THE UNIVERSITY OF HULL

“The Application of Microwaves to some Heterogeneously Catalysed Reactions.”

being a thesis submitted for the Degree of

Doctor of Philosophy
in the University of Hull.

by

Christopher J Bool, B.Sc.

July, 1997.

1. Introduction

2. Oxidative Coupling of Methane

3. Steam Reforming of Methane and Methane Combustion

4. Experimental

5. Results

6. Other Reactions

7. Discussion

Abstract

Three heterogeneously catalysed reactions have been investigated using both conventional and microwave heating of the catalyst bed.

The oxidative coupling of methane reaction has been widely studied using conventional methods of catalyst heating but only limited works have investigated the continuous microwave heating of catalysts. This research compares the two methods of catalyst heating in detail. Catalysts based on rare - earth oxides and chloride containing materials were studied.

The combustion of methane reaction has also been studied under microwave and conventional heating methods. The reaction has attracted some attention in recent years with the increasing research in the area of natural gas powered vehicles. Emission regulations for the automotive industry are becoming increasingly stringent and the clean up of exhaust emissions from natural gas vehicles is of increasing interest.

For both of the above reactions, the microwave heated example occurred at lower bulk temperatures than the conventionally heated reaction. However, documented equilibrium constant calculations show that the actual reaction temperature was far in excess of the observed bulk temperature. It is therefore postulated that there exist within the catalyst bed small areas which are at elevated temperature relative to the observed bulk temperature. Such areas are thought to be where the reaction actually occurs and have been termed “hot spots”.

Temperature measurement in a microwave field is not a simple matter and the observations from the studies of the above reactions prompted further investigation into the "hot spot" theory.

The well documented steam reforming of methane reaction was studied under microwave conditions. Equilibrium constant calculations enabled the reaction to be used as a "chemical thermometer". Reference to temperature - equilibrium constant data for the reaction revealed that temperatures well in excess of the observed bulk temperatures were indeed achieved and provided confirmation of the "hot spot" theory.

1. Introduction

1.1 The Use of Microwaves to Heat Materials

Microwave equipment has been available since the 1950s and was popularised in the USA. However it was not until the late 1970s and early 1980s that domestic microwave ovens were a common feature in UK households. There is now a whole industry devoted to pre - packaged microwave meals. However, the impact of microwaves on Chemistry has not been so dramatic. This is unfortunate since the mode of heating under microwave conditions depends upon the dielectric properties of the material. Therefore certain chemical reactions may exhibit different product selectivities when microwaves are used depending upon the way in which the materials under irradiation interact with the applied field.

1.2 Origins of Microwave Radiation

During the development of RADAR during the Second World War, Randall and Booth invented the magnetron, a device which generates fixed frequency microwave radiation.

The magnetron (shown in Fig. 1.1) is a cylindrical diode with an anode and cathode. A magnetic field aligned with the cathode is superimposed on the diode. A ring of mutually coupled resonant cavities is in the anode so that as a potential of several thousand volts is reached across the diode, the released electrons under the influence of the magnetic field, resonate and the magnetron oscillates. The oscillating electrons surrender energy to the microwave field that radiates from an antenna enclosed in the vacuum envelope of the tube.

The microwave region of the electromagnetic spectrum lies between infra-red and radio frequencies at frequencies of between 300 MHz and 30 GHz and this corresponds to wavelengths of 1 cm to 1m. Wavelengths between 1 cm and 25 cm are extensively used for RADAR applications and the remaining wavelength range is used for telecommunications. In order not to interfere with these uses, domestic and industrial microwave apparatus are required to operate at one of four frequencies these being 0.915 ± 0.025 GHz, 2.450 ± 0.013 GHz, 5.800 ± 0.075 GHz and 22.125 ± 0.125 GHz. Of these, 2.450 GHz is the most commonly used and is the frequency used in domestic microwave equipment.

The theory of microwave heating has been studied by many workers and several excellent reviews of the subject have been published.[1,2,3]

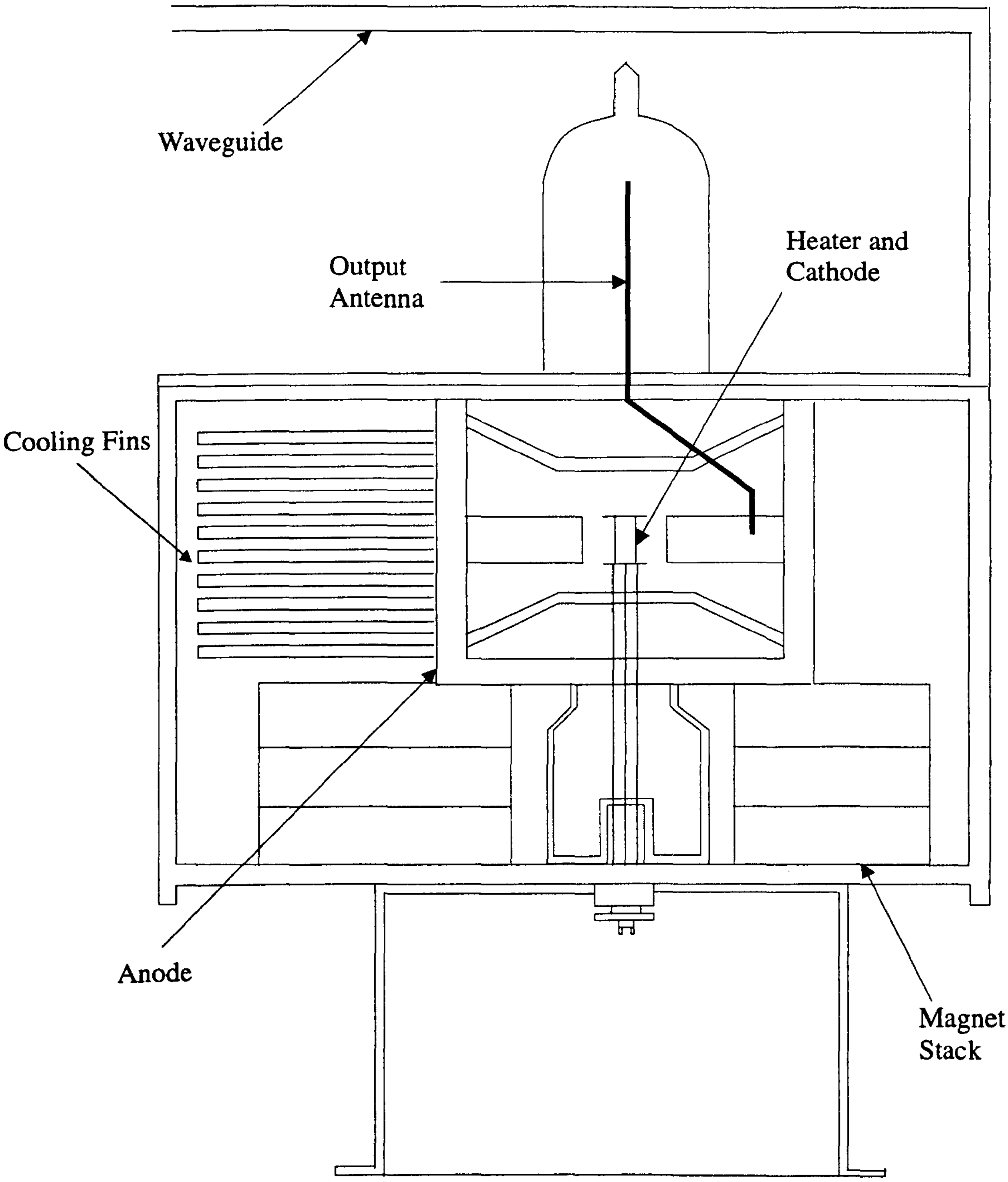


Figure 1.1. Schematic Representaion of a Fixed - Tuned Magnetron

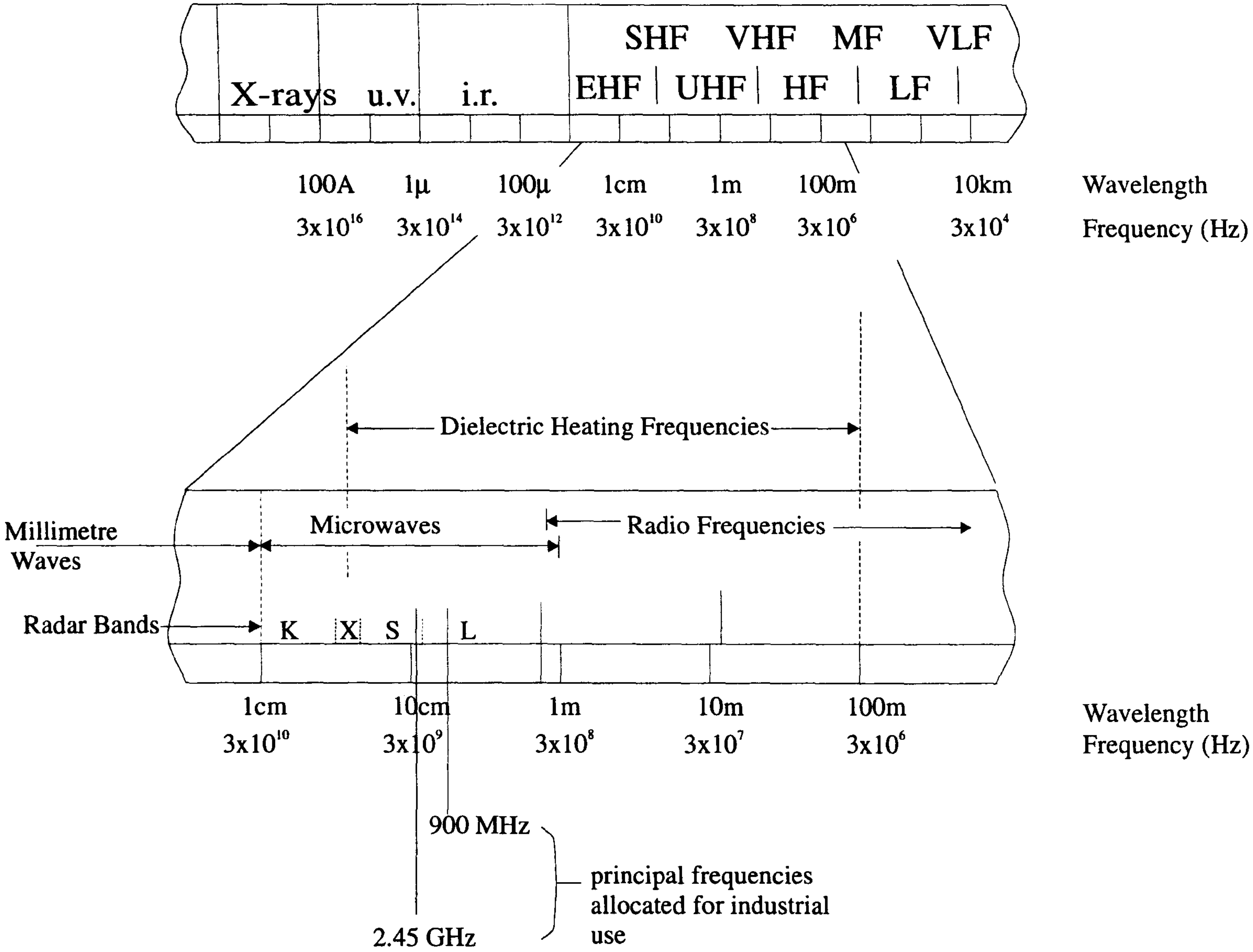


Figure 1.2. Schematic Diagram of the Electromagnetic Spectrum showing the Microwave Region

1.2.1 Mechanisms of Microwave Heating

The two principal mechanisms whereby microwave energy is lost to a sample are ionic conduction and dipole rotation.

1.2.1.1 Ionic Conductance

Ionic conductance is the migration of ions within a sample due to the applied microwave field. This migration results in heat production due to I^2R losses. This form of microwave heating is particularly important when considering the heating of liquid samples containing dissolved ions. The magnitude of the contribution to heating of ionic conductance depends on ionic concentration and mobility.

1.2.1.2 Dipole Rotation

Dipole rotation refers to the alignment and rotation of charges and dipoles within a sample due to the applied field. The inability of the resulting polarisation to follow rapid reversals in the direction of the field results in the heating of the sample.

1.2.1.3 Dielectric Polarisation

The total polarisation effect is defined as the following:

$$\alpha_t = \alpha_e + \alpha_a + \alpha_d + \alpha_i + \alpha_v$$

Where:

α_e is the electronic polarisation arising from the realignment of electrons around specific nuclei.

α_a is the atomic polarisation which results from the relative displacement of nuclei due to unequal distribution of charge in the molecule.

α_d is the dipolar polarisation resulting from the orientation of permanent dipoles by the electric field.

α_i is the interfacial polarisation (Maxwell - Wagner effect) which occurs when there is a build up of charge at interfaces.

α_v is the vibrational polarisation.

When an electric field is applied to a material at low frequency, the dielectric polarisation is able to keep in phase with the field. This field is able to bring the molecules within the sample into alignment. Some energy is transferred each time a molecule is disturbed and realigned but this is insufficient to increase the temperature of the material.

The polarisation of α_e and α_a are far too rapid when a material is exposed to an oscillating electric field and as such do not contribute to the heating effect as there is no phase lag between the changes in direction of the field and the polarisation. However, α_d and possibly α_i are polarised and depolarised in a timescale comparable to microwave frequencies.

If a high frequency field is applied, its direction changes faster than the response time of the dipoles and as such there no energy is absorbed and no increase in temperature is observed.

If the timescale of the change in direction of the electric field is comparable to the response time of the dipoles within the sample, the dipole rotates but the polarisation lags behind the field. When the electric field is removed and the molecules return to their natural disorder, thermal energy is released. At a frequency of 2.45 GHz, this occurs 4.9×10^9 times a second and therefore very rapid heating may result. This heating is dependent on a number of properties of the material including dielectric properties and the relaxation time of the sample.

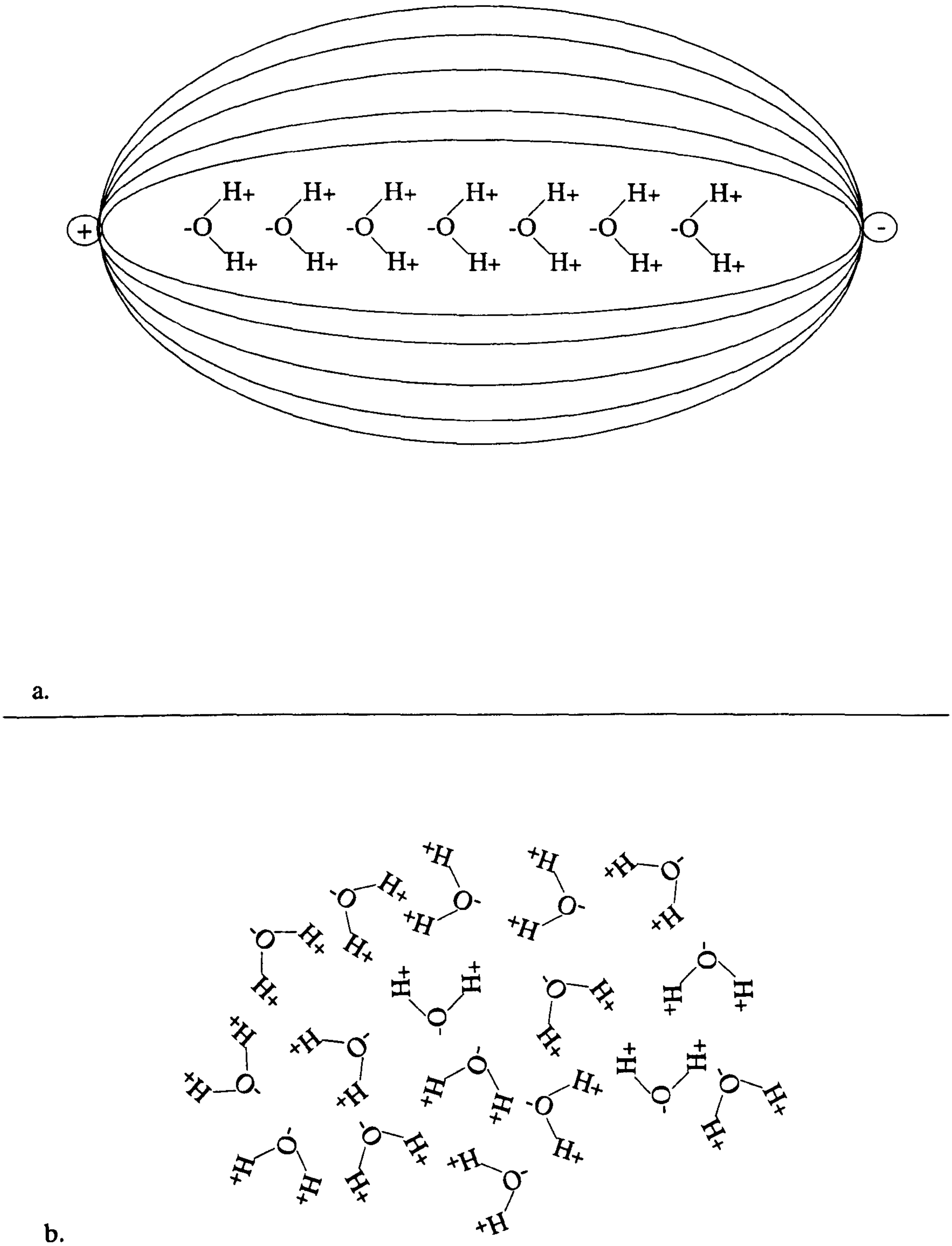


Figure 1.3. Schematic Representation of the Molecular Response to an Electromagnetic Field
a) polarised molecules align with the field
b) thermally induced disorder as field is removed

1.2.2 Dielectric Properties

The ability of a sample to be heated in a microwave field is very much dependent upon its dielectric properties.

The dielectric constant, ε′, of a material is a measure of its ability to be polarised by the incoming microwaves.

$$\varepsilon' = \frac{C}{C_0}$$

Where C is the capacitance or ability to store charge by the material and C_0 is the capacitance of air.

The dielectric loss of a sample ,ε″, is a measure of the efficiency with which the radiation is converted to thermal energy.

$$\varepsilon'' = \frac{\sigma}{2\pi f}$$

Where f is the frequency of the applied microwaves and σ is the dielectric conductivity.

From these properties a quantity known as tan δ can be calculated. Tan δ (the dissipation factor) is defined as the ability of a sample to convert electromagnetic energy into heat at a given temperature and pressure. It is calculated by taking the ratio of the dielectric loss to the dielectric constant.

1.2.3 Penetration Depth

The penetration depth of a material is an important factor in microwave chemistry as it influences the efficacy or otherwise with which samples may be heated in the microwave field. The penetration depth of a sample is defined as the depth into the material where the power is reduced to ½ the value at the surface of the material. The penetration depth may be calculated using the following equation:

$$Dp = \lambda o \frac{\varepsilon'}{2\pi\sqrt{\varepsilon''}}$$

Where ε'' is small and λ_0 is the wavelength of the microwave radiation. Throughout this study, the wavelength of microwave radiation was 12.2 cm.

1.2.4 Dielectric Relaxation Time

The dielectric relaxation time is the time taken for 63% of the molecules in the medium to return to their natural disorder. This will occur when

$$\omega = \frac{1}{\tau}$$

Where $\omega=2\pi f$.

If $1/\tau$ corresponds to the angular frequency of the microwave radiation, as is the case for a non-ionic polar sample, the dissipation factor (tan δ) will be high. If $1/\tau$ is different from ω then the dissipation factor will be low.

If water is considered as a model example, when it is heated in the microwave field, the dielectric relaxation time and dissipation factor are changed and hence the penetration depth will change. As the temperature of the water is increased, tan δ is decreased since $1/\tau$ increases with temperature.

1.2.5 Interfacial Polarisation (Maxwell-Wagner Effect)

Interfacial polarisation is the build up of charge in a non homogeneous system at the interface between conducting and non conducting particles. Wagner[4] devised a simple model for the effect involving conducting spheres distributed through a non conducting medium A model for interfacial polarisation was devised by Maxwell and Wagner and consisted of a two layer capacitor configuration. The total effect is seen as a composite produced by areas having different dielectric constants and conductivity.

1.2.6 Thermal Runaway

Thermal runaway is an uncontrollable increase in the temperature of a material whilst under microwave irradiation. Following initial exposure to the microwave field, the temperature of the material increases with a corresponding increase in the dielectric loss (ε''). This continues so that for a given power input, more and more is converted to heat and ε'' increases more rapidly with time. If a critical temperature is reached, tan δ achieves such a value that the material is converting a large proportion of the applied energy to heat and the runaway effect is observed.

1.2.7 Types of Microwave Cavity

There are two major types of microwave cavity currently in wide usage. These are designated multi - mode and single mode cavities.

1.2.7.1 Multimode Cavities

The multi - mode cavity has been in existence for many years. The traditional domestic microwave oven is an example of the multi - mode variety. Multi - mode devices have also found use in chemistry for tasks such as acid digestion of inorganic materials and organic syntheses. The components of the multi - mode cavity are relatively basic and comprise a magnetron, section of waveguide and the actual cavity itself. For domestic use, a turntable is usually included in an attempt to increase the uniformity food heating. Multi - mode devices in the laboratory often utilise a mode stirrer in order to create a more uniform microwave field in the cavity.

1.2.7.2 Single Mode Cavities

Single mode microwave cavities are more complex than multi - mode systems and utilise certain components which are not always included in the latter. The components of the single mode device used for catalytic experiments during this study will be discussed in greater detail later. At this stage a brief description may suffice. A single mode microwave cavity is able to produce a stronger electric field than multimode devices and the radiation can be tuned to produce a maximum in the E field at the sample which is being irradiated. This may be particularly useful when non - lossy materials are being tested. A device known as a circulator is included in the apparatus to prevent any reflected radiation which is not absorbed from damaging the magnetron.

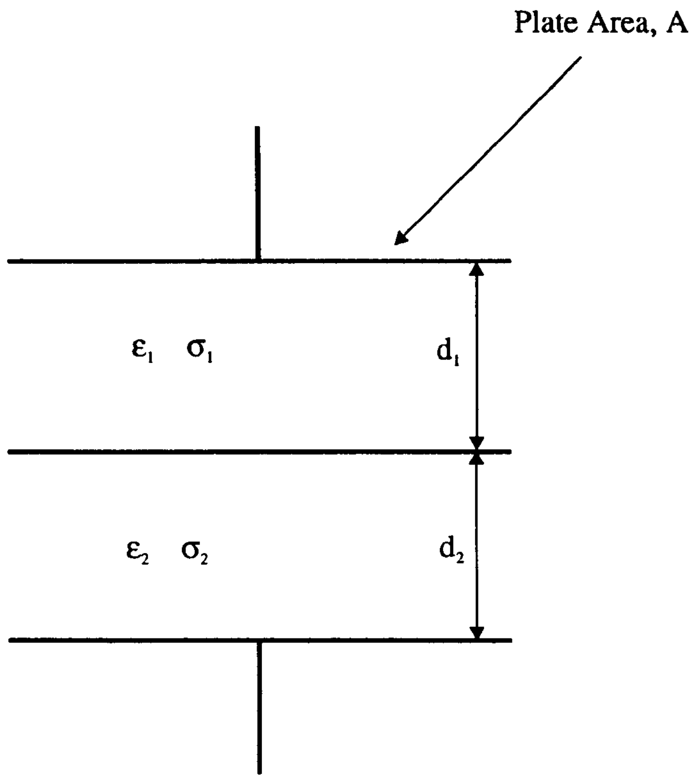


Figure 1.4. The Maxwell - Wagner two layer capacitor model

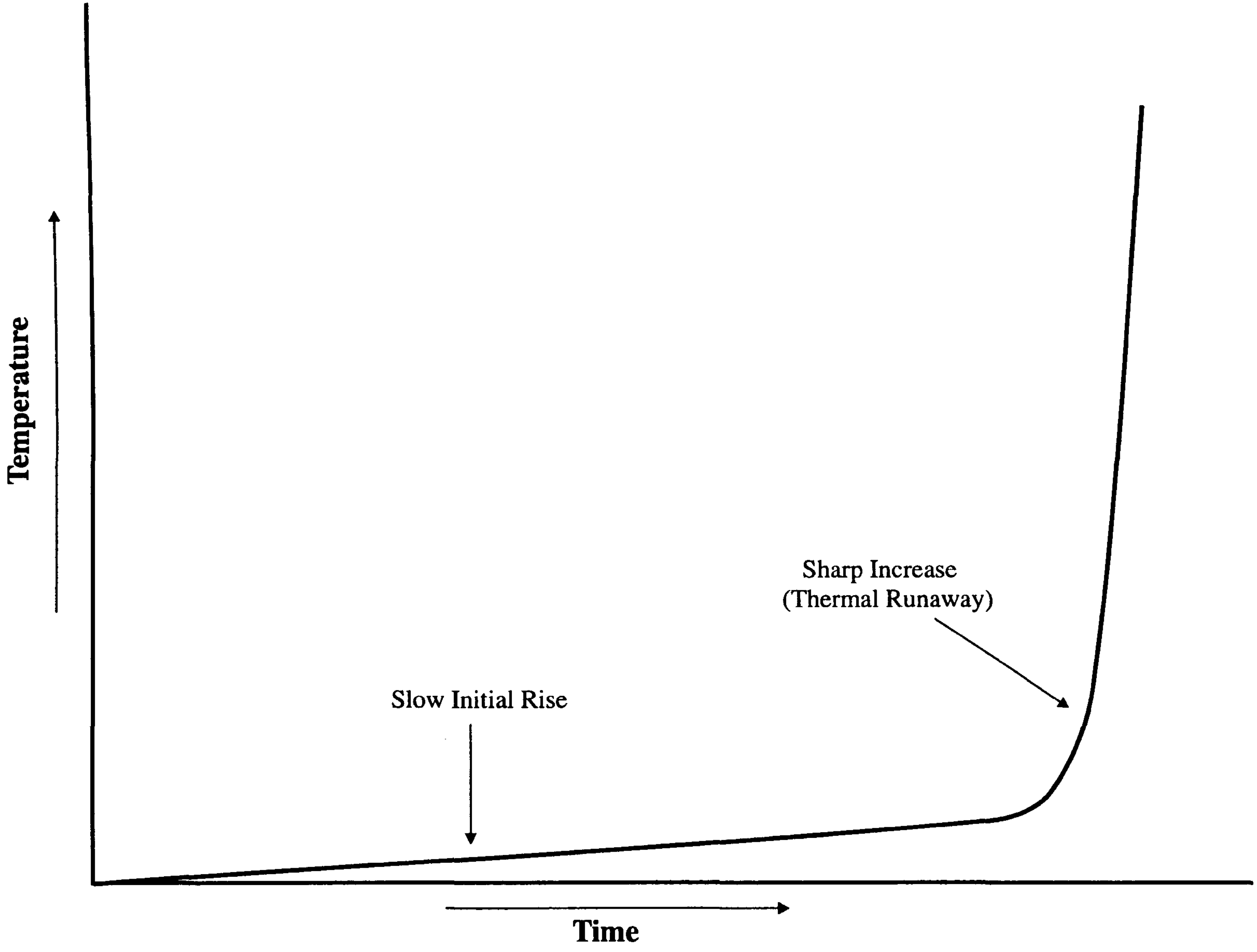


Figure 1.5. Illustration of Thermal Runaway Effect

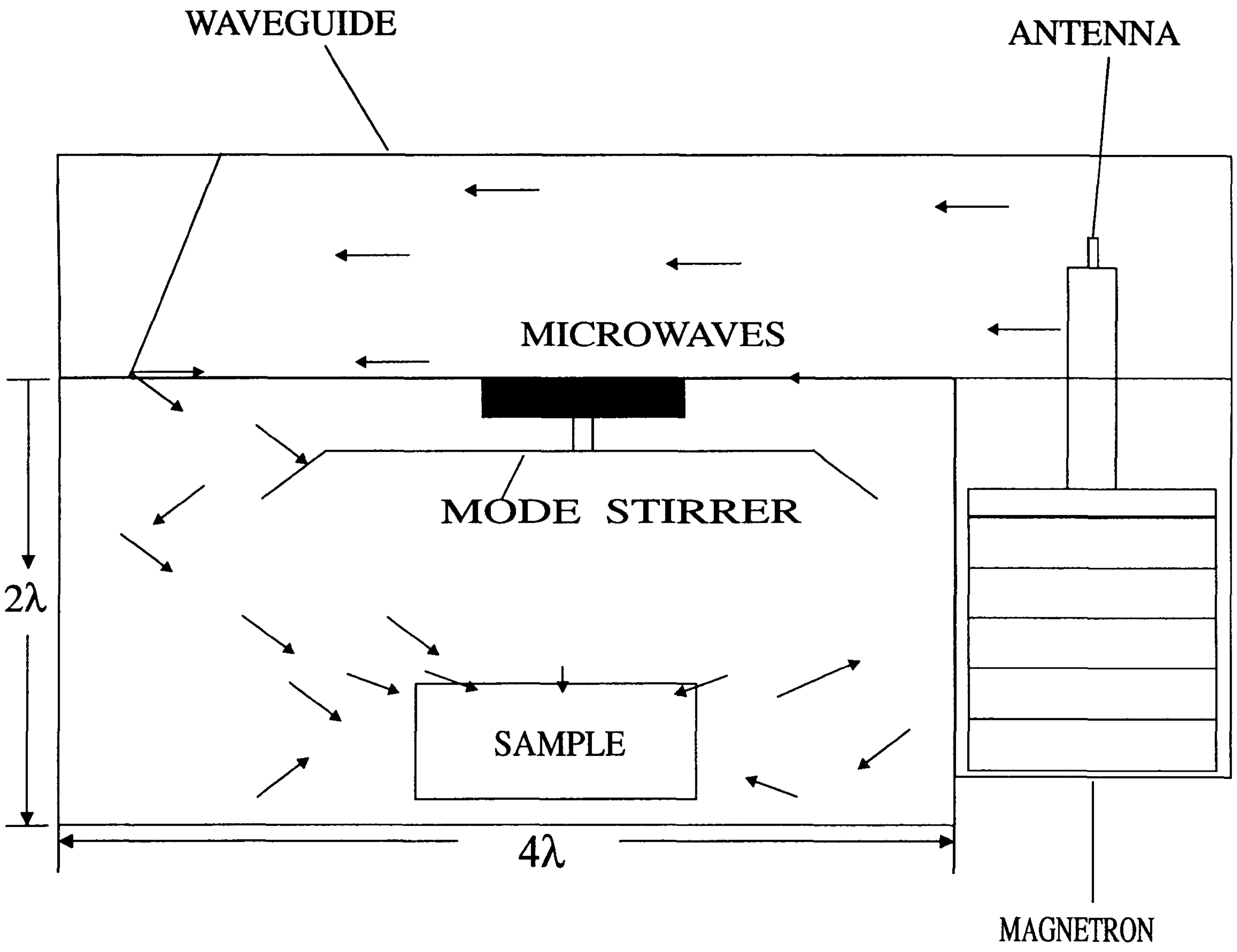


Figure 1.6. Schematic Representation of a Multi - Mode Microwave Cavity

1.2.8 Microwaves in Chemistry

The early uses of microwaves in laboratories were for relatively simple tasks such as moisture analysis and wet ashing procedures of geological and biological materials. The fact that microwaves could rapidly heat a variety of samples led to them being used subsequently for the heating of acid and ore samples as greatly reduced processing times were observed by their use.

It was not until the mid 1980s that research into the use of microwaves as the heat source for organic chemical reactions was performed. Giguere et al and Gedye and co-workers[5 - 9] noticed that massive rate enhancements (sometimes as large as 200 times) were achieved for a series of organic reactions when microwaves were used to heat the reactants. The work was performed in modified domestic microwave ovens using sealed containers.

What was not realised at the time was the fact that large pressures were obtained during irradiation due to the use of sealed reaction vessels. This in addition to the superheating of reactants (which is a well known phenomenon in the microwave heating of certain liquids) was found to be the cause of the observed rate enhancements. When this fact came to light, it led Gedye to conclude that there was no so called "Microwave Effect" during his microwave heated reactions.

In addition to synthetic applications, microwaves have also found use in analytical chemistry for tasks such as acid dissolution of samples prior to spectroscopic analysis.

1.2.9 Microwaves in Catalysis

The use of microwaves in the field of catalysis is very much still in its infancy but today there are several active research groups throughout the world. The work in the field is quite diverse and a number of different experimental techniques have been investigated. For example, Wan and co-workers in Canada have used pulsed microwave techniques for a number of reactions including a mimicry of photosynthesis, reactions over wetted carbon catalysts and the production of higher hydrocarbons from carbon dioxide and water.[10 - 12] This work utilised high power micro and millisecond "pulse packets" of radiation in order to perform the required reactions. It was noted that microwaves had the potential to perform reactions which would otherwise be extremely difficult or even impossible under conventional methods of heating. Wan introduced the concept of a "sensitiser" which he described as a conducting particle in a non - conducting medium.[12] This sensitiser selectively absorbed the applied microwave energy and was rapidly heated to high temperatures. The heat thus generated would then be dissipated by the support medium.

Further use of microwaves in catalysis has been found in catalyst characterisation and preparation.

1.2.9.1 Catalyst Characterisation

The use of microwaves for temperature programmed techniques such as thermogravimetric analysis and temperature programmed decomposition has been studied by Bond et al.[13] Using a continuous irradiation heating method a catalyst sample was heated at a constant rate in a single mode microwave cavity using the continuous irradiation technique. It was found that a more linear rate of heating was achieved by microwave heating and also that a sharper more distinctive decomposition profile was obtained by use of the microwave technique. A further advantage was the fact that following a microwave decomposition, the sample cooled far more rapidly than under conventional heating clearly suggesting that a higher throughput of samples was possible for the microwave experiment.

1.2.9.2 Catalyst Preparation

In addition to the use of microwaves to heat catalytic reactions, they have also found use in chemistry in the preparation of catalysts.

The use of microwave radiation for drying purposes has been well established in the ceramic industry[14 20] and recently microwaves have been used to dry supported metal catalyst precursors. Bond et al[13] have shown that the use of microwaves gives several advantages over conventional methods of catalyst drying. It was reported that reduced drying times (of between a factor of two and three) and increased crush strengths of the prepared pellets were observed. The observations were attributed to the different methods of water removal between microwave and conventional heating. Water interacts very strongly with microwave radiation (due to the presence of dipoles) and it was stated that during microwave catalyst drying, the region of the catalyst with the highest water content (i.e. the wettest part) interacted more strongly with the applied field than other parts of the catalyst and therefore this area became the hottest region of the sample. The heat generated from this area was imparted to other areas within the catalyst (containing less water) and allowed an enhanced rate of evaporation from the cooler regions. This produced a small moisture gradient within the sample and this process is commonly known as moisture levelling. During conventional heating, the sample is heated form the outside and this leads to a moisture flow from the wet inside to the outside of the material resulting in a high moisture gradient across the sample and tension at the surface. The lack of tension for microwave prepared samples results in a stronger catalyst pellet. These observations coupled with energy dispersive X-ray analysis (EDXA) evidence also revealed that the distribution of active metal within the sample was far more homogeneous for the microwave dried sample than for that dried using conventional methods. The authors attributed this to the lack of moisture flow from the interior to the exterior of the sample during microwave heating and thus there was no migration of the metal ions from the centre of the sample to the outside.

Microwave radiation has also been used in the synthesis of catalytic materials in the form of zeolites. Jansen et al[20] reported that the use of microwaves facilitated abundant nucleation and gave crystal growth at a rate ten times grater than that observed for conventionally heated syntheses. Other workers have investigated the microwave dehydration of zeolites.[21] The authors reported that water could be rapidly desorbed from the internal cage of 13X zeolite when microwaves were used.

Zerger et al[22] used microwave discharge methods to produce highly dispersed and reduced metal atom clusters in zeolite materials. It was reported that the microwave method of synthesis offered advantages over the conventional method as the metal particle size may be selected by suitable optimisation of the microwave discharge conditions.

1.2.10 Microwaves and Methane Conversion

The use of microwaves to convert methane to more valuable products is another active area of research in microwave chemistry. Several research groups currently have an interest in this area and a number of different experimental techniques and reactions have been investigated.

Wan and co-workers[23] in Canada have investigated the use of high power micro and millisecond pulses of radiation to convert methane to higher hydrocarbons such as ethane and ethene. Metal particles (often nickel) dispersed in non-lossy non-conducting medium served as the catalyst. The particles were rapidly heated by the "pulse packets" of radiation and any reactant molecules adsorbed at such sites would undergo rapid conversion to products otherwise the energy would dissipate into the matrix by conduction. Wan reported that the conversion of methane by the pulsed microwave technique was a highly selective process with C_2 hydrocarbon selectivity being consistently between 85% and 97% and C_3 selectivity reported as between 3% and 15%. Clearly, this represents total selectivity to coupled products which is highly advantageous since minimising (or in this case totally eliminating) the production of undesirable carbon oxide products is one of the prime considerations when converting methane to higher hydrocarbons.

Zerger and co-workers[24,25] used a different microwave method for methane conversion. A methane/oxygen microwave plasma operating at pressures of between 3 and 500 torr was used to activate methane. A variety of catalysts were studied and all were able to produce higher hydrocarbons and all with the exception of the Fe catalyst produced the oxygenated products of methanol or formaldehyde. It was reported that in a high frequency plasma reactor, significant concentrations of free radicals (essential in the production of higher hydrocarbons from methane) and excited species are created. Under the experimental conditions described, the gas temperature was far lower than the electron temperature and as a result the microwave plasma created thermally sensitive species. It was concluded that the use of a microwave plasma selectively activated C-H bonds and enabled a thermally difficult and thermodynamically unfavourable reaction to be performed.

A further microwave method has been reported by Kawahara.[26] The use of a microwave discharge for decomposition of methane is described and the effect of power is investigated. Again working at low pressure (10 torr) and at microwave power of between 200 and 500W, methane is converted to higher hydrocarbons. The author states that when conversion is high, acetylene and hydrogen are the principal products, whilst at low conversion, ethene and ethane are also obtained in significant quantities. Trace amounts of other hydrocarbons were also detected.

Continuous microwave irradiation is another way of converting methane to form higher hydrocarbons. Roussy and co-workers[27] studied the oxidation of methane over $SmLiO_2$ and $(SmLiO_2)_{0.8}(CaOMgO)_{0.2}$ catalysts under continuous irradiation and concluded that the microwave field selectively activated what they termed the "electrical sites" of the catalyst which were responsible for the first step of the reaction. It was also stated that the production of coupled products (i.e. higher hydrocarbons) was increased as the production of carbon oxides decreased.

Bond et al[13,28] studied the oxidative coupling of methane over sodium aluminate catalysts and reported several interesting phenomena. Firstly, similar C_2 selectivity was observed for both conventional and microwave heated experiments but in the microwave heated experiment, the observed temperature of the catalyst bed was some 400°C lower. It was postulated that the temperature across the catalyst bed was non-uniform and as a result certain areas of the bed were achieving temperatures in excess of the observed bulk temperature. This was said to be especially likely when dealing with a non-uniform system, the components of which interacted to differing degrees with the microwave field. The overall result was that heating occurred at sites which preferentially absorbed the incoming radiation and hot spots occurred within the catalyst bed. The authors stated that the hot spot theory had neither been proved nor disproved but stated it as a possible explanation for the large difference in the temperatures of the microwave and thermally heated reactions. Other benefits of the microwave heating of the oxidative coupling of methane reaction were also mentioned. These included an increased selectivity to CO at the expense of CO_2 and an increased ethene to ethane ratio.

Chen et al[29] also studied the oxidative coupling of methane over proton conductive catalysts under continuous microwave radiation and made the same observations as Bond et al regarding a reduction in temperature of the oxidative coupling reaction when microwaves were used. They also observed a change in selectivity and product species under microwave conditions.

1.3 Nature of this Study

This study was initially focused at the oxidative coupling of methane (OCM) using rare earth oxide catalysts. Such catalysts had previously been shown to be both active and selective for the reaction under thermal conditions. The initial aim was to investigate the observations of other researchers (regarding reduced reaction temperature etc.) but using catalysts which had not previously been studied under conditions of continuous microwave irradiation.

Another reaction studied was the steam reforming of methane. This well documented reaction was used in an attempt to ascertain the temperature of the "hot spots" within the catalyst bed using thermodynamic data. In addition, this reaction had not previously been studied under conditions of continuous microwave irradiation.

A third reaction investigated was the combustion of methane. The reaction is important in environmental catalysis and has been studied under conventional heating conditions but not previously under microwave conditions.

2. Oxidative Coupling of Methane

2.1 Reasons for the Oxidative Coupling of Methane

The existence of vast world-wide reserves of natural gas, of which methane is the major constituent has focused attention on the possibility of converting it directly to other forms of fuel and more valuable chemicals. The need for such a direct conversion arises at least in part from the remoteness of the reserves and the high costs involved in the transportation of gaseous fuels over long distances.

Additionally, the methane molecule is a highly stable entity with a low energy density and current methods for the conversion of methane to more valuable products such as ethene, methanol, formaldehyde, petrochemicals and liquid transportation fuels involve costly, highly energy intensive processes. An example is the Mobil methanol to gasoline (MTG) process which initially converts methane to syngas via steam reforming prior to a conversion process to yield methanol and ultimately gasoline.

Clearly, a single step conversion of methane to more valuable products would be of immense industrial significance and economic advantage.

The conversion of methane to higher hydrocarbons via dehydrogenative coupling requires high temperatures in order to achieve practical yields. However, conversion via the oxidative coupling of methane whereby methane and a suitable oxidant are fed to a heated reaction zone favourably alters the thermodynamics of the conversion and appears to solve the heat of reaction problem. Selectivity to desired products then becomes a major consideration since although the oxidative coupling of methane to higher hydrocarbons is possible in the absence of a catalyst under certain experimental conditions, a suitable catalyst is required in order to alter the reaction pathway so as to modify the conversion - selectivity curve to higher values than those predicted for the non-catalysed reaction.

2.2 Background to the Oxidative Coupling of Methane

The oxidative coupling of methane has been one of the most active areas in catalytic research over recent years since the pioneering work of Keller and Bhasin[30] in 1982. These workers used a sequential feed system whereby methane and oxygen. were fed individually over the catalyst interspaced by a short purge of inert gas as their work had concluded that the simultaneous feeding of reactants produced non selective oxidation products. A large number of metal oxides supported on α-alumina were investigated and they found that C_2 species (primarily ethene) were formed over many of them. It was noted that most of the catalysts exhibiting activity for C_2 formation lay in the low melting metal part of the periodic table i.e. groups IIIA, IVA and VA. It was reported that of the catalysts studied, manganese oxide gave the best results.

Later studies[31,32] showed that cyclic feeding of the reactants was not necessary to produce good selectivity to coupled products and as a result, the majority of subsequent work has employed the co-feed system whereby reactants are fed simultaneously to the reactor.

A major work was produced by Ito and Lunsford[33] who investigated MgO and Li doped MgO as catalysts for the OCM reaction and it was stated that the latter gave much improved catalytic performance.

2.3 The Oxidative Coupling Reaction

The dehydrogenative coupling of methane to higher hydrocarbons is thermodynamically unfavourable at temperatures below 950°C.

$$2CH_4 \rightarrow C_2H_6 + H_2 \qquad \Delta G^\circ = 71.0 \text{ kJ mol}^{-1} \text{ at } 1000K \qquad (2.1)$$

However, if methane is reacted with an oxidant, this thermodynamic limitation is overcome.

$$2CH_4 + \tfrac{1}{2}O_2 \rightarrow C_2H_6 + H_2O \qquad \Delta G^\circ = -121.6 \text{ kJ mol}^{-1} \text{ at } 1000K \qquad (2.2)$$

In the oxidative coupling of methane, the major challenge is to achieve high conversion and selectivity to desired products without significant loss of hydrocarbon to carbon oxides via complete combustion. The formation of carbon oxides is thermodynamically favourable and it is therefore important to kinetically suppress the rates of formation of carbon oxides relative to those of coupled hydrocarbons. A catalyst is utilised in order to accomplish this.

The reaction between methane and oxygen to yield higher hydrocarbons is generally carried out at temperatures in excess of 650°C. In addition to ethene and ethane, carbon monoxide, carbon dioxide, water, hydrogen and small amounts of higher hydrocarbons are formed.

The stoichiometry of the reactions occurring may be represented by the following equations:

$$2CH_4 + 0.5O_2 \rightarrow C_2H_6 + H_2O \tag{2.3}$$

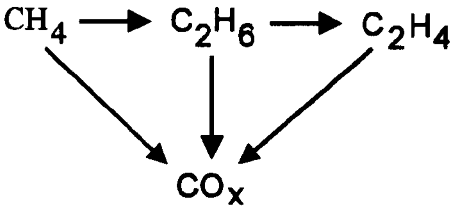
$$2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O \tag{2.4}$$

$$CH_4 + 1.5O_2 \rightarrow CO + 2H_2O \tag{2.5}$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{2.6}$$

In addition to the coupling and total oxidation reactions, steam reforming and the water gas shift reactions may also take place at reaction temperatures. Indeed, Ekstrom[34] reported that at temperatures in excess of 700°C, the shift reaction may make a significant contribution to the yield of CO_x.

A simplified reaction network can be used to describe the reaction:



2.4 Nature of the Oxidant

The use of an oxidant in methane conversion to higher hydrocarbons overcomes the thermodynamic barrier encountered when no oxygen is present[35] (e.g. in the case of dehydrogenative coupling). The use of molecular oxygen, nitrous oxide and ozone amongst other oxidants has been studied.

Early work reviewed by Foster[36] indicated that ozone could be active for methane oxidation at temperatures lower than those observed when molecular oxygen was utilised. This was ascribed to the greater oxidising ability of the species. However, a comparative study by Hutchings et al[37] showed that no enhancement in production of C_2 or oxygenated species was achieved by the use of ozone at lower temperatures. Ozone was found to be active at temperatures of less than 500°C but the only products observed were carbon oxides and hydrogen.

The use of nitrous oxide as an oxidant over Sm_2O_3, MgO and Li/MgO catalysts has been investigated[38 - 40] and was found (under comparable conditions) to give reduced conversion but enhanced selectivity to coupled hydrocarbons in comparison to molecular oxygen. This observation was ascribed to the fact that N_2O can supply only half the oxidising capability of molecular oxygen and also it may have a slow decomposition to an active oxidising species under reaction conditions. Additionally, nitrous oxide has been shown to be a selective oxidant at temperatures below 600°C.

Molecular oxygen is still the most widely used oxidant for the OCM reaction. Although not as selective as nitrous oxide it is more economical to acquire and greater conversions are achieved. Catalyst design is therefore important in the OCM reaction using molecular oxygen in order to re-dress the balance between selectivity and conversion.

Aika et al.[41,42] investigated the effect of introducing CO_2 to the methane/oxygen feed and observed an increased C_2 yield over certain catalysts. This was explained by the transfer of an oxygen atom from the carbon dioxide directly to the lattice or catalyst surface to enable H atom abstraction.

Shepelev and Ione[43] researched the suitability of NO, NO_2 and H_2O_2 as oxidants for the OCM reaction but found that due to their facility to readily donate oxygen, they were unselective oxidising materials.

2.5 Oxidative Coupling Catalysts

Much of the periodic table has been scanned in an attempt to find the definitive oxidative coupling catalyst. The screening of such a large number of catalysts has revealed some common features. It has been concluded that the majority of active and selective co-feed oxidative coupling catalysts are composed of basic, irreducible surface oxides many of which form stable surface carbonate species. These systems are invariably p-type semiconductors under reaction conditions.

Alkali metal promoted alkaline earth oxides and the rare-earth oxides have been shown to be some of the most active and selective and will be considered in more detail later.

Several excellent reviews on oxidative coupling catalysts have been produced and it is beyond the scope of this study to attempt to comment on such a great body of work. However, it is important to comment on systems which have received some of the greatest attention of researchers (such as the lithium doped magnesia catalyst) and also to assess research into systems which relate directly to those studied during this work, namely rare earth oxide based catalysts and chloride containing catalysts.

2.6 Alkaline Earth Oxide Catalysts

Work on unpromoted alkaline earth oxides (BeO, MgO, CaO, SrO and BaO) has shown them to possess both activity and selectivity for the OCM reaction.[44 - 50]. Among this series, MgO is the most widely studied. Magnesia has the most basic character and contains a significant number of one electron donor centres on its surfaces.[51 - 53] Mehandru[54] reported that within the MgO structure there were oxygen atoms with different co-ordination number and that these different species exhibited different catalytic behaviour. The method of preparation of the MgO was found by Hargreaves et al[55] to be crucial to its catalytic properties since different preparation methods gave catalysts possessing different structures. The work investigated the different performances of samples prepared by different methods and concluded that the sample prepared by thermal decomposition of the basic carbonate produced a more most selective and active catalyst than that produced by burning magnesium ribbon in air. Examination of the samples by TEM showed that the sample originating from the carbonate comprised agglomerates of crystallites while the other sample was more highly structured and made up of regular crystallites of MgO. This work is however in contrast with the work of Lunsford et al[56] who concluded that the morphology of the magnesia was of limited importance relative to the effect of the alkali promoter.

Alkaline earth oxide catalysts doped with alkali metal are some of the most widely studied catalysts. Li/MgO and Na/CaO are good examples this genre of catalysts. These systems are in fact not simply alkali metals deposited on the alkaline earth. When the ionic radii of both cations are similar (as in the case of both these catalysts), replacement of the alkaline earth by the alkali may take place.[57] Such substitution of a monovalent cation into the lattice of the oxide forms a true mixed oxide which requires that an equivalent number of O^- centres be present to maintain electrical neutrality. Such species have been detected by EPR spectroscopy and have been proved to be the species responsible for methane activation over such catalysts.[58]

Lunsford and co-workers[57 - 59] investigated the influence of alkali dopants on the performance of magnesia and found that a magnesia catalyst doped with 7wt% Li produced a very effective system. This catalyst has been intensively investigated by the group of Lunsford. Many analytical techniques have been utilised in an attempt to elucidate the reaction mechanism over this catalyst. The active species on the catalyst surface was an oxygen species which was stabilised by the presence of Li^+ O^- pairs within the catalyst. As a result of extensive testing, Lunsford et al formulated the following mechanism:

The centres are formed by oxygen vacancies ([]) trapped at O^{2-} ions adjacent to Li^+ ions.

$$2Li^+O^{2-} + [] + \frac{1}{2}O_2 \leftrightarrow 2Li+O- + O^{2-}$$

$$Li^+O^- + CH_4 \rightarrow Li^+OH^- + CH_3\bullet$$

The $[Li^+O^-]$ centres are regenerated by the following:

$$2Li^+OH^- \rightarrow Li^+O^{2-} + Li^+[\,] + H_2O$$

$$Li^+O^{2-} + Li[\,] + \tfrac{1}{2}O_2 \rightarrow 2Li^+O^-$$

or

$$2Li^+OH^- \rightarrow Li^+O^- + Li^+[e^-] + H_2O$$

$$Li^+[e^-] + \tfrac{1}{2}O_2 \rightarrow Li^+O^-$$

Thus, in agreement with the work of Wang et al[52], O^- species are responsible for the activation of methane.

2.7 Rare-Earth Oxide Catalysts

Rare-earth oxide catalysts such as La_2O_3 and Sm_2O_3 have been researched by many groups and were found to be of the most effective coupling catalysts. Lin et al[59] studied pure La_2O_3 and found it to be a good producer of methyl radicals which are essential to the reaction (See section 2.9). Using a matrix isolation electron spin resonance apparatus (MIESR), methyl radicals were isolated and the activity of lanthana for their production quantitated. A C_2 selectivity of 47% and methane conversion of 9.4% at 725°C were reported.

The structure sensitivity of the OCM reaction over samaria and lanthana has been studied. Samaria exists in two different forms - cubic and the more thermally stable monoclinic the transition between the two crystalline phases occurring between 875°C and 950°C. It has been reported that the calcination temperature of Sm_2O_3 has an effect on C_2 selectivity.[60] Calcination at a temperature of 1000°C produced a catalyst comprised entirely of the monoclinic phase and this was detrimental to C_2 selectivity. It was postulated that calcination at lower temperatures retained some of the less stable cubic form and such catalysts performed better in the OCM reaction. It was therefore concluded that although the cubic form is less thermally stable it is the more selective morphology of samaria. This finding is supported by considering the differing structures of the two morphologies. In the cubic structure, a quarter of the oxygen atoms are missing from the lattice and oxygen vacancies are in their place whereas the monoclinic structure has fewer vacancies. This means that lattice/gas phase oxygen exchange is more rapid over cubic samaria and the rate of this exchange has been related to enhanced C_2 selectivity. The issue does not however appear to be easily understood since work by others[61] reports that a mixture of the two phases gives enhanced catalytic performance.

Several studies of the structure sensitivity, kinetics and mechanism of the oxidative coupling reaction over lanthana have been performed. Le Van et al[62] reported that the reaction was structure sensitive. It was stated that lanthana catalysts could form different morphologies depending upon the method of preparation and that two different types of lanthanum oxycarbonate species could be formed. These were a monoclinic form of lanthanum oxycarbonate denoted type 1a and a hexagonal form, type 2. Type 2 was favoured by low temperature catalyst preparation (650°C) and this observation was attributed to morphological differences in the lanthana. The type 1a oxycarbonate was found from thermogravimetric data to be less thermally stable than type 2. The type of oxycarbonate species formed was said to affect the overall performance of the catalyst since it was believed that much of the CO_2 produced during the OCM reaction originated from decomposition of the oxycarbonate. Hence, the more thermally stable the oxycarbonate species formed, the less selective for C_2 formation the catalyst. Lanthana prepared by low temperature calcination was therefore found to be the more selective catalyst since the formation of the more thermally stable type 2 oxycarbonate was favoured by such preparation conditions. However, a more recent study by Squire et al[63] used in-situ X-ray diffraction methods to study lanthana under reaction conditions. The authors concluded that although La_2O_3 formed both types of oxycarbonate species during the reaction, there did not seem to be a direct relationship between the amount of bulk oxycarbonate formed and catalyst selectivity.

Transient isotope techniques have been used to study the mechanism of the oxidative coupling reaction.[64] Ekstrom et al[34] reported that the rate of methane conversion was dependent upon the rate of exchange between gas phase and lattice oxygen. It is well known that rare-earth oxides are able to exchange lattice oxygen with gas phase oxygen.[65] Winter performed exchange experiments with $^{18}O_2$ and found that of the lanthanides, lanthana had the lowest activation energy and highest rate of exchange. A high rate of lattice/gas phase oxygen exchange shows high oxygen mobility within the material and these factors are important to the selectivity of the catalyst.

The actual nature of the active oxygen species on the surface of the catalyst which is responsible for the activation of methane has been the focus of much research. In 1986, Lin et al[59] used EPR spectroscopy to study lanthana and found evidence for the generation of superoxide (O_2^-) on the surface. This form of oxygen is however known to be inactive for the activation of methane[66,67] thus it was concluded that a different oxygen species was responsible for the activation. Following this work, Wang and Lunsford suggested that the active species was a transient O^- moiety formed from O^{2-} during the reaction. A further suggestion was that superoxide was in equilibrium with surface peroxide and oxygen:

$$O_2 + O_2^{2-} \Leftrightarrow 2O^{2-} \qquad (2.7)$$

More recently, comprehensive studies by Otsuka et al[67] have revealed that the most likely activating species is superoxide O_2^{2-}. Their findings were supported by EPR measurements obtained for a sodium peroxide catalyst. Peroxide catalysts were found to be able to convert methane and since the only oxygen species present in the system could be related to peroxide, it was concluded that this particular form was the active species. The peroxide anion (O_2^{2-}) may be regarded as the diamagnetic, resting form of O^-. A further suggestion was made by DuBois et al[68]. Using XPS, the work of Wang et al[58] was confirmed, as superoxide was detected on the catalyst surface. However, evidence of a peroxycarbonate species (CO_4^{2-}) was also found, this species being formed from surface carbonate produced during the OCM reaction. The authors stated that it was unlikely that this species was responsible for methane activation but suggested that it may play a part in the generation of the active species mentioned previously via the following equations:

$$CO_3^{2-} + O^{2-} \Leftrightarrow CO_4^{2-} + O^- \qquad (2.8)$$

$$2O^- \Leftrightarrow O_2^{2-} \qquad (2.9)$$

$$O_2 + 2CO_3^{2-} \Leftrightarrow 2CO_2 + O_2^{2-} \qquad (2.10)$$

It was found that in order to activate methane over rare-earth oxide catalysts that gas phase oxygen was required since it was fundamental in the generation of active oxygen sites on the catalyst surface.[69]

The large amount of research into the suitability of rare-earth oxides for the OCM reaction revealed that only the irreducible oxides such as lanthana and samaria appear to exhibit any degree of selectivity to C_2 hydrocarbons. Oxides which possess more than one stable oxidation state such as CeO_2, Pr_6O_{11} and Tb_4O_7 tend to exhibit largely total oxidation behaviour. That is to say that the main products of the coupling reaction over such catalysts are carbon oxides (CO and CO_2). Tong et al[70] explained this by a reductive addition cycle indicated overleaf.

$$CH3\bullet \ + \ M^{(n+1)+}\,O^{2-} \ \rightarrow \ M^{n+}\,(OCH3)^- \qquad (2.11)$$

It was postulated that the methoxy species formed in such a scheme would undergo further reaction to yield CO_2 and hence make the reducible rare-earth oxides unselective catalysts.

2.8 Doped Rare-Earth Oxide Catalysts

As discussed in section 2.7, rare-earth oxides are among the most effective oxidative coupling catalysts. Studies have been conducted to investigate the effects of dopants on their catalytic performance.

It was noted previously that Pr_6O_{11} was not an effective coupling catalyst. However, if promoted with alkali metal it becomes a highly effective system.[71] The addition of Na_2CO_3 to CeO_2 dramatically transformed its performance under reaction conditions. Pure ceria favours total oxidation whereas upon addition of the sodium compound it became an effective coupling catalyst. However, the transformation was explained by the fact that the sodium species was totally coating the ceria meaning that none of the CeO_2 was available for reaction. This phenomenon was observed on other lanthanides and it was concluded that the lanthanide acts merely as a carrier for the active alkali centres. Therefore such catalysts may be regarded as lanthanide supported peroxides.

Significant improvements in the catalytic performance of La_2O_3 have been demonstrated by the incorporation of dopants into the catalyst formulation[72 - 74]. Group II metal ions such as barium calcium and strontium have been investigated and have been shown to increase C_2 selectivity and yield as well as methane conversion.

DeBoy and Hicks[47] investigated the effect of a number of alkali and alkaline earth metal dopants on the performance of lanthana.

Their findings revealed that the best performance was achieved by a 1wt% Sr/La_2O_3 catalyst. This catalyst achieved a maximum C_2 selectivity of 78.8% and methane conversion of 12.4%. This compares with values for pure lanthana of 71.1%and 10.8% respectively.

The favourable effects of strontium doping on the performance of lanthana are reported to be a combination of factors.

Strontium has a similar ionic radius to lanthana (1.15 Å cf 1.13 Å[75]) and as such solubility and conductivity are maximised while structural constraints and activation energies are minimised. The dissolution of strontium in lanthana leads to an increase in the number of defect sites which is important to oxygen conductivity through the sample (i.e. lattice/gas phase oxygen exchange). Sr/La_2O_3 exhibits p-type semiconductor behaviour meaning that positive holes are the means of conduction. The dissolution of strontium in lanthana therefore increases the number of holes present and enables faster exchange of lattice and gas phase oxygen. This is important since it has been shown that the rate of oxygen exchange is directly related to the rate of methane conversion.[76]

As previously mentioned, the oxidative coupling of methane over lanthana has been shown to be structure sensitive and selectivity was also dependent on catalyst preparation conditions[149]. A thin platelet morphology favoured by lower temperature preparation was found to be more selective than the tridimensional, smaller particles formed at higher temperatures. It is thought that strontium doping preserves the favourable platelet structure of the oxide during the catalytic reaction.

Other work has reported that Sr doping may improve the catalytic performance of lanthana by replacing some of the surface La_2O_3 with less active but more selective $SrCO_3$ under reaction conditions.[78]

2.9 Chloride Containing Catalysts

The maximisation of the ethene to ethane ratio during oxidative coupling is most desirable since ethene is the potentially more valuable product and it has been reported[79 - 82] that the selectivity of the OCM reaction towards ethene can be enhanced if a chlorine containing gaseous compound is passed over the catalyst during the reaction. This observation has also been reported when chloride ions are included in the catalyst formulation.[82 - 93]

Some excellent work in the area of chloride oxidative coupling catalysis has been performed by the group of Burch.

Manganese catalysts have attracted some interest due to their stability and activity. In fact manganese oxide was found to be one of the best simple oxide coupling catalysts.[94,79,95 - 99] Manganese chloride was investigated by Baldwin and workers for its suitability and it was found that in isolation this catalyst had a low selectivity for ethene formation.[100] However, when partially oxidised, a good ethene selectivity was achieved. This system was unstable under reaction conditions and ethene selectivity diminished quickly with time on stream due to loss of chloride from the catalyst. The incorporation of an alkali promoter to the catalyst formulation was found to give greater stability under reaction conditions and therefore more long term ethene selectivity.

It is widely accepted that the majority of ethene formed during the OCM reaction derives from secondary reactions of ethane which is regarded as the primary coupling product. Baldwin and co-workers utilised a small post catalytic reactor volume and therefore concluded that gas phase dehydrogenation to ethene was not an important reaction in their studies. They reported that gas phase radical reactions involving chlorine were important to the formation of ethene over chloride catalysts and postulated a mechanism whereby ethene could be generated in such a manner.

$$HCl = H\bullet + Cl\bullet \tag{2.12}$$

$$C_2H_6 + Cl\bullet = C_2H_5\bullet + HCl \tag{2.13}$$

$$C_2H_5\bullet = C_2H_4 + H\bullet \tag{2.14}$$

$$H\bullet + HCl = H_2 + Cl\bullet \tag{2.15}$$

The HCl may be released by the reaction of the $MnCl_2$ with water formed during the reaction. The critical step was reported to be the initial dissociation of HCl to give chlorine radicals since all other radical reactions were regarded as fast. It was postulated that methyl radicals could be involved in HCl dissociation via the following radical reaction:

$$CH_3\bullet + HCl = CH_4 + Cl\bullet \tag{2.16}$$

This route was said to enable radical formation at a fast enough rate to account for most of the ethene observed during the tests.

Burch et al[150] investigated the use of pulses of dichloromethane onto the catalyst during reaction. A manganese oxide catalyst was used and the influence of promotion with potassium was also investigated. It was found that ethene selectivity was greatly increased when pulses of CH_2Cl_2 were introduced. However, the ethene selectivity decreased with time on stream due to the loss of chlorine from the catalyst.

The use of a potassium promoter into the catalyst formulation was found to yield a KCl/Mn_3O_4 - like species which was found to be both highly selective and stable under reaction conditions.

Other researchers have investigated the use of other chloride containing catalysts. Thomas et al[101] reported that using a bismuth oxychloride catalyst, conversions of up to 42% and ethene to ethane ratios of up to 35 were achieved. It must be noted however that this system was unstable under reaction conditions and activity was lost in a matter of a few hours.

Lunsford et al[102] used a Li^+ - MgO - Cl^- catalyst and added controlled amounts of HCl during the reaction. It was found that the addition of HCl increased the ethene to ethane ratio from 5 to 11 and that following cessation of the HCl feed, the ratio remained high for many hours. This observation prompted the suggestion that surface chloride species were responsible for the ethene production and this is in agreement with the work of Burch et al[103] who reported that over samarium based chloride catalysts chlorine induced reactions occurred within the voids between particles in the catalyst bed and not in the free space outside the catalyst.

2.10 Proposed Reaction Mechanism

There have been several studies regarding the mechanism of the oxidative coupling reaction and it has been found that many complex reactions occur both on the catalyst surface and in the gas phase near to the catalyst.

It is known that methane and other hydrocarbons are dissociatively adsorbed on the surfaces of many metal oxides[104 - 132] and it is widely accepted that the initial step in the mechanism is the abstraction of a proton from the methane molecule by an active oxygen species on the catalyst surface to produce a methyl radical. The presence of such radicals has been confirmed by matrix isolation experiments.[133] This step is also regarded as the rate determining step of the oxidative coupling reaction.[134] It was shown by Lunsford[135] that methyl radicals so formed desorb from the catalyst surface and undergo further reactions. Once formed, they may combine with other methyl radicals to produce ethane, undergo further oxidation to undesirable carbon oxides or they may react with gas phase oxygen in a radical reaction to form a methylperoxy radical ($CH_3OO\bullet$). The final two options will be considered later but at this stage the fate of ethane formed by the interaction of two gas phase methyl radicals will be discussed.

Ethane is recognised as the primary coupled product in the oxidative coupling reaction[66] and is accepted as the precursor to ethene. Ethane molecules may interact with lattice oxygen species and lose a proton to yield an ethyl radical ($C_2H_5\bullet$)[136]. These radicals may then interact with oxygen species on the catalyst surface and undergo further proton abstraction to yield C_2H_4 and $H\bullet$. A further but somewhat unlikely suggestion is that ethane is selectively oxidised to ethene in the gas phase away from the catalyst surface. The possibility of the formation of ethene as a primary coupling product has largely been discarded by the vast majority of researchers. However, Hutchings et al[39,40,137 - 139] conducted studies which suggested that primary ethene production was not negligible for all catalysts. By varying the reactant feed rate at constant reaction temperature and reactant ratio it was found that over several catalysts including pure lanthana and samaria that ethene and ethane were primary hydrocarbon products.

In addition to the desired coupled products of the OCM reaction, undesirable oxides of carbon are usually formed since 100% C_2 selectivity is generally only achieved at extremely low levels of conversion. The methylperoxy radical referred to earlier has been postulated by Iwamatsu and Aika[140] to be responsible for both C_2 products and carbon oxides. However, other groups including Lunsford et al[141,142] suggest that the methylperoxy radical is plays a very important part in the formation of undesirable carbon oxides during the OCM reaction. The following scheme was suggested to account for the reaction of methylperoxy radicals to CO_x.

$$CH_3\bullet + C_2H_6 \rightarrow CH_3O_2H + C_2H_5\bullet \qquad (2.17)$$

$$2CH_3O_2\bullet \rightarrow CH_2O + CH_3OH + O_2 \qquad (2.18)$$

$$CH_2O,\ CH_3OH \rightarrow CO,\ CO_2 \qquad (2.19)$$

Lee and Oyama suggested in their review[35] that the radical is in fact in equilibrium with methyl radicals and gas phase oxygen (from which it is formed).

$$CH_3\bullet + O_2 \Leftrightarrow CH_3O_2\bullet \qquad (2.20)$$

At high temperatures, the reverse of the above equilibrium is favoured and thus more methyl radicals are released. Therefore, at high reaction temperatures, C_2 selectivity should increase at the expense of CO_x. Since the OCM reaction is usually performed at temperatures of between 700° and 900°C, they argued that the methylperoxy radical should have little or no contribution to the production of carbon oxides under normal reaction conditions.

A general scheme for catalytic oxidation on solid oxide catalysts was proposed by Sokolovskii.[85]

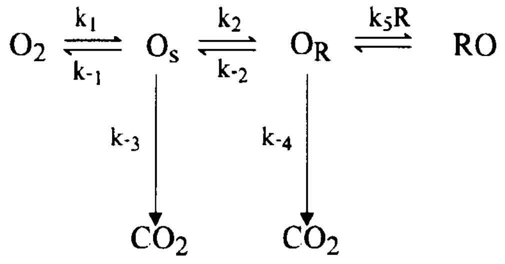


Figure 2.1. Sokolovskii General Scheme for OCM on Solid Oxide Catalysts

As mentioned at the beginning of the section, the mechanism of the oxidative coupling of methane is a series of complex surface and gas phase reactions involving both radical and molecular species. Evenso, several workers have attempted to schematically summarise the major steps. A very general reaction scheme was represented in section 2.3 but in no way did this account for any of the radical processes or surface interactions which occur under reaction conditions. Lunsford[142] produced a more detailed scheme similar to that shown below which included intermediates of coupled products and interactions of gas phase species with active oxygen species on the catalyst surface (Figure 2.2).

In their review on the oxidative coupling reaction, Hutchings and co-workers[66] expanded the work of Lunsford and derived the scheme illustrated in figure 2.3.

As described in section 2.7, the actual nature of the active oxygen species is still open to some argument but it is reasonable to assume from current evidence that it is either a transient O^- species or a peroxide species (O_2^{2-}).

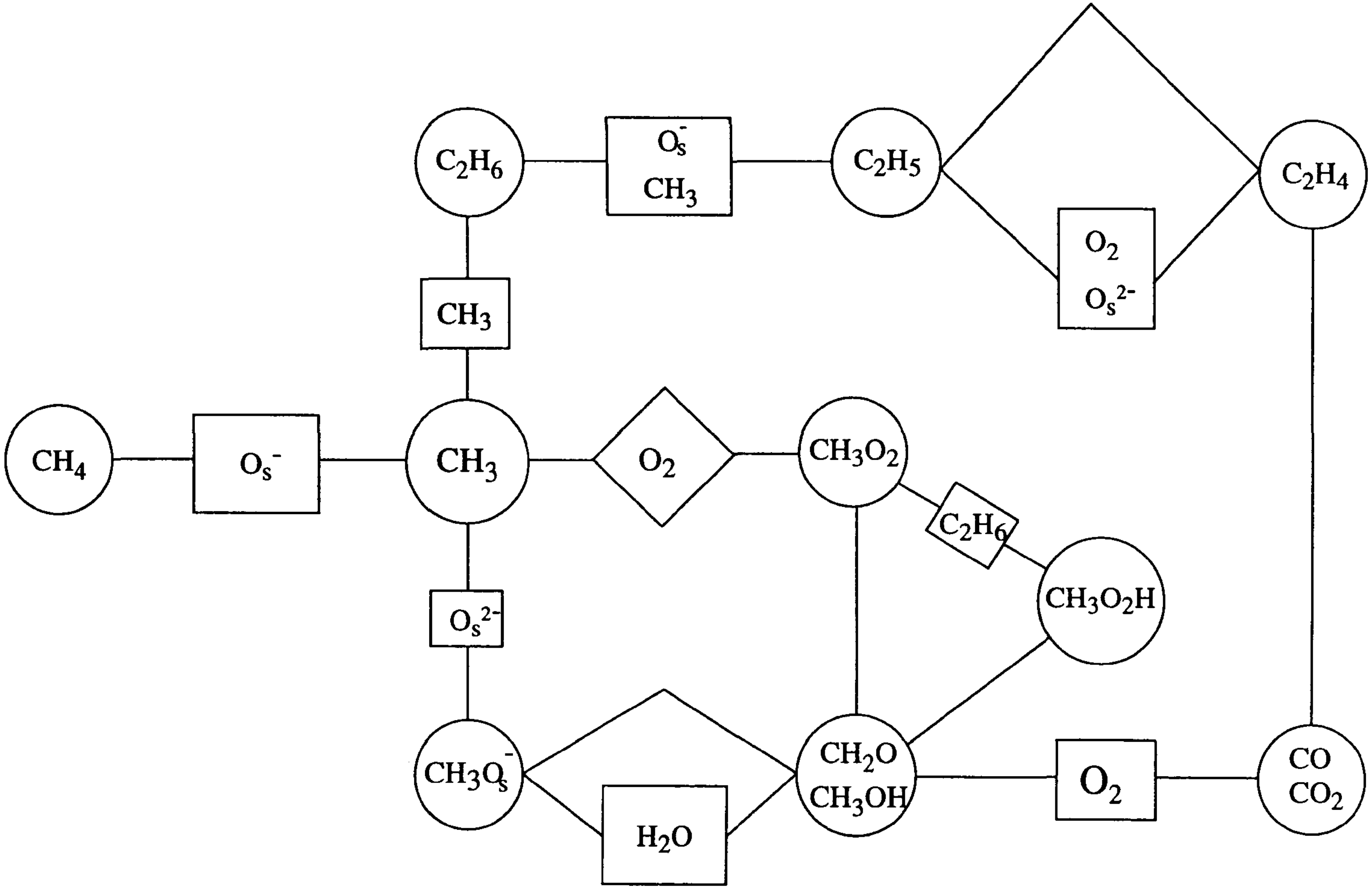


Figure 2.2. Reaction Scheme Proposed by Lunsford et al

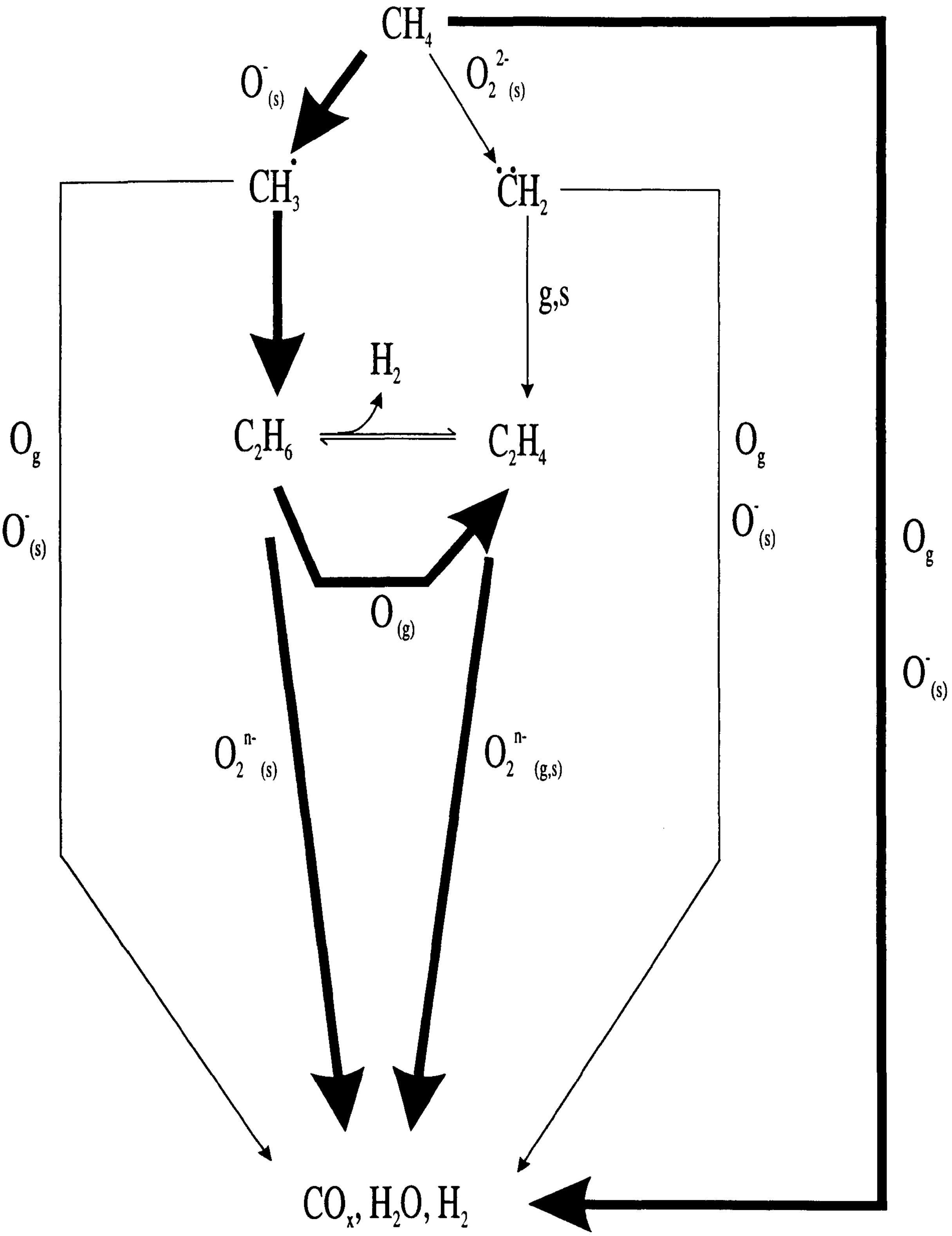


Figure 2.3. Proposed Mechanism for the OCM Reaction (Hutchings et al[66])

Though it is clear that much research has been devoted to the mechanism of the oxidative coupling reaction, a definitive path has yet to be defined due to the complex nature of the many interactions which may take place during the reaction. Following analysis of kinetic modelling data, van der Wiele et al[144] reported a scheme of 164 different reactions which could take place under reaction conditions and the area is still currently under investigation.

2.11 Scope of This Study

The focus of this study was to investigate the use of microwave radiation to stimulate the oxidative coupling of methane reaction. Two types of catalyst were investigated: rare - earth oxide based systems and a chloride containing catalyst. Effects of the use of microwave heating on catalyst selectivity, yield of desired coupled hydrocarbon products and methane conversion were investigated. Conventionally heated experiments performed during this study served as a comparison for microwave heated experiments. It was beyond the scope of the work to attempt to further any of the conventionally heated experiments performed by many other researchers. However, a novel catalyst system (1wt% Sr/15wt% La_2O_3/MgO) was investigated using both conventional and microwave methods of catalyst heating.

It is believed that this is the first study of the use of microwave radiation for the OCM reaction using the various catalysts investigated during this work.

3. Steam Reforming of Methane and Methane Combustion

3.1 Introduction

The need for large supplies of cheaply produced hydrogen arose in the early 20th Century when ammonia synthesis plantswere being developed. Initially, hydrogen was produced in a water-gas generator but by 1917, the classical Haber Bosch process was complete and hydrogen was being produced by the reaction of coke with steam followed by the water gas shift reaction (Eqs 3.1 -3.2)

$$C + H_2O \rightarrow CO + H_2O \qquad (3.1)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (3.2)$$

In areas where natural gas was abundant, this was used as the feedstock instead of coke. This made the reforming process more efficient since the hydrogen content of the hydrocarbon increased the yield of hydrogen from the reaction. This technology was pioneered by BASF in the first quarter of the 20th century. The reaction occurred over catalyst mounted in vertical tubes in a furnace. Naphthas were also reformed using a process pioneered by ICI but in more recent years, the increasing availability of natural gas has meant that it is the major feedstock for reforming processes.

3.2 The Steam Reforming Reaction

The steam reforming of natural gas (of which methane is the major constituent) is generally performed at temperatures of 800°C or higher at pressures up to 35 bar. The industrial reformer consists essentially of two main sections: the furnace which houses tubes of catalyst and the convection section where heat is recovered from the flue gas. The feedstock must be desulphurised prior to reaction as sulphur containing compounds are known catalyst poisons.

The catalyst used for the reaction must meet a number of criteria in order to be useful under the extreme conditions within the reformer unit. As with all catalysts, selectivity to desired products is a major consideration. Good reforming catalysts should be as inactive as possible to unwanted side reactions especially the formation of carbon. Carbon formation can usually be avoided by the use of a suitable steam to hydrocarbon ratio. Resistance to poisoning is also important on the industrial scale. As stated above, industrial reformers operate at temperatures of 800°C upwards and therefore thermal stability of the catalyst is fundamental. Physical strength of the catalyst is a further consideration since the reaction is performed at high pressure.

Nickel catalysts are the most widely used for reforming duties. Other metals such as cobalt, iridium, palladium, platinum, ruthenium and rhodium are suitable and in some cases are more active than nickel but nickel is far cheaper and sufficiently active for the task.

The reaction takes place on the nickel surface of the catalyst so it is important to maximise the stable nickel surface area. This is achieved by dispersing the nickel as small crystallites on a refractory support medium. The catalyst is reduced before reaction using pure hydrogen which maximises the available surface area. The temperature of reduction is an important variable and generally temperatures of around 600°C are utilised. At temperatures below this, incomplete reduction may occur whilst at higher temperatures significant sintering may take place and this has the obvious effect of decreasing the nickel area and reducing the efficiency of the process.

Two equilibria occur during the reaction: the steam reforming equilibrium and the water gas shift reaction.

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H = +206\ kJmol^{-1} \qquad (3.3)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H = -41\ kJmol^{-1} \qquad (3.4)$$

Clearly the reforming reaction is endothermic so the forward reaction is favoured by high temperature as well as low pressure. The shift reaction on the other hand is exothermic and the forward reaction is therefore favoured by low temperature and high pressure. To maximise the overall efficiency of carbon to carbon dioxide and hydrogen, the reforming reaction conditions mentioned previously are employed. In industry, this is followed by the shift process which enables the shift reaction to be brought to equilibrium by using two different catalysts.

3.2.1 The Industrial Importance of Steam Reforming

The steam reforming of natural gas is an important industrial process as the products of the reaction find use in many applications in the chemical industry.

Ammonia synthesis plant use reformers to produce the hydrogen required for their reaction. A two stage process is used. Following the primary reforming (endothermic) the partially reformed gas with added nitrogen is fed to a secondary reformer where air is added. Any carbon monoxide in the exit stream is converted to CO_2 in shift reactors and then removed by scrubbing. Residual oxides of carbon are converted to methane by a methanator before the hydrogen and nitrogen are compressed to synthesis pressures.

Obviously, the reforming reaction is an efficient way of generating large amounts of hydrogen and as such has found use in the area of fuel cells. Fuel cells provide a means of electricity from a chemical feedstock and certain types of fuel cell (for example the molten carbonate variety) require hydrogen as their fuel. There are two possibilities regarding the reformer for fuel cells. The simplest option is to perform external reforming. In this case, existing reforming catalysts are perfectly acceptable for the task. However, in order to make the fuel cell unit as compact as possible internal reforming may be used. The molten carbonate fuel cell operates near reforming temperatures so the heat supply for the reaction would not pose a problem. Unfortunately, the environment within the molten carbonate fuel cell is highly corrosive and therefore a suitably sturdy catalyst is required in order to make internal reforming a viable proposition.

The gas mixture produced by the steam reforming process is commonly known as synthesis gas and this forms the raw materials for the synthesis of many chemicals. Methanol synthesis is a good example. In this synthesis only hydrogen and carbon oxides are required and therefore the reformer unit is required to convert as much of the natural gas as possible to these gases. This means that the process should be operated at as low a pressure and as high an exit temperature as is economically viable.

Synthesis gas is also used in the Fischer - Tropsch process which is used to produce linear paraffins and olefins. The oxo process which is a means of converting an olefin to an aldehyde requires hydrogen and carbon monoxide which are obtained form the reforming reaction.

A scheme outlining some of the major uses of syngas is shown below.

3.2.2 Steam Reforming of Methane in This Study

The steam reforming reaction is one of the best understood catalytic reactions. Mathematical data relating equilibrium constant to temperature of reaction may be readily found in publications such as the Catalyst Handbook[145]. The calculation for the equilibrium constant is as follows.

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad (3.5)$$

$$K_p = pCH_4\ pH_2O/pCO\ pH_2^3\ atm^{-2} \qquad (3.6)$$

$$K_p=\exp(Z(Z(Z(0.2513Z-0.3665)-0.58101)+27.1337)-3.2770)$$

where $Z = (1000/T) - 1$, with T being the absolute temperature (Kelvin)

In previous catalytic work many reactions have been shown to occur at much reduced temperatures when microwaves are used to supply the heat. However, it has been postulated that within the catalyst bed there are areas which are at temperatures far higher than the observed bulk temperature. These "hot spots" are believed to be the areas within the catalyst where the reaction actually occurs. Due to the method of temperature measurement and the fact that the hot spots in the bed are extremely small, the actual temperature of these areas cannot be measured by such methods as optical fibre thermometry. Therefore, with the wealth of knowledge of the equilibrium constant - temperature relationship of the reforming reaction, the aim of this study was to use the reaction as a "chemical thermometer." By calculation of the equilibrium constant of the experiments performed in this study and comparison with the literature values, it is possible to suggest the actual temperature of the "hot spots" within the catalyst bed.

3.3 Methane Combustion

Natural gas is a relatively clean source of hydrocarbons and as such, interest is growing rapidly into its use as an environmentally friendly fuel for motor vehicles. In addition to its relative cleanliness compared to conventional gasoline, the use of natural gas reduces the emission of SO_x[146]. However, environmental legislation regarding emissions dictate that the exhaust gases be further cleaned up. Such legislations are now including the removal of trace amounts of methane which as stated earlier is the major component of natural gas. Tests performed on both automotive and stationary combustion engines revealed that although traditional three way exhaust catalysts are efficient in NO_x and carbon monoxide removal, their efficiency in removal of methane was not satisfactory (<50% for the stationary engine and <15% for the automotive engine). Such a low conversion of methane is achieved by conventional three way catalysts since the optimum air : fuel ratio for a natural gas fuelled engine is different to that for gasoline engines. As a result, the conventional catalysts would require operation at temperatures far higher than those achieved by the exhaust gases. Burch and Loader[147] investigated Pt/Al_2O_3 and Pd/Al_2O_3 catalysts for their suitability for methane combustion and concluded that platinum did have a role to play in catalysts for emission control for natural gas vehicles.

In the light of this work and also the environmental applications, it was decided to investigate a range of catalysts with different Pt loadings and assess their behaviour under stoichiometric feed conditions.

The application of microwaves to the reaction had not been previously studied. Microwaves are known to facilitate rapid heating of metal catalysts and this may have implications in the future of automotive catalysts. Exhaust catalysts experience a "dead time" upon start up since when the engine is first started, the catalyst is below its operating temperature. Incorporation of a microwave preheater which is activated before engine start up would mean that the catalyst achieves operating temperature before the engine is ignited.

The combustion reaction also occurs at lower bulk temperatures under conditions of microwave irradiation and therefore, the use of a small microwave generator to heat the catalyst may overcome the short comings of the abilities of traditional three way systems to remove methane form exhaust gases.

4. Experimental

4.1 Experimental Equipment

4.1.1 Oxidative Coupling of Methane

Two different sets of experimental equipment were used. One was used to perform experiments using resistive electrical (thermal) heating of the reactor while the other was used for microwave tests. Both apparatus were designed to enable methane and oxygen to be co-fed continuously to the catalyst in the reactor.

4.1.1.1 Thermal Apparatus

A schematic representation of the thermal apparatus is shown in Figure 4.1. The equipment may be divided into three basic components: the gas feed system, the micro-reactor and furnace, and the analysis system.

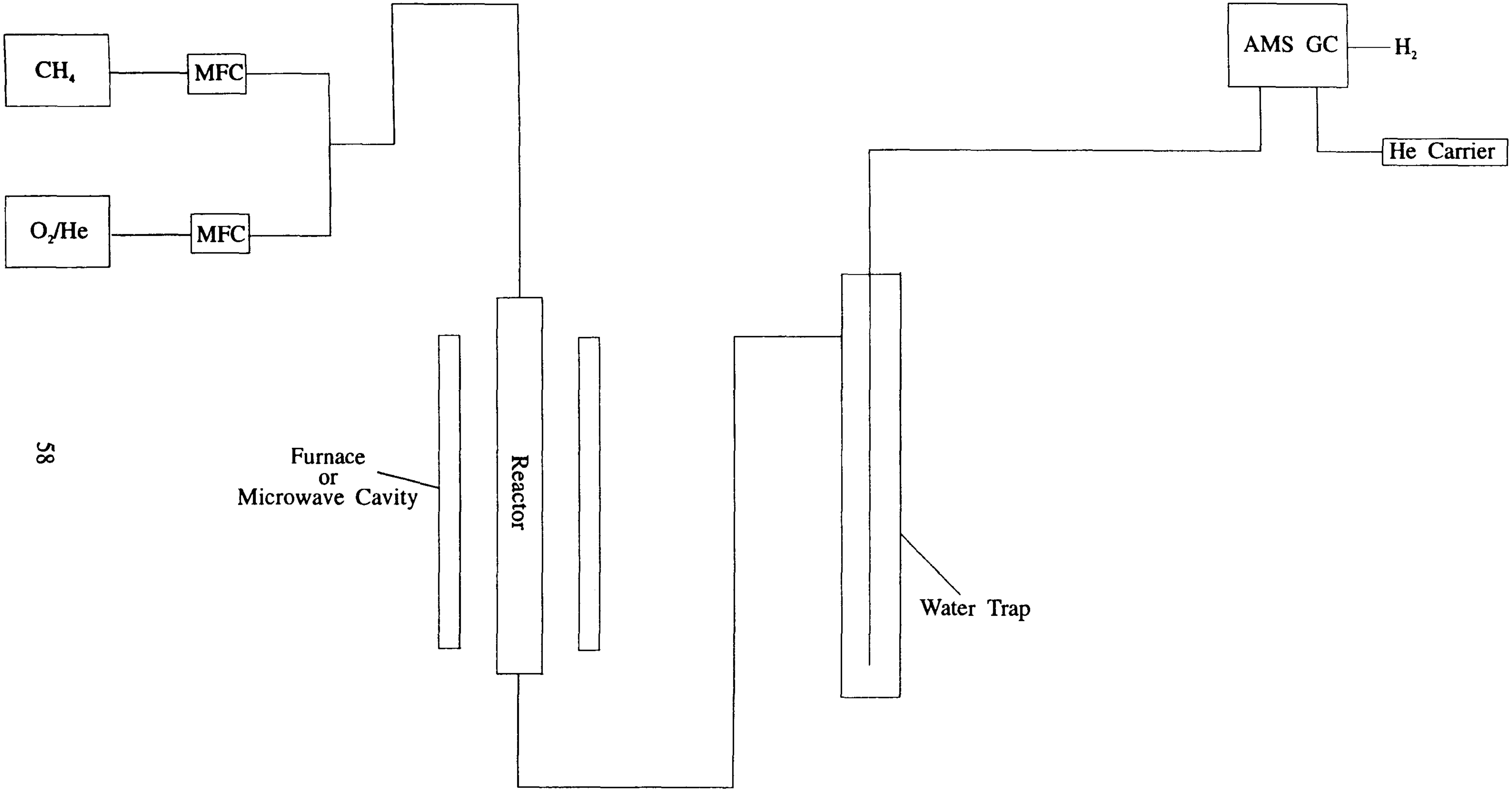


Figure 4.1. Schematic Representation of Oxidative Coupling Apparatus

4.1.1.1.1 The Gas Feed System

Ultra high purity methane (99.999%) and a 5% mixture of oxygen in helium (both of 99.9% purity) both obtained from Engineering and Welding Supplies were fed to the reactor at the required flow rates using separate mass flow controllers (MFCs). The oxygen/helium flow was controlled by a Brooks 5850TR MFC which itself was controlled by a personal computer equipped with an IEEE-488 interface card and digital to analogue converter. The methane flow was controlled by a Chell HA 6568 MFC. The required flow of methane being set using a supply voltage from a potentiometer. The flow rates were monitored using an analogue to digital converter through the IEEE-488 bus.

The MFCs were calibrated by connecting the output to a bubble flow meter and re calibration was performed at regular intervals and minimal drift was observed.

Non return valves were incorporated in the flow system to ensure uni-directional flow of the feed gases.

Flash traps were fitted to the feed gas lines as a precaution against fire.

The feed gases were mixed in a mixing chamber prior to being passed to the reactor. The mixing chamber was simply a Wade Couplings Tee piece fitting.

4.1.1.1.2 The Microreactor and Furnace

Down-flow, fixed-bed microreactors fabricated from silica were used for all tests. Silica was the material of choice since it is able to withstand the high temperatures required for the oxidative coupling reaction and is also transparent to microwave radiation. The reactor was fitted with a central thermowell which housed a thermocouple to enable the temperature of the catalyst bed to be accurately monitored.

The electrically powered furnace was cylindrical and lined with silica. The temperature of the furnace was controlled by a temperature controller linked to a variable output transformer. The transformer was used to control the maximum temperature of the furnace. The furnace temperature was monitored by a thermocouple which was connected to the temperature controller.

The temperature of the catalyst bed was monitored using a K type thermocouple which was placed in the central thermowell of the reactor. The thermocouple was connected to a Digitron 2310 scanner which supplied a digital temperature readout.

A water trap was located beyond the exit of the reactor. This consisted of a pyrex tube loaded with self indicating silica gel. The gel was dried in an oven at 100°C following each test.

4.1.1.1.3 The Analysis System

Two gas chromatographs (GCs) were used to perform the required effluent gas analyses. An AMS Model 93 GC fitted with a 6 ft 1/8 in external diameter PTFE Porapak Q column was used for the quantitation of methane and all products. The detector consisted of a flame ionisation detector fitted with a catalytic methanator (a nickel catalyst). The use of a methanator enabled the quantitation of both carbon monoxide and carbon dioxide by converting these products to methane following separation by the chromatograph. Samples were injected via an air actuated sample loop which was connected to a ten port Valco sampling valve. The column was initially conditioned by heating to 150°C in a helium flow for a period of 8 hours. The chromatographic conditions utilised are shown below.

Carrier Gas	Helium
Carrier Flow	35 ml min^{-1}
Sample loop volume	0.1694 cm^3
Initial Temperature	35°C
Ramp Rate	10°C min^{-1}
Final Temperature	100°C
Final Time	1 min

A Perkin-Elmer 8410 GC fitted with a thermal conductivity detector was also used. The main function of this chromatograph was to monitor oxygen consumption but methane, carbon monoxide and carbon dioxide were also measured. Two columns were utilised: a 6ft. 1/8 in o.d. stainless steel Carbosphere column and a Porapak N column of the same dimensions. The direction of carrier gas flow was reversed after 13 minutes of the analysis to enable the removal of hydrocarbons from the columns. Injection of gas samples was facilitated via an air activated sample loop which was connected to a ten port injection valve. The connections of the ten port valve are shown in Figure 4.2.

Initial column conditioning was carried out as above. The conditions and temperature programme are shown below.

Carrier Gas	Helium
Carrier Flow	30 ml min^{-1}
Sample loop volume	0.5 cm^3
Initial Temperature	25°C
Isothermal Time 1	3.5 min
Ramp Rate 1	30°C min^{-1}
Isothermal Time 2	7 min
Ramp Rate 2	30°C min^{-1}
Isothermal Time 3	5 min
Backflush Time	13 min
Detector Temperature	180°C

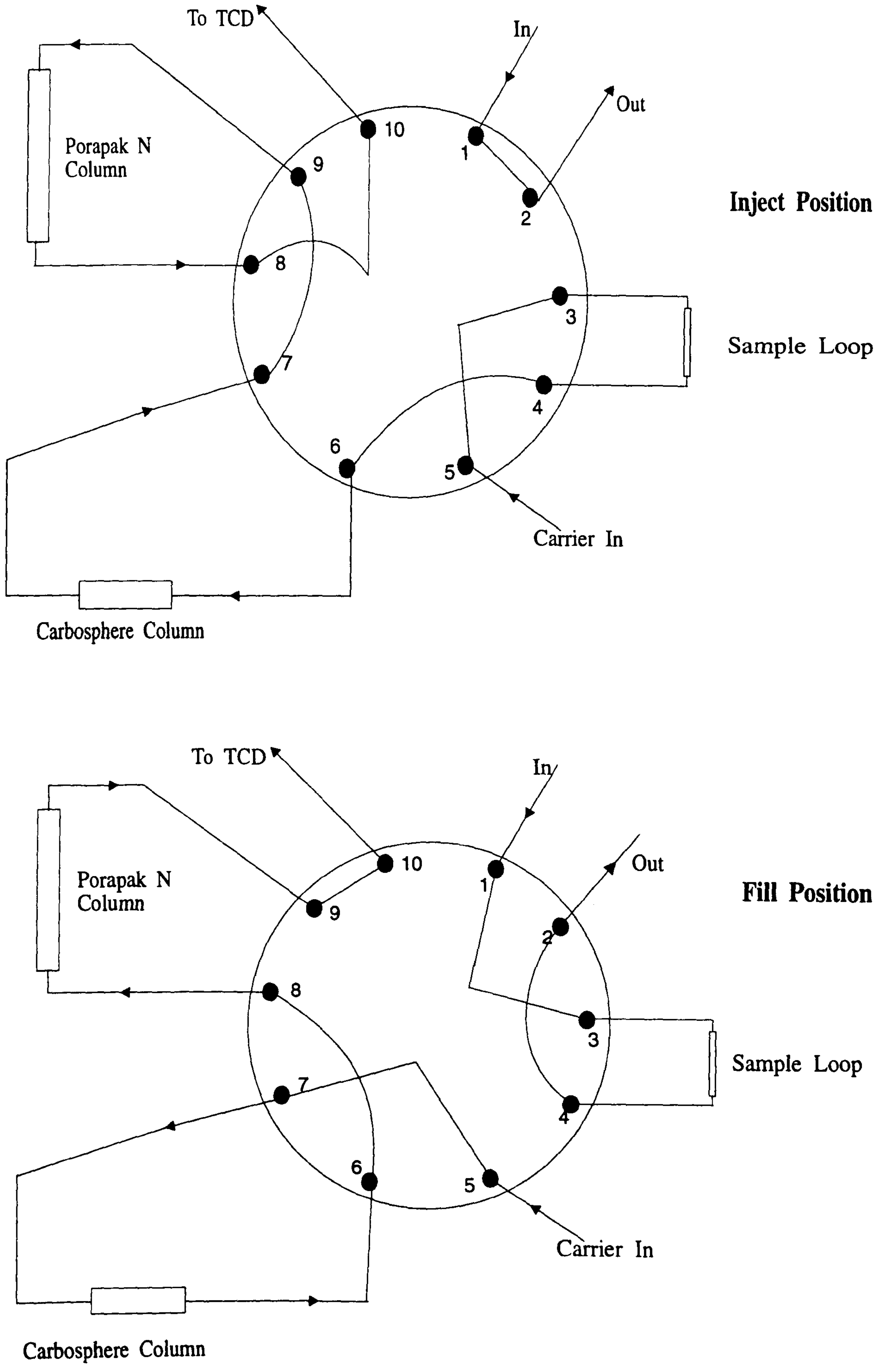


Figure 4.2. 10 Port Gas Sampling Valve

4.1.1.2 Microwave Apparatus

Reactions under microwave conditions were performed using a tuneable single mode microwave cavity which is shown schematically in figure 4.3. The various components of the apparatus are described below.

4.1.1.2.1 The Gas Feed System

The gas feed system of the microwave apparatus was similar to that described above for the thermal equipment. The feed gases were fed to the reactor using computer controlled MFCs and flows were monitored by a personal computer via an analogue to digital converter. Flash traps and non-return valves were again positioned in the feed lines.

4.1.1.2.2 The Magnetron

The magnetron supplied microwave radiation to the sample under study. The output power of the magnetron was continuously variable to a maximum of 700W. The operating frequency was 2.45 GHz. The output of the magnetron was controlled by a personal computer or the temperature measurement device so as to maintain a constant pre-set temperature.

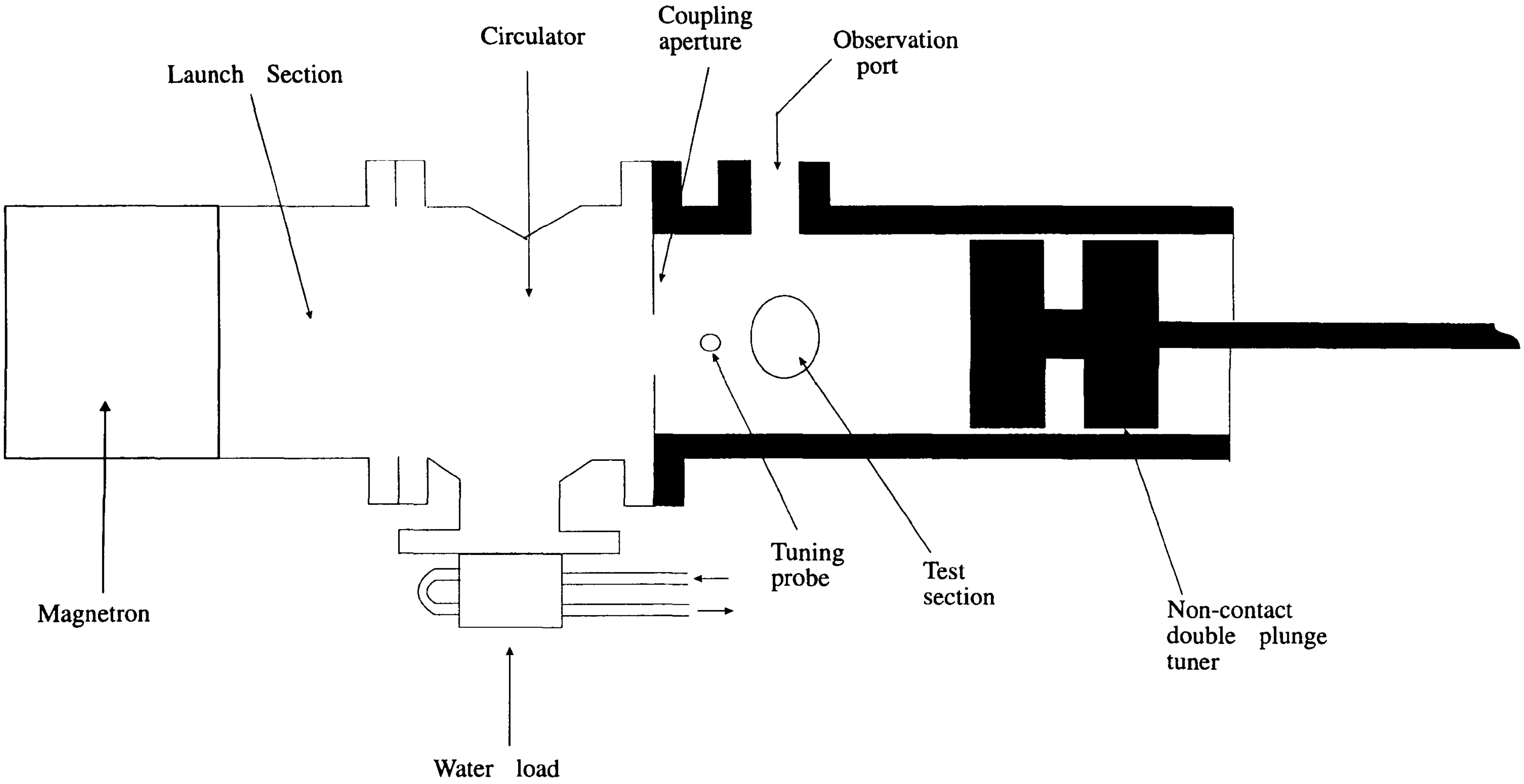


Figure 4.3. Schematic Representation of a Single Mode Microwave Cavity

4.1.1.2.3 The Circulator

The function of the circulator was to prevent the magnetron being damaged by reflected radiation. Microwaves exiting the launch zone were deflected through an angle of 120° prior to passing to the sample cavity. Any radiation reflected from the waveguide that was not absorbed by the sample was prevented from reaching the magnetron by a further deflection by the circulator. This radiation was harmlessly dissipated by the water cooled dummy load.

4.1.1.2.4 The Waveguide

The waveguide incorporated a non-contact double plunge tuner which enabled constructive interference of the microwave energy to be established at the sample. The setting up of a "standing wave" was confirmed by monitoring the signal received by the antenna on an oscilloscope. This enabled the region of maximum E field to be concentrated at the sample.

4.1.1.2.5 Temperature Measurement Devices

Temperature measurement in a microwave field is not a simple task and will be discussed in greater detail later. Several devices were investigated including an infra red pyrometer and optical fibre thermometer These devices were mounted in the observation port of the single mode cavity. A gas thermometer was also tested.

The infra red pyrometer was interfaced to the microwave power controller via a personal computer to enable the catalyst temperature to be accurately controlled by continuously varying the amount of microwave power supplied to the sample under study. The optical fibre thermometer performed the same function without the requirement of the computer.

4.1.1.2.6 The Coupling Aperture

The coupling aperture enabled the focusing intensity of the microwave radiation at the sample to be varied. Apertures of various sizes were investigated. A narrower aperture provided stronger focusing of the radiation.

4.1.1.2.7 The Microreactor

Down flow fixed bed reactors fabricated from silica were used for all microwave tests. Silica is transparent to microwave radiation and is able to withstand the high temperatures required for the oxidative coupling reaction. During testing, the reactor was mounted vertically in the test section part of the single mode cavity.

4.1.1.2.8 The Analysis System

The analysis system used for microwave tests was identical to that described for thermal experiments.

4.2 Experimental Procedures

4.2.1 Mass Flow Controller Calibration

All mass flow controllers were calibrated before any catalyst testing was performed.

Calibration of the MFCs was achieved by connecting a bubble flow meter to the outlet of the MFC and noting the observed gas flow at a variety of input voltages. A computer program was used to calculate an equation relating flow and input voltage and the coefficients of this equation were incorporated into a BASIC computer program which controlled the MFCs. Thus by inputting the desired flow rate into the Basic program, the computer supplied the MFC with the correct voltage to produce the required gas flow. The correct reactant flow was ensured by checking with a bubble flow meter.

4.2.2 Furnace Temperature Profile

The temperature profile of the furnace used for conventionally heated reactions was measured by setting a value on the furnace temperature control box and positioning a thermocouple at various points within the furnace. By noting the temperature at different distances from the bottom of the furnace, a temperature profile was obtained as shown in figure 4.4.

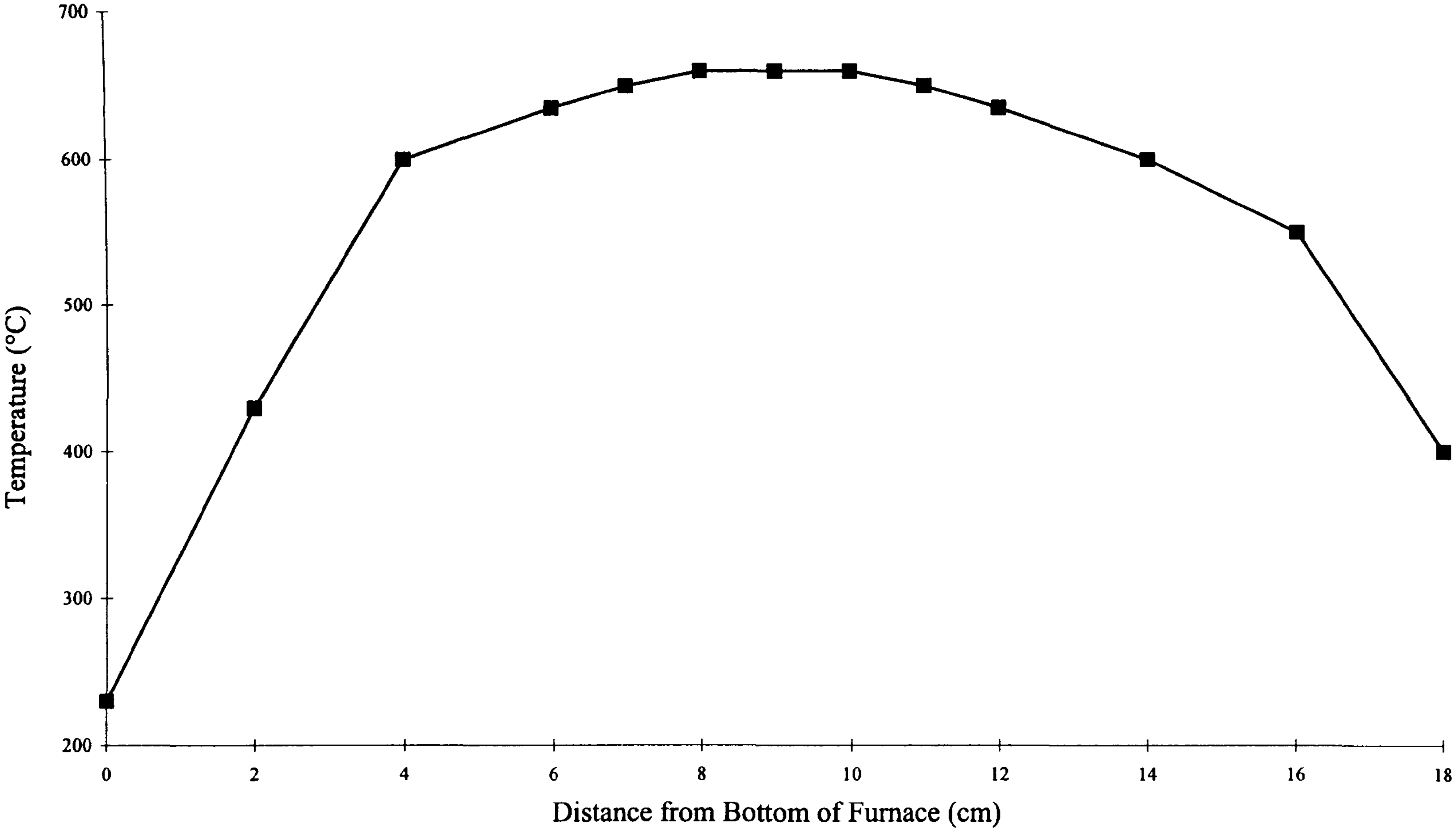


Figure 4.4. Furnace Temperature Profile

The temperature profile clearly shows that the hottest region of the furnace lay between 8 and 10 cm from the bottom of the furnace. For all tests, the reactor was mounted in the furnace such that the catalyst bed resided in this optimal heating zone.

4.2.3 Calibration of the Gas Chromatographs

Both of the GC systems used were calibrated in a similar manner. Standard calibration gases supplied by Phase Separations Ltd. were injected via the sample loops and the resulting peak area for each component noted. Response factors for each required component were then calculated using the following expressions:

$$\text{Moles Component x injected} = \frac{\text{\% Component x}}{100} \times \frac{\text{Volume of Sample Loop (ml)}}{22414}$$

$$\text{Response Factor Component x} = \frac{\text{No moles injected}}{\text{Observed Peak Area}}$$

The response factors were incorporated into a computer spreadsheet program for the calculation of the various reaction parameters which will be discussed in the in the data reduction section.

4.2.4 Reactant Flow Rates

The required flow rate of the reactant gases was set by inputting the required flows into a computer program which then supplied the correct voltage to the mass flow controllers. The exception being the methane flow for thermal tests which was set by setting the required voltage on a calibrated potentiometer.

Typical reactant flow rates were either 5 or 10 ml min^{-1} methane and 20, 30 or 40 ml min^{-1} O_2/He depending on the reactant ratio and space velocity required for a particular test.

Flow rates were varied to determine if any effect on product distribution was observed.

4.2.5 Data Reduction

Product selectivity, yield and reactant conversion are fundamental terms in catalysis and the following defines these terms and outlines the methods used in this study for their calculation.

4.2.5.1 Product Selectivity

Product selectivity is defined as the concentration of the product as a percentage of the total concentration of products formed and may be calculated using the following expression:

$$\% \text{Selectivity Product x} = \frac{\text{Molar Concentration Product x}}{\text{Sum of Molar Product Concentrations}} \times 100$$

4.2.5.2 Methane and Oxygen Conversion

Methane conversion is defined as the fraction of the total amount of methane fed to the reactor that is converted to hydrocarbons and carbon oxides.

Chromatographic calculation of methane conversion is possible in theory using the following expression:

$$(\text{Peak area})_a - (\text{Peak area})_t = (\text{Peak area})_c$$

where $(\text{Peak area})_a$ = ambient methane peak area

$(\text{Peak area})_t$ = Methane peak area at temperature t°C

$(\text{Peak area})_c$ = Area of methane consumed

By using the calculated response factor, peak area values can be converted to molar concentrations and the percentage methane conversion calculated.

Calculation of methane conversion is also possible on a product summation basis and for spreadsheet data manipulation, this method was used. The following expression was employed:

$$\text{CH}_4\ \text{Conversion}\ (\%) = \frac{[CO] + [CO_2] + 2[C_2H_4] + 2[C_2H_6] + 3[C_3]}{[CH_4] + [CO] + [CO_2] + 2[C_2H_4] + 2[C_2H_6] + 3[C_3]} \times 100$$

This assumes that one mole of methane is consumed in the production of one mole of carbon oxides, two moles of methane are consumed in the production of C_2 hydrocarbons and three moles are consumed for C_3 hydrocarbon production.

Oxygen consumption was calculated in a similar fashion to methane conversion. The following expression was used for the calculation:

$$\text{Oxygen Consumption}\ (\%) = \frac{1.5[CO] + 2[CO_2] + [C_2H_4] + 0.5[C_2H_6]}{[O_2]_{\text{inital}}} \times 100$$

4.2.5.3 Product Yield

The yield of a product is defined as its selectivity multiplied by methane conversion:

$$\text{Yield Product x} = \frac{\text{Selectivity x}\ (\%) \times \text{Methane Conversion}\ (\%)}{100}$$

4.2.6 Catalyst Preparation

4.2.6.1 1wt % Sr/La_2O_3

A 1wt% Sr/La_2O_3 catalyst was prepared by the wet impregnation method. 29.7g La_2O_3 was mixed with a dilute (0.228M) solution of $Sr(NO_3)_2$ (total volume of solution was 150 ml). The suspension was heated to dryness with constant stirring. The resulting solid was dried in an oven at 100°C for 12 hours.

Catalysts were calcined at either 650°C or 800°C in air for 4 hours prior to use since previous research (ref 10 from 1st year report) has shown that the calcination temperature has a marked effect on the activity and selectivity of lanthana based catalysts. Further samples were calcined in air for 1 hour at 350°C and in a flow (40 ml min^{-1}) for 1 hour.

4.2.6.2 Magnesia Supported Catalysts

Two catalysts of different composition were prepared. A 1wt% Sr/15wt% La_2O_3/MgO catalyst and a sample consisiting of 1.1wt% Sr/17.2wt% La_2O_3/MgO.

Both catalysts were prepared by the wet impregnation of appropriate amounts of $SrCO_3$ and $MgCO_3$ (the latter in the form of $Mg_2(CO_3)(OH)_2$) with a 0.1M solution of $La(NO_3)_3 \cdot 6H_2O$. The solution was heated with constant stirring to dryness and the resulting solid dired in an oven at 100°C for 12 hours.

The catalysts were calcined in an identical manner to the unsupported catalysts with the exception of the 800°C condition.

4.2.6.3 Other Catalysts

The majority of other catalysts studied required little or no preparation. Diluted formulations were prepared by taking appropriate amounts of catalyst and diluent and intimately mixing them using a mortar and pestle.

Pure lanthana (Gold Label 99.99%) was obtained from Aldrich Chemical Company and was either used as received or calcined before use.

The catalysts supplied by British Gas plc were either used as received or calcined at 700°C for 8 hours between silica wool plugs in a silica reactor before use.

4.2.7 Nature of the Oxidant

Two different oxidants were investigated: - a 5% mixture of oxygen in helium was used with all catalysts and nitrous oxide was used for some of the lanthana containing catalysts.

4.3 Catalyst Characterisation

Catalysts were characterised by performing surface area measurements, X-ray diffraction analysis, scanning electron microscopy, simultaneous differential scanning calorimetry/thermogravimetric analysis (DSC)/(TGA) and investigation using a network analyser.

4.3.1 Surface Area

Surface area measurements were performed on selected catalysts using a Micromeritics Pulse Chemisorb 2700 instrument. A single point determination was used for all tests.

Samples were initially de-gassed by heating to 260°C in a mixture of 30% nitrogen in helium. The instrument was then calibrated by injecting 1ml of nitrogen.

The volume of nitrogen adsorbed at liquid nitrogen temperature and the amount desorbed upon returning the sample to room temperature was measured.

The surface area of the samples was calculated using the following equation:

$$S = v\left[\frac{273.2}{\text{Amb.T.}}\right]\left[\frac{\text{Atm Press.}}{760}\right]\left[\frac{6.023\times10^{23}\times16.2\times10^{-20}}{22414}\right]\left[1-\left[\frac{(\%N_2/100)\times\text{Atm Press.}}{\text{Sat.Press.}}\right]\right]$$

Where: S = Surface area in square metres

v = Volume of nitrogen adsorbed at STP

4.3.2 X-ray Diffraction Studies

Selected catalyst samples were submitted for X-ray diffraction analysis to determine which crystalline phases were present. A Philips X-ray diffractometer using the Cu K_α line at a voltage of 40 kV and current of 30 mA was used for all analyses.

4.3.3 Scanning Electron Microscopy

Selected catalysts were submitted for analysis by scanning electron microscopy (SEM). A Stereoscan 360 electron microscope (Leica-Cambridge) utilising an electron beam energy of 15 keV.

4.3.4 Network Analysis

Network analysis was performed using a Hewlett - Packard apparatus at the University of Nottingham. A schematic diagram of the apparatus is shown in figure 4.5.

Samples were loaded into 6mm o.d. silica tubing such that a 10 cm length of material was formed.

The sample was heated to pre-set temperatures in a conventional electrical furnace before being rapidly lowered into a low power cylindrical microwave cavity operating at a frequency of 2.45 GHz. Whilst the sample was in the microwave cavity, the analyser was used to measure frequency shifts from which both real and imaginary permittivities of the sample could be calculated.

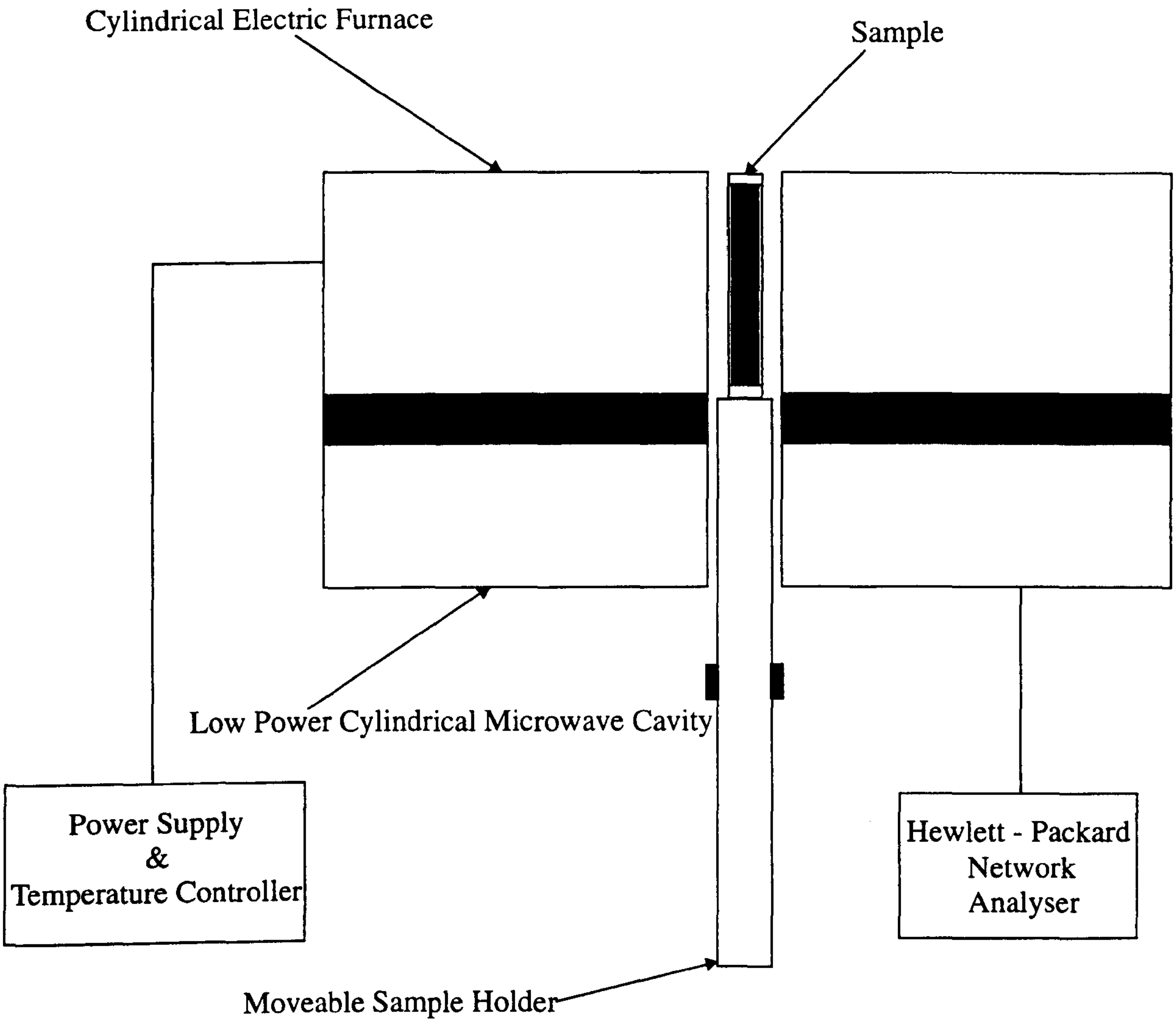


Figure 4.5. Schematic Representation of Network Analysis Equipment

4.3.5 DSC/TGA

Simultaneous DSC/TGA was performed on selected catalysts using a Stanton Redcroft apparatus at Leeds Metropolitan University.

Approximately 10 mg of alumina was used as the reference. 10 mg of sample was loaded into an alumina dish and heated in a flow of helium (30 ml min^{-1})at a ramp rate of 10°C min^{-1} from ambient temperature to a temperature of 600°C. Data was collected automatically every 0.5 seconds and downloaded to a personal computer.

The experimental data obtained were was manipulated using a computer spreadsheet package.

4.3.5.1 Catalysts Studied

1% Sr/La_2O_3

1% Sr/15% La_2O_3/MgO

1.1%Sr/17.2%La_2O_3/MgO

15% La_2O_3/MgO

10% $Sr/La_2O_3/SiC$

80% $Sr/La_2O_3/SiO_2$

La_2O_3

MgO

British Gas "mixed oxide" catalyst

British Gas Catalyst designated CIW1

4.4 Steam Reforming of Methane

4.4.1 Experimental Equipment

The majority of hardware used for steam reforming experiments was identical to that described for the oxidative coupling of methane. A schematic representation of the equipment is given in figure 4.6.

A water bubbler in a thermostatted water bath at known temperature was used to introduce a known vapour pressure of water to the feed gas.

4.4.2 Experimental Procedures

Methane was co-fed with a helium diluent using mass flow controllers to the reactor via the water bubbler. All pipework downline of the bubbler was heated with heating tape to prevent condensation of the water.

Microwave tests were performed with the reactor in a vertical configuration and also mounted transversely across the single mode cavity.

Duplicate effluent gas samples were taken at each temperature of choice.

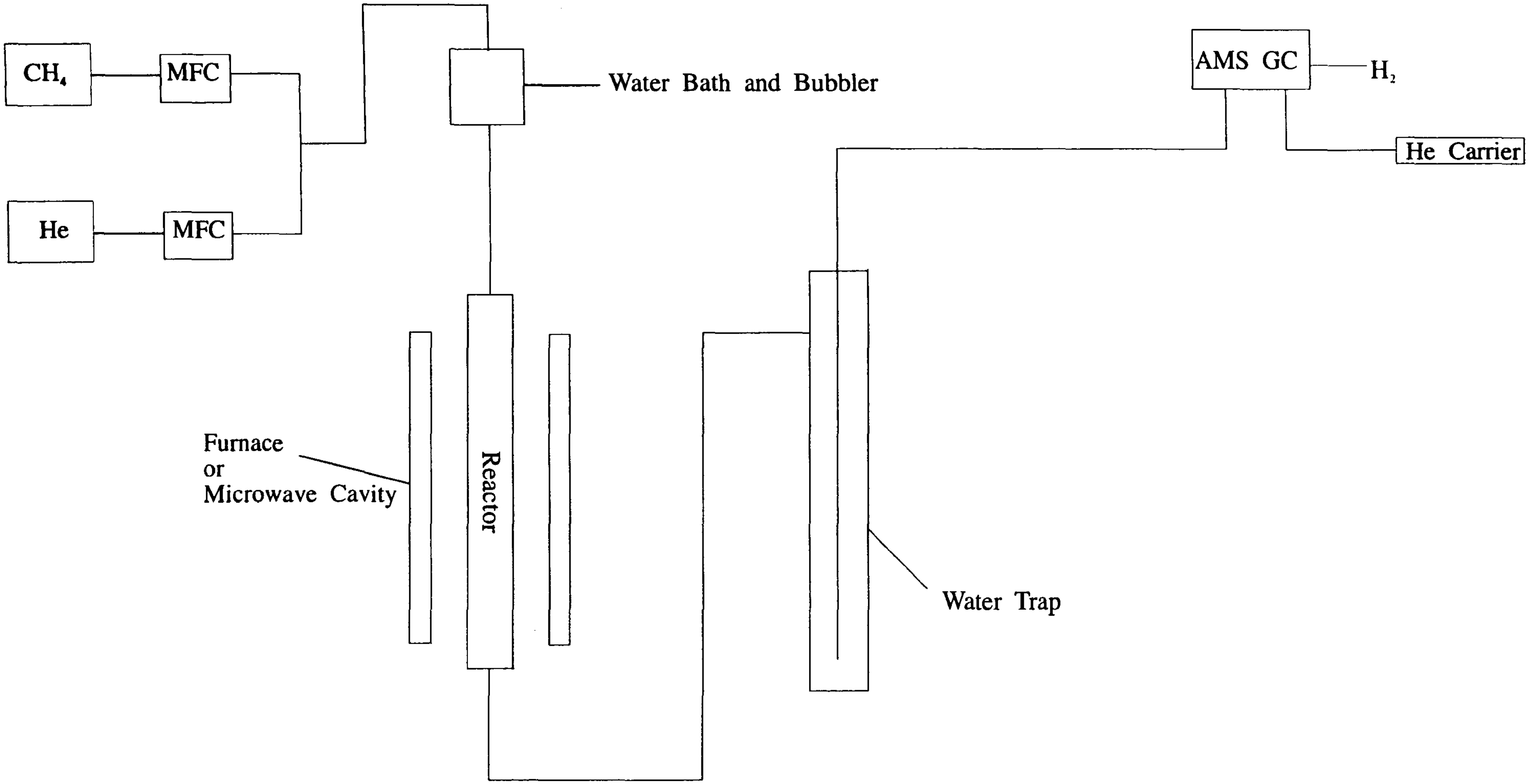


Figure 4.6. Schematic Representation of Steam Reforming Apparatus

4.4.3 Catalysts Tested

A British Gas supplied catalyst designated LH was used for much of the reforming work.

In addition, a selection of alumina supported nickel catalysts were assessed as was a physical mixture of 50wt% LH/50wt% Al_2O_3.

4.4.4 Catalyst Preparation

The only preparation required for the British Gas supplied catalyst was a reduction step. The catalyst was loaded into a silica reactor and heated to 600°C in hydrogen flowing at 40 ml min^{-1} for 12 hours.

The physical mixture of LH and alumina was prepared in the same way as the physically mixed oxidative coupling catalysts.

The nickel - alumina systems were prepared by the wet impregnation of the required amount of alpha alumina with a solution of $Ni(NO_3)_2.6H_2O$.

4.4.5 Catalyst Characterisation

Catalysts were characterised by performing surface area measurements, simultaneous DSC/TGA and network analysis using the same methods as outlined above.

4.5 Methane Combustion

The combustion of methane to oxides of carbon and water was studied under both microwave and thermal conditions.

4.5.1 Experimental Equipment

The equipment used for combustion studies was essentially the same as that described for the oxidative coupling reaction with the exception that only the FID equipped GC was used to monitor the composition of the effluent gas.

4.5.2 Experimental Procedures

Methane, a 5% mixture of oxygen in helium and a nitrogen diluent were fed to the reactor at various flow rates such that different feed gas compositions could be investigated.

The catalyst was heated either in a cylindrical electric furnace or single mode microwave cavity and duplicate GC analyses were performed at each selected temperature.

4.5.3 Catalysts Studied

Pre-prepared platinum - alumina catalysts of a variety of Pt loadings were studied. The loadings investigated were 0.8%, 1%, 3% and 5% Pt by weight.

4.6 Catalyst Preparation using Microwaves

Attempts were made to calcine selected coupling catalysts and reduce reforming catalysts using microwave radiation.

4.6.1 Experimental Procedures

4.6.1.1 Calcination

Approximately 1g of 1wt% Sr/15wt% La_2O_3/MgO was loaded into a silica reactor and mounted verically in the single mode microwave cavity. A 40 ml min^{-1} flow of oxygen helium was fed to the reactor and the sample irradiated.

4.6.1.2 Reduction

1g of fresh LH catalyst was loaded into a silica reactor and placed in the single mode cavity. A flow of 40 ml min^{-1} H_2 was established and the sample irradiated.

5. Results

5.1 Oxidative Coupling of Methane using Rare - Earth Oxide Catalysts

A range of supported and unsupported lanthana catalysts were investigated. The effect of calcination conditions, strontium doping, variation of reactant ratio and flow rate were studied.

5.1.1 Conventionally Heated Reactions

5.1.1.1 Blank Reaction

An experiment was conducted on an empty reactor in order to determine the extent of any non-catalysed gas phase reactions. The test was performed using identical experimental techniques to those employed for catalytic experiments.

Analyses of the reactor effluent gas showed small amounts of CO between 726°C and 730°C the yield increasing with temperature.

Very small amounts of ethane were produced over the same temperature range but the overall yield of coupled hydrocarbons was found to be negligible and never exceeded 0.1%.

5.1.1.2 Effect of Strontium Doping

Strontium doping of both the supported and unsupported catalysts led to an increase in C_2 selectivity and yield. Enhanced methane conversion was achieved by the strontium doping of magnesia supported lanthana. However, the strontium doping of unsupported lanthana led to a decreased level of methane conversion. The beneficial effects of strontium doping on selectivity and yield of coupled hydrocarbons were most evident for the unsupported catalyst where improvements in selectivity of greater than 7% were achieved.

Typical results are presented in Table 5.1.

Catalyst (Calc. Temp./°C)	C_2 Selectivity % (Temp/°C)	C_2 Yield % (Temp/°C)	CH_4 Conversion % (Temp/°C)
La_2O_3 (650)	48.3 (742°C)	11 (742°C)	22.7 (742°C)
Sr/La_2O_3 (650)	55.9 (759°C)	12.2 (759°C)	21.9 (759°C)
15wt% La_2O_3/MgO	58.8 (790°C)	12.6 (790°C)	21.5 (790°C)
1wt% Sr/15wt% La_2O_3/MgO	60.3 (789°C)	13.4 (789°C)	22.3 (789°C)

Table 5.1. Effect of Strontium Doping on Catalyst Performance

5.1.1.3 Effect of Reactant Ratio

Methane to oxygen ratios of 5:1 and 3:1 were investigated for both the doped and undoped catalysts. A general observation was that the yield of coupled products was increased by the use of the lower ratio but often at the expense of C_2 selectivity. A substantial increase in CO_2 selectivity and yield was observed by the use of the lower ratio. Methane conversion was also enhanced at the 3:1 ratio. Typical results are presented in Table 5.2.

Methane to Oxygen Ratio	3	5
C_2 Selectivity (%)	53.5	60.3
C_2 Yield (%)	12.5	13.4
Methane Conversion (%)	29.8	22.3

Table 5.2. Effect of Reactant Ratio on C_2 Selectivity, Yield and CH_4 Conversion for 1wt% Sr/15wt% La_2O_3/MgO Catalyst

5.1.1.4 Effect of Reactant Flow Rate

The use of higher reactant flow rates (greater space velocity) gave enhanced C_2 selectivity at the expense of selectivity to CO_2. C_2 yield and methane conversion for both unsupported and supported catalysts were also increased by use of a higher reactant flow rate. (Table 5.3)

Catalyst (Reactant Flow Rate/ml min-1)	C_2 Selectivity % (Reaction Temp/°C)	C_2 Yield % (Reaction Temp/°C)	CH_4 Conversion % (Reaction Temp/°C)
Sr/La_2O_3 (25 ml min^{-1})	55.9 (759°C)	12.2 (759°C)	21.9 (759°C)
Sr/La_2O_3 (50 ml min^{-1})	57.8 (775°C)	13.9 (775°C)	24 (775°C)

Table 5.3. Effect of Flow Rate on Catalytic Performance for 650°C calcined Catalyst (Reactant Ratio:5)

5.1.1.5 Effect of Catalyst Calcination Conditions

The effect of calcination conditions was found to be dependent upon the nature of the catalyst. This is in contrast to the parameters reported above where it was noted that both supported and unsupported catalysts exhibited many common trends with changing experimental conditions,.

1wt% Sr/La_2O_3 calcined at 650°C for 4 hours in air exhibited greater C_2 selectivity than those calcined at either 800°C or 350°C (the latter for 1 hour). The C_2 yield was also improved by calcination at 650°C.

At reaction temperatures below 740°C, the catalyst calcined at the lower temperature shows greater conversion whilst at temperatures in excess of this, the opposite is true.

Calcination of the catalyst at 350°C for 1 hour either in air or a 5% mixture of oxygen in helium had a deleterious effect on catalytic performance compared to the other calcination conditions investigated. C_2 yield and selectivity and methane conversion were all reduced when the catalyst was calcined at 350°C. Maximum C_2 selectivity for the 350°C calcined samples was 47% compared to 56% for the 650°C calcined sample and 51% for the 800°C sample. The results are summarised in table 5.4.

Catalyst (Calcination Temp/°C)	C_2 Selectivity % (Reaction Temp/°C)	C_2 Yield % (Reaction Temp/°C)	CH_4 Conversion % (Reaction Temp/°C)
Sr/La_2O_3 (650)	55.9 (759°C)	12.2 (759°C)	21.9 (759°C)
Sr/La_2O_3 (800)	47.3 (765°C)	11.2 (765°C)	23.7 (765°C)
Sr/La_2O_3 (350°C O_2/He)	45.6 (779°C)	11.5 (779°C)	25.3# (779°C)
Sr/La_2O_3 (350°C Air)	38.9 (747°C)	8.1 (747°C)	20.7 (747°C)

Table 5.4. Effect of Calcination Conditions on 1wt% Sr/La_2O_3 Catalyst Performance

For magnesia supported catalysts, samples calcined at 350°C for 1 hour in air exhibited the best performance of the calcined materials. This is clearly in contrast to the unsupported systems. It was observed that the uncalcined material was the most selective of the supported catalysts. Clearly, a catalyst which requires non-energy-intensive preparation and can achieve selectivity enhancements relative to other catalysts while suffering only small deficits in terms of yield and conversion is an attractive system. A summary of results for supported catalysts is shown in Table 5.5.

The observed results clearly indicate that the magnesia-supported catalysts exhibited better catalytic performance than the unsupported systems under the reaction conditions studied. Maximum C_2 selectivity of 60.3% was achieved by the strontium doped supported catalyst whilst the corresponding figure for the unsupported material was 55.9%. The yield of coupled products and methane conversion was generally found to be greater for supported catalysts. This is advantageous since these catalysts utilised less lanthana which is the most expensive component of the catalyst formulation. Clearly, enhanced catalytic performance for reduced cost suggests an attractive catalyst system.

Catalyst (Calcination Temp.)	C_2 Selectivity % (React. Temp. °C)	C_2 Yield % (React. Temp. °C)	CH_4 Conv. % (React. Temp. °C)
SLM (650)	57.5 (782°C)	13.2 (782°C)	23 (782°C)
SLM (350°C Air)	58.2 (782°C)	13.9 (782°C)	23.8 (782°C)
SLM (350 O2/He)	56.9 (806°C)	13.7 (806°C)	24.1 (806°C)
SLM (Uncalcined)	60.3 (789°C)	13.4 (789°C)	22.3 (789°C)
LM (650)	59.7 (749°C)	12.7 (749°C)	21.4 (781°C)
LM (350°C Air)	60.0 (793°C)	13 (793°C)	21.3 (793°C)
LM (Uncalcined)	58.8 (790°C)	12.6 (790°C)	21.5 (790°C)

Table 5.5. Effect of Calcination Conditions on Performance for Magnesia Supported Catalysts

(SLM = 1wt% Sr/15wt% La_2O_3/MgO; LM = 15wt% La_2O_3/MgO)

5.1.1.6 Reactions in the Absence of Gas Phase Oxygen

Supported and unsupported catalysts were tested in the absence of gas phase oxygen. A methane flow of 5 ml min^{-1} was used.

Two tests were conducted, one in which the reactor temperature was increased from 620°C to 760°C and a second where the reactor was maintained at a constant temperature of 754°C for a period of 7½ hours.

The incremental test showed an increase in the yield of CO_2 with temperature. CO was detected at temperatures in excess of 700°C and the yield of this product also increased with temperature.

Coupled products were formed in very small quantities at temperatures above 715°C. The total yield of C_2 hydrocarbons did not exceed 0.04% over the temperature range investigated.

The isothermal test again showed carbon oxides to be the major reaction products. The yield of CO_2 initially increased but then showed a general decrease with time on stream. The CO yield was fairly constant but showed a dramatic increase approximately 6 hours into the test. After this time, the amount of CO_2 in the effluent gas was negligible. After 7½ hours, the amount of carbon monoxide decreased markedly.

C_2 products were produced in negligible amounts throughout the duration of the test.

5.1.1.7 Reactions using Nitrous Oxide as Oxidant

Both supported and unsupported catalysts were investigated using nitrous oxide as the oxidant. As reported in previous sections, other tests had utilised molecular oxygen as the oxidant.

The use of nitrous oxides as the oxidant for the OCM reaction over pure lanthana led to increased selectivity and yield of coupled hydrocarbon products relative to the molecular oxygen reaction. Methane conversion was however reduced relative to the molecular oxygen tests. Figure 5.1. shows C_2 selectivity for lanthana using molecular oxygen and nitrous oxide as oxidants.

An important observation of the N_2O tests over lanthana was that the C_3 yield was some two to three times greater than that achieved when oxygen was used as the oxidant.

In contrast to tests which utilised molecular oxygen as the oxidant, the supported and doped catalyst did not perform as well as pure lanthana when N_2O was employed. Carbon dioxide yield and selectivity were far higher for the supported system whilst C_2 yield and selectivity were reduced. The C_2 yield was less than that observed over lanthana regardless of the reaction temperature. No enhancement in C_3 yield was observed over this catalyst when N_2O was used as the oxidant. Figure 5.2 shows a comparison of C_2 selectivity for both catalysts (calcined at 350°C in 5% O_2/He for 1 hour)

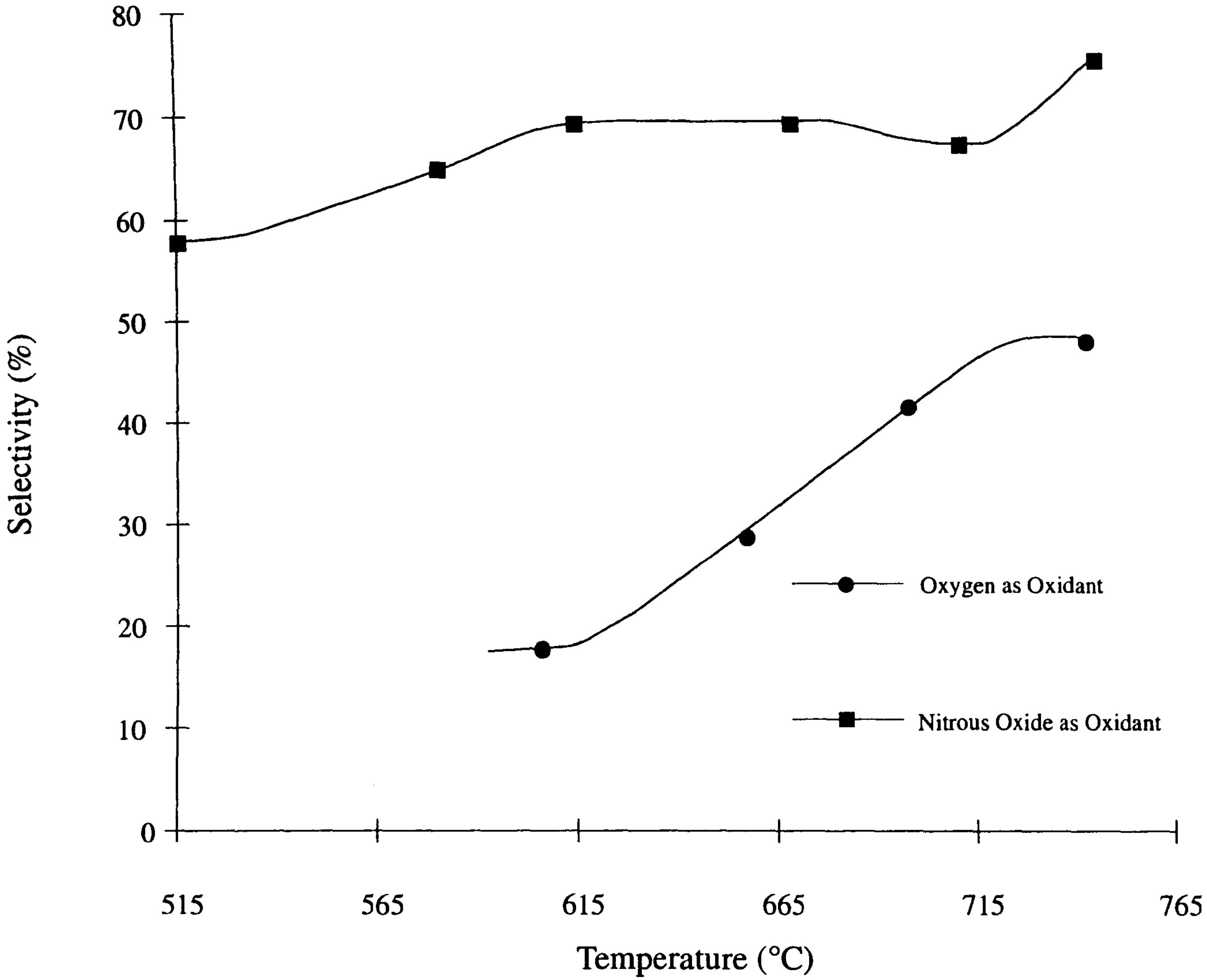


Figure 5.1. Effect of Nature of Oxidant on C_2 Selectivity

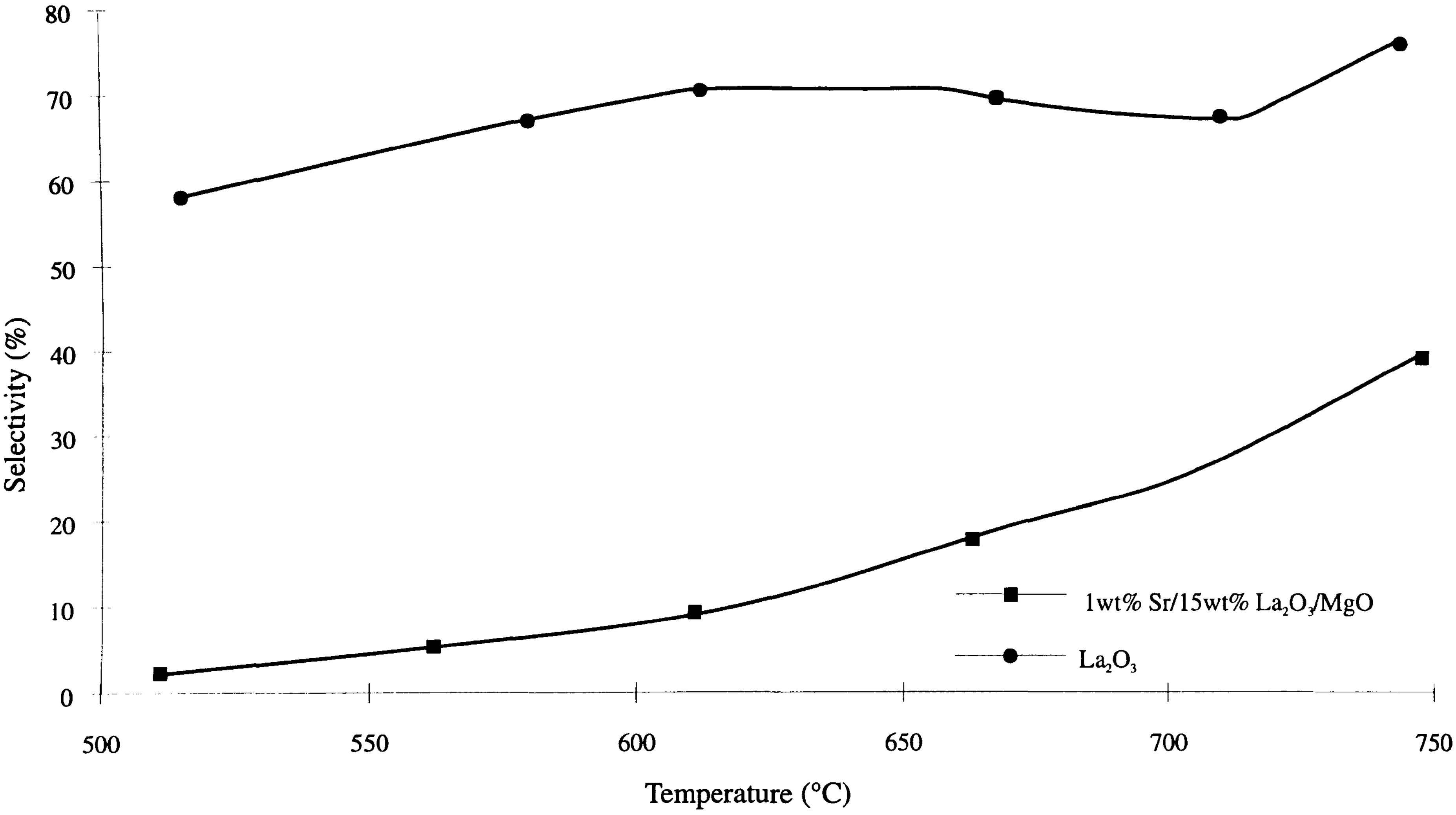


Figure 5.2. Comparison of C_2 Selectivity for La_2O_3 and SLM Catalysts using N_2O as Oxidant

The use of strontium as a dopant and magnesia as a support therefore appears to have a detrimental effect on catalyst performance when nitrous oxide is used as the oxidant.

5.1.1.8 Comparison of Catalytic Performance of Unsupported and Magnesia - supported Catalysts

In general, under the reaction conditions studied, both the strontium doped and undoped magnesia supported catalysts performed better than the unsupported systems regardless of calcination conditions. Enhanced C_2 selectivity and yield was achieved by both undoped and strontium doped supported catalysts compared to either pure lanthana or 1wt% Sr/La_2O_3. Figure 5.3 shows C_2 selectivity against temperature for supported and unsupported strontium - lanthana catalysts.

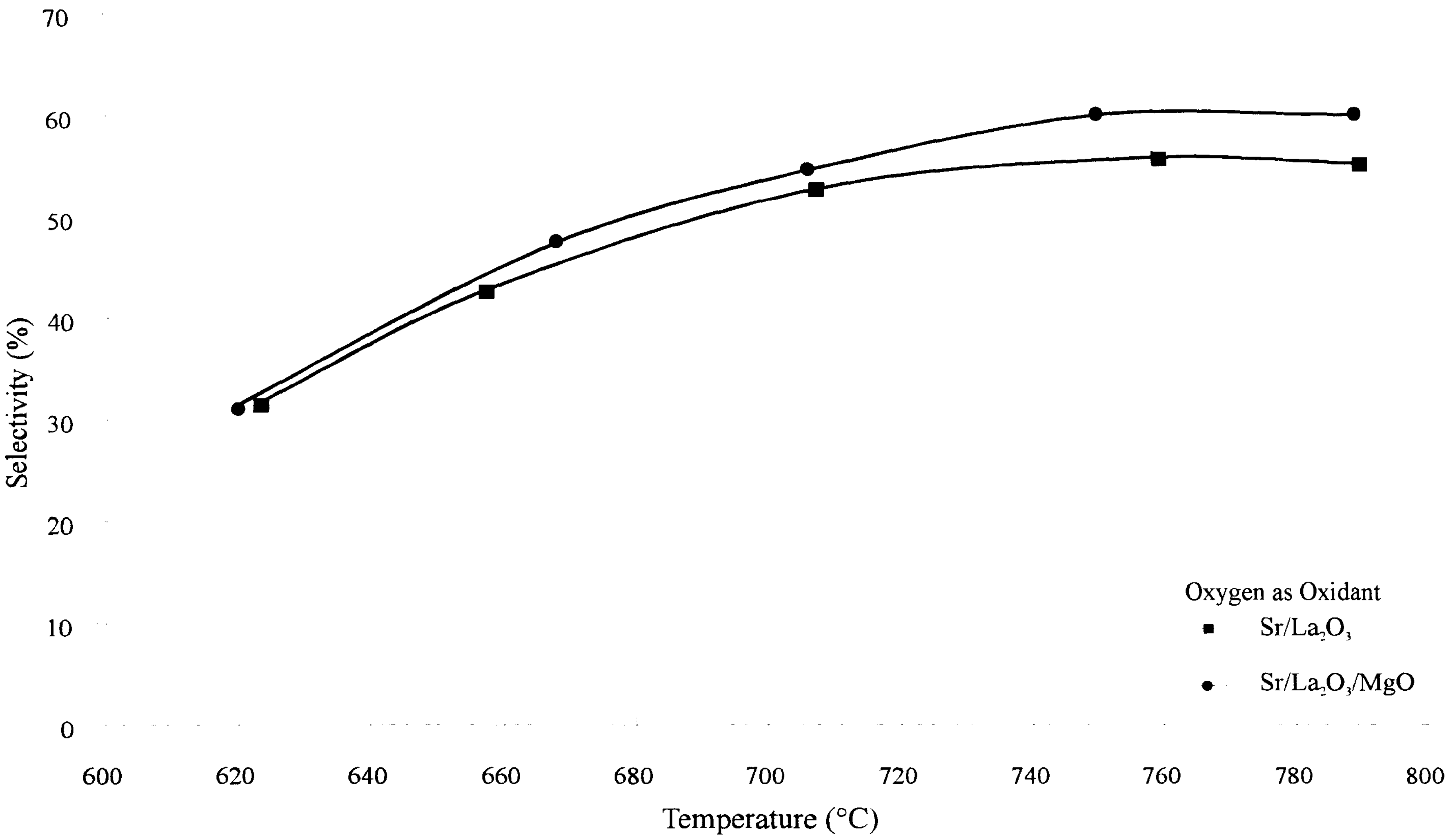


Figure 5.3. Comparison of C_2 Selectivity for Supported and Unsupported Sr/La$_2$O$_3$ Catalysts

5.1.2 Microwave Heated Reactions

5.1.2.1 La_2O_3

Pure lanthana could not be heated in the single mode microwave cavity even when maximum microwave power was used.

5.1.2.2 1wt% Sr/La_2O_3

The microwave heating of this catalyst was found to be extremely difficult. Initial heating required the application of high microwave power and the rate of heating was extremely slow. Following the initial slow heating, a temperature rise was maintained at reduced levels of microwave power.

However, at temperatures in excess of 250°C, the catalyst began to glow and discharges were observed within the reactor. Clearly under such conditions, temperature control of the catalyst bed was impossible.

Gas samples were analysed by GC over the temperature range where discharges were not observed (i.e. below 250°C). Ethene and ethane were produced between temperatures of 165°C and 250°C as indicated by the optical fibre thermometer. The amounts of these products formed at 250°C were similar to those achieved at 730°C under thermal conditions. C_2 products were therefore produced at temperatures several hundred degrees lower than those required under conditions of conventional heating. An important observation was that a higher yield of ethene was achieved under microwave conditions. The major reaction product was CO with CO_2 being produced but in smaller quantities.

Small amounts of acetylene were produced sporadically during the microwave testing of the catalyst. Acetylene production was normally associated with the production of discharges within the reactor.

It is clear from these observations that the catalyst undergoes a dramatic change in dielectric properties with temperature when heated in a microwave field.

In an attempt to heat the catalyst more controllably, the size of the coupling aperture in the microwave cavity was increased. This action had the effect of reducing the degree of focus of the microwave radiation on the sample. However, the result of increasing the size of aperture was that the catalyst could not be heated at all.

The reactor was charged with increased amounts of catalyst in an attempt to provide a larger area of material for the incoming microwave radiation to interact with. Heating of the catalyst again required the use of high microwave power and discharges were observed at an indicated temperature of 250°C.

A further attempt to encourage higher temperatures to be achieved before the production of discharges was made by heating the reactor in a conventional furnace and transferring the hot vessel to the microwave cavity. Once exposed to the radiation, the temperature of the catalyst decreased rapidly from 500°C to 170°C and it could not be increased above 200°C even when irradiated with full microwave power.

The observations of the tests on the Sr/La_2O_3 catalyst suggest that it is unsuitable as a coupling catalyst under microwave conditions. However, thermal tests during this study and by other workers had shown that it is a very effective coupling catalyst. In an attempt to allow its use under microwave conditions, "diluted" forms of the catalyst were prepared and investigated.

Silicon carbide was the material chosen to be mixed with the catalyst. This compound is known to interact strongly with microwave radiation whilst being inert in the OCM reaction. It was hoped that its inclusion in the catalyst formulation would enable more uniform and controlled heating than had been achieved by the Sr/La_2O_3 system in its "pure" form. A 10wt% mixture of 1%Sr/La_2O_3 in SiC was prepared and irradiated in the cavity. A temperature of 475°C was achieved without the production of discharges. However, upon trying to further increase the temperature, the catalyst began to glow and discharges were observed. No significant amounts of product were formed over this catalyst whilst under conventional heating, coupled products were formed at temperatures in excess of 600°C.

A second set of diluted catalysts were tested. 80% and 30% by weight mixtures of Sr/La_2O_3 in silica were prepared as an intimate physical mixture. Silica was the material of choice for this system since it is known to be virtually transparent to microwaves and it was hoped that its inclusion would suppress any discharges. However, the temperature of the catalyst could not be increased above 180°C even when exposed to full microwave power. No products were formed from either of the silica diluted catalysts.

It should be stated at this point that attempts to calcine Sr/La_2O_3/MgO catalysts in the single mode microwave cavity were unsuccessful due to the repeated production of discharges within the reactor.

5.1.2.3 15wt% La_2O_3/MgO

Initial heating of this sample required the use of high microwave power. Temperature control could not be established due to the production of discharges in the reactor.

5.1.2.4 Uncalcined 1wt% Sr/15wt% La_2O_3/MgO

Initial heating of this catalyst also required the use of high microwave power. The catalyst could be heated controllably to a temperature of 500°C without the production of discharges. Coupled hydrocarbon products were detected in the effluent gas between 350°C and 450°C.

The use of microwave radiation to heat the catalyst bed resulted in an enhanced ethene to ethane ratio compared to that obtained using conventional methods of catalyst heating. (Figure 5.4.) Methane conversion under microwave conditions was comparable to that achieved using thermal conditions but at much reduced temperatures.

Selectivity of coupled products was higher than the conventionally heated reaction at lower temperatures. The same observation also applied to the yield of coupled products. (Figures 5.5 & 5.6.)

Attempts to increase the temperature of the catalyst beyond 500°C resulted in the production of a discharge. Following this, the application of low microwave power to the sample resulted in the recurrence of the discharge. Network analysis results for this sample presented in figure 5.7 show a significant increase in tan δ at 550°C. This is 50°C greater than the temperature recorded by the optical fibre thermometer at the moment of discharge. (Max. C_2 Selectivity: 69.8%@ 500, Max. C_2 Yield: 16%, Max. CH_4 Conv.: 23%)

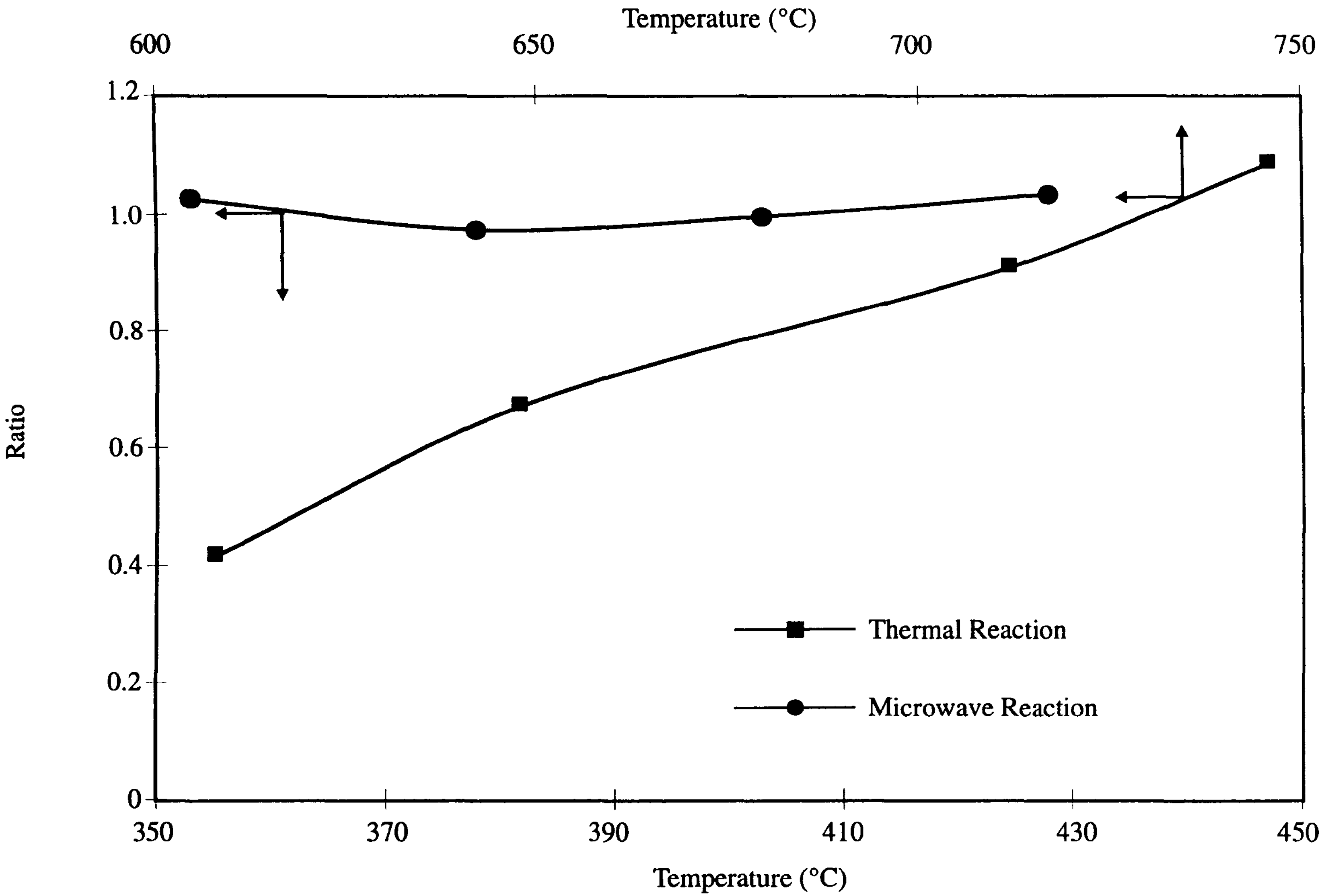


Figure 5.4. Effect of Mode of Heating on Ethene to Ethane Ratio

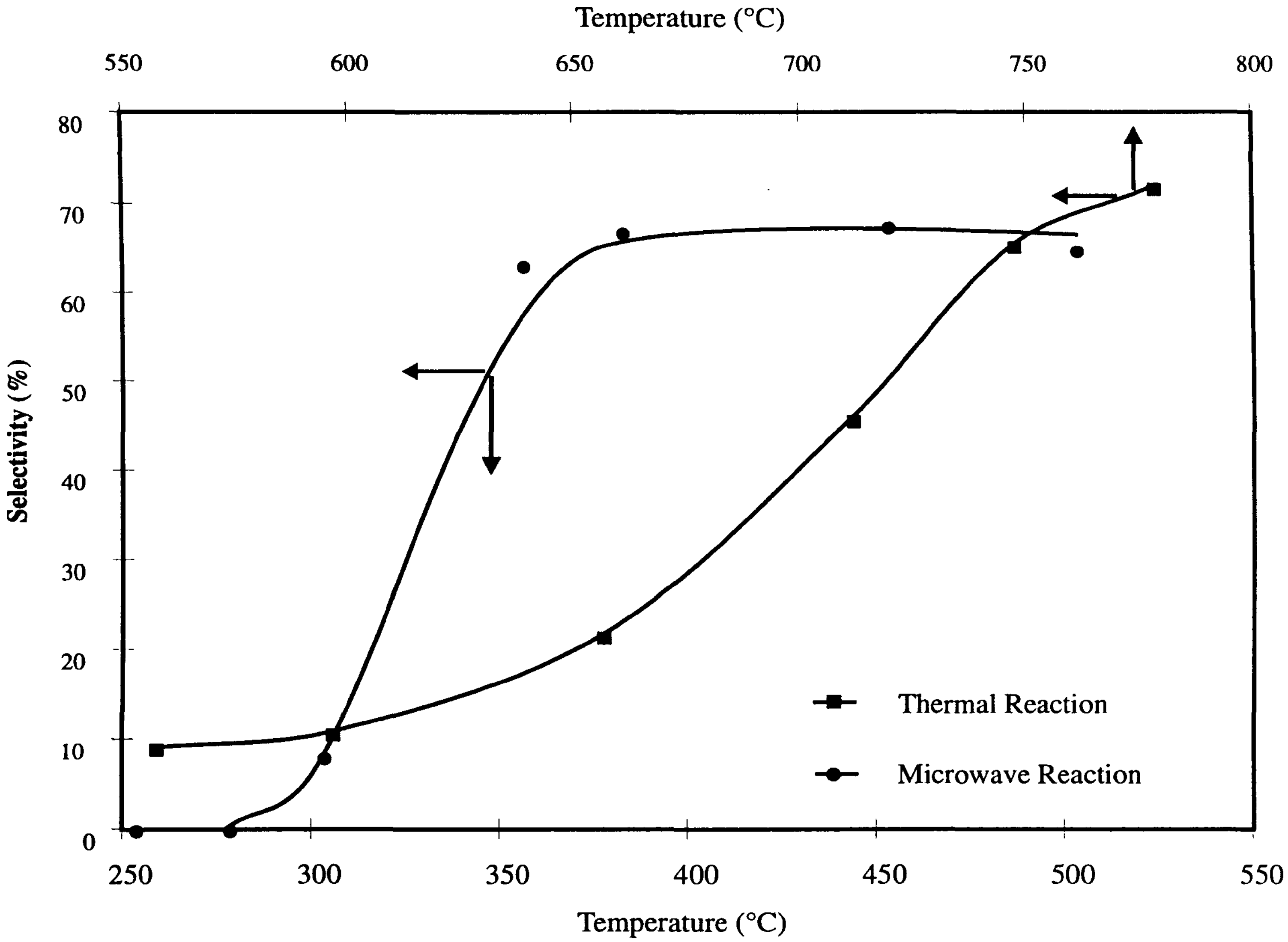


Figure 5.5. Effect of Mode of Heating on C_2 Selectivity

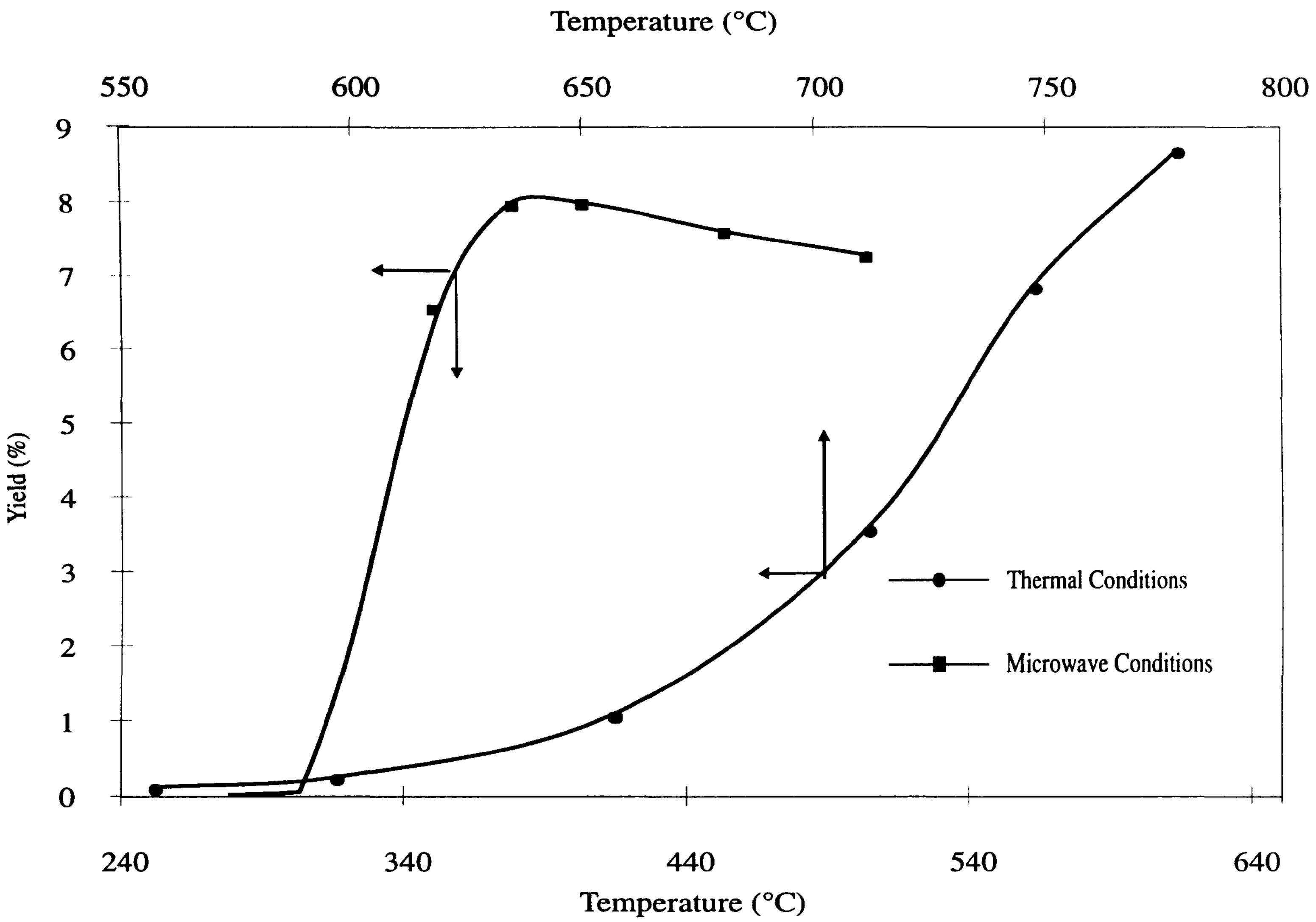


Figure 5.6. Comparison of C_2 Yield for Microwave and Thermal Reactions over SLM

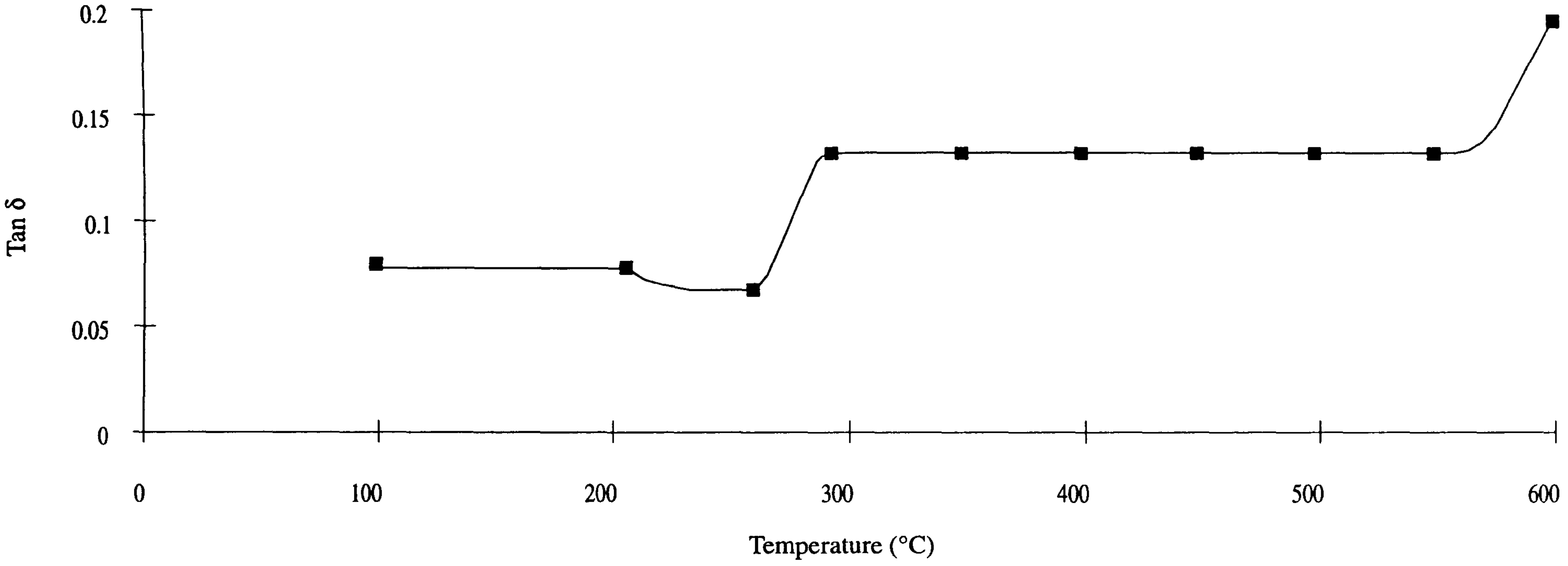


Figure 5.7. Plot of Tan delta vs Temperature fo 1wt% Sr/15wt% La_2O_3/MgO

5.1.2.5 1wt% Sr/15wt% La_2O_3/MgO calcined at 650°C for 4 hours

Initial heating of the calcined catalyst again required the use of high microwave power. However, at an indicated temperature of 200°C, a discharge was observed. The discharge was less vigorous than that produced by the uncalcined catalyst but occurred at a significantly lower temperature.

Due to the mode of operation of the microwave power control system, the microwave power supply was terminated upon the production of the discharge. This caused the catalyst to cool. When the temperature of the catalyst had fallen below the set temperature for the test (i.e. less than 200°C), the control system applied a pulse of microwave power and this resulted in a recurrence of the discharge and discontinuation of the microwave power. As a result of these observations, steady state reaction conditions could not be achieved and therefore the behaviour of the system under discharge conditions was investigated.

The system was allowed to continue under discharge conditions and the observed temperature (as indicated by the Accufiber optical fibre thermometer) varied between 190°C (following the cooling of the catalyst) to 270°C (upon the production of a discharge).

Analysis of the reactor effluent gas under these pulsing conditions revealed that CO was the major reaction product. The second most abundant product under these conditions was acetylene. The amount of acetylene produced increased with increasing time on line. Other products of the coupling reaction were produced in very small quantities.

5.1.2.6 Reactions in the Absence of Gas Phase Oxygen

Tests were conducted on the magnesia supported catalyst using a methane only feed. Initial catalyst heating required high microwave power but temperatures up to 700°C were achieved without the production of discharges. Ethane was produced at temperatures as low as 300°C. Carbon oxides were the major products at lower temperatures but significant amounts of coupled products were formed above 500°C with ethene being the most abundant product after approximately 30 minutes steady state reaction at 505°C. The CO_2 yield decreased with time on stream until becoming negligibly small. Upon increasing the temperature to 550°C, the yield of carbon monoxide increased again and further temperature increases led to CO becoming the most abundant product. The yield of coupled products decreased with time.

A microwave discharge experiment in the absence of gas phase oxygen was also performed. The catalyst used for this test had previously been tested under discharge conditions in the presence of gas phase oxygen and was therefore known to induce discharges in the reactor. Carbon monoxide was the major product in the early stages of the test but the yield of carbon oxides decreased with increasing time on stream whilst the yield of coupled products (including acetylene) was seen to increase. With further time on stream at an observed temperature of 450°C, ethene became the most abundant product whilst acetylene was the next most abundant. Upon increasing the temperature to 550°C, the yield of CO increased with a corresponding decrease in yield of ethene. Worthy of note is that the yield of acetylene continued to increase. The maximum selectivities for ethene and acetylene were 56% and 28% respectively whilst the corresponding yields of these products were 0.9% and 0.7%.

The maximum selectivities for ethene and acetylene were 56% and 28% respectively whilst the corresponding yields of these products were 0.9% and 0.7%.

5.1.2.7 Reactions using Nitrous Oxide as Oxidant

Uncalcined 1wt% Sr/15wt% La_2O_3/MgO

Initial heating of the uncalcined material in the single mode cavity was found to be facile and temperature control was established at temperatures up to 500°C without the production of discharges. No coupled products were observed at temperatures below 300°C although some carbon oxides were produced between 250 and 300°C. A small amount of ethane was produced at 300°C.

At a bulk temperature of 353°C, the yield of CO_2, ethene and ethane increased dramatically and C_3 products were also detected.

In general, the yield of coupled products increased with temperature although an optimum yield was achieved at ca. 400°C (figure 5.8). It can be seen that C_2 yields achieved under microwave conditions were comparable to those obtained using conventional heating but at much lower bulk catalyst temperatures.

A similar observation was made for the C_2 selectivity as illustrated in figure 5.9.

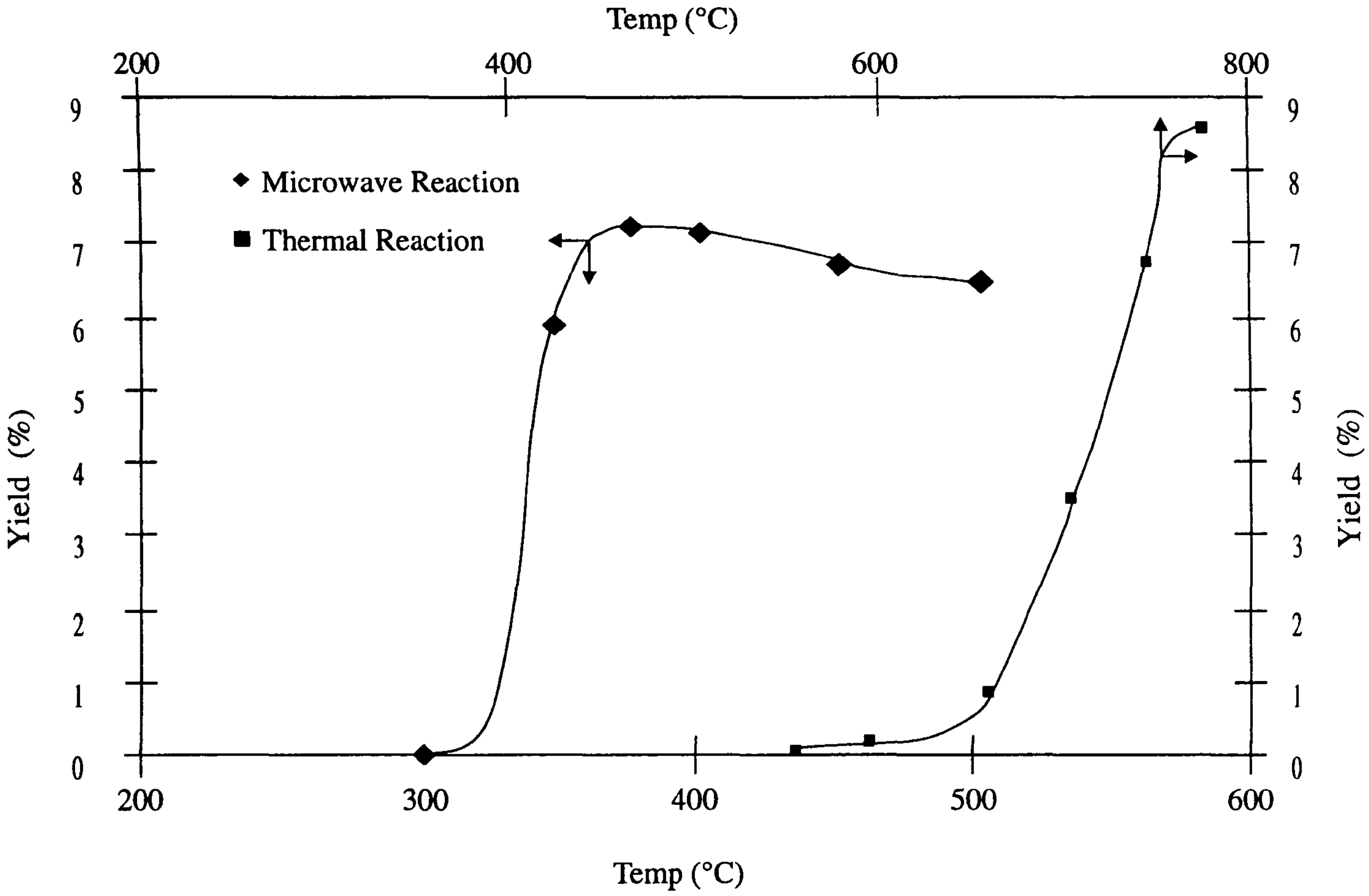


Figure 5.8. Comparison of C_2 Yield for Microwave and Thermal Reactions using Nitrous Oxide as the Oxidant

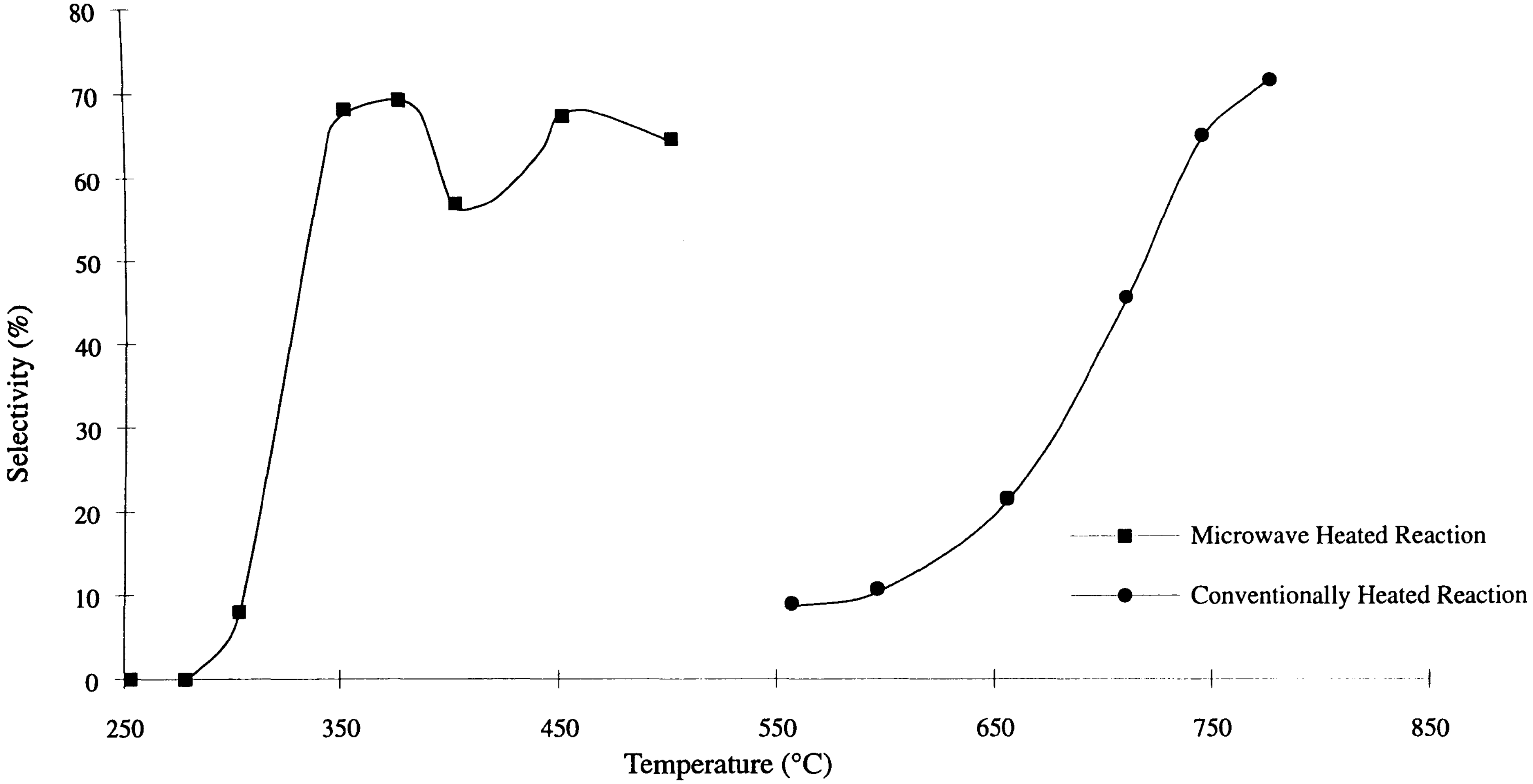


Figure 5.9. Comparison of C_2 Selectivities for Microwave and Conventionally Heated Reactions

5.1.2.8 Microwave Reaction over SLM using trace amount of N_2O in the feed

A reaction was performed over the 1wt% Sr/15wt% La_2O_3/MgO catalyst using the standard reactant feed of methane and 5% O_2/He but a small amount (approx. 4%) of nitrous oxide was included. The test was conducted in an attempt to suppress discharges since it had been found previously that the catalyst could be heated to 700°C in the microwave field in the presence of N_2O without the production of discharges. A temperature of 400°C was achieved without the production of a discharge but after a short period at this temperature a discharge was observed. No increase in the achieved temperature before observation of a discharge was observed compared to "normal" microwave tests. Therefore trace N_2O does not suppress the occurrence of a discharge when the magnesia supported catalyst is heated in a microwave field.

Selectivity to coupled hydrocarbons was reduced relative to both the thermal and conventional microwave reactions. The yield of C_2 compounds was equivalent to that achieved under thermal conditions but at a lower bulk temperature but was far lower than that for the conventional microwave reaction. Methane conversion however was increased by the inclusion of a small amount of N_2O in the reactant mixture. Comparative results are presented in table 5.8.

Conditions	Max. C_2 Selectivity %	Max. C_2 Yield %	Max. CH_4 Conversion %
Thermal	60.3	13.4	22.3
Microwave	69.8	16	23
Microwave + N_2O	55.5	13.4	25.4

Table 5.8. Comparison of Catalyst Performance for 1wt% Sr/15wt% La_2O_3/MgO under different Experimental Conditions

5.1.2.9 Summary of Magnesia Supported Catalyst Experiments

The uncalcined samples could be heated easily in the single mode cavity. The samples appear to undergo changes in dielectric properties with temperature as modification of the amount of microwave power is often required to achieve or maintain a desired temperature.

Steady state microwave tests produced coupled hydrocarbon products at bulk temperatures 300 to 400 degrees lower than those required for the conventionally heated reaction. Furthermore, evidence has been found to suggest that an enhancement of the yield and selectivity of coupled hydrocarbons is achieved under microwave conditions whilst the yield of CO_2 is reduced. An enhanced ethene to ethane ratio has been observed when microwaves are used to heat the catalyst.

A platelet-like structure may be formed within the catalyst during microwave reactions and is thought to encourage the production of discharges during catalyst testing.

The tests in the absence of gas phase oxygen have shown that under microwave conditions, methane can be activated over the rare-earth based catalysts investigated in this study.

The pulse/discharge experiments in the absence of gas phase oxygen produced ethene and acetylene as the major reaction products. The production of these C_2 hydrocarbons followed a period during which carbon oxides were also formed. It is suggested that carbon oxides are formed by interaction of methane with the lattice oxygen of the rare earth oxide and that as the supply of this is depleted, coupled products become more abundant. The coupled products may be formed by recombination of radicals produced from methane during the discharge.

The use of N_2O as the oxidant enabled the catalyst to achieve far higher temperatures than those attained when molecular oxygen was the oxidant.

It is believed that the discharge is originated by the oxygen in the system.

5.1.3 Catalyst Characterisation

5.1.3.1 Surface Area Measurements

BET surface area measurements were performed on selected catalysts. The results are summarised in table 5.9. (Bracketed figures indicate calcination temperature). A higher calcination temperature for the strontium - lanthana catalysts favoured a lower surface area material. The surface areas of these catalysts was found to increase following reaction under both thermal and microwave conditions. The incorporation of magnesia as a catalyst support resulted in a much higher surface area material.

Catalyst	Specific Surface Area (m2g-1)
1wt% Sr/La_2O_3 (650°C)	8.24
1wt% Sr/La_2O_3 (800°C)	3.53
1wt% Sr/La_2O_3 (650°C) after testing in the absence of gas phase oxygen	4.95
1wt% Sr/La_2O_3 (650°C) after testing under microwave conditions	10.34
1wt% Sr/La_2O_3 (650°C) after conventionally heated reaction	9.45
1wt% Sr/15wt% La_2O_3/MgO (350°C)	33.27

Table 5.9. BET Surface Area Measurements for some rare-earth oxide catalysts

5.1.3.2 Network Analysis Results

The results shown in figure 5.10 show the variation of tan δ with temperature for 1wt% Sr/La_2O_3. Three strong and distinctive changes in the dielectric properties of the sample with temperature can be seen. At low temperatures, the system interacts only weakly with the applied field whereas at a temperature between 150 and 200°C, the catalyst interacts very strongly resulting in the production of discharges.

This first change in dielectric properties may be attributed to the removal of water from the sample. Lanthana is known to be strongly hygroscopic and it is not surprising that water vapour from the air was retained by the catalyst. The properties change further between 300°C and 350°C and the tan δ value decreases indicating that the material interacts weakly with the applied microwave field. The range of weak coupling with the microwave field extends to a temperature of 500°C when the third change is observed. These results suggest that the sample undergoes phase changes with temperature.

Figure 5.7 presented a plot of tan δ against temperature for the magnesia supported Sr/La_2O_3 system. An increase in tan δ was observed between 250°C and 300°C but this value then remained constant up to 550°C. Between 550°C and 600°C, tan δ began to increase further. This shows that the catalyst undergoes a change in dielectric properties between 250°C and 300°C.

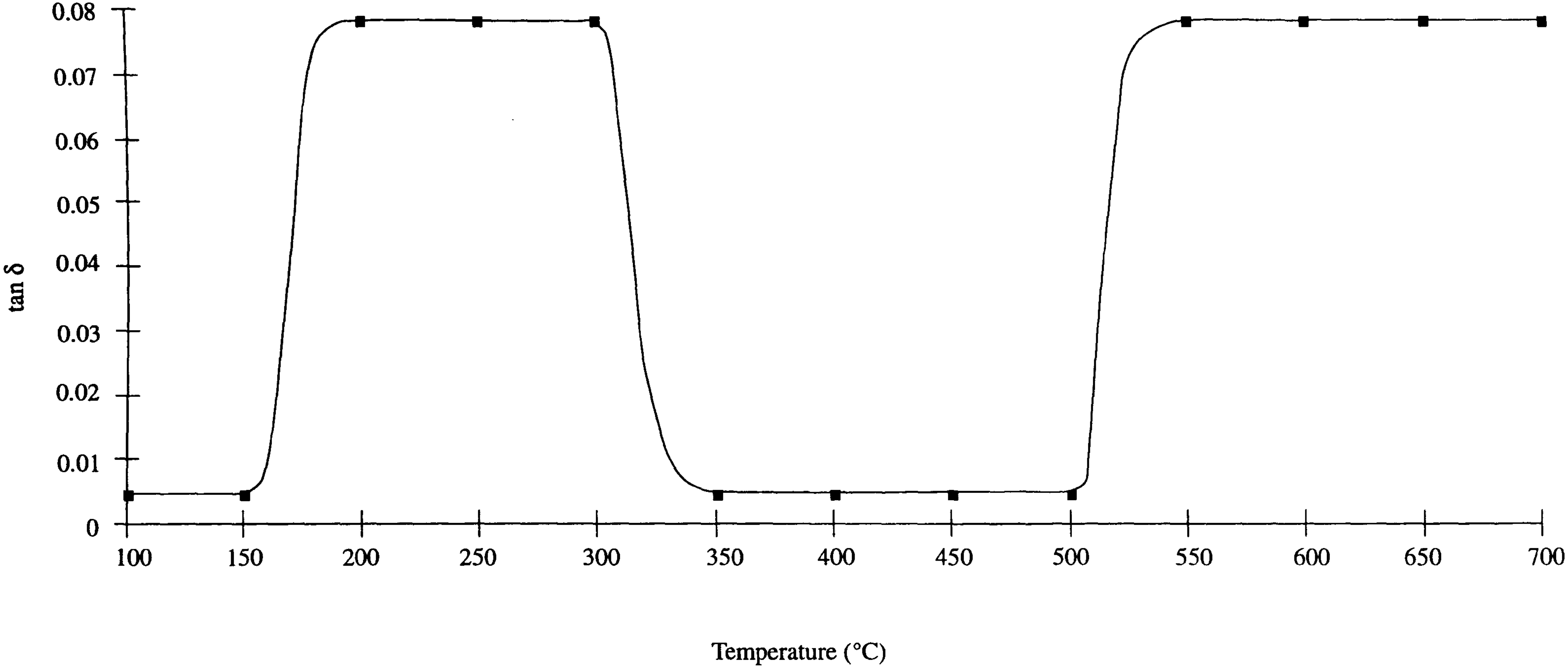


Figure 5.10. Plot of tan δ against Temperature for 1wt% Sr/La_2O_3 Catalyst

5.1.3.3 DSC/TGA Results

Figure 5.11 represents the DSC/TGA data for the strontium lanthana catalyst. At 375°C, a large endotherm and simultaneous weight loss are observed. This suggests that the catalyst is losing a species either from the surface or the bulk at this temperature.

5.1.3.4 Scanning Electron Microscopy

Samples of the strontium - lanthana catalyst both before and after the microwave heated experiments were analysed by scanning electron microscopy. The micrographs of the sample following exposure to microwave radiation revealed that the structure of the sample had been changed and that small plate-like areas were present in the catalyst. Plates 5.1 and 5.2 show scanning electron micrographs of strontium lanthana samples before and after microwave reaction.

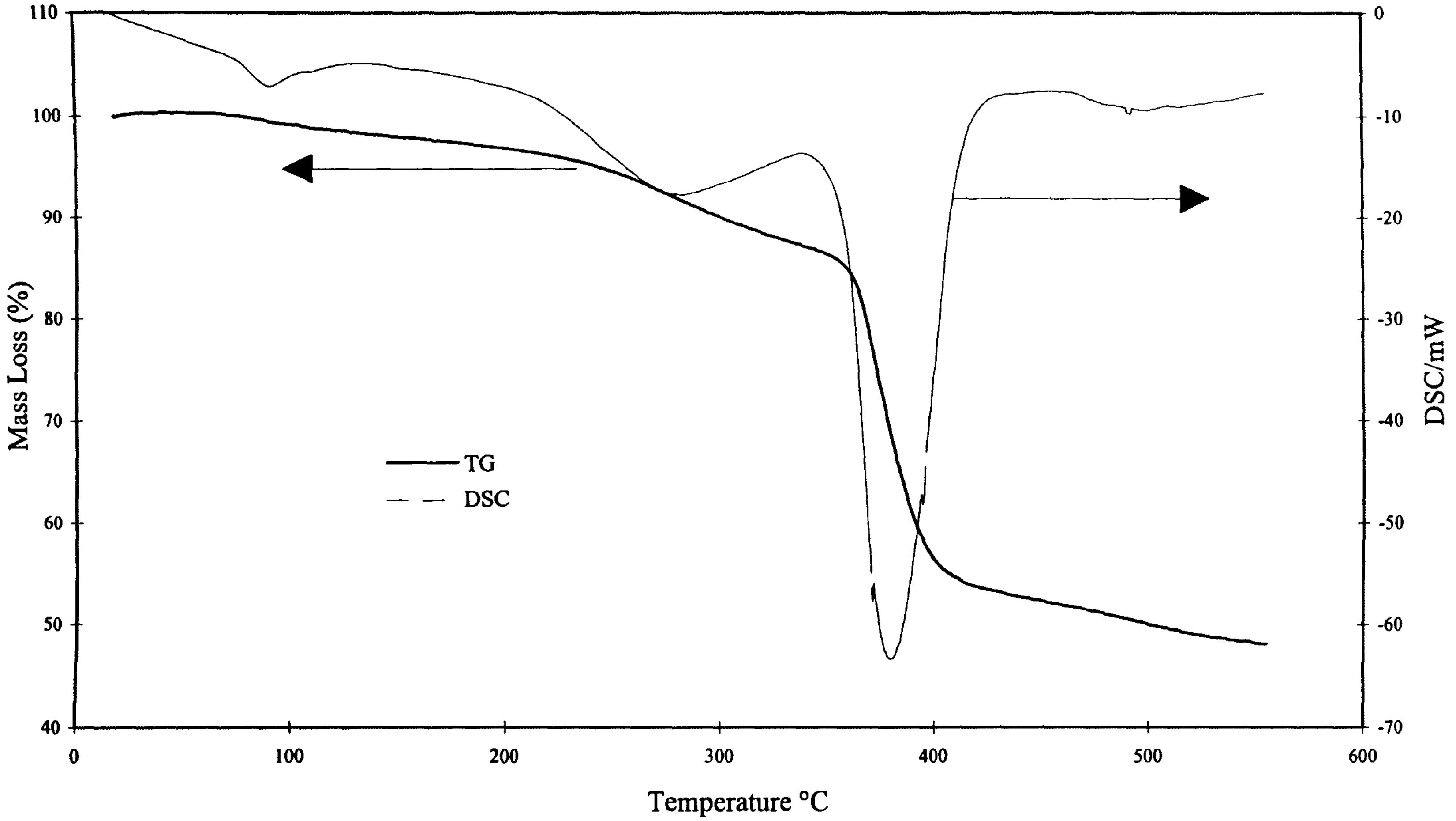


Figure 5.11. DSC/TGA Plot for SLM Catalyst

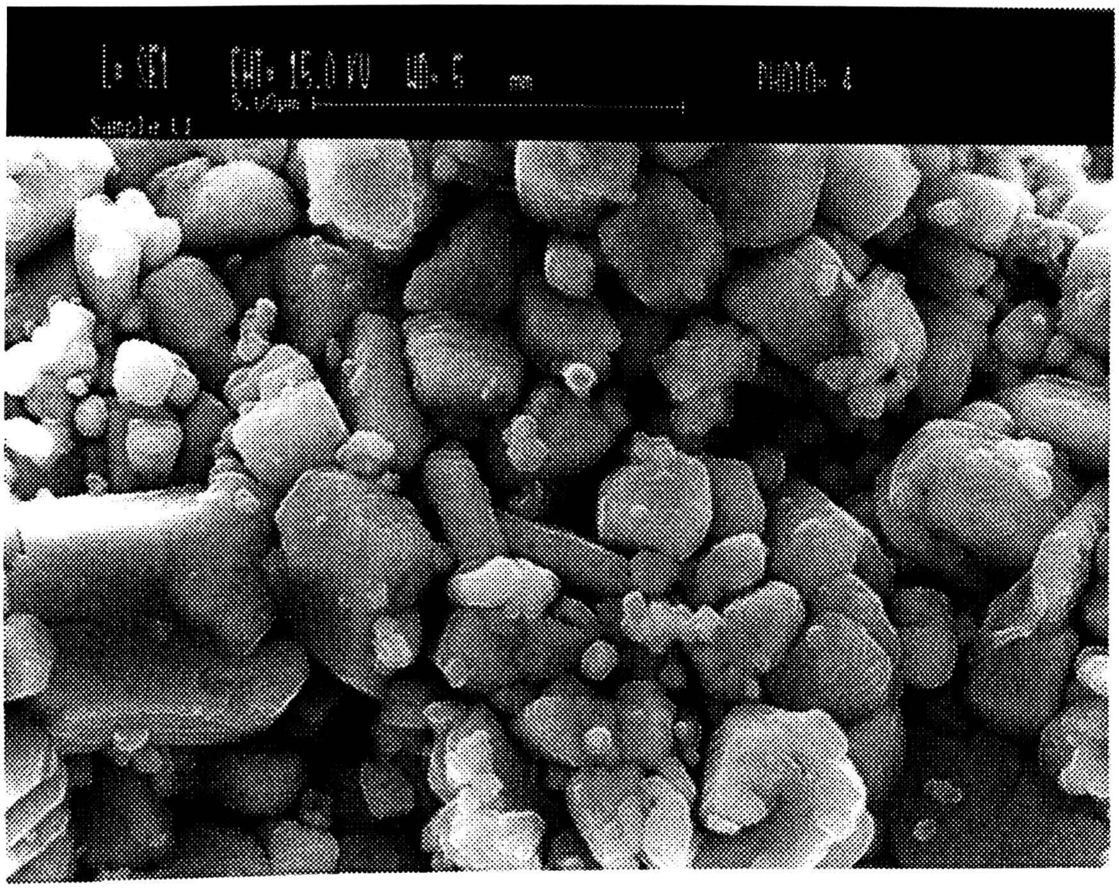


Plate 5.1. SEM Photograph of strontium lanthana catalyst before microwave reaction

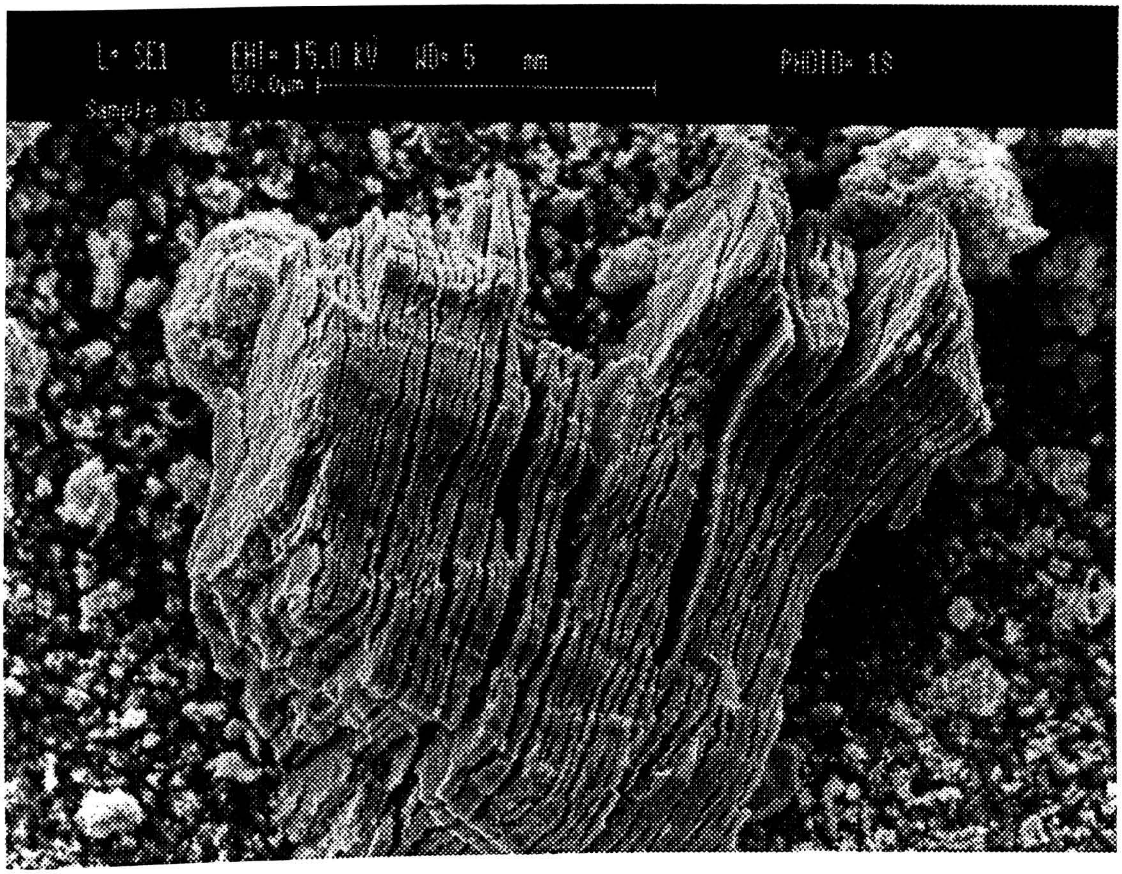


Plate 5.2. SEM Photograph of strontium lanthana catalyst after microwave reaction

5.2 Oxidative Coupling of Methane using Chloride Containing Catalyst

A chloride containing catalyst designated CIW1 supplied by British Gas plc was tested for its suitability for the oxidative coupling reaction. The effects of variation of reactant flow rate and ratio were studied as was the effect of calcination of the catalyst. The catalyst had a high TiO_2 content and this material was tested in order to determine any activity it may have had for the oxidative coupling reaction.

Under the secrecy agreement, details of the formulations of the catalysts cannot be published.

5.2.1 Conventionally Heated Reactions

5.2.1.1 Reaction on TiO_2

The OCM reaction on titanium dioxide was performed using conditions identical to those employed for the testing of the CIW1 catalyst. Over the temperature range studied, no coupled products were produced. The only products formed were carbon oxides. This suggests that under conventional heating, TiO_2 is a total oxidation catalyst.

5.2.1.2 Effect of Calcination

Calcination of the chloride containing catalyst was performed by loading an amount of the material into a silica tube between two quartz wool plugs and heating at 700°C for 7 hours. Under the majority of reaction conditions studied, the calcined material performed better in terms of C_2 selectivity and yield. Although the uncalcined material was not as selective as the calcined sample, it was found to be the more active catalyst. Table 5.6 presents typical results.

Catalyst	C_2 Selectivity %	C_2 Yield %	CH_4 Conversion %
Calcined	82.7	14.5	22
Uncalcined	78.2	17.3	24.2

Table 5.6. Effect of Calcination on Performance of CIW1 Catalyst

5.2.1.3 Effect of Reactant Ratio

Methane to oxygen ratios of 5:1 and 3:1 were again used for the chloride system. Common effects of decreasing the methane to oxygen ratio are increased methane conversion and product yield but often at the expense of reduced selectivity to coupled products. The CIW1 catalyst exhibited this type of behaviour when the reactant ratio was reduced from 5 to 3. Table 5.7 shows the effects of variation of the reactant ratio.

Catalyst and Reactant Ratio	C_2 Selectivity %	C_2 Yield %	CH_4 Conversion %
Calcined Ratio 5	82.7	14.5	22
Calcined Ratio 3	75.8	24.1	36.1
Uncalcined Ratio 5	78.2	17.3	24.2
Uncalcined Ratio 3	71.9	25.0	38.5

Table 5.7. Effect of Reactant Ratio on Catalyst Performance

5.2.1.4 Effect of Reactant Flow Rate

The effect of variation of the reactant flow rate depended upon whether or not the catalyst had been calcined. For the calcined material, a two fold increase in the reactant flow rate led to increased C_2 yield and methane conversion but had little effect on selectivity. For the uncalcined material, increased C_2 selectivity was observed at the higher flow rate but yield and methane conversion were decreased. For both calcined and uncalcined catalysts, the CO_2 yield and selectivity were decreased by the use of a higher reactant flow rate whilst the production of CO was enhanced.

5.2.1.5 Lifetime Tests

A 48 hour thermal test was conducted on the CIW1 catalyst to assess any decline in catalytic activity and/or selectivity with time on line. A temperature of 720°C ± 5°C was chosen and reactant flow rates were as follows: CH_4: 5.3 ml min^{-1}; O2/He: 19.9 ml min^{-1}.(Methane to oxygen ratio = 5.3)

As with previous thermal tests, the catalyst exhibited high yield and selectivity to ethene. With increasing time on line, ethane became the second most abundant product. The yield of ethene decreased from an initial value of 10.1% to 5.5% after 48 hours on line. The yield of all other products remained fairly constant throughout the duration of the test. Examination of the catalyst following the test showed a marked darkening of the sample.

5.2.1.6 Production of Higher Hydrocarbons

For both the calcined and uncalcined catalysts, liquid residues were observed in the reactor exit following many of the tests. Samples of these residues were analysed by GC - MS and the results revealed the presence of C_5+ oxygenated species. This is an interesting observation as it has not apparently been previously reported that such higher hydrocarbons may be produced during the OCM reaction. The production of such species was however erratic and difficult to reproduce.

5.2.2 Microwave Heated Experiments

5.2.2.1 General Observations

Coupled hydrocarbon products were formed in similar yield and with similar selectivity to the conventionally heated reaction at temperatures up to 250°C less than those required for the thermal reaction. Figure 5.12. shows a comparison of C_2 selectivity for conventionally heated and microwave heated reactions.

Initial heating of the catalyst required the use of maximum microwave power but as the temperature increased, the power could be gradually decreased.

At a temperature of approximately 230°C, a large, instantaneous increase in the catalyst temperature was observed. The maximum temperature achieved during this surge was approximately 450°C. The control system was able to re-establish temperature control following the surge. A similar observation was made between temperatures of 270°C and 280°C. However, following the rapid temperature increase at this higher temperature, control was re-established around the desired setpoint using a much reduced amount of power than was previously required. This suggests a dramatic change in the dielectric properties of the sample between the temperatures of 270°C and 280°C.

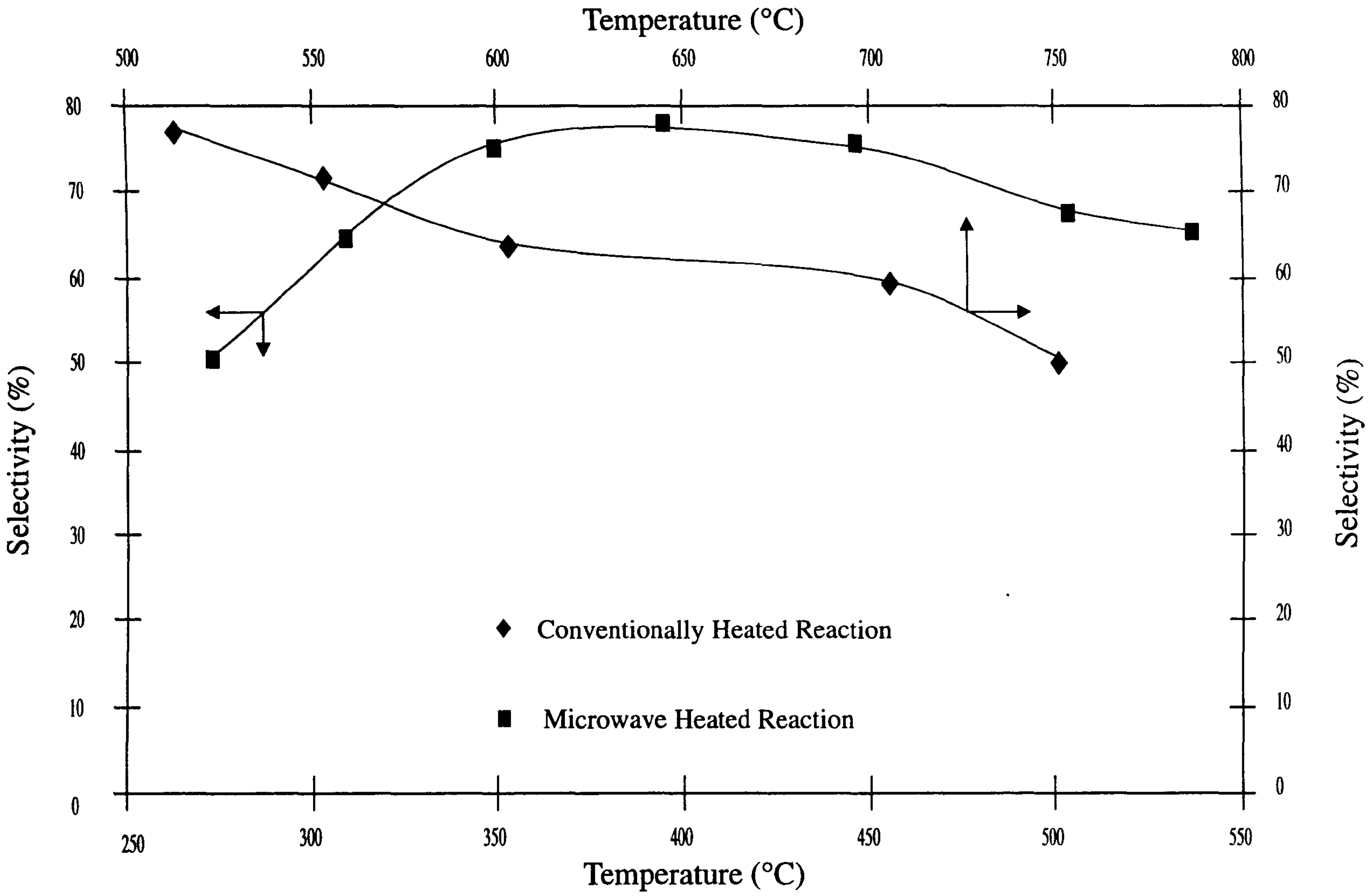


Figure 5.12. Comparison of C_2 Selectivity for Microwave and Thermally Heated Reactions on CIW1 Catalyst

Examination of the catalyst following the microwave reaction revealed some yellow and black particles. Also, liquid had accumulated in the exit of the reactor. Analysis of this liquid by gas chromatography - mass spectrometry showed that it consisted of several higher hydrocarbon components including oxygenated species and cyclic compounds. Software library searches of the mass spectrometry data provided information as to the nature of the various species. Compounds detected were as follows:-

1,1,2,2, - tetramethyl - cyclopropane
4-hydroxy - 4 - methyl - 2 - pentanone
4 - methyl - 4 - penten - 2 - one
3 - methyl - 4 - penten - 2 - one
2,4, - dimethyl - 2 pentanol.

This is the first catalyst tested during this project which has produced oxygenated species and compounds containing more than three carbon atoms.

The production of C_6 and C_7 oxygenated products suggests that lower molecular weight oxygenates may also have been formed during the reaction. The presence of species such as methanol and formaldehyde was not detected because of the nature of the analysis system. Another test incorporated a cold trap in an attempt to isolate any lower oxygenates that may have been formed but GC - MS analysis of washings from the cold trap revealed only the presence of a dimethyl substituted pentanol.

5.2.2.2 Effect of Reaction Temperature

Products were observed at temperatures in excess of 300°C. The yield of ethene and CO increased with temperature and at temperatures of 400°C and above, ethene was the major reaction product with CO being the second most abundant. Trace amounts of acetylene were also produced at temperatures of 500°C and above. At a temperature of approximately 650°C, the product distribution changed dramatically. CO_2 and CO became the major products whilst coupled products were produced only in small amounts.

5.2.2.3 Effect of Calcination

Using a methane to oxygen ratio of 5, the uncalcined material exhibited better performance in the microwave heated reaction than the catalyst calcined at 700°C for 8 hours. However, the reverse was observed when the flow rate of the reactants was doubled as the calcined material was the better catalyst (see Section 5.7.4). Maximum selectivity to C_2 hydrocarbons was greater for the thermal reaction but for the calcined material, the use of microwaves enhanced the yield of C_2 compounds and also the degree of methane conversion.

Under microwave conditions it may be concluded that the calcined catalyst is a better coupling catalyst than its uncalcined counterpart. Furthermore it is able to operate efficiently at lower temperatures than the uncalcined sample. Table 5.10 represents a comparison of catalytic performance for calcined and uncalcined samples. (Bracketed figures show reaction temperature).

Catalyst	Max. C_2 Select. %	Max. C_2 Yield %	Max. CH_4 Conv. %
Calcined	83.7 (450°C)	19 (655°C)	25.3 (505°C)
Uncalcined	77.6 (450°C)	15.8 (603°C)	23.3 (551°C)

Table 5.10. Effect of Calcination on Catalyst Performance

5.2.2.4 Effect of Reactant Flow Rate

Doubling the reactant flow rate over the CIW1 catalyst produced enhanced performance for both calcined and uncalcined materials. The yield and selectivity of coupled products was increased as was methane conversion. Table 5.11 presents a summary of experimental data. (Bracketed figures show reaction temperature).

Catalyst & Conditions	Max. C_2 Selectivity %	Max. C_2 Yield %	Max. CH_4 Conversion %
Calcined 25 ml min^{-1} total flow	70.9 (302°C)	15 (302°C)	23 (352°C)
Calcined 50 ml min^{-1} total flow	83.7 (450°C)	19 (655°C)	25.3 (505°C)
Uncalcined 25 ml min^{-1} total flow	73.7 (456°C)	15.2 (602°C)	24.1 (602°C)
Uncalcined 50 ml min^{-1} total flow	77.6 (450°C)	15.8 (603°C)	23.3 (551°C)

Table 5.11. Effect of Reactant Flow Rate on Catalyst Performance

5.2.2.5 Effect of Reactant Ratio

The effect of reactant ratio on catalyst performance was largely similar for both calcined and uncalcined samples. The use of a methane to oxygen ratio of 3 as opposed to 5 produced enhanced C_2 yield and methane conversion for both catalysts but an enhancement in C_2 selectivity at the lower ratio was only observed for the calcined material. Table 5.12 summarises the data.

Catalyst & Ratio	CH_4 : O_2 Ratio	Max. C_2 Selectivity %	Max. C_2 Yield %	Max. CH_4 Conversion %
Calcined	5	70.9	15	23
Calcined	3	77.9	15.8	26.1
Uncalcined	5	73.7	15.2	24.1
Uncalcined	3	72.1	16.2	27.9

Table 5.12. Effect of Reactant Ratio on Catalyst Performance

5.2.2.6 Lifetime Test of CIW1 Catalyst

A lifetime test under microwave conditions was performed at 540°C for 5 hours. The initial product distribution was similar to that observed during previous microwave tests with a high selectivity to ethene being observed. During the mid-section of the test (between 1.5 and 3.5 hours), the distribution of the products changed markedly. The yield of carbon monoxide increased from approximately 4% to a maximum of 38% before decreasing again in the later stages. This increase was accompanied by a corresponding decrease in the production of coupled hydrocarbon products. The C_2 selectivity and yield were seen to fluctuate to a great extent during the test. Maxima for C_2 selectivity and yield of 61.7% and 13.1 % respectively were recorded while the corresponding minima were 3% and 4.1%. Large amounts of acetylene were produced during the test and this may have been due to the occurrence of small discharges within the catalyst bed as it has been noted previously that acetylene production is promoted by the occurrence of discharges. Due the large fluctuation of the performance of the catalyst during the 5 hour test, the catalyst is considered to be unstable under long term microwave irradiation.

5.2.2.7 Kinetic Considerations

Experimental data was processed to yield plots of ln k against 1000/T for both thermal and microwave coupling tests. Thermal data generally produced linear plots . However, for both thermal and microwave tests, some levelling of the plots was observed at the highest temperatures studied.

Unique to the microwave tests was a levelling of the plots at the lower end of the temperature range.

5.2.3 Comparison Between Microwave and Conventionally Heated Reactions

The clear and major discrepancy between conventionally heated and microwave heated reactions was the observed temperature of reaction. Microwave heated reactions occurred at bulk temperatures of up to 400°C lower than the conventionally heated reactions. Table 5.13 presents a comparison of the performance for both modes of catalyst heating. The results indicate that generally the catalyst performed better under conditions of conventional heating although enhanced selectivity to coupled hydrocarbon products was achieved by the use of microwaves. However, in order to attain the enhancements in conversion and yield observed for the conventionally heated reaction, higher temperatures than those required for the microwave reaction were needed. The production of higher hydrocarbons (e.g. C_5+ species) was noted earlier. It should be stated that the production of such species was reproducible under conditions of microwave heating but erratic under conventional heating. Furthermore, the amount of higher liquid hydrocarbons was greater for microwave heated reactions. The reasons for these observations will be discussed in chapter 7.

	Maximum Values %		
Mode of Heating	C_2 Selectivity (React. Temp. °C)	C_2 Yield (React. Temp. °C)	CH_4 Conversion (React. Temp. °C)
Microwave	83.7 (450°C)	19 (655°C)	27.9 (453°C)
Thermal	82.7 (660°C)	25 (733°C)	38.5 (796°C)

Table 5.13. Effect of Mode of Heating on Catalyst Performance

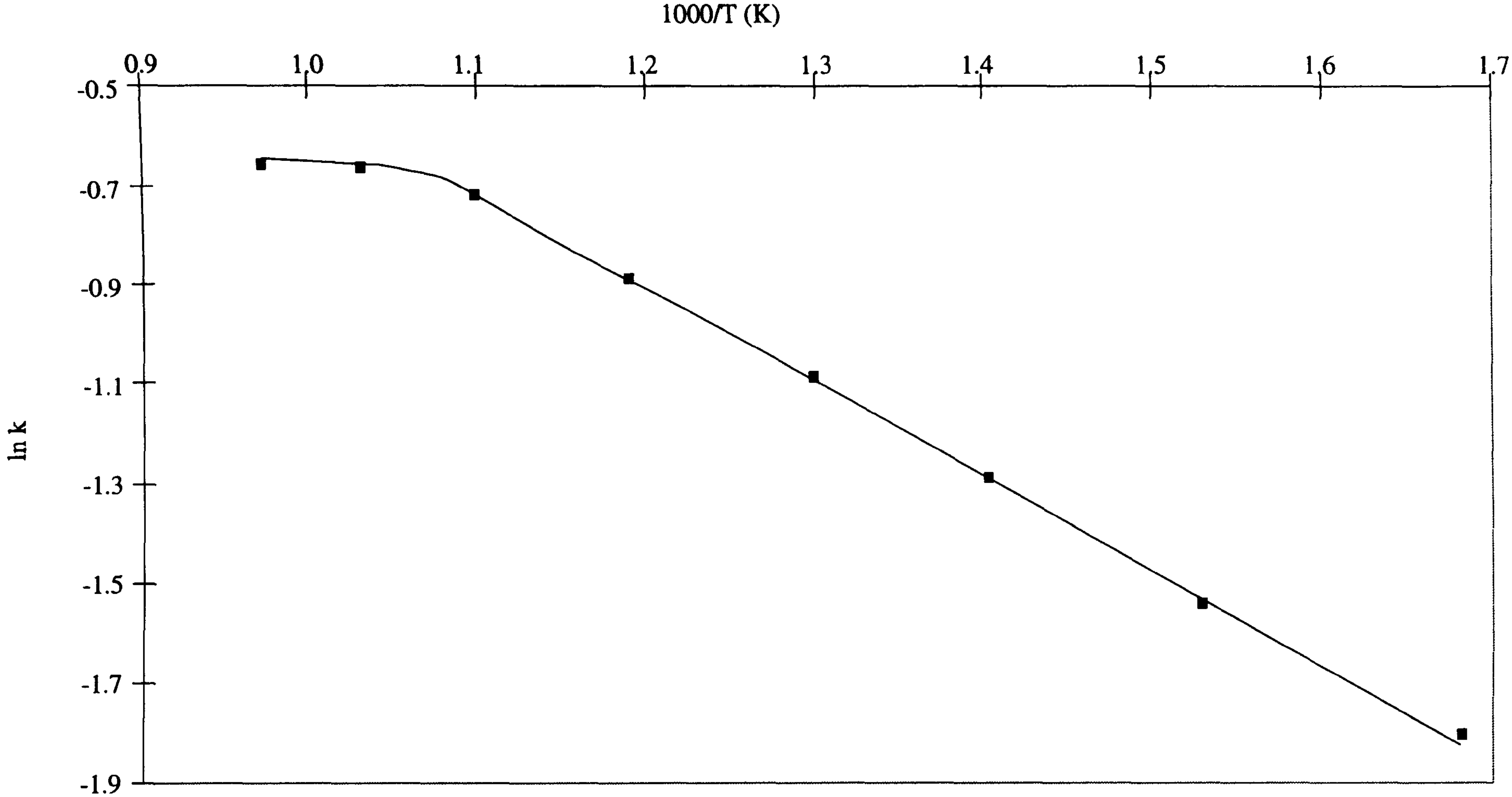


Figure 5.13. Typical Plot ofln k against 1000/T for a Conventionally Heated Experiment

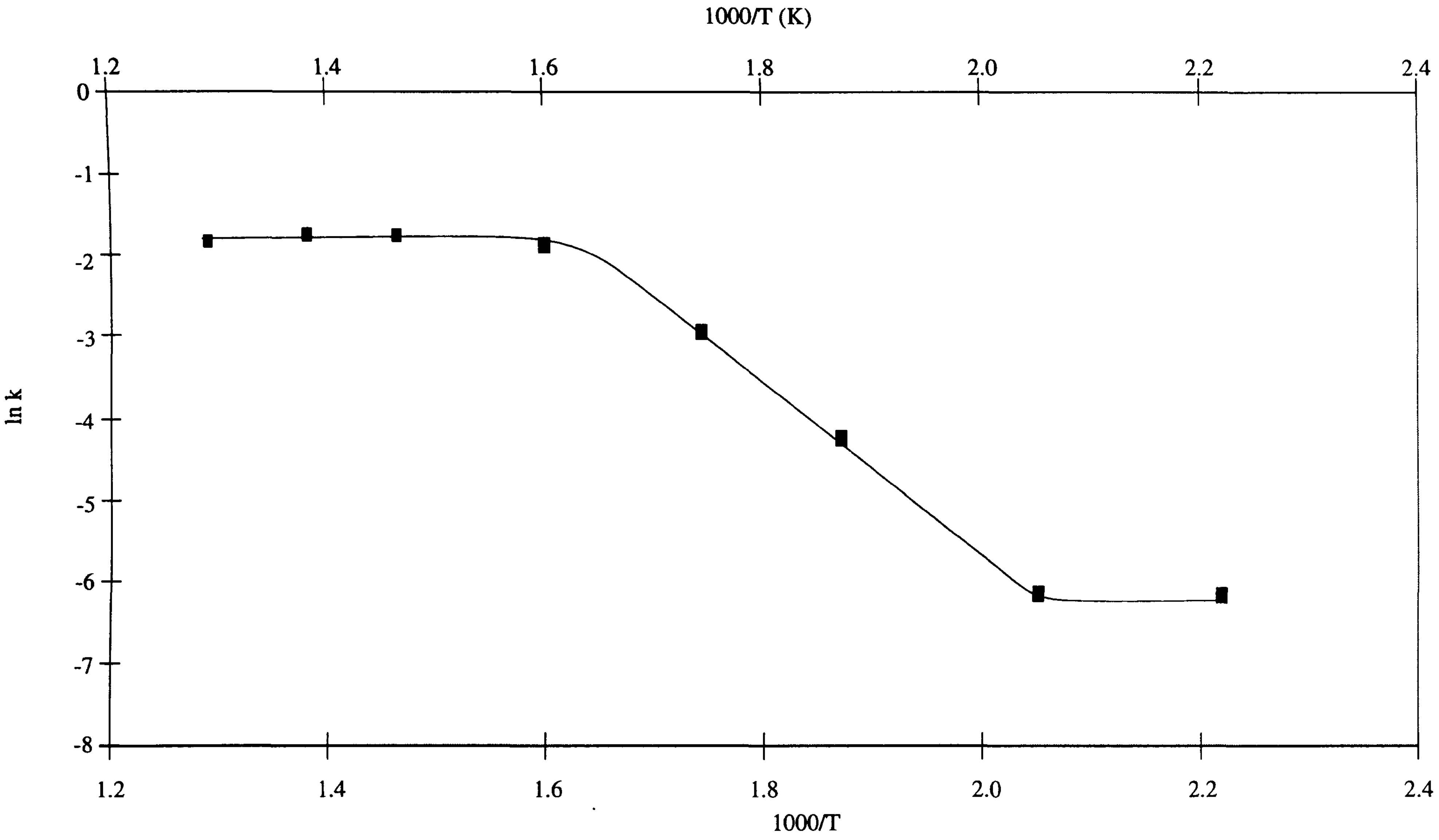


Figure 5.14. Plot of ln k vs 1000/T for Microwave Heated reaction on CIW1

5.2.4 Catalyst Characterisation

5.2.4.1 Surface Area Measurement

BET surface area measurements performed on the CIW1 catalyst revealed that its surface area was low (approximately 1 m^2g^{-1}).

5.2.4.2 DSC/TGA

The DSC/TGA trace for the British Gas CIW1 catalyst is shown in figure 5.13. A sharp endothermic peak at 425°C is clearly visible but this is not accompanied by a corresponding change in mass. Such a trace suggests that the catalyst may be undergoing a phase change.

5.2.4.3 Network Analysis Results

The variation of tan δ with temperature was investigated for the CIW1 catalyst was investigated using a network analyser.

The CIW1 sample (figure 5.15)exhibited a large change in tan δ between 250°C and 350°C indicating that between these temperatures the ability of the catalyst to interact with microwave radiation had increased.

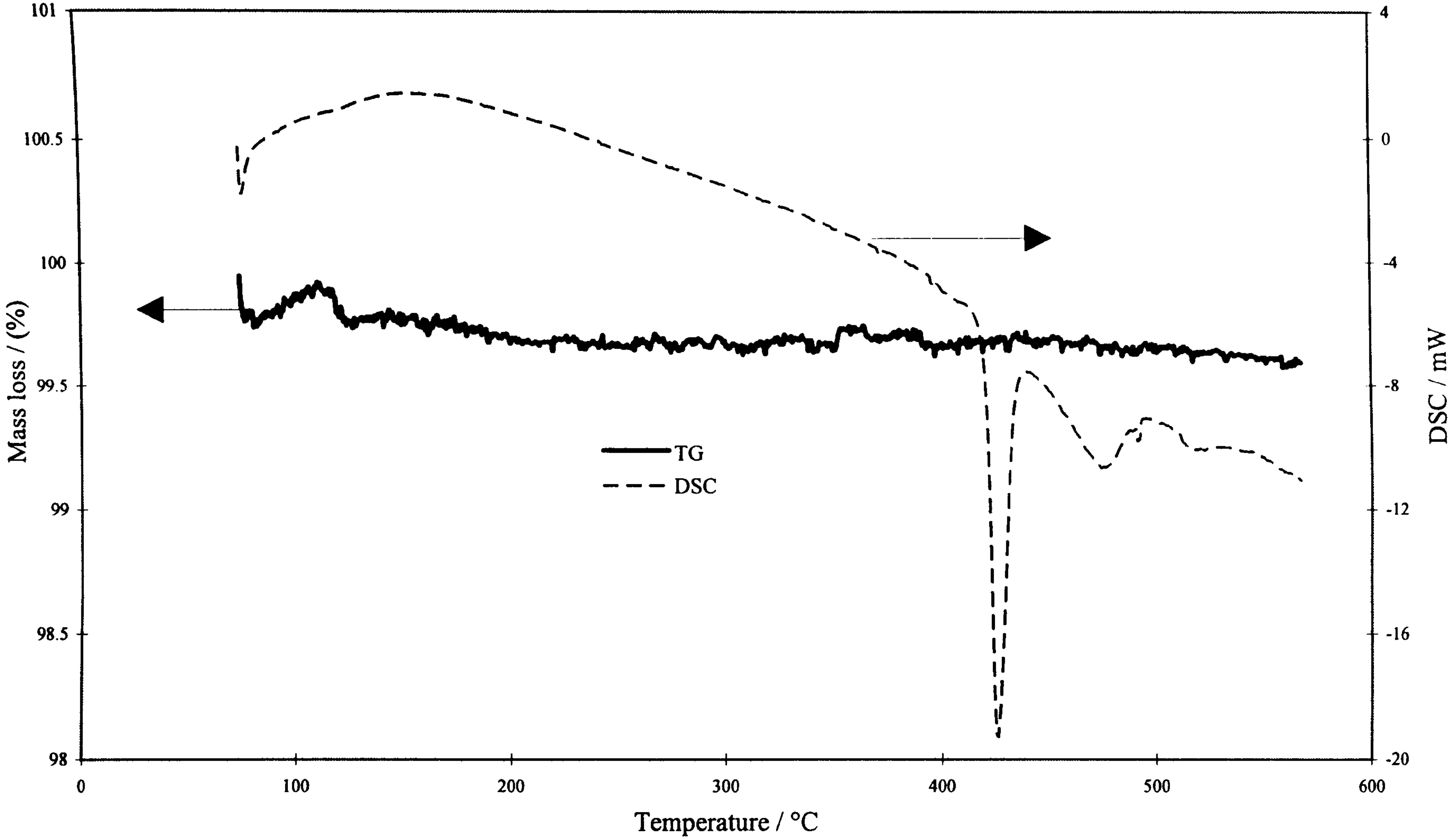


Figure 5.15. DSC/TGA Plot for CIW1 Catalyst

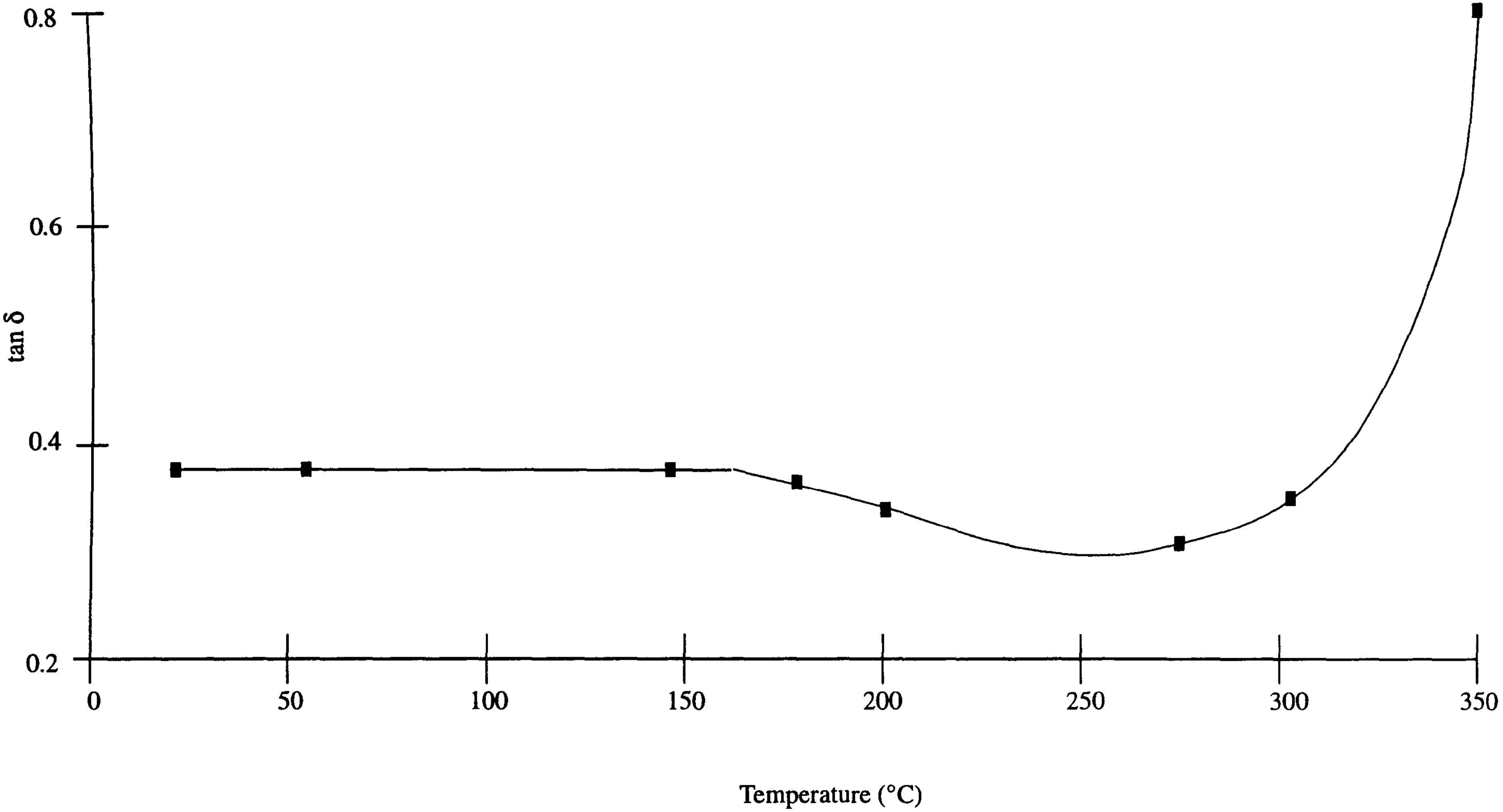


Figure 5.16. Plot of tan δ Against Temperature for CIW1 Catalyst

6. Other Reactions

6.1. Steam Reforming of Methane

6.1.1. Thermal Reforming

British Gas LH Catalyst

The reforming reactions performed under conventional heating served as a comparison for those carried out under microwave conditions. The equilibrium constant for the reaction was calculated for all experiments and related to reaction temperature using literature values in the Catalyst Handbook.[145]

The equilibrium constants for given reaction temperatures observed during these tests were in excellent correlation to the temperature/equilibrium constant tables found in the literature. This showed that the thermal results were valid and could be used for comparative purposes against the microwave heated experimental data. Figure 6.1 shows the correlation between results obtained from conventionally heated experiments in this study and literature values.

The results presented in table 6.1 show the maximum values for methane conversion and product yields achieved over the British Gas catalyst. Bracketed figures represent the steam ratio used where the steam ratio is the ratio of steam to hydrocarbon in the feed gas mixture.

Methane Conversion (%)	CO Yield (%)	CO_2 Yield (%)	H_2 Yield (%) (by calculation)
94.2 (6)	10.5 (6)	11.44 (5)	73.2 (6)

Table 6.1. Maximum Conversion and Product Yields for British Gas LH Catalyst

A number of different steam ratios were investigated for thermal tests and it was found that the use of a ratio of 6 gave the best overall catalyst performance under the experimental conditions used in this study. The only product produced in greater yield by the use of a different ratio was CO_2 (see table 6.2). Methane conversion at a steam ratio of 6 was over 20% higher than that achieved at a ratio of 5 and the hydrogen yield was 17% greater. The use of steam ratios of less than 4 resulted in reduced conversion and yield of products. At ratios of 2 or less, carbon deposition on the catalyst surface was appreciable and negligible amounts of products were formed. Table 6.2 shows the variation in conversion and product yields for a variety of steam ratios.

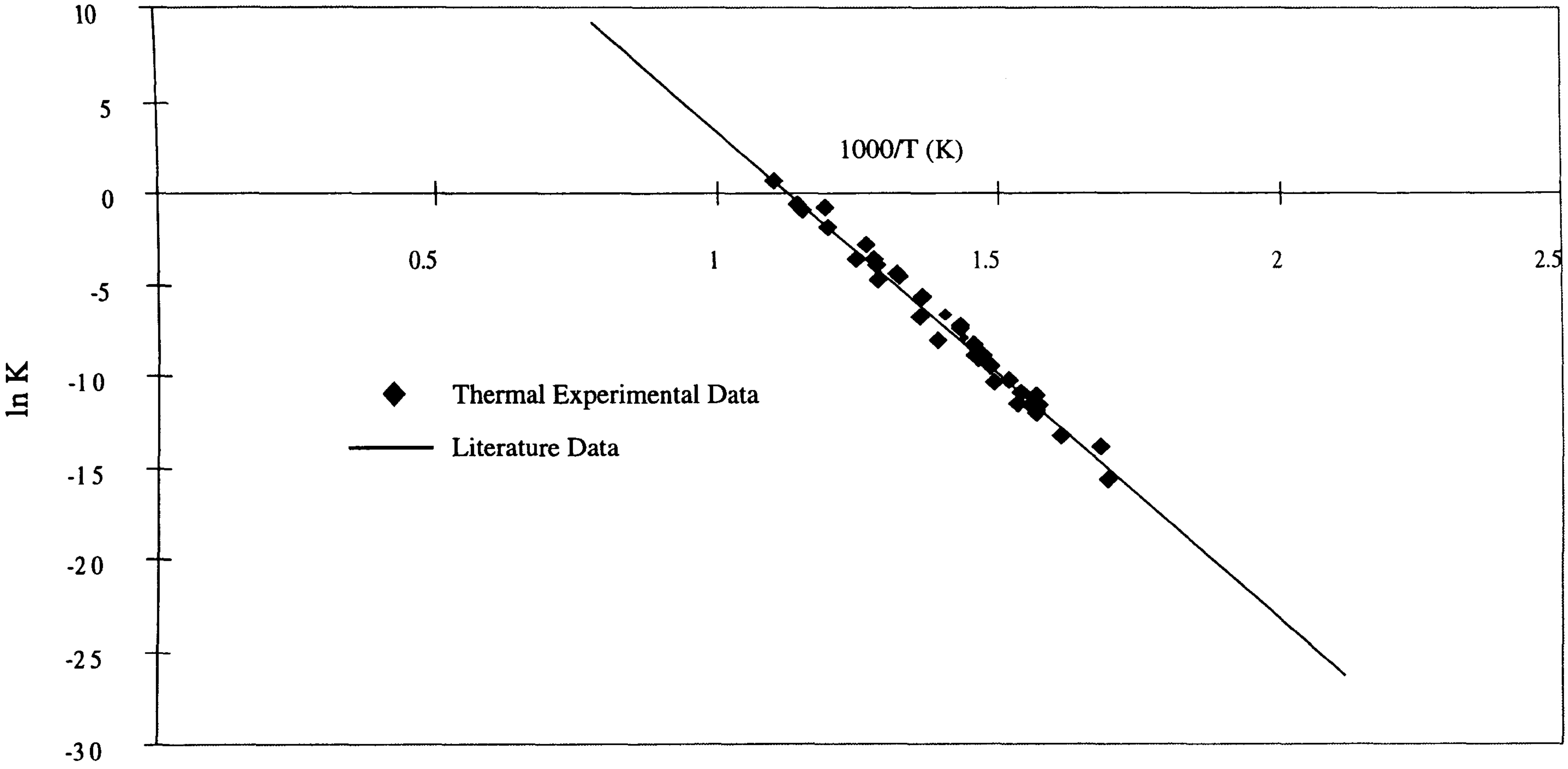


Figure 6.1. Comparison of Literature and Conventionally Heated Reaction Data

	Maximum Values			
Steam Ratio	CH_4 Conv. (%)	CO Yield (%)	CO_2 Yield (%)	H_2 Yield (%)
3	5.2	0	1.04	4.16
4	65.8	8.0	6.8	51.0
5	71.1	3.5	11.4	56.1
6	94.2	10.5	10.4	73.2

Table 6.2. Effect of Steam Ratio on Product Distribution and Methane Conversion

Nickel - Alumina Catalysts

A range of nickel - alumina catalysts were prepared with nickel contents of 10, 16 and 20% by weight. A summary of the results is presented in Table 6.3.

It can be seen that as the nickel content of the catalyst is increased, the yield of all products increased. In addition, the temperature of initial product formation was seen to decrease with increasing nickel loading. Bracketed figures in the table indicate the temperature in degrees Celsius at which the reported values were observed.

	Maximum Product Yields (%)		
Catalyst	CO	CO_2	H_2
10% Ni/Al_2O_3	4.6 (581)	5.9 (581)	37.5 (581)
16% Ni/Al_2O_3	6.2 (605)	9.8 (605)	45.7 (605)
20% Ni/Al_2O_3	10.6 (711)	11.1 (665)	66.1 (711)

Table 6.3. Comparison of Product Yields for Nickel - Alumina Catalysts

As observed for the British Gas LH catalyst, the equilibrium constant calculations for the nickel - alumina catalysed reactions were in excellent agreement with the literature values for any given temperature.

Chromatographic evidence in the form of a carbon balance of substantially less than 100% indicated the deposition of carbon on the catalyst surface at the higher temperatures investigated.

6.1.2. Microwave Reforming

British Gas LH Catalyst

Initial microwave heating of this catalyst required the use of high microwave power. However, once the catalyst had achieved a temperature of approximately 130°C, reduced power was required to maintain the catalyst at constant temperature. Increasing the temperature of the catalyst required the application of higher microwave power but once the required setpoint temperature was achieved, control was established using reduced power. The temperature of the catalyst could not however be increased above 400°C as attempts to do so resulted in the production of discharges in the reactor. Upon the occurrence of discharges, experiments were terminated.

At very low bulk temperatures (<190°C) only CO_2 was detected in the reactor effluent. However, CO was detected at temperatures in excess of 190°C. This temperature is much reduced compared to the equivalent thermal tests.

Plots of ln (equilibrium constant) against 1000/T showed that the catalyst experienced changes in performance during a typical microwave heated experiment and these changes were directly related to time on line and temperature of reaction. Figures 6.2 to 6.5 show such plots at different stages of an experiment. In the initial stages of a run (figure 6.2), the equilibrium constant is higher than would be expected for the given reaction temperature indicating that the catalyst activity is high.

Following this initial period, a "steady state" condition was observed and the plot for this portion of the experiment is presented in figure 6.3. Methane conversion increased with temperature during this period.

After operation at high temperatures, chromatographic evidence suggested that appreciable amounts of carbon were being deposited on the catalyst surface. The plot shown in figure 6.4 is indicative of the performance of the catalyst following carbon deposition on the surface. Chromatographic evidence also suggested that following the observed decrease in activity the previous levels of activity were not re-established. This shows that following operation at high temperature, the catalyst had been irreversibly de-activated to a certain extent.

Figure 6.5 is a compilation of the previous three plots and clearly illustrates the different activities of the catalyst throughout the duration of an experiment under microwave conditions. In summary, it can be seen that the fresh catalyst exhibits enhanced activity for the steam reforming reaction relative to the "steady state" results and those obtained over the catalyst which had been subjected to carbon deposition and that following carbon deposition activity is diminished relative to the results for both the fresh catalyst and the "steady state" results.

Figure 6.5 also shows that as the temperature of reaction is increased, the line for the fresh catalyst converges towards that of the "steady state" conditions. Additionally, the line representing results obtained over the carbonised catalyst diverges away form the "steady state" line.

Attempts to reduce the LH catalyst by heating in the single mode microwave cavity were unsuccessful due to the production of discharges within the reactor.

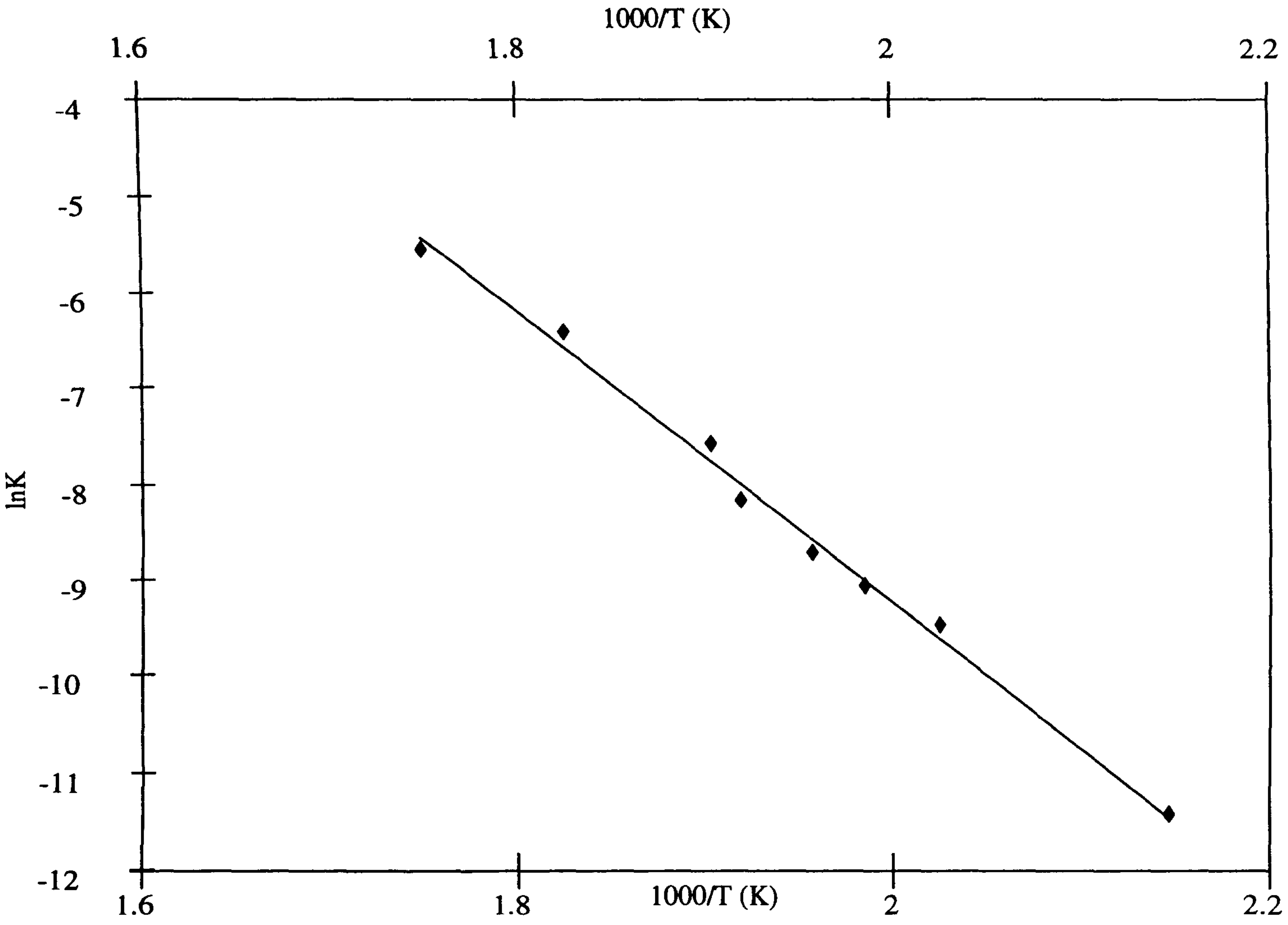


Figure 6.2. Plot of ln K against 1000/T for Freshly Reduced LH Catalyst

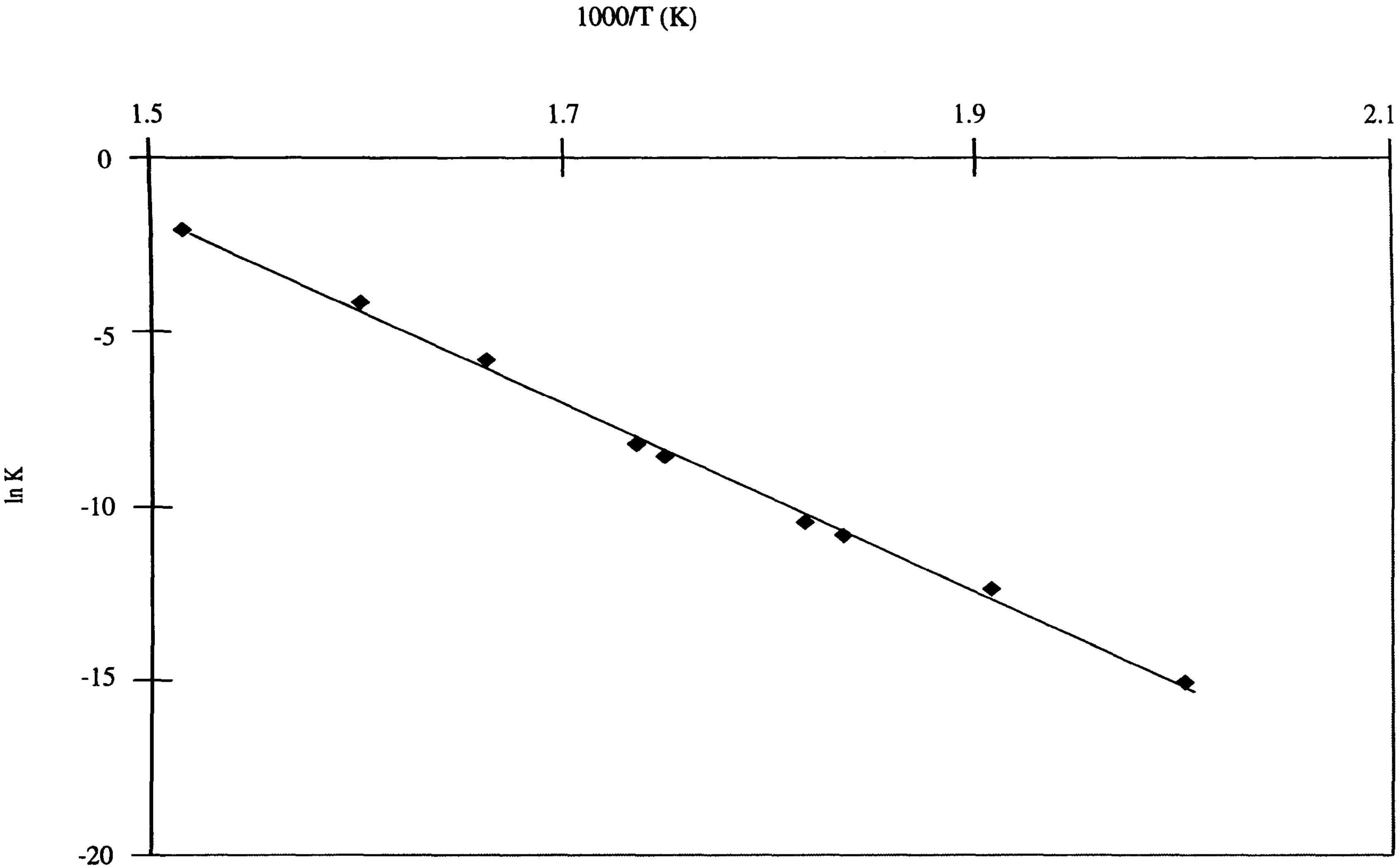


Figure 6.3. Plot of ln K against 1000/T for "Steady State" Microwave Experiments

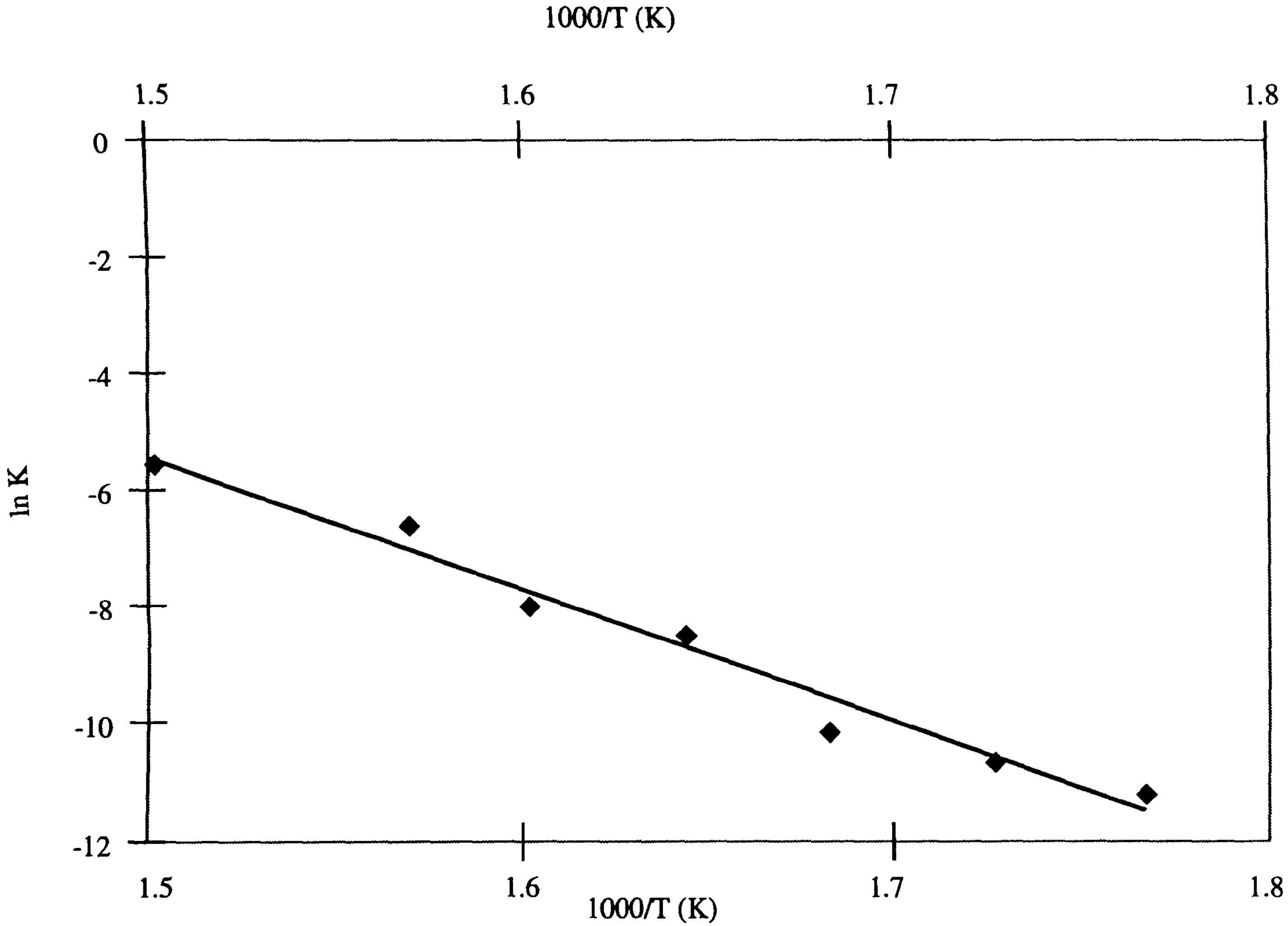


Figure 6.4. Plot of lnK against 1000/T for LH Catalyst following Carbon Deposition

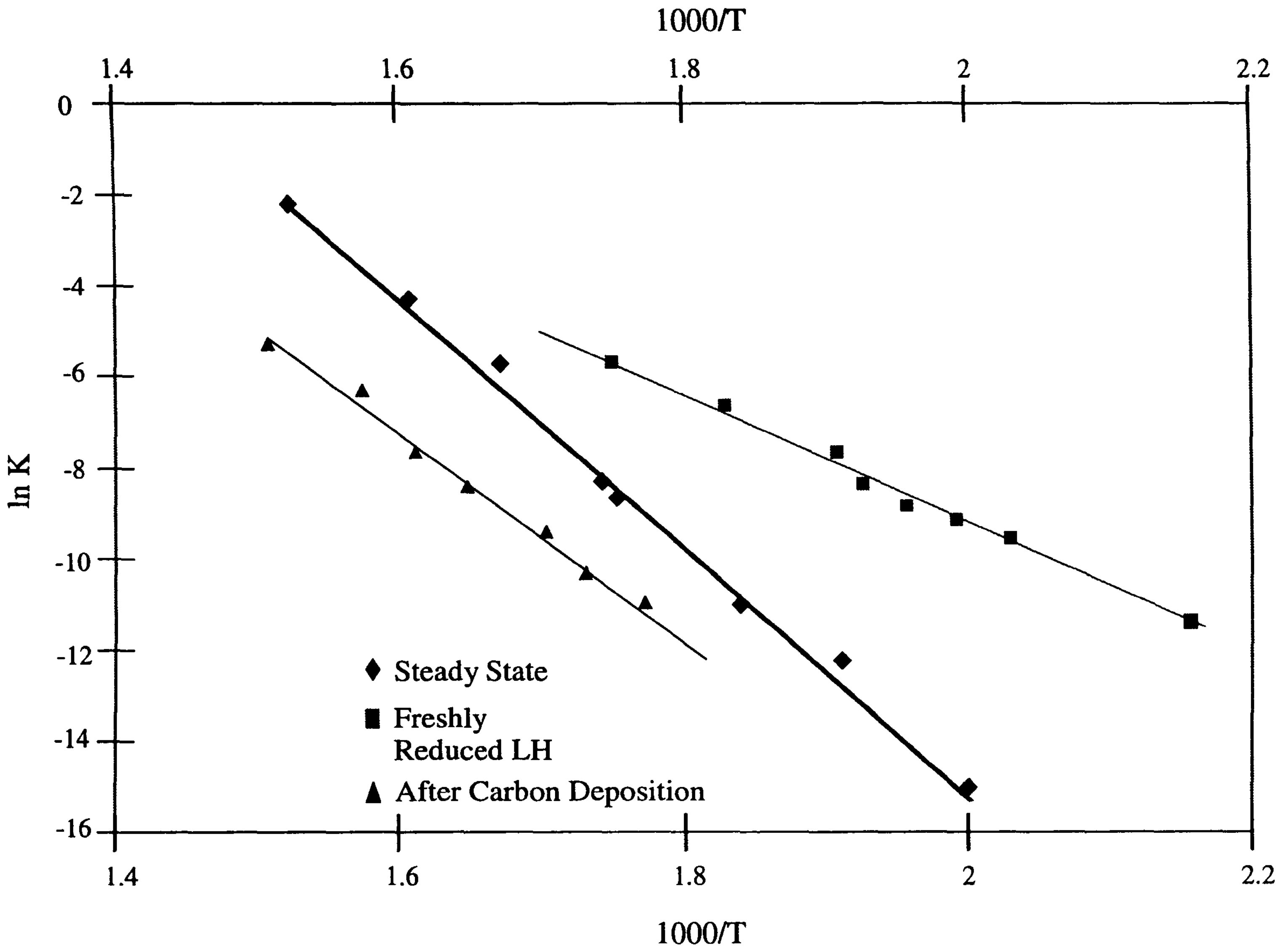


Figure 6.5. Plots of 1000/T against ln K for LH Catalyst at various Stages of a Microwave Heated Run

Nickel - Alumina Catalysts

The microwave heating characteristics of these catalysts were similar to those of the British Gas catalyst i.e. high microwave power was required for the early stages of heating. However, as observed for the commercial catalyst, once initial heating had been achieved, reduced microwave power was required to maintain a constant temperature. Temperature increases during the experiment again required the use of higher microwave power but control was achieved at the desired temperature using a reduced level of microwave power.

In general, the nickel - alumina catalysts could be heated to higher temperatures than the commercial catalyst without the production of discharges. The 10% nickel catalyst could in fact be heated to temperatures in excess of 500°C before discharges were observed. However, at such elevated temperatures, chromatographic data showed that significant amounts of carbon had been deposited on the catalyst surface. In general, the maximum temperature achieved before the production of discharges increased as the nickel loading was reduced. There was little difference in the maximum "non-discharge" temperature for the 20% and 16% nickel catalyst but as noted above, the 10% catalyst was heated to >500°C before discharges were observed.

The performance of all of the nickel - alumina catalysts was poorer than the commercial catalyst in terms of conversion and product yields. However, similar observations to those noted for the commercial catalyst regarding the reduction in bulk reaction temperature under microwave heating were true for these catalysts. The reforming reaction occurred at lower bulk temperatures under conditions of microwave heating.

Greater conversion and product yields were achieved by increasing the nickel loading of the catalyst. The catalyst containing 20% nickel by weight therefore produced the best performance. Table 6.4 shows the effect of nickel loading on catalyst performance. Values quoted are maxima and were achieved using a steam ratio of 6.

% Ni (by weight)	CH_4 Conv. (%)	CO Yield (%)	CO_2 Yield (%)	H_2 Yield (%) (by calc.)
20	47.5	1.2	8.6	37.8
16	40.7	0.3	7.9	32.5
10	27.6	0.02	5.4	21.7

Table 6.4. Effect of Nickel Content on Catalyst Performance

6.1.3. Effect of Variation of Reactant Flow Rate

Tests were performed at constant temperature using a variety of reactant flow rates in order to determine any effect of this variable on the distribution of products. Table 6.5 shows typical results of such experiments. Clearly, the variation of reactant flow rate (and hence space velocity) had negligible effect on the product distribution under the conditions used.

				Product Yields (%)		
Temp (°C)	CH_4 (ml min^{-1})	He (ml min^{-1})	Steam Ratio	CO	CO_2	H2
446	1.2	18.9	3.96	0.44	7.58	31.65
451	2.1	36.0	4.25	0.46	7.72	32.25
446	3.4	58.9	4.28	0.48	7.16	30.07
444	5.0	84.2	4.14	0.39	6.93	28.92

Table 6.5. Effect of Variation of Reactant Flow Rate on Product Distribution

6.1.4. Comparison between Conventionally Heated and Microwave Heated Experiments

The conventionally heated experiments provided an excellent point of comparison for the microwave heated tests. As presented in figure 6.1, the conventionally heated reactions in this study produced results which were in good correlation with those presented in the literature. In order to assess any effects of the application of microwaves to the steam reforming of methane, it is necessary at this stage to compare and contrast the results obtained from both modes of catalyst heating.

A comparison of maximum product yields and methane conversion together with the temperatures required for the values is presented in table 6.5. (Bracketed figures indicate the temperature for the observed value in degrees Celsius)

Mode of Heating	CH_4 Conv. (%)	CO Yield (%)	CO_2 Yield (%)	H_2 Yield (%) (by calculation)
Thermal	94.2 (806)	10.5 (806)	10.4 (806)	73.2 (806)
Microwave	96.6 (398)	10.5 (398)	12.8 (398)	73.3 (398)

Table 6.6. Effect of Mode of Heating on Catalyst Performance

It is clear form the table 6.6 that the reforming reaction occurs at much lower bulk temperatures than the thermally heated equivalent. In addition, enhanced methane conversion and yields of both CO_2 and hydrogen are achieved by the use of microwaves. The maximum yield of CO using microwave heating is identical to that observed using conventional methods of catalyst heating but obviously at a much reduced temperature. Microwave heating of a catalyst bed therefore enables the reforming reaction to occur to the same degree as conventional heating but with the advantage that the catalyst achieves enhanced activity relative to the conventionally heated reaction at much lower bulk temperatures. It should be emphasised that for the microwave heated experiments, all quoted temperature values are bulk temperatures.

This is due to the nature of operation of the temperature measurement device which is able only to record the temperature of the outer wall of the reaction vessel.

The use of equilibrium constant calculations enabled the actual temperature of the active sites within the catalyst bed to be estimated. The initial formation of products was in some cases more than 200°C lower for the microwave reaction compared to the conventionally heated reaction. Figure 6.6 presents a comparison of ln K versus 1000/T plots for the conventionally heated reaction and the "steady state" microwave reaction (i.e. after initial heating and before the deposition of carbon on the catalyst surface). The two lines are nearly parallel and the average temperature difference between thermal and microwave heated experiments for a given equilibrium constant was found to be approximately 140°C.

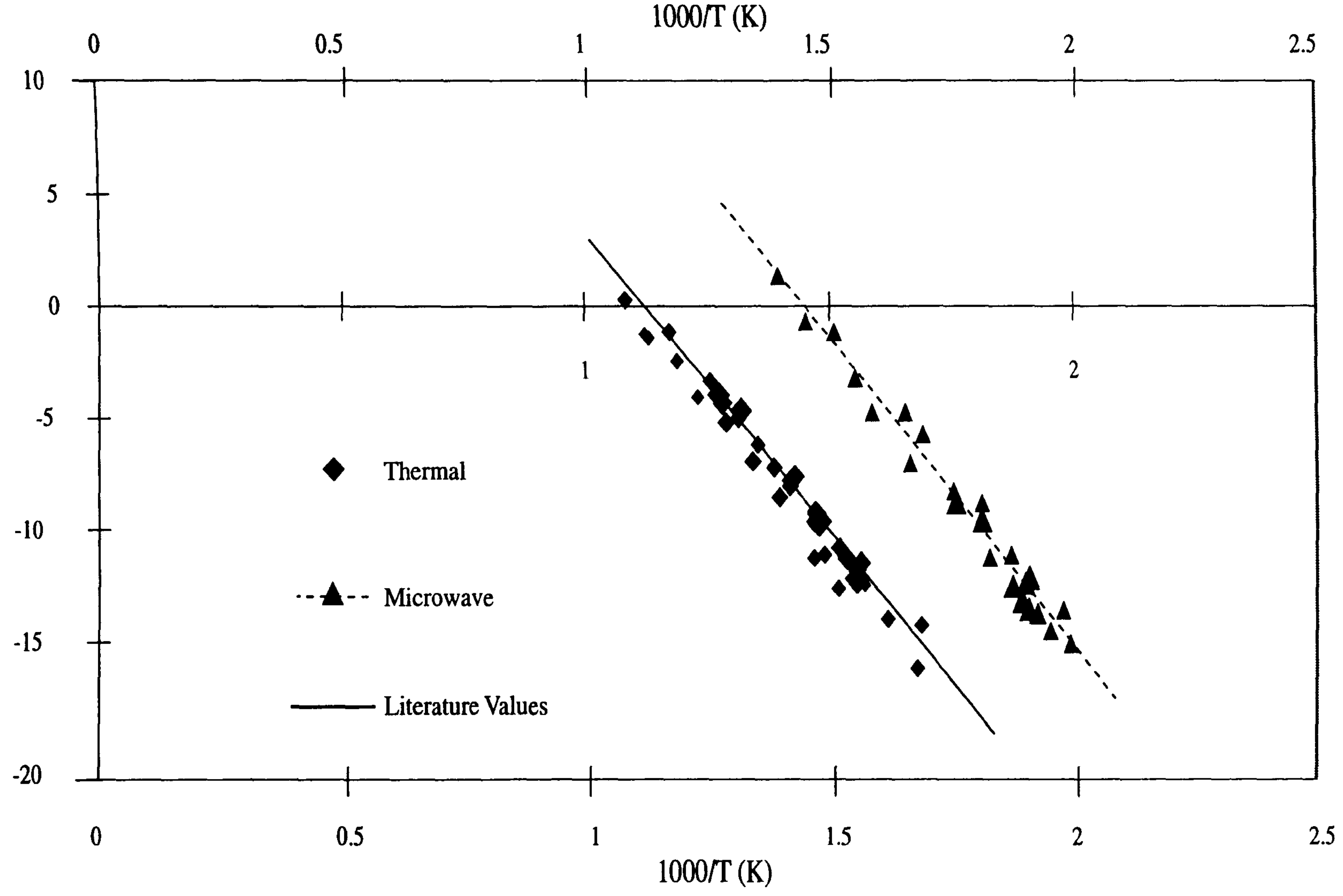


Figure 6.6. Comparison of Microwave, Thermal and Literature Reforming Data

6.1.5. Catalyst Characterisation

6.1.5.1.Surface Area Measurements

Surface area measurements of the LH catalyst revealed that there was negligible change in surface area following reaction under conventional heating conditions. However, significant loss of surface area was observed for the catalyst which had been tested under microwave conditions. The results are summarised in table 6.7.

Catalyst	Specific Surface Area (m^2g^{-1})
Freshly Reduced	74.4
Following Thermal Reaction	74.2
Following Microwave Reaction	63.0

Table 6.7. Specific Surface Area Measurements for British Gas LH Catalyst

6.1.5.2.Network Analysis Results

The use of a network analyser enabled the dielectric properties of the catalyst to be investigated. Figure 6.7 shows the result for the freshly reduced LH catalyst. It can be seen that the catalyst shows erratic dielectric behaviour with temperature. A large increase in tan δ is clearly visible between 200°C and 225°C. Further oscillations in the value of tan δ occurred throughout the temperature range studied.

6.1.5.3.DSC/TGA

Further investigations of any changes in the properties of the catalyst with temperature were made by performing simultaneous differential scanning calorimetry and thermogravimetric analysis. Figure 6.8 shows no clear peaks in either the DSC or TG traces are up to a temperature of 525°C. Only a small weight loss (4%) with increasing temperature was observed. The DSC plot gradually decreases with increasing temperature indicating a small endotherm. However, this may be ascribed to baseline drift on the instrument.

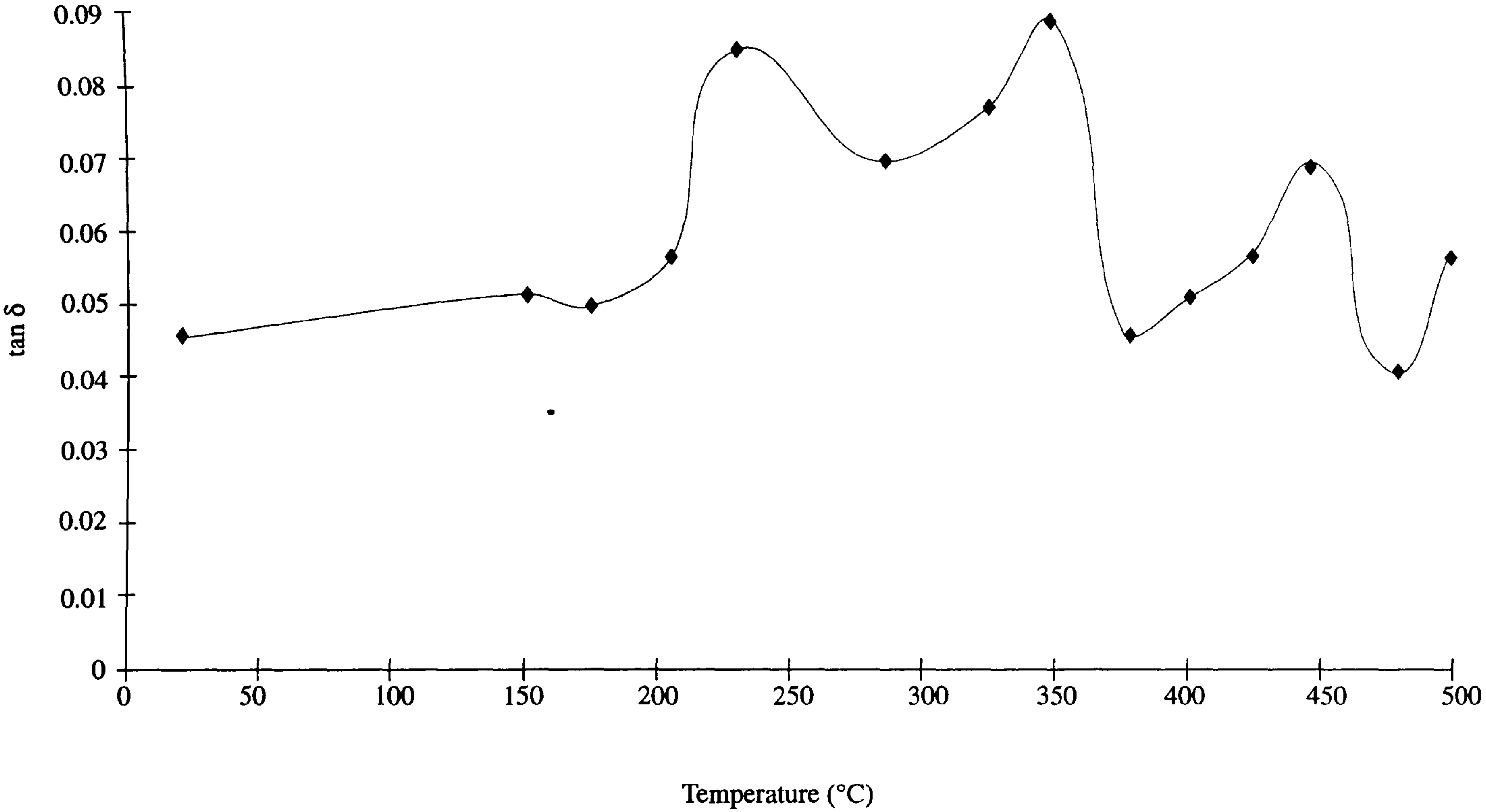


Figure 6.7. Plot of tan δ against Temperature for Freshly Reduced LH Catalyst

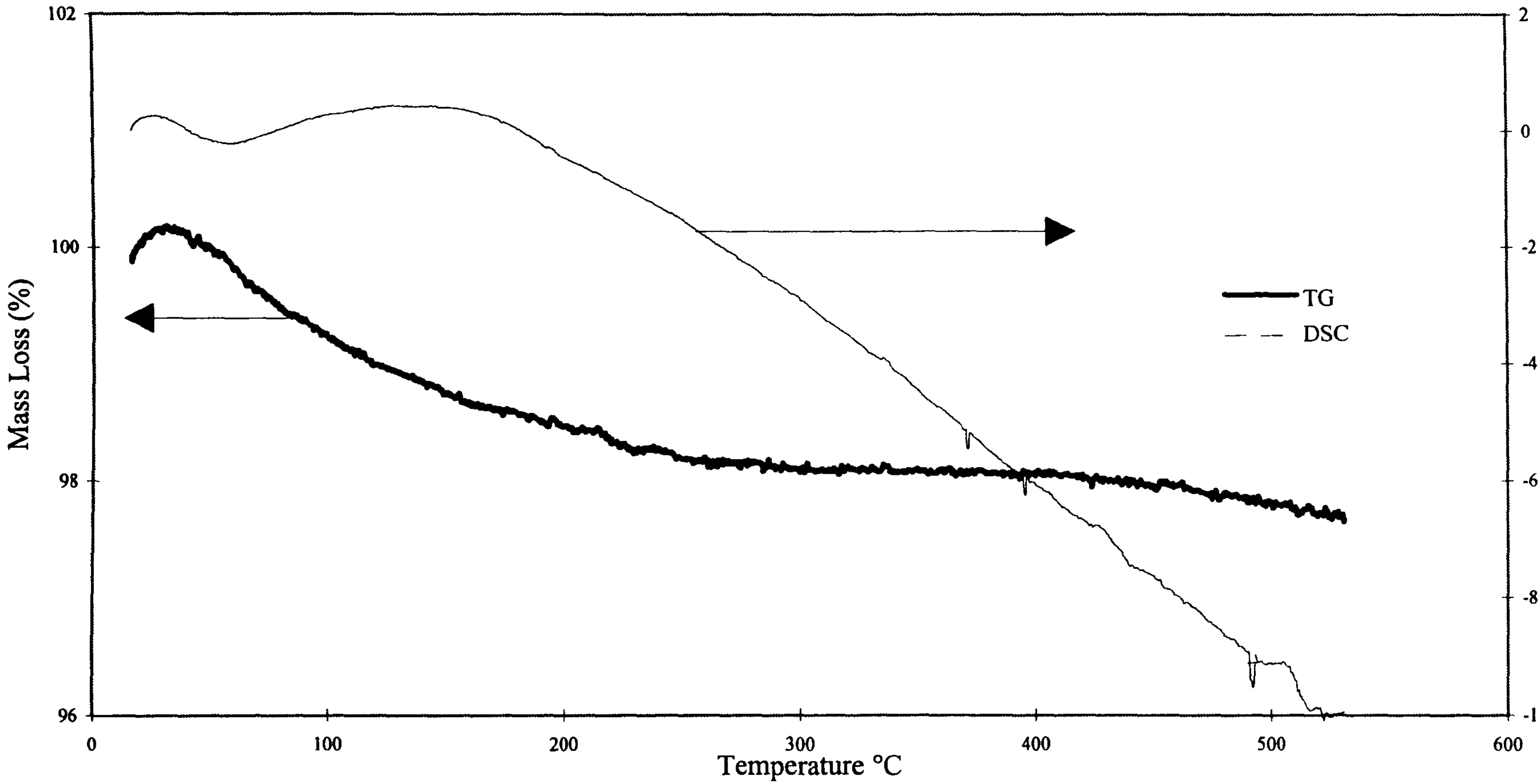


Figure 6.8. DSC/TGA Plot for Freshly Reduced LH Catalyst

6.2. Methane Combustion

6.2.1. Conventionally Heated Reactions

Platinum/alumina catalysts with platinum loadings of 1, 3 and 5% by weight were investigated for their ability for the combustion of methane under an oxygen to methane ratio of 2 (i.e. stoichiometric mixture). Typical results are presented in Table 6.8.

Catalyst	Temperature of Total Combustion (°C)
5% Pt/Al_2O_3	450
3% Pt/Al_2O_3	460
1% Pt/Al_2O_3	505

Table 6.8. Comparison of Temperature of Total Combustion for Pt/Al_2O_3 Catalysts

The results show that as the platinum content of the catalyst increased, the temperature required for complete methane combustion decreased. Furthermore, a "light off" temperature was observed for all of the catalysts. This phenomenon can be clearly seen in figure 6.9

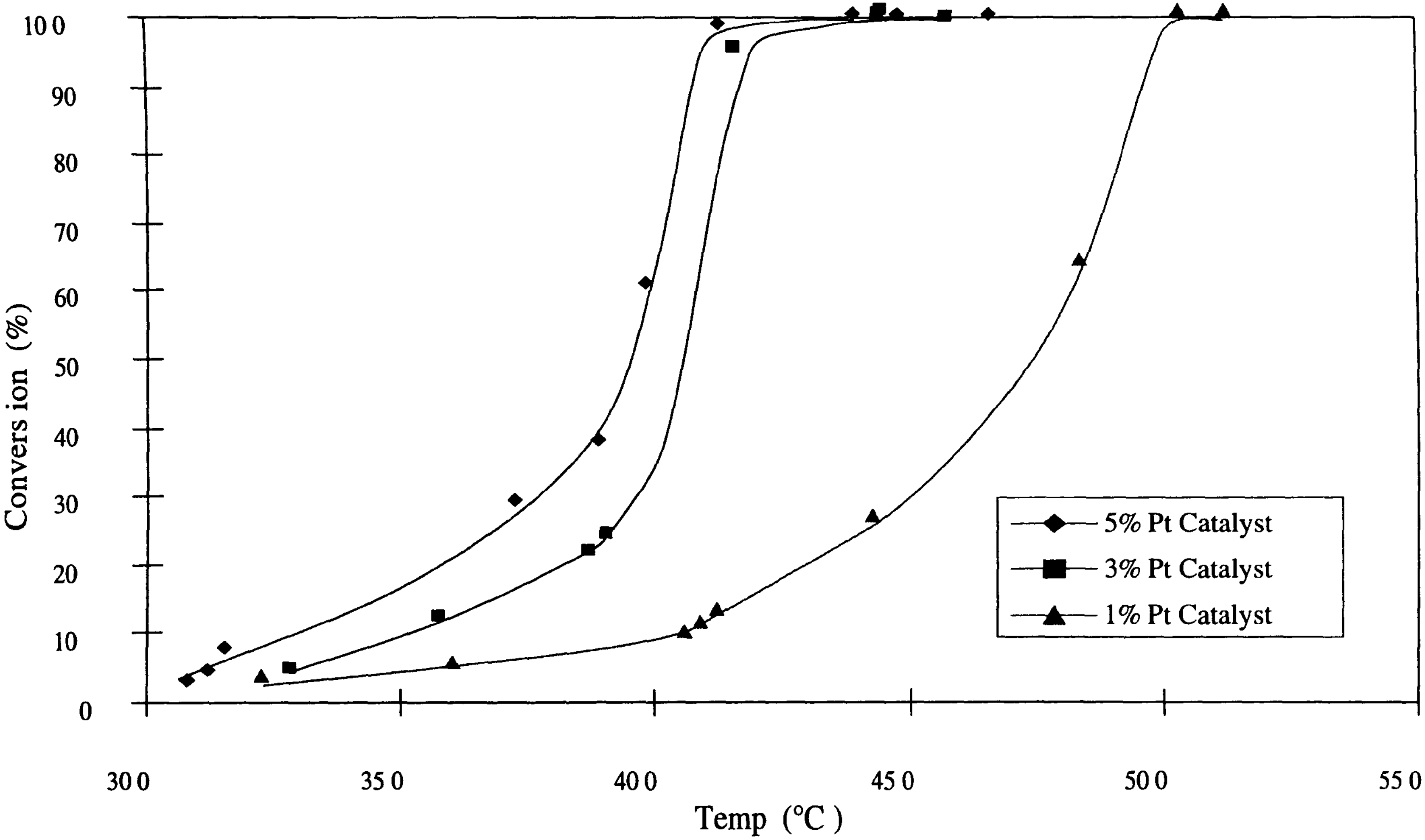


Figure 6.9. Effect of Platinum Loading on Methane Conversion

Below certain temperatures, (the magnitude of which was found to be dependent on the catalyst), negligible amounts of products were formed. However, once the "lightoff" temperature had been achieved and surpassed, conversion increased rapidly and a corresponding increase in the yield of carbon oxides was observed. For all of the catalysts studied, methane conversion was below 40% at temperatures below 400°C. However, figure 6.9 clearly illustrates that for the 5 and 3% platinum catalysts, the conversion is dramatically increased between 400°C and 425°C. The temperature for total conversion by the two catalysts varied by only 10°C (see table 6.7). The "lightoff" temperature for the 1% platinum catalyst was however far higher than that of those containing greater amounts of metal. A large increase in conversion was observed between 400°C and 450°C but maximum conversion was achieved at a far higher temperature relative to the other two catalysts (505°C cf. 450°C and 460°C for the 5%Pt and 3%Pt catalysts respectively).

Although higher reaction temperatures were required to facilitate complete methane conversion over the 1% Pt catalyst, higher yield of CO was achieved by this catalyst than either of the others. Table 6.9 shows a comparison of maximum product yields for the catalysts tested.

Catalyst	Max. CO Yield (%)	Max. CO_2 Yield (%)
5%Pt/Al_2O_3	2.1	97.9
3%Pt/Al_2O_3	1.9	98.1
1%Pt/Al_2O_3	2.5	97.5

Table 6.9. Comparison of Maximum Product Yields for Platinum - Alumina Catalysts

6.2.2. Microwave Heated Reactions

The same catalysts tested under conditions of conventional heating were also tested in the single mode microwave cavity under conditions identical to those used for the conventional tests.

The 5% platinum - alumina catalyst required the application of high microwave power in order to stimulate initial heating. However, once a temperature of 140°C had been achieved, reduced microwave power was required to maintain this temperature; temperature control below this temperature was found to be impossible.

Under microwave heating conditions, the 5% platinum - alumina catalyst was found to be active for methane combustion at bulk temperatures far below those observed under conventional heating. Figure 6.10 shows a comparison between the two modes of heating for the reaction over this catalyst.

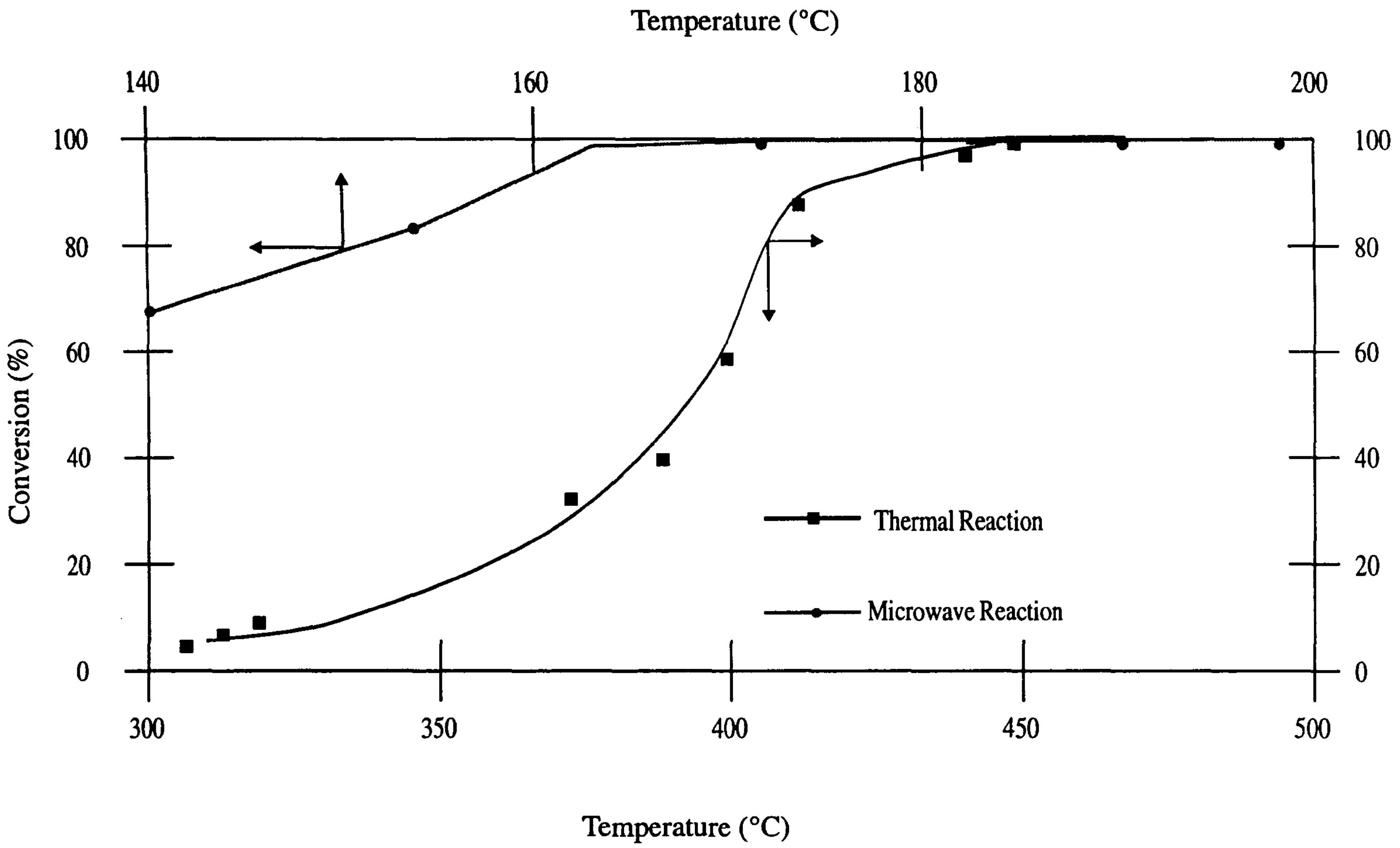


Figure 6.10. Plots of Methane Conversion against Temperature for Conventionally and Microwave Heated Methane Combustion

It is clear that a large temperature difference for total conversion exists between the microwave and conventionally heated reactions. Near total conversion is achieved using microwaves for catalyst heating at approximately 170°C whereas for the conventionally heated reaction, the figure is 450°C.

Furthermore, under microwave conditions a greatly enhanced yield of CO was achieved relative to the conventionally heated experiments. This enhanced yield was obviously achieved at lower bulk temperatures under microwave heating. Table 6.10 shows comparative values for product yields at total conversion. (Bracketed figures show the reaction temperature in degrees Celsius for the corresponding values).

Due to the heating characteristics of the 5% platinum - alumina catalyst in the single mode microwave cavity, analyses of the reactor effluent gas at temperatures below 140°C were not possible. It is therefore impossible to determine whether or not such a strong "lightoff" temperature phenomenon which was observed under conventional catalyst heating is also true for the microwave heated reaction.

Many difficulties were experienced during the attempts to heat both the 3% and 1% platinum catalysts. As was observed for the 5% Pt catalyst, high microwave power was required for the initial heating of both of the catalysts. However, it was found to be impossible to raise the temperature of the 3% Pt catalyst above 160°C The corresponding value for the 1% Pt catalyst was 125°C. No products were formed over either of these catalysts under microwave heating at the temperatures achieved during this study.

Mode of Heating	Max. CO Yield (%)	Max. CO_2 Yield (%)
Thermal	2.1 (450)	97.9 (450)
Microwave	18.2 (200)	81.8 (200)

Table 6.10. Effect of Mode of Heating on Product Yields for Methane Combustion over 5wt% Pt/Al_2O_3 Catalyst

6.2.3. Surface Area Measurements

The specific surface area of the platinum - alumina catalysts increased with decreasing platinum loading. With increasing platinum loading, greater reduction in specific surface area was observed following reaction. Typical results are presented in table 6.10. It is clear from the table that the use of microwaves to heat the catalyst resulted in a much greater loss of catalyst surface area than when conventional heating was utilised.

	Specific Surface Area (m^2g^{-1})		
Pt loading (wt%)	Fresh Catalyst	After Thermal Reaction	After Microwave Reaction
1	17.1	17.1	16.2
3	15.1	14.6	12.8
5	14.2	11.7	9.4

Table 6.11. Specific Surface Area Measurements for Platinum - Alumina Catalysts

7. Discussion

Oxidative Coupling of Methane

7.1. Conventionally Heated Experiments

7.1.1. Rare - Earth Oxide Catalysts

7.1.1.1. Blank Reaction

The blank reaction produced negligible amounts of C_2 hydrocarbon products and only very small amounts of CO. This shows that a catalyst is required for the activation of methane under the conditions of choice. It is therefore suggested that under the experimental conditions used, the contribution of non-catalysed gas phase reactions to the overall oxidative coupling mechanism is negligible and can be disregarded.

7.1.1.2. Reaction in the absence of Gas Phase Oxygen

CO and CO_2 were the only products formed in non-negligible quantities during the test. Coupled products were formed in negligibly small amounts.

It is known that CO is formed by an interaction between methane and the lattice oxygen of the catalyst. Subsequent reaction of the CO thus formed with further lattice oxygen leads to the production of CO_2. As the amount of lattice oxygen available for reaction decreases (i.e. with increasing time on stream), less CO_2 is formed from the CO and a decrease in the amount of CO_2 produced is observed. This decrease is accompanied by an increase in the amount of CO produced.

As the lattice oxygen supply nears exhaustion, the amount of CO and CO_2 produced decreases markedly.

These tests appear to show that carbon oxides are produced in a pathway parallel to the oxidation of coupled hydrocarbons in the oxidative coupling of methane.

The negligible amounts of C_2 hydrocarbons produced during this test suggests that gas phase oxygen is required for the production of methyl radicals over 1wt% Sr/La_2O_3 and that in the absence of gas phase oxygen, methane is not activated by the catalyst for the formation of coupled hydrocarbon products. This is in agreement with the findings of other workers[69] who have shown that gas phase oxygen is required for the activation of methane over rare earth oxide catalysts.

7.1.1.3.Effect of Strontium Doping

The doping of La_2O_3 with 1wt% strontium improved the overall catalytic performance. Both C_2 selectivity and yield were enhanced relative to the pure oxide.

The beneficial effect on catalytic performance by strontium doping is thought to be due to a combination of factors.

Much faster exchange between lattice and gas phase oxygen is possible when lanthana is doped with strontium[151] and this is important in the activation of the methane molecule as it has been shown[76] that the rate of methane conversion is dependent on the rate of exchange of gas phase with lattice oxygen exchange.

Improvements in catalyst selectivity may be explained by active La_2O_3 being replaced at the surface by less active (yet more selective)$SrCO_3$[78].

Under the conditions of the oxidative coupling reaction lanthana can form two types of surface oxycarbonate species which have different thermal stabilities.[148] Strontium doping appears to suppress the formation of the unselective Type 2 oxycarbonate thus leading to a more selective catalyst.

The oxidative coupling of methane over lanthana has been shown to be structure sensitive and selectivity was also dependent on catalyst preparation conditions.[149] A thin platelet morphology favoured by lower temperature preparation was found to be more selective than the tridimensional, smaller particles formed at higher temperatures. It is thought that strontium doping preserves the favourable platelet structure of the oxide during the catalytic reaction.

7.1.1.4.Effect of Reactant Ratio

The use of a higher methane to oxygen ratio resulted in higher selectivity to coupled products. The lower partial pressure of oxygen present in the system under these conditions results in a smaller proportion of the desired products being further oxidised to the undesired carbon oxides.

Little effect was noted upon the C_2 yield at the higher reactant ratio and this is probably due to there being insufficient oxygen to activate large amounts of methane.

Lowering the methane to oxygen ratio from 5 to 3 produced a significant increase in methane conversion. This is not surprising since the presence of a proportionally greater amount of oxygen in the system means that larger amounts of methane can be activated. The higher oxygen partial pressure at the lower reactant ratio led to a decrease in C_2 selectivity and a corresponding increase in CO_x yield and selectivity due to the further oxidation of coupled hydrocarbons to carbon oxides.

7.1.1.5.Effect of Flow Rate

The use of higher reactant flow rates (i.e. shorter residence times) improved C_2 yield and selectivity and gave enhanced methane conversion.

Shorter residence times appear to limit the extent to which carbon oxides formed by interaction with the lattice oxygen of the catalyst can be formed and hence the importance of this pathway for carbon oxide formation is reduced at higher reactant flow rates. This accounts for the observed increase in C_2 selectivity.

The increase in C_2 yield may be explained by the fact that coupled products once formed, spend a shorter time in the heated zone of the reactor and are therefore less likely to undergo further oxidation to carbon oxides.

7.1.1.6.Effect of Catalyst Calcination Conditions

Unsupported catalysts calcined at 650°C showed improved performance relative to those calcined at 800°C. Previous work[62] has shown that lower temperature calcination favours the formation of a platelet structure which is thought to be responsible for improvements in C_2 selectivity.

The fact that catalysts calcined at 350°C exhibited poorer catalytic performance than either of the samples calcined at higher temperatures cannot be easily explained. It may be that calcination at this lower temperature does not enable the generation of more active and selective catalytic sites.

Clearly, for the 1wt% Sr/La_2O_3 system, a volcano type relationship exists between catalytic performance and calcination temperature whereby the best results are achieved by the use of an "intermediate" calcination temperature. The use of higher or lower calcination temperatures results in a reduction in performance.

7.1.1.7.Reactions using Nitrous Oxide as Oxidant

The use of nitrous oxide as the oxidant for the oxidative coupling reaction resulted in enhanced C_2 selectivity in comparison to tests in which molecular oxygen was used. The explanation for this observation may be found by considering a possible reaction mechanism for the N_2O oxidised reaction.

Clearly, nitrous oxide contains only one atom of oxygen per mole whereas dioxygen possesses two. The use of nitrous oxide therefore introduces ~~less~~ fewer oxygen atoms to the system. As a result, methane conversion decreases due to the unavailability of a pool of oxygen but correspondingly, undesirable total oxidation reactions are reduced. Thus C_2 selectivity is increased by the use of N_2O as the oxidant. It has also been suggested that the observed reduction in methane conversion when using nitrous oxide as the oxidant may be due to the slow breakdown of N_2O to an active oxidising species.[66]

7.1.1.8.Methane Conversion and Oxygen Consumption

Oxygen consumption for the majority of tests was in excess of 90% and at temperatures of 650°C and above, total oxygen consumption was observed. The fact that the reaction was occurring under oxygen limited conditions dictates that methane conversion should not be used as an assessment of the activity of the catalyst since the rate of methane conversion is limited by oxygen availability.

Magnesia Supported Catalysts

Similar trends regarding the effects of strontium doping, reactant ratio and reactant flow rate to those observed for 1wt% Sr/La_2O_3 were also noted for the magnesia supported catalysts but these catalysts exhibited better catalytic performance than their unsupported counterparts.

An interesting observation was the fact that for the strontium doped supported system, the best results were obtained using a calcination temperature of 350°C. Calcination at temperatures above this value led to a decrease in C_2 selectivity and yield. It is possible that calcination at higher temperatures generates non-selective active sites on the magnesia which leads to greater selectivity and yield of carbon oxides. However the opposite was true for the undoped catalyst and calcination at 650°C enabled performance on a par to that of the 350°C calcined doped system to be achieved.

The beneficial effect of strontium doping on catalytic performance is therefore best observed when lower calcination temperatures are utilised. Strontium doping enables less energy intensive preparation conditions to be used which represents financial savings. In order for the undoped catalyst to achieve comparable performance, harsher calcination conditions are required which entail the use of larger amounts of energy.

7.1.1.9.Summary

An obvious advantage of the supported catalyst is the fact that less lanthana was used in the preparation (15wt% compared to 99wt% for the unsupported formulation) and catalytic performance was improved. Lanthana is the most expensive component of the formulation and the use of less of this substance and any reduction in the amount used in the catalyst preparations will lead to financial savings. Clearly the fact that financial savings are accompanied by an improvement in C_2 yield and selectivity represents an advance in catalyst development for the conditions used in this study.

The performance of the unsupported catalysts was not significantly better than the supported systems at lower temperatures to justify the greater financial outlay required for their preparation. The fact that comparable performance was achieved using a system that utilised substantially less of the most expensive component far outweighs the small enhancements in selectivity and yield observed.

Furthermore, less energy intensive calcination conditions were required to produce the enhanced catalytic performance exhibited by the supported systems and this suggests further financial savings.

7.1.2. Chloride Containing Catalysts

7.1.2.1. Effect of Calcination

The British Gas CIW1 catalyst calcined at 700°C for 7 hours produced greater selectivity to coupled products than the uncalcined sample. The uncalcined material was however the more active catalyst. It is therefore suggested that the calcination procedure alters the structure of active surface sites in such a way to make them more selective yet less active.

7.1.2.2. Effect of Reactant Ratio

The use of a higher methane to oxygen ratio increased the selectivity to coupled products whilst a reduction in the ratio produced increased methane conversion at the expense of C_2 selectivity. The reasons for these observations were noted in section 7.1.1.4. i.e. at a higher methane to oxygen ratio, there is insufficient oxygen in the reactant stream to enable deep oxidation of C_2 products to carbon oxides.

7.1.2.3.Effect of Reactant Flow Rate

Increasing the reactant flow rate over the uncalcined chloride containing catalysts had the same effect on product distribution as for the rare-earth oxide catalysts i.e. C_2 selectivity was increased and methane conversion was decreased. However, for the calcined material, increased methane conversion was observed but little effect on selectivity was seen. It may be that the calcination process alters the structure of the catalyst.

7.1.2.4.General Observations

The CIW1 chloride containing catalyst supplied by British Gas performed better than any of the rare-earth oxide catalysts under the experimental conditions investigated in this study. The chloride component of the catalyst is the key to the enhancement in catalyst performance. Burch et al have investigated a number of chloride containing catalysts.[44,80,81,100,103] As a result of their extensive studies, it has been stated that the chloride species in the catalyst do not simply act as promoters for the reaction but in fact play an active role in the overall oxidative coupling mechanism. Since the chloride catalyst investigated in this work is of a very similar nature to the systems investigated by Burch, it is reasonable to assume that a similar mechanism was occurring during the reactions performed in this study.

7.2. Microwave Heated Experiments

7.2.1. Rare - Earth Oxide Catalysts

7.2.1.1.Heating Characteristics

La_2O_3

Pure lanthana could not be heated in the microwave field and this is ascribed to the homogeneity of the material and lack of dipoles within the sample. This means that the sample was unable to interact with the applied microwave field and therefore no heating occurred.

1wt% Sr/La_2O_3

This catalyst could be heated in the microwave cavity but high power was required to facilitate any temperature increase. Discharges were observed at temperatures in excess of 250°C. Network analysis results clearly showed that the dielectric properties of the sample changed with temperature and three distinct variations in the value of tan δ were observed. At low temperatures the value of tan δ was low indicating that the sample was not interacting strongly with the applied microwave field. This is consistent with the behaviour of the sample during initial heating where maximum microwave power was required.

The first major change in the value of tan δ occurred between 150°C and 200°C. Between these temperatures, the value of tan δ increased markedly indicating that the catalyst was interacting strongly with the applied field. Again, this is consistent with experimental observations as following the initial heating period, reduced microwave power was required to further increase the temperature. This change in dielectric properties may be attributed to the removal of water from the sample. Lanthana is known to be strongly hygroscopic and it is not surprising that water vapour from the air was retained by the catalyst.

The properties change further between 300°C and 350°C and the tan δ value decreases indicating that the material interacts weakly with the applied microwave field. The range of weak coupling with the microwave field extends to a temperature of 500°C when the third change is observed. These results suggest that the sample undergoes phase changes with temperature.

The final change increase in the value of tan δ is thought to coincide with the production of discharges. However, it should be noted that the network analysis results showed that this change occurred at temperatures greater than 500°C whereas discharges were observed during catalytic experiments at bulk temperatures of 250°C. It is therefore suggested that areas within the catalyst achieved temperatures far higher than the recorded bulk temperatures. Such "hot spots" within the catalyst bed may have been the "seed points" for the production of discharges.

A further explanation for the production of discharges by the 1wt% Sr/La_2O_3 catalyst may be found in scanning electron microscopy evidence. Micrographs of the catalyst (plates 1 - 2) following a microwave reaction clearly showed the presence of a plate - like structure which was not evident for catalysts which had been tested using conventional methods of heating. It is possible that the plates formed during the microwave reaction acted in a capacitor - like manner and charge was built up between the surfaces of the plates creating a Maxwell - Wagner type effect and initiating discharges.

1wt% Sr/15wt% La_2O_3/MgO

During initial heating, this catalyst behaved in a similar way to the unsupported system in that high power was required to facilitate heating. However, the supported catalyst could be controllably heated to a temperature of 500°C before discharge production. The network analysis results showed that tan δ for this catalyst remained constant between temperatures of 300°C and 550°C before increasing as the temperature was increased to 600°C. Clearly, the supported catalyst did not undergo such a dramatic change in dielectric properties and as a result could be controllably heated to higher temperatures. It is suggested that the use of magnesia as a catalyst support in some way alters the dielectric properties of the sample.

7.2.1.2.Reaction in The Absence of Gas Phase Oxygen

The microwave coupling reaction in the absence of gas phase enabled the production of coupled hydrocarbon products. This was not the case for the conventionally heated reaction. The catalyst could be heated to higher temperatures (700°C cf. 500°C) when oxygen was not present in the system This suggests that oxygen may play a part in the production of discharges.

Previous studies of rare earth oxide catalysts in the absence of gas phase oxygen[69] have led researchers to believe that methane could not be activated over these catalysts in the absence of gas phase oxygen. However, the use of microwave radiation to heat the catalyst bed appears to enable methane activation in the absence of gas phase oxygen. The discharge experiment in the absence of gas phase oxygen also yielded coupled hydrocarbons (notably acetylene) with high selectivity but low yield.

It is suggested that the use of microwave radiation to heat the catalyst bed stimulates the lattice oxygen of the catalyst either making it available itself for reaction with methane or enabling the generation of active surface sites. Using conventional methods of catalyst heating, exchange between gas phase and lattice oxygen has been postulated to be responsible for the generation of catalytic sites capable of activating methane to form higher hydrocarbons.[69] However, it is possible that microwave energy interacts with the rare-earth oxide catalyst in such a way as to eliminate the requirement of such oxygen exchange for the generation of these sites.

The performance of the catalyst deteriorated with time on stream however due to appreciable carbon deposition on the catalyst surface.

7.2.1.3.Reactions using Molecular oxygen as Oxidant

1wt% Sr/La_2O_3

The heating characteristics of this catalyst in the single mode microwave cavity revealed that it was unsuitable for use in the microwave heated oxidative coupling reaction at temperatures in excess of 250°C as the production of discharges was common. However, at temperatures below this figure, coupled hydrocarbon products were formed at bulk temperatures far lower than those required for similar product yields using conventional methods of catalyst heating. This observation is thought to be due to the presence of active catalytic sites within the catalyst which achieve temperatures far in excess of the observed bulk temperature as measured by the optical fibre thermometer. It is postulated that such "hot spots" within the catalyst bed achieve a sufficiently high temperature to enable the oxidative coupling reaction to occur.

1wt% Sr/15wt% La_2O_3/MgO

The dielectric properties of this sample were significantly different to those of the unsupported catalyst and enabled the heating of the supported material to higher temperatures. It is postulated that the use of magnesia as a support has the effect of dispersing the strontium to a greater effect over the catalyst. The strontium component of the catalyst is thought to contribute to the production of discharges since pure strontium nitrate could not be heated above 160°C without the production of discharges. In the unsupported material, the strontium may form larger clusters on the catalyst surface (this is supported by surface area measurements) and thus may interact more easily with the applied field in the unsupported material promoting the production of discharges at lower bulk temperatures.

The reaction over the magnesia supported catalyst also occurred at much reduced bulk temperatures relative to the conventionally heated reaction and this observation is again ascribed to the presence of "hot spots" within the catalyst bed.

A higher ethene to ethane ratio was achieved by the use of microwaves to heat the magnesia supported catalyst. It is possible that the proposed "hot spots" within the catalyst bed can on occasion achieve temperatures sufficiently high to abstract a proton from methyl radicals formed on the surface. It is also feasible to suggest that small point discharges may occur periodically in the catalyst bed under conditions of microwave irradiation and such discharges may also be able to remove a proton from the $CH_3\bullet$ species. Clearly, this would produce $CH_2\bullet$ species which may couple to form ethene.

7.2.1.4.Reactions Using Nitrous Oxide as Oxidant

When nitrous oxide was used as the oxidant for the microwave heated oxidative coupling reaction, the catalyst could be heated to bulk temperatures of 300°C higher than when molecular oxygen was used. This provides further evidence that the presence of oxygen in the reactant feed mixture contributes to the production of discharges in the reactor during microwave experiments. Enhanced C_2 selectivity relative to molecular oxygen experiments was observed and the reasons for this are suggested to be identical to those for the thermally heated experiments which were discussed in section 7.1.7. As observed for the tests using molecular oxygen, the microwave experiments using N_2O as the oxidant were seen to occur at bulk temperatures far lower than the conventionally heated equivalent.

7.2.1.5.Reactions using Trace Amount of N_2O in the Reactant Mixture

Reactions using a trace amount of nitrous oxide in the reactant mixture provided no improvement in terms of increased selectivity or yield of coupled products relative to experiments which used a mixture of 5% O_2/He. The catalyst could not be heated to higher temperatures by the incorporation of a small amount of nitrous oxide in the reactant feed before the production of discharges. It is suggested that there was insufficient N_2O in the reactant mixture either to enhance the yield and selectivity of coupled hydrocarbons or to suppress the formation of discharges.

7.2.1.6.Reactions under Discharge Conditions

As reported in previous sections, the production of discharges by the rare-earth oxide catalysts was commonplace under conditions of microwave heating. Under such conditions controlled heating of the catalysts was not possible. The product distribution for reaction under discharge conditions was considerably different to that obtained under conditions of controlled heating. The production of acetylene under discharge conditions is worthy of note since it is a potentially more valuable material than the "conventional" products of the oxidative coupling reaction.

Acetylene was only observed in trace amounts during controlled heating experiments and its production was erratic. However, under discharge conditions, its production was reproducible. The discharge may have removed a proton from the methyl radicals formed in the initial reaction step thus producing CH_2 radical species.

A further abstraction of a proton from such species by the discharge would yield CH species which may then dimerise in the gas phase to produce acetylene.

Another suggested route to the production of acetylene under these experimental conditions may apply. It is possible that the "discharge" observed during the experiments was in fact a methane plasma which previous studies have shown[24] produces methyl radicals, CH_2 species or CH species. Radicals produced in this manner may interact with the catalyst surface and undergo further proton abstraction. In the case of methyl radicals, this would lead to a surface CH_2 species whilst for the CH_2 species formed from the discharge, proton abstraction would yield a CH moiety. Two successive proton abstractions from the methyl radical would also generate CH species. Desorption of such CH species followed by their coupling may explain the production of acetylene. If CH species are formed directly from the methane molecule, their subsequent dimerisation in the gas phase may also lead to the production of acetylene.

One of the limiting factors to this suggested route to acetylene is the fact that it is known that La_2O_3 is a relatively poor radical scavenger[70] and therefore the interaction of methyl radicals or CH_2 species with the catalyst surface may occur to only a small extent. However, it should be noted that the major component of the catalyst formulation is in fact MgO which may have better radical scavenging abilities than La_2O_3 and thus enable interaction between the catalyst surface and the radical species to occur to a greater extent.

It is possible that the discharge created in the reactor is able to remove hydrogen atoms from methyl radicals formed on the catalyst surface.

Carbon monoxide was found to be the major reaction product under discharge conditions and this may be due to an oxygen deficiency in the system during the period of the microwave pulse. This may limit the extent to which CO is further oxidised to CO_2.

7.2.2. Chloride Containing Catalysts

7.2.2.1.Heating Characteristics

The CIW1 chloride containing catalyst supplied by British Gas could be heated to temperatures in excess of 650°C in the single mode cavity before discharges were observed. Analysis of the variation of tan δ with temperature shows an increase in the value of tan δ between 300°C and 350°C. The network analysis apparatus was unable to record dielectric property values above 350°C. However, it is reasonable to assume that the value of tan δ would continue to increase at higher temperatures. This is in correlation to the heating characteristics of the catalyst in the microwave field where following the requirement for the application of high power to enable initial heating, subsequent heating required reduced microwave power. The ability to use reduced microwave power to maintain catalyst heating following the need for high power application suggests a change in dielectric properties of the sample. During experiments it was noted that a large temperature increase occurred when a bulk temperature of 230°C had been achieved. This is indicative of the sample interacting more strongly with the applied microwave field. It should be noted however that the bulk temperature at which this occurred under experimental conditions is more than 100°C less than that measured during network analysis investigations. It is therefore suggested that by combining experimental observations with network analysis measurements, further evidence for the presence of "hot spots" within the catalyst bed has been found.

7.2.2.2.Reaction in the Absence of Gas Phase Oxygen

As was observed for the rare-earth oxide catalysts the microwave heated reaction in the absence of gas phase oxygen over chloride containing catalysts was found to produce coupled hydrocarbon products. It is suggested that the reasons for this observation over the chloride catalyst are identical to those discussed in section 7.2.2.

7.2.2.3.Reactions using Molecular Oxygen as Oxidant

The chloride containing catalyst produced similar performance under conditions of microwave heating as for conventional heating Again, the bulk temperature for similar yields and selectivities of C_2 hydrocarbons was much reduced by the use of microwaves. As for the rare-earth oxide results, it is suggested that the presence of "hot spots" within the catalyst bed are responsible for these observations.

The chloride catalyst also produced quantities of C_5+ liquid hydrocarbon products. It is thought that areas of the catalyst were achieving temperatures even greater than those required to produce conventional coupling products. At such elevated temperatures, it is suggested that C_2 and C_3 hydrocarbons may be cracked and radicals thus formed may recombine to produce heavier hydrocarbon products. Such products were rapidly quenched upon exit from the catalyst bed due to the post catalytic zone being cool. GC - MS data for the products of a number of microwave heated experiments provides further evidence for the suggested route to the formation of the heavier hydrocarbons. Rarely were two analyses of the liquid products identical. This suggests that the radicals formed by high temperature cracking in the catalyst bed recombine at random to produce a large range of higher hydrocarbon products.

An observation unique to the microwave heated reaction over the chloride containing catalyst was the dramatic switch in the behaviour of the catalyst from a highly selective coupling catalyst to a near total oxidation catalyst. This transformation in catalytic behaviour was generally observed at the higher end of the temperature range studied and after several hours on line. A possible cause of the transformation in behaviour may be that at higher temperatures, the selective oxidation sites of the catalyst are destroyed. Another possibility is that the chloride contained within the catalyst is leached with increasing time and temperature. It is reasonable to suggest that this process would occur more rapidly in a microwave heated experiment due to the presence of "hot spots" within the catalyst. A further suggestion is that the selective oxidation sites of the catalyst were poisoned. A strong sulphur smell was evident following microwave tests and the exposure of the catalyst to microwave radiation may have liberated otherwise trapped sulphur. The sulphur may then have acted as a poison by blocking the selective oxidation sites of the catalyst.

7.2.2.4.Catalyst Lifetime Test

The operational lifetime of the chloride containing catalyst was found to be limited. The product distribution and selectivity to coupled hydrocarbons fluctuated greatly over the duration of the 5 hour test. This variation in catalyst behaviour is ascribed to the removal of chloride species from the catalyst during the experiment. The chloride component of the catalyst is thought to be an important factor for high selectivity to coupled hydrocarbons and its removal will inevitably be detrimental to catalyst performance. It was noted that acetylene was produced during the test and this may have been due to the occurrence of small discharges within the catalyst bed. It was noted in section 7.2.1.6 that acetylene was a major reaction product over rare-earth oxide catalysts under discharge conditions and it is reasonable to assume that similar processes to those described previously were occurring within the chloride containing catalyst during the 5 hour experiment.

7.3. Catalyst Characterisation Studies

7.3.1. Surface Area Measurements

7.3.1.1.Rare - Earth Oxide Catalysts

The surface area of the unsupported lanthana catalysts was found to be below $10m^2g^{-1}$ in all cases. The catalyst was reasonably selective for the production of coupled hydrocarbons under the conditions used in this study. This is in agreement with the work of other researchers[35] who have made tentative correlations between good selectivity of oxidative coupling catalysts and their possession of low surface areas. However, other workers have concluded that the results of their studies showed no conclusive relationship between selectivity and surface area of the catalyst.[152]

The magnesia supported catalysts had much increased specific surface areas in relation to their unsupported counterparts. This may have been due to a greater dispersion of strontium and lanthana over the surface of the support material. It appears from the work in this study that under the conditions used, there is no direct relationship between a "good" catalyst and a low surface area.

7.3.1.2.Chloride Containing Catalyst

The chloride containing coupling catalyst ClW1 was found to have a low surface area and was far more selective than the rare-earth oxide catalysts. This observation may suggest that a low specific surface area is in fact beneficial to C_2 selectivity. However, the argument is still yet unresolved.

7.3.2. DSC/TGA

7.3.2.1.Rare Earth Oxide Catalysts

The DSC/TG trace for the strontium- lanthana catalysts exhibited, a large endotherm and simultaneous weight loss at 375°C. This suggests that the catalyst is losing a species either from the surface or the bulk at this temperature. This is consistent with the work of others[153 - 155] who have studied the decomposition of lanthanide carbonates and their counterparts which is represented below:

$$\begin{array}{c} La(OH)_3 \\ La_2(OH)_4CO_3.nH_2O \end{array} \xrightarrow{377\,^{\circ}C} \begin{array}{c} LaO(OH) \\ La_2O_2CO_3 \end{array}$$

It is therefore suggested that at a temperature of 375°C, the Sr/La_2O_3 catalysts may form a lanthanum oxycarbonate species on the surface. This species has been suggested by other researchers to play a significant role in the overall selectivity of lanthana containing oxidative coupling catalysts.[62,63,78]

7.3.2.2.Chloride Containing Catalyst

The DSC/TG analysis of the CIW1 catalyst showed a sharp endothermic peak at 425°C but this was not accompanied by a corresponding change in mass. This type of trace is characteristic of a phase change in the sample. It may be that the chloride within the catalyst is reacting with other components of the material to form different chloride species at this elevated temperature. It is reasonable to suggest that at temperatures in excess of those achievable by the DSC/TGA apparatus used, further changes may occur in the catalyst. Thus it may be possible that such an occurrence has an effect on the observed switch in catalyst behaviour under microwave conditions from a selective coupling material to a total oxidation catalyst. It is possible that at elevated temperatures, the selective oxidation sites are destroyed. It has been suggested previously that areas of the catalyst bed may achieve temperatures far in excess of the observed bulk temperature under microwave conditions and as such, the morphology of the catalyst may be changed in such a way as to be detrimental to performance.

7.3.3. Network Analysis Experiments

7.3.3.1. Rare - Earth Oxide Catalysts

The investigation of the dielectric properties of the rare-earth oxide oxidative coupling catalysts revealed that significant changes occurred with temperature. The 1wt% Sr/La_2O_3 catalyst exhibited three distinctive changes in the value of tan δ with temperature. These changes consisted of two increases in the value of tan δ at 150 - 200°C and 500°C and a decrease between 300°C and 350°C.

The first change in dielectric properties may be attributed to the removal of water from the sample. Lanthana is known to be strongly hygroscopic and it is not surprising that water vapour from the air was retained by the catalyst. The decrease in the value of tan δ shows that the catalyst was not interacting strongly with the applied field and this is in agreement with the microwave heating characteristics of the catalyst as high microwave power was required to heat this catalyst. The increase in tan δ at 500°C shows that the catalyst was transformed from a non - lossy to a lossy material at this temperature. Again this is in agreement with the heating characteristics as discharges were produced by the catalyst following the initial heating period. There is however a large discrepancy between the measured value of the large increase in tan δ and the bulk temperature at which discharges were observed under experimental conditions. This is seen as further evidence for the production of "hot spots" within the catalyst bed under conditions of microwave heating.

It is possible as suggested in section 4.1.1 that the sample undergoes a phase change with temperature and the formation of a new lanthana phase may be responsible for the change in ability of the catalyst to interact with the applied microwave field.

The magnesia supported catalyst could be controllably heated to higher temperatures in the microwave field than the unsupported sample. The dielectric property measurements for this sample revealed that the final increase in tan δ occurred at a greater temperature for this material than the unsupported catalyst. This explains the fact that increased temperatures could be achieved by this catalyst in the microwave cavity. The reason for the final increase in dielectric properties occurring at a higher temperature for the supported sample is thought to be due to the incorporation of magnesia into the catalyst formulation. Strontium was found to play a role in the production of discharges during microwave heated tests and since the surface area of the supported catalyst was greater than that of the unsupported one it is reasonable to suggest that the strontium was more highly dispersed in the supported catalyst. This may result in the microwave field interacting less strongly with the strontium component and hence higher bulk catalyst temperatures could be achieved before discharges were observed.

7.3.3.2.Chloride Containing Catalysts

The chloride catalyst did not exhibit as many changes in dielectric properties with temperature as the rare-earth oxide samples.

7.4. Kinetic Considerations

Plots of ln k vs 1000/T for the thermally heated reforming reactions produced the expected straight line plot assuming that the reaction is first order in methane. Some levelling of the plots for both the thermal and microwave experiments was observed at the higher temperatures investigated. This is ascribed to the depletion of oxygen in the system. At higher reaction temperatures, oxygen consumption was calculated to be at least 100% indicating that the reaction was proceeding under oxygen limited conditions.

For microwave heated tests, levelling of the plot was also observed during the initial stages of catalyst testing and at the lower end of the temperature range studied. This shows that the rate constant for the reaction during this part of the experiment is greater for the microwave heated reaction than the thermally heated counterpart. This is ascribed to initial activation of the catalytic sites by the microwave energy. It is suggested that the microwave energy was able to produce more active catalytic sites in the fresh catalyst and at lower bulk reaction temperatures. At low bulk temperatures it is suggested that the applied microwave energy specifically activates the active catalytic sites such that enhancements in the rate of reaction are observed. A further consideration is the presence of "hot spots" within the catalyst bed. Although the presence of sites within the catalyst bed at temperatures far in excess of the observed bulk temperature are thought to exist over the whole temperature range investigated, it is possible that the effect is enhanced at the lower end of the temperature range thus increasing the rate of reaction.

8. Discussion

8.1. Steam Reforming of Methane

8.1.1. Conventionally Heated Reactions

Conventionally heated steam reforming experiments served two major purposes in this study. The first function of conventionally heated reactions was to provide process validation because an untried method of water introduction was being used. Secondly, the conventionally heated experiments served as a direct means of comparison for the microwave heated experiments.

British Gas LH Catalyst

The impracticality of constructing and installing a high temperature steam generator as used for industrial and pilot scale steam reforming dictated that an alternative method of introducing water to the reactant stream was required. A water bubbler mounted in a thermostatted water bath was used to perform the task. The vapour pressure of water at a particular temperature is well documented[156] and thus by monitoring the temperature of the water in the bubbler, the exact amount of water introduced to the reactant stream could be determined.

The LH catalyst used for the first steam reforming experiments is a commercial catalyst and it was therefore unsurprising that high activity for the reforming reaction was observed.

The use of a steam ratio of 2 or less resulted in an appreciable degree of carbon deposition on the catalyst surface and this is in agreement with literature guidelines regarding steam ratios.[145]

Equilibrium constant calculations obtained from chromatographic results of the experiments were in excellent agreement with the well documented literature values which relate equilibrium constant to temperature[145] thus indicating that the experimental procedures used were indeed valid.

Nickel - Alumina Catalysts

Equilibrium constant calculations for the nickel - alumina catalysts showed the same excellent correlation with literature values as the commercial reforming catalyst. However in general, the catalysts were not as active for the reforming reaction as the commercial catalyst. This is not surprising since the commercial catalyst had been designed and developed for optimum performance over a number of years of costly research. The 20% nickel - alumina catalyst gave the best performance of all the catalysts studied.

Carbon deposition at the higher end of the temperature range was greater for the nickel - alumina catalysts than the LH catalyst. This shows that the catalysts produced in - house were not as durable under reaction conditions as the commercial material. This observation was expected since the commercial catalyst formulation included the use of components which provided the stability and durability required for an industrial catalyst.

8.1.2. Microwave Heated Reactions

British Gas LH Catalyst

The microwave heating characteristics and network analysis results for this catalyst showed that a change in dielectric properties with temperature occurred. The material showed a transition from a non - lossy to a reasonably lossy material.

At very low bulk reaction temperatures the water gas shift equilibrium appeared to predominate but CO was detected as the temperature was increased indicating that the steam reforming equilibrium was contributing to a greater extent.

The temperature at which products were first observed under conditions of microwave heating was some 200°C lower than the conventionally heated reaction.

Equilibrium constant calculations revealed a marked deviation from the observed bulk reaction temperature and the quoted literature temperature values for a given equilibrium constant.

Plots presented in chapter 6 (figures 6.2 - 6.5) show that the catalyst exhibits three different characteristics during a typical run. Straight line plots of ln K versus 1000/T of different slope were obtained depending upon the length of time on line.

During initial stages of an experiment, equilibrium constants were higher than those obtained under "steady state" microwave conditions. The reasons for this observation are suggested to be two - fold. At the start of an experiment, the catalyst was freshly reduced and possibly at its most active. It is suggested that the microwave radiation is able to interact with the catalytically active sites to a greater extent during this time thus creating enhanced activity. Such a higher initial catalyst activity was not observed for conventionally heated reactions.

Furthermore, it is suggested that the active sites of the catalyst achieve temperatures far in excess of the observed bulk temperature during this time thus accounting for the deviation from the "steady state" equilibrium constant/temperature relationship. The plot of ln K against 1000/T (figure 6.5.) for the catalyst during the initial period of the experiment converged towards the steady state line as the temperature was increased.

The "steady state" period spanned the middle region of the experiment and extended to a temperature of approximately 380°C. However, at temperatures in excess of this, carbon deposition on the catalyst became appreciable and the catalyst entered the third stage of its behaviour.

Following carbon deposition, the equilibrium constants were generally much lower than the "steady state" values for a given bulk temperature. This indicates that the active sites had been poisoned by carbon deposition. In contrast to the plot for the freshly reduced catalyst, the plot during this region of the experiment diverged from that of the "steady state" line.

The upper temperature achieved by the catalyst under conditions of microwave irradiation was limited to approximately 400°C. This is thought to be due to the experimental conditions which were used. The nature of the experimental apparatus meant that the exit of the reactor could not be heated in the same manner as the reactor entrance. This resulted in the condensation of water vapour in the post catalytic zone.

The resulting water regressed towards the catalyst and reduced the temperature of the catalyst. Water interacts well with microwave energy but because the amount of catalyst was small, it is thought that it became saturated with water and the applied microwave energy had insufficient power and could not be strongly focused enough to remove all of the deposited water.

Nickel - Alumina Catalysts

Observations for the nickel - alumina catalysts were very similar to those for the commercial catalyst and it is suggested that similar arguments to those for the LH catalyst apply to the catalysts produced in - house.

8.1.3. Comparison between Microwave and Conventionally Heated Experiments.

In order to make a valid comparison between the two methods of heating it is necessary to consider the "steady state" microwave results. The use of data during the initial stages or following carbon deposition may cause misleading conclusions to be drawn.

As stated in section 8.1.1 the conventionally heated reactions produced data which was in excellent agreement to that cited in the literature. However, when comparing this information with that obtained from the steady state microwave experiments there is a clear discrepancy. The plot of ln K vs 1000/T is parallel to the thermal line but offset to lower temperatures. This indicates that the same degree of reaction is occurring under microwave conditions but at a lower bulk temperature.

Clearly, the thermodynamics dictate that the reaction cannot proceed to the same extent at lower temperatures. It is therefore concluded that although the bulk catalyst temperature as measured by the optical fibre thermometer is some 140°C lower for the microwave heated reaction, there exist within the catalyst bed active sites which are heated to the actual temperature required for the observed degree of reaction. Such sites have been termed "hot spots".

The conventional view of catalytically active sites was proposed by Taylor.[157] Taylor stated that the active catalytic sites were seen as **small** particles having atoms of different co-ordination number at their surface and postulated that the most co-ordinatively unsaturated atoms constituted the "active centres" for certain reactions.

If the Taylor definition of active sites is applied to the supported nickel catalyst used in this study, it can be assumed that the "active sites" (nickel particles) are dispersed throughout the support material. When conventional heating is used, the whole of the catalyst (support and active material) is heated to the same temperature. However, when microwave heating is used, the small nickel particles are preferentially heated relative to the support and may therefore achieve higher temperatures than the support material. The small size of the active sites in the catalyst and the sensitivity limitations of the available temperature measurement equipment dictated that the actual temperature of the sites could not be measured by conventional means.

The use of the thermodynamics of the steam reforming reaction has however provided irrefutable chemical evidence of the existence of "hot spots" within a catalyst bed under conditions of microwave irradiation.

Clearly, the methods available during this study for the measurement of temperature in a microwave field were not sufficiently sensitive for the actual temperature of the active catalytic sites to be monitored and some microwave temperature measurement techniques are considered in appendix A. The use of the thermodynamics of the reaction to obtain a good estimate of the temperature of active sites within the catalyst bed is a novel way to gain information which the available technology cannot provide.

The use of microwave energy to heat the catalyst for the steam reforming of methane offered advantages over the conventionally heated reaction in terms of methane conversion and product yield. This may be due to the presence of the "hot spots" within the catalyst bed which were discussed previously.

It is possible that due to the nature of the microwave heating of the active sites that certain sites achieve temperatures in excess even of the highest achieved during conventionally heated reactions. This is not to say that the majority of active sites achieve such temperatures and this is not implied as it is reasonable to suggest that the majority of active sites ("hot spots") achieve the same temperatures as the temperatures observed for the conventionally heated reaction. However, even a relatively small amount of sites at "super - elevated" temperatures may account for the observed increase in conversion.

Mathematical modelling of catalysts and heat transfer characteristics may have enabled the calculation of the actual number of active sites achieving temperatures in excess of the observed bulk temperatures. However, such investigations were not conducted during this study.

8.2. Methane Combustion

The methane combustion reaction was investigated as it was thought that under microwave conditions the same "hot spot" phenomenon observed for both the oxidative coupling of methane and the steam reforming of methane would apply to this reaction.

8.2.1. Conventionally Heated Reactions

As was the case for the coupling and reforming reactions, the main purpose of conventionally heated reactions was to serve as a comparison for subsequent microwave heated tests.

The observation of a "light - off" temperature for all of the catalysts tested is in agreement with recent work by Burch and Loader.[147] As the active component of the catalyst is platinum, it is not surprising that the magnitude of the "light off" temperature decreased with increasing platinum content. Additionally, the temperature required for complete combustion decreased with increasing platinum loading. The results of the thermal experiments performed in this study appear to suggest that the greater the platinum content of the catalyst, the lower the temperature required to achieve complete combustion. However, it should be noted that the high price of platinum metal requires consideration when designing and producing catalysts. Therefore, the 5% Pt material appears to be a compromise catalyst since although temperatures in excess of 400°C were required for >90% conversion, production costs would be bearable. However, under the experimental conditions used in this study, the

3% catalyst required only a further 10°C than the 5% material to achieve complete combustion. Unfortunately, the conditions used in this study in no way simulate the conditions which would be experienced by the catalyst in one of the major applications for catalysts of this genre i.e. automotive exhaust systems. Natural gas powered vehicles are the subject of much research at present and as a result, methane emissions from such vehicles is a major consideration. Clearly it is beyond the scope of this study to simulate "real" conditions.

8.2.2. Microwave Heated Reactions

Of the catalysts tested, only the material containing 5% platinum was able to perform satisfactorily under microwave conditions. The 1% and 3% Pt materials could not be heated to sufficiently high temperatures to facilitate the reaction. It is suggested that insufficient platinum was present in these catalysts to enable efficient interaction of the catalyst with the applied microwave field.

The results achieved by the 5% platinum catalyst clearly showed that the combustion reaction occurred at significantly lower bulk temperatures than the conventionally heated reaction. As was mentioned when considering the other reactions performed during the course of this study, it is suggested that under conditions of microwave irradiation areas of the catalyst achieve temperatures far in excess of the observed bulk temperature. The existence of such "hot spots" within the catalyst bed would account for the apparent discrepancy in the temperature required for complete methane conversion between the conventionally and microwave heated reactions.

The heating characteristics of the catalyst in the microwave field dictated that temperatures below 140°C could not be investigated and therefore no evidence of a "light off" temperature could be found. However, the shallow slope of the microwave data line in figure 6.10 suggests that it is unlikely that a sharp "light off" phenomenon is observed under conditions of microwave heating.

8.2.3. Comparison between Microwave and Conventionally Heated Experiments.

Clearly the major difference between the two modes of catalyst heating is the difference in the temperature required for complete methane combustion. The microwave heated reaction showed complete combustion at a temperature some 280°C lower than the conventionally heated reaction. This observation is ascribed to the presence of "hot spots" within the catalyst bed when heated by the microwave field.

Clear evidence of a "light off" temperature was observed for the conventionally heated reaction but not for the microwave reaction. It is suggested that this may be due to the way in which the catalyst is heated under microwave conditions. When exposed to microwave radiation, the active sites of the catalyst are heated directly and possibly achieve temperatures far higher than the observed bulk temperature almost instantaneously. It is therefore reasonable to suggest that upon exposure to the applied field, reaction temperatures are achieved and the "light off" phenomenon is not observed.

An interesting observation was the large difference in product distribution between the two modes of heating. The conventionally heated reaction showed a distribution of carbon oxides heavily favouring CO_2 (98%). However, the microwave heated reaction showed a significant amount of CO (18.2%) at total combustion. This observation may have been caused by the presence of small discharges within the catalyst bed which may have caused the partial decomposition of CO_2 to CO.

The use of microwaves for methane combustion offers the advantage that the catalyst is heated directly and almost instantaneously which is obviously not the case for the conventionally heated reaction. This may have applications in automotive catalysis where the catalyst requires a certain amount of time to achieve reaction temperatures. Automotive exhaust catalysts are at their least efficient during a cold start of the engine and as a result the greatest emission of pollutants occurs during this time. If a small microwave generator could be incorporated into the exhaust catalyst system in order to pre - heat the catalyst very quickly before start up then the problems associated with cold start catalyst inefficiency may be significantly reduced.

9. Conclusions

9.1. Microwave Heating of a Catalyst Bed

For all of the reactions investigated during this study, the use of microwave radiation to heat the catalyst bed resulted in the reaction occurring at an apparently reduced temperature relative to the conventionally heated reaction. However, it is apparent, particularly from the thermodynamic data obtained from the steam reforming studies, that the it was not feasible for the reaction to occur at such a reduced temperature. It is therefore concluded that under conditions of microwave heating, areas of the catalyst achieve temperatures far in excess of the observed bulk catalyst temperature. Such areas within the catalyst have been termed "hot spots" and it is thought that the reaction occurs at these sites.

It is therefore concluded that no "microwave effect" was observed for any of the reactions investigated. Microwave radiation served only as a means of catalyst heating.

A possible advantage to the use of microwaves to heat a catalyst bed is that the active sites are heated directly while the post catalytic area remains relatively cool. this may lead to increased yields of products of low stability compared to conventional methods of heating due to a quenching effect.

9.2. Temperature Measurement in a Microwave Field

This subject is considered in greater detail in Appendix A. However, it can be concluded that the methods available for catalyst temperature measurement during this study were insufficiently sensitive to enable the measurement of the temperature of the proposed "hot spots" within the catalyst bed. As a result of this, the apparent reaction temperature was greatly reduced when microwaves were used to heat the catalyst as only the overall bulk temperature of the catalyst could be measured.

The investigation of the steam reforming of methane under microwave conditions provided an indirect means of temperature measurement in a microwave field. The use of other well documented reactions to serve as a "chemical thermometer" for microwave heated reactions may be an area for future investigation.

9.3. Advantages of Microwave Heating of a Catalyst Bed

The work performed during this study has revealed that the microwave heating of a catalyst bed may offer advantages over conventional methods of catalyst heating.

Firstly, the use of microwave radiation enables the catalyst to be heated directly whereas when conventional electrical furnaces are utilised, the pre and post catalytic zone is also heated. This suggests that the use of microwave heating leads to less energy wastage and hence a more economic and efficient process.

Secondly, as a result of direct catalyst heating, the post catalytic zone remains cool in relation to the catalyst bed thus minimising the occurrence of any undesirable gas phase reactions in the post catalytic area. Furthermore, products of low thermal stability may be produced in higher yield by the use of microwave catalyst heating as they may be quenched in the cold post catalytic zone.

9.4. Oxidative Coupling of Methane

Of the catalysts investigated for the OCM reaction during this study, the chloride containing catalysts offered significant advantages in terms of yield and selectivity of unsaturated coupled hydrocarbon products. However, the lifetime of such catalysts is questionable particularly under microwave conditions due to the leaching of chloride species from the catalyst during reaction. Small discharges within the catalyst bed under microwave conditions led to a more rapid removal of chloride species than when conventional heating was employed.

9.5. Suitability of Catalysts for Microwave Heated Reactions

Throughout this study, several problems were encountered during the microwave heating of the majority of the catalysts tested. The most common problem was the production of discharges in the reactor and within the catalyst bed during microwave heating. Clearly it can be concluded that the catalysts investigated during this study were not entirely suitable for use under conditions of microwave heating. However, this is not surprising since the materials had previously only been tested using conventional heating methods. The area of catalyst design therefore requires careful attention if an effective catalyst suitable for use under microwave conditions is to be formulated. The problem of microwave catalyst design is a difficult one since one must consider several factors. The catalyst must interact suitably with the applied microwave field, have stable dielectric properties over a wide temperature range and obviously be both active and selective for the reaction of choice.

References

1. Mingos D. M. P. and Baghurst D. R., Chem. Soc. Rev., **20**, 1 (1991).
2. Metaxas A. C. and Meredith R. J., "Industrial Microwave Heating", Peter Peregrinus Ltd, (1983).
3. Neas E. D. and Collins M. J., in "Introduction to Microwave Sample Preparation", H. M. Kingston and L. S. Jassie (Eds.), American Chemical Society, 7, (1988).
4. Wagner K. W., Arch. Elektrotech, **2**, 371, (1914).
5. Giguere R. J., Bray T. L. and Duncan S. M., Tet. Letts., **27**, No. 41, 4945, (1986).
6. Giguere R. J., Namen A. M., Lopez B. O., Arepally A., Ramos D. E., Majetich G. and Defauw J., Tet. Letts., **28**, No. 52, 6553 (1987).
7. Gedye R. N., Smith F. E. and Westway K. C., Can. J. Chem., **66**, 17, (1988).
8. Gedye R. N., Rank W. and Westaway K. C., Can. J. Chem., **69**, 706, (1991).
9. Gedye R., Smith F., Westaway K.,, Ali H., Baldisera L., Laberge L. and Rousell J., Tet. Letts., **27**, No. 3, 279, (1986).
10. Wan J. K. S., Bamwenda G. and Depew M. C., Res. Chem. Interm., **16**, 241, (1991).
11. Wan J. K. S., Res. Chem. Interm., **19**, No. 2, 147, (1993).
12. Bamwenda G., Moore E., and Wan J. K. S. Res. Chem. Interm., **17**, 243, (1992).
13. Bond G., Moyes R. B. and Whan D. A., Catal. Today, **17**, 427, (1993).

14. Thuery J., "Microwaves: Industrial, Scientific and Medical Applications" Artech House, Boston London (1991).

15. Kenkre V. M., Skala L., Weiser M. W., and Katz J. D. J. Mat. Sci., **26**, 2483, (1991).

16. Mingos D. M. P. and Baghurst D. R., J. British Ceramics Trans., **91**, 124, (1992).

17. Palaith D. and Silberglitt R., Ceramic Bulletin, **68**, 1601, (1989).

18. Jones P., in "Drying 1992", Mujundar A. S. (Ed.), Elseveir Science Publishers B. V., 114, (1992).

19. Roy R., Komarneni S. and Yang L. J., J. Am. Ceram. Soc., **68**, 392, (1985).

20. Jansen J. C., Arafat A., Barakat A. K. and van Bekkum H., in "Molecular Sieves: Synthesis of Microporous Materials". Occelli M. L. and Robson H. E. (Eds.), Vol. I, Van Nostrand Reinhold, 507, (1992).

21. Roussy G., Zoulalian A., Charreyre M. and Thiebaut J. M., J. Phys. Chem., **88**,5702, (1984).

22. Zerger R. P., McMahon K. C., Seltzer M. D., Michel R. G. and Suib S. L., J. Catal., **99**, 498, (1986).

23. Wan J. K. S., Tse M Y., Husby H. and Depew M. C., J. Microwave Power and Electromagnetic Energy, **25**, 32, (1990).

24. Suib S. L., Zerger R. P. and Zhang Z., Symposium on Natural Gas Upgrading II., Div. Petroleum Chem., ACS, Washington D. C., 344, (1992).

25. Suib S. L., and Zerger R. P. J. Catal., **139**, 383, (1993).

26. Kawahara Y., J. J. Phys, Chem., 73, 1648, (1969).

27. Roussy G., Thiebaut J. M., Souiri M., Kiennemann A., and Maire G., Proc. 28th Symposium IMPI, 79, (1993).

28. British Patent No. 9115655 (1994).

29. Chen C., Hong P., Dai S. and Kan J., J. Chem. Soc. Faraday Trans., **91**, (7), 1179, (1995).

30. Keller G. E. and Bhasin M. M., J. Catal., **73**, 9, (1982).

31. Hinsen W. and Baerns M., Chem. Ztg., **107**, 223, (1983).

32. Hinsen W., Bytyn W. and Baerns M., Proc. 8th ICC Verlag Chemie, Weinheim **3**, 581, (1984).

33. Ito T. and Lunsford J. H., Nature (London), **314**, 7211, (1985).

34. Ekstrom A., Lapszewicz J. A. and Campbell Appl. Catal., **117**, 416, (1989).

35. Lee J. S. and Oyama S. T., Catal. Rev., **30**, (2), 249, (1988).

36. Forster N. R., Appl. Catal., **19**, 1, (1985).

37. Hutchings G. J., Scurrell M. S. and Woodhouse J. R., Stud. Surf. Sci. Catal., **36**, 415, (1988).

38. Otsuka K. and Nakajima K., J. Chem. Soc. Faraday Trans., **83**, 1315, (1987).

39. Hutchings G. J., Scurrell M. S. and Woodhouse J. R., Proc. 1st Workshop on Catalytic Methane Conversion, Bochum 1988.

40. Hutchings G. J., Scurrell M. S. and Woodhouse J. R., J. Chem. Soc. Chem. Commun., 1388, (1987).

41. Aika K. and Nishiyama T., Proc. 9th ICC Calgary 1988.

42. Aika K. and Nishiyama T., J. Chem. Soc. Chem. Commun., 70, (1988).

43. Shepelev S. S. and Ione K. G., Kin. Katal., **25**, 347, (1984).

44. Burch R., Squire G. D. and Tsang S. C., Appl. Catal., **43**, 105, (1988).

45. Carriero J. A. S. P., Foumer G., Lehmann L. and Baerns M., Proc. 9th ICC **2** 891, (1988).

46. Roos J. A., Korf S. J., Veehof R. J. H., van Ommen J. G. and Ross J. R. H., Proc. 1st Workshop on Catalytic Methane Conversion, Bochum 1988.

47. DeBoy J. M. and Hicks R. F., J. Chem. Soc. Chem. Commun., 982, (1988).

48. Otsuka K., Jinno K. and Morikawa A., Chem. Lett., 499, (1985).

49. Otsuka K., Liu Q., Hatano M. and Morikawa A., Inorg. Chim. Acta, **118**, L24, (1986).

50. Asami K., Hashimoto S., Shikada T., Fujimoto K. and Tominaga H., Chem. Lett., 1233, (1986).

51. Kijensky J. and Malinowski S., J. Chem. Soc. Faraday Trans., I74, 250, (1978).

52. Tench A. I. and Nelson R. L., Trans. Faraday Soc., **63**, 2254, (1967).

53. Che M., Naccache C. and Imelik B., J. Catal., **24**, 328, (1972).

54. Mehandru S. P., Anderson A. B. and Bradzil J. F., J. Am. Chem. Soc., 110, 1715, (1988).

55. Hargreaves J. S. H., Hutchings G. J. and Joyner R. W., Catal. Today, **6**, 481, (1990).

56. Lunsford J. H., Cisneros M. D., Hinson P. G., Tong Y. and Zhang H., Faraday Discuss. Chem. Soc., **87**, 13, (1989).

57. Driscoll D. J., Wilson M., Wang J. X. and Lunsford J. H., J. Am. Chem. Soc., **107**, 58, (1985).

58. Wang J. X. and Lunsford J. H., J. Phys. Chem., **90**, 5883,(1986).

59. Lin C. H., Campbell K. D., Wang J. X. and Lunsford J. H., J. Phys. Chem., **90**, 534, (1986).

60. Lo M. Y., Agarwal S. K.and Marcelin G. E., Prepr. 196th ACS Nat. Meetg., **33**, (2), 378, (1988).

61. Sokolovskii V.D., in "Direct Methane Conversion by Oxidative Processes", E. E. Wolf (Ed.), Van Nostrand Reinhold, New York, 1991, p. 368

62. Le Van T., Che M., Kermarec M., Louis C. and Tatibouët J. M., Cat. Lett., **6**, 395, (1990).

63. Squire G. D., Luc H. and Puxley D. C., Appl. Cat. A: General, **108**, 261, (1994).

64. DeBoy J. M. and Hicks R. F., J. Catal., **113**, 517, (1988).

65. Winter E. R. S., J. Chem. Soc. (A), 1832, (1969).

66. Hutchings G. J., Scurrell M.S. and Woodhouse J. R., Chem. Soc. Rev., **18**, 251, (1989).

67. Otsuka K., in "Direct Methane Conversion by Oxidative Processes", E. E. Wolf (Ed.), Van Nostrand Reinhold, New York, 1991, p. 78

68. Dubois J. L., Bisiaux M., Mimoun H. and Cameron C. J., Chem. Lett., 967, (1990).

69. Otsuka K., Jinno K and Morikawa A., J. Catal., **100**, 353, (1986).

70. Tong Y., Rosynek M. P. and Lunsford J. H., J. Phys. Chem., **93**, 2896, (1989).

71. Gaffney A. M., U.S. Patent No. 4,499,323, (1985).

72. Becker S. and Baerns M.,, J. Catal., **128**, 512, (1991).

73. DeBoy J. M. and Hicks R. F., Ind. Eng. Chem. Res., **27**, 1577, (1988).

74. Yamagata N., Abe Y., Igarashi K., Ishikawa T., Sahara M. and Okazaki S., Chem. Lett., 1893, (1990).

75. "Handbuch des Chemikers" G. Faust (Ed.), VEB Verlag Technik Berlin Vol. 1, 1956.

76. Ekstrom A. and Lapszewicz J. A., J. Phys. Chem., **93**, 5230, (1989).

77. Feng Y., Niiranen J. and Gutman D., J. Phys. Chem. **95**, 6558, (1991).

78. Conway S. J., Grieg J. G. and Thomas G. M., Appl. Catal. A: General **86**, 199, (1992).

79. Withers H. P., Jones C. A., Leonard J. J. and Sofranko J. A., U.S. Patent No. 4,,634,800, (1987).

80. Burch R., Squire G. D. and Tsang S. C., Appl. Catal., **46**, 69, (1989).

81 Burch R., Crabb E. M., Squire G. D. and Tsang S. C., Catal. Lett., **2**, 249, (1989).

82. Kimble J. B. and Kolts J. H., U.S. Patent No. 4,620,057, (1986).

83. Otsuka K., Liu Q., Hatano M. and Morikawa A., Chem. Lett., 903, (1986).

84. Otsuka K., Sekiyu Giakkaishi, **30**, 385, (1987).

85. Shigapov A. N., Novozhilova M. A., Vereshchagin S. N., Anshits A. G. and Sokolovskii V. D., React. Kinet. Catal. Lett., **37**, 397, (1988).

86. Ueda W. and Thomas J. M., J. Chem. Soc. Chem. Commun., 1148, (1988).

87. Wohlfahrt K., Bergfeld M. and Zengel H., German Patent No. 3,503,664, (1986).

88. Otsuka K., Hatano M. and Komatsu T., in "Methane Conversion", D. M. Bibby, C. D. Chang, R. F. Howe and S. Yurchak (Eds.), Elsevier, Amsterdam, 1988, 383.

89. Larkins F. P. and Nordin M. R., in “Methane Conversion”, D. M. Bibby, C. D. Chang, R. F. Howe and S. Yurchak (Eds.), Elsevier, Amsterdam, 1988, 409.

90. Fujimoto K., Hashimoto S., Asami K. and Tominaga H., Chem. Lett. 2157, (1987).

91. Minachev Kh. M., Usachev N. Ya., Udut V. N. and Khodakov Yu. S., Russ. Chem. Revs., **57**, 22, (1988).

92. Otsuka K. and Komatsu T., J. Chem. Soc. Chem. Commun., 388, (1987).

93. Otsuka K., Liu Q. and Morikawa A., J. Chem. Soc. Chem. Commun., 586, (1986).

94. Sofranko J. A., Leonard J. J. and Jones C. A., J. Catal., **103**, 302, (1987).

95. Jones C. A., Leonard J. J. and Sofranko J. A., J. Catal., **103**, 311, (1987).

96. Sofranko J. A., Leonard J. J., Jones C. A., Gaffney A. M. and Withers H, P., Catal. Today, **3**, 127, (1988).

97. Labinger J. A., Ott K. C., Mehta S.,, Rockstead H. K. and Zoumalan S., J. Chem. Soc. Chem. Commun., 543, (1987).

98. Thomas J. M., Kuan X. and Stachurski J., J. Chem. Soc. Chem. Commun., 162, (1988).

99. Otsuka K. and Komatsu T., J. Chem. Soc. Chem. Commun., 388, (1987).

100. Baldwin T. R., Burch R., Crabb E. M., Squire G. D. and Tsang S. C., Appl. Catal., **56**, 219, (1989).

101. Thomas J. M., Ueda W., Williams J. and Harris K. D. M., Faraday Discuss. Chem. Soc., **87**, 33, (1989).

102 Lunsford J. H., Hinson P. G., Rosynek M. P., Shi C., Xu M. and Yang X., J. Catal., **147**, 301, (1994).

103. Burch R., Chalker S., Loader P. and Rice D. A., Appl. Catal. A: General, **79**, 265, (1991).

104. Ekstrom A. and Lapszewicz J. A., J. Am. Chem. Soc., **110**, 5226, (1988).

105. Berlowitz P., Driscoll D. J., Lunsford J. H., Butt J. B. and Kung H. H., Comb. Sci. Technol., **40**, 317, (1984).

106. Murgulescu I.G. and Schneider I. A., J. Pract. Chem., **18**, 121, (1962).

107. Wroblowa H., Priesma B. J. and Bockris J. O'M., Electroanal. Chem., **6**, 401, (1963).

108. Grubb W. T. and Michalske C. J., J. Electrochem. Soc., **111**, 1015, (1964).

109. Grubb W. T., J. Electrochem. Soc., **111**, 1086, (1964).

110. Lucchesi P. J., carter L. J. and Sinfelt J. H., J. Am. Chem. Soc., **86**, 1494, (1964).

111. Niedrach L. W., J. Electrochem. Soc., **113**, 645, (1966).

112. Taylor G. F., Thomson S. J. and Webb G., J. Catal., **12**, 150, (1968).

113. Taylor A. H. and Brummer S. B., J. Phys. Chem., **73**, 2397, (1969).

114. Brummer S. B. and Turner M. J., Proc. 23rd Annual Power Sources Conf., 1969, p. 26.

115. Bockris J. O'M., Gileadi E. and Stoner G. E., J. Phys. Chem., **73**, 427, (1969).

116. Kemball C., Catal. Rev., **5**, 33,, (1971).

117. Vasiliev Yu. B.,, Bagotskii V. S. and Khazowa O. A., Elektokhimiya, **11**, 1505, (1975).

118. Kolyadko E. A., Menyailova M. V. and Podlovchenko V. I., Elektrokhimiya, **13**, 273, (1977).

119. Sarkany A., Matusek K. and Tetenyi P., J. Chem. Soc. Faraday Trans. I, **73**, 1699, (1977).

120. Tetenyi P., Guczi L. and Sarkany A., Acta Chim. Acad. Sci. Hung. **97**, 221, (1978).

121. Sustercic M. G., Cordova R., Triaca W. E. and Arvia A. J., J. Electrochem. Soc., **127**, 1242, (1980).

122. Castro Luna A. M., Delgado A. and Arvia A. J., An. Assoc. Quim. Argent., **69**, 301, (1981).

123. Lisowski W. and Dus R., Surf. Sci., **118**, 208, (1982).

124. Tanaka K., Yaegashi I. and Aomura K., J. Chem. Soc. Chem.Commun., 938, (1982).

125. Palfi S., Lisowski W., Smutek M. and Cerny S., J. Catal., **88**, 300, (1984).

126. Muzyka I., Zubkov S. A., Borokov V. Yu. and Kazanskii V. B., Dokl. Akad. Nauk SSSR. Ser. Fiz. Khim., **284**, 391, (1985).

127. Quinlan M. A., Wood B. J. and Wise H., Chem. Phys. Lett. **118**, 478, (1985).

128. Coche D. L. and Yoon C., in "Rapidly Quenched Metals", S. Steeb and H. Warlimot (Eds.),, Elsevier, 1985, p. 1497.

129. Madix R. J., Science, **233**, 1159, (1986).

130. Wang P. K., Ansermet J. P., Rudaz S. L., Wang Z., Shore S., Slichter C. P. and Sinfelt J. H., Science, **234**, 35, (1986).

131. Lee M. B., Yang Q. Y, Tan S. L. and Ceyer S. T., J. Phys. Chem., **85**, 1693, (1986).

132. Mehandru S. P., Anderson A. B. and Bradzil J. F., J. Am. Chem. Soc., **110**, 1715, (1988).

133. Campbell K. D. Morales E. and Lunsford J. H., J. Am. Chem. Soc., **109**, 7900 (1987).

134. Cant N. W., Lukey C. A., Nelson P. F. and Tyler R. J., J. Chem. Soc. Chem. Commun., 766, (1988).

135. Lunsford J.H., in “Direct Methane Conversion by Oxidative Processes”, E. E. Wolf (Ed.), Van Nostrand Reinhold, New York, 1991, p. 1.

136. Garibyan T. A. and Margolis L. Y., Cat. Rev. Sci. Eng. **31**, (4), 355 (1989).

137. Hutchings G. J., Scurrell M. S. and Woodhouse J. R., J. Chem. Soc. Faraday Trans. I, **85**, 2507, (1989).

138. Hutchings G. J., Scurrell M. S. and Woodhouse J. R., Catal. Today, **4**, 371 (1989).

139. Hutchings G. J., Scurrell M. S. and Woodhouse J. R., J. Chem. Soc. Chem. Commun., 1862, (1987).

140. Iwamatsu E. and Aika K. J., J. Catal., **117**, 416, (1989).

141. Ito T., Wang J. X., Lin C. H. and Lunsford J. H., J. Am. Chem. Soc., **107**, 5062, (1985).

142. Lin C. H.,, Wang J. X. and Lunsford J. H., J. Catal., **111**, 302, (1988).

143. Sokolovskii V. D. React. Kinet. Catal. Lett., 35, 337, (1987).

144. Van der Wiele K., Geerts J. W. M. H. and van Kasteren J. M. N., in “Direct Methane Conversion by Oxidative Processes”, E. E. Wolf (Ed.), Van Nostrand Reinhold, New York, 1991, p. 267.

145. Catalyst Handbook, 2nd. Edition, M. V. Twigg (Ed.), Wolfe Publishing Ltd., 1989.

146. der Kinderen J. M., van der Waal W. J. J., Heijkoop G. and Geus J. W., Proc. 1989 International Gas Research Conference, Tokyo, 1989, p. 1373.

147. Burch R. and Loader P. K., Appl. Catal. B: Environmental, **5**, 149, (1994).

148. Mimoun H., Robine A., Bonnaudet S. and Cameron C. J., Chem. Lett., 2185 (1989).

149. Le Van T., Che M. and Tatibouet J. M., Catal. Lett., **14**, 321, (1992).

150. Burch R., Chalker S., Squire G. D. and Tsang S. C., J. Chem. Soc. Faraday Trans., **86**(9), 1607, (1990).

151. Kalenik Z. and Wolf E. E., Catal. Today, **13**, 255, (1992).

152. Martin G. A. and Mirodatos C., in "Direct Methane Conversion by Oxidative Processes", E. E. Wolf (Ed.), Van Nostrand Reinhold, New York, 1991, p. 351.

153. Bernal S., Botana F. J., Garcia R. and Rodrigues - Izquierdo J. M., Thermochimica Acta, **66**, 139, (1983).

154. Turcotte R. P., Sawyer J. O. and Eyring L., Inorg. Chem., **8**(2), 238, (1969).

155. Bernal S., Diaz J. A., Garcia R. and Rodrigues - Izquierdo J. M., J. Mat. Sci., **20**, 537, (1985).

156. CRC Handbook of Chemistry and Physics, No. 65, 1984 - 1985.

157. Taylor, H.S. Proc Roy Soc., A108, 105, (1925)

Acknowledgements

I would like to thank my supervisor Dr. Richard Moyes for his help, understanding and support throughout the duration of this work. British Gas plc. are acknowledged for their financial support of this project. I would like to thank all members past and present of the Microwave Catalysis Group at Hull for their support, advice and friendship. Particular thanks go to Gary Bond, Ian Theaker and Steve Pollington.

My thanks must also be extended to the excellent Technical Staff in the Department of Chemistry.

Last but by no means least I would like to thank my parents for everything. Without them, none of this would have been possible!

Appendix A

Temperature Measurement in a Microwave Field

Due to the nature of microwave radiation, conventional metallic thermocouples cannot be used for temperature measurement in a microwave field. Not only are such probes subject to charging resulting in the production of arcs and discharges but they can also distort the applied microwave field. As a result, alternative methods of temperature measurement for microwave heated experiments have been developed.

Gas Thermometers

Attempts to construct and use a simple gas thermometer for the measurement of temperature in microwave heated experiments were made during this study.

The gas thermometer consisted of a 0.1 mm bore capillary tube attached to a sealed air bulb. This apparatus was located in the centre of the silica reactors. To the top of the tube was attached a small pressure transducer. As the temperature of the reactor increased, the air in the bulb at the bottom of the capillary tube expanded and exerted a pressure on the transducer. The transducer converted the pressure to a voltage which was recorded by a digital voltmeter. Calibration of the thermometer was performed by noting the magnitude of the voltage output of the transducer at a variety of temperatures, while the apparatus was mounted in a conventional electrical furnace.

The gas thermometer proved unreliable during experiments performed during this study as a gas tight seal between the capillary and pressure transducer could not be adequately maintained. An additional problem of the gas thermometer for catalyst testing is the fact that it is likely to disrupt the gas flow through the reactor.

Infra - red Pyrometers

Infra - red pyrometers provide a means of remotely measuring the temperature of a catalyst which is being irradiated in a microwave cavity. The instrument measures infra - red emissions from the sample and provides an output voltage which is directly proportional to the temperature of the sample. By linking the pyrometer to a personal computer and with the appropriate software, the output of the magnetron could be controlled so as to maintain the catalyst at a desired temperature.

Advantages of the pyrometer arrangement include the fact that it is a non-intrusive method of temperature measurement.

The pyrometer used in the initial stages of this study was however found to be unsuitable for the measurement of temperature for the oxidative coupling of methane reaction. This was due to it having a working temperature range of 100°C to 500°C whereas temperatures in excess of 700°C are generally required to perform the OCM reaction. An additional disadvantage was the fact that the device was not sensitive to light in the visible range of the spectrum. Because substances at elevated temperatures emit visible as well as infra - red radiation, the pyrometer was substituted by an optical fibre thermometer (Luxtron).

Optical Fibre Thermometers

Theory of Operation

All substances above absolute zero emit radiant energy as a result of the atomic and molecular agitation associated with the temperature of the substances. The rate of emission per unit area increases with increasing temperature. The temperature of a substance can therefore be measured by means of a suitable device which is responsive to such radiant energy. This radiant energy is considered to be in the form of electromagnetic waves having a wide range of wavelengths.

Luxtron Accufiber Model 10 Optical Fibre Thermometer (OFT)

The OFT device used in this study was obtained from Megatech Ltd. The apparatus consisted of a sapphire light pipe which was connected to a combined control box and digital readout by an optical fibre cable. The light pipe was positioned remotely from the sample and collected radiant emissions from the sample. Software incorporated into the control/readout apparatus converted the collected radiation to an accurate temperature readout. The control box was connected to the magnetron power controller and enabled the power of the magnetron to be continuously varied so as to maintain a constant pre-set temperature.

The optical probe offered several advantages over the other methods of temperature measurement that were investigated. These include the fact that the probe had an operating range of 100°C to 1000°C which is by far the widest range of any of the sensors investigated. A further advantage of the optical probe was that it could be the sensors investigated. A further advantage of the optical probe was that it could be directly connected to the microwave power control box to enable a pre-set temperature to be maintained without the need for separate computer software or the use of an analogue to digital converter this was not the case for any of the other devices which demanded both such things in order to control the microwave power output. The OFT probe also focused on a smaller area than the infra - red pyrometer thus possibly providing a greater insight to the temperature of "hot spots" within the catalyst. However, it is suggested that the hot spots are extremely small points in the catalyst bed which would require a far more sensitive method of temperature measurement in order to gain information of their true temperature.

It should therefore be noted that only the bulk temperature of the catalysts was measured during this study due to the limitations of the available equipment.