Sordelli *et al.* [24] recently found that Rh-catalysed propene hydroformylation is promoted by alkalis. Exactly how alkali promotes CO insertion in the present system remains to be established. Two possible effects are (i) K-induced increase in CO coverage [25] and (ii) enhanced population of the CO π^* orbital induced by K favours CO insertion. As to methanol formation, it has been shown Cu-catalysed methanol synthesis results from the hydrogenation of CO₂, rather than the hydrogenation of CO [26]. However, under the highly reducing conditions of our experiments, it seems unlikely that significant amount of CO₂ were present at steady state. Therefore, in the present case hydrogenation of CO to formyl seems the likely first step [15].

5. Conclusions

In summary, electrochemical promotion by K of Rh-catalysed FTS at high pressure can be used to reversibly alter the product distribution. Most noteworthy is the K-promoted increased selectivity towards alkenes and primary alcohols, which results from actual increases in the rates of formation of these products. Alkane formation is progressively suppressed by added alkali. These findings are consistent with K-induced acceleration and retardation of the (different) rate limiting steps for alkene and alkane formation, respectively. A possible mechanism involves the opposite effects of K on the chemistry of adsorbed alkyl species: alkene formation and desorption *via* β -hydrogen elimination is promoted, hydrogenation to alkane is retarded.

Acknowledgments

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