

**NEW ENERGY-EFFICIENT PROCESS ROUTES IN INDUSTRY :
THE ONE-STEP CONVERSION OF METHANE TO ETHYLENE,
METHANOL AND FORMALDEHYDE**

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Contract JOE3-CT95-0010

PUBLISHABLE REPORT

Research funded in part by
THE EUROPEAN COMMISSION
in the framework of the
Non Nuclear Energy Programme
JOULE III

2. TITLE

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3. ABSTRACT

The main goals of the Project were:

1. To study the scale-up of a novel oxidative coupling of methane (OCM) reactor-separator (*Science* **264**, 1583, 1994) for ethylene production.
2. To construct and test similar reactor-separator units for the production of methanol/formaldehyde from methane.

Both goals have been met during the Project. The OCM reactor-separator has been successfully scaled up from the microreactor unit described in the Science publication (catalyst mass 0.1 g, molecular sieve mass 2-3 g, gas feed flowrate 3 cm³ STP/min) to a large bench scale unit (catalyst mass 4 g, molecular sieve mass 40 g, gas feed flowrate 250 cm³ STP/min, recycle flowrate 900 cm³ STP/min). This near 100-fold scale-up in gas feed flowrate has been achieved without any significant loss in C₂ hydrocarbon selectivity and yield. This C₂ yields up to 53% and C₂H₄ yields up to 45% have been obtained. It is the first time that such high C₂ and C₂H₄ yields are obtained at such high gas flowrates (240 cm³ STP/min).

The same concept was used to study and scale-up the partial oxidation of methane to methanol and formaldehyde (MMF process). Maximum formaldehyde yield of 6% at a selectivity of 45% was obtained at feed flowrates of 30 cm³ STP/min using 2 g of catalyst, 20 g of trapping material and recycle flowrates of 380 cm³ STP/min. Although the maximum achieved formaldehyde yield was significantly lower than that originally anticipated on the basis of literature values reported for single pass (no recycle) operation, still the achieved value (6%) is the highest reported in the literature. Since our best single pass formaldehyde yield was of the order of 1% the values achieved with recycle operation (6%) show the significant advantages of the recycle reactor separator.

In the course of this Project significant advances were made both in terms of developing novel state-of-the-art catalysts for the OCM process as well as for the development of efficient trapping materials for the selective adsorption of ethylene at higher temperatures (250°C).

4. PARTNERSHIP

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5. OBJECTIVES

The development of direct (one-step) and energy efficient processes for the conversion of methane to ethylene and to methanol/formaldehyde has been a long-sought goal. Despite intensive research during the last twelve years the maximum ethylene and formaldehyde yield obtained in laboratory-scale reactors until 1994 were of the order of 20% and 5% respectively. This is due to the much higher reactivity with oxygen of the partial oxidation products (ethylene and methanol/formaldehyde respectively) than that of methane.

In 1994 one of the participating research teams (University of Patras) developed a novel laboratory scale gas-recycle reactor separator which gave ethylene yields up to 85% for the oxidative coupling of methane (OCM) (Science **264** (1994) 1583). In this novel reactor-separator ethylene and ethane are trapped, and thus protected from further oxidation, in a molecular sieve trap in the recycle loop. They are then released by subsequent heating of the molecular sieve trap. The above very encouraging results were obtained in a small microreactor (catalyst mass: 0.1 gram, molecular sieve mass: 2-3 gram) able to handle up to 3 ccSTP/min of methane.

The main strategic objectives of the present program are:

1. To study the scale-up of the novel reactor-separator for ethylene production by building bench-scale units able to convert up to 1000 ccSTP/min of methane each to ethylene. The units will employ a fixed-bed reactor with an optimised catalyst composition, and an optimally designed swing-bed molecular sieve trap.
2. To construct and test a similar catalytic reactor-separator for the direct production of methanol/formaldehyde from methane (up to 1000 ccSTP/min). The differences from case 1 is in the selection of the catalytic and adsorbent materials.

These new one-step processes are both exothermic and will have a very strong potential to replace the existing two- or three-step commercial routes for the production of ethylene and methanol which involve severely endothermic steps.

More specifically the objectives were :

OCM catalyst testing

- To synthesise, characterise and evaluate a range of OCM catalysts comprising samaria-based mixed oxide materials and trimetallic systems consisting of Na tungstate supported on silica.
- To synthesise samples of the most promising materials on a larger scale and send them for evaluation in the Patras recycle-separator reactor.
- To supply catalyst samples for evaluation in the Imperial College electrochemical reactor

- To discover how the ultimately chosen catalytic system works. This to be achieved by "taking apart" the catalyst with a view to understanding role of the various constituents.
- To use the understanding acquired under 4, above, to assist in the development of an improved system. A key question is "what, if anything, is the role of the Na?".
- To develop a catalyst which shows promise for industrial implementation.

Electrochemical Route

The principal objectives were:

- To investigate the conversion of methane to ethylene in an electrochemical reactor which would allow oxygen supply by two different modes, a) through the gas-cofed (catalytic mode) or b) by oxygen ions through the electrolyte (electrocatalytic mode).
- To compare both methane conversion and C₂ selectivities, specially ethylene selectivity, for both modes of oxygen supply

In order to achieve such objectives the following procedure was adopted:

- To design and construct the electrochemical reactor. Two electrolyte materials were to be investigated: (i) CGO and (ii) YSZ
- To synthetise and characterise both electrolyte materials
- To assemble a gas flow system including the appropriate gas analysis techniques
- To provide open and close-circuit kinetics measurements for both electrochemical systems. Those were to be carried out initially with catalyst A and finally with the most promising catalysts materials supplied by our Cambridge partners
- To optimise reactor performance for optimum ethylene yield in the electrochemical oxidation of methane

Scale-up of the reactor-separator

The principal objectives were to test the most promising catalysts that were identified and tested in microreactors in activities 1.3 and 1.2 in bench-scale reactors. The main single-pass reactor performance were :

OCM process : ethylene selectivity > 70% , ethylene yield per pass > 12%, space time < 5 sec, CH₄ feed 1 lt/min and operating temperature 700° C-800 °C.

MMF process : CH₃OH/HCHO selectivity > 60%, CH₃OH/HCHO yield per pass >2% , CH₄ feed 1 lt/min and operating temperature 550-600 °C.

The next step was to operate the reactor-separator under recycle operation for both OCM and MMF processes using the most promising reactors identified in activities 1.1, 1.2(as far as the catalyst) and 1.3(as far as the reactor itself). The goal was to

scale-up the reactor separator compared to the very first studies of the reactor-separator. The main targets were:

OCM process : ethylene yield $>65\%$, Recycle ratio <8 , CH_4 feed 1lt/min.

MMF process : Formaldehyde yield $>55\%$, Recycle ratio <50 , CH_4 feed 1lt/min.

6. TECHNICAL DESCRIPTION

OCM Catalyst testing

The principal objectives were to identify, synthesise, characterise and test heterogeneous catalysts for the oxidative coupling of methane (OCM). The most promising materials would then be synthesised on a larger scale and sent for evaluation in the Patras recycle-separator reactor. The desired characteristics are high ethylene selectivity at relatively high methane conversion coupled with stable performance. A key goal was to understand as fully as possible the factors controlling the performance of the of action of the "best" class of catalysts, so as to optimise their performance as effectively as possible.

A promising OCM catalyst based on a Mn/Na/W oxide formulation supported on silica was therefore synthesised and evaluated. It became clear that this material was promising respects, in particular with respect to high methane conversion at high *ethylene* selectivity. In due course, we delivered to our Patras partners ~ 200 g of the Na/Mn/W catalysts for use in the recycle separator reactor, along with a specification of the optimum operating conditions.

We then set out to "take apart" the trimetallic catalyst with a view to understanding role of the various constituents and then to use this information to assist development of an improved system. A key question is "what, if anything, is the role of the Na?". This point has been entirely overlooked by other researchers in the field: *our work indicates that alkalis play a vital role in the production of high performance catalysts*. We showed that the presence of Na in the catalyst precursor is of critical importance for the formation of catalysts that are both active and selective for the OCM reaction, especially with respect to the production of good ethylene yields.

It was demonstrated that the alkali component plays a dual role. First, as a "structural promoter" whereby it induces the amorphous silica \rightarrow α -cristobalite transition ~ 700 K below the normal transition temperature. The result is a highly crystalline catalyst support which, unlike amorphous silica, is totally inactive towards the burning of methane. Second, as a "chemical promoter" whereby it stabilises a monolayer of the catalytically active species (the alkali tungstate) on the support surface. Other bimetallic and trimetallic catalyst formulations were also investigated.

Electrochemical Reactor

The principal objective was to was to investigate the conversion of methane to ethylene in an electrochemical reactor which would allow oxygen supply by two different modes, a) through the gas-cofed (catalytic mode) or b) by oxygen ions through the electrolyte (electrocatalytic mode). Our previous experience led us to the idea that electrochemically supplied oxygen for partial oxidation of methane may have substantial selectivity benefits. Thus, our main goal was to prove this.

The option of electrochemically-supplied oxygen was proposed to eliminate unwanted deep oxidation reactions due to the presence of gaseous oxygen. This electrochemical supply of oxygen in the oxidative coupling reactor has several advantages, including a

fine control of the CH_4 to O_2 ratio and also simultaneous generation of electrical power by-product which benefits the overall energy efficiency of the process. An additional advantage of the electrochemical route is that the methane and the oxygen (from the air) are fed to separate reactor compartments avoiding any possible formation of explosive mixtures. Moreover, such a mode of operation could lead to important catalyst selectivity and activity enhancement.

The reactor performance for methane conversion to ethylene was to be investigated using the most promising catalyst materials (note that the catalysts is in form of an electrode). The catalysts were entirely synthesised and supplied by our Cambridge partners. In order to compare the performance ($\text{SC}_2\%$) of the system by both modes of oxygen supply, three candidate catalysts were employed, namely catalyst A, B and C.

After thorough examination of the literature two classes of materials were investigated for their use as electrolyte: (i) mixed conductor ceria-gadolinia doped oxide, CGO, and (ii) pure oxygen conductor yttria-stabilised-zirconia, YSZ. Those materials were used to supply all the oxygen required for the partial oxidation reaction electrochemically in the temperature range of 700-900°C. After early preliminary work, it became clear that the later material was superior. This was therefore selected as the most promising system for further investigation and development.

Accordingly, a totally new electrochemical reactor was design and constructed. In addition, a gas flow system including the appropriate gas analysis techniques was assembled. All the components of the electrocatalytic cell were also prepared in our laboratory and characterised for optimum performance. It was then demonstrated that for the catalyst A system, in the whole range of temperature studied (700-900°C), electrochemical supplied oxygen was more selective towards C_2 formation than oxygen co-fed in the gas-phase. At that stage, it was also clear that oxygen utilisation was higher for the electrochemical supplied oxygen (100% current efficiency). Even so, optimisation for maximum performance was still required.

Having decided to focus on the optimisation of the reaction conditions, two effects were comparatively investigated for both catalytic and electrochemical modes of operation. Those were the effect of rate of oxygen supply (or optimum CH_4/O_2 ratio) and the operating temperature on methane conversion and selectivity to C_2 formation. This study was carried out for the three catalyst systems in order to achieve maximum C_2 yields.

Regarding the optimum operating temperature, preliminary studies on catalyst A and B indicated that the optimum temperature of operation for OCM was in the range of 850-900°C, although there were signs of carbon deposition on the electrode above 850°C which would cause a decrease in methane conversion. Therefore, further work was carried out at 850°C. As far as the feed rate of oxygen is concerned, it was found that increasing the oxygen flux led to a decrease in C_2 selectivity. This can be ascribed to an excess of oxygen in the gas-phase which would promote total oxidation at high oxygen feed rates. Optimum $\text{SC}_2\%$ were found at low oxygen feed rates for the catalyst A system. Optimisation of the feed rate was still required for catalysts B and C.

The main experimental problem at this stage was found to be the catalyst application method on the YSZ electrolyte. Due to the poor electrical conductivity of the as received-catalysts employed, it was necessary to mix them with a metal conductor in order to form a conductive slurry to apply on the YSZ tubular electrolyte. Preliminary application methods resulted in a masking effect of the true catalyst behavior, i.e. the morphology of the applied catalyst indicated that the active sites were significantly blocked by the metal content, thus masking its true catalytic behavior. Much effort was focussed on an optimisation of the application method in order to prevent this masking effect from happening. We carried out a systematic evaluation of different compositions of the metal/catalyst mixture until maximum performance was achieved. This occurred at a composition of 50:50% in volume (the catalysts weight being 0.1g and the catalyst geometric area being approximately 16 cm²).

Having focussed in this composition, further investigations were carried out in order to determine which of the three catalyst systems would give the highest C₂ selectivity, particularly the highest ethylene selectivity at high methane conversion, hence optimum ethylene yield. The effect of rate of oxygen supply on selectivity to C₂ formation was comparatively investigated for the three systems at 850°C for both catalytic and electrochemical modes of oxygen supply. It was demonstrated that for the whole of oxygen fluxes studied (0.01-0.6A) electrochemically supplied oxygen was more selective towards C₂ compounds, especially ethylene, than the correspondent co-fed oxygen in the gas-phase. This happened for the three catalyst systems employed. Reproducibility of the results was perfect in all cases.

For the catalyst A case, increasing the electrochemical oxygen flux from 0.01 to 0.6 A (XCH₄=18%) decreases the total SC₂% by 59% (S%ethylene decreasing by 54%). Therefore, the reaction should be operated with low oxygen fluxes as far as the selectivity for C₂ compounds is concerned. In the case of catalyst B, increasing the electrochemical oxygen flux from 0.1 to 0.6 A only decreases the total SC₂% by 24% (S%ethylene decreasing by 17%) while maintaining 20% XCH₄%. Thus, the reaction can be operated under a wider range of oxygen feed rates than for catalyst A. The optimum performance was found for the catalyst C system which showed maximum SC₂% of 95% at low oxygen flux and 75% (Sethylene =55%) at high flux with around 20% methane conversion. Co-fed SC₂% are in very good agreement with those reported by Cambridge's group and C₂ selectivities achieved electrochemically are the highest ever reported.

Adsorption-separation unit optimisation

The adsorption-separation unit plays a key role in the novel laboratory scale gas recycle reactor-separator developed at the University of Patras. In the original work the molecular sieve trap comprised two packed bed units in a swing-bed arrangement. One unit was maintained at 30°C to continuously trap the reactor products, while the other was heated for 15 min to 400°C to release the products in an inert gas stream.

The main objective for the adsorption-separation unit is an energy-efficient separation of the reaction products in the OCM and MMF process. Both processes suffer from low product yields and are operated at high temperature (850°C and 550°C respectively). Conventional hydrocarbon separations are done by cryogenic distillation,

involving high-pressure/low-temperature units. During recycling of the unconverted methane a considerable effort has to be made to heat and cool the whole gas stream between the low-temperature separation unit (-100°C) and the high-temperature reaction unit (850°C/550°C). A typical plant would involve a large number of heat exchangers, recycle pumps and gas compressors. This will make the process capital intensive. One way to reduce these capital investments, is the development of an alternative, high-temperature separation unit. In this way, it may be possible to separate the reaction products from methane at temperatures much closer to the reaction temperature, so that considerable savings in the overall heat transfer duty and related with that the capital investments in heat-exchanger equipment can be made.

Reactor optimisation / MMF catalysts

In this task a preparation method for catalysts used in the partial oxidation of methane to formaldehyde(MMF process) was developed. Kinetic measurements were performed, a reaction network was established and the kinetic parameters were evaluated for modelling the MMF process.

The analysis procedure for quantitatively analysing all components was improved. It is now possible to analyse all substances within the MMF process by GC during one run. Kinetic measurements were performed investigating activity and selectivity of a state-of-the-art-catalyst at various temperatures. These data were used to evaluate kinetic parameters based on a reaction network. With these data it is now possible to model the MMF process.

Recycle operation and scale-up of the gas recycle reactor-separator

The main target was to scale-up the novel gas recycle separator for the oxidative coupling of methane reaction(OCM) and to test a similar reactor for the partial oxidation of methane to formaldehyde or methanol(MMF).

OCM process

The OCM reaction was carried out using the Mn/Na₂WO₄/SiO₂ catalyst developed and prepared at Cambridge and Sr/La₂O₃ catalyst prepared at Patras.

Initially the reactor was operated under single-pass conditions, i.e. without gas recycling and trapping. The goal was to scale-up from the microreactor used at Cambridge (reactor volume of 2.8 cm³, catalyst mass 0.4gr) to a bench scale reactor of volume 43cm³ containing 4gr of the catalyst. The reactor was operated at total volumetric flowrate up to 1300 cm³/min using the three catalysts. It was found that C₂-selectivity is not strongly affected upon the scale-up. The only problem that has to be taken into account is the pronounced temperature rise in the reactor due to the high exothermicity of the reaction(up to 70°C). The obtained yield values are : 20 % for the Mn/Na₂WO₄/SiO₂ catalyst and 10% for the Sr/La₂O₃ catalyst.

The next step in our investigation was to operate the reactor-separator under recycling conditions. The trap was loaded with molecular sieve Linde 5A material which adsorbs

and protects from further oxidation the desired products, i.e. ethane and ethylene. The improvement in the yield values due to the design of the reactor-separator is clear for all three catalysts. The maximum C₂-yield value obtained was 53% (with a corresponding C₂H₄-yield of 45%). The present studies were carried at flowrate range up to 250 ml/min which is a 100-fold scale-up compared with the initial studies of 3ml/min. Recycle ratio values are of the order of 10.

MMF process

The catalyst used for the partial oxidation of methane to formaldehyde was V₂O₅(1.3wt% V)/SiO₂. Preparation of the catalyst was done according to *Spencer and Pereira, J.Cat 116, 399, 1989*. Testing of the catalyst in microreactors showed that it is very selective to formaldehyde giving selectivity values up to 80% at low methane conversion (<1%). Thus the obtained formaldehyde yield values are up to 1%.

In order to operate the reactor-separator a suitable trapping material for the formaldehyde should be used. It was found that water is the best “adsorbent” for HCHO, so that formaldehyde solution is formed in the trap unit. So the trap unit was loaded with 15-20 ml of water. The reactor used was a quartz plug flow reactor of volume 7 cm³ loaded with 1.09 gr of catalyst. The obtained yield value under recycle operation was 6% (S_{HCHO}=41 % at 14.3% CH₄ conversion) which is much higher than the 0.6% under single-pass conditions. To the best of our knowledge this is the highest reported value in literature.

Modelling

A model which comprises the mass and heat balances in the unit for OCM process, has been used to estimate the kinetic constants of the reactions involved and the main features for the industrial application of the process.

7. RESULTS AND DISCUSSION

7.1 TASK 1, ACTIVITY 1.1 (*U. of Cambridge*)

Preparation of Li doped samaria catalysts

Since true incorporation of the alkali into the oxide lattice appears to be a key point, we used more than one synthetic method to prepare the $\text{Li}/\text{Sm}_2\text{O}_3$ catalysts:

Solid State Reaction (SSR): Two different routes were employed. In each case, the mixed precursor compounds were very slowly heated until they had completely decomposed.

Preparation of the $\text{Mn}/\text{Na}_2\text{WO}_4/\text{silica}$ catalyst

We followed the basic method described by the inventors [Jiang *et al* [*J. Phys. Chem.* 97 12870 (1993)] except that we used silica directly, rather than silica gel. We used the catalyst loading that was found to be optimum by Lunsford *et al* [*J. Catal.*, 155 390 (1995)]: 1.9% Mn; 5% Na_2WO_4 . This corresponds to $\sim 1\text{ML}$ WO_4 on silica.

Microreactor testing of the LiSmO_2 and $\text{Mn}/\text{Na}_2\text{WO}_4/\text{silica}$ catalysts

Catalytic measurements were performed using a single-pass, plug-flow microreactor, equipped with continuous on-line gas-chromatograph (G.C.) analysis.

Testing was carried out using the system whose commissioning was described in Periodic Report No 1, at the agreed GHSV (2000), in order to find the optimum conditions of temperature and feed composition. Durability was examined by accelerated ageing procedures involving application of (i) high temperatures and (ii) prolonged exposure to high levels of CO_2 . Of the two catalysts, LiSmO_2 exhibited C_2 production at lower temperatures than $\text{Mn}/\text{Na}_2\text{WO}_4/\text{silica}$. However, it had a

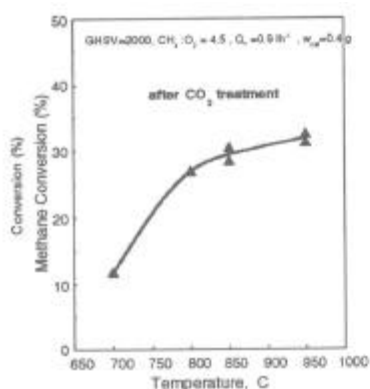


Figure 1: Methane conversion for the $\text{Mn}/\text{Na}_2\text{WO}_4/\text{silica}$ catalyst as a function of reaction temperature.

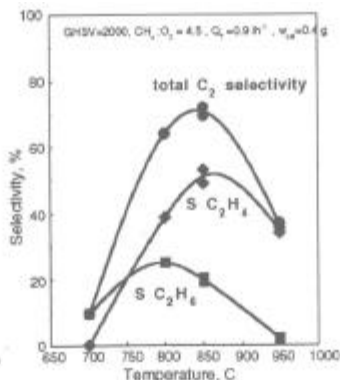


Figure 2: Total C_2 selectivity and ethane and ethylene selectivity for the $\text{Mn}/\text{Na}_2\text{WO}_4/\text{silica}$ catalyst as a function of reaction temperature

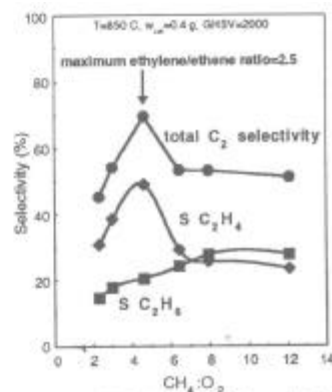


Figure 3: Total C_2 selectivity and ethane and ethylene selectivity for the $\text{Mn}/\text{Na}_2\text{WO}_4/\text{silica}$ catalyst as a function of CH_4/O_2 ratio.

significantly inferior performance at higher temperatures where useful levels of methane conversion are reached. In particular, *the selectivity towards ethylene* was substantially lower than in the case of Mn/Na₂WO₄/silica.

It is also less robust than Mn/Na₂WO₄/silica. The XRD data indicated that under reaction conditions, it appears to decompose to lithium carbonate and samarium oxide. We therefore concentrated on Mn/Na₂WO₄/silica and our findings for this catalyst are summarised below.

We found stable performance over 12 h and did not investigate longer intervals. The catalyst activity rose steeply above 700 C (Figure 1) and at ~ 2000 GHSV useful conversions (~ 30%), total C₂ selectivities (~ 80%) and *ethylene selectivities* (> 50%) were obtained in the interval 800 C - 950 C (Figure 2). We therefore concentrated on this regime and found that the best performance was obtained with CH₄:O₂ ~ 4 - 5 (Figure 3).

Catalyst characterisation

Representative samples of (i) fresh catalyst, (ii) used, active catalyst and (iii) used, deactivated catalyst were examined by TPR/TPO, XRD and XPS measurements. TPR and TPO measurements on the Mn/Na₂WO₄/silica catalysts showed the presence of two reducible sites. One of these appeared to react preferentially with methane. The fully reduced material was air stable for long enough to permit *ex situ* transfer to XPS spectrometer enabling XP spectra to be obtained for the Mn, Na and W constituents. XRD revealed little evidence of catalyst decomposition under normal operating conditions, the only detectable Mn was present as Mn₃O₄. It also showed that the initially amorphous silica underwent complete conversion highly crystalline cristobalite at ~ 800°C, i.e. far below the normal transition temperature. Deliberate deactivation of the catalyst with CO₂ or at high temperatures leads to the appearance of sodium carbonate. The deactivated catalyst showed pronounced loss of C₂ selectivity (~ 25% ethylene) and greatly increased activity for production of carbon oxides.

In order to understand the catalytic behaviour more fully, appropriate materials were prepared containing 1, 2, and 3 metal components on the SiO₂ support.

The XRD results clearly demonstrate that good catalysts are produced only when the preparation technique leads to conversion of the originally amorphous SiO₂ to highly crystalline cristobalite. It is remarkable that in the case of the full trimetallic formulation this phase transition occurs at 750 C- i.e. far below the normal silica □ cristobalite transition temperature (1500 C). Neither the Mn nor the W alone or in combination induce this remarkable low temperature phase transition. From these results it seems clear that Na plays a dual role in determining catalyst performance. Firstly it acts as a structural promoter, converting the high surface area amorphous silica (which is very active for methane burning) into low surface area α-cristobalite (which is inactive for methane burning). Secondly, it acts as a chemical promoter, apparently stabilising the active site for OCM. Our hypothesis is that this site is a (tetrahedrally co-ordinated) WO₄ species interacting with the alkali. We propose that in the absence of alkali, calcination leads to formation of (octahedrally co-ordinated)

WO₃ surface species which are unselective towards OCM. This model is consistent with the well known oxidation properties of oxo-tungsten species in solution.

It is clear that the nature of the silicon dioxide support and its interaction with the catalytically active phase are critically important. To investigate this further, appropriate materials were prepared containing 1, 2, and 3 metal components on 4 different SiO₂ supports, including synthetic *α*-cristobalite, with surface areas of 345, 150, 10 and 1 m²/g. The effect of substituting other metals was systematically investigated by means of microreactor studies of the OCM reaction over these materials, coupled with detailed XPS studies. Alkali free formulations were synthesised by using (NH₄)₂WO₄ as a precursor for the W component.

Principal findings

Reactor studies over the temperature range 700 - 900 C and with methane/oxygen ratios between 8.0 and 2.0 showed that certain other formulations also generated a highly efficient OCM catalysts. For example, 52% ethylene selectivity (67% C₂ selectivity at 30% CH₄ conversion). Guided by these results, we then investigated other formulations which led to the discovery of an extremely efficient catalyst with optimum performance characteristics as follows: 850 C; methane/oxygen ratio of 4.5; **64 % ethylene selectivity** (90 % C₂ selectivity at 29 % CH₄ conversion). This could be a significant breakthrough. Our Shell partners estimate that ~ 60% ethylene selectivity is the critical minimum necessary for commercialisation to become feasible.

The XPS results revealed that Na is critically important in obtaining good dispersion of the W-containing phase, regardless of the surface area of the support. In conjunction with the reactor data, the XPS data also show that the stronger the interaction between Na/W and SiO₂, the better the catalyst. The results show clearly that a strong interaction is best achieved by contacting the Na and W precursors on the silica prior to calcination.

7.2 TASK 1, ACTIVITY 1.2 (U. of Karlsruhe)

Experimental set-up

For the microreactor testing and evaluation of the kinetic data an experimental set-up as shown in figure 4 was used.

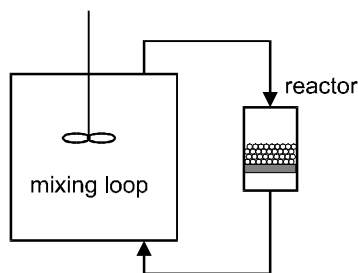


Figure 4 : Schematic of the experimental set-up.

The set-up consists of a quartz reactor in a recycle system. By use of a mixing loop, an ideal continuously stirred tank reactor (CSTR) can be simulated. Initially, the mixing loop is filled with the reactants, methane and oxygen. At time zero the mixing loop is connected to the reactor. A constant flow is driven through the reactor filled with a fixed bed of catalyst and led back into the mixing loop again. This experimental set-up offers the advantage of realising a lower temperature in the mixing loop than in the reactor itself. Thus homogenous reactions in the gas phase outside the reactor are minimised, while a temperature above ambient is sufficient to prevent condensation of products.

A small amount of substance from the mixing loop is frequently analysed by GC. In a single experiment, starting with the initial reaction gas mixture and monitoring the development of product composition as a function of time, a set of data is obtained that allows for the determination of kinetic model parameters. By use of the described experimental installation, catalyst screening as well as detailed kinetic investigations are possible.

Analysis

A Varian 3400 GC is used for analysis of the reactants. Due to the wide range of chromatographic properties of the involved species a complex three-column system is required for the analysis procedure. The scheme is shown in figure 5, whereas a typical chromatogram is depicted in figure 6.

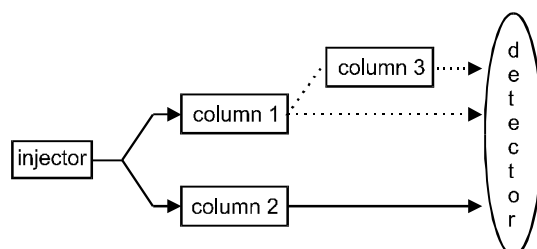


Figure 5 : Scheme of the three-column system.

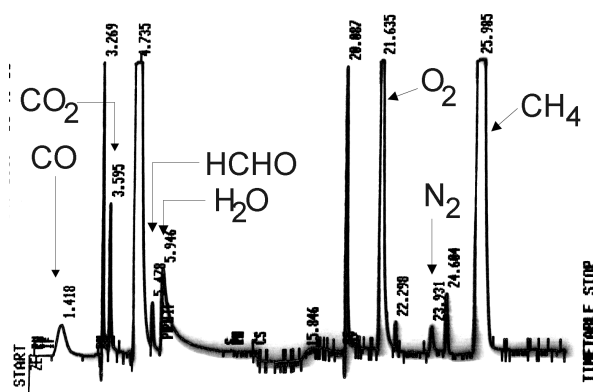


Figure 6 : Example of a chromatogram using a three-column system.

The sample is split and led into columns 1 and 2. During an isothermal run, column 1 is initially connected to column 3. The permanent gases except carbon dioxide (methane, oxygen, carbon monoxide and nitrogen) elute without interaction and enter column 3. Then column 1 is connected directly to the TCD and carbon dioxide is detected, while the gases are being trapped in column 3. On column 2, formaldehyde and water are separated from the other components. After the liquid components have left column 2, column 3 is reconnected and the gases are analysed. Connection and disconnection of the columns is performed by use of an air actuated valve. Whenever the valve is switched, a short interruption of the carrier gas occurs resulting in a peak. These peaks can be seen in figure 6 with retention times of 3.3 and 20.1 minutes, respectively.

Considering the broad range of concentrations depicted in this chromatogram (methane to formaldehyde $\approx 200 : 1$), the achieved degree of separation appears to be very reasonable. Only the water peak exhibits some tailing.

Experimental results

Experiments were performed using sieve fractions of vanadia/silica catalyst supplied by the participating group in Patras. An initial molar methane-to-oxygen ratio of 3.5 to 1 was chosen and the catalyst temperature was varied between 830 and 930 K. The amount of catalyst was varied between 50 and 250 mg according to the reaction temperature.

Figure 7 shows the results obtained at a catalyst temperature of 930 K. The upper part depicts the three major components, methane, oxygen and water, whereas the lower part shows the development of the products, formaldehyde, carbon monoxide and carbon dioxide. It has to be noted that no methanol could be detected.

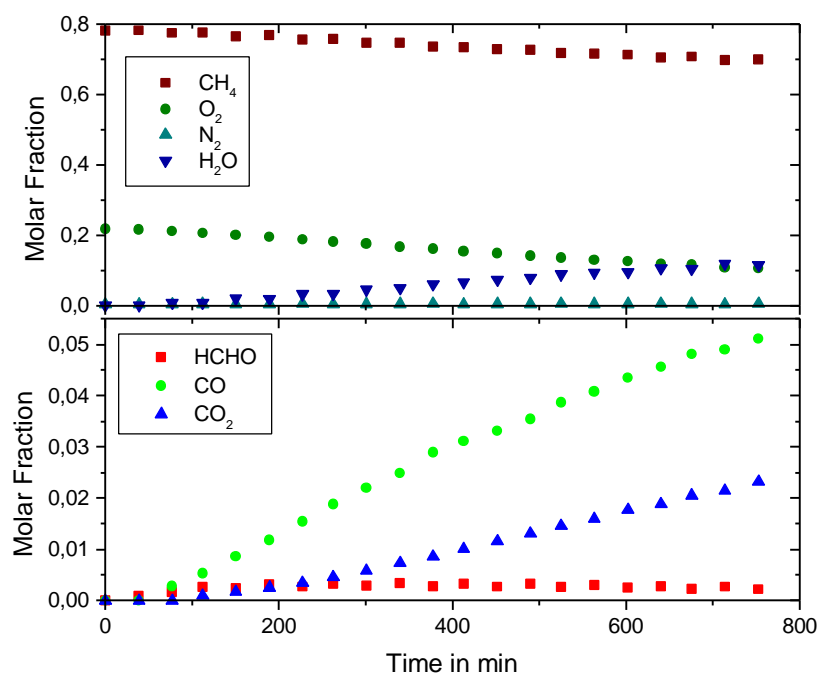


Figure 7 : Experimental results: Product composition over vanadia catalyst (1.3 weight-% V on SiO₂) at 930 K as a function of time.

Reaction kinetics

For determination of the reaction kinetics, a reaction network was established. In this network, methane can react towards formaldehyde, carbon monoxide and carbon dioxide, whereas in subsequent reactions formaldehyde can be converted to carbon monoxide and carbon dioxide. Finally carbon monoxide is oxidised to carbon dioxide. A scheme of this reaction network is depicted in figure 8.

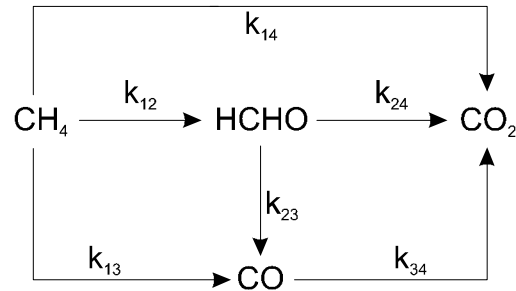


Figure 8 : Scheme of the reaction network.

Using dimensionless carbon fractions of the form

$$z_i = \frac{n_i}{n_{\text{Me},0}}$$

where n_i is the amount of methane, formaldehyde, carbon monoxide or carbon dioxide, a set of differential equations is obtained assuming first order reaction for all paths:

$$\frac{dz_i}{dt} = \sum (n_{ij} \cdot k_{ij} \cdot z_j)$$

with n_{ij} the stoichiometric coefficient and k_{ij} the first-order rate constant in reaction path ij .

The modified time

$$t = \frac{T_M}{T_R} \frac{m_{\text{cat}}}{V_M} \cdot t$$

takes into account the temperatures of the mixing loop and of the reactor, T_M and T_R , respectively, as well as the volume of the mixing loop, V_M . m_{cat} is the mass of catalyst in the reactor, and t is the real time.

The obtained set of four differential equations can be solved analytically. One example below shows the as-obtained equation for formaldehyde:

$$z_F = \frac{k_{12}}{(k_{23} + k_{24}) - (k_{12} + k_{13} + k_{14})} \cdot \left\{ \exp[-(k_{12} + k_{13} + k_{14}) \cdot t] - \exp[-(k_{23} + k_{24}) \cdot t] \right\}$$

The kinetic parameters in these equations, k_{ij} , are determined by performing a non-linear least square fit. The resulting values for the reaction temperature of 830 K, 880 K and 930 K are summarised in table 1.

Table 1 Kinetic parameters k_{ij} in $l/(g \cdot \text{min})$.

kinetic parameter	k_{12}	k_{13}	k_{14}	k_{23}	k_{24}	k_{34}
at 830 K	0.0011	0.0010	0.0008	0.477	0	0.053
at 880 K	0.0101	0	0.001	2.90	0	0.053
at 930 K	0.0186	0.0192	0.006	4.66	0	0.204

Interestingly, the value calculated for k_{24} , the rate constant for the reaction of formaldehyde to carbon dioxide, is zero. This is true for the complete range of temperatures investigated. Hence over the catalysts used no formaldehyde is directly converted to carbon dioxide. Additionally, it can be seen that the rate constant k_{14} is considerably smaller than k_{12} and k_{13} . Unfortunately, the reaction rate of methane to carbon monoxide has the same order of magnitude as the rate to formaldehyde. Therefore it is not possible to obtain high formaldehyde yields using this catalyst. Furthermore, formaldehyde is a very unstable intermediate product as can be seen from the ratio of k_{12} to k_{23} , which amounts to about $4 \cdot 10^{-3}$. In figure 9 the carbon fractions are plotted versus the modified time as symbols, whereas the calculated data are depicted by lines. The calculated lines fit the measured data quite well. The reaction network is therefore suitable for description of the reaction kinetics.

During the fitting procedure, only the carbon containing species were considered, but oxygen and water were not taken into account. However, using the stoichiometry of the reactions involved in the reaction network, the concentrations of these components can be calculated with the kinetic data. In figure 10 the as-obtained data for oxygen and water (lines) are compared to the measured data (symbols).

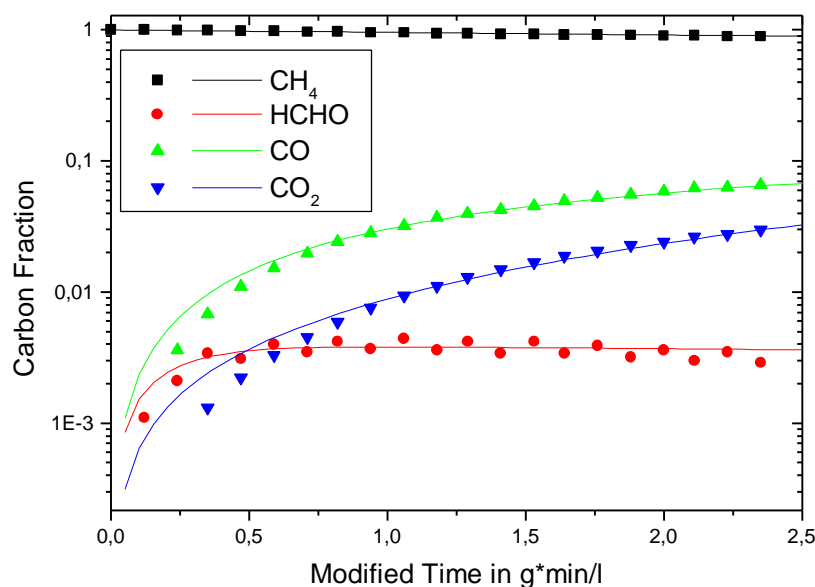


Figure 9 : Plot of the measured (symbols) and calculated (lines) carbon fractions.

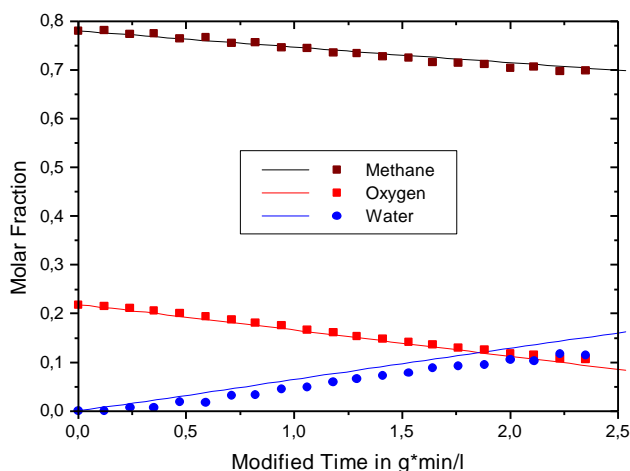


Figure 10 : Comparison of measured (symbols) and calculated data for water and oxygen (lines).

It is evident that the agreement for oxygen is good and even for water, the component being most difficult to analyse, it is quite reasonable.

Furthermore, with the kinetic data the selectivities with respect to the formation of formaldehyde, carbon monoxide and carbon dioxide can be calculated. The selectivity S_i is defined as

$$S_i = \frac{n_i}{n_{\text{CH}_4,0} - n_{\text{CH}_4}} .$$

The selectivities towards the products are plotted versus methane conversion in figure 11; the symbols depict the measured data and the lines the data calculated with the kinetic parameters. Again it can be seen that the measured and the calculated data agree well. The selectivity with respect to formaldehyde decreases monotonously whereas the selectivity towards carbon monoxide reaches a maximum and decreases again. This is the typical behaviour of intermediate products which subsequently react to a more stable final product, carbon dioxide. Hence the selectivity towards carbon dioxide increases with increasing conversion of methane.

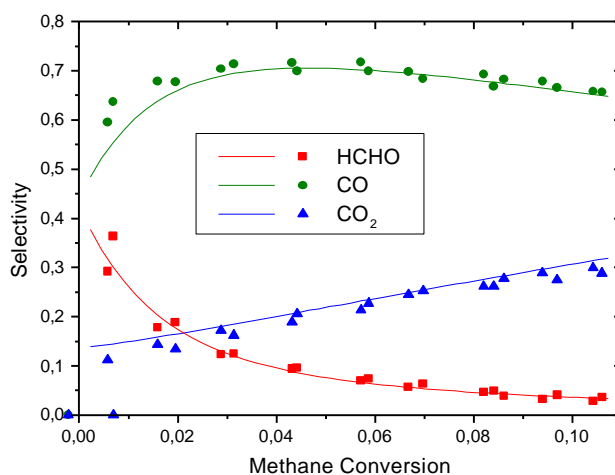


Figure 11 : Selectivity vs. methane conversion: Measured (symbols) data and calculated (lines) at $T = 930 \text{ K}$.

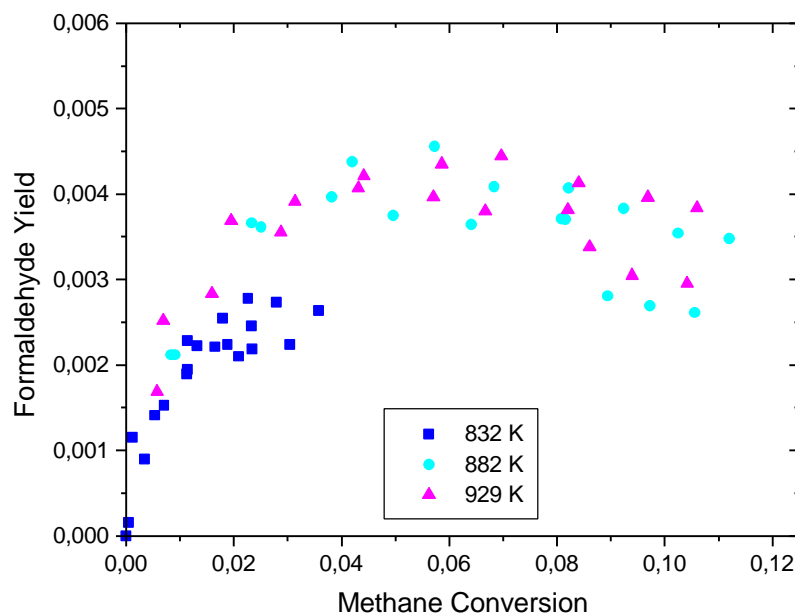


Figure 12 : Formaldehyde yield versus methane conversion at different temperatures.

For comparing the results obtained at different temperatures, the formaldehyde yield (selectivity with respect to the formation of formaldehyde times methane conversion) versus methane conversion is shown in figure 12.

The formaldehyde yield appears to be independent of the reaction temperature. The maximum formaldehyde yield observed with this catalyst is about 0.5 % at a methane conversion of 6 %. These values were found to be not dependent on the initial methane-to-oxygen ratio, which was varied between 2.5 to 1 and 5.5 to 1.

Other catalysts used (e.g. molybdena on silica) exhibited very similar maximum formaldehyde yields. In any case, no methanol was formed under the reaction conditions used. Thus the determined kinetic data describe the present state-of-the-art regarding the direct catalytic formation of formaldehyde from methane. The obtained data can be used for modelling of the reaction/separation process.

7.3 TASK 1 , ACTIVITY 1.3 (*U. of Patras*)

7.3.1 Reactor optimization for the OCM process

Results with the Mn/Na₂WO₄/SiO₂ catalyst

The oxidative coupling of methane (OCM) reaction was carried out using the 2%Mn/5%Na₂WO₄/SiO₂ catalyst prepared at Cambridge. The goal of the experiments was to scale-up from the microreactor used at Cambridge (reactor volume 2.8 cm³, catalyst mass 0.4 g, total volumetric flowrate 15 cc STP/min) to a reactor of volume 43 cm³ containing 4 g of catalyst and total single-pass flowrates up to 1200 cm³ STP/min.

The reactor was operated under single-pass conditions, i.e. without gas recycling and

molecular sieve trapping. This is a necessary first step before testing for gas recycle operation.

Figure 13 shows the effect of total flowrate on the selectivity to C_2 hydrocarbons and to ethylene selectivity ($S_{C_2H_4}$). Interestingly both S_{C_2} and $S_{C_2H_4}$ increase slightly with flowrate: S_{C_2} increases from 60% to 70% and $S_{C_2H_4}$ increases from 45% to 54%. The inlet CH_4/O_2 ratio was kept near 5 (± 1) and the oxygen conversion was complete ($>98\%$). Reactants were 20% CH_4 diluted in He and 20% CH_4 in He. As shown in Fig. 13 the CH_4 conversion increases slightly from 20% to 28% as the inlet flowrate increases from 100 to 1200 cm^3 STP/min. This small increase is consistent with the corresponding slight decrease in inlet CH_4/O_2 ratio in this set of experiments. Figure 14 shows the corresponding single-pass yields of ethylene ($Y_{C_2H_4}$) and ethane ($Y_{C_2H_6}$). At high total flowrates and GHSV values $Y_{C_2H_4}$ is up to 15% and $Y_{C_2H_6}$ is up to 5%. Consequently the total C_2 -yield is up to 20%. The Gas Hourly Space Velocity (GHSV) values are computed on the basis of the catalyst bed volume. The GHSV is up to 7000 on the basis of the total flowrate and up to 1400 on the basis of the CH_4+O_2 flowrate.

In the experiments of Figure 13 the reactor temperature prior to introduction of reactants was $820^\circ C$. However due to the exothermicity of the reaction, there is a significant, up to $70^\circ C$, steady-state temperature rise ΔT (Fig. 15) in the reactor at high flowrates. The near-linear increase in ΔT with flowrate is due to the fact that the heat generated is proportional to the reaction rate and thus proportional to the total flowrate, since oxygen conversion is always complete.

Results with the Sr/La_2O_3 catalyst

Single-pass experiments were carried out so as to check the performance of this catalyst. The reactor used was a quartz plug flow reactor of a volume 30 cm^3 ($d=3\text{ cm}$ and $length=4\text{ cm}$). The amount of catalyst used was 4.4 gr, that is 8 times more than the amount (0.5 gr) used in earlier studies [2].

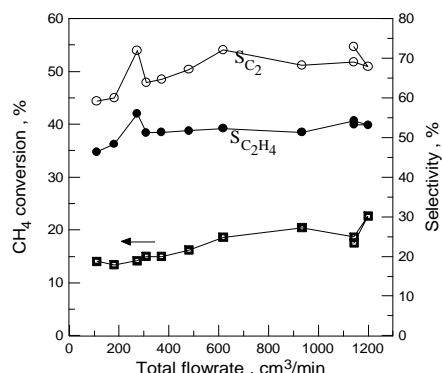


Figure 13 : Effect of total flowrate on selectivity and conversion

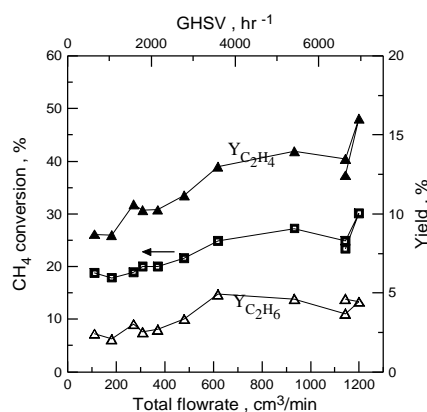


Figure 14 : Effect of the total flowrate on ethylene and ethane yield

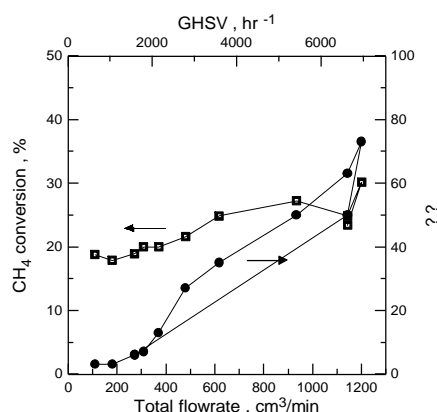


Figure 15 : Effect of the total flowrate on the temperature rise in the reactor

Figure 16 depicts the effect of methane conversion on selectivity and yield. As shown at low methane conversion 5%, C_2 -selectivity is 80% and the maximum C_2 -yield is 10%. Thus one can utilize this catalyst in order to get the high selectivity value of 80% even at high methane conversions by operating the recycle unit at appropriate conditions. In order to check the influence of the catalyst bed volume a second reactor

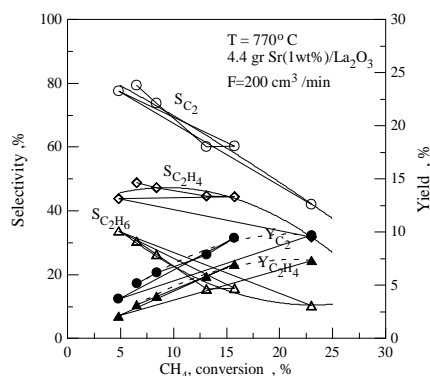


Figure 16 : Dependence of selectivity and methane conversion upon methane conversion

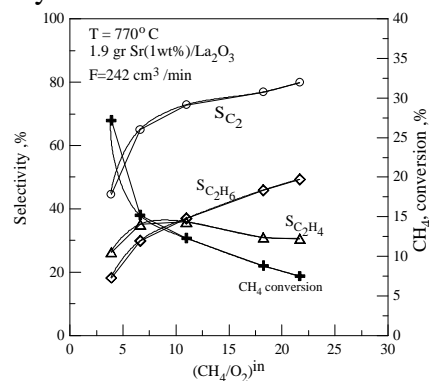


Figure 17 : Effect of the $(CH_4/O_2)^{in}$ ratio on selectivity and CH_4 conversion

was tested with 1.9 gr of the Sr(1wt%)/La₂O₃ catalyst. The single-pass performance of this reactor was similar to the previous one as shown in figure 5 which depicts the effect of the $(CH_4/O_2)^{inlet}$ ratio on methane conversion and on the corresponding C_2H_4 , C_2H_6 and C_2 selectivities at constant flowrate. As shown increasing the CH_4/O_2 ratio from 4 to 22, methane conversion decreases from 28% to 7% while the corresponding C_2 -selectivity increases from 43% to 80%. The obtained C_2 -hydrocarbon yield values are up to 10%. Oxygen conversion was complete in all the above experiments.

Comparing the two catalysts as far as the operating temperature we see that the operating temperature of the Sr(1wt%)/La₂O₃ is almost 100°C lower than that of the Mn/Na₂WO₄/SiO₂(770°C compared with the 850°C of Mn/Na₂WO₄/SiO₂).

7.3.2 Reactor optimization for the MMF process

The partial oxidation of methane to formaldehyde (MMF) was carried out in a microreactor of volume 3.5 cm³ containing 0.325 gr of V₂O₅/SiO₂ catalyst which was prepared by incipient wet impregnation[3]. Figure 18a shows the effect of the total flowrate on CH_4 conversion and formaldehyde selectivity. The operating temperature was 560°C. As shown, increasing the total flowrate up to 200 ml STP/min methane conversion decreases while HCHO selectivity increases reaching a value of 70% at very low methane conversion (<0.5%). Crossplotting HCHO selectivity with methane conversion one can get the dependence of HCHO selectivity upon methane conversion as shown in Fig. 18b

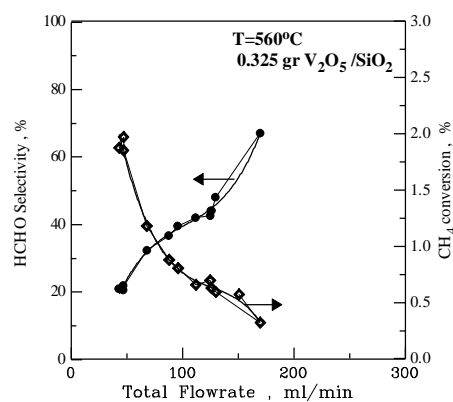


Figure 18a: Effect of the total flowrate on HCHO selectivity and CH_4 conversion

where CO and CO₂ selectivities are also presented. CO₂ selectivity is almost constant with increasing methane conversion while CO selectivity increases. This implies that CO is a secondary product in the reaction

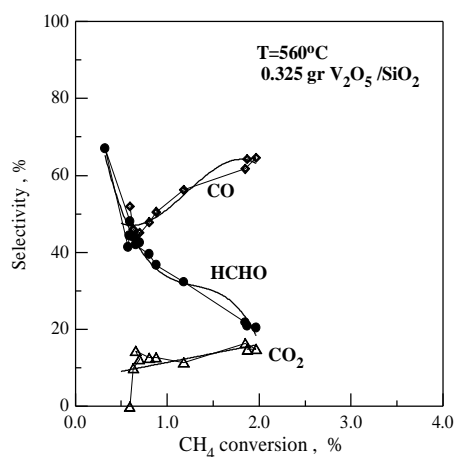


Figure 18b:Dependence of HCHO,CO and CO₂ selectivity upon methane conversion

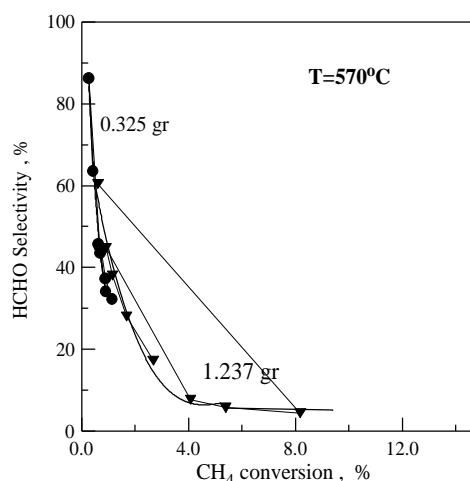


Figure 19:Dependence of HCHO selectivity upon methane conversion for the microreactor(cycles) and the scaled-up reactor(triangles)

network while CO₂ is a primary one.

A scale-up was done using bigger reactors and larger amount of catalyst. Figure 19 shows the results of the scale-up (1.237 gr of catalyst) in comparison with the microreactor(0.325 gr). The total flowrate is up to 500 cm³/min for the scaled-up reactor. As shown, for the same CH₄ conversion HCHO selectivity is not affected with the scale-up.

7.4 TASK 2, ACTIVITIES 2.1, 2.2 (Imperial College)

The oxidative coupling of methane can be studied over a wide range of temperatures from (typically) 500 to 900 °C. In order to cover such a range, with electrochemically supplied oxygen, it is desirable to use solid electrolytes with high ionic conductivities. Yttria stabilised zirconia does not perform satisfactorily below 700°C, whereas ceria-

gadolinia ($\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$) can be used down to about 450 °C. Conversely, CGO does not perform so well at the higher temperatures, due to instability, whereas YSZ perform excellently at temperature from 800°C upwards. Thus, in order to cover the entire temperature range both types of electrolyte have been studied. Moreover, the catalytic properties of the two electrolyte materials (and the activity of the generated oxygen species) are believed to be different. This is the second reason why both types of material have been chosen for study. The nature of the cell design and construction were different for the two materials. In the case of CGO, the design centred on the use of flat discs of the electrolyte, whereas in the case of YSZ, the design centred on the use of open ended tubes.

Both the anode and the cathode must exhibit thermal expansivities compatible with the electrolyte to prevent delamination during heat up. They should have high electronic conductivities and preferably high oxygen-ion conductivities (if an electrode is non-conductive to oxygen ions, the oxygen exchange between the electrode and electrolyte will only take place at the triple phase boundary between the gas/electrode/electrolyte). They must also be chemically stable in contact with the electrolyte. i.e. the presence of interfacial reactions resulting in the production of third phases can be detrimental to oxygen-ion exchange.

Anode materials should be good catalysts for hydrocarbon activation. The anode should not promote carbon deposition. For partial oxidation of methane catalyst A, B and C were investigated.

The oxidation of methane was studied at the atmospheric pressure in the temperature range 600 to 900°C for both catalytic and electrochemical operation modes of the electrochemical reactor. Comparison was made between co-fed and electrochemically supplied oxygen in a sequence of experiments. In the catalytic mode, the cell's electric circuit was broken and a mixture of CH_4 and O_2 was fed to the working electrode. In this case, the silver electrode was acting as a conventional catalyst. For the reaction with the electrochemically pumped oxygen, the feed rate of oxygen was equivalent to the flux of oxygen supplied through the YSZ. Since only oxygen ions can pass through the electron-conducting leads when the circuit is closed, the flux of oxygen was controlled by the electrical potential applied between the electrodes.

7.4.1 Design and Assembly of the Electrochemical Reactor

catalyst /CGO Electrochemical Reactor

The electrochemical reactor was constructed from a CGO flat disk. Electrical connections to the cell were made by spot welding Au wires to the Ag mesh current collectors. The whole assembly was mounted on to the end of a vertical YSZ tube with the anode facing inwards and the cathode outwards. The cell was sealed by a low-melting point glass onto the edge of the support tube. The reactant gas was fed to the anode and the cathode was exposed to the ambient air inside the furnace chamber.

catalyst /YSZ Electrochemical Reactor

The design concept was based on the use of pre-sintered zirconia tubes. The electrodes were applied on both sides of the tube so that the inside became the cathode and the outside the anode. In order to keep the anode gas within the confines of the outside wall, the zirconia tube was inserted concentrically down the inside of a quartz tube of a slightly wider diameter. This provided a narrow annular channel for the anode gases to pass. The anode material, containing the catalyst was applied in a band near the middle of the tube. By contrast, the cathode material was applied all over the inside wall of the tube. The two tubes were sealed together at the ends using either silicone rubber adhesive, or by specially adapted swagelock fittings. The furnace which was required to heat up only the middle portion of the tubes so the ends of the tubes projected sufficiently outside to be maintained at room temperature. This meant that the seals could be kept cool, thus completely removing the problem with high temperature seals.

7.4.2 Testing the Reactor Performance (Results)

The principal objectives of this activity were to investigate the conversion of methane to ethylene over candidate catalysts in an electrochemical reactor based on ceria gadolinia (CGO) or Ytria-stabilised-zirconia (YSZ) solid electrolyte, and to compare the results with conversions carried out in co-feed experiments. Initial experiments were done with catalyst A. Subsequent experiments were focussed on the incorporation of the more selective catalysts supplied by our Cambridge partners, with particular attention to electrode fabrication and material compatibility.

catalyst A/CGO Electrochemical Reactor

The behaviour of the system at 650°C was initially investigated in the absence of methane, by current pumping in the presence of helium (at a flow rate of 50 ml/min). When electrochemical oxygen was supplied (in absence of methane) to the anode, the relationship between the amount of oxygen detected by the mass spectrometer and the current pumped through the electrolyte was found to be non-linear. Moreover, when a constant current was held over a period time, the oxygen response exhibited oscillatory behaviour. Oscillations in the measured electrode potential were also observed. The rate of oxygen supply was not constant with time and therefore, higher currents were required to observe the same oxygen level. In addition, the emf was found to decrease substantially after applying current. This behaviour may be associated with the mixed ionic-electronic properties of the electrolyte.

In presence of methane, comparison was made between co-fed and electrochemically supplied oxygen in a sequence of experiments. In the electrochemical pumped case, (when 20% CH₄ in He (50ml/min) was fed to the anode at 650°C whilst oxygen was supplied electrochemically by pumping 100 mA) the mass spectrometer only detected CO and hydrogen in the products. There was no trace of CO₂ or C₂ compounds. This

may be due to the low rate of oxygen driven through the electrolyte at this temperature. These experiments showed that electrochemically supplied oxygen does not significantly enhance the formation of C₂ compounds at this temperature (650°C). The low selectivities observed are consistent with previous work which shows a volcano relationship between selectivity and temperature, the peak of which is centred at about 850°C.

The main perceived benefit in using ceria-gadolinia based electrolyte (CGO) was its low temperature of operation. However, preliminary co-fed results indicated that the optimum ethylene production occurs at temperature closer to 800°C and above. In this range of temperature, yttria stabilised zirconia, YSZ, is more appropriate because it is intrinsically more stable. CGO was also found to be non-stable under the reducing conditions required for methane conversion experiments, in particular some of the oscillating behavior observed on CGO could be related to the effect of mixed conductivity in this electrolyte material. In addition, CGO has been reported to be a deep oxidation catalyst. Therefore, work carried out in this phase of the project has focused on YSZ electrolytes.

catalyst /YSZ Electrochemical Reactor

The effect of both the rate of oxygen supply and the operating temperature on methane conversion and selectivity to C₂ formation were comparatively investigated for both modes of operation. In order to make a comparison between co-fed and electrochemically supplied oxygen, it is useful to express the oxygen content in both cases as a flux measured in amperes. This can be obtained from the measured flow rate of oxygen in the case of the co-fed experiments, and from the measured current in the electrochemical case.

The OCM reaction was carried out over catalysts A, B and C. The main products were CO₂, C₂H₆, and C₂H₄. Formation of CO was negligible only when supplying the reactant oxygen electrochemically. Other oxygenated products and heavier hydrocarbons were not found in the outlet stream. In all experiments, methane conversion was found to be dependent on the oxygen flux and always less than 30%. This is a consequence of our reactor design. The methane concentration in the cell was constant and equal to the initial concentration in the feed (50%). Oxygen conversions higher than 90% were generally achieved. Utilisation of oxygen was found to be higher for the electrochemical case where almost 100% current efficiency was achieved. This happened for the three catalyst systems studied.

Optimisation of the reaction temperature

The effect of temperature in methane conversion and C₂, particularly ethylene, selectivities was investigated on the three catalyst systems for catalytic and electrochemical operational modes. Comparison was made in a sequence of experiments.

Oxidative coupling of methane over the three catalysts was investigated in the range of temperatures of 550-900°C, under identical conditions, i.e. 50% CH₄, and total flow

rate of 60 ml/min. At temperatures lower than 750°C C₂ compounds were found only in very low concentration. C₂ selectivities, in particular ethylene selectivity was found to be maximum at 900°C for catalyst A and 850°C for catalysts B and C. The highest methane conversion was achieved at 850°C in all cases, above this temperature carbon deposited in the catalyst-electrode decreasing conversion. This suggested that the optimum operation temperature was in the range of 850-900°C. This was in close agreement with the optimum temperature reported by our partners in Cambridge.

Effect of Rate of Oxygen Supply

Having optimised the optimum reaction temperature the next objective was to optimise the oxygen feed rate. All results presented here were carried out at 850°C. For co-fed operation, the oxygen concentration in the inlet flow was varied from 2.4 to 9.6% corresponding to 2.33-9.33 10⁻⁵ moles of oxygen per minute respectively. This corresponds to a variation from 0.01 to 0.6 A in electrochemical operation. The concentration of both carbon oxides and C₂ hydrocarbons increased with increasing the oxygen flow velocity resulting in decrease of CO and C₂ products selectivities in favour of CO₂ selectivity. The optimum range of operation corresponds to a compromise between C₂ selectivity and methane conversion. This has been studied for the three catalyst systems.

catalyst A

Figure 20 shows the comparative study of the dependence of rate of oxygen supply in the inlet flow on methane conversion for the OCM at 850°C. As expected, methane conversion increased linearly both with increasing the oxygen flux and temperature for both modes of operation. This happened over the entire range of temperatures studied. Carbon deposited on the catalyst surface causing a decrease in catalytic methane conversion below at 850°C. Electrochemical conversions agreed with those predicted by the Faraday's law, and the highest value (16%) was obtained at maximum temperature (900°C). For the whole range of oxygen feed rates studied, electrochemical methane conversions were found to be higher than those obtained in co-fed operation. This may be due to the 100% oxygen utilisation found in the electrochemical case. This is also in agreement with the CO formation and excess oxygen detected only in co-fed operation.

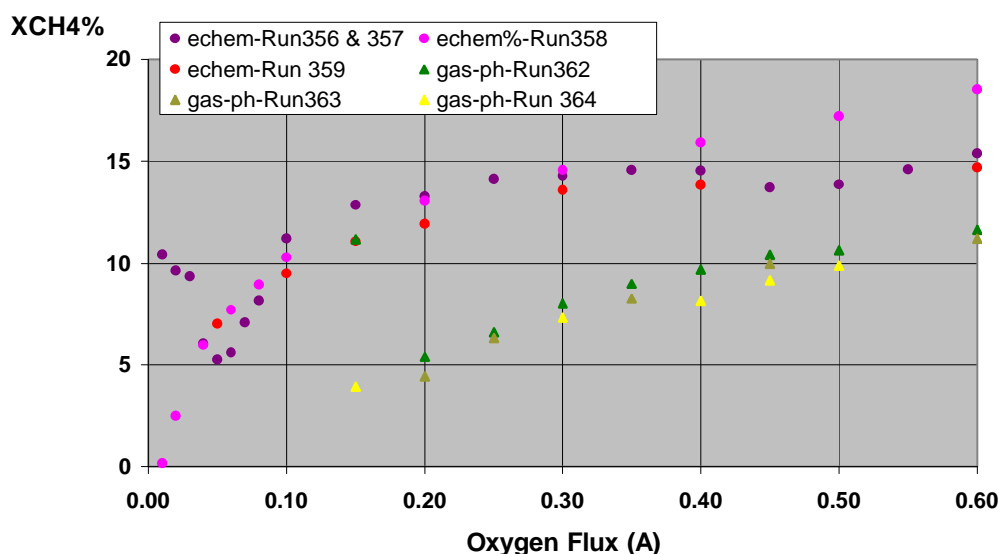


Figure 20 : Effect of the oxygen flux in XCH₄% for catalytic & electrocatalytic operation for the catalyst A/YSZ cell at 850°C, 50% CH₄, FRt=60 ml/min.

Figure 21 shows the dependence of the C₂ selectivity with respect to the oxygen flux (current in A) during the oxidation of methane at 850°C for electrochemical and co-fed operation. C₂ selectivity decreased progressively with increasing oxygen flux for both modes of operation, but the loss was found to be more pronounced in the case of co-fed oxygen. The decrease in C₂ selectivity at high oxygen content can be ascribed to the burning of C₂H₆ and C₂H₄ produced, i.e. conversion to CO₂.

Reproducibility of the results was found to be excellent. Ethylene selectivities were always found to be higher than those for ethane in both modes of operation and were approximately 36% higher for the electrochemical case. Increasing the electrochemical oxygen flux from 0.01 (low XCH₄%) to 0.6 A (XCH₄=18%) decreased the total SC₂% by 59%, from 93 to 40% (S%ethylene decreasing by 54%, from 50 to 23%). Therefore, in the case of the silver catalyst the reaction should be operated with low oxygen fluxes as far as the selectivity for C₂ compounds is concerned.

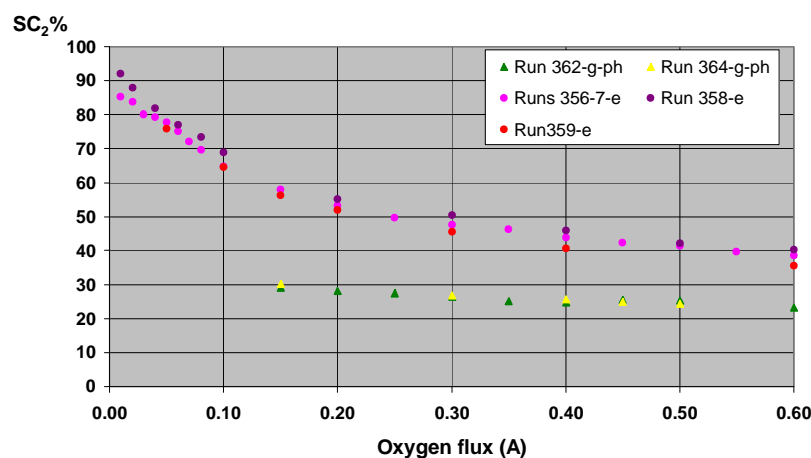


Figure 21 : Effect of the oxygen flux in SC₂% for catalytic & electrocatalytic operation for the catalyst A/YSZ cell at various temperatures, 50% CH₄, FRt=60 ml/min.

Results (for temperatures in the range of 720-840°C) follow the same trend observed by Belyaev and co-workers⁴⁻⁶ who carried out similar research in a Ag/YSZ (0.9%Zr + 0.1% Y₂O₂)/Ag symmetrical electrochemical cell. It is worthy noting that their C₂ selectivities were much lower (< 40%) than the ones reported here and likewise methane conversions were also lower than those observed in our experiment.

catalyst B

The trends observed with catalyst B were similar to those observed for catalyst A except that the C₂ selectivities were significantly higher, especially for ethylene. This is shown in Figure 22. Methane conversion increased with increasing oxygen flux and with increasing temperature for both modes of operation. Carbon deposited on the catalyst surface decreasing catalytic methane conversion below 850°C.

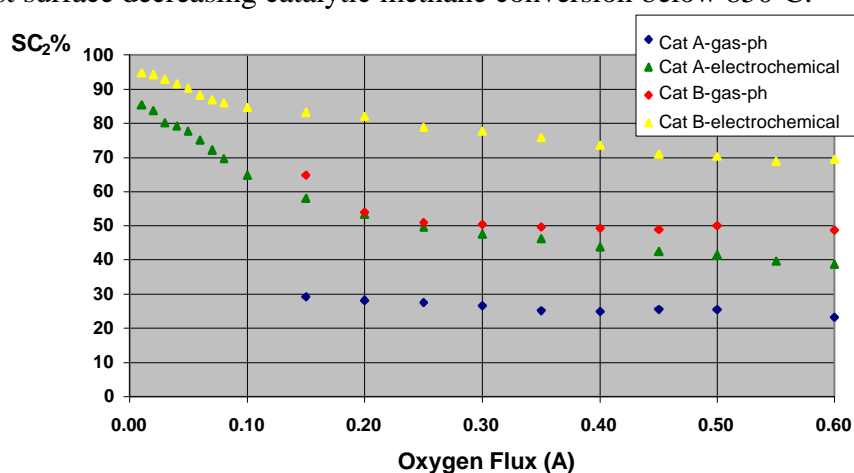


Figure 22. Comparative study of the effect of the oxygen flux in SC₂% for catalytic & electrocatalytic operation for the catalyst A/YSZ and catalyst B/YSZ electrochemical cells at 850°C, 50% CH₄, FRt=60 ml/min.

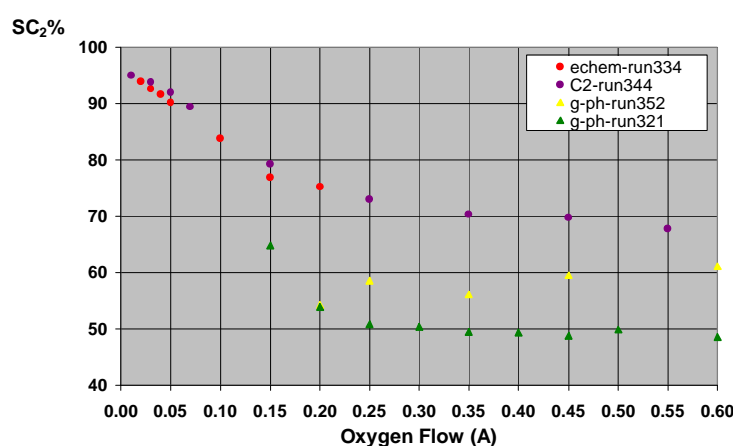


Figure 23 : Effect of the oxygen flux in SC₂% for catalytic & electrocatalytic operation for the catalyst B/YSZ cell at 850°C, 50% CH₄, FRt=60 ml/min.

Electrochemical C₂ selectivities were found to be approximately 29% higher than those achieved in co-fed operation. In particular, ethylene selectivities were approximately

13% higher for the electrochemical case and always higher than ethane selectivities. C_2 selectivity decreased slightly with increasing oxygen flux for both modes of operation, as shown in Figure 23. Increasing the electrochemical oxygen flux from 0.1 to 0.6 A only decreased total $SC_2\%$ by 24%, from 93 to 70% (S%ethylene decreasing by 17%, from 58 to 48%) while maintaining 20% $XCH_4\%$. Thus, the reaction can be operated under a wider range of oxygen feed rates than for catalyst B.

The selectivities achieved in the co-fed case are in a very close agreement with those obtained by our Cambridge partners.

catalyst C

The trends observed were similar to the other cases except that C_2 selectivities and in particular ethylene selectivities achieved in both modes of oxygen supply are higher. This confirms the catalyst C as the most promising system for OCM.

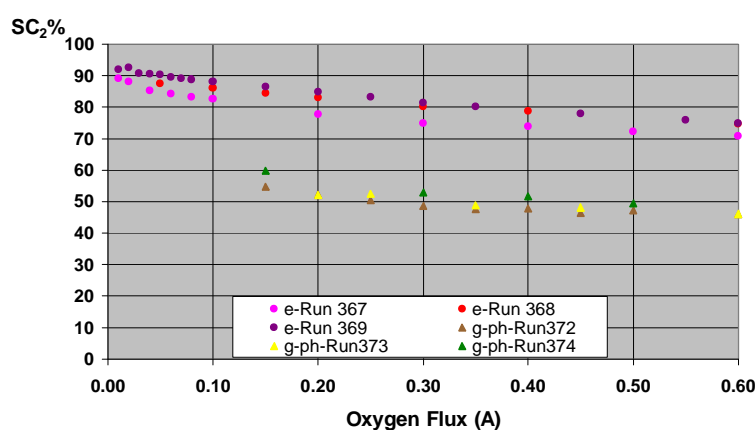


Figure 24 : Effect of the oxygen flux in $SC_2\%$ for catalytic & electrocatalytic operation for the catalyst C/YSZ electrochemical cells at 850°C, 50% CH_4 , $FRt=60$ ml/min.

Methane conversion increased with increasing oxygen flux and with increasing temperature for both modes of operation. Carbon deposited on the catalyst surface decreasing catalytic methane conversion below 850°C. Electrochemical conversion were found to be higher than those achieved in co-fed operation. Reproducibility of results was excellent. This is shown in Figure 24. Electrochemical C_2 selectivities were also found to be approximately 36% higher than those achieved in co-fed operation. In particular, ethylene selectivities were approximately 31% higher for the electrochemical case and always higher than ethane selectivities. C_2 selectivity decreased slightly with increasing oxygen flux for both modes of operation, as shown in Figure 24. Increasing the electrochemical oxygen flux from 0.01 to 0.6 A only decreased total $SC_2\%$ by 19%, from 93 to 75%, while maintaining 20% $XCH_4\%$. In other words, increasing the oxygen flux did not decrease C_2 selectivity dramatically (minimum $SC_2\%=75\%$) but increased methane conversion. This gives a wider range of oxygen feed rates for optimum operation compared to catalysts A & B.

To summarise, a comparison of the three catalysts systems at 850°C is given in Figure 25.

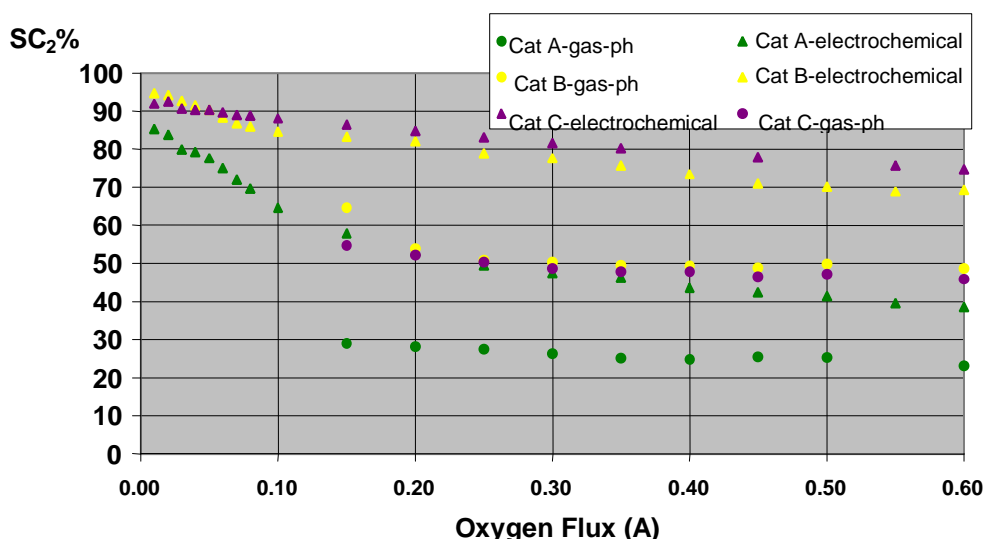


Figure 25 : Comparative study of the effect of the oxygen flux in SC₂% for catalytic & electrocatalytic operation for the catalyst A/YSZ, catalyst B/YSZ and catalyst C/YSZ electrochemical cells at 850°C, 50% CH₄, FRt=60 ml/min.

Figure 26 shows a comparative study of the optimum ethylene selectivity achieved for the electrochemical and co-fed route for methane oxidation (OCM) for the three catalyst systems. The best performance was found when supplying the oxygen electrochemically for the catalyst C system at 850°C which showed maximum SC₂% of 95% at low oxygen flux and 75% (S_{ethylene} = 55%) at high flux with around 20% methane conversion. Co-fed SC₂% at 0.6A (corresponding to a CH₄/O₂ ratio=5) are in very good agreement with those reported by Cambridge’s group and C₂ selectivities achieved electrochemically are the highest ever reported.

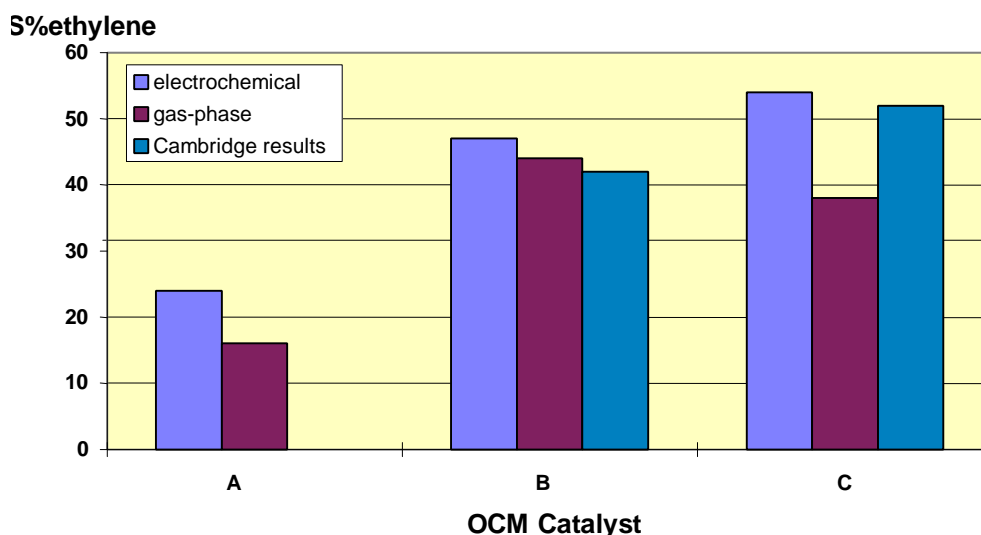


Figure 26 : Comparative study of the maximum ethylene selectivity at XCH₄= 20% for catalytic & electrocatalytic operation of the catalyst A/YSZ, catalyst B/YSZ and catalyst C/YSZ electrochemical cells at 850°C, 50% CH₄, FRt=60 ml/min.

7.5 TASK 3, ACTIVITIES 3.1, 3.2 (*Shell Laboratory, U. of Karlsruhe*)

Adsorption-separation unit optimisation

The adsorption-separation unit plays a key role in the novel laboratory scale gas recycle reactor-separator developed at the University of Patras. In the original work the molecular sieve trap comprised two packed bed units in a swing-bed arrangement. One unit was maintained at 30°C to continuously trap the reactor products, while the other was heated for 15 min to 400°C to release the products in an inert gas stream.

The main objective for the adsorption-separation unit is an energy-efficient separation of the reaction products in the OCM and MMF process. Both processes suffer from low product yields and are operated at high temperature (850°C and 550°C respectively). Conventional hydrocarbon separations are done by cryogenic distillation, involving high-pressure/low-temperature units. During recycling of the unconverted methane a considerable effort has to be made to heat and cool the whole gas stream between the low-temperature separation unit (-100°C) and the high-temperature reaction unit (850°C/550°C). A typical plant would involve a large number of heat exchangers, recycle pumps and gas compressors. This will make the process capital intensive. One way to reduce these capital investments, is the development of an alternative, high-temperature separation unit. In this way, it may be possible to separate the reaction products from methane at temperatures much closer to the reaction temperature, so that considerable savings in the overall heat transfer duty and related with that the capital investments in heat-exchanger equipment can be made.

OCM process: Separation of ethylene

In the current project research has been primarily focused on chemical adsorption processes, and more specific on the adsorption properties of modified zeolite A.

Several adsorbents were experimentally evaluated for the separation of ethylene from methane. It was discovered that modifying zeolite A with silver ions resulted in an adsorbent with unique ethylene adsorption characteristics. With this silver-exchanged zeolite A ethylene can be separated from a gas mixture containing methane, carbon dioxide and ethylene at temperatures up to 250°C.

Unfortunately, the extreme reactivity of silver-exchanged zeolite A with water prevents applications in which water is present. For this reason also a high-temperature water and carbon dioxide removal system was evaluated. Based on thermodynamic calculations it was demonstrated that magnesium oxide could be used to chemically remove carbon dioxide and water at about 200°C. Regeneration of the formed magnesium carbonate and hydroxide can be done by raising the bed temperature to 400-500°C. Additional experiments have to be carried out to demonstrate the feasibility of this high-temperature carbon dioxide and water removal system.

A proposed oxidative coupling process scheme with the two high-temperature separation units is presented in Figure 27.

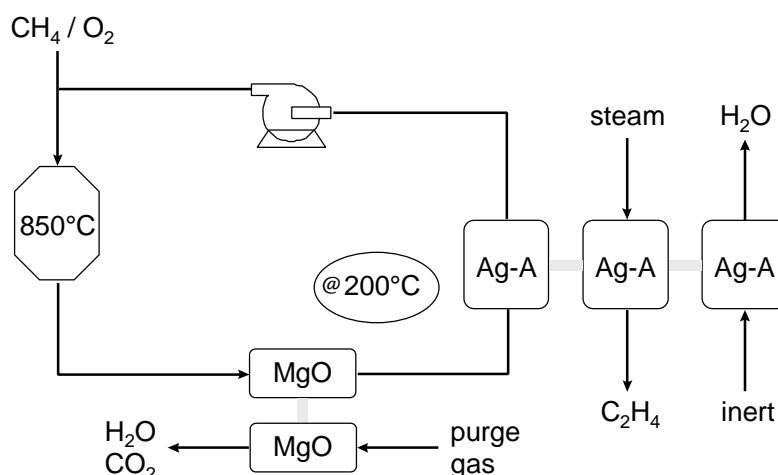


Figure 27 : Proposed oxidative coupling process scheme

One of the main problems we are still dealing with is the choice of a proper stripping agent. In the proposed oxidative coupling process scheme steam is used to strip the ethylene from the adsorbent. In this way ethylene can be isolated simply by condensing the gas stream. However, the regeneration of the adsorbent will be very difficult and time consuming (compare: Shell's Total Isomerisation Process uses adsorption bed cycles of about 6 minutes).

At the moment no suitable alternative stripping agent is available. The choice of a proper stripping agent strongly depends on the raw material specifications in subsequent ethylene consuming processes. Another point of concern is the reaction of acetylenes with silver(I)-ions. Exposing silver(I)-ions to acetylene leads to the formation of an explosive acetylide, Ag_2C_2 . For safe operation the occasionally formed acetylenes have to be removed from the OCM-effluent stream prior to ethylene adsorption in silver-exchanged zeolite A. One possibility to remove these acetylenes, often applied in refineries, is selective hydrogenation over a supported palladium catalyst. This purification step has, however, great implications on the process economics and on the safe handling of both oxygen and hydrogen in the same plant.

Still, we believe that considerable progress is made in the development of a high-temperature ethylene separation unit. The separation process is still not mature enough at the moment to give a thorough evaluation and quantification of its potential advantages. There are several difficulties (some already stated above) to be overcome prior to commercial application. Further exploratory research, mainly technologically driven, is needed to evaluate the economic feasibility of the proposed alternative process scheme.

MMF process: Separation of formaldehyde

The separation of formaldehyde from methane-rich streams is much more complicated than it is for ethylene. Due to the extreme reactivity of formaldehyde only high

selectivities can be achieved at extremely low conversions (yields less than 3-5%). Separation of the reaction products from the gas stream can only be achieved by rapid quenching of the gas stream. This is necessary to avoid polymerisation and further decomposition of the formaldehyde. Even at room temperature it is not easy to handle gaseous formaldehyde. Therefore, formaldehyde is commercial handled mainly in the form of aqueous solutions and as formaldehyde-containing resins. For energy-efficient recycling of the unconverted methane a separation unit at room temperature with low concentrations of formaldehyde in the methane stream is not applicable. Maybe, the formaldehyde yield can be improved if the formaldehyde can be separated immediately after its formation at the reaction temperature (450°C). Unfortunately, no suitable separation methods are available at the moment. There are some developments in membrane technology, but these processes are mainly operated at room temperature and demand for high concentration gradients in order to get high separation selectivities.

In our view it seems that, at this moment, the most efficient way to separate the reaction products from the methane stream is by condensation with water.

Note: methanol would be a more valuable product than formaldehyde, because this is a directly transportable chemical. Unfortunately, the currently investigated catalytic system produces mainly formaldehyde.

7.6 TASK 4, ACTIVITY 4.1 (*U. of Patras*)

Experimental

The experimental setup of the reactor-separator has been described in detail elsewhere[1].The trapping material used for the experiments is Molecular Sieve 5A, which was the best trapping material for the OCM reaction until recently that our Shell partners developed a Ag modified zeolite. However at the time when the experiments were carried out the new Ag modified zeolite had not been developed yet so Molecular Sieve 5A was used. The amount of the mass used in the two traps ,placed in a swing-bed arrangement for continuous flow operation of the recycle unit [1], was 60 gr .This amount of mass was found to be enough so as to trap effectively the desired products, ethylene and ethane.Ethylene was trapped quantitatively while ethane was partially trapped.CO₂ and H₂O were also trapped effectively while CO was not trapped at all.

Experiments were carried out keeping a constant inlet CH₄ flowrate(20% CH₄ in He) and increasing the oxygen inlet flowrate(20% O₂ in He) resulting in higher methane conversions.Oxygen was supplied in a co-feed mode with methane, while oxygen conversion was always complete.During operation of the reactor one of the traps was kept at low temperatures (< 50 °C) so as ethylene and ethane produced per each gas cycle were trapped while the other trap was heated up to 250 °C to release the products in a He stream.In order to check the steady state of the operation 3-6 switches were made between the two traps.The trapping period was one hour.

Results and Discussion

Figure 28 shows the effect of the oxygen inlet flowrate, $F_{O_2}^{in}$, on the product selectivity and CH_4 conversion keeping a constant inlet CH_4 flowrate of $67 \text{ cm}^3/\text{min}$. Increasing oxygen flowrate from 20 to $70 \text{ cm}^3/\text{min}$ methane conversion increases from 40% to 80%, while ethylene selectivity remains almost constant at 60%, which is the best value one can get using this catalyst according to single-pass experiments.

Figure 29 refers to the same experiments (solid lines) and shows the corresponding effect of methane conversion on the yield of ethane and ethylene. Dashed lines in this figure refer to single-pass operation conditions at a constant flowrate $275 \text{ cm}^3/\text{min}$. The increase in the yield during recycle operation is due to the fact that selectivity remains at the high values, even at high methane conversions.

In order to meet the requirements of the project, that is scale-up of the reactor-separator, a second set of experiments was carried out at higher inlet methane flowrate, of $118 \text{ cm}^3/\text{min}$.

Figure 30 compares the yield values for the two set of experiments. As shown for the higher methane flowrate selectivity is lower, especially

at high methane conversions, and thus the obtained C_2 -yield is up to 40% compared to the 50% C_2 -yield obtained at the lower methane flowrate. This is attributed to the lower recycle ratio values, RR (defined as the ratio of the recirculation flowrate, F_r , to the inlet flowrate, F^{in}) when the flowrate is high. Recycle ratio varies from 3.8 to 6.2 in the case of the inlet methane flowrate $118 \text{ cm}^3/\text{min}$ and between 6.6-11.6 in the case of methane flowrate $67 \text{ cm}^3/\text{min}$. These values meet well the requirements of the project which is $RR < 8$.

The present results show that with this catalyst, 2% Mn/5 % Na_2WO_4/SiO_2 , C_2 -yield

up to 50 % is obtained operating the reactor at flowrates up to $140 \text{ cm}^3/\text{min}$ and up to

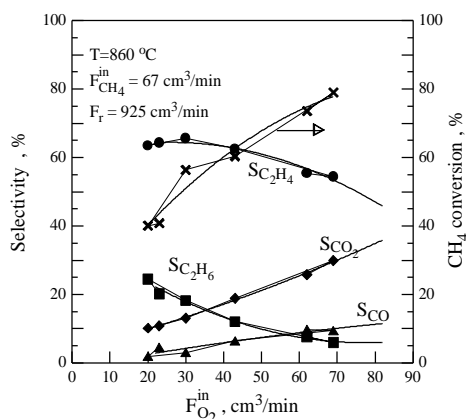


Figure 28 : Effect of the oxygen flowrate on product selectivity and methane conversion

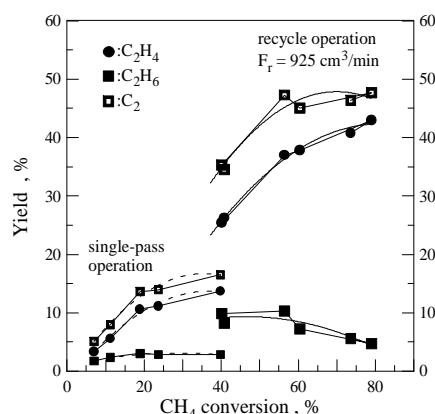


Figure 29: Effect of methane conversion on yield for single pass and recycle operation

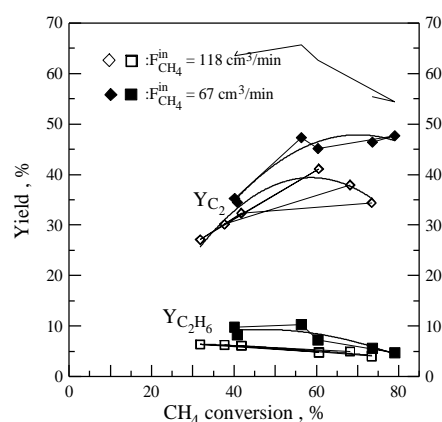


Figure 30 : Comparison of the yield values for the two set of experiments

40% at flowrates up to $240 \text{ cm}^3/\text{min}$. To the best of our knowledge these values are the highest reported so far at such flowrate range. However comparing this catalyst with other OCM catalysts from the literature, i.e. $\text{Sr}(1\text{wt}\%)\text{La}_2\text{O}_3$ we can see that there is a difference in their behaviour. While the general trend for the OCM catalysts is selectivity increasing at low methane conversions, with this catalyst selectivity goes through a maximum upon methane conversion as shown from experiments under single-pass conditions. This behaviour can be attributed to a parallel scheme of the reaction network.

So, the next step in our investigation was to use a catalyst with which one can get high C_2 -selectivity (>80%) at low methane conversions. For this purpose we prepared a $\text{Sr}(1\text{wt}\%)/\text{La}_2\text{O}_3$ catalyst which has been used in earlier studies of the reactor separator [2]. The preparation method followed was incipient wet impregnation as reported in *J. Cat 113, (517-524), 1988*. Figure 31 shows the effect of the $(\text{CH}_4/\text{O}_2)^{\text{in}}$ ratio on CH_4 conversion, C_2H_4 , C_2H_6 and C_2 -selectivity. Increasing the $(\text{CH}_4/\text{O}_2)^{\text{in}}$ ratio CH_4 conversion decreases from 87% to 40% while the C_2 -selectivity increases from 43% to 80%. The effect of the amount of mass of trapping material is also presented. Using larger amount of mass (stars) leads to more effective trapping of ethane, and, as a result, ethane selectivity is higher. On the other hand ethylene selectivity is lower and C_2 -selectivity is unaffected. The obtained yield values are up to 50% C_2 -yield with a corresponding 42% C_2H_4 -yield.

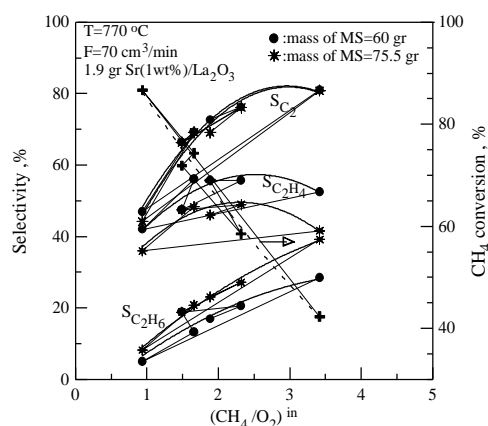


Figure 31 : Effect of the $(\text{CH}_4/\text{O}_2)^{\text{in}}$ inlet ratio on CH_4 conversion and on ethane, ethylene and C_2 -selectivities.

7.7 TASK 4 , ACTIVITY 4.2 (U. of Patras)

MMF Reactor-Separator

Having carried out the single-pass experiments for the MMF reaction (partial oxidation of methane to formaldehyde) it was found that V_2O_5/SiO_2 is a good catalyst for this reaction achieving HCHO selectivity of the order of 80%, but at very low methane conversion (<1%). In order to operate the reactor-separator a suitable trapping material for the formaldehyde should be used. It was found that water is the best "adsorbent" for HCHO, so that formaldehyde solution is formed in the trap unit. So the trap unit was loaded with 15-20 ml of water. Formaldehyde in the solution was measured with an F.I.D. detector. The experimental setup for the reactor separator is similar to the one used for the OCM process with a slight difference in the trap unit where there is only one trap instead of two traps placed in a swing bed arrangement. The reactor used for the recycle operation was a quartz plug flow reactor of volume 7 cm^3 filled with 1.09 gr of catalyst.

Experiments were carried out keeping a constant flowrate and varying the $(CH_4/O_2)^{\text{inlet}}$ ratio. The total inlet flowrate was 30 cm^3 while the recycle flowrate was $F_r=380\text{ cm}^3$ resulting in a recycle ratio $RR=12.7$. The results are shown in Figure 32 where HCHO selectivity (32a) and yield (32b) is plotted upon CH_4 conversion for both single-pass and recycle operation. As shown HCHO selectivity in the recycle operation is higher compared to that at single-pass operation conditions at high methane conversion (of the order of 10%). The obtained yield value under recycle operation is 6% which is much higher than the 0.6% obtained under single-pass conditions as better presented in figure 18. To the best of our knowledge this is the highest reported value in literature.

An important parameter that one should take care of is oxygen conversion to be less than 100% as it was found from the single-pass experiments that at conditions of complete oxygen conversion formaldehyde selectivity is lower. In table 1 are presented the data from experiments under recycle operation where it is shown that in case of complete oxygen conversion (No 5) the corresponding formaldehyde selectivity is 9.3%, compared to 48.3% when oxygen conversion is 92% (No 4) and at the same time methane conversion is almost the same.

Table 1

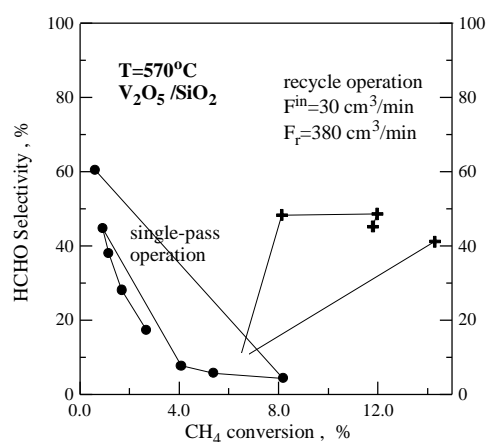


Figure 32a : Effect of CH_4 conversion on HCHO selectivity for both single-pass (·) recycle operation (+)

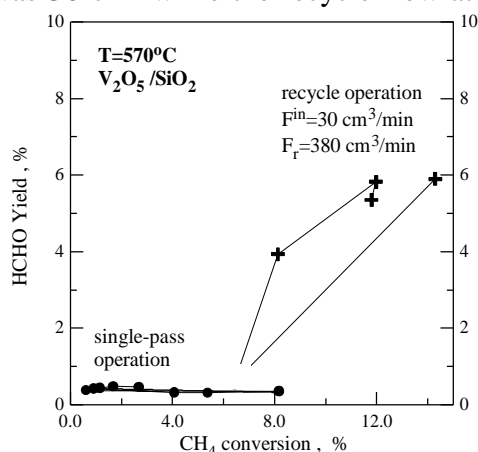


Figure 32b : Effect of CH_4 conversion on HCHO yield for both single-pass (·) recycle operation (+)

No	CH ₄ ⁱⁿ (%)	O ₂ ⁱⁿ (%)	X _{CH₄} (%)	X _{O₂} (%)	S _{HCHO} (%)	Y _{HCHO} (%)
1	43.21	13.66	11.8	67	45.22	5.35
2	45.56	14.26	11.98	81	48.63	5.82
3	48.52	12.35	14.3	79	41.2	5.9
4	64.33	9.7	8.13	92	48.35	3.93
5	60.38	9.32	6.43	100	9.3	0.59

From the above it is clear that the design of the novel gas recycle reactor separator favours the obtained yield in formaldehyde for the partial oxidation of methane. The trap unit protects from further oxidation formaldehyde and thus one can maintain high formaldehyde selectivity at higher methane conversion resulting in higher yield values.

7.8 TASK 4, ACTIVITY 4.3 (LPC Hellas)

KINETIC MODEL (mass balance)

A model which describes the continuous flow operation experimental data for O.C.M. reaction, has been developed. This model can describe the dependence of product distribution on the recycle ratio. We assume that the reactor is a CSTR and that we have linear kinetics for all the chemical reactions taking place. For simplicity, we also assume 100% trapping of water in the trap.

One can write the mass balance equations as follow:

Total mass balance equations

$$CH_4: G_E y_1^E = G_F y_1^O - k_1 A y_1^R y_O^R$$

$$C_2H_6: G_E y_2^E = (1/2) k_1 A y_1^R y_O^R - k_2 A y_2^R y_O^R - k_{t2} A_t y_2^R$$

$$C_2H_4: G_E y_3^E = k_2 A y_2^R y_O^R - k_3 A y_3^R y_O^R - k_{t3} A_t y_3^R$$

$$CO_2: G_E y_4^E = 2k_3 A y_3^R y_O^R - k_{t4} A_t y_4^R$$

$$O_2: G_E y_O^E = G_O y_O^O - (1/4) k_1 A y_1^R y_O^R - (1/2) k_2 A y_2^R y_O^R - 3k_3 A y_3^R y_O^R$$

$$He: G_E (1 - y_1^E - y_2^E - y_3^E - y_4^E - y_O^E) = G_F (1 - y_1^O) + G_O (1 - y_O^O)$$

Mass balance equations for the reactor

$$CH_4: G_R y_1^R = G_F y_1^O + (R G_F) y_1^E - k_1 A y_1^R y_O^R$$

$$C_2H_6: G_R y_2^R = (R G_F) y_2^E + (1/2) k_1 A y_1^R y_O^R - k_2 A y_2^R y_O^R$$

$$C_2H_4: G_R y_3^R = (R G_F) y_3^E + k_2 A y_2^R y_O^R - k_3 A y_3^R y_O^R$$

$$CO_2: G_R y_4^R = (R G_F) y_4^E + 2k_3 A y_3^R y_O^R$$

$$H_2O: G_R y_5^R = (1/2) k_1 A y_1^R y_O^R + k_2 A y_2^R y_O^R + 2k_3 A y_3^R y_O^R$$

$$\begin{aligned}
 O_2: \quad G_R y_O^R &= G_O y_O^O + (R G_F) y_O^E - (1/4) k_1 A y_1^R y_O^R - (1/2) k_2 A y_2^R y_O^R - 3 k_3 A y_3^R y_O^R \\
 He: \quad G_R (1 - y_1^R - y_2^R - y_3^R - y_4^R - y_5^R - y_O^R) &= \\
 &= G_O (1 - y_O^O) + G_F (1 - y_1^O) + (R G_F) (1 - y_1^E - y_2^E - y_3^E - y_4^E - y_O^E)
 \end{aligned}$$

The above sets of equations are used in a dimensionless way. Independent variables are O_2 feed and recycle ratio, whereas adjustable parameters are the kinetic constants. These sets have been used to fit the experimental data. As shown in figures 33 this model provides a satisfactory fit to the data.

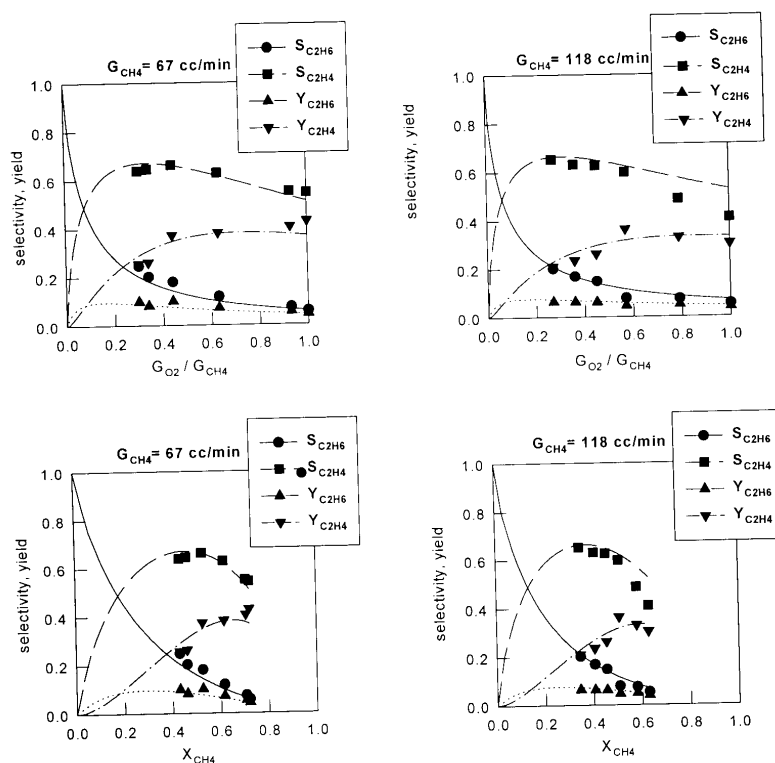


FIGURE 33 : C_2H_6 and C_2H_4 selectivity and yield versus O_2 dimensionless feed rate and CH_4 conversion, for different CH_4 feed rates. Lines are plotted by model (2% Mn/5% Na_2WO_4/SiO_2 , recycle ratio 8-14, $T=860^\circ C$)

Industrial application - Conclusions

Using the kinetic model and the estimated dimensionless kinetic constants for the same catalyst and reaction temperature, according to the above assumptions, it is calculated that 1180 kt NG/year are consumed for the production of 800 kt C_2H_4 / year. The yield of the unit concerning C_2H_4 production is up to 79% (carbon balance), where as the yield per pass through the reactor is only 18%. The combination of hot and cold steams optimizes the energy saving. The exceeding amount of heat co-produced is extremely high, up to 256 Gcal/h or 300 MW and can be used for the heating of the adsorbers as well as for other needs. In the outlet of the unit, the gas

stream contains 42% CH₄ and 2.5% C₂H₆. It can be used to generate 150 MW electrical power, assuming 35% total yield of the unit (diesel engines-generators). This is also an extremely high power able to satisfy needs beyond the process. This is totally the 33% of the thermal power produced in the case of total combustion of the same amount of Natural Gas. The financial advantages of the industrial application of this process are obvious.

8. EXPLOITATION PLANS AND ANTICIPATED BENEFITS

For a proper technological and economic evaluation of the proposed alternative methane conversion process two potential markets can be considered: (a) the production of ethylene as a commodity for the petrochemical industry, and (b) the production of liquid fuels for the fuel industry, each with its specific economic implications.

For the fuel industry, natural gas based technology (either direct or indirect) may only be attractive in remotely located areas where large quantities of inexpensive natural gas are available. A competitive process in this field is the indirect route via synthesis gas using Fischer-Tropsch technology. To evaluate the oxidative coupling of methane with this indirect conversion process, assumptions have to be made with respect to the subsequent conversion of ethylene to gasoline. Because of lack of reliable data for the atmospheric conversion of diluted ethylene streams to gasoline, we have only evaluated the oxidative coupling of methane for the production of ethylene for the petrochemical industry.

In the petrochemical industry, ethylene production is currently based on steam cracking technology. Feedstocks range from ethane to gas oil depending on availability, location and price. In North America the preferred feedstocks are Natural Gas Liquids (C₂-C₁₀) and particularly ethane, because of abundant low-cost natural gas. In Europe, (more expensive) naphtha is the predominant ethylene feedstock. Several research institutes and chemical companies have already made extensive process economics evaluations for the oxidative coupling of methane, almost all compared with conventional ethane steam cracking. A comparison with naphtha steam cracking is more complicated: in the case of naphtha steam cracking the feedstock price is higher and the distillation train is more sophisticated resulting in higher capital investments. But, from naphtha steam cracking more value-added products besides ethylene are formed which can justify the capital investments. Roughly said, an evaluation with ethane steam cracking technology as base case suffices for a preliminary economic evaluation of the oxidative coupling of methane. In the study of Chem Systems Inc. (1994) a catalytic system comparable with the OCM catalyst developed at Cambridge University was compared with ethane steam cracking. A cryogenic distillation train was used for the separation of the products and a caustic scrubber and a molecular sieve trap were used for the removal of carbon dioxide and water. The main conclusion of this study was that oxidative coupling of methane is not competitive with ethane steam cracking at the moment (due to about 21% higher capital investments). The main capital investments (67%) were however related with the recovery of ethylene. They stated that a simplification of the recovery unit has the greatest potential for reduction of the capital requirements.

The development of a new separation unit obviously has a great impact on the installed capital costs. However, this alternative separation process still is not mature enough to give a thorough evaluation and quantification of its potential advantages. There are some difficulties to be overcome prior to commercial application. Further exploratory research, mainly technologically driven, is needed to evaluate the economic feasibility of the proposed alternative process set-up. Some follow-up R&D efforts and active gate-keeping programs shall be initiated within Shell to keep up with the developments in this field, and to be able to make a proper economic evaluation of the proposed alternative process set-up.

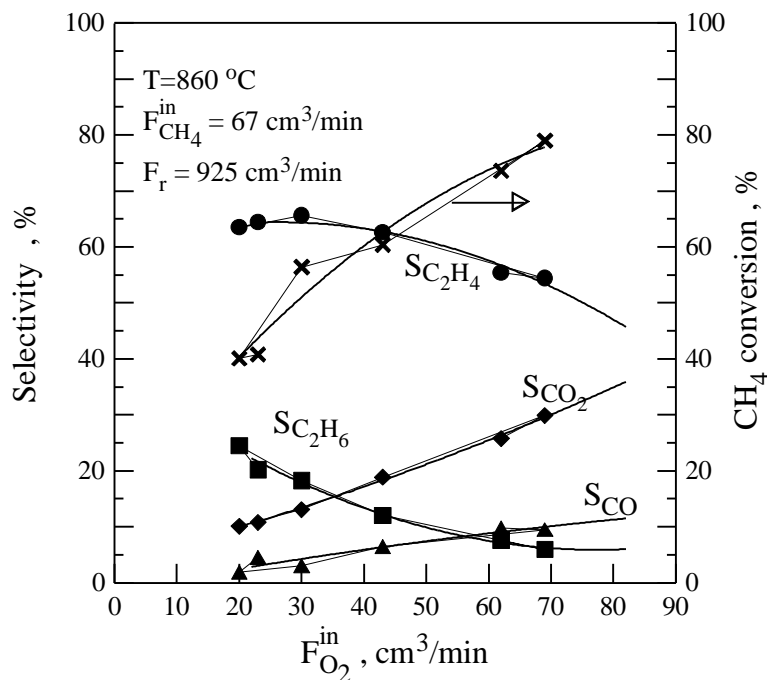
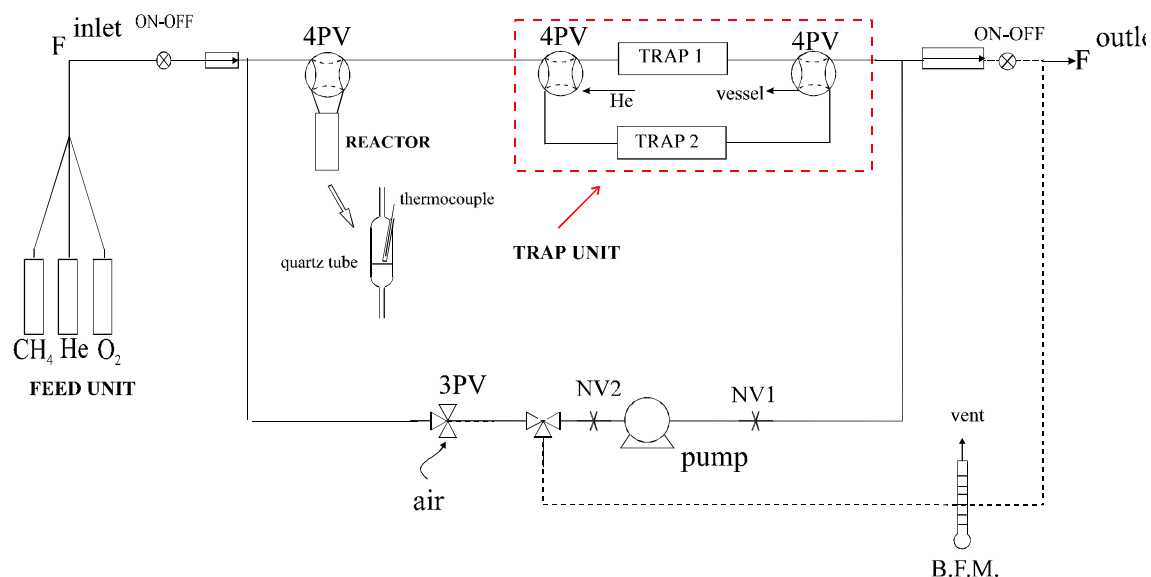
Concluding, at this moment of time there is no economic, commercial drive for alternative processes to ethylene. For an OCM concept at present there are no cost advantages. Shell has not the intention to commercialise an oxidative coupling process in the near future, because no real breakthrough technology is developed so far, which justifies a switch to an alternative ethylene production process. However, in the future, when the feedstock slate might change drastically, economics may become more favourable.

Concerning the other part of the project for the direct conversion of methane to formaldehyde the formaldehyde market is still growing. Due to its great variety of applications, it will not be replaceable in the near future. The large fluctuations in the price of the basic product for the usual formaldehyde production process, methanol, would favour a new technique in which methanol can be replaced. The process investigated in this project uses the primary raw materials, methane and air, for a direct conversion to formaldehyde. Methane is available at many locations at relatively low costs. Additionally this process has the advantage of using exothermic reaction paths, the highly endothermic production of synthesis gas can be avoided. Furthermore, this process could be used for the production of a chemical easy to store and transport, i.e. formaldehyde in the commercial form of aqueous solutions. Using the investigated one-step process this could be performed even at locations where methane is presently being flared due to missing transport facilities. Hence the energy efficiency of the newly developed process is without question; economically, the process has to be calculated based upon industrial figures regarding manpower, investment and operating costs.

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10. NOVEL REACTOR-SEPARATOR FOR THE OXIDATIVE COUPLING OF METHANE : SCHEMATIC AND PERFORMANCE



Effect of oxygen inlet flowrate on product selectivity and methane conversion.