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Combined steam reforming of methane and Fischer–Tropsch synthesis for the formation of hydrocarbons: A proof of concept study

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The concept of combining the reactions of methane steam reforming and the Fischer–Tropsch synthesis is explored in an attempt to convert methane directly to hydrocarbons. Consideration of the thermodynamics and kinetics of the two processes confirms that the combined reaction could give small conversions. The controlled addition of small quantities of oxygen to the reactants could further enhance conversion without loss of selectivity. The catalyst design for the new combined process requires a catalyst capable of both methane steam reforming and Fischer–Tropsch synthesis that is tolerant to high concentrations of steam at elevated temperatures. Ru and Co catalysts were selected for study and the initial results at 573 K indicate that conversion of methane of ca. 4% to C_2–C_4 hydrocarbons can be achieved with unoptimized catalysts. It is concluded that catalysts with enhanced activity are required to achieve more realistic conversions, but the current data provide a proof of the concept of combining the reforming and Fischer–Tropsch reactions.

KEY WORDS: methane steam reforming; Fischer–Tropsch synthesis; hydrocarbon formation; methane conversion.

1. Introduction

The synthesis of hydrocarbons from methane remains at the core of the economically important gas to liquids technology [1,2]. In particular, it is important with respect to utilization of the extensive remote supplies of natural gas that have been discovered in recent years. At present, methane is converted primarily by steam reforming to form $CO + H_2$ [3]. This reaction is carried out at high temperatures under thermodynamic control and is central to many production processes using methane as a source of carbon and/or hydrogen [3]. The $CO + H_2$ produced can then be reacted in the Fischer–Tropsch synthesis to form linear hydrocarbons [1,2]. Recently, there has been a significant revival of interest in the Fischer–Tropsch synthesis. This is due in part to the commercialization of the Shell Middle Distillate Synthesis in Malaysia in 1993 [4], as well as recent work on the use of air-blown methane partial oxidation, which could eliminate the requirement for pure oxygen in the overall process [5,6]. There remains a major target in the design of a new process that could achieve the direct formation of hydrocarbons from methane without the requirement for the synthesis and purification of the intermediate $CO + H_2$. In view of this, we have investigated the coupling of the two processes to give the Combined Reforming and Fischer–Tropsch (CRAFT) process. There have been a number of previous studies in which processes involving $CO + H_2$ as reactants have been combined with other process steps. Minderhoud *et al.* [7] have described a process for the synthesis of C_{9+} hydrocarbons from C_{4+} hydrocarbons with steam reforming and a separate Fischer–Tropsch stage using a cobalt catalyst. Minderhoud [8] has also examined the use of a dual function catalyst that combines the Fischer–Tropsch synthesis with the water–gas shift reaction ($CO + H_2 \rightleftharpoons CO_2 + H_2$) using Cu/ZnO as catalyst, which can use molar ratios of H_2 : CO as low as 0.25–1.0 in the synthesis reaction. Loffler *et al.* [9] have investigated a system in which a zeolite catalyst containing a Fischer–Tropsch catalyst is coated with a thin film of a water–gas shift catalyst. This was used to produce higher hydrocarbons. Maatschappij [10] combined three catalysts: (a) an Fe–Cu Fischer–Tropsch catalyst, (b) a zeolite, and (c) a Cu/ZnO catalyst for the water–gas shift reaction, and over 70% C_{3+} hydrocarbons could be produced from $CO + H_2$. Similar approaches using water–gas shift catalysts with Fischer–Tropsch synthesis catalysts have been proposed by Minderhoud *et al.* [11] and Satterfield [12]. In addition, there have been numerous studies in which Fischer–Tropsch synthesis catalysts were combined with zeolites to modify the product distribution [13–16], and we have recently shown that this arrangement can lead to a significant decrease in the yield of non-desired methane [17]. However, to date, there have been no reported studies combining methane steam reforming and the Fischer–Tropsch synthesis. In this paper, we describe our initial approach to the possible use of a

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combined process. Our results indicate that with the design of catalysts with improved activity, this approach could provide a new way of exploiting methane.

2. The CRAFT concept

The combined steam reforming and Fischer–Tropsch process involves the conversion of methane and steam to hydrocarbons without isolating the intermediate $CO + H_2$:

$$nCH_4 + nH_2O \rightleftharpoons nCO + 3nH_2 \rightleftharpoons C_nH_{2n+2} + nH_2O + (n-1)H_2.$$

CO/CO_2 interconversion via the water–gas shift reaction does not affect these overall reactions.

The overall success of this approach will depend on the consideration of the thermodynamics and kinetics of the two combined processes and this is discussed in this section.

The steam reforming of methane and the Fischer–Tropsch synthesis require very different operating conditions to achieve optimal performance. The steam-reforming reaction is usually carried out at temperatures above 900 K using Ni catalysts [3] and under thermodynamic control. The Fischer–Tropsch synthesis is carried out at much lower temperatures < 500 K under kinetic control for product selectivity and Fe, Co and Ru are all effective catalysts for this reaction [1]. To combine these processes requires operation of a single catalyst at an intermediate temperature. However, this temperature must be closer to the operating range of the Fischer–Tropsch catalysts since, at higher temperatures, methanation would dominate as a reaction.

The following reactions are all important in the proposed CRAFT process:

Dry	$CH_4 + CO_2 \rightleftharpoons 2H_2 + 2CO$
Steam reforming	$CH_4 + H_2O \rightleftharpoons CO + 3H_2$
Water–gas shift reaction	$CO + H_2O \rightleftharpoons CO_2 + H_2$
Methane decomposition	$CH_4 \rightleftharpoons C + 2H_2$
Boudouard reaction	$2CO \rightleftharpoons C + CO_2$
Hydrocarbon synthesis (including methane)	$nCO + (2n+1)\ H_2 \rightleftharpoons C_nH_{2n+2} + nH_2O$

The dependence of ΔG_r with temperature is shown in figure 1 [18]. It is apparent that below 900 K only carbon formation from the Boudouard reaction and methane formation are thermodynamically viable. Steam reforming of methane represents the least preferred reaction and, consequently, only very low concentrations of $CO + H_2$ could be expected to form on catalyst surfaces at temperatures of ca. 500–600 K, the possible temperature range for the proposed CRAFT reaction. It is known that, for the Fischer–Tropsch synthesis reaction, methane is thermodynamically preferred over all other hydrocarbons and oxygenates [18,19]. The dependence of ΔG_r on temperatures for the conversion of methane into higher hydrocarbons is shown in figure 2. It is apparent that ΔG_r increases with the product carbon number and the reaction temperature. Thermodynamic limits to the proposed CRAFT reaction were explored in the following way. Two typical and desirable overall reactions are the conversion of methane to either pentane or decane, reactions (1) and (2).

$$5CH_4 \rightarrow C_5H_{12} + 4H_2 \qquad (1)$$

$$10CH_4 \rightarrow C_{10}H_{22} + 9H_2. \qquad (2)$$

As steam is conserved in the overall CRAFT process, reactions (1) and (2) can be expressed as simple dehydrogenations/oligomerizations. The equilibrium constants for reactions (1) and (2) are calculated at 600 K from standard data [18]:

$$K_1 = 5.0 \times 10^{-15}$$

$$K_2 = 4.2 \times 10^{-50}.$$

These values are so small that the CRAFT reaction appears to be essentially impossible. However, this is a misleading simple conclusion for several reasons.

First, there is the general consideration that thermodynamic limits to kinetics in multicomponent systems have been shown [20,21] to be more complex than those applicable to two-component systems. Further, there is experimental evidence from multicomponent catalytic systems that apparent equilibrium limits do not necessarily apply. In systems well short of total equilibrium, it is possible for the concentrations of components in subsystems to cross apparent equilibrium limits relevant only to the subsystems [21]. At full equilibrium, of course, all the subsystems, as well as the total system, must be at equilibrium. In this preliminary analysis of the CRAFT reaction, only full-equilibrium conversions are calculated. The possibilities of higher conversions to some selected products at partial conversions are not considered further here, but they could be considered at a later stage for a better-defined process and catalyst.

Further indications can be obtained from the calculation of limiting equilibrium conversions. Conversions in the general CRAFT reactions, giving alkanes only, are independent of pressure. Maximum yields of pentane and decane from methane can be calculated from the values of K_1 and K_2 to be 0.046 and 1.6×10^{-4} %mol mol, or 0.21 and 0.0014 wt/wt%. Pentane is one of three isomers of the alkane C_5H_{12}, and decane is one of 72 isomers of the alkane $C_{10}H_{22}$. Each of these isomers has a separate equilibrium limit, but these limits are of the same order as those of the equivalent pentane or decane. Thus, the corresponding conversions for a highly branched C_{10} alkane, 2,2,5,5-

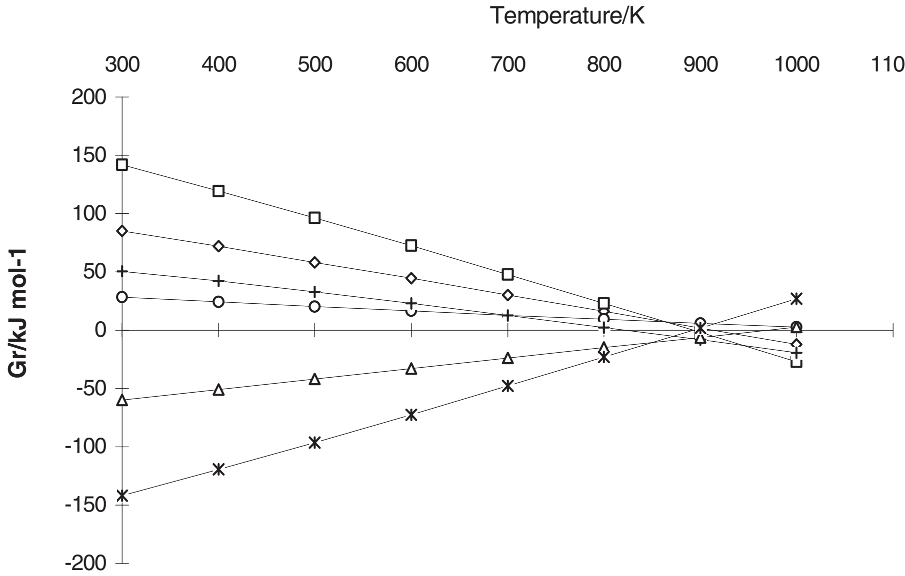

Figure 1. Dependence of ΔG_r with temperature [18]. Key: ◇ dry reforming; □ steam reforming; ○ water gas shift reaction; + methane decomposition; △ Boudouard reaction; * methanation.

tetramethylhexane (TMH), are 1.4×10^{-4}mol% or 0.0012 wt%. Some other C_{10} alkanes give somewhat lower conversions, so the limiting conversion to all C_{10} alkanes is about 72 × 0.0012 wt%, i.e., about 0.1 wt%. Similarly, the limiting equilibrium conversion for the three C_5 alkanes is on the order of 0.5 wt%. This is close to yields that could be of commercial interest. Further, if we consider a CRAFT reaction producing a naphtha fraction, typically $C_5{-}C_{12}$ fraction of alkanes with some alkene, cycloalkane and aromatic products, then the equilibrium limit to the production of naphtha is likely to be on the order of several percent. The experimental yields obtained in this work are in qualitative agreement with this analysis.

A feature of the selectivity of the CRAFT process emerges from this analysis. The desired commercial products are liquid hydrocarbons, at least C_5^+ and preferably higher. The selectivity at equilibrium favors a lighter hydrocarbon isomer over a heavy hydrocarbon isomer, but this is counterbalanced by the rapid increase (with carbon number) in the multiplicity of hydrocarbon isomers for each carbon number. Thus, a satisfactory selectivity could be expected for a CRAFT process operating at close to equilibrium. In contrast, the equilibrium product in conventional Fischer–Tropsch processes is methane and these processes have to be operated well short of equilibrium to obtain selectivity to liquid hydrocarbons.

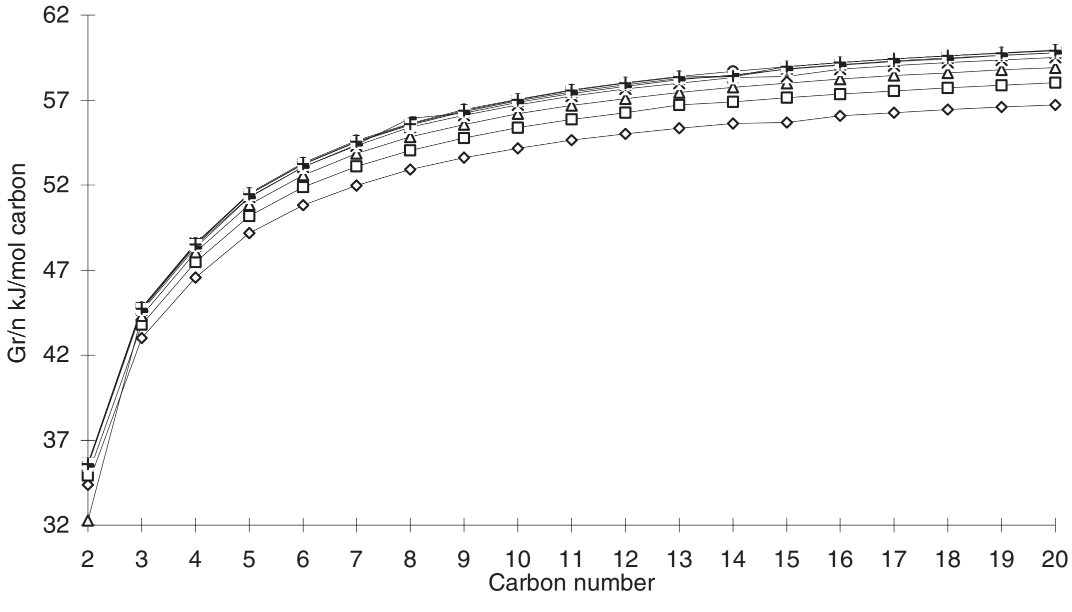

Figure 2. Dependence of ΔG_r per mole of carbon for methane conversion to hydrocarbons. Key: ◇ 300 K; □ 400 K; △ 500 K; ×600 K.

Although, with appropriate process design, these limiting conversions might be commercially acceptable, it would clearly be preferable to use a further reaction to drive the process to higher yields. It needs to be emphasized that any driving reaction must be intrinsic to the process to provide the needed free energy. In processes where extra enthalpy alone is required, as in primary methane/steam reforming, the supply of heat from outside the catalytic reactor is sufficient.

Some limited supply of oxygen to the CRAFT reaction system is the most direct way of driving the process by additional reactions. An estimate of the oxygen required (and the extra methane used, directly or indirectly) can be made in the following way. Let us suppose that a 10 wt% conversion of methane to decane (reaction (2)) would be acceptable. Note that this would imply, on the reasoning used above, a very substantial total conversion of methane to C_5–C_{12} hydrocarbons. Then the equivalent K_2 would need to be about 10^{-10} and $\Delta G_2^o = +115\,\mathrm{kJ\,mol^{-1}}$. Without any driving reaction, $\Delta G_2^o = +567\,\mathrm{kJ\,mol^{-1}}$, so the extra Gibbs free energy required to drive reaction (2) is $+453\,\mathrm{kJ\,(mol\ reaction)^{-1}}$ or $+45\,\mathrm{kJ\,(mol\,CH_4)^{-1}}$.

Four possible driving reactions are given below with the corresponding free energy changes at 600 K. All three methane conversions are only partial oxidations, so these reactions, like the partial oxidation of hydrogen, are fully compatible with operation inside the reducing atmosphere of the CRAFT reaction. Thus, with suitably controlled oxygen addition, possible undesirable consequences, such as catalyst oxidation or homogeneous combustion, should not occur.

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2 \qquad (3)\ \Delta G_3^o = -142\ \mathrm{kJ\,mol^{-1}}$$

$$CH_4 + O_2 \rightarrow CO + H_2 + H_2O \qquad (4)\ \Delta G_4^o = -356\ \mathrm{kJ\,mol^{-1}}$$

$$CH_4 + \tfrac{3}{2}O_2 \rightarrow CO + 2H_2O \qquad (5)\ \Delta G_5^o = -570\ \mathrm{kJ\,mol^{-1}}$$

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \qquad (6)\ \Delta G_6^o = -214\ \mathrm{kJ\,mol^{-1}}$$

Then, the extra methane required for reaction (3) to provide the necessary extra free energy of $45\,\mathrm{kJ\,(molCH_4)^{-1}}$ is $(45/142) = 0.32\,\mathrm{mol\,CH_4}$, per mol CH_4 used in reaction (2). Similar values of 0.13 mol CH_4 by reaction (4), 0.08 mol CH_4 by reaction (5), and 0.21 mol H_2 by reaction (6) can be calculated. It is clear that the amount of extra methane or of by-product hydrogen, and of oxygen, required to drive the CRAFT reaction to substantial conversions should not cause practical difficulties.

As it is essential that driving reactions run concurrently with the CRAFT reaction through the reactor, careful reactor design, especially related to continuous and low-level oxygen addition, will be required. As noted above, the mere generation of enthalpy will not be sufficient. In principle, several ways of achieving suitable oxygen addition are possible. For fixed-bed flow reactors, a variation on "cold shot" systems could be used to give frequent, small oxygen additions down the catalyst bed, although the number of injection points needed would be greater than in the usual "cold shot" reactor. Alternatively, a tube-and-still reactor, constructed with tube walls of an appropriate porosity, could operate with catalyst and steam/hydrocarbon reactants in the tubes and oxygen (possibly air) outside the tubes. Similar systems could be used in fluid-bed or slurry reactors, where the movements of catalyst and reactant should help to ensure a near-constant, low level of oxygen. Any further analysis of possible reactor systems would be premature at this stage of process evaluation.

Although the steam reforming of methane and the Fischer–Tropsch synthesis reactions are the composite of many interconnecting equilibria and reaction processes, at a simplistic kinetic level, the proposed CRAFT process can be considered as two consecutive processes where k_1, k_2, and k_3 are the composite of many rate constants.

$$nCH_4 + nH_2O \underset{k_3}{\overset{k_1}{\rightleftharpoons}} nCO + 3nH_2 \xrightarrow{k_2} C_nH_{2n+2} + nH_2O + (n-1)H_2.$$

Since, at the temperature of 500–600K the steam reforming reaction will be very slow and the Fischer–Tropsch reaction rapid (i.e., $k_2 \gg k_1$ for catalysts currently available), it is possible that the proposed CRAFT process could be feasible. In particular, low concentrations of $CO + H_2$ formed on the catalyst surface would react rapidly to form hydrocarbons rather than reform methane as $k_2 \gg k_3$. The central problem that remains is that the methanation reaction, i.e., the reverse reaction, would need to be controlled if higher hydrocarbons C_{2+} are to be observed.

3. Catalyst design

In this initial study, we decided to select a single catalyst capable of both steam reforming and Fischer–Tropsch synthesis. The selected catalyst needed to satisfy two further criteria: (a) it would have to be stable to high concentrations of steam at elevated temperatures and (b) it would need to be active with very low concentrations of $CO + H_2$.

The effect of water on Fischer–Tropsch catalysts has been extensively investigated and it has been reported that the addition of water increases the average carbon number of the product [22–27]. Consequently, operating with high-water concentrations in the reactor feed is not anticipated to pose a problem.

Table 1
Rate expression for the Fischer–Tropsch synthesis reaction for metal catalysts

Metal	Rate expression	References
Ni	$r = k\ P_{CO}P_{H_2}{}^{0.5}$	[29]
	$r = k\ P_{CO}/(1 + kP_{CO})^2$	[30]
	$r = k\ P_{H_2}{}^{0.9}P_{CO}{}^{-0.2}$	[31]
	$r = k\ P_{H_2}{}^{0.9}P_{H_2O}{}^{-0.9}$	[32]
Co	$r = k$	[33]
	$r = k\ P_{H_2}{}^{2}P_{CO}{}^{-1}$	[34]
Fe	$r = k\ P_{H_2}{}^{0.6}P_{CO}{}^{-0.4} - fr^{0.5}P_{H_2O}{}^{-0.5}$	[35]
	$r = k\ P_{H_2}(1 + aP_{H_2O}P_{CO}{}^{-1})^{-1}$	[36]
Ru	$r = k\ P_{H_2}{}^{2}$	[37]
	$r = k\ P_{H_2}{}^{1.33}P_{CO}{}^{-0.13}$	[38]
	$r = k\ P_{H_2}{}^{2}P_{CO}(1 + mP_{CO} + nP_{H_2})^{-3}$	[39]
	$r = k\ P_{H_2}{}^{1.5}P_{CO}{}^{-0.6}$	[40]

The kinetics for Fischer–Tropsch catalysts has also been extensively studied and the rate expressions for Ni, Co, Fe and Ru catalysts are shown in table 1. Ni, Co and Ru, and also rhodium, catalysts are known to act as steam reforming catalysts. Since very low concentrations of $CO + H_2$ are expected to be formed on the catalyst under CRAFT conditions, a catalyst with negative order of reaction with respect to CO will be preferred. Nickel can be rejected not only as a potential catalyst as it has a positive reaction order with respect to CO but also as it acts exclusively as a methanation catalyst in the temperature range 500–600 K. Ru can have a negative order with respect to CO and can also be expected to be the most stable catalyst under CRAFT conditions in the presence of H_2O and O_2 [23]. In addition, Ru has the highest rate of chain propagation, thereby favoring the formation of higher hydrocarbons [1]. Co has a negative reaction order with respect to CO and is also relatively stable to H_2O at elevated temperatures. Hence, in the initial study, Ru and Co catalysts were selected for study. It was further decided to use catalyst formulations already known in the literature in this initial study.

4. Experimental

Ru and Co catalysts supported on γ-Al_2O_3 (Sasol Chemie), SiO_2 (Cab-O-Sil M5) and MnO (Strem) were prepared using impregnation. A solution of the metal salt in distilled water at the required concentration was impregnated onto the predried support at 353 K, the excess water was then evaporated and the material dried (373 K, 24 h). $Co(NO_3)_2 \cdot 6H_2O$ (Aldrich) was used as the cobalt source, and $RuBr_3$ and ruthenium nitrosyl nitrate was used as the Ru source. KBr and KNO_3 were added as promoters to the impregnating solutions. Catalysts were pelleted and sieved to give particles (0.6–1 mm) and were pre-reduced in the reactor with H_2 at 400 °C prior to evaluation in the CRAFT process. The CRAFT reaction was investigated using a standard laboratory microreactor with a stainless-steel reactor described previously [28]. Ultrapure methane or $CO : H_2$ (BOC, 1 : 3) and diluent nitrogen were fed via a calibrated mass flow controller to the reactor. Water was fed via a calibrated HPLC pump to a vaporizer. All lines were heated before and after the reaction. Pressure control was achieved via a back-pressure regulator. Reaction products were analyzed using on-line gas chromatography.

5. Results and discussion

A series of supported Ru and Co catalysts were initially investigated for the Fischer–Tropsch reaction at 573 K and the results are given in table 2. This temperature was initially selected for evaluation of the CRAFT reaction and, consequently, it was necessary to establish the potential C_{2+} product selectivity for the reaction of $CO + H_2$ with these catalysts at this temperature. In addition, highly dilute $CO + H_2$, diluted with N_2, was employed to simulate the expected conditions in the CRAFT reaction. These reaction

Table 2
CO hydrogenation with dilute $CO + H_2$[a]

Catalyst	CO conversion (%)	Product selectivity (wt%)[b]				
		CH_4	C_2	C_3	C_4	C_{5+}
20% Co/Al_2O_3	23.0	65.8	4.4	13.4	14.8	1.6
1% Ru/Al_2O_3	77.8	86.9	9.1	4.0	0.4	0
1% Ru/Al_2O_3[c]	91.4	95.2	3.6	1.2	0	0
1% Ru/SiO_2	63.9	85.3	8.1	6.5	0	0
1% Ru/0.1% KNO_3/Al_2O_3[d]	58.3	99.5	0.1	0.4	0	0
1% Ru/0.1% KBr/Al_2O_3[d]	78.8	99.9	tr	0.1	0	0
1% Ru/0.1% KBr/Al_2O_3	78.0	82.8	10.2	5.8	0.8	0.4
1% Ru/0.5% KBr/Al_2O_3	59.5	78.1	8.0	7.5	3.8	2.6

[a] Reaction conditions: 1.25% CO/3.75% H_2, balance N_2, 573 K, gas hourly space velocity 2000 h^{-1}, 2.2 Mpa.
[b] Products are hydrocarbons, alkene and alkane selectivity combined.
[c] 2.5% CO/7.5% H_2, balance N_2.
[d] Catalysts precalcined at 550 °C before reduction.

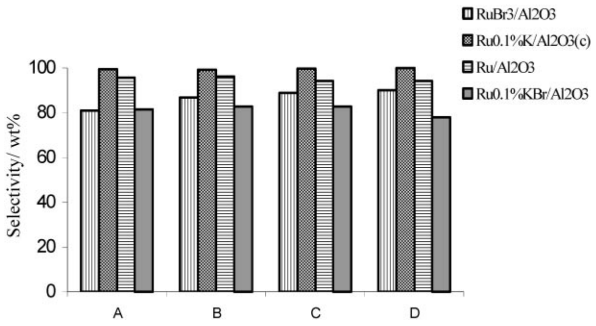

Figure 3. Methane selectivity in CO hydrogenation with dilute $CO + H_2$. Reaction conditions: 1.25% CO/3.75% H_2, 573 K, 2.2 MPa. A, 20–30 h time-on-stream; B, 40–50 h; C, 60–70 h; D, 85–100 h.

conditions are considerably different from those employed for the standard Fischer–Tropsch reaction [1,2]. As expected, at the high temperature, all the catalysts were very active giving high CO conversions. In addition, the catalysts mainly catalyzed the methanation reaction due to the high temperature and the high molar ratio of $H_2 : CO$ employed [1,2]. However, although these catalysts are not at all optimal to be used under these reaction conditions, they do synthesize some C_{2+} products and, hence, can be used for the proof of concept study. In particular, promotion of the 1% Ru/Al_2O_3 with KBr leads to a significant decrease in the formation of methane, and this effect was maintained for ca. 100 h of catalyst testing (figure 3). The Ru compound used for the catalyst preparation was also found to be important. In early studies, we find that $Ru_3(CO)_{12}$-derived catalysts were less active and gave only methane as product, hence, studies with this type of precursor were abandoned. The best catalysts with respect to C_{2+} formation were prepared using ruthenium nitrosyl nitrate promoted with KBr. Calcination of the catalysts at 573 K prior to reduction gave catalysts with enhanced methane formation. It is possible that the influence of the Ru particle size is important with respect

Table 3
CO hydrogenation with dilute $CO + H_2$ in the presence of water[a]

Time-on-line (h)	CO conversion (%)	Product selectivity (wt%)[b]				
		CH_4	C_2	C_3	C_4	C_{5+}
20–30	71.1	84.5	6.8	6.8	0.9	1.0
	68.7[c]	88.4	7.1	1.1	0.5	2.6
40–50	78.1	82.8	10.2	5.8	0.8	0.4
	68.0[c]	88.4	8.1	1.1	0.5	2.0
85–95	76.1	83.4	9.9	5.4	0.9	0.4
	76.9[c]	89.9	6.1	2.3	0.7	1.0
110–120	68.0	83.4	9.7	5.8	0.7	0.3
	69.7[c]	97.4	0.7	1.0	0.2	0.8

[a] Reaction conditions: 1% Ru/0.1% KBr/Al_2O_3, 1.25% CO/3.75% H_2, balance N_2, 573 K, gas hourly space velocity 2000 h^{-1}, 2.2 Mpa.
[b] Total hydrocarbon selectivity, alkene, and alkane selectivity combined.
[c] Water added to feed 0.3 ml/min, total gas hourly space velocity 2680 h^{-1}.

Table 4
Reaction of methane and steam

Catalyst[a] promoter KBr (%)	Temperature (K)	GHSV[b] (h^{-1})	H_2O/CH_4[c]	CH_4 conversion to C_{2+} hydrocarbons (%)[d]	
				5–7 h	20–50 h
0.5	573	2000	4	0	0
0.1	573	2000	4	2.2[e]	4.4[f]
0.1	623	1000	1.4	0.1[f]	0.5[f]
0.1	623	2000	1.4	0.9[e]	0.1[f]
0.1	623	4000	1.4	5.5[e]	0.2[f,g]
0.1	623	4000	1.4	0.6[e]	0

[a] Catalyst KBr-promoted–1% Ru/Al_2O_3.
[b] Total gas hourly space velocity.
[c] $H_2O : CH_4$ mol ratio.
[d] CH_4 conversion averaged over two periods of reaction.
[e] Products, mainly C_3, C_4 alkanes.
[f] Product, mainly ethane.
[g] 0.18 vol% O_2 added to reactants.

Table 5
Reaction of methane with steam[a]

Catalyst	GHSV[b] (h^{-1})	H_2O/CH_4[c]	CH_4 conversion to C_{2+} hydrocarbons (%)
RuMnO	400	3.0	0.2
RuMnO	800	3.0	0.6
1% Ru/0.1% KBr/Al_2O_3[d]	400	3.0	0.4
5% Ru/0.1% KBr/Al_2O_3[e]	400	3.0	0.1
5% Ru/0.1% KBr/Al_2O_3[e]	1200	1.0	0.2
5% Ru/0.1% KBr/Al_2O_3[f]	1300	1.0	tr
5% Ru/0.1% KBr/Al_2O_3[g]	400	3.0	tr
5% Ru/0.1% KBr/Al_2O_3[g]	1200	1.0	tr
5% Ru/0.1% KBr/Al_2O_3[g,f]	1300	1.0	tr
5% Ru/0.5% O_3/Al_2O_3	400	3.0	tr
5% Ru/0.5% O_3/Al_2O_3	1200	1.0	tr
5% Ru/0.5% NO_3/Al_2O_3[f]	1300	1.0	tr
20% Ru/0.5% KBr/Al_2O_3[h]	400	3.0	0.6
20% Ru/0.5% KBr/Al_2O_3[h]	1200	1.0	0.1
20% Ru/0.5% KBr/Al_2O_3[f]	1300	1.0	0

[a] Data obtained 2–10 h time-on-stream, 573 K, 2.2 MPa, ethane only observed C_{2+} product.
[b] Total gas hourly space velocity.
[c] H_2O : CH_4 mol ratio.
[d] Ru source: ruthenium nitrosyl nitrate.
[e] Ru source: $RuBr_3$.
[f] 0.18 vol% O_2 added to reactants.
[g] Catalyst calcined at 550 °C prior to reduction.
[h] Ru source: $Ru_3(CO)_{12}$.

to controlling methane formation. Also, *K* concentrations and distribution will also be a significant factor.

Following these initial studies, the effect of the addition of steam to the $CO/H_2/N_2$ reaction gases was investigated for the 0.1% KBr/1.0% Ru/Al_2O_3 catalyst and the results are shown in table 3. The addition of steam did not significantly affect conversion after ca. 85 h, although, at earlier reaction times, some decrease in Co conversion was observed. Most significantly, the addition of water to the reactants resulted in an increase in the C_5^+ products, and this is consistent with a number of previous studies concerning the effect of added water [24–30].

The KBr-promoted 1% Ru/Al_2O_3 catalyst was then evaluated in the CRAFT process at 573 and 623 K and the results are shown in table 4 for initial reaction data at 5–7 h time-on-line and also for reaction data collected at 20–50 h time-on-line. In these reactions, methane : steam mixtures were fed to the reactor in the absence of a nitrogen diluent. In the absence of water vapor, neither methane conversion nor C_{2+} products were observed. Under these conditions, it is apparent that the 0.1% KBr-promoted 1% Ru/Al_2O_3 gave small amounts of conversion to C_2–C_4 products indicating that the CRAFT process may provide a viable pathway for hydrocarbon formation from methane. These results are qualitatively in agreement with the equilibrium limits on yield calculated above. Increasing the reaction temperature from 573 to 623 K tended to decrease C_{2+} hydrocarbon formation and, in addition, the inclusion of 0.18% O_2 in the reaction gases did not lead to any improvement in hydrocarbon synthesis. Hydrogen was also observed as a reaction product in most cases. On the basis of the thermodynamic analysis above, oxygen addition would be expected to provide additional driving reactions, which would in turn give higher yields of C_{2+} hydrocarbons. However, the reactions of all the components in the CRAFT system (except steam) with oxygen over Ru catalysts are very fast at 623 K. It is likely then that, with the simple reactor used here, all the oxygen reacted at the top of the catalyst bed, leaving reactions in the major part of the catalyst bed as without oxygen addition.

In view of the initial potentially promising results, a broader range of catalysts were evaluated at 573 K and the results are given in table 5. It is apparent that Ru-based catalysts give enhanced CH_4 conversion compared with Co-based catalysts although, under most conditions, only trace levels of conversion were observed and ethane was the only observed product. The highest CH_4 conversion to C_{4+} hydrocarbons we have observed is 5.5% (table 4). It should be stressed that this study was not undertaken with optimized catalysts and, consequently, under the extreme conditions required for the CRAFT process, compared with more standard Fischer–Tropsch conditions, it is not unexpected that only low conversion of methane to C_{2+} hydrocarbons was observed. However, the initial results presented in this study do confirm the proof of concept that methane can be converted to higher hydrocarbons, although these may be in the range C_2–C_4 in carbon number with the catalysts we have used. Oxygen addition, in suitably designed reactors, may be able to enhance the yields of higher hydrocarbons. It is now apparent that significant catalyst design effort is required to capitalize on these initial results. In particular, it will be necessary to design a Fischer–Tropsch catalyst capable of operating at 573–623 K, which gives much lower levels of methanation. If this is possible, then it is feasible that the concept of the CRAFT reaction can be exploited in the formation of hydrocarbons.

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