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THE PARTIAL OXIDATION OF METHANE TO METHANOL USING MODIFIED MIXED METAL OXIDES

THESIS SUBMITTED IN ACCORDANCE WITH THE
REQUIREMENTS OF THE UNIVERSITY OF WALES
FOR THE DEGREE OF DOCTOR IN PHILOSOPHY BY
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Abstract

The current steam reforming process for the production of CH_3OH is complicated and difficult, and therefore the direct partial oxidation of CH_4 to CH_3OH would be economically desirable. Other economic factors are the lowering of transportation costs from the remote locations that the vast worldwide reserves of natural gas are situated. Up to the present date, no catalytic systems have demonstrated outstanding performance, even though the reaction has been subject to an extensive amount of research.

In previous work a design approach for a selective partial oxidation catalyst has been investigated, which comprises the combination of components with a desired reactivity, producing a successful selective partial oxidation catalyst. In this approach, it is considered a successful partial oxidation catalyst must activate methane, activate oxygen and not destroy the desired product, methanol. All these properties could not be found in a single catalyst, so it was proposed that two synergistic components could be combined, one responsible for methane activation and the other for oxygen activation/insertion.

Previous work has studied the CH_4/D_2 exchange reaction as an indication of the ability of a metal oxide surface to activate CH_4. Two metal oxides demonstrated appreciable activity for the activation of CH_4, these being Ga_2O_3 and ZnO. These oxides were then doped with different metals in order to try and increase the activity of the catalyst. The doping of Ga_2O_3 with Zn or Mg did not improve the methane oxidation properties of Ga_2O_3, and the doping of ZnO with Ga significantly lowered the light off temperature, the temperature at which CH_4 was first detected, and increased its oxidative capacity. The addition of precious metals, namely Au and Pt, by coprecipitation to GaO(OH) and ZnO significantly affected the catalysts ability to activate CH_4. The addition of Au to the Ga and Zn catalysts dramatically reduced the light off temperature, and increased its rate of oxidation at lower temperatures, with the optimum loading 2% for both catalysts. For GaO(OH) and ZnO, the addition of 1%Au and 1%Pt by coprecipitation produced a synergistic effect, producing lower light offs and higher CH_4 conversion than the singly doped catalysts with Au and Pt separately.

When the methane activation catalysts were combined with MoO_3 in a physical mixture, a number of the mixtures produced higher methanol per pass percentage yields than its constituent parts. Therefore it is concluded that the increased methane activation properties beneficially interact with the oxygen activation and insertion properties of MoO_3. However, none of the yields reported were significantly higher.

A dual bed system, with the lower layer comprising the methane activation catalysts, and the upper layer consisting of MoO_3 was tested. The results for this system were promising, with the low temperature activation of CH_4, combined with the oxygen insertion ability of MoO_3, producing high selectivities of CH_3OH at much lower temperatures. The best results were obtained when the ratio of the two layers was 50:50 with respect to 2%Au ZnO and MoO_3.

Micro Abstract

In previous work a design approach for a selective partial oxidation catalyst has been investigated, by combining components with a desired reactivity to produce a successful selective partial oxidation catalyst, which must activate methane and oxygen, and not destroy methanol. All these properties could not be found in a single catalyst, so it was proposed that two synergistic components could be combined, one responsible for methane activation and the other for oxygen activation/insertion.

The doping of ZnO with Ga significantly lowered the light off temperature, and increased its oxidative capacity, an effect which was not seen with the doping of Ga_2O_3 with Zn or Mg. The addition of Au to the Ga and Zn catalysts dramatically reduced the light off temperature, and increased its rate of oxidation at lower temperatures, both with optimum loading of 2%. The addition of 1%Au and 1%Pt produced a synergistic effect, producing lower light offs and higher CH_4 conversion than the singly doped catalysts with Au and Pt separately.

When the methane activation catalysts were combined with MoO_3 in a physical mixture, a number of the mixtures produced higher methanol per pass percentage yields than its constituent parts. It is concluded that the increased methane activation properties beneficially interact with the oxygen activation and insertion properties of MoO_3.

The dual bed system, with the lower layer comprising the methane activation catalysts, and the upper layer consisting of MoO_3 produced promising results, with the low temperature activation of CH_4, combined with the oxygen insertion ability of MoO_3, producing high selectivities of CH_3OH at much lower temperatures. The best results were obtained when the ratio of the two layers was 50:50 with respect to 2%Au ZnO and MoO_3.

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Finally, thanks to my family, Mum, Dad, Hales, Peter, James, Jess, George, Gran, and all those who are no longer with us but are not forgotten.

Contents

Chapter 1

Introduction

1.1 General Introduction

The partial oxidation of CH_4 to CH_3OH has presented a major challenge for catalysis, with research into the catalytic oxidation of hydrocarbons being one of the main areas of interest in chemistry for over 100 years. Many different catalyst systems have been investigated and varying degrees of success achieved, however, to date none have demonstrated outstanding performance. The reaction has proved to be a very difficult problem to solve:-

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CH_3OH \quad \text{and} \quad CH_4 + O_2 \rightarrow HCHO + H_2O$$

The main problem for the reaction is that CH_4 is one of the most stable hydrocarbons, with the C-H bond energy being 435 kJ mol^{-1}, an extremely high value. The activation of the C-H bond is also difficult due to the high stability of the CH_4 molecule imposed by the sp^3 hybridisation of the C atom. Therefore the thermal activation of CH_4 occurs at high temperatures, making the control of product selectivity difficult. Thermodynamically the CH_4 to CH_3OH reaction is favourable, but the large negative free energy changes for carbon oxide formation make the formation of total oxidation products preferable. Due to the fact that thermodynamically the reaction is favourable, it can be assumed that the partial oxidation of CH_4 to CH_3OH, rather than total oxidation, is a kinetic problem.

One of the main driving forces behind this interest concerns a longer term strategy for the chemical industry, since currently crude oil is the preferred feedstock for the petrochemical industry. Recent reports suggest that worldwide reserves of crude oil will become depleted within 20-30 years. At the same time worldwide reserves of natural gas, which is mainly CH_4, are large, therefore the potential of CH_4 for the manufacture of chemicals is quite apparent, and worthy of a great deal of research. Another consideration is the cost and ease of transportation of CH_4. As a number of the main gas fields are in remote locations, the preferred method of transportation is via a pipeline, and costs for this are high. Conversely, the cost of transporting liquids is much lower, and is easier to transport than gases. Hence the conversion of CH_4 to a liquid such as CH_3OH would help to alleviate the problem of transportation.

Currently CH_3OH is an important feedstock in the chemical industry, producing many products, including HCHO, acetic acid, methyl formate and methyl terbutyl ether (MTBE). The use of HCHO in the plastics industry is vast, so a CH_3OH to HCHO production process is desirable. Due to the need for a replacement for lead in gasoline and petroleum, MTBE has been used as an octane improving agent. As mentioned previously, worldwide reserves of crude oil are finite, and gasoline transport fuels are derived from this. Therefore new transport fuels will be needed, and CH_3OH can be converted by Mobils MTG (methanol to gasoline) process. The preliminary step is the conversion of methanol to dimethyl ether over an alumina catalyst, and then the conversion of dimethyl ether to C_5-C_8 hydrocarbons over H-ZSM5 catalyst [1]. It is obvious that as time goes on the use of CH_3OH as a chemical feedstock will become increasingly important as the energy needs of the world change.

1.2 Current Production of Methanol and Formaldehyde

The current production technology for the oxidation of CH_4 to CH_3OH involves a three stage process. The first, and most costly, is the catalytic steam reforming of natural gas to produce the synthesis gas.

$$CH_4 + H_2O \xrightarrow[\text{Heat}]{\text{Ni}} CO + 3H_2$$

The reaction is highly endothermic, with $\Delta H = 206$ kJ mol^{-1}, with the forward reaction being favoured by low pressures and high temperatures. The products from this reaction are called synthesis gas. The supported Ni catalyst used is produced by impregnation of MgO and/or α-Al_2O_3 with a Ni salt solution. The second step is a shift reactor to obtain the desired ratio of H_2:CO, and the third step is carried out by passing the synthesis gas over a Cu/ZnO/Al_2O_3 catalyst, summarised below.

$$CO + 2H_2 \xrightarrow[\text{50-100 bar}]{\text{Catalyst}} CH_3OH$$

The third stage is endothermic, with high pressures of 50-100 bar, and temperatures of around 250°C. CO_2 may also be added, and the reaction ratios usually used are in the region of 80-86 : 8-10 : 6-10 for H_2 : C_2 : CO_2 respectively. CH_3OH selectivity is high, usually greater than 99%. The exit stream of the reactor contains around 4-7 vol.% of CH_3OH, and this is removed before the synthesis gas is recycled.

There are a number of problems with this process, including the relative inefficiency of carrying out the oxidation of natural gas followed by the reduction of CO, as well as having complicated engineering steps. The synthesis gas must also be free from any contaminants, including chloride and sulfur, which poison the catalyst. One of the major challenges in CH_4 oxidation is the high temperatures required to activate the CH_4 molecule. The use of these high temperatures often leads to the production of more thermodynamically stable products than CH_3OH. Therefore the ability to intercept the oxidation process at the point of initial oxidation, and where the reaction yields a liquid product, and is energetically more favourable.

Fox et al. [2] and Edwards and Foster [3] concluded that the direct oxidation of CH_4 to CH_3OH would be competitive with current technology if CH_4 conversion of 5.5% and CH_3OH selectivities of 80% could be achieved. Because in many countries in the world CH_3OH is now fast becoming an alternative fuel, mixed with gasoline, and a starting material for many industrial processes, this makes the one step conversion of CH_4 to CH_3OH both economically and environmentally viable.

1.3 Early Studies into the partial oxidation of methane

The partial oxidation of CH_4 to CH_3OH has now been studied for a century or more. No evidence for the formation of CH_3OH in CH_4 oxidation was found until the reaction was carried out at high pressure. The first CH_3OH synthesis at the start of the 20th century was published in 1906 by Lance and Elworthy [4], who reported that CH_3OH could be produced by the oxidation of CH_4 with H_2O_2, at elevated pressure, at a temperature of 120°C and in the presence of $FeSO_4$. In 1932 Newitt and Haffner [5] reported the formation of CH_3OH during CH_4 oxidation. A static system was used, with temperatures from 360°C to 393°C. At a pressure of 150bar, and a CH_4 to air ratio of 8:1, upon raising the temperature from 343°C to 375°C a 21.1% CH_3OH yield was reported. The product CH_3OH to HCHO ratio was 52.7:1 and CO to CO_2 ratio was 2.1:1. Early research into the subject concentrated on identifying suitable catalysts. It soon became apparent that metal oxides were potentially good catalysts due to the formation of gas methyl radicals at the oxide surface. The reaction was deduced to be dominated by rapid gas phase reactions, with limitations imposed by radical chemistry. In later work by Newitt, with Szego [6], the slow high pressure oxidation of CH_4 in a flow system was investigated. A maximum CH_3OH yield of 51% was reported, using low reaction times and oxygen concentrations.

Wiezevich and Frolich [7] carried out a comprehensive study of the partial oxidation of CH_4 in a flow system. Their studies showed an optimum pressure for CH_3OH production at 132 bar, with the flow rates of the reactants not significantly affecting the CH_3OH per pass yield. When CH_4 was tested, the reaction began at 500°C. When natural gas was used, the reaction temperature was lowered, and at 390°C, at a pressure of 132 bar with a 5.4% oxygen content, gave up to 30% CH_3OH in the condensed liquids, although this represented only 3.7% in terms of reacted CH_4. Most of their research involved the use of natural gas, which contains approximately 2% ethane, and upon increasing this level CH_3OH yield increased from 14% to approximately 32%. In their conclusions they could not explain the increase in CH_3OH yield upon the increase of ethane, and merely concluded that the CH_3OH was formed by the presence of ethane sensitising the oxidation of CH_4.

The theory of using catalysts to increase the yield of CH_3OH was pursued further by Boomer and co-workers [8,9,10]. Their work was carried out at pressures of 180 bar, using natural gas, which had a composition of $CH_4/C_2H_6/N_2$ with respective ratios of 90/3.5/5, and using oxygen as the oxidant at varying levels between 4.1% and 12%. They discovered that copper was an effective catalyst for increasing the yield of CH_3OH. The study identified some important points, the first being that the yield of CH_3OH increased as the percentage of oxygen in the feed was decreased, and it was also seen that flow rate variation is more pronounced at low oxygen concentrations than at high concentrations, with only a slight decrease in CH_3OH yield observed upon decreasing the flow rate. They reported the production of H_2, and that trace amounts of sulphur poisoned the copper catalyst, halving its catalytic activity. When CH_4 containing 5.7% N_2 was used as a reactant, much higher temperatures were necessary for the reaction when compared to the natural gas feed. Boomer et al. also showed that other catalysts were effective for the production of CH_3OH, and these included steel, silver and glass. These results agree with the previous results reported by Wiezevich and Frolich, that the lower temperatures required for reactions with natural gas were attributed to the presence of higher hydrocarbons, catalysing the overall oxidation of CH_4.

1.4 Design approach for methane partial oxidation catalysts

Several approaches in the area of CH_4 selective partial oxidation have attempted to adopt a design approach to identify new and efficient catalysts. Dowden et al. [11] proposed a virtual mechanism for the partial oxidation of CH_4 to CH_3OH in a 1968 publication. In this study it was concluded that the functions of a suitable catalyst were dehydrogenation and oxygen insertion, and a hydration function to suppress total oxidation of the product. A hypothetical surface scheme, where the preferred products are formed, is shown in figure 1.1

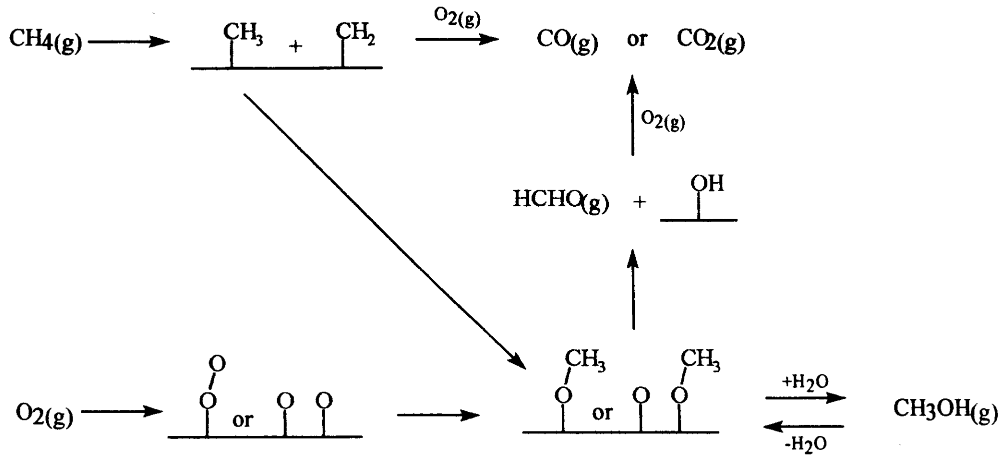

Figure 1.1 Virtual mechanism for the design of CH_4 partial oxidation catalysts

In order to prevent the total oxidation of CH_4, the dehydrogenation of the intermediate methyl of methylene groups should be suppressed with respect to their migration. The formation of the methyl intermediate is preferable over the methylene, which would be more strongly bound to the surface and therefore more susceptible to dehydrogenation. This was taken to indicate that an oxide catalyst would be preferable to a metal catalyst, with the surface of the oxide preventing methylene formation. It was suggested that the surface methyl bond should be weaker than the surface oxygen bond to promote methyl migration onto the oxygen. On the basis of the above they proposed that a relatively weak dehydrogenation function was required, suggesting that d^0, d^1, d^5, d^{10} or d^4 configurations would be suitable, while the oxygen insertion properties should be those of n-type oxides. Examples of these are TiO_2, V_2O_5, MoO_3, Fe_2O_3 and ZnO. It was also proposed that the catalyst should be of a single crystallographic phase to allow rapid migration of reaction intermediates.

To prevent over oxidation it was proposed that a hydration function, that would also increase CH_3OH production compared to HCHO, should also be incorporated into the catalyst. This would generate methylene glycol, which is relatively slowly attacked by one electron oxidising species in aqueous solution. The ions suggested were V^{5+}, Fe^{3+} and Cu^{2+} for dehydrogenation and V^{5+}, Fe^{3+}, Zn^{2+}, Mo^{6+} and Ti^{4+} for oxygen insertion. Thus the use of phosphate or tungstate catalysts are suitable for the dehydration function. Due to the mechanism being hypothetical no detailed catalytic data is reported, but preliminary studies based on B, Al, Cr, Mn, Fe and Ce phosphates showed Cr^{3+} and Mn^{3+} to be the most active, and Fe^{3+} as the most selective.

A study by Otsuka and Hatano [12] investigated the synthesis of HCHO from CH_4 using silica supported oxides. It was noted that the greatest CH_4 conversion was observed using metal oxides with cations of intermediate electronegativity. When CH_4 conversion was plotted versus cation electronegativity, the results showed a volcano type distribution. As the electronegativity of the cation increased, so did formaldehyde selectivity. In light of this information Otsuka proposed the following mechanistic pathway, displayed below:-

$$CH_4 \xrightarrow[1]{\text{H abstraction}} CH_{4-x} \xrightarrow[2]{\text{O addition}} HCHO \xrightarrow[3]{\text{H abstraction}} CO, CO_2$$

This pathway hypothesised that HCHO selectivity was determined by the rates of the second and third steps. The oxidative abstraction of H from CH_4 was thought to be dependent on the amount of negative charge on the oxygen, with the most active oxide having the greatest charge. At the same time as the negative charge on the oxygen approached zero, the likelihood of electrophilic addition of oxygen increased. The negative charge on the adsorbed oxygen of the oxide changed according to the electronegativity of the cation, for example the lower the electronegativity, the lower the electrophilicity of the adsorbed oxygen. The rates of steps 1 and 2 determined CH_4 conversion. It was argued that for the more basic oxides the CH_4 conversion rate was controlled by step 2, and for these oxides conversion increased as the electronegativity increased. As the oxygen electrophilicity increased with increasing electronegativity, the ability of an oxide to abstract H from CH_4 was decreased and the rate determining step was step 1. The higher HCHO selectivity of the more electronegative oxides was due to the increased rate of step 2 in relation to step 3, as O addition was increased, the electrophilicity of the oxygen increased. It was thought that the most acidic oxides were the most selective, but their ability for H abstraction was poor, and the more basic oxides were ineffective due to poisoning of the acidic component. Thus it was concluded that acid-base bifunctional catalysts would be most effective for HCHO production.

Lyons and co-workers [13,14,15] have used iron sodalite based catalysts for the oxidation of CH_4 to CH_3OH. Their studies involved the creation of a design approach using biological enzymes, Cytochrome P450, a heme iron catalyst, and Methane Monooxygenase, a non-heme iron catalyst with a diiron centre. Both are thought to function via a high oxidation state ferryl species, which is effective for alkane activation. In the model proposed, the redox potential of the Fe^{2+} was modified so as to favour the formation of the μ-peroxo species , Fe^{3+}-O-O-Fe^{3+}, which would then cleave to form ferryl sites.

The Fe-sodalite catalysts tested showed promising activity for CH_4 oxidation to CH_3OH, and the catalyst was a sodalite lattice, with more than 10wt% iron. The catalysts that exhibited the highest activity had been calcined at high temperature, approximately 550°C. This causes some framework collapse contributing to the improvement in activity, and also drives iron into exchangeable positions associated with residual framework iron to create an active centre. CH_3OH selectivity was also increased when Fe-sodalite was exchanged with Fe^{2+} ions. It was postulated that a surface generated ferryl intermediate caused CH_4 activation, leading to the release of methyl radicals to the gas phase.

A review by Hutchings et al. [16] discusses recent developments in the design of oxidation catalysts, and highlights recent successes and the problems faced within this field. For CH_4 Taylor and Hutchings [17] adopted a simplified approach for the design of oxidation catalysts, based on three components for selective oxidation, identifying catalysts that:-

1) Do not catalyse the oxidation of the required product under the reaction conditions
2) Activate the oxidant
3) Activate the substrate

Their studies involved a variety of metal oxides in an attempt to combine the necessary functions in a single catalyst. The activation of CH_4 was probed by studying CH_3OH oxidation over single oxides, as one of the prime requisites is that a catalyst must not readily destroy CH_3OH under reaction conditions. The activation of CH_4 was investigated by studying the rate of CH_4/D_2 exchange, and oxygen activation characterised by $^{16}O_2/^{18}O_2$ exchange. Thus, simplistically it can be imagined that synergistic conditions may exist in which one component is responsible for CH_4 activation and another for oxygen activation/insertion. Their approach was not without precedent, as one of the currently accepted views of the mode of operation of the bismuth molybdate catalyst for propene oxidation and ammoxidation is that the bismuth component is responsible for hydrocarbon activation, whilst the molybdenum component effects oxygen activation and insertion [18]. Studies to assess CH_3OH stability show that it is most stable over the oxides MoO_3, WO_3, Nb_2O_5, Ta_2O_5 and Sb_2O_3. The full set of results are displayed in figure 1.2.

In particular, the conversion of CH_3OH to carbon oxides over MoO_3 was very low whilst showing high selectivity towards HCHO. Additionally the oxygen exchange reaction over MoO_3 takes place with the entire bulk of the oxide. This suggests that the diffusion of oxygen through the lattice of these solids is faster than the surface exchange, which is therefore the rate determining process. This is an important concept for selective oxidation reactions in which labile lattice oxygen is the active oxygen species.

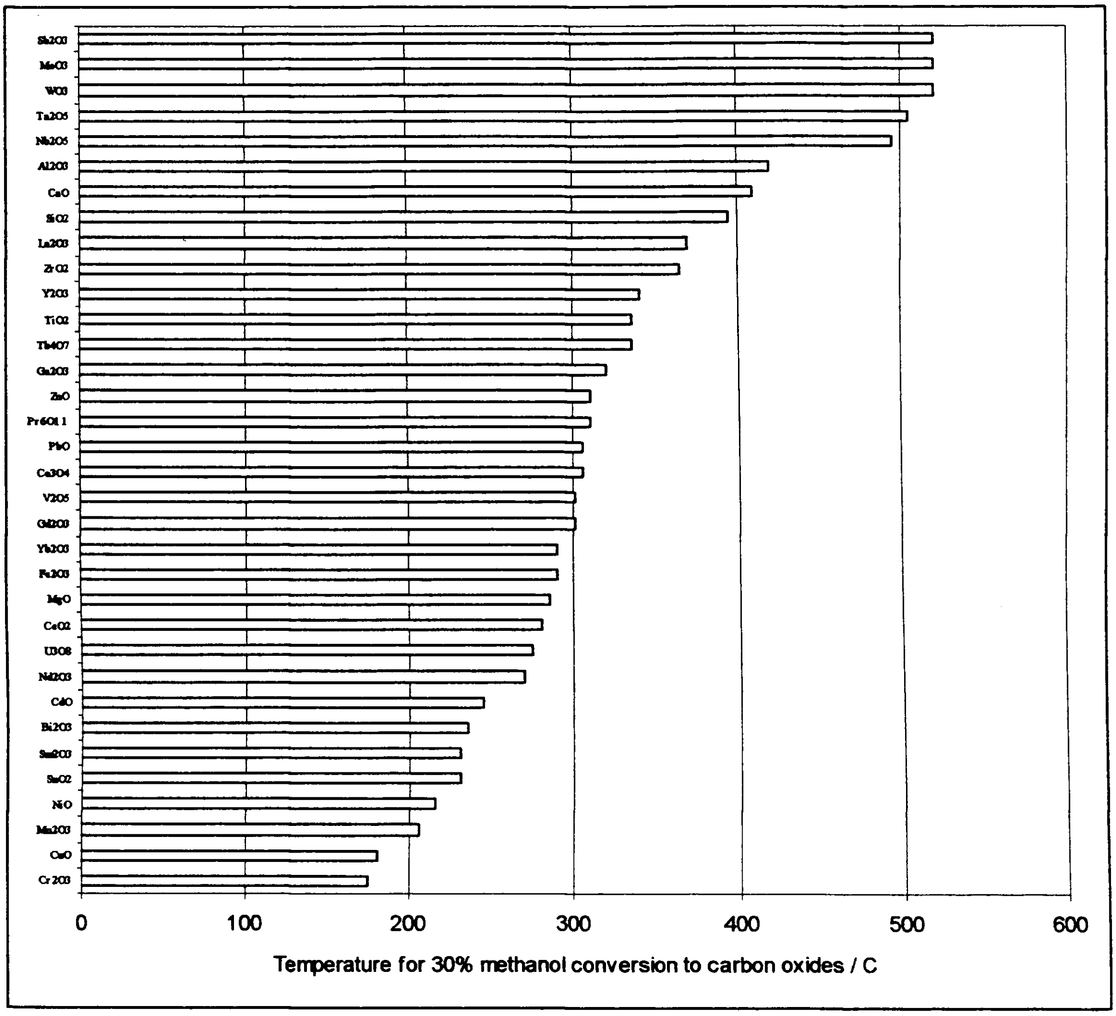

Figure 1.2 Temperature for 30% CH_3OH conversion to carbon oxides

CH_4/D_2 exchange studies are displayed in figure 1.3. These show that Ga_2O_3 is significantly more active for the activation of CH_4 compared with other catalysts by several orders of magnitude [19]. ZnO also exhibited high activity for the exchange reaction and it must be noted that both elements show high activity for alkane activation, such as aromatization processes of short chain alkanes, when in combination with MFI type zeolites [20].

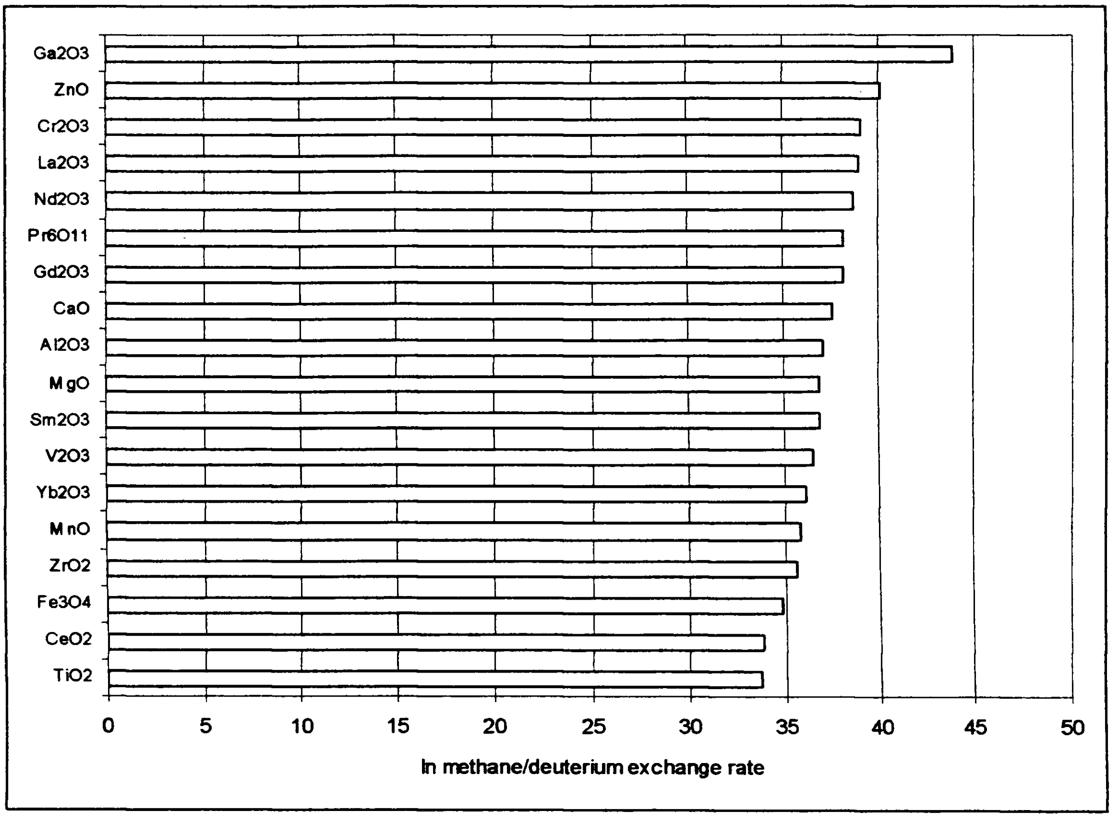

Figure 1.3 ln CH_4/D_2 Exchange Rate

Based on the results detailed above, a Ga_2O_3/MoO_3 catalyst was prepared, and results for CH_4 oxidation are shown in table 1.4.1:-

Table 1.4.1 Methane oxidation over Ga_2O_3/MoO_3 physical mixture.

Catalyst	Temp (°C)	CH_4 Conv. (%)	Selectivity (%)				CH_3OH *Per Pass* Yield
			CH_3OH	CO	CO_2	C_2H_6	
Ga_2O_3/MoO_3	455	3.0	22	50	27	1	0.66
Ga_2O_3	455	1.5	3	27	68	2	0.05
MoO_3	455	0.3	13	69	18	-	0.04
Quartz packing	455	0.1	-	-	100	-	0.00
Empty tube	455	8.1	29	63	7	1	2.34

Conditions : $CH_4/O_2/He = 23/2/5$, 15 bar, GHSV = 5,000 h^{-1}.

The Ga_2O_3/MoO_3 catalyst produced the highest catalytic yield of CH_3OH which was greater than the comparative homogeneous gas phase reaction over a quartz chips packed reactor. The CH_3OH yields over MoO_3 and Ga_2O_3 were also low in comparison with Ga_2O_3/MoO_3. CH_4 oxidation over MoO_3 showed that the oxide was relatively selective for CH_3OH, whilst Ga_2O_3 was more active, showing a much higher CH_4 conversion. These observations are consistent with the high activity for CH_4 activation of Ga_2O_3, as discussed previously in relation to CH_4/D_2 exchange, as well as the oxygen exchange mechanism and the selective oxidation function exhibited by MoO_3 during CH_3OH oxidation studies. These aspects were beneficially combined for CH_4 partial oxidation by the physically mixed Ga_2O_3/MoO_3 system.

The results obtained clearly indicate that their design approach is valid and the concept has resulted in the manufacture of a novel catalyst system based on gallium and molybdenum oxides, which shows promising activity for the partial oxidation of CH_4 to CH_3OH. However, the yield of CH_3OH from the empty reactor tube was considerably higher than from the Ga_2O_3/MoO_3 catalyst. This was primarily a consequence of the higher CH_4 conversion and was not due to an increase in CH_3OH selectivity. The increase in conversion can be explained in terms of increased residence time within the heated zone of the empty reactor compared with the reactor packed with catalyst.

Sun et al. [21] have developed the use of a double layered bed for CH_4 partial oxidation, consisting of two separate layers of 1%Sr La_2O_3 and MoO_3/SiO_2. The first layer of 1%Sr La_2O_3 was chosen to provide a flux of methyl radicals to the molybdenum bed, which converted the radicals to HCHO. The experiment was carried out at atmospheric pressure with air as the oxidant. The addition of the 1%Sr La_2O_3 bed to the MoO_3/SiO_2 bed reduced HCHO selectivity, at 630°C reduced from 100% to 3.3%, however CH_4 conversion was markedly increased at this temperature, rising from 0.08% to 8.2%. The overall result of these changes in selectivity and conversion was an increase in the space time yield of HCHO by a factor of 3.4. In further experiments an increase in the space velocity also increased the HCHO yield, as the radical flux to the molybdenum layer increased. When the double layered bed was replaced with a single physically mixed bed of the same catalyst composition its HCHO yield was markedly reduced, with all the HCHO appearing to be converted to CO. The study concluded that the formation of HCHO occurred on the surface of the MoO_3/SiO_2 catalyst surface rather than in the gas phase.

1.5 Short Review of Catalytic Methane Partial Oxidation

There have been several reviews of the partial oxidation of CH_4 to CH_3OH and HCHO, with some of the most notable by Hall et al. [22], Herman et al. [23] and Lunsford [24]. One of the most widely studied catalysts for the partial oxidation of CH_4 is molybdenum oxide, MoO_3. The Mo catalysts can be split into two groups, the ones that have used a highly dispersed molybdenum species supported on silica, and the catalysts that have used the bulk MoO_3.

A virtual mechanism for the oxidation of CH_4 over MoO_3 is shown in figure 1.1 in section 1.4, and an early patent was awarded to the same authors [25] in 1971 for the development of multi-component molybdenum based oxides based on this mechanism. The patent stated that for a catalyst to be successful one oxide must be responsible for the oxidation of hydrocarbons and the other responsible for the catalysing the hydration of alkenes. They also found that it was advantageous to support the catalyst e.g. using 25% silica / 75% alumina with a surface area of approximately $0.1m^2g^{-1}$. A CH_4:O_2 mix of 97:3, at a pressure of 50bar, with temperatures of 430-500°C, at high space velocities high methanol selectivities were obtained over several catalysts. In order to maintain selectivity to CH_3OH the reactor effluent was cooled to 200°C within 0.3 seconds of leaving the catalyst bed, by the injection of water. The most successful was based on Fe_2O_3 / $(MoO_3)_4$ which yielded 869g $(kg\ cat)^{-1}h^{-1}$ of CH_3OH.

Unsupported two component oxides have been reported by Stroud [26] in a 1975 patent. The first component should have variable valency, and the best result was that of CuO with MoO_3. They reported oxygenated products with a yield of 490g $(kg\ cat)^{-1}h^{-1}$, containing CH_3OH, HCHO, ethanol and acetaldehyde, due to the presence of ethane at levels of 6.1% in the hydrocarbon feed.

Crystalline MoO_3 has been used for CH_4 partial oxidation with O_2 by Smith and Ozkan [27]. In this study two MoO_3 catalysts were tested, the first, MoO_3-R, had the basal (010) plane preferentially exposed, while the other, MoO_3-C, had a greater number of the side (100) planes. Results show that by varying the ratio of basal planes to side planes, it was discovered that when the ratio of side planes was increased, then the selectivity to HCHO also increases. It was stated that the basal planes (which consist mainly of Mo-O-Mo bridging), were responsible for complete oxidation of the products, to CO_2 and CO. However the side planes of a crystal (mainly consisting of Mo=O) shows a great selectivity for partial oxidation, to CH_3OH and HCHO.

Characterisation studies indicated that the re-oxidation of the Mo-O-Mo sites took place via gas phase oxygen, while the Mo=O sites were re-oxidised by diffusion of oxygen from the lattice.

The combination of Fe and Mo oxides have been previously mentioned [25], and this has also been investigated by Otsuka et al. [28], by testing $Fe_2(MoO_4)_2$ for CH_4 partial oxidation with O_2. The catalysts were prepared via coprecipitation from iron nitrate and ammonium heptamolybdate solutions. The experiments were carried out at atmospheric pressure with a gas feed ratio of 1/1/2 for $CH_4/O_2/He$ respectively. At low conversions of 0.24% and at 650°C selectivity for HCHO was greater than 75%. As the temperature was raised to 750°C, and as CH_4 conversion rose to 7.8%, HCHO selectivity decreased to 30%. The results indicated that HCHO was formed by the sequential oxidation of CH_3OH, with the further oxidation of HCHO the main route for the production of carbon oxides. The presence of large amounts of CH_4 had the effect of improving HCHO selectivity. The conclusions for the study stated that the reaction was completely heterogeneous, which, if the high temperatures are taken into account, may seem unlikely. At the same time the same authors investigated the activity of the same catalyst using N_2O as an oxidant [29]. The main products in this study were ethane and ethane, different to the oxygenated products when O_2 was used as the oxidant.

The most studied catalysts for CH_4 partial oxidation have been those of MoO_3 supported on high area SiO_2. Spencer et al. [30] have investigated the MoO_3/SiO_2 system using O_2 as the oxidant. In this study the major reaction products were HCHO, CO and CO_2. Traces of CH_3OH and H_2 were also detected. At low conversions

HCHO was produced with a selectivity of 71%. The best catalyst was MoO_3/Cab-O-Sil prepared by the physical milling of the components, with catalysts prepared by impregnation having lower selectivity but comparable activity. The effects of impurities were also investigated, and it was found that the presence of Na, at levels as low as 300ppm, had a detrimental effect on conversion and selectivity. This was investigated more fully in a more recent publication by the same author [31]. From kinetic analysis the authors suggested that Na retarded the direct oxidation of CH_4 to formaldehyde and CO_2, whilst promoting the further oxidation of HCHO to CO. They also proposed that the initial CH_4 activation took place on a Mo-O· surface radical species, generated thermally by the temperature of the reaction. Mo(V) was very important in several steps of the reaction scheme.

Several research groups have used nitrous oxide as an oxidant instead of oxygen. Liu et al. [32] reported an 84.6% selectivity toward CH_3OH and HCHO with a conversion of 8.1%, using a 1.7% Mo/SiO_2 catalyst, under conditions of 560°C and at a pressure of 1 bar. They found that the addition of steam increased the selectivity of CH_3OH by inhibiting further oxidation, but in a later paper reported they were unable to reproduce the results [33]. However they did report a selectivity of 78.1% for CH_3OH and HCHO using 1.7wt% MoO_3 supported on Cab-O-Sil M-5 silica. When they considered the nature of the mechanism and the kinetics of the reactions, their studies indicated a rate law:-

$$\frac{d[CH_4]}{dt} = -k[N_2O]^1[CH_4]^0$$

An Arrhenius plot of the rate of conversion of CH_4, linear over the temperature of 500-594°C gave an activation energy of 176± 8 $kJmol^{-1}$. Using ESR they showed that if O^{2-} instead of O^- was a product of surface decomposition of N_2O then the total oxidation process was preferred. They concluded that it was the more active O^- species was responsible for the initiation of the selective oxidation cycle. The O^- species was shown to be formed by the interaction of N_2O with a surface Mo(V). ESR also found evidence for the existence of methyl radicals and IR found the existence of CH_3O^- at the surface. Using this information, Liu et al proposed the following mechanism for the partial oxidation of CH_4:-

$\mathrm{Mo(V)} + N_2O \rightarrow \mathrm{Mo(VI)}O^- + N_2$

$\mathrm{Mo(VI)}O^- + CH_4 \rightarrow \mathrm{Mo(VI)}OH^- + CH_3\cdot$

$\mathrm{Mo(VI)}O^{2-} + CH_3\cdot \rightarrow \mathrm{Mo(V)}OCH_3^-$

$\mathrm{Mo(V)}OCH_3^- + H_2O \rightarrow \mathrm{Mo(V)}OH^- + CH_3OH$

$\mathrm{Mo(VI)}OH^- + \mathrm{Mo(V)}OH^- \rightarrow \mathrm{Mo(V)} + \mathrm{Mo(VI)}O^{2-} + H_2O$

Khan and Samorjai [34] also investigated supported Mo catalysts, also on silica. Their experiments produced a similar set of results, but with some important differences. They were able to derive rate equations for both the formations of CH_3OH and HCHO, finding that for the formation of CH_3OH the rate was approximately first order in CH_4 and water and zero in N_2O. HCHO formation was zero order with respect to all reactants. An Arrhenius plot for CH_3OH formation showed a linear relationship up to 540°C, with an approximate activation energy of 172 ± 17 $kJmol^{-1}$ which is in good agreement with that of Dowden and Walker. A similar plot for HCHO formation presents two distinct linear regions, with activation energies of 344 ± 17 $kJmol^{-1}$ below 540°C and 168 ± 8 $kJmol^{-1}$ above 540°C. This indicates that CH_3OH and HCHO were formed simultaneously from the same intermediate via two independent pathways. Above 540°C the activation energies were almost identical which implies that the formation of HCHO is by the sequential oxidation of CH_3OH. They also proposed that the increased selectivity of CH_3OH by the presence of steam could be due to the prevention of coking of the catalyst, as this is what happened in the absence of steam.

Spencer et al have also investigated Vanadium based catalysts [35]. In contrast to the proposed parallel pathway formation of CO_2 and HCHO from CH_4 and O_2 over MoO_3 based catalysts, it was concluded that over V_2O_5/SiO_2 catalysts the following sequential reaction led to the formation of CO_2:-

$$CH_4 \rightarrow HCHO \rightarrow CO \rightarrow CO_2$$

Over the V_2O_5/SiO_2 catalyst, the sequential pathway theory was supported by the very low selectivities for CO_2 at low CH_4 conversions, and higher selectivity for CO_2 at high CH_4 conversions. Compared to the corresponding MoO_3/SiO_2, this catalyst appeared to be more active, however when the data was extrapolated the CH_4 conversions and HCHO selectivities at 575°C were similar, at levels of 3% and 32.5% respectively.

The modification of the reaction conditions to control the selectivity of the products was investigated by Hargreaves, Hutchings and Joyner [36]. With a CH_4:O_2:He feed ratio of 6:1:6, the consumption of O_2 was controlled by the variation of the flow rate in the GHSV range of 1,000-48,000 h^{-1}. When the O_2 conversion was high, at levels above 70%, CO_2 was the major product. As O_2 conversion decreased, and was in the 10-70% region, CO was the most selective product. When O_2 conversion was low, at levels of 3-5%, the selectivity to HCHO was approximately 60%, with CO and CO_2 selectivity both in the 20% region. It was proposed that the partial oxidation of CH_4 was controlled by the balance between methyl radical coupling and oxidation. With the surface area of the catalyst being unchanged, the concentration of intermediate methyl radicals decreases linearly with flowrate. As the rate of ethane formation is proportional to the square of the concentration of the radicals, it too decreases. For example, at low O_2 conversion there is a relatively high pressure of O_2 in the catalyst bed, and so the oxidation of methyl radicals to HCHO is the dominant process. This study demonstrated that homogeneous non-surface catalyzed reactions must always be considered, and in CH_4 oxidation they tend to be dominant.

1.6 Introduction to Gold Catalysts

Gold had long been regarded as a poorly active catalyst. Early published reviews brought light to this fact and attempted to excuse the low catalytic activity of gold. One of the earliest major reviews was by Bond in 1972 [37], which stated "Although the catalytic reviews properties of gold are surpassed by those of the Group VIII metals, especially palladium and platinum, possible applications of gold in catalytic processes have been widely studied." In a later review, by Schwank in 1985 [38], it was commented that "In spite of its low intrinsic activity, gold can influence the activity and selectivity of Group VIII metals". Although gold had been shown to be active for oxidation reactions, it did not exhibit any significant advantages over other metal catalyst systems. These quotations were used in a review by Hutchings [39] to highlight the early misconception of gold as an inactive catalyst.

In another review by Bond [40], it was stated that the reason that gold was seen to be a poor catalyst was due to its low power of chemisorption in comparison to the platinum group metals, whose superior performance for many reactions was seen to be due to their stronger chemisorption tendency. This is highlighted in the review by Bond who states that gold was seen as a poor catalyst because under the Tanaka-Tamaru rule the initial enthalpies of chemisorption of oxygen were linearly related to the enthalpies of formation of the most stable oxides. This implied that the chemisorbed oxygen atoms are energetically similar to atoms or ions in bulk oxides. Due to the nobility of gold, as the oxide of gold, Au_2O_3, is unstable ($\Delta H_f = +19.3$ $kJmol^{-1}$), it was thought that this determined its inability to chemisorb oxygen in the bulk state. Another aspect of gold is its high ionisation potential, and consequently, its poor affinity towards molecules. In a review by Haruta [41] it states that surface science investigations and theoretical calculations have concluded that no dissociative adsorption of hydrogen and oxygen takes place over the smooth surfaces of gold below 200°C, indicating that gold is catalytically inactive for hydrogenation and oxidation.

The interest in gold catalysts increased markedly after work by Haruta [42], that found when gold is deposited as hemispherical nanoparticles on selected metal oxides, high catalytic activity for CO oxidation was seen. It was noted that gold catalysts prepared using a conventional impregnation procedure were less active than platinum group metals prepared in the same way. It is probably due to this that gold catalysts had been overlooked as an oxidation catalyst. It was showed that the method of catalyst preparation was crucial to the activity of the catalyst. The method of preparation prior to this study, by impregnation, produced large gold particles, maybe due to the coagulation of gold nanoparticles during calcination, as the melting point of gold is much lower than the other precious metals. Haruta prepared the catalysts via a coprecipitation method, which produced an uniform distribution of small metallic gold particles on the support. In this work by Haruta it was decided the smaller the gold particles, the more active the catalyst, with the optimum size in the 2-5nm range. Building on this work by Haruta, Graham Hutchings [38] has elaborated on the preparation method, through the ageing of the precipitate, as it was found that when gold is present in the coprecipitation mixture the initial precipitate that forms is amorphous. Hutchings has suggested that during the ageing process the precipitate generally crystallises and it is these more crystalline materials that give enhanced activity.

The Gold Bulletin paper by Hutchings mentioned earlier covers two of the main uses of gold catalysts, the hydrochlorination of ethyne, and the low temperature oxidation of CO. A recent review by Bond and Thompson [43] thoroughly looks at the many and diverse uses of gold catalysts. An earlier publication by Haruta et al. [44] makes mention of the different uses of gold catalysts in complete and partial oxidation reactions. A later paper by Haruta [45] detailed the advances made in gold catalyst chemistry, and highlights the huge increase in the number of publications involving gold catalysis, indicating the huge amount of recent interest in the field. From these reviews it can be concluded that the vast majority of work reported for gold catalysts is for low temperature CO oxidation, though some work has been published in the literature for CH_4 oxidation. Grisel et al. [46] conducted a study into the influence of catalyst preparation on the CH_4 oxidation ability of Au/Al_2O_3. They found that the pH used for coprecipitation had a large effect on the gold loading on the catalyst, and at pH values above 8.5 the gold loading dramatically decreased. The results for coprecipitation in this study were not that impressive, but their method of preparation did not involve any ageing of the precipitate in the mother liquor, which may have been a factor in the poor activity of the catalyst. In this study the best preparation method for catalysts was by homogeneous deposition precipitation. In further work by Grisel [47], it was reported that the addition of gold lowered the activation energies of the catalysts, and that the gold was responsible for the activation of CH_4 at lower temperatures. It was reported that for CH_4 oxidation activity was dependent on both the gold particle size and the identity of the metal oxide used. This study concluded that their results supported a single model for oxidation of CO and CH_4 over gold catalysts. This models states that the reaction takes place solely at the perimeter of the metal oxide and the gold, with the reductant adsorbed on the gold and the metal oxide being the supplier of O. However when the metal oxide is itself active in oxidation reactions, the reaction also partly takes place on the metal oxide itself.

Au/MgO catalysts were also found to be active for CH_4 oxidation [48]. The addition of already small amounts of gold, at levels of 0.04wt%, was found to inhibit the production of CH_4 coupling products, which are characteristic of MgO. The yield of CO was found to increase with low gold loadings, at levels lower than 2wt%, but higher loadings produced high selectivity to CO_2. The study concludes that as the gold loading is increased, the proportion of gold present as discrete particles increases and that these are considered active for CH_4 oxidation to CO_2 and CO. Gold catalysts have also been reported as being very effective as total CH_4 oxidation catalysts. Waters et al. [49] reported that coprecipitated gold on several transition metal oxides was extremely active for total oxidation. The catalysts chosen for this study had already shown excellent results for CO oxidation, and that is the reason the authors decided to test them for CH_4 oxidation. The addition of gold lowered the temperature that the catalyst became active at, in the case of Co_3O_4, 50°C lower. One of the conclusions of the study was that because the supports showed a measurable level of activity without gold, a dual site mechanism may explain the enhanced activity upon the addition of gold, with the two sites being the gold and the support. Another conclusion was that the degree of oxidation of gold in the oxidised state affects the ability of the site to bind oxygen, the more oxidation the higher the activity the catalytic activity for CH_4 oxidation.

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Chapter 2

Experimental Details

2.1 Catalyst preparation

2.1.1 Oxide Catalyst Preparation for Initial Studies.

A series of gallium oxide based catalysts were prepared. The β-Ga_2O_3 was prepared by thermal decomposition of precipitated $Ga(OH)_3$ by calcination in air [1], using a temperature programmed regime from ambient to 700°C at 20°C min^{-1}, and then maintained at 700°C for 14 hours. According to the paper published in 1952, the preparation methods of the different phases of Ga_2O_3 [2] are summarised in figure 2.1

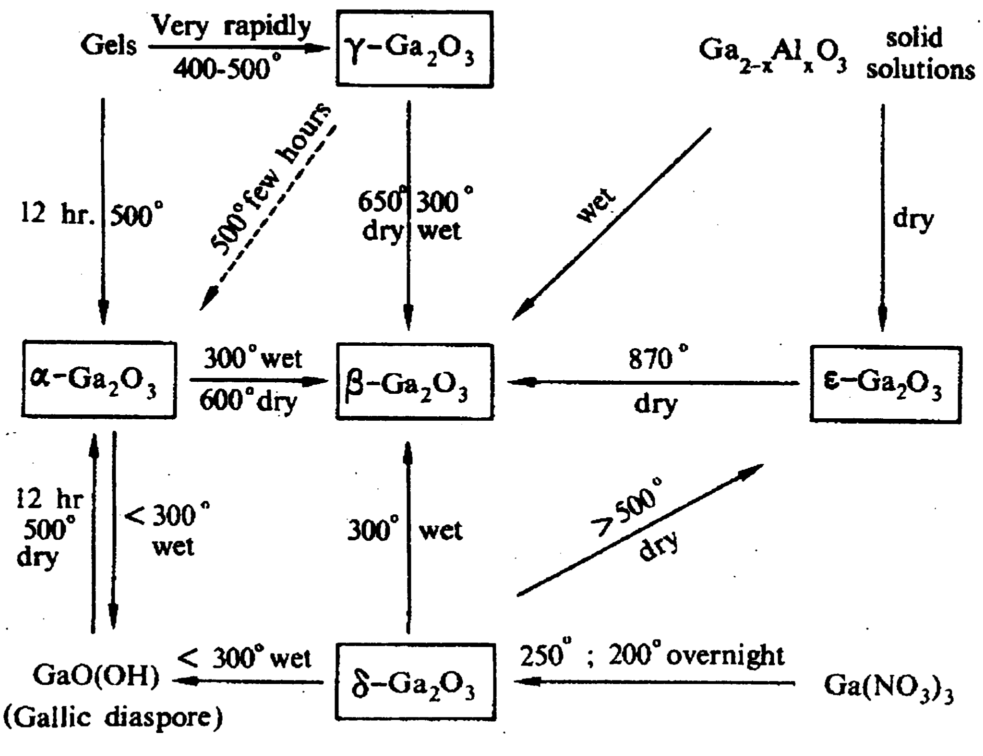

Figure 2.1 Preparation method for the different phases of Ga_2O_3

The hydroxide was prepared by dissolving gallium nitrate in deionised water. The solution was thoroughly stirred for 30 minutes and dilute ammonia solution was added dropwise until pH 8.5 was attained. The gelatinous precipitate was stirred in the liquor for a further 30 minutes and then collected by filtration.

The Zn coprecipitated Ga_2O_3 (Zn:Ga=1:99, 2:98 and 5:95 wt%) was obtained by a coprecipitation method. A mixed solution of gallium and zinc was prepared by dissolving appropriate quantities of the respective nitrates in deionised water. The resulting solution was thoroughly stirred for 30 minutes and dilute ammonia solution was added dropwise until pH 8.5 was attained. The gelatinous precipitate was stirred in the liquor for a further 30 minutes and then collected by filtration. The precipitate was calcined using the same procedure used for the Ga_2O_3 preparation.

It was not possible to prepare a magnesium doped gallium oxide catalyst (Mg:Ga=1:99 wt%) using the same coprecipitation method. The variation in preparation method was adopted as gallium and magnesium nitrates precipitate at vastly different pH, resulting in catalysts with poor homogeneity. For comparison a coprecipitated magnesium/gallium catalyst was prepared from magnesium phosphate and gallium nitrate as they precipitate at similar pH. The coprecipitated magnesium phosphate doped Ga_2O_3 (Mg:Ga=1:99 wt%) was prepared from a mixed solution of the salts by dissolving appropriate quantities of the chemicals in deionised water. The resulting solution was stirred for 30 minutes and dilute ammonia solution was added dropwise until a pH of 8.5 was attained. The gelatinous precipitate was then stirred for a further 30 minutes and then collected by filtration. The precipitant was again calcined using the same procedure as in the preparation of the Ga_2O_3.

For comparison zinc oxide and magnesium phosphate catalysts were prepared by precipitation methods. The zinc oxide system was precipitated from zinc nitrate solution by raising the pH to ca. 8.5. The gelatinous precipitate was stirred for a further 30 minutes, and then filtered. The magnesium catalyst was precipitated from a phosphate solution using a similar method and both catalysts prepared by calcination of the precursors using the same method described in the previous preparations. The physical mixture catalysts were produced by the physical tumbling or physical grinding of respective amounts of the relevant oxides. For comparison a fumed silica (BDH cab-o-sil) was used. MoO_3 was supplied by Aldrich.

The Zn impregnated Ga_2O_3 was prepared by the mixing of Ga_2O_3 (prepared as earlier) and a suitably concentrated zinc nitrate solution into a paste, and this was then calcined as before, at 700°C for 14 hours.

2.1.2 Precious metal modified catalyst preparation

The catalyst preparation that was adopted for these catalysts produced highly dispersed Au particles on ZnO, which resulted in highly active CO oxidation catalysts [3]. The catalysts were produced from a coprecipitation method. For the Au modified catalysts, a set amount of the relevant nitrate was mixed with a relevant amount of $HAuCl_4$, with stirring at 80°C. However unlike the method quoted, aqueous ammonia was used to raise the pH to 8.5. Then the precipitate formed was left to age in the mother liquor for 300 minutes at 80°C in an air atmosphere. The precipitate was recovered by filtration, washed with cold distilled water, and dried in air at 90°C for 12 hours.

The platinum modified catalysts were prepared in an identical manner, except with the addition of the appropriate amount of $HAuCl_4$ and/or H_2PtCl_4 in the starting solution. The precious metal concentration was calculated using the weight ratio between the precious metal and the support content.

2.2 Atmospheric pressure methane oxidation

2.2.1 Reactor Design

The lower and upper explosion limits for CH_4 with O_2 are 5.4% and 59.2% respectively [4], and the conditions chosen in this study are above the upper limits of safety. Methane activation experiments were carried out in a conventional plug flow microreactor, shown schematically in figure 2.2.

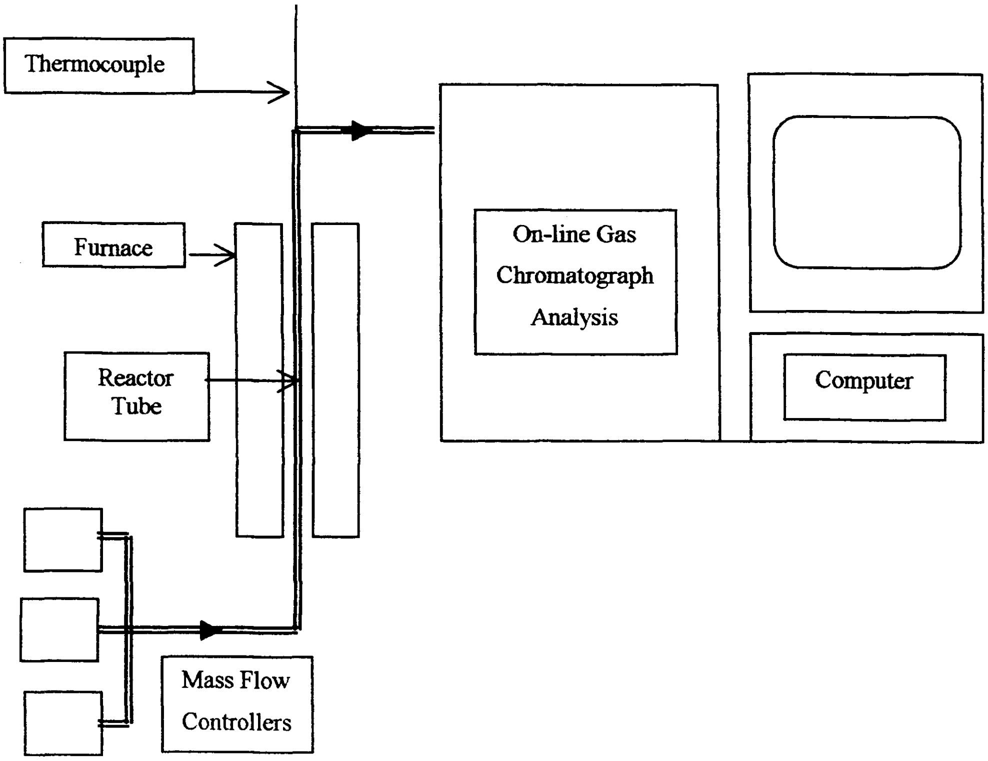

Figure 2.2 Microreactor design for Methane Activation studies

The reactor was constructed of ½" O.D. stainless steel piping operated at atmospheric pressure. Studies were performed using methane (99.99%), oxygen (99.5%) and helium (99.5%) gases. The gas flow rates were controlled using three mass flow controllers (Brooks Mass Flow 5850 Series). To ensure accuracy of flow rates the flow at the reactor outlet was checked regularly using a bubble flow meter. Catalysts were pelleted to uniform particle size and were secured in place at the centre of the reactor tube using two silica wool plugs. The catalyst bed was heated using a furnace (Carbolite) with a 50mm uniform heated zone, capable of maintaining temperatures up to 1000°C. Reaction temperatures were measured using a thermocouple, which was placed in intimate contact with the catalyst bed within the reactor tube, with the temperature displayed electronically. Analysis was carried out on-line using gas chromatography with Porapak Q and Molsieve 13X columns in a series bypass configuration with thermal conductivity and flame ionisation detectors.

2.2.2 Experimental Procedure

The catalysts used in this study were first pelleted to uniform size (250-600μm) by pressing the catalyst in a 5cm die under 5 tonnes pressure for one minute. The resulting disc was then pressed through 0.25mm and 0.6mm standard brass sieves. In each experiment, 0.25cm^3 of catalyst was used. The gas flow used was 23/2/5 ml min^{-1} for CH_4/ O_2/He gases respectively. The reason for the low O_2 flow in relation to CH_4 is because methane activation is preferred to full oxidation, making oxygen deficient conditions necessary. These flows produced a Gas Hourly Space Velocity (GHSV) of approximately 7200 h^{-1}.

Once flow rates were set and stabilised, the reactor temperature was set to approx 250°C and allowed to equilibrate for half an hour. No catalysts showed any activity at this temperature. Catalytic activity was monitored up to the temperature where high methane conversion was detected. Methane conversion was calculated on the basis of products detected, namely CO_2, in accordance with the following equation:-

$$CH_4 \text{ Conversion} = \frac{\text{Volume \% of } CO_2}{\text{Volume \% } CH_4 \text{ in feed gas}} \times 100$$

This proved more accurate than calculating the conversion based on CH_4 peak area by difference, as it did not rely on the small difference between two large values.

2.3 High Pressure Methane Oxidation Experiments

2.3.1 Reactor Design

The methane oxidation experiments were carried out in a conventional high pressure plug flow microreactor, essentially similar to the reactor shown in figure 2.1. The reactor was constructed of ½" O.D. stainless steel. Studies were performed using methane (99.99%), oxygen (99.5%) and helium (99.5%) gases. The gas flow rates were controlled using three mass flow controllers (Brooks Mass Flow 5850 Series). To ensure accuracy of flow rates the flow at the reactor outlet was checked regularly using a bubble flow meter. All gas lines and main parts of the rig were constructed of ⅛" o.d. stainless steel tubing. Catalysts were uniform particle size range and were secured in place at the centre of the reactor tube using two silica wool plugs. The catalyst bed was heated by a furnace (Carbolite) with a 50mm uniform heated zone, capable of maintaining temperatures up to 1000°C. The temperature was maintained using a thermocouple, which was placed in intimate contact with the catalyst bed within the reactor tube. The outlet of the reactor was heated at approx 150°C with heating tape in order to avoid possible condensation of products. Analysis was carried out on-line using gas chromatography with Porapak Q and Molsieve 13X columns in a series bypass configuration with thermal conductivity and flame ionisation detectors. The pressure was kept at 15 bar and regulated using a Tescom back pressure regulator and pressure release valve. The pressure within the system was indicated by a Bourdon Gauge.

2.3.2 Experimental Procedure

The catalysts used in this study were first pelleted to uniform size (250-600μm) by pressing the catalyst in a 5cm die under 5 tonnes pressure for one minute. The resulting disc was then pressed through 0.25mm and 0.6mm standard brass sieves. In each experiment, 0.25cm^3 of catalyst was used. The gas flow used was 92/8/20 ml min^{-1}for CH_4/ O_2/He gases respectively. The reason for the low O_2 flow in relation to CH_4 is because methane activation is preferred to full oxidation, making oxygen deficient conditions necessary. These flows, and being at 15 bar pressure, produced a Gas Hourly Space Velocity (GHSV) of approximately 1920 h^{-1}.

Once flow rates were set and stabilised, the reactor temperature was set to approx 250°C and allowed to equilibrate for half an hour. Catalytic activity was monitored up to the temperature where oxygen conversion was almost complete. As in section

2.2.2, conversion was calculated on the products detected. Product selectivities were calculated using the following equation:-

$$\text{Selectivity} = \frac{\text{Product}}{\text{Total Number of Products}} \times 100$$

Where the product is the volume % of a product containing carbon, multiplied by the number of carbon atoms it contains per molecule. Oxygen conversion was based on the difference in area of the peaks, summarised in the following equation:-

$$\text{Oxygen conversion} = \frac{\text{Oxygen}_{\text{in}} - \text{Oxygen}_{\text{out}}}{\text{Oxygen}_{\text{in}}} \times 100$$

2.4 GC Analysis System

The Gas Chromatograph (GC) used for these experiments was a Varian Star 3400CX. The columns used were Poropak Q (2m x 2mm internal diameter) and Molecular Sieve 13X (2m x 2mm i.d.) also known as Molsieve. These two columns were connected in series, and reactants and products were monitored by a TCD and FID. The two columns were respectively chosen to separate light gases and oxygenated products, such as CH_4, O_2, CO, CO_2, HCHO and CH_3OH. The use of two separate columns was also necessary to prevent CO_2 entering the Molsieve, leading to irreversible absorption and resulting in column deactivation. A simplified summation is shown below:-

Sample in → 10 Port Valve → Poropak Q → Molsieve / Restrictor / 6 Port Valve → TCD + FID

The valve positions are simplified in table 2.1:-

Table 2.1 Summary of Valve Positions

Valve	Off (-)	On (+)
1	Backflush / Fill	**Inject**
2	**Series**	**Bypass**

In the method used for the methane oxidation experiments, the sample loop was allowed to fill whilst the poropak column was being cleaned using the backflush. Once the loop was filled it was injected into the poropak via the ten port valve, with the two valves in series. By using the valves in both bypass and series configurations, it was possible to fully separate all the gases that were detected, namely CH_4, O_2, CO, CO_2, HCHO and CH_3OH. In order to obtain quantitative results from the GC analysis, it was essential to use correction factors, known as response factors. For the TCD Dietz et al determined relative response factors for some hydrocarbons and many oxygenated products. These response factors are independent of carrier gas, temperature, flow rate and concentration. The conversion was calculated on the basis of reaction products.

For the atmospheric pressure experiments the only gases that were detected were O_2, CH_4 and CO_2. The column temperature used was 50°C, thus ensuring full separation of the peaks, and each run took approximately 6 minutes. For the high pressure experiments the initial column temperature used was 40°C, beginning with both columns in series, before switching to bypass after 1.8 minutes. The run continued in bypass until 4 minutes, where it switched to series before switching back after 6.7 minutes. After 8 minutes the temperature of the oven was ramped up to 150°C at a rate of 50°C a minute, so that the methanol peaks could be observed. Each run took approximately twenty three minutes.

2.5 Methods of catalyst characterisation

2.5.1 X-Ray Diffraction (XRD)

A crystalline powder will consist of a large number of microcrystalline particles. If this powder is packed in a completely random manner, then this will contain crystal lattice planes in every orientation. When an impinging x-ray beam is aimed at this sample, a number of crystal planes may produce in phase diffraction, shown in figure 2.2.

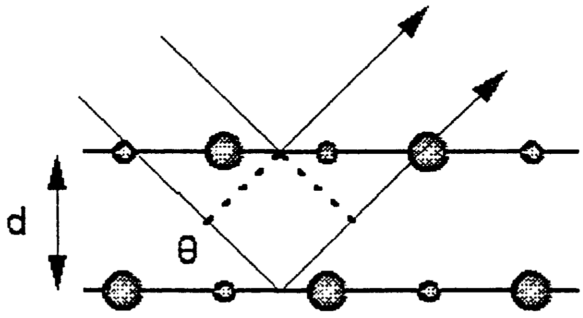

Figure 2.2 Diffraction from a set of lattice planes.

The in phase diffracted x-ray beams are due to the additional distance travelled by the x-ray photon between the neighbouring A and D planes. The difference in path, BD + DC, will depend on the lattice spacing (d_{hkl}), the Miller indices of these planes. Due to BD + DC being related to the angle of incidence of the x-ray beam, θ, a relationship between θ and d_{hkl} can be obtained, through the Bragg Equation:-

$$n\lambda \quad = \quad 2\, d_{hkl} \,.\, \sin\theta$$

Therefore when a sample is moved through an angular range θ, different sets of crystal planes will satisfy the criteria in the bragg equation producing a diffracted beam at an angle 2θ. The plot 2θ against the intensity of the diffracted x-ray pattern gives rise to the powder diffraction pattern, from which phase identification is possible. Only reflections following Braggs law will be detected, and just crystalline samples with a crystallite range above 20Å – 50Å will give a diffraction pattern.

Diffraction studies on the powdered samples were performed using an Enraf Nonius FR 590 instrument with a monochromatic radiation provided by an X-ray source of Cu with a Ni filter to obtain the Cu K_{α} ($K_{\alpha 1}$ + $K_{\alpha 2}$) radiation with a wavelength of 1.54066Å. The X-ray power was set at 1.2 kW (30mA and 40kV). Each sample was scanned from 2θ = 4.4 to 124.6. The powdered samples were compressed on an aluminium sample holder, which was rotated during exposure to the X-ray radiation to increase randomness in the orientation of the crystallites. The diffraction pattern is registered by means of a position sensitive detector (Inel PSD120), which is a curved wire counter which covers all 2θ in the range highlighted earlier, and can simultaneously register all Bragg reflection. All samples were tested over half hour periods.

Data was analysed using Traces 4.0 software, which allowed the removal of the contribution of the background, and peak positions and relative intensities determined.

Phase identification was performed using Fein Marquart Associates Micro Powder Diffraction Search and Match (μ-PDSM), and with the JCPDS database.

2.5.2 BET Surface Area Analysis

Catalyst surface areas were measured in accordance with Brunauer, Emmet and Teller (B.E.T.) method [5]. In this method the physical adsorption of an inert gas (N_2) onto the catalyst surface is used to calculate the total surface area of the solid. The method is based on a theoretical model, with the adsorption isotherm measured, which is the nitrogen adsorbed volume (Va) against its relative pressure, which is the actual pressure (P) divided by the vapour pressure (Po) of the adsorbing gas at the experimental temperature. From this by a mathematical analysis the calculation of the monolayer capacity of the adsorbent can be determined. The BET equation has the form:-

$$P / Va (Po - P) = [(C - 1) / (VmC) . P / Po] + 1 / VmC$$

Where P / Po = Pressure / Saturated Vapour Pressure at experimental T

= Relative Pressure

Va = Adsorbed Volume

Vm = Monolayer Capacity

C = Constant Related to Adsorption and Liquefaction

Once the monolayer volume has been calculated the surface area can be determined by the following equation :-

$$\text{Surface Area} = V_m \sigma N_a / M V_o$$

Where σ = Area of Adsorbate = $0.162m^2$ at 77K

N_a = Avagadro's Number

M = Mass of Sample

V_o = Molar Volume of Gas

The apparatus use for these experiments were a Micromeritics ASAP 200 and a Micromeritics Gemini system, and both were computer controlled. To ensure accurate measurements, approximately 0.2-0.4g of sample was used. All calcined samples were measured on the ASAP apparatus and were degassed under vacuum to remove any contaminating physisorbed species, and each sample took on average 4-5 hours, at a temperature of 120°C. All uncalcined samples were measured on the Gemini apparatus and were also degassed for similar periods of time, however at a temperature of 50°C, and not under vacuum. After cooling, the dead volume of the apparatus was measured accurately by expansion of He from a known volume. The glass tube was immersed in liquid N_2 and the dead volume was measured, following which all He was pumped out and replaced with a known volume of N_2 at a temperature of 77K, and the pressure was determined. From these measurements an adsorption isotherm was constructed and the surface area derived as explained above. For these surface area experiments there was a ±10% error in the values recorded, taking into account different degassing times, and differing amounts of catalyst tested. The lowest reliable surface areas are in the region of 4-5 m^2g^{-1}.

2.6 References

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Chapter 3

Initial Methane Activation Experiments

3.1 Introduction

As was explained more fully in chapter 1, the selective activation of CH_4 remains one of the biggest challenges in the design of heterogeneous catalysts. In previous work by this group a design approach for a selective partial oxidation catalyst has been investigated [1]. This design approach comprises the combination of components with a desired reactivity, producing a successful selective partial oxidation catalyst. In this approach, it is considered a successful partial oxidation catalyst must activate CH_4, activate oxygen and not destroy the desired product, CH_3OH. All these properties could not be found in a single catalyst, so it was proposed that two synergistic components could be combined, one responsible for CH_4 activation and the other for oxygen activation/insertion.

Previous work has studied the CH_4/D_2 exchange reaction as an indication of the ability of a metal oxide surface to activate CH_4 [2]. Two metal oxides demonstrated appreciable activity for the activation of CH_4, these being Ga_2O_3 and ZnO. The activity of Ga_2O_3 was particularly noteworthy as the rate of exchange was at least two orders of magnitude greater than any other material examined.

One of the major aims for selective CH_4 oxidation by heterogeneous catalysts is to activate the C-H bond, under realistic oxidation conditions, at the lowest possible temperature. Activation at lower temperatures offers the greatest potential to carry out the chemistry on the catalyst surface and thereby control the product selectivity. The use of higher temperatures tends to promote gas phase reactions as the activated CH_4 species desorb from the surface, often as a methyl radical, and consequently the catalyst surface exerts minimal influence over the product selectivity. One of the best ways to distinguish the ability of a catalyst to activate the CH_4 is to measure the catalyst light off temperature. For the entirety of this study the light off temperature is defined as the temperature at which 0.01% conversion was observed.

The activation of CH_4 was probed by studying the CH_4 oxidation activity of the catalysts at atmospheric pressure. By performing these studies at ambient pressure the influence of gas phase chemistry was reduced when compared with measurements made at elevated pressure. Gas phase reactions initiated by the walls of the reactor tube were not significant in these studies as conversion was only observed above 550°C in blank experiments. The CH_4 conversion over the catalysts was observed at significantly lower temperatures and consequently the activation of CH_4 on the catalysts surface was probed. The present study has probed the activity of Ga_2O_3 and ZnO for CH_4 activation under conditions relevant for selective oxidation.

The work carried out in this chapter aims to investigate further the CH_4 activation steps in the partial oxidation reaction. The efficacy for CH_4 activation by Ga_2O_3 is significant, and the present studies hope to probe the relationship between Ga_2O_3 structure and its ability to activate CH_4. These studies aim to investigate the effect of doping Ga_2O_3 with zinc and magnesium as these components have also shown promising activity for CH_4 activation [3], also the ions are of comparable ionic radii to Ga^{3+} and it is hoped their incorporation in the lattice will increase defect concentration. As well as doping Ga_2O_3, this study will investigate the effect of doping ZnO with gallium. This is due to previous results by Sojka [4], where ZnO was doubly doped with Cu and Fe at levels of 1% each, who reported an increase in selectivity toward partial oxidation products at the expense of total oxidation and coupling products.

3.2 Initial Methane Activation Studies Results

3.2.1 Characterisation

Catalysts used for the initial CH_4 activation experiments were characterised before use by powder X-ray diffraction. Analysis of the single oxides indicated the most stable phases were present, β-Ga_2O_3 for gallium oxide, and for zinc oxide, ZnO. The precipitated magnesium phosphate catalyst showed that the crystal structure was $Mg_2P_2O_7$. The coprecipitated gallium oxide catalysts, namely the 1wt% Zn and Mg, did not show anything except the pattern for β-Ga_2O_3. The coprecipitation levels of Zn and Mg were only 1 wt% and we can deduce this was not a high enough percentage to be detected by XRD.

The surface areas of the catalysts were distributed over a relatively wide range. The gallium oxide catalyst had a surface area of 40 m^2g^{-1}, and the coprecipitation of gallium oxide with 1 wt% magnesium and 1 wt% zinc showed a large increase in the surface area of the catalyst. The data presented in table 3.2.1 indicates that the addition of magnesium may have an important structural promotional effect as the surface area of the coprecipitated system was considerably higher than Ga_2O_3. The value for zinc oxide and magnesium phosphate were at the bottom end of scale of reliability. The molybdenum oxide was tested for comparison to the other catalysts, as it will feature later in this study. The fumed silica was amorphous and the surface area was much greater than the other catalysts at 276 m^2g^{-1}.

The results of powder XRD and surface area measurements for the catalysts prepared in the initial part of this study are summarised in table 3.2.1.

Table 3.2.1. Results of BET surface area and phases identified by powder X-ray diffraction.

Catalyst	**Surface area/m^2g^{-1}**	**Phase**
Ga_2O_3	40	β-Ga_2O_3
1%Zn Ga_2O_3	58	β-Ga_2O_3
1%Mg Ga_2O_3	96	β-Ga_2O_3
ZnO	4	ZnO
$Mg_3(PO_4)_2$	3	$Mg_2P_2O_7$
MoO_3	0.5	MoO_3
SiO_2	276	Amorphous

Maximum error ±10%

3.2.2 Catalytic Activity for initial methane activation catalysts

The activation of CH_4 has been by studied by conversion to products, namely CO_2. One of the most important properties a CH_4 activation catalyst must have is to activate CH_4 at a low temperature. The light-off temperatures for the catalysts are displayed in table 3.2.2. All the gallium based catalysts displayed initial CH_4 activation at the same temperature, called the light-off temperature, 350°C. The precipitated magnesium phosphate catalyst showed activation twenty five degrees higher, and the zinc oxide twenty five degrees higher again.

Table 3.2.2. Light-off temperatures for initial studies catalysts

Catalyst	Light off Temperature (°C)
Ga_2O_3	350
1%Zn/Ga_2O_3	350
1%Mg/Ga_2O_3	350
ZnO	400
$Mg_2P_2O_7$	375
MoO_3	425
SiO_2	520

Maximum error ±9 °C

The CH_4 conversion results for all the catalysts tested are shown in Figure 3.1. The only reaction product observed was carbon dioxide. No other products, such as CH_3OH, HCHO, CO or ethane were detected above the limits of analytical sensitivity.

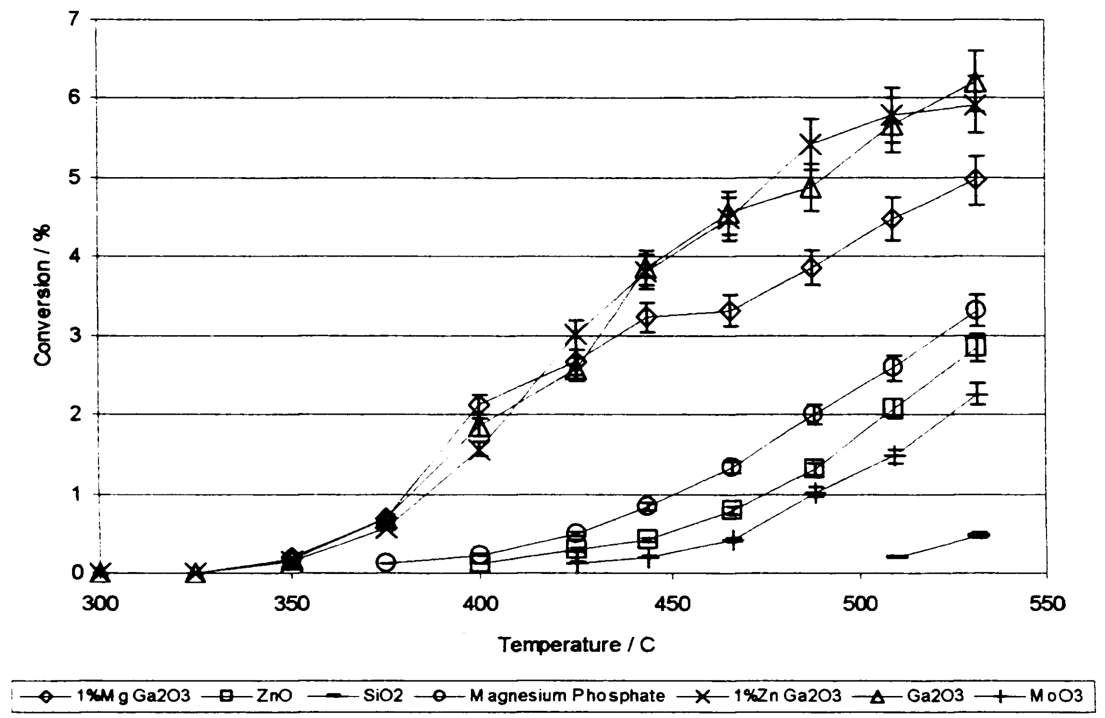


Figure 3.1 Methane conversion plot for initial studies catalysts - showing error bars

Comparison with a relative inert packing of fumed SiO_2 showed that all the catalysts were more active. Although the SiO_2 may have some residual surface activity it provides a comparison to gauge the contribution from homogeneous gas phase reactions. The Ga_2O_3 catalyst and Ga_2O_3 coprecipitated with magnesium and zinc showed broadly similar activity at lower temperatures, but the Ga_2O_3 coprecipitated magnesium catalyst's activity did reduce at higher temperatures. It can also be seen that compared to the Ga_2O_3, CH_4 activation by precipitated zinc and magnesium catalysts was lower. To determine the accuracy of the conversions measured, the standard deviation of three runs for each catalyst was calculated, resulting in an average error of ±6%. This error is displayed using error bars in figure 3.1, and this average error for conversion is taken as the uniform error for this study.

The data presented in figure 3.1 is representative of the catalyst formulations and is therefore normalised in terms of catalyst volume. To compensate for the effect of varying surface area reaction rates have been normalised per unit area. A comparison of the normalised rates is shown in table 3.2.3.

Table 3.2.3. Methane oxidation rates at 444°C normalised for the effect of surface area

Catalyst	**Rate/mol s^{-1} m^{-2}**
Ga_2O_3	1.078×10^{16}
1%Zn/Ga_2O_3	5.75×10^{15}
1%Mg/Ga_2O_3	3.24×10^{15}
ZnO	1.04×10^{16}
$Mg_2P_2O_7$	2.71×10^{16}
MoO_3	1.49×10^{16}
SiO_2	0

Comparison of the gallium oxide systems in terms of surface area normalised reaction rates showed that the Ga_2O_3 catalyst was the most active. It is therefore evident that coprecipitating Ga_2O_3 with zinc and magnesium produces similar rates of reaction, but when the rates are surface normalised it shows that coprecipitation actually has the opposite effect and suppresses the activity. Due to their low surface areas, the $Mg_2P_2O_7$, MoO_3 and ZnO catalysts show high reaction rates.

The activation energies for the various catalysts were calculated from the Arrhenius equation obtained at low conversions. A plot of the Arrhenius behaviour is shown in Appendix A. This data is displayed in table 3.2.4.

Table 3.2.4. Activation energies for initial studies catalysts (Errors ± 8 kJ mol^{-1})

Catalyst	Activation Energy (kJ mol^{-1})
Ga_2O_3	123
1%Zn/Ga_2O_3	132
1%Mg/Ga_2O_3	166
ZnO	124
$Mg_2P_2O_7$	112
MoO_3	128

As can be seen, the majority of activation energies were similar. The coprecipitation of gallium oxide with 1 wt% zinc did not significantly alter the activation energy. The coprecipitation with magnesium increased the activation energy by more than 40 kJ mol^{-1} and is consistent with the lower rate observed for the 1 wt% Mg gallium oxide catalyst.

3.3 Varying the levels of Zn in Ga_2O_3 catalysts

After the coprecipitation of Zn with Ga_2O_3 at levels of 1%, the effect of increasing the loading to higher levels was undertaken. In order to assess whether the creation of defects due to coprecipitation was the reason for the catalysts oxidation behaviour, physical mixtures of ZnO in Ga_2O_3 were also tested, at levels of 1% and 10%. This was in order to determine whether defects created in the crystal structure by Zn, or just by the presence of ZnO itself.

3.3.1 Varying the levels of Zn in coprecipitated Ga_2O_3 catalysts

Due to the nature of the initial results for Zn coprecipitated gallium catalysts, a series of other Zn coprecipitated catalysts were prepared, with wt% of 2 and 5 respectively. This was done to try and ascertain if increasing the loading of Zn by coprecipitation increases defect formation within the Ga_2O_3 catalyst.

3.3.1.1 Characterisation

Even though zinc oxide has a substantially lower surface area than gallium oxide, the addition of Zn by coprecipitation raises the surface area of the catalyst. For example, the addition of just 1wt% Zn raises the surface area of the gallium catalyst by 50%, and 2wt% and 5wt% by over 75%. The catalysts prepared in this study and the results of powder XRD and surface area measurements are summarised in table 3.3.1.

Table 3.3.1. Results of BET surface area and phases identified by powder X-ray diffraction.

Catalyst	Surface area/m^2g^{-1}	Phase
Ga_2O_3	40	β-Ga_2O_3
1% Zn coprecipitated Ga_2O_3	58	β-Ga_2O_3
2% Zn coprecipitated Ga_2O_3	71	β-Ga_2O_3
5% Zn coprecipitated Ga_2O_3	71	β-Ga_2O_3
ZnO	4	ZnO

Maximum error ±10%

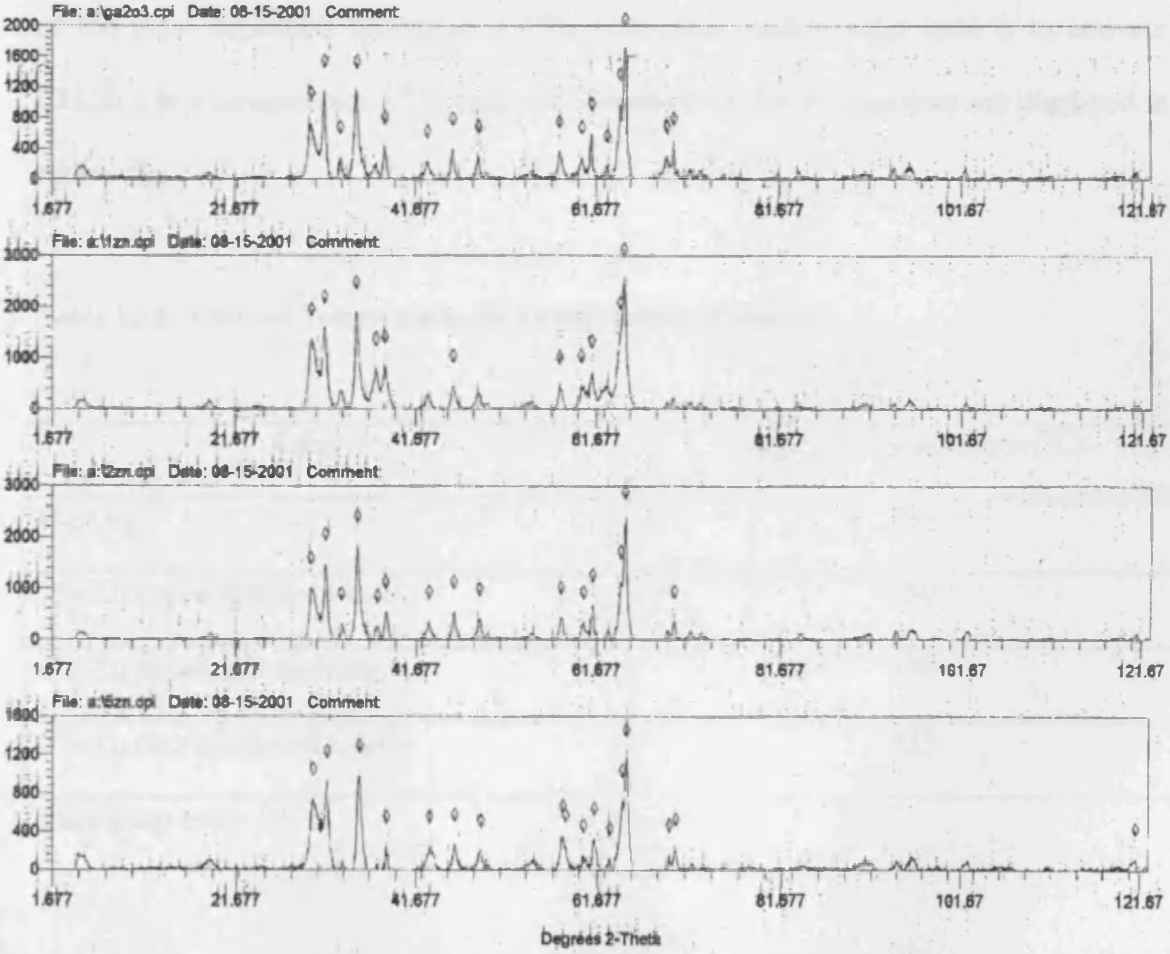


Figure 3.2 X-ray pattern for Zn coprecipitated Ga_2O_3 catalysts

To highlight the similarity in the X-ray patterns of the Gallium Oxide and the Zn coprecipitated catalysts a copy of the patterns are displayed in Figure 3.2. The patterns are from top to bottom: Ga_2O_3, 1wt% Zn, 2 wt% Zn, 5 wt% Zn.

It can be observed that all the gallium catalysts have similar patterns, but it can also be noted that at a loading of 5 wt% Zn, no peaks corresponding to Zn can be seen.

3.3.1.2 Catalytic Activity

The activation of CH_4 has been studied by conversion to products, namely CO_2. One of the most important properties a CH_4 activation catalyst must have is to activate CH_4 at a low temperature. The light-off temperatures for the catalysts are displayed in table 3.3.2.

Table 3.3.2. Light-off Temperatures for Zn coprecipitated catalysts

Catalyst	Light off Temperature (°C)
Ga_2O_3	350
1% Zn coprecipitated Ga_2O_3	350
2% Zn coprecipitated Ga_2O_3	350
5% Zn coprecipitated Ga_2O_3	325

Maximum error ±9 °C

All of the catalysts have very similar light-off temperatures, but in the studies the 5 wt% Zn catalyst did activate the CH_4 at slightly lower temperatures.

The results for all the catalysts tested are shown in Figure 3.3. The only reaction product observed was carbon dioxide. No other products, such as CH_3OH, HCHO, CO or ethane were detected above the limits of analytical sensitivity.

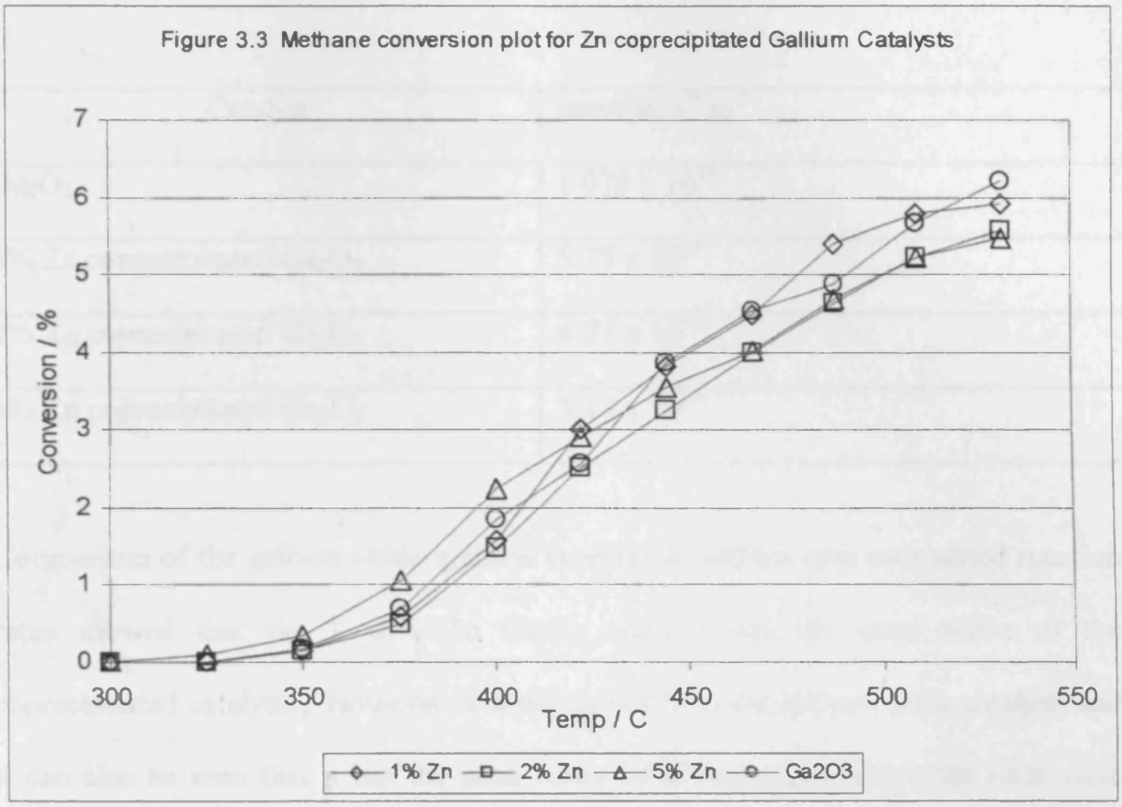


Figure 3.3 Methane conversion plot for Zn coprecipitated Gallium Catalysts

The 5% Zn catalyst shows higher conversion at lower temperatures, whereas at higher temperatures the 1% Zn catalyst does show higher conversion. The data presented in figure 3.3 is representative of the catalyst formulations and is therefore normalised in terms of catalyst volume. The order of activation at 444°C was:-

Ga_2O_3>1% Zn coprecipitated Ga_2O_3>5% Zn coprecipitated Ga_2O_3>2% Zn coprecipitated Ga_2O_3

In the middle of the temperature range the Ga_2O_3 catalyst has higher conversion than the coprecipitated catalysts. To compensate for the effect of varying surface area reaction rates have been normalised per unit area. A comparison of the normalised rates is shown in table 3.3.3.

Table 3.3.3. Methane oxidation rates at 444°C normalised for the effect of surface area

Catalyst	rate/mol s^{-1} m^{-2}
Ga_2O_3	1.078×10^{16}
1% Zn coprecipitated Ga_2O_3	5.75×10^{15}
2% Zn coprecipitated Ga_2O_3	4.23×10^{15}
5% Zn coprecipitated Ga_2O_3	5.14×10^{15}

Comparison of the gallium oxide systems in terms of surface area normalised reaction rates showed that the 1 wt% Zn Ga_2O_3 catalyst was the most active of the coprecipitated catalysts. However, it is not as active as the gallium oxide catalyst, and it can also be seen that it has the same order of activation as before the rates were surface normalised.

The activation energies for the various catalysts were calculated from the Arrhenius equation obtained at low conversions. This data is shown in table 3.3.4.

Ga_2O_3 has the lowest activation energy, with the loadings of 1wt% and 2wt% having similar activation energies. The 5wt% catalyst had the highest activation energy, nearly 20 kJ mol^{-1} higher than Ga_2O_3.

Table 3.3.4. Activation energies for Zn coprecipitated catalysts (Errors ± 8 kJ mol^{-1})

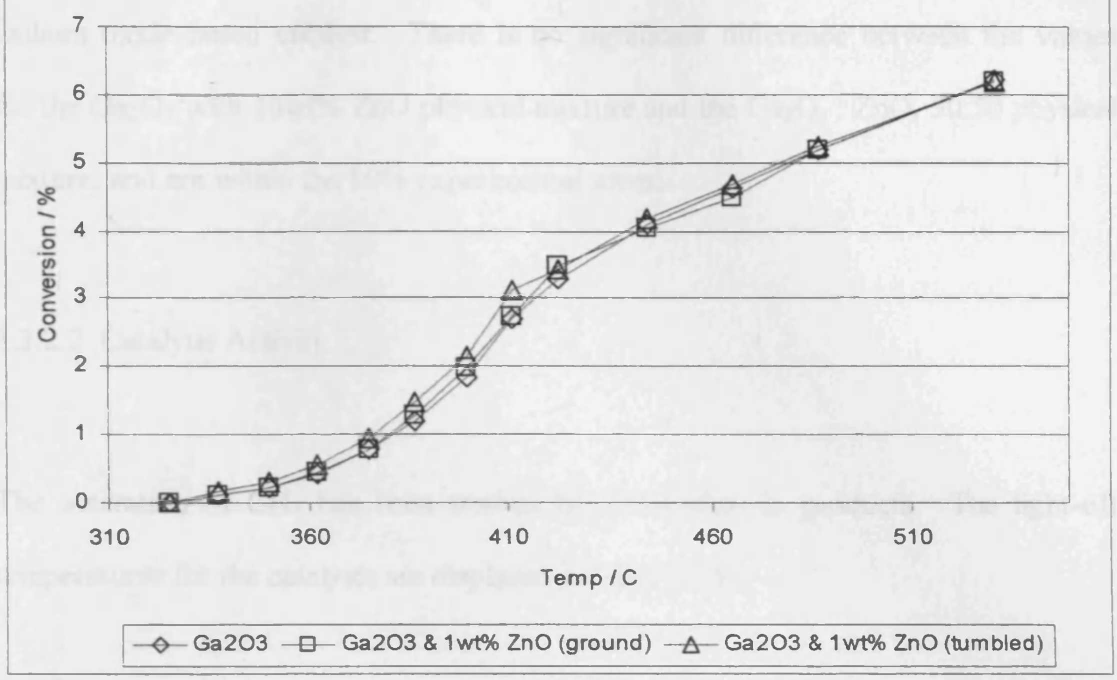
Catalyst	Activation Energy (kJ mol^{-1})
Ga_2O_3	123
1% Zn coprecipitated Ga_2O_3	132
2% Zn coprecipitated Ga_2O_3	130
5% Zn coprecipitated Ga_2O_3	142

3.3.2 Ga_2O_3 with different levels of ZnO physical mixtures

In order to determine whether the coprecipitation of Zn into the Ga_2O_3 lattice did in fact create defects that affect the CH_4 activation properties within the catalyst, a different set of catalysts was prepared. These catalysts were created by the physical mixing of certain amounts of ZnO into Ga_2O_3. These were then tested to see if this different preparation method produced catalysts with different results to the coprecipitated catalysts

To ensure the method of physical mixing did not affect the result of the experiment, two different methods were tested. The first was tumbling the two oxides together for 30 minutes in a sample vial, the second 30 minutes grinding together with a pestle and mortar. A slight difference was seen, in figure 3.4, but it is negligible. For the remainder of this report the tumbling method of physical mixing was used.

Figure 3.4 Methane conversion plot for different preparation methods of gallium oxide and zinc oxide physical mix catalysts



3.3.2.1 Characterisation

Table 3.3.5. Results of BET surface area and phases identified by powder X-ray diffraction.

Catalyst	**Surface area/m^2g^{-1}**	**Phase**
Ga_2O_3	40	β-Ga_2O_3
Ga_2O_3 with 1wt% ZnO Physical mixture	35	β-Ga_2O_3
Ga_2O_3 with 10wt% ZnO Physical mixture	20	β-Ga_2O_3
Ga_2O_3 : ZnO, 50:50 Physical mixture	24	ZnO/β-Ga_2O_3
ZnO	4	ZnO

Maximum error ±10%

It is interesting to note that the addition of just 1wt% of ZnO reduces the surface area by over 12%, and the addition of 10 wt% ZnO in fact halves the surface area of the gallium oxide based catalyst. There is no significant difference between the values for the Ga_2O_3 with 10wt% ZnO physical mixture and the Ga_2O_3 : ZnO, 50:50 physical mixture, and are within the 10% experimental error.

3.3.2.2 Catalytic Activity

The activation of CH_4 has been studied by conversion to products. The light-off temperatures for the catalysts are displayed in table 3.3.6.

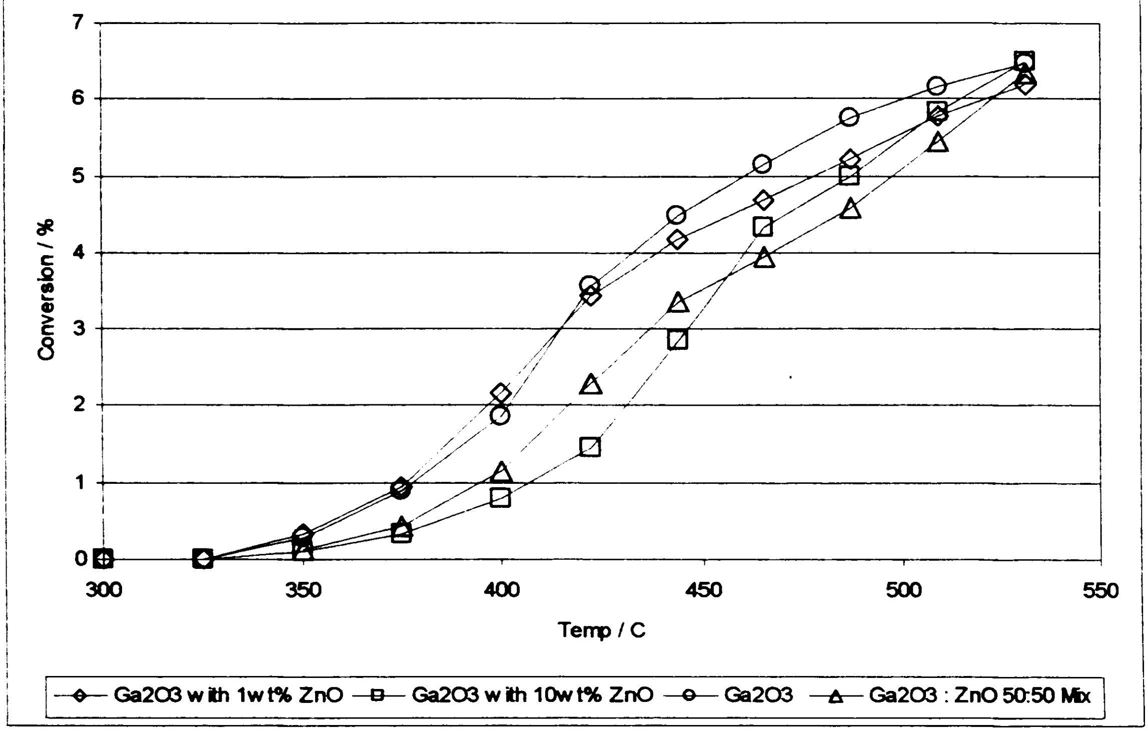
Table 3.3.6. Light-off Temperatures for Ga_2O_3 : ZnO physical mixture catalysts

Catalyst	**Light off Temperature (°C)**
Ga_2O_3	350
Ga_2O_3 with 1wt% ZnO Physical mixture	350
Ga_2O_3 with 10wt% ZnO Physical mixture	350
Ga_2O_3 : ZnO, 50:50 Physical mixture	375
ZnO	400

Maximum error ±9 °C

There is no difference in the light-off temperature upon the addition of ZnO by physical mixture at lower loadings, but once the loading is raised to 50%, the addition of ZnO begins to inhibit CH_4 activation.

Figure 3.5 Methane conversion plot for ZnO physical mixture gallium catalysts



Data representative of CH_4 conversion is shown in figure 3.5. This plot shows that the physical mixing of ZnO into Ga_2O_3 does in fact significantly reduce its activation properties. At lower temperatures it seems the addition of a large amount of ZnO to Ga_2O_3 actually lowers the methane activation properties of the catalyst, but at higher temperatures this effect is reduced. Also, at lower temperatures, the 1wt% Zn catalyst exhibited the highest CH_4 conversion.

Upon considering the surface areas of the catalysts, given in table 3.3.5, the following surface area normalised rates were obtained, shown in table 3.3.7.

Table 3.3.7. Methane oxidation rates at 444°C normalised for the effect of surface area

Catalyst	rate/mol s^{-1} m^{-2}
Ga_2O_3	1.08×10^{16}
Ga_2O_3 with 1wt% ZnO Physmix	1.15×10^{16}
Ga_2O_3 with 10wt% ZnO Physmix	1.37×10^{16}
Ga_2O_3 : ZnO 50:50 Physical mixture	1.35×10^{16}
ZnO	1.04×10^{16}

It can be seen that once the results are normalised for surface area, the physical mixture catalysts have higher oxidation rates. The Ga_2O_3 has higher CH_4 activation, but the lower surface area of the physical mixes makes their normalised oxidation rates higher. The activation energies for the various catalysts were calculated from the Arrhenius equation obtained at low conversions. This data is shown in table 3.3.8.

Table 3.3.8 Activation Energies for Ga_2O_3 : ZnO physical mixture catalysts (Errors ± 8 kJ mol^{-1})

Catalyst	Activation Energy (kJ mol^{-1})
Ga_2O_3	123
Ga_2O_3 with 1wt% ZnO Physical mixture	131
Ga_2O_3 with 10wt% ZnO Physical mixture	128
Ga_2O_3 : ZnO, 50:50 Physical mixture	144
ZnO	124

For the lower loadings of ZnO, very similar activation energies were seen, within experimental error. The 50:50 physical mixture catalyst had the highest activation energy, higher than the activation energies of its constituent parts.

3.3.3 Comparison of 1wt% Zn Ga_2O_3 catalysts

To see whether the method of addition of 1% Zn to Ga_2O_3 catalysts greatly affects the methane activation, figure 3.6 was plotted showing the CH_4 conversion properties for 3 different 1% Zn catalysts, made by different preparation methods. The three preparation methods are physical mixture, coprecipitation and impregnation.

3.3.3.1 Characterisation

The results of powder XRD and surface area measurements for the catalysts prepared in the initial part of this study are summarised in table 3.3.9.

Table 3.3.9. Results of BET surface area and phases identified by powder X-ray diffraction.

Catalyst	**Surface area/m^2g^{-1}**	**Phase**
Ga_2O_3	40	β-Ga_2O_3
Ga_2O_3 with 1wt% ZnO Physical mixture	35	β-Ga_2O_3
Ga_2O_3 with 1% Zn by coprecipitation	58	β-Ga_2O_3
Ga_2O_3 with 1wt% Zn by impregnation	21	β-Ga_2O_3
ZnO	4	ZnO

Maximum error ±10%

As described earlier the addition of ZnO by physical mixture lowers the surface area of gallium oxide, and the addition of Zn by coprecipitation raises the surface area. The addition of 1wt% Zn by impregnation lowers the surface area, effectively halving it when compared to the unmodified gallium oxide catalyst.

3.3.3.2 Catalytic Activity

The light-off temperatures for the catalysts are displayed in table 3.3.10. As has been seen in previous sections, all the gallium oxide catalysts had the same CH_4 activation temperature, except the impregnated catalyst which had a higher temperature.

Table 3.3.10. Light-off Temperatures for 1wt% Zn gallium catalysts

Catalyst	Light off Temperature (°C)
Ga_2O_3	350
Ga_2O_3 with 1wt% ZnO Physmix	350
Ga_2O_3 with 1% Zn coprecipitation	350
Ga_2O_3 with 1wt% Zn impregnation	375
ZnO	400

Maximum error ±9 °C

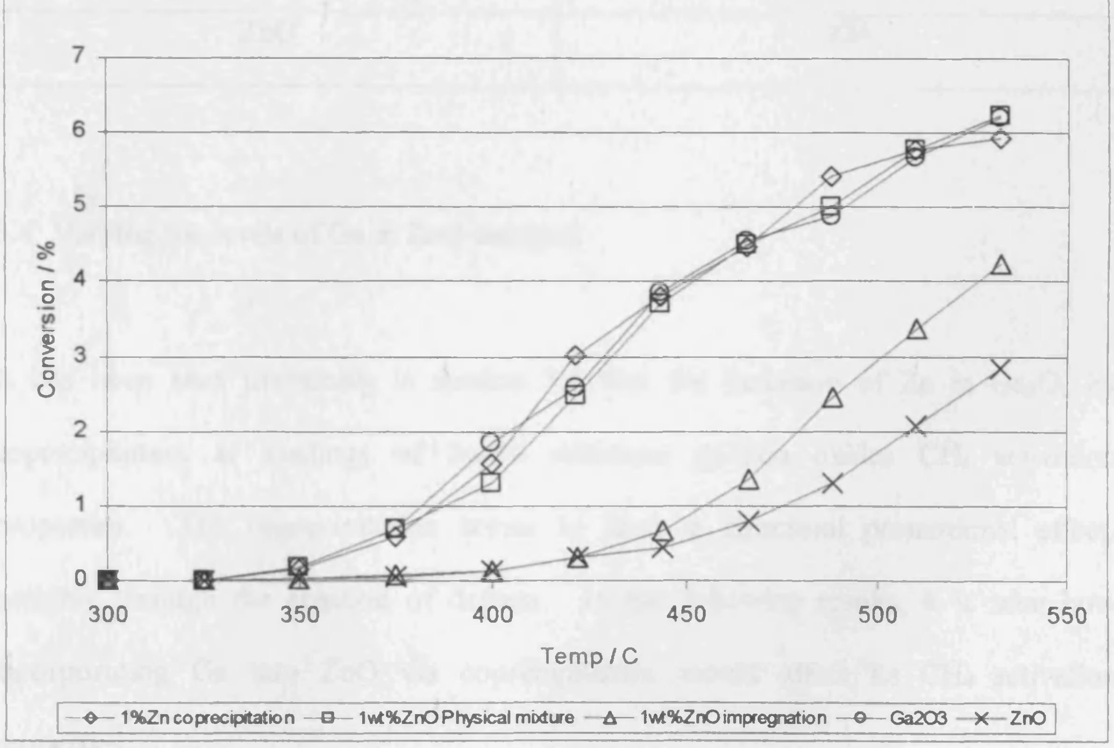
Data representative of catalytic activity is shown in figure 3.6. The gallium oxide, coprecipitated and physical mixture catalysts all had similar CH_4 conversion properties, and the impregnated catalyst in comparison had a much lower conversion at all temperatures. It can be seen from these results that the addition of 1wt% Zn to a

Ga_2O_3 catalyst does not greatly affect its CH_4 conversion properties. At 450 °C, with the exception of the impregnation catalyst, all the Ga_2O_3 exhibit similar activation properties.

Table 3.3.11. Methane oxidation rates at 444°C normalised for the effect of surface area

Catalyst	rate/mol s^{-1} m^{-2}
Ga_2O_3	1.078×10^{16}
Ga_2O_3 with 1wt% ZnO Physmix	1.15×10^{16}
Ga_2O_3 with 1% Zn coprecipitation	5.75×10^{15}
Ga_2O_3 with 1wt% Zn impregnation	3.01×10^{15}
ZnO	1.04×10^{16}

Figure 3.6 Methane conversion plot for different 1wt% Zn Gallium Oxide catalysts



It can be seen from these results that the addition of 1wt% Zn to a Ga_2O_3 catalyst does not greatly affect its CH_4 conversion properties. At 444 °C, with the exception of the impregnation catalyst, all the Ga_2O_3 exhibit similar activation properties. However, once surface areas are considered, the Ga_2O_3 with 1wt% ZnO physical mixture is marginally the best catalyst. The activation energies for the various catalysts were calculated from the Arrhenius equation obtained at low conversions. This data is shown in table 3.3.12.

Table 3.3.12. Activation energies (Errors ± 8 kJ mol^{-1})

Catalyst	Activation Energy (kJ mol^{-1})
Ga_2O_3	123
Ga_2O_3 with 1wt% ZnO Physmix	131
Ga_2O_3 with 1% Zn coprecipitation	132
Ga_2O_3 with 1wt% Zn impregnation	113
ZnO	124

3.4 Varying the levels of Ga in ZnO catalysts

It has been seen previously in section 3.3 that the inclusion of Zn in Ga_2O_3 by coprecipitation at loadings of 5wt% enhances gallium oxides CH_4 activation properties. The coprecipitation seems to have a structural promotional effect, possibly through the creation of defects. In the following results, it is seen how incorporating Ga into ZnO via coprecipitation would affect its CH_4 activation properties.

3.4.1 Varying the levels of Ga coprecipitation in ZnO

3.4.1.1 Characterisation

When the catalysts were characterised using XRD, the Ga coprecipitated ZnO catalysts have patterns very similar to ZnO. To highlight the similarity in the X-ray patterns of the zinc oxide and the Ga coprecipitated catalysts a copy of the patterns are displayed in Figure 3.7. The 1 wt% Ga ZnO displays no sign of any Ga peaks, however, at 10 wt% three prominent Ga_2O_3 peaks are visible on the spectrum. The patterns are from top to bottom:- 10% Ga coprecipitated Zn, 1% Ga coprecipitated Zn, ZnO, Ga_2O_3.

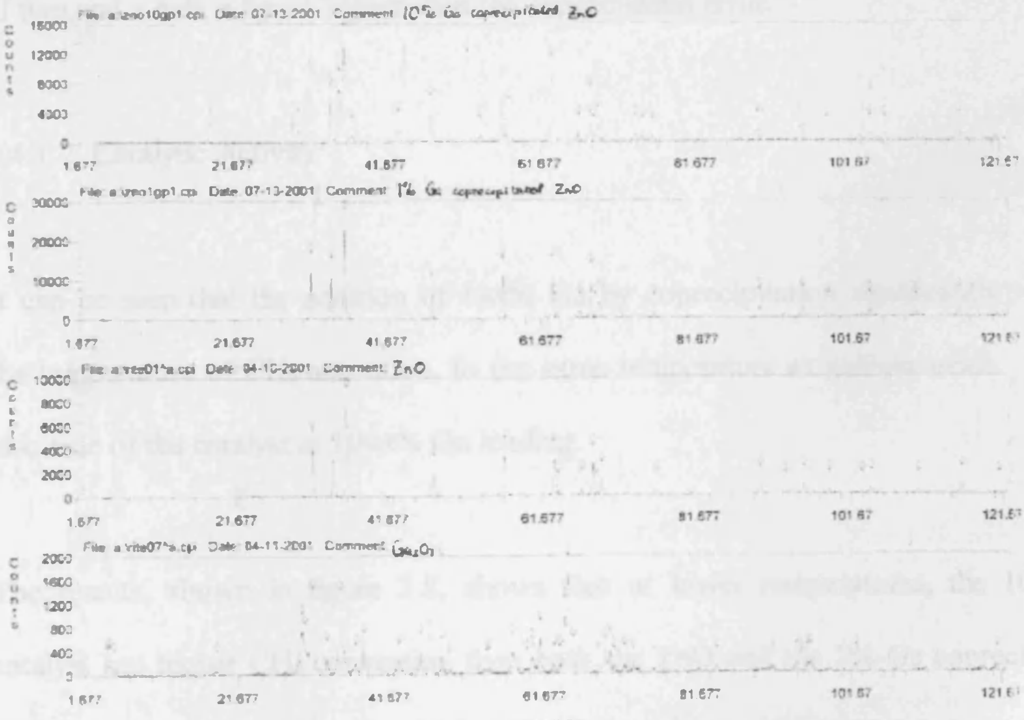


Figure 3.7 X-ray patterns of the ZnO and Ga coprecipitated catalysts

Table 3.4.1. Results of BET surface area and phases identified by powder X-ray diffraction

Catalyst	Surface area/m^2g^{-1}	Phase
ZnO	4	ZnO
1% Ga coprecipitated ZnO	6	ZnO
10% Ga coprecipitated ZnO	10	ZnO
Ga_2O_3	40	β-Ga_2O_3

Maximum Error ± 10%

As we have seen earlier, coprecipitation seems to raise the surface area of catalysts, and these results are no exception. The addition of just 1wt% Ga sees the ZnO catalysts surface area go up by half, and 10wt% Ga raises the surface area by a factor of two and a half, a figure higher than the experimental error.

3.4.1.2 Catalytic Activity

It can be seen that the addition of 1wt% Ga by coprecipitation significantly reduces the temperature of CH_4 activation, to the same temperature as gallium oxide. This is also true of the catalyst at 10wt% Ga loading.

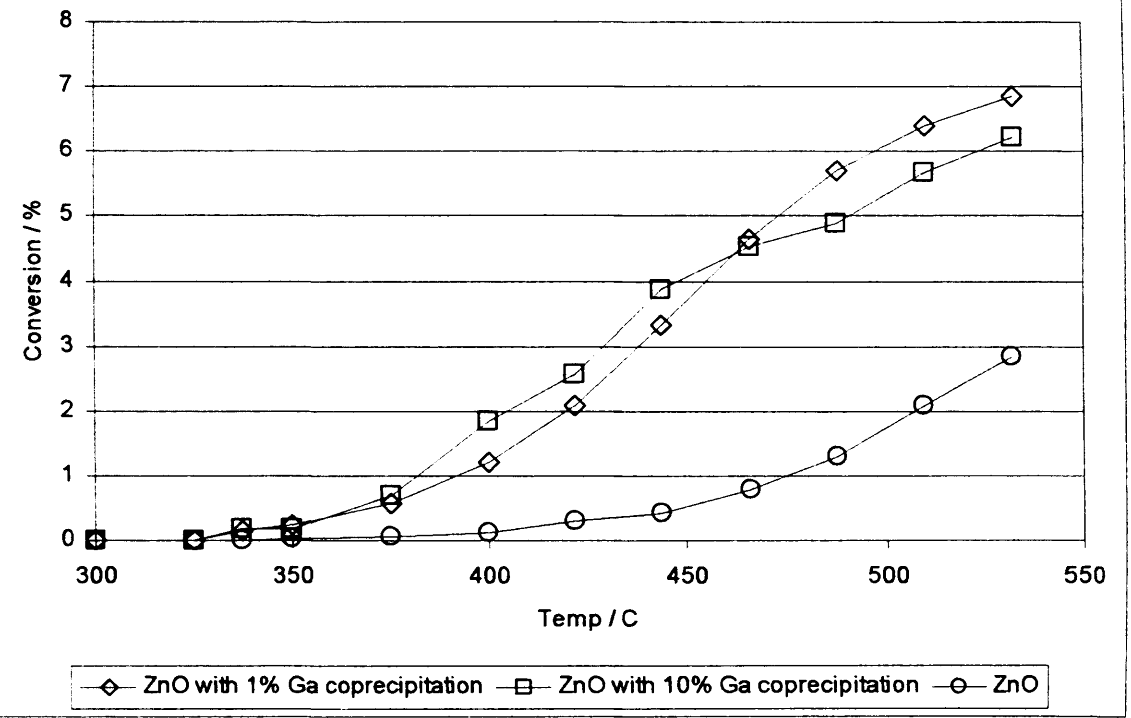
The results, shown in figure 3.8, shows that at lower temperatures, the 10% Ga catalyst has higher CH_4 conversion than both the ZnO and the 1% Ga coprecipitated ZnO, which seems to tail off at high temperatures, but at higher temperatures the 1% Ga coprecipitated ZnO has higher CH_4 conversion. The interesting part of these results is they show that incorporating Ga into the ZnO lattice, even at levels of only 1%, affects CH_4 conversion by several orders of magnitude.

Table 3.4.2. Light-off Temperatures for Ga coprecitated ZnO catalysts

Catalyst	**Light off Temperature (°C)**
ZnO	400
1% Ga coprecipitated ZnO	350
10% Ga coprecipitated ZnO	350
Ga_2O_3	350

Maximum error ±9 °C

Figure 3.8 Methane conversion plot for ZnO and ZnO : Ga coprecipitated catalysts



The data presented in figure 3.8 is representative of the catalyst formulations and is therefore normalised in terms of catalyst volume. To compensate for the effect of varying surface area reaction rates have been normalised per unit area. A comparison of the normalised rates is shown in table 3.4.3.

Table 3.4.3. Methane oxidation rates at 444°C normalised for the effect of surface area

Catalyst	rate/mol s^{-1} m^{-2}
ZnO	1.04×10^{16}
1% Ga coprecipitated ZnO	5.35×10^{16}
10% Ga coprecipitated ZnO	2.48×10^{16}
Ga_2O_3	1.078×10^{16}

The surface normalised rates are very interesting, as they show that coprecipitation of Ga into ZnO creates catalysts with excellent methane oxidation rates, with 1wt% Ga by far the best, even better than Ga_2O_3 itself. The reason for this is that they exhibit similar CH_4 conversion to Ga_2O_3, but with a much lower surface area. The activation energies for the various catalysts were calculated from the Arrhenius equation obtained at low conversions. This data is shown in table 3.4.4.

The addition of Ga by coprecipitation lowers the activation energy of the ZnO catalysts, especially so for the 10 wt% catalyst, which is lowered by more than 20 kJ mol^{-1}.

Table 3.4.4. Activation Energies for Ga coprecitated ZnO catalysts (Errors ± 8 kJ mol^{-1})

Catalyst	Activation Energy (kJ mol^{-1})
ZnO	124
1% Ga coprecipitated ZnO	113
10% Ga coprecipitated ZnO	98
Ga_2O_3	123

3.4.2 ZnO with different levels of Ga_2O_3 physical mixtures

In order to determine whether it is the presence of Ga within the ZnO lattice or just the presence of Ga_2O_3 itself within the catalyst that increases CH_4 conversion, a series of ZnO catalysts were tested with different levels of Ga_2O_3 physically mixed by the tumbling method used earlier.

3.4.2.1 Characterisation

Table 3.4.5. Results of BET surface area and phases identified by powder X-ray diffraction

Catalyst	**Surface area/m^2g^{-1}**	**Phase**
ZnO	4	ZnO
ZnO with 1% Ga physical mixture	4	ZnO
ZnO with 10% Ga physical mixture	8	ZnO
ZnO : Ga_2O_3 50:50 physical mixture	24	ZnO /β-Ga_2O_3

Maximum Error ± 10%

The addition of gallium oxide at 1 wt% levels show no difference to the surface area, unlike coprecipitation, and the increase at the 10 wt% level is smaller. The mixing of identical amounts of the two oxides produced a catalyst with a surface area roughly mid-way between the two constituent parts.

3.4.2.2 Catalytic Activity

The light-off temperatures for the catalysts are displayed in table 3.4.6.

Table 3.4.6. Light-off Temperatures for ZnO with Ga_2O_3 physical mixture catalysts

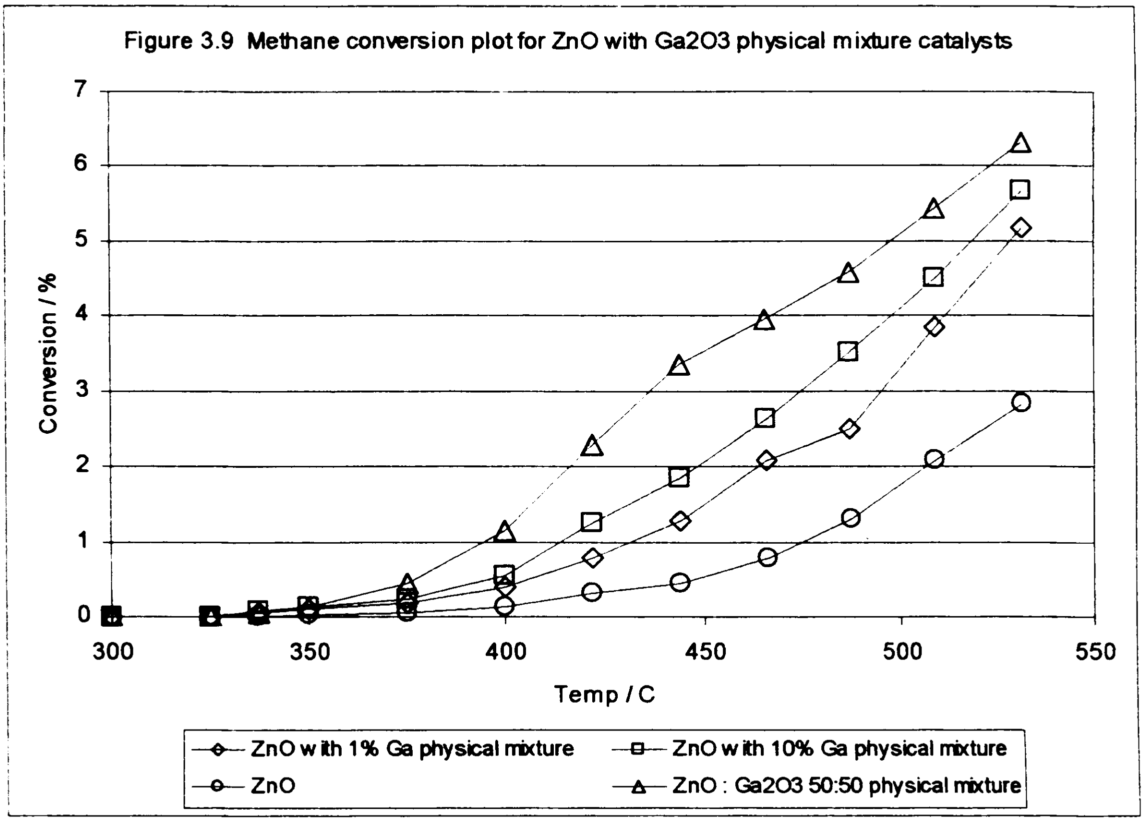
Catalyst	**Light off Temperature (°C)**
ZnO	400
ZnO with 1% Ga physical mixture	350
ZnO with 10% Ga physical mixture	350
ZnO : Ga_2O_3 50:50 physical mixture	375

Maximum error ±9 °C

Again it can be seen that the addition of gallium oxide by physical mixture, even at levels of 1 wt%, reduces the light-off temperatures for the zinc oxide catalysts down to the same level as that of gallium oxide. As can be seen from the results, shown in figure 3.9, the addition of Ga_2O_3 to the catalyst does increase its CH_4 conversion, but not to the same extent as it does from coprecipitation. It is also interesting to note that as the loading of Ga_2O_3 in the catalyst increases, so does the CH_4 conversion. Therefore it can be seen that the addition of Ga_2O_3 to ZnO does affect the CH_4 activation in a favourable way. The 50:50 physically mixed catalyst has activation properties closely comparable to Ga_2O_3, but has a much lower surface area.

Table 3.4.7. Methane oxidation rates at 444°C normalised for the effect of surface area

Catalyst	rate/mol s^{-1} m^{-2}
ZnO	1.04×10^{16}
ZnO with 1% Ga physical mixture	3.075×10^{15}
ZnO with 10% Ga physical mixture	1.475×10^{15}
ZnO : Ga_2O_3 50:50 physical mixture	1.345×10^{16}



Therefore it can be seen that the addition of Ga_2O_3 to ZnO does affect the CH_4 activation in a favourable way. The 50:50 physically mixed catalyst has the highest surface area normalised rate, as it has a similar activation properties to Ga_2O_3, but has a much lower surface area. The activation energies for the various catalysts were calculated from the Arrhenius equation obtained at low conversions. This data is shown in table 3.4.8.

The addition of 1 wt% and 10 wt% Ga significantly lowers the activation energy of the ZnO catalysts, and even though the 50:50 physical mixture has higher CH_4 conversion properties, it has a much higher activation energy.

Table 3.4.8. Activation Energies ZnO with Ga_2O_3 physical mixture catalysts (Errors ± 8 kJ mol^{-1})

Catalyst	Activation Energy (kJ mol^{-1})
ZnO	124
ZnO with 1% Ga physical mixture	100
ZnO with 10% Ga physical mixture	102
ZnO : Ga_2O_3 50:50 physical mixture	144

3.4.3 Comparison of 1wt% Ga ZnO catalysts and also other 1wt% coprecipitated ZnO catalysts

3.4.3.1 Characterisation

Table 3.4.9. Results of BET surface area and phases identified by powder X-ray diffraction

Catalyst	**Surface area/m^2g^{-1}**	**Phase**
ZnO	4	ZnO
ZnO with 1% Ga Physical Mixture	4	ZnO
ZnO with 1% Ga Coprecipitated	6	ZnO

Maximum Error ± 10%

3.4.3.2 Catalytic activity

Figure 3.10 is included to show how the different 1wt% Ga ZnO catalysts compare. It can be seen that the coprecipitated catalyst has significantly higher CH_4 conversion properties.

Figure 3.10 Methane conversion plot for 1wt% Ga ZnO catalysts

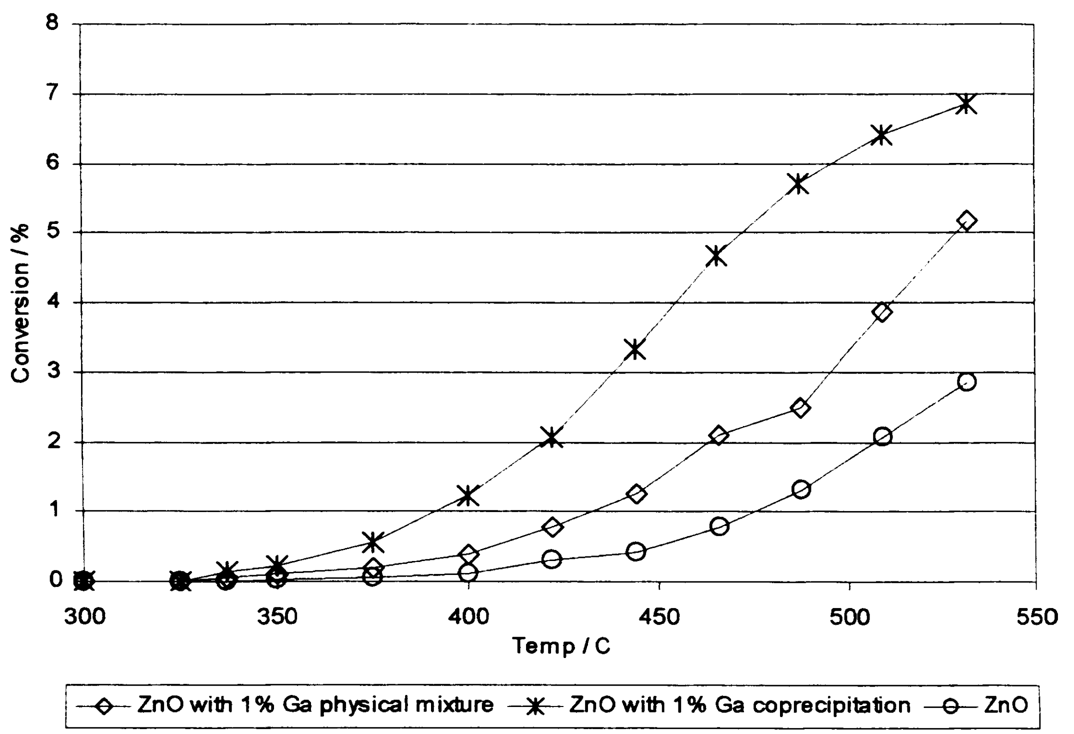


Table 3.4.10. Methane oxidation rates at 444°C normalised for the effect of surface area

Catalyst	rate/mol s^{-1} m^{-2}
ZnO	1.04×10^{16}
ZnO with 1% Ga physical mixture	9.175×10^{15}
ZnO with 1% Ga coprecipitation	1.967×10^{16}

As was expected from the CH_4 conversion plot earlier, the coprecipitated catalyst has the highest surface area normalised rate.

3.5 Discussion

3.5.1 Discussion for initial studies results

The coprecipitation of gallium oxide with elements with similar ionic radii at low levels produced interesting results. A feature of the coprecipitated catalysts is the large increase in surface area when compared to the unmodified catalyst. There is no decrease in the light-off temperature for CH_4 activation upon the addition of these dopants. At lower temperatures, all the gallium based catalysts have similar CH_4 conversion, but at higher temperatures the conversion of the 1wt% Mg catalyst does significantly drop. Due to the higher surface areas of the coprecipitated catalysts, when the reaction rates are normalised for surface area, the coprecipitated catalysts are not as high as the gallium oxide catalyst. With the exception of the 1 wt% Mg catalyst all had similar activation energies. It can be deduced that the addition of the dopants certainly has an effect on the structure of the gallium oxide lattice, significantly raising the surface area of the catalysts. However, their addition does not increase the CH_4 activation properties of the catalyst. This can lead us to the conclusion that defects are more than likely created within the gallium oxide lattice by coprecipitation, but they are not beneficial for CH_4 activation.

It must be noted that the results in this section are different to those previously published [5,6]. The results published in these papers were the initial results. Upon further synthesis of the catalysts for repeat experiments the surface areas of the Ga_2O_3 were different, falling from the 60 m^2g^{-1} in the paper to 40 m^2g^{-1} in the results quoted here. This was also true for the 1% Zn Ga_2O_3 which had a surface area of 16 m^2g^{-1} for the paper, and this was 58 m^2g^{-1} in repeat experiments.

3.5.2 Discussion for Zn/Ga_2O_3 catalysts

In the same manner as in section 3.2, coprecipitation raises the surface area of the gallium oxide catalyst, which may be a structural promotional effect. At Zn levels of 5 wt% there are no Zn peaks visible on the XRD pattern of the catalyst. All but one of the gallium oxide catalysts have the same light-off temperature, with the 5 wt% exhibiting CH_4 activation at a slightly lower temperature. Due to the higher surface areas of the coprecipitated catalysts, the surface normalised rates are lower than gallium oxide. Apart from the slightly higher activation energy of the 5 wt% Zn, all the coprecipitated gallium oxide catalysts are in a similar range. Raising the level of Zn addition by coprecipitation, in an attempt to create more defects, does create a catalyst with a lower light off temperature, and higher CH_4 conversion at low temperatures. It seems that a higher wt% of dopant is required, maybe to create a higher number of defects, before gallium oxides CH_4 activation properties are enhanced. The physical mixture of ZnO into gallium oxide lowers the surface area of the catalyst, at higher levels by a signifant amount. All exhibited the same light-off temperature. For CH_4 conversion it seems the addition of ZnO suppresses activity, with larger amounts of ZnO suppressing the activity further. However, due to their lower surface areas, the normalised rates are higher, but are not representative of activity.

3.5.3 Discussion for Ga/ZnO catalysts

Coprecipitation of Ga into ZnO raises the surface area of catalysts, with some Ga peaks visible in the XRD pattrern of the 10 wt% ZnO catalyst. The coprecipitation of Ga into ZnO lowers the light-off temperatures to the same levels as gallium oxide. At lower temperatures, the 10% Ga coprecipitated catalyst has higher CH_4 activation properties, but at higher temperatures the 1 wt% has higher activity. There is a significant effect with the coprecipitation of Ga into ZnO at levels as low as 1 wt%, exhibiting high activity and low surface area. The activation energies of the coprecipitated catalysts are also much lower. With the physical mixture catalysts the rise in surface area is much less, however the light-off temperatures are also the same as the gallium oxide catalyst. The addition of Ga_2O_3 increases the CH_4 conversion of ZnO, but not to the same extent as by coprecipitation. The addition of more Ga_2O_3 to the ZnO increases the CH_4 conversion, and also low additions of Ga_2O_3 decrease the activation energy. In comparison of the addition of Ga to ZnO catalysts, by coprecipitation or physical mixture, the coprecipitated catalysts show much higher CH_4 conversion. Therefore it could be concluded that the coprecipitation of Ga with ZnO has a structural promotional effect, which may be due to the creation of defects within the catalyst. However, if previous studies involving doping ZnO, by Sojka [4], are correct, it may be that the ZnO has low activity, and acts as a relatively low surface area support, with the supported Ga responsible for CH_4 activation. This may explain why the coprecipitated Ga/ZnO catalysts have higher CH_4 activity, in the same region as that of Ga_2O_3.

3.6 Conclusions

For Ga_2O_3 the addition of Zn by coprecipitation does not significantly affect the CH_4 activation properties when compared to the unmodified catalyst. The addition of Zn by coprecipitation at lower loadings produce catalysts with the same activation as the unmodified gallium oxide catalyst. The addition of ZnO by physical mixture at a loading of 1wt% does not greatly affect the catalysts activation properties, however, at higher concentrations it begins to inhibit CH_4 conversion. These studies show that the physical mixing of ZnO into Ga_2O_3 does in fact significantly reduce its activation properties, which is not the case when Zn is coprecipitated into Ga_2O_3. The addition of Zn into Ga_2O_3 by coprecipitation, even at percentages as low as 1 wt.%, increases the surface area of the Ga_2O_3 considerably, therefore it seems that coprecipitation has a significant structural effect on Ga_2O_3.

For ZnO, the addition of Ga_2O_3 into the catalyst improves its CH_4 conversion capabilities, especially if the addition is done by coprecipitation. However the addition of Ga_2O_3 just by physical mixture greatly improves its CH_4 conversion properties. Coprecipitation increases the surface area and lowers the activation energy of the catalysts, to a much higher extent than by physical mixture.

Therefore the addition of another element, with a similar ionic radius to zinc, by coprecipitation does in fact improve the catalysts CH_4 activation properties, by increasing its surface area, increasing its CH_4 conversion, and at the right loading lowering its light off temperature. Due to the comparison of similar loadings by different preparation methods, it can be concluded that coprecipitation, maybe through the creation of defects, has a promoting effect on the structure of the catalyst, for the zinc catalysts. However it may be that the ZnO has low activity, and acts as a relatively low surface area support, with the supported Ga responsible for CH_4 activation.

3.7 References

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Chapter 4

Methane Activation Using Precious Metal Modified Catalysts

4.1 Introduction

As was explained more fully in section 3.1, the activation of the C-H bond at the lowest possible temperature is one of the major aims for a successful and selective CH_4 catalyst. The activation at lower temperatures is preferable as then the majority of the reaction will occur on the surface of the catalyst, so the product selectivity can be better controlled. Lower temperatures are also preferable, as at higher temperatures there tend to be a lot more gas-phase reactions. This is due to the activated CH_4 leaving the surface of the catalyst, usually as a methyl radical, resulting in gas phase reactions controlling product selectivity, not the catalyst. In this study the activation ability of the catalyst tested is measured by at which temperature 0.01% conversion was recorded. This is known as the catalysts light off temperature.

As also described in section 3.1, previous studies have indicated that the metal oxides Ga_2O_3 and ZnO have demonstrated good ability for CH_4 activation, using the CH_4/D_2 exchange reaction as a design tool. The purpose of finding a catalyst with a low light off temperature is to find a suitable CH_4 activation component of a mixed metal oxide catalyst.

In the search for catalysts that would activate CH_4 at low temperatures, catalysts that are known for their low temperature CO oxidation have been investigated. Among these were catalysts with highly dispersed Au nanoparticles on oxide supports. A catalyst preparation was found that produced highly dispersed Au particles on ZnO, which resulted in highly active CO oxidation catalysts [1]. This preparation method was adopted for the Au modified catalysts used in this study. Previous studies on CH_4 activation with Au modified catalysts, by Waters et al [2] have produced catalysts with low light off temperatures. A range of Au modified metal oxides were tested, including Co_3O_4, NiO, MnO_x, Fe_2O_3 and CeO_2. Apart from Waters' study the use of Au modified catalysts has not been widely studied.

Other precious metals have been identified with the activity to activate CH_4 at low temperatures, namely Pd [3], and the use of Pt crystals under UHV conditions [4]. In a follow up to Waters' study on Au modified catalysts, where Au modified Co_3O_4 exhibited the lowest light off temperature, other precious metals, namely Pt and Pd, were also added with Au to create catalysts with even lower light off temperatures [5]. The addition of Au and Pt to Co_3O_4 at low wt% levels produced catalysts with lower light off temperatures than the singly modified oxides.

The experiments in this chapter were carried out at atmospheric pressure in order to reduce the effect of gas phase reactions. Gas phase reactions influenced by the reactor tube walls were not significant for these experiments as CH_4 conversion was only detected above the temperature of 500°C in blank runs. The catalysts tested in this chapter were not calcined, but were thoroughly dried. Because of this, the catalysts were repeatedly tested for CH_4 oxidation to see if subsequent runs were different from the initial run. Some of these results have been published in a paper by this group [6].

4.2 Gallium Based catalysts

4.2.1 Au Modified Catalysts

For the catalysts used in this study the bulk phases identified by XRD and the BET surface areas are shown in table 4.2.1. The surface areas (S_{BET}) for the gallium catalysts were all relatively low and of similar magnitude. Before reaction the phase identified by XRD was GaO(OH), gallium sub-oxide, and this was converted to β-Ga_2O_3 after use. There was no evidence from diffraction for metallic Au crystallites.

Table 4.2.1 Results of BET surface area and phases identified by powder X-ray diffraction.

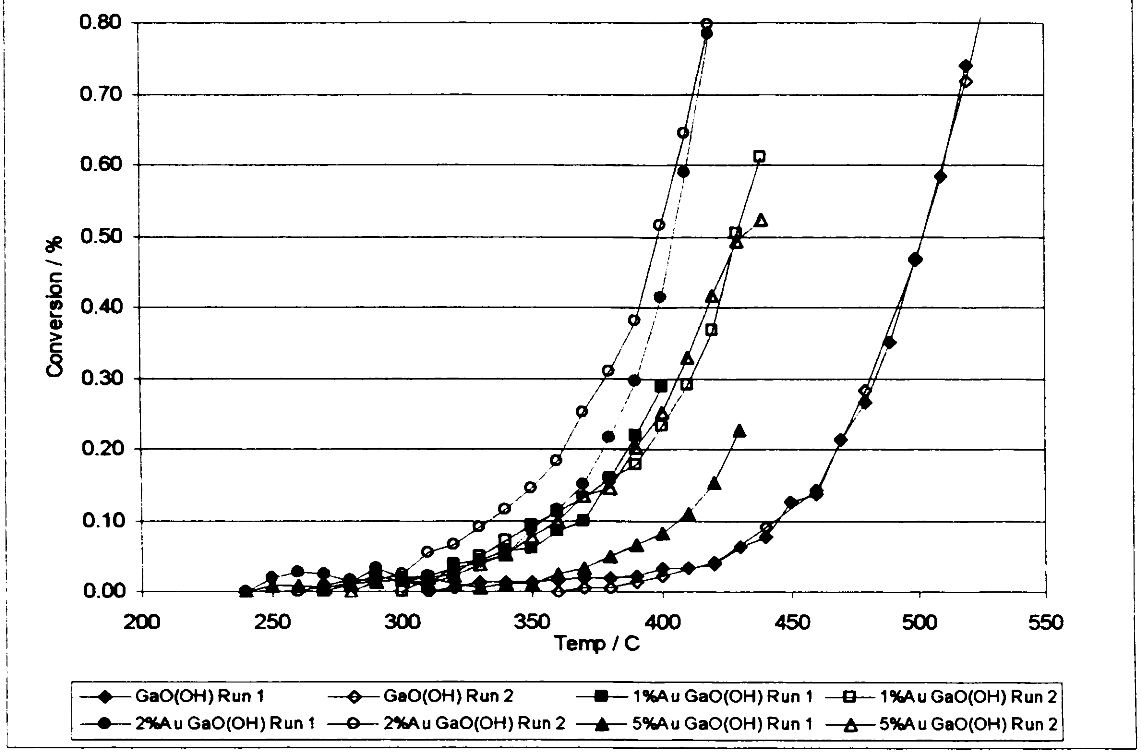
Catalyst	$S_{BET}/m^2\ g^{-1}$	Phases identified by XRD	
		As synthesised	After use
GaO(OH)	7	GaO(OH)	β-Ga_2O_3
1%Au GaO(OH)	3	GaO(OH)	β-Ga_2O_3
2%Au GaO(OH)	7	GaO(OH)	β-Ga_2O_3
5%Au GaO(OH)	10	GaO(OH)	β-Ga_2O_3

Maximum Error ± 10%

Data representative of the CH_4 oxidation over the Au modified and unmodified Ga catalysts are shown in figure 4.1. The order of activity for the initial runs for these catalysts was:

2%Au GaO(OH) > 1%Au GaO(OH) > 5%Au GaO(OH) > GaO(OH)

Figure 4.1 Methane Conversion plot for uncalcined Au modified GaO(OH) catalysts



The modification of the gallium catalysts by the addition of Au lowered the light off temperature. The amount of Au added influenced the light off temperature, with the 2% loading having the lowest, followed by the 5% then the 1% loading. After the initial test, the catalyst was allowed to cool and the experiment was repeated. It can be seen that for all catalysts that the light off temperature for the successive runs all increased. The light off temperatures for the initial and successive runs are displayed in table 4.2.2

The activation energies for all the gallium catalysts in the initial studies, shown in table 4.2.3, were in a similar range, around 120kJ mol^{-1}. For the unmodified gallium catalyst, the activation energy increased for successive temperature cycles, while the Au modified catalysts decreased after successive runs. The final activation energies for the modified catalysts were broadly similar.

Table 4.2.2. Light-off temperatures for Au modified gallium catalysts

Catalyst	Light off temperature/°C	
	Initial run	Successive runs
GaO(OH)	320	340
1%Au GaO(OH)	270	300
2%Au GaO(OH)	250	270
5%Au GaO(OH)	260	290

Maximum error ±9 °C

Table 4.2.3 Activation energies for Au modified gallium catalysts (Errors ± 8 kJ mol^{-1})

Catalyst	Activation energy/kJ mol^{-1}	
	Initial run	Successive runs
GaO(OH)	118	123
1%Au GaO(OH)	115	102
2%Au GaO(OH)	124	90
5%Au GaO(OH)	120	89

4.2.2 Pt Modified Catalysts

The bulk phases identified by XRD and the BET surface areas for the Au/Pt modified gallium catalysts are shown in table 4.2.4. Similarly to the Au modified catalysts the surface areas (S_{BET}) were all relatively low and of similar magnitude. Before reaction the phase identified by XRD was GaO(OH), gallium sub-oxide, and this was converted to β-Ga_2O_3 after use. Again there was no evidence from diffraction for metallic Au or Pt crystallites.

Table 4.2.4 Results of BET surface area and phases identified by powder X-ray diffraction.

Catalyst	$S_{BET}/m^2 g^{-1}$	Phases identified by XRD	
		As synthesised	After use
GaO(OH)	7	GaO(OH)	β-Ga_2O_3
1%Pt GaO(OH)	3	GaO(OH)	β- Ga_2O_3
1%Au 1%Pt GaO(OH)	4	GaO(OH)	β- Ga_2O_3
2%Au 2%Pt GaO(OH)	6	GaO(OH)	β- Ga_2O_3

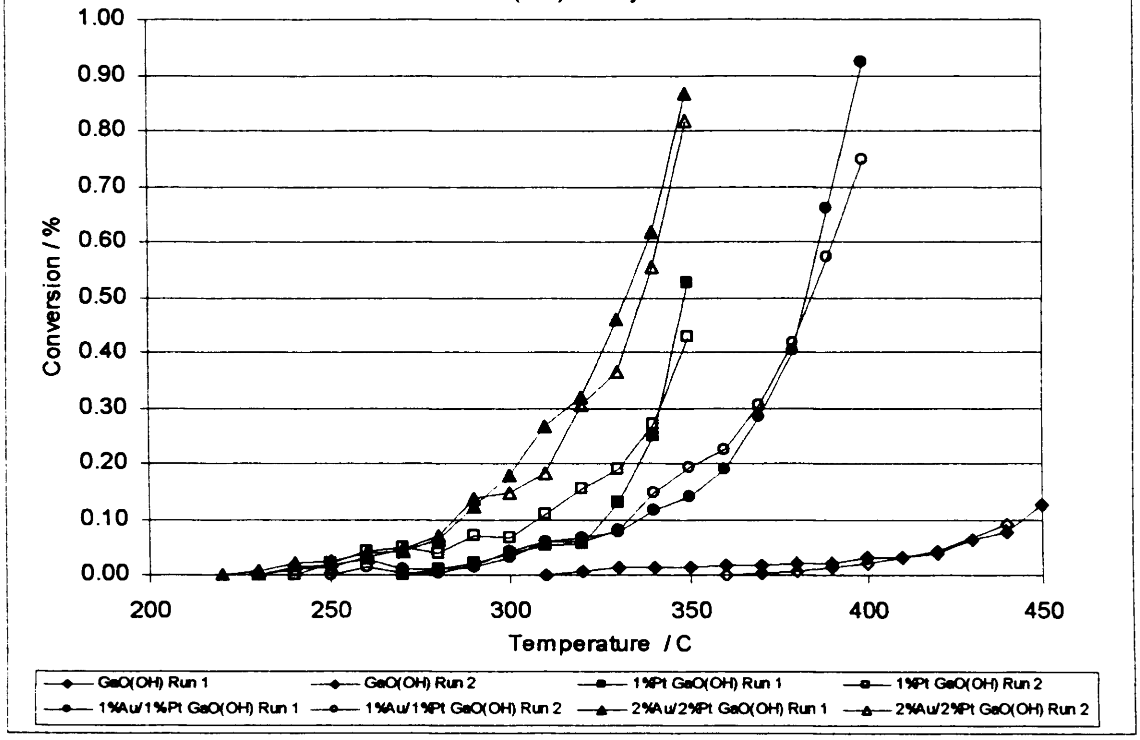
Maximum Error ± 10%

Data representative of the CH_4 oxidation over the Pt and Pt/Au modified and unmodified Ga catalysts are shown in figure 4.2. The order of activity at lower conversions for the initial runs was:

2%Au 2%Pt Ga > 1%Pt Ga > 1%Au 1%Pt Ga > GaO(OH)

As the temperatures rose, the catalysts containing Pt had a large jump in conversion, to total oxidation. The 1%Pt catalyst exhibited total CH_4 conversion at 360°C, with the 2%Au 2%Pt catalyst exhibiting total conversion at 390°C. Data displaying the large jumps in oxidation for the Pt catalysts are displayed in figure 4.3.

Figure 4.2 Methane Conversion Plot for uncalcined Pt and Pt/Au modified GaO(OH) Catalysts



For the initial runs, the Pt/Au modified catalysts showed a large decrease in light off temperature in comparison to the unmodified gallium catalyst, shown in table 4.2.5. The 1% Pt catalyst also showed a drop in light off temperature, but to a lesser degree. In successive runs, like the unmodified gallium catalyst, the 1% Au 1% Pt catalyst and the 2% Au 2% Pt catalyst had a higher light off temperature. The 1% Pt catalyst had a lower light off temperature, but still did not have as low an activation temperature as the 2% Au 2% Pt catalyst, which retained its low activation temperature. The light off temperature for the 2% Au 2% Pt GaO(OH) was 100°C lower than for the unmodified GaO(OH) catalyst. The light off temperatures for the Pt modified gallium catalysts are displayed in table 4.2.5

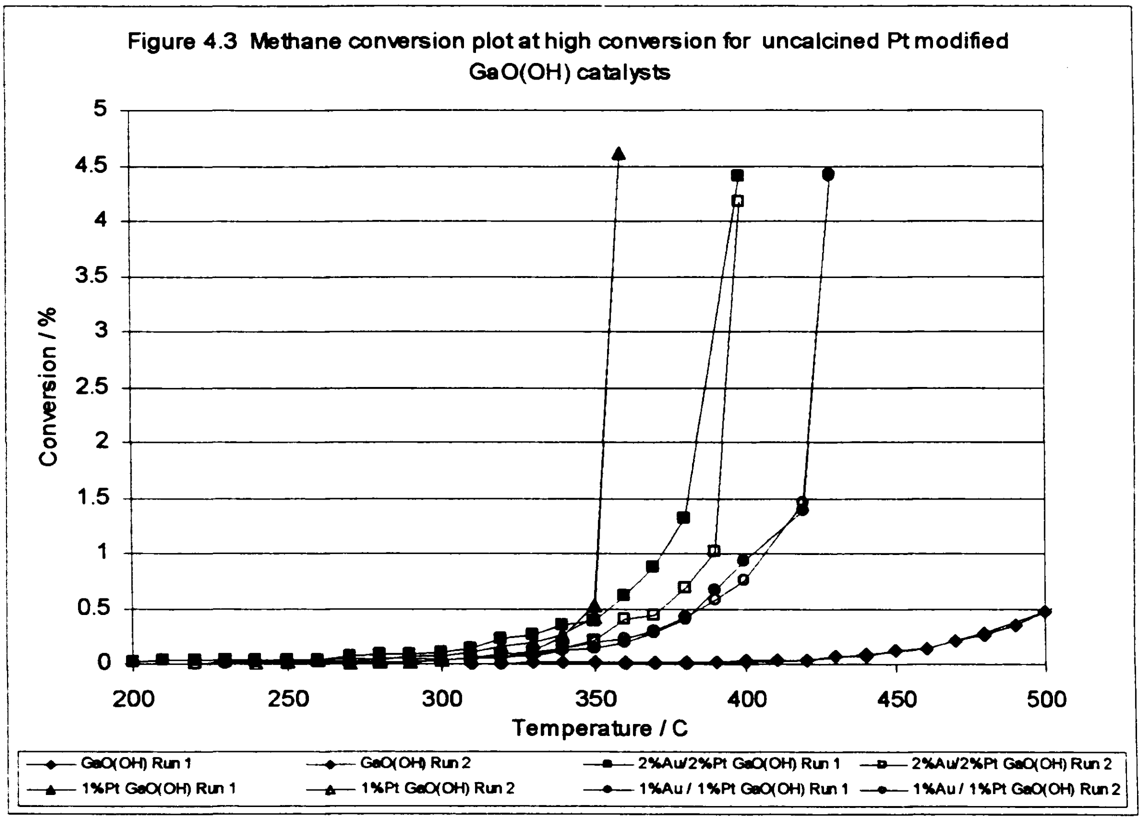


Figure 4.3 Methane conversion plot at high conversion for uncalcined Pt modified GaO(OH) catalysts

Table 4.2.5 Light-off temperatures for Pt and Au/Pt modified gallium catalysts

Catalyst	Light off temperature/°C	
	Initial run	Successive runs
GaO(OH)	320	340
1%Pt GaO(OH)	280	250
1%Au 1%Pt GaO(OH)	260	280
2%Au 2%Pt GaO(OH)	230	240

Maximum error ±9 °C

The activation energies for the Pt modified gallium catalysts are shown in table 4.2.6. The 2%Au 2%Pt GaO(OH) catalyst, with the lowest light off temperature, also had the lowest initial run activation energy, at 95 kJ mol^{-1}. The other two Pt modified catalysts had similar initial activation energies, both higher than the unmodified catalyst. On successive runs all the modified catalysts had lower activation energies, with the 2%Au 2%Pt GaO(OH) again being the lowest, and the other two modified catalysts again were in a similar range to each other.

Table 4.2.6 Activation energies for Pt and Au/Pt modified gallium catalysts (Errors ± 8 kJ mol^{-1})

Catalyst	Activation energy/kJ mol^{-1}	
	Initial run	Successive runs
GaO(OH)	118	143
1%Pt GaO(OH)	144	105
1%Au 1%Pt GaO(OH)	137	102
2%Au 2%Pt GaO(OH)	95	88

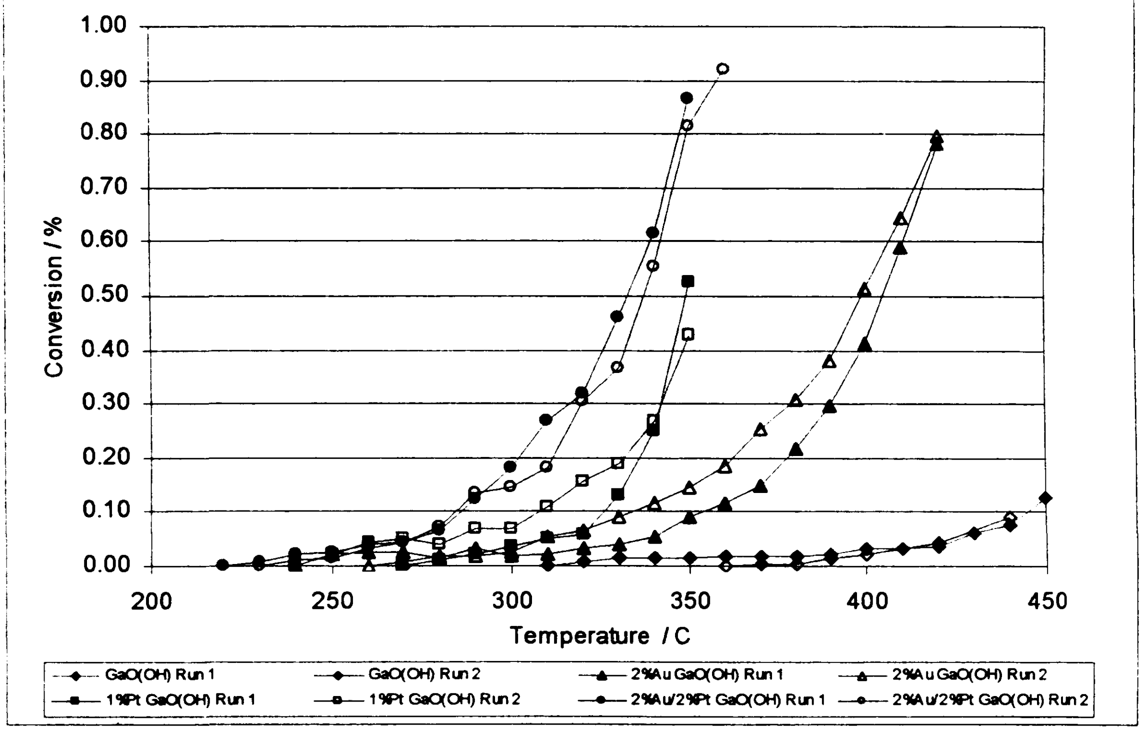
4.2.3 Comparison of Gallium Based Catalysts

The addition of precious metals to the gallium system did not significantly change the surface area of the uncalcined catalysts, and all of the catalysts were GaO(OH) previous to use. However, the modification of gallium oxide with precious metals resulted in a significant change in the catalysts oxidation properties. For the most impressive modified gallium catalysts, this included lower light off temperatures, lower activation energies and higher CH_4 oxidation abilities at lower temperatures. All the modified catalysts, with Au, Pt and Au/Pt respectively had higher methane oxidation rates. The addition of Pt promoted the rate of oxidation to a significant extent, but was not as active as the 2%Au 2%Pt catalyst. The order of activity at lower conversions for the most impressive uncalcined gallium based catalysts was:-

2%Au/2%Pt GaO(OH)>1%Pt GaO(OH)>1%Au/1%Pt GaO(OH)>2%Au GaO(OH)>GaO(OH)

However, above certain temperatures, for the catalysts containing Pt, there was a huge jump in conversion, from levels of 1.5% conversion to 4.5% conversion upon the raising of the temperature by just 10°C. Data representative of CH_4 oxidation over the most impressive uncalcined catalysts at low conversion; unmodified gallium, Au modified, Pt modified and Pt/Au modified gallium catalysts are shown in figure 4.4.

Figure 4.4 Methane Conversion plot for most impressive uncalcined Au, Pt and Pt/Au modified GaO(OH) catalysts



After initial testing, the catalysts were then re-run again, and for the uncalcined catalysts this resulted in a general rise in light off temperatures. The only exception was the 1% Pt gallium catalyst, as this then had a 30°C reduction in the light off temperature for successive runs when compared to the initial runs light off temperature, going from 280°C in the initial run to 250°C in successive runs. The modification of the gallium catalysts by the addition of Pt or Au, or Pt and Au, lowered the light off temperatures significantly. The Au loading influenced the light off temperature, with 1% and 5% Au having not as low a light off temperature as the 2% Au gallium catalyst, 250°C in the initial run rising to 270°C in successive runs. The addition of Au and Pt at the same time produced a catalyst with a lower light off temperature than by the addition of Au and Pt separately, with the 2%Au 2%Pt catalyst having an initial light off temperature of 230°C, only rising to 240°C in later runs. This was a drop of over 100°C when compared to the unmodified catalyst.

The initial activation energies for the uncalcined catalysts, determined at low conversion to minimise concentration gradients through the catalyst bed, for the unmodified and Au modified gallium catalyst were similar, in the range of 120kJ mol^{-1}. After successive temperature cycles the activation energy of the unmodified catalyst rose, and the Au modified catalysts activation energies rose. Apart from the low activation energy for the 2% Au 2% Pt catalyst, at 95kJ mol^{-1}, the addition of Pt and Pt/Au raised the initial activation energy. For successive temperature cycles, all the modified catalysts exhibited similar activation energies, much lower than that of the unmodified gallium catalyst.

4.3 Zinc Based Catalysts

4.3.1 Au Modified Catalysts

The surface area of the precipitated ZnO was increased by the addition of the precious metal. With the exception of the 1% Au ZnO catalyst the modified ZnO catalysts had similar surface areas. With these catalysts there was no change of phase identified between the as synthesised and the catalyst after repeated use.

Table 4.3.1 Results of BET surface area and phases identified by powder X-ray diffraction.

Catalyst	$S_{BET}/m^2\ g^{-1}$	Phases identified by XRD	
		As synthesised	After use
ZnO	4	ZnO	ZnO
1% Au ZnO	11	ZnO	ZnO
2% Au ZnO	22	ZnO	ZnO
5% Au ZnO	26	ZnO	ZnO

Maximum Error ± 10%

Data representative of the CH_4 oxidation over the Au modified and unmodified ZnO catalysts are shown in figure 4.5. The order of activity for the initial runs for these catalysts was:-

2%Au ZnO > 1%Au ZnO > 5%Au ZnO > ZnO

After the initial test, the catalyst was allowed to cool and the experiment was repeated. It can be seen that for most catalysts that the light off temperature for the successive runs all increased. The 2%Au ZnO catalyst had the lowest initial and successive light off temperature of the range, 100°C lower than the unmodified ZnO and a minimum of 40°C lower than the other Au modified catalysts.

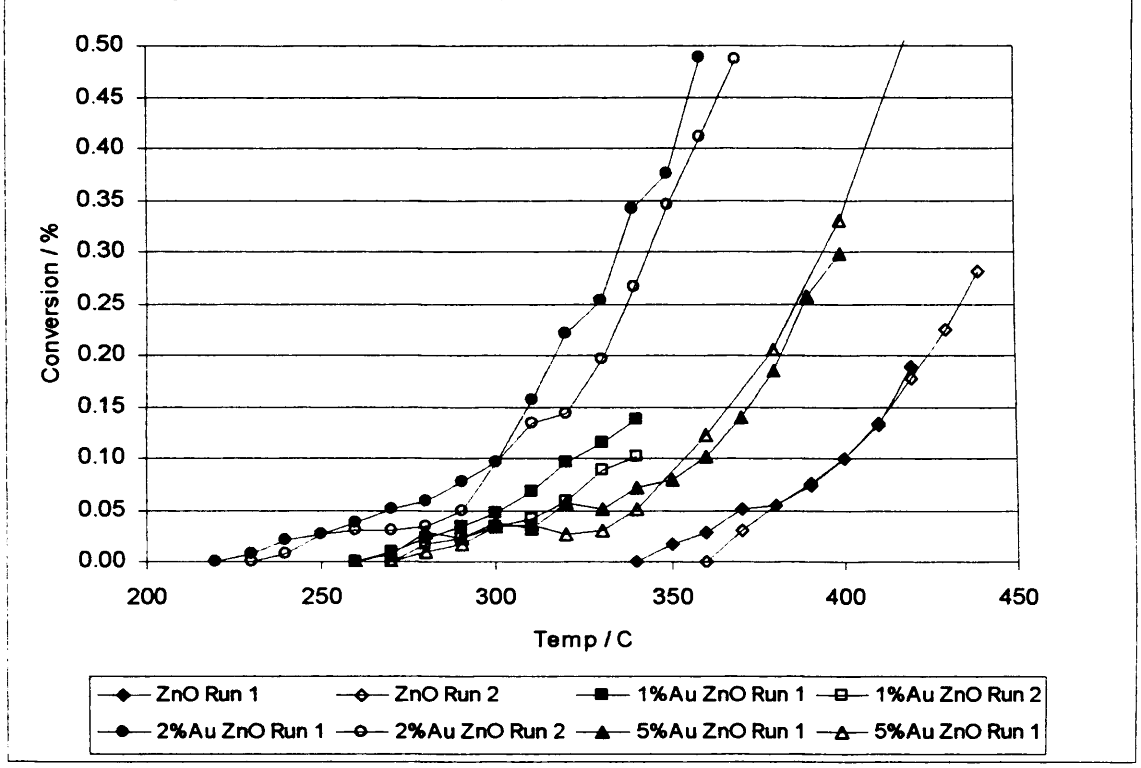


Figure 4.5 Methane Conversion plot for uncalcined Au modified ZnO catalysts

Table 4.3.2 Light-off temperatures for Au modified ZnO catalysts

Catalyst	Light off temperature/ °C	
	Initial run	Successive runs
ZnO	340	360
1% Au ZnO	270	280
2% Au ZnO	230	240
5% Au ZnO	270	270

Maximum error ±9 °C

Modification of ZnO with 1%Au had little effect on the activation energy of the catalyst, but the addition of higher Au loadings had a much bigger effect. The 5% Au catalyst exhibited a drop of approximately 20kJ mol^{-1} over both runs, whilst the 2% was 50kJ mol^{-1} lower than the unmodified catalyst on the first run, and just under 40kJ mol^{-1} on successive runs.

Table 4.3.3 Activation energies for Au modified ZnO catalysts (Errors ± 8 kJ mol^{-1})

Catalyst	Activation energy/kJ mol^{-1}	
	Initial run	Successive runs
ZnO	120	116
1% Au ZnO	117	127
2% Au ZnO	70	82
5% Au ZnO	102	91

4.3.2 Pt Modified Catalysts

The surface area of the precipitated ZnO was increased by the addition of the gold and platinum. The modification of zinc oxide with Pt, and also mixed with Au, resulted in a large increase in the surface area of the catalysts, and the modified ZnO catalysts had similar surface areas. With these catalysts there was no change of phase identified between the as synthesised and the catalyst after repeated use.

Table 4.3.4 Results of BET surface area and phases identified by powder X-ray diffraction.

Catalyst	$S_{BET}/m^2\ g^{-1}$	Phases identified by XRD	
		As synthesised	After use
ZnO	4	ZnO	ZnO
1%Pt ZnO	20	ZnO	ZnO
1%Au 1%Pt ZnO	19	ZnO	ZnO
2%Au 2%Pt ZnO	23	ZnO	ZnO

Maximum Error ± 10%

Data representative of the CH_4 oxidation over the Pt and Pt/Au modified and unmodified ZnO catalysts are shown in Figure 4.6. The order of activity at lower conversions for the initial runs was:-

2%Au 2%Pt ZnO > 1%Pt ZnO > 1%Au 1%Pt ZnO > ZnO

As the temperatures rose, the catalysts containing Pt had a large jump in conversion, to total oxidation. The 1%Au 1%Pt catalyst exhibited total CH_4 conversion at 370°C, with the 2%Au 2%Pt catalyst exhibiting total conversion at 390°C. Data displaying the large jumps in oxidation for the Pt catalysts are displayed in figure 4.7.

Figure 4.6 Methane conversion plot for uncalcined Pt and Pt/Au modified ZnO catalysts

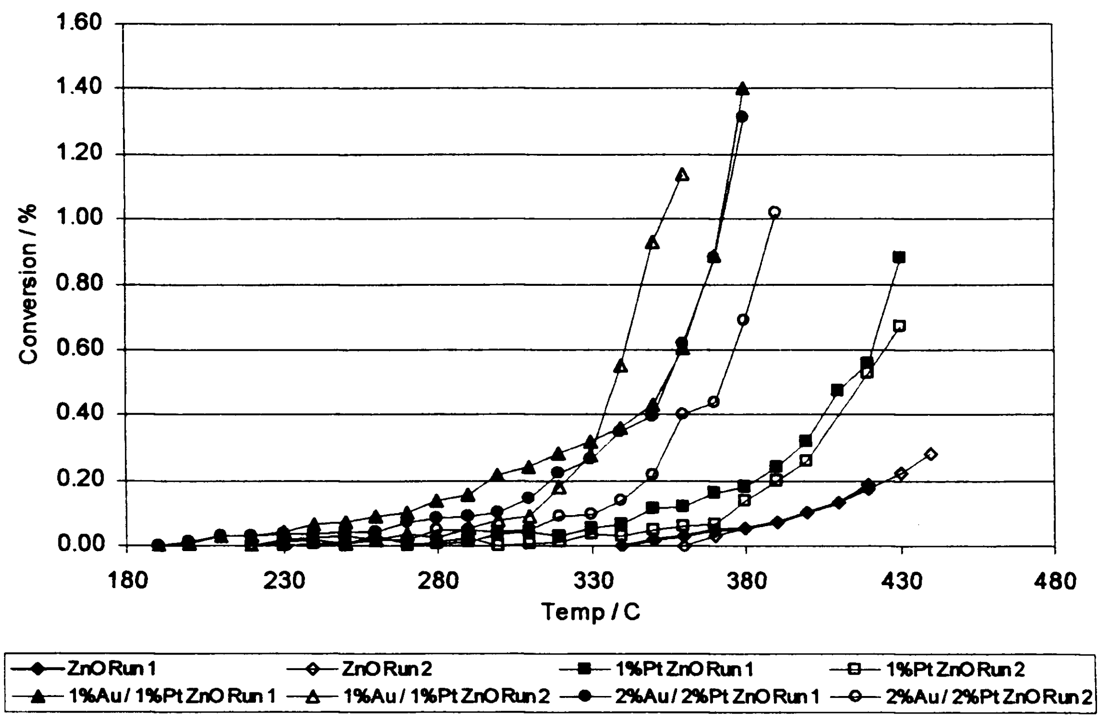
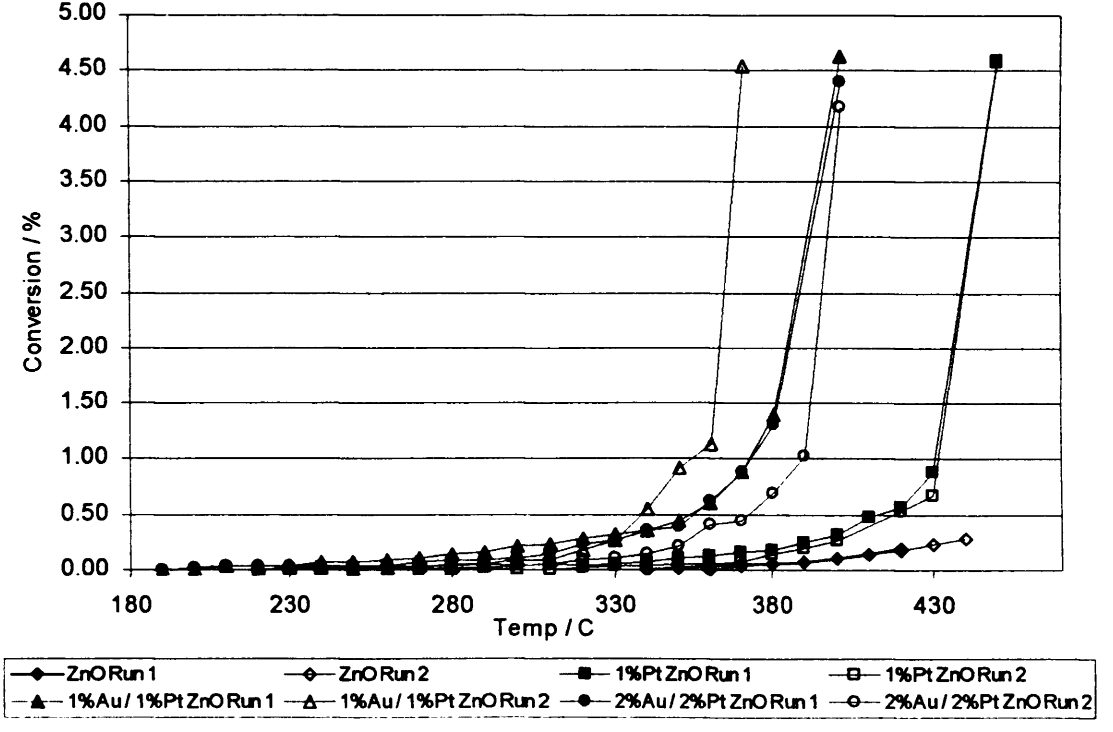


Figure 4.7 Methane conversion plot for high conversions for Pt and Au/Pt modified ZnO catalysts



As would be expected, the modification of ZnO with 1% Pt resulted in a large decrease of the light off temperature when compared to the unmodified catalyst, in this case 100K lower on the initial run, and 80K lower on successive runs. However, the modification of ZnO with 1% Au and 1% Pt, and also with 2% Au and 2% Pt, resulted in a decrease in light off temperature of 140°C lower on the initial run, and 120°C on successive runs. The light off temperatures for the initial and successive runs are displayed in table 4.3.5.

Table 4.3.5 Light-off temperatures for Pt and Au/Pt modified ZnO catalysts

Catalyst	Light off temperature/ °C	
	Initial run	Successive runs
ZnO	340	360
1%Pt ZnO	240	280
1%Au 1%Pt ZnO	200	230
2%Au 2%Pt ZnO	200	230

Maximum error ±9 °C

Although the modification of ZnO with 1% Pt increased surface area, and lowered the light off temperature of the catalyst, it resulted in a very similar activation energy in initial and successive runs when compared to the unmodified ZnO catalyst. The ZnO catalysts modified with a mixture of Au and Pt had much lower activation energies, over both initial and successive runs. The 2%Au 2%Pt catalyst had the lowest activation energy, at 42kJ mol^{-1} for all runs, approximately 80kJ mol^{-1} lower than the unmodified catalyst.

Table 4.3.6 Activation energies for Pt and Au/Pt modified ZnO catalysts (Errors ± 8 kJ mol^{-1})

Catalyst	Activation energy/kJ mol^{-1}	
	Initial run	Successive runs
ZnO	120	116
1%Pt ZnO	117	127
1%Au 1%Pt ZnO	54	62
2%Au 2%Pt ZnO	42	42

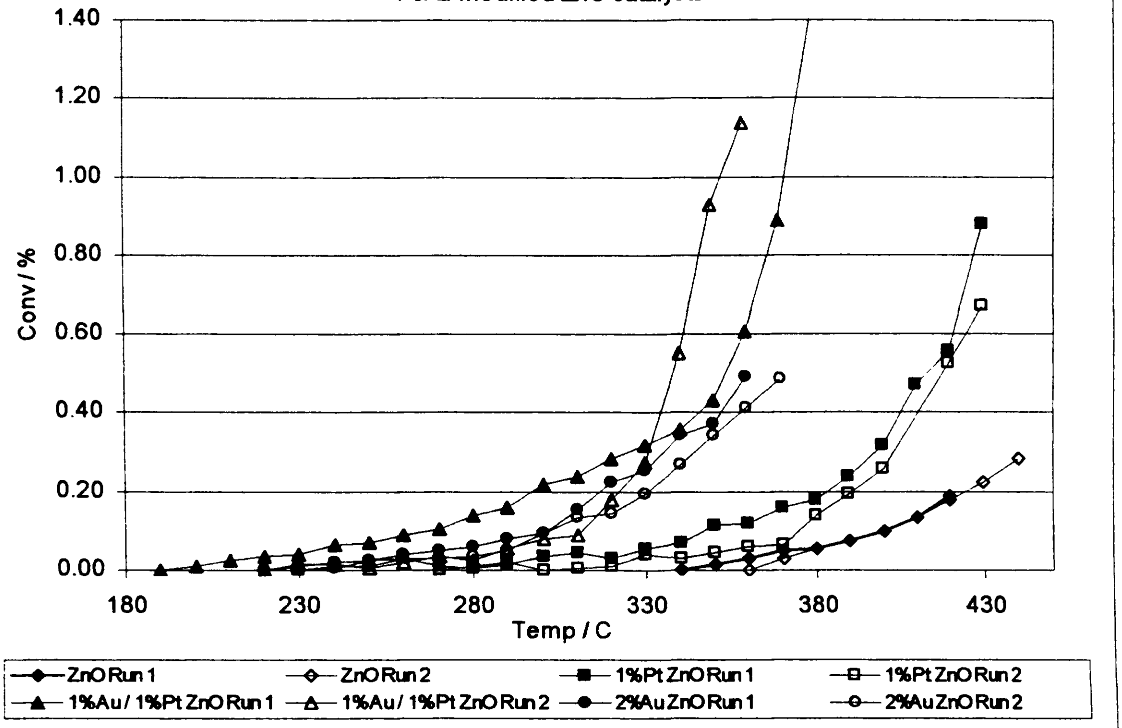
4.3.3 Comparison of Zinc Based Catalysts

For the uncalcined catalysts, the surface area of the precipitated ZnO was increased by the addition of the precious metals. With the exception of the 1% Au ZnO catalyst all the modified ZnO catalysts had similar surface areas. With the zinc based catalysts there was no change of phase identified between the as-synthesised and the catalyst after repeated use.

Representative data for CH_4 oxidation over zinc and the most impressive uncalcined modified zinc catalysts are presented in Figure 4.8. The addition of the precious metals increased the rate of CH_4 oxidation relative to the unmodified zinc catalyst. The order of activity of the catalysts was:

1% Au 1% Pt ZnO > 2% Au ZnO > 1% Pt ZnO > ZnO

Figure 4.8 Methane conversion plot for most impressive uncalcined Au, Pt and Pt/Au modified ZnO catalysts



The addition of Pt did not result in such a dramatic increase of the oxidation rate as the other modified catalysts. The addition of Au resulted in a greater increase in the rate of oxidation. However, the simultaneous addition of Au and Pt resulted in the greatest increase of CH_4 oxidation rate. Above certain temperatures, for the catalysts containing Pt, there was a huge jump in conversion, from levels of 1.5% conversion to 4.5% conversion upon the raising of the temperature by just 10°C.

In regard to the light off temperatures for CH_4 oxidation of the uncalcined catalysts, the addition of precious metals all had an effect, the addition of Pt lowered the initial light off temperature by 100°C when compared to the unmodified catalyst, which had a light off temperature of 240°C changing to 280°C lower in successive runs. The most impressive gold modified catalyst is the 2%Au ZnO catalyst, and that has an initial light off temperature 110°C lower, rising to 120°C lower on following runs.

The lowest light off temperature, however was exhibited by the 1%Au 1%Pt catalyst, with the initial light off temperature 140°C lower, with successive runs 130°C lower than the unmodified catalyst

The activation energy for the uncalcined unmodified ZnO catalyst remained constant between the initial and repeat temperature cycles. For the uncalcined catalysts, the introduction of gold on to the zinc catalyst reduced the activation energy for CH_4 activation, whilst the introduction of platinum alone had little effect. The most dramatic lowering of the activation energy was observed for the zinc based catalysts modified with both Au and Pt. For the 1% Au 1% Pt ZnO catalyst the activation energy was reduced by ca. 60 kJ mol^{-1} compared to the ZnO catalyst, and by the addition of 2% Au 2% Pt the energy required for CH_4 activation was lowered by approximately 80 kJ mol^{-1}. The combination of adding Au and Pt to the zinc catalyst was particularly interesting. The combination of both precious metals resulted in a synergistic enhancement of CH_4 activation.

4.4 Calcined Au modified catalysts

A sample of the same catalysts used in sections 4.2 and 4.3 were calcined in air at 500°C for 5 hours. These were then run in an identical manner to the uncalcined Au modified catalysts in the previous section.

4.4.1 Calcined Au Modified Ga_2O_3 Catalysts

The bulk phases identified by XRD and the BET surface areas are displayed in table 4.4.1. The same phase was identified before and after use, and this was the most stable phase of gallium oxide, β-Ga_2O_3.

Table 4.4.1 Results of BET surface area and phases identified by powder X-ray diffraction.

Catalyst	$S_{BET}/m^2\ g^{-1}$	Phases identified by XRD	
		As synthesised	After use
Ga_2O_3	40	β-Ga_2O_3	β-Ga_2O_3
1% Au Ga_2O_3	30	β-Ga_2O_3	β-Ga_2O_3
2% Au Ga_2O_3	38	β-Ga_2O_3	β-Ga_2O_3
5% Au Ga_2O_3	45	β-Ga_2O_3	β-Ga_2O_3

Maximum Error ± 10%

Data representative of the CH_4 oxidation over the Au modified and unmodified Ga catalysts are shown in figure 4.9. Due to the catalysts being pre heat treated, there was no difference between initial and successive runs. The order of activity for these catalysts was:-

$$2\%Au\ Ga_2O_3 > 1\%Au\ Ga_2O_3 > 5\%Au\ Ga_2O_3 \approx Ga_2O_3$$

Figure 4.9 Methane Conversion plot for calcined Au modified Ga2O3 catalysts

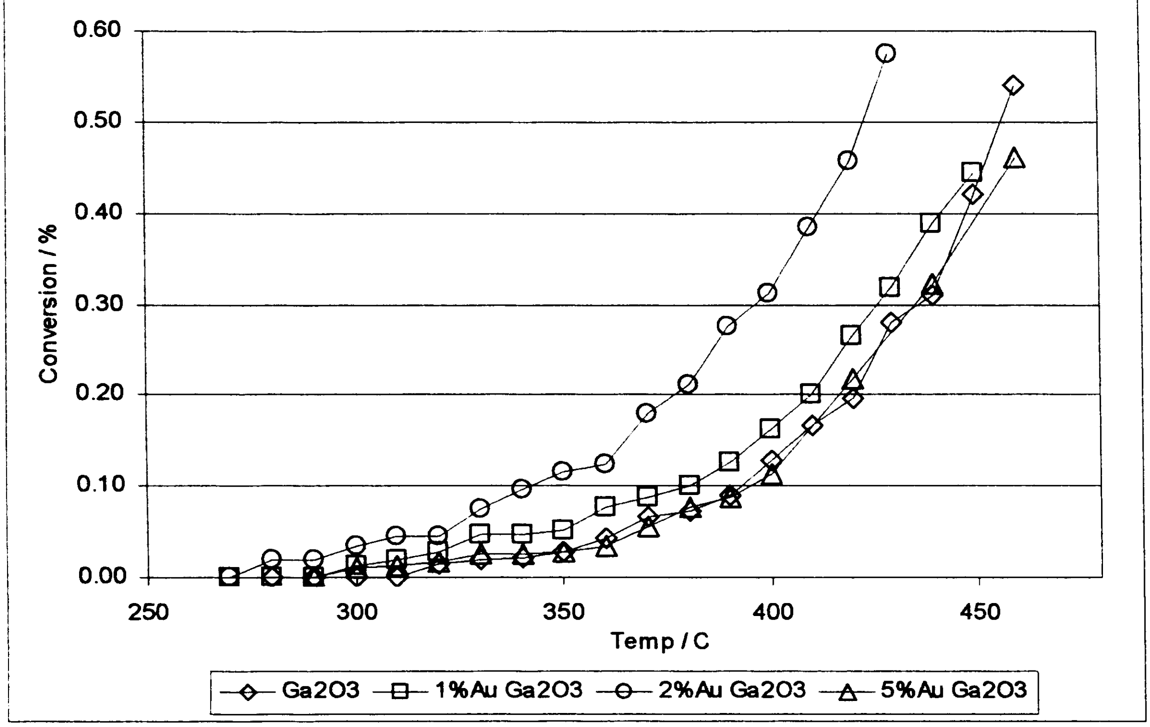


Table 4.4.2 Light off temperatures for calcined Au modified gallium catalysts

Catalyst	Light off temperature / °C	
	Initial run	Successive runs
Ga_2O_3	320	320
1% Au Ga_2O_3	300	300
2% Au Ga_2O_3	280	280
5% Au Ga_2O_3	300	300

Maximum error ±9 °C

As with the uncalcined modified catalysts, the addition of Au to Ga_2O_3 lowered the light off temperature of the catalyst, with the addition of 2%Au having the greatest effect, being 40K lower than the unmodified catalyst. There was no difference however between the light off temperatures for the initial run and the runs successive to that.

For the activation energies, in a similar trend to the light off temperatures, there was no great difference between the results for the initial and successive runs. Unlike the unmodified catalyst, there was a very slight rise in activation energy after the initial run, but these rises are all within experimental error. The catalyst with the lowest activation energy was the 2%Au gallium oxide catalyst.

Table 4.4.3 Activation energies for calcined Au modified gallium catalysts(Errors ± 8 kJ mol^{-1})

Catalyst	Activation energy/kJ mol^{-1}	
	Initial run	Successive runs
Ga_2O_3	123	121
1% Au Ga_2O_3	90	96
2% Au Ga_2O_3	75	81
5% Au Ga_2O_3	85	86

4.4.2 Calcined Au Modified ZnO Catalysts

A sample of the same catalysts tested in section 4.3 were calcined in air at 500°C for five hours. These were then run in an identical manner to the uncalcined Au modified catalysts. The bulk phases identified by XRD and the BET surface areas are shown in table 4.4.4. The same phase was identified both prior to and after use, and this was ZnO.

Table 4.4.4 Results of BET surface area and phases identified by powder X-ray diffraction.

Catalyst	$S_{BET}/m^2\ g^{-1}$	Phases identified by XRD	
		As synthesised	After use
ZnO	4	ZnO	ZnO
1% Au ZnO	36	ZnO	ZnO
2% Au ZnO	38	ZnO	ZnO
5% Au ZnO	42	ZnO	ZnO

Data representative of the CH_4 oxidation over the Au modified and unmodified ZnO catalysts are shown in figure 4.10. The order of activity for these catalysts was:-

5%Au ZnO > 2%Au ZnO > 1%Au ZnO > ZnO

In the same manner as the uncalcined catalysts, but not to the same degree, the modification of ZnO with Au lowered the light off temperatures of the catalysts. There was not much difference between the light off temperatures for the modified catalyst, with the 5%Au modified catalyst displaying the lowest, only 10°C lower than the next best, the 2%Au modified catalyst. For all the catalysts there were no significant changes for the light off temperatures between the initial light off temperature and the successive temperatures.

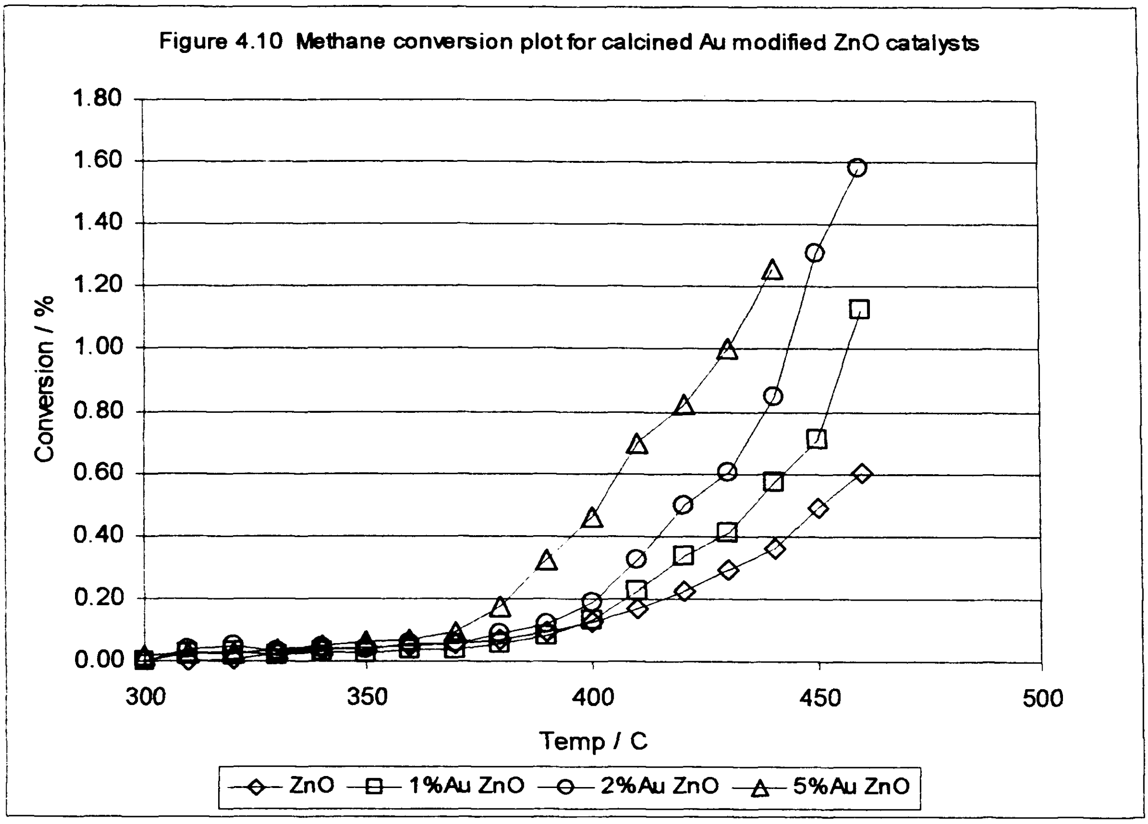


Table 4.4.5 Light off temperatures for calcined Au modified gallium catalysts

Catalyst	Light off temperature / °C	
	Initial run	Successive runs
ZnO	330	330
1% Au ZnO	300	310
2% Au ZnO	300	300
5% Au ZnO	290	290

Maximum error ±9 °C

Upon calculation of the activation energies for the catalysts, shown in table 4.4.6, the unmodified ZnO and the 1% and 2% Au catalysts exhibited similar values. The 5% Au catalyst however showed a lower activation energy, 40K lower than the unmodified catalyst, and this may contribute to the slightly lower light off temperature exhibited. Apart from the 5% Au catalyst, whose activation energy rose by a large amount in successive runs, all of the calcined ZnO showed a slight decrease in activation energy in successive runs.

Table 4.4.6 Activation energies for calcined Au modified zinc catalysts(Errors ± 8 kJ mol^{-1})

Catalyst	Activation energy/kJ mol^{-1}	
	Initial run	Successive runs
ZnO	120	116
1% Au ZnO	112	108
2% Au ZnO	123	105
5% Au ZnO	80	103

4.4.3 Calcined Au modified Fe_2O_3 catalysts

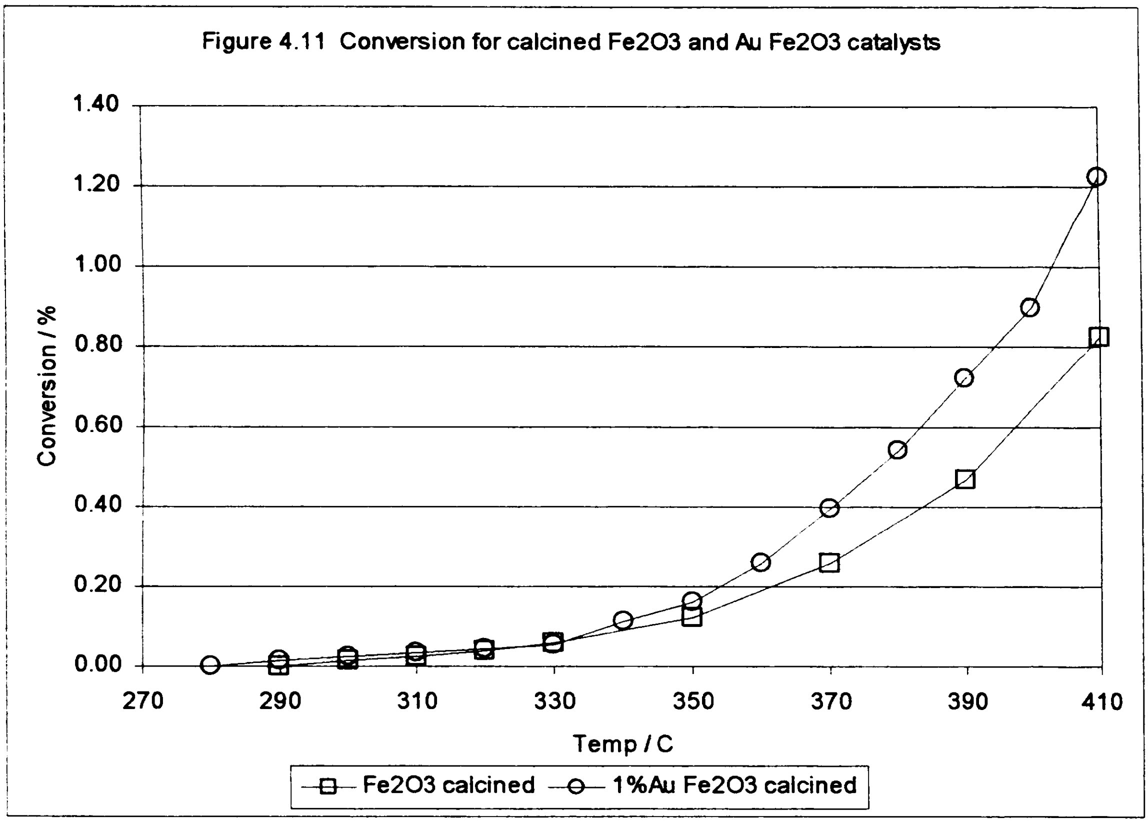
The addition of Au by coprecipitation to iron oxide slightly lowered the surface area compared to the unmodified catalyst.

Table 4.4.7 Results of BET surface area and phases identified by powder X-ray diffraction.

Catalyst	S_{BET}/m^2 g^{-1}	Phases identified by XRD	
		As synthesised	After use
Fe_2O_3	30	Fe_2O_3	Fe_2O_3
1% Au Fe_2O_3	28	Fe_2O_3	Fe_2O_3

Maximum Error ± 10%

Data representative of CH_4 conversion for the iron based catalysts is displayed in figure 4.11. This plot shows that at lower temperatures and conversions, the two catalysts have similar activity. However, above 330°C the CH_4 conversion of the Au modified catalyst rapidly to a higher level than the unmodified iron oxide catalyst.



The light off temperatures for the iron oxide catalysts are displayed in table 4.4.8. The addition of Au to iron oxide lowered the light off temperature of the catalyst, and the light off temperature was not any different on successive runs. There were small variations in the activation energies for initial and successive runs, but these were within experimental error. The modification of iron oxide with gold lowered the activation energy of the catalyst.

Table 4.4.8 Light off temperatures for calcined Au modified iron catalysts

Catalyst	Light off temperature °C	
	Initial run	Successive runs
Fe_2O_3	300	300
1% Au Fe_2O_3	270	270

Maximum error ±9 °C

Table 4.4.9 Activation energies for calcined Au modified iron catalysts(Errors ± 8 kJ mol^{-1})

Catalyst	Activation energy/kJ mol^{-1}	
	Initial run	Successive runs
Fe_2O_3	117	121
1% Au Fe_2O_3	110	106

4.5 Discussion

The activation of CH_4 was probed by studying CH_4 oxidation at ambient pressure over gallium and zinc based catalysts prepared by precipitation and modified with Au and Pt. The unmodified gallium and zinc based catalysts were both active for CH_4 oxidation. Under the reaction conditions typical for CH_4 oxidation, CH_4 activation by gallium oxide is not significantly better than the zinc based catalyst. In this study the light off temperature for the unmodified zinc catalyst was greater than the unmodified gallium catalyst, but only by a maximum of 20°C. These results are consistent with earlier studies investigating CH_4 activation using D_2 exchange [7].

The addition of Au to the zinc and gallium catalysts increased the oxidation activity. The low temperature activity for CO oxidation of highly dispersed Au nanoparticles on oxide supports has been extensively studied. The preparation method used in the present work is one that is known to produce highly dispersed Au particles on ZnO giving highly active CO oxidation catalysts [1]. The Au modified catalysts after use were of a vivid violet colour, indicating that highly dispersed small Au particles were in fact present. The promotion of CH_4 oxidation rate by adding Au to a series of metal oxides, including Co_3O_4, NiO, MnO, Fe_2O_3 and CeO_2, has been studied by Waters et al. [2]. These conclusions are consistent with our observations in this study. Waters et al. reported a correlation between the rate of CH_4 oxidation and the concentration of Au in an oxidised state. The redox behaviour of supported Au catalysts has been proposed as an important feature of the catalyst for ambient temperature CO oxidation, although surface hydroxyl species and defects at the junction between the metal particle and the oxide support are also thought to be a factor [8]. The use of Au catalysts for CH_4 oxidation has not been studied widely, but in addition to the Au oxidation state the Au particle size distribution and the interface region between Au particles and the support are also expected to be important factors influencing the effectiveness for CH_4 activation.

It is interesting to consider the change in catalyst activity between the initial and successive tests. The decrease in activity may simply be due to sintering of the active metal particles under the reaction conditions. However, the involvement of surface hydroxyl species at the interface between Au particles and the metal oxide support are implicated directly in the oxidation mechanism of CO [8]. Surface hydroxyl species have also been shown to promote alkane activation over other metal oxide catalysts

[9]. It is possible that the initial catalysts have a considerable surface concentration of hydroxyl species that are successively removed until the catalyst achieves a steady state concentration. Some supporting evidence for the latter case is provided by the gallium catalyst, as the initial hydroxylated GaO(OH) phase was more active than Ga_2O_3. This is given further credence as a theory when the calcined Ga_2O_3 Au modified catalysts are considered, as the light off temperatures of the calcined catalysts are very similar to those of the successive runs for the uncalcined catalysts. The calcined Au ZnO catalysts had higher light off temperatures than the successive runs for the uncalcined catalysts, though this may be due to a number of factors, including the calcination temperature [10]. Another possible reason for the lower light off temperature for the 5%Au ZnO after calcinations can be found in a study by Bailie et al. [11]. It was found that the calcination of 5%Au ZnO produced cuboctahedral gold particles of 2-5nm size, whereas for the 5%Au ZnO catalyst that was dried, small gold particles were not seen. The calcined catalyst showed high activity, whilst the uncalcined catalyst was inactive. For comparison of the conditions used in this study, and that of Waters et al., calcined 1%Au Fe_2O_3 was tested, and had very similar light off and reactivity.

4. 6 Conclusions

The activation of CH_4 was probed by studying CH_4 oxidation at ambient pressure over gallium and zinc based catalysts prepared by precipitation and modified with Au and Pt. The unmodified gallium and zinc based catalysts were both active for CH_4 oxidation. The addition of Au to the ZnO and Ga based catalysts markedly increased its activity when compared to the unmodified catalysts. In general, the modification with Au had a greater effect in lowering the light off temperatures of the zinc based catalysts compared to the gallium based catalysts. The optimum Au loading for both the Ga and ZnO catalysts was 2%, with higher light off temperatures recorded for loadings of 1% and 5%. However, when these catalysts were calcined before use, the 2%Au Ga_2O_3 had the lowest light off, and the Au modified ZnO catalyst with the highest activity was the 5% loading. The addition of Pt at levels of 1% decreased the light off temperature when compared to the light off temperatures of the unmodified catalysts. This was particularly true for the gallium 1%Pt catalyst, whose light off temperature decreased by 30°C for successive runs, and whose CH_4 oxidation was almost comparable with the best Ga catalyst. These results are in correlation with previous results where Pt surfaces at UHV were shown to activate CH_4 at low temperatures [4].

The greatest decrease in light off temperature over the Ga based catalysts was observed on the addition of Au and Pt together, at levels of 2% each, being 90°C lower than the unmodified catalyst on the initial run, and 110°C lower on subsequent runs. This catalyst also exhibited the highest CH_4 activation properties of all the Ga catalysts tested. The greatest decrease in light off temperature over the Zn based catalysts was also observed on the addition of both Au and Pt together, this time at levels of 1% each. The loadings of 2%Au 2%Pt had the same light off temperatures as the 1%Au 1%Pt loadings, but it did not have as high an activity. Therefore for both the Ga and ZnO systems there seems to be a synergistic effect on the Au and Pt, which has been reported before for CH_4 activation over Au/Pt Co_3O_4 catalysts [5]. The origin of the synergistic effect is not yet clear, it may be due to the alloying of the metal components or by modification of the dispersion of the supported metals during coprecipitation.

The activation energies for both the Ga and Zn catalysts were very similar for the initial runs, but the ZnO values remained constant for subsequent runs, whereas the Ga catalysts had a tendency to rise on subsequent runs. When the same Au modified Ga catalysts were calcined before use, the light off temperature for these heat treated catalysts were very similar to those of the successive runs for the uncalcined catalysts. The light off temperatures for the calcined Au ZnO catalysts were higher than the uncalcined, even on successive runs of the uncalcined catalyst. The modification of Fe_2O_3 with Au lowered its light off temperature and increased its activity

The results from this chapter are very encouraging from a CH_4 activation point of view, with lower light off temperatures, higher oxidation properties and lower activation energies. However, the one concern from the use of these catalysts containing Pt is that they can jump from a relatively low conversion to total oxidation within a short temperature range.

4.7 References

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Chapter 5

High Pressure Studies

5.1 Introduction

The dual oxide approach for the design of new CH_4 oxidation catalysts has been previously introduced in chapter 1. The design approach is based on MoO_3 being the oxygen insertion component, and in chapters 3 and 4 suitable catalysts for CH_4 activation were investigated. The oxides chosen in these chapters were chosen for their CH_4 activation, CH_3OH stability and oxygen exchange activity. The catalysts chosen to be tested in the early pressure studies were the catalysts with the best CH_4 activation results from chapters 3 and 4. The most promising calcined catalysts from chapter 3 and uncalcined catalysts from chapter 4 were tested. These include both unmodified and modified catalysts.

In this chapter these modified catalysts were tested in a similar manner to previous studies by Taylor et al. [1], by being physically mixed with MoO_3. In addition to this method of catalyst preparation, other studies [2] have identified a double layered catalyst bed as producing more selective oxidation than with single bed catalysts or mechanically mixed catalyst beds. Therefore as well as physically mixed catalysts, for the most impressive CH_4 activation catalysts a dual bed system was investigated, varying the levels of the catalysts involved. Molybdenum oxide was chosen as the oxygen insertion component of the mixed oxide catalyst, due to its CH_3OH stability, and that the oxygen exchange reaction takes place over the entire bulk of the oxide.

This suggests that the diffusion of oxygen through the lattice of these solids is faster than the surface exchange, which is the rate determining process.

The reaction conditions used for the CH_4 partial oxidation experiments in this chapter were chosen to try and favour CH_3OH production. Previous studies by Taylor et al. used a pressure of 15 bar [1]. This was chosen as elevated pressure has been known to enhance CH_3OH selectivity [3]. Previous studies by Boomer and Thomas [4] and Morton et al. [5] suggests there is an optimum pressure range for CH_3OH formation, reporting CH_3OH selectivity falls off at 177 and 98 bar respectively.

5.2 Initial High Pressure Studies – Catalytic Activity

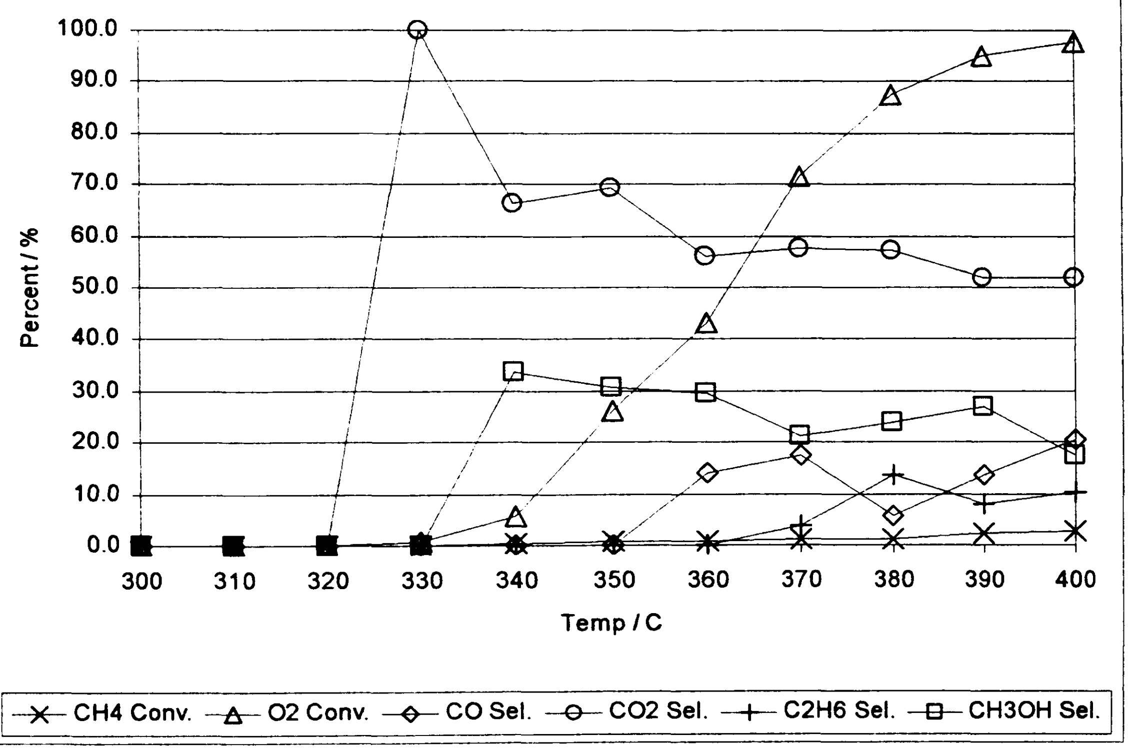
The gas flows used in chapters 3 and 4 had a ratio of 23/2/5 ml min^{-1} for $CH_4/O_2/He$ respectively. Initial runs at these gas flows at 15 bar pressure did not show distinguishable results between different catalysts. It was found that increasing the flows by a magnitude of 4, keeping the same overall ratio of gases, gave results easier to distinguish. It also ensured the conditions, in which the catalysts demonstrated excellent CH_4 activation properties, were not vastly changed. Therefore the flows used for the runs at pressure were 92/8/20 ml min^{-1} for $CH_4/O_2/He$ respectively. A low O_2/CH_4 ratio in the gas feed was also chosen in the previous studies as previous studies have reported that the lower the percentage of O_2 in the reactant feed, the higher the selectivity to CH_3OH [6].

The most impressive catalysts from the last two chapters have been tested at 15 bar pressure, using the experimental conditions outlined in section 2.3. From chapter 3, the most impressive Ga based catalyst was 5%Zn Ga_2O_3, and for Zn it was 10%Ga ZnO. In chapter 4 it was 2%Au GaO(OH) and 2%Au ZnO that exhibited the most promising results for Ga and Zn catalysts respectively. The unmodified catalysts have also been tested for comparison. Also tested were iron oxide, Au modified iron oxide and MoO_3. The molybdenum oxide was tested to gauge its CH_4 oxidation behaviour before being mixed with other catalysts.

5.2.1 Ga based catalysts

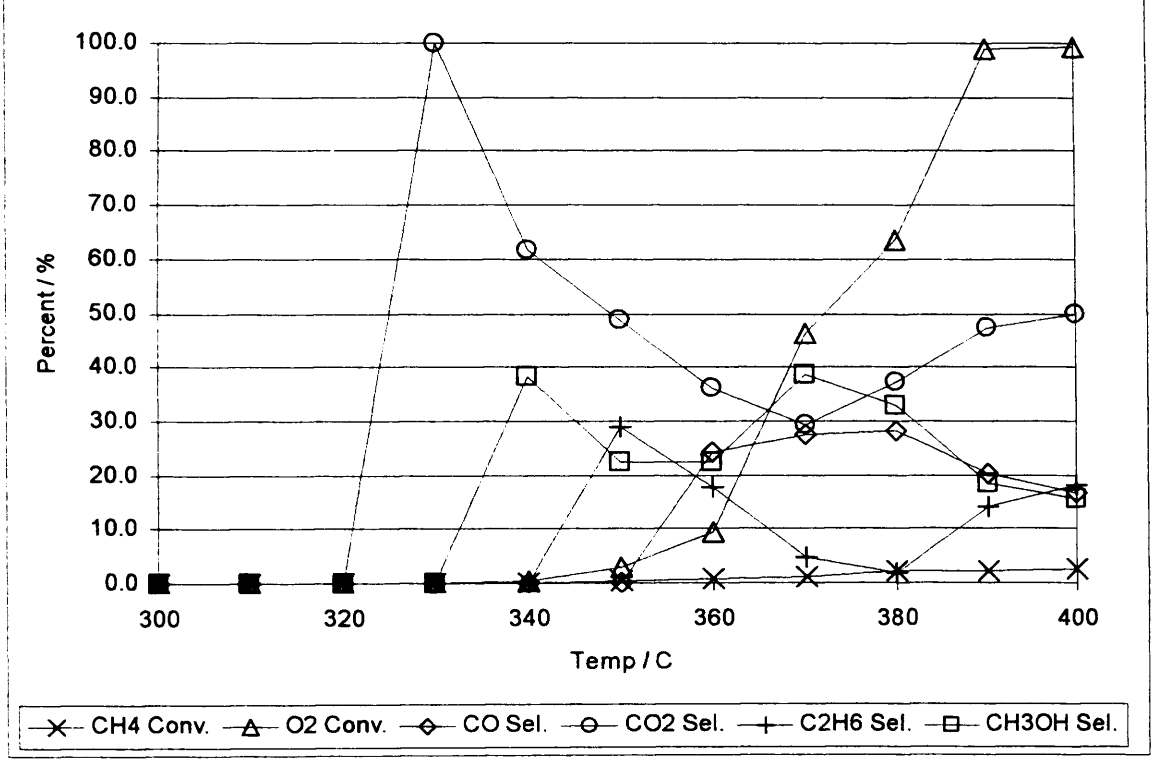
Results for the partial oxidation of CH_4 over GaO(OH) are shown in figure 5.1.

Figure 5.1 Methane Partial Oxidation over GaO(OH)



Activity was first seen for this catalyst at 330°C, with a CH_4 conversion of just 0.1% and O_2 conversion of 0.6%. The only product seen at this temperature is CO_2. The oxygen conversion stays at a low percentage until 340°C, at 5.8%, rising sharply to 26.1% at 350°C, then to 43.1% upon the next 10°C step. Throughout the entire temperature range CO_2 was the most selective product, staying at levels between 50-70% in the temperature range 340-400°C. At lower temperatures and conversions, CH_3OH is the second most selective product, with a maximum of 34% at 340°C. From 350°C CO is detected, and ethane is detected at low selectivity. Oxygen conversion rose above 90% at 390°C.

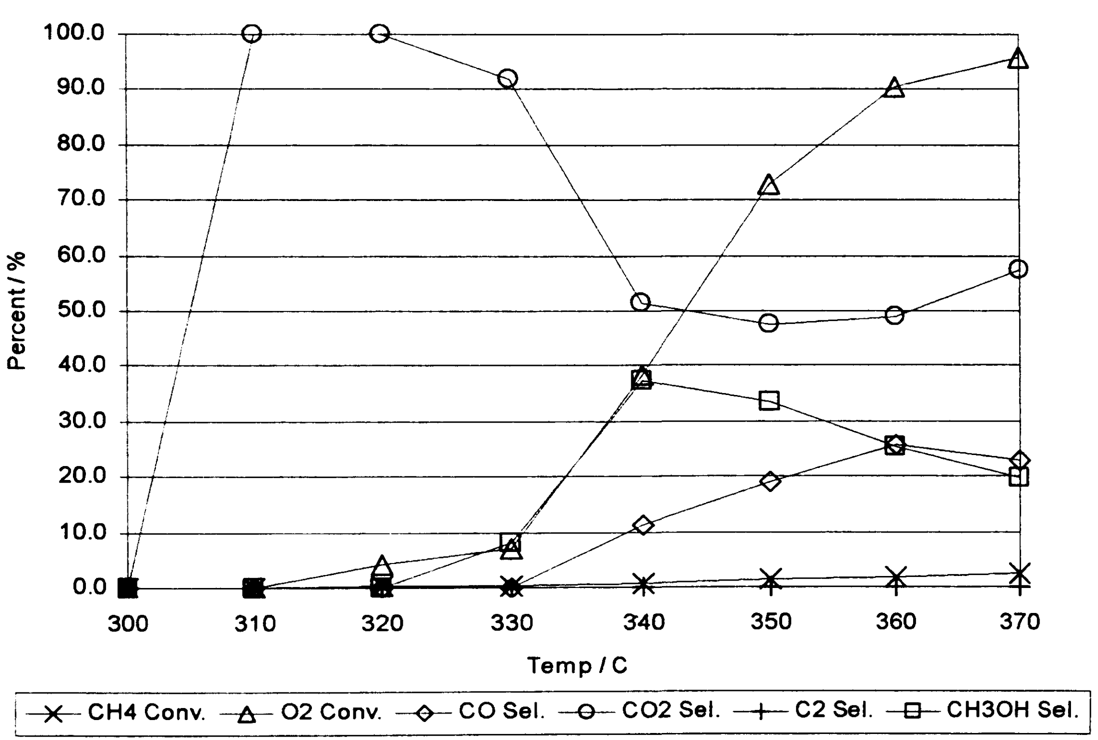
Figure 5.2 Methane Partial Oxidation over 5%Zn Ga2O3



Initial activity for the most impressive Zn modified Ga based catalyst began at 330°C, with CO_2 the only product. After this temperature CO_2 selectivity fell steadily to a minimum of 29% at 370°C, the only temperature where it was not the most selective product, before rising again as temperature rose to 400°C. At 370°C the most selective product was CH_3OH, at 39%, with an oxygen conversion of 46.2%. CO was first seen above 360°C and ethane above 350°C, with their respective selectivities never rising above 30%. Oxygen conversion rose above 90% at 390°C.

Initial activity for the 2%Au GaO(OH) was seen at 310°C, with CO_2 the only product detected. Selectivity for CO_2 stayed above 90% until 330°C, before dropping to levels of approximately 50%, where it stayed for the rest of the temperature range. CH_3OH was the second most selective product, with a maximum of 37% at 340°C, before decreasing gradually with increasing temperature. There was no ethane detected and O_2 conversion rose above 90% at 360°C.

Figure 5.3 Methane Partial Oxidation over 2%Au GaO(OH)



5.2.2 Zn based catalysts

Initial activity for ZnO was seen at 340°C, with CO_2 the only product detected, and this was the most selective product throughout the temperature range. There was low O_2 conversion until 360°C, at 6.4%, rising sharply to 40.1% at 370°C and 78.9% at 380°C. The maximum CH_3OH selectivity was 47% at 360°C, however this was at a temperature where conversion was very low. There was no ethane detected in the experiment and 90% O_2 conversion was detected at 390°C

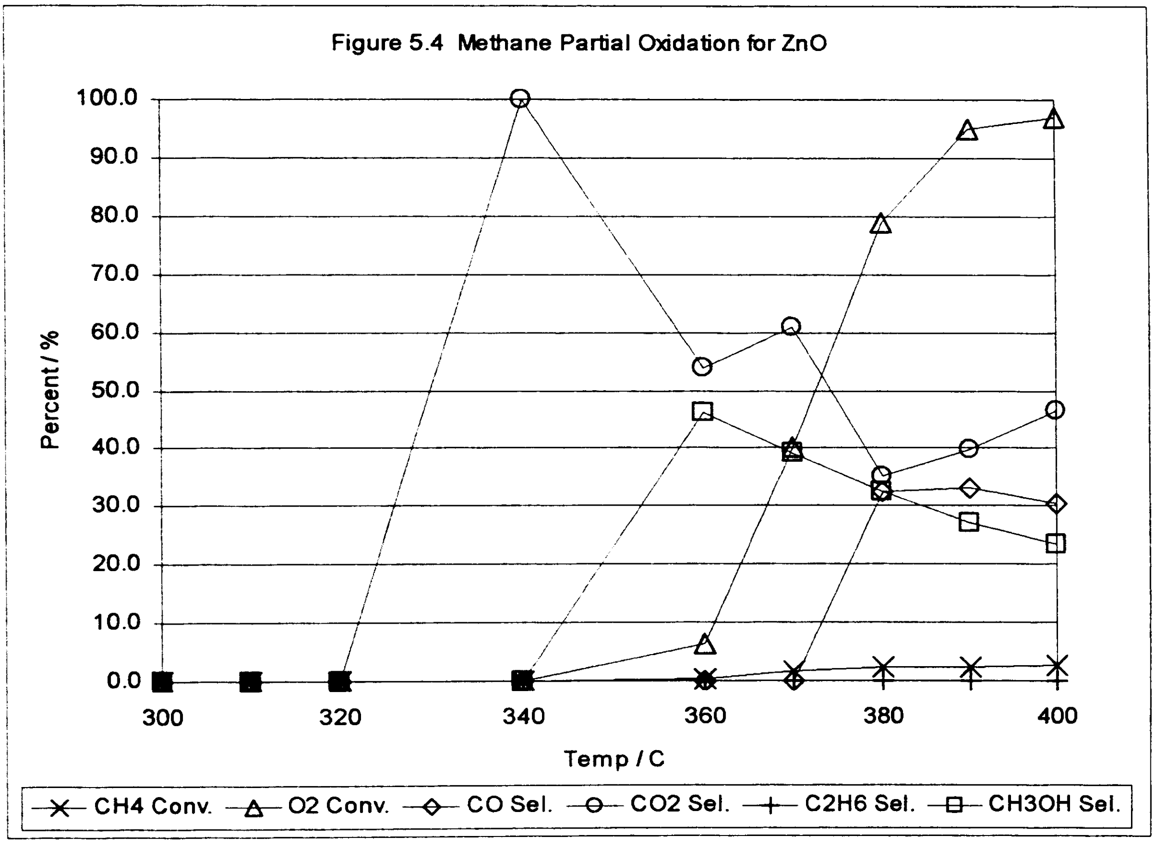
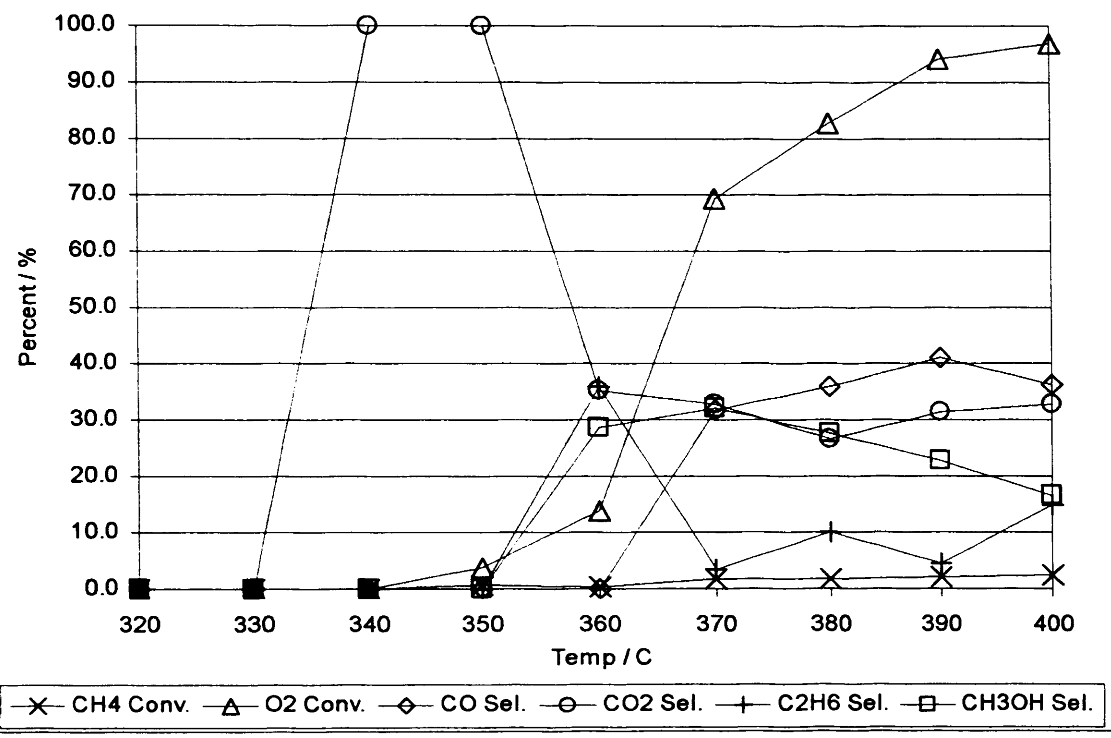


Figure 5.4 Methane Partial Oxidation for ZnO

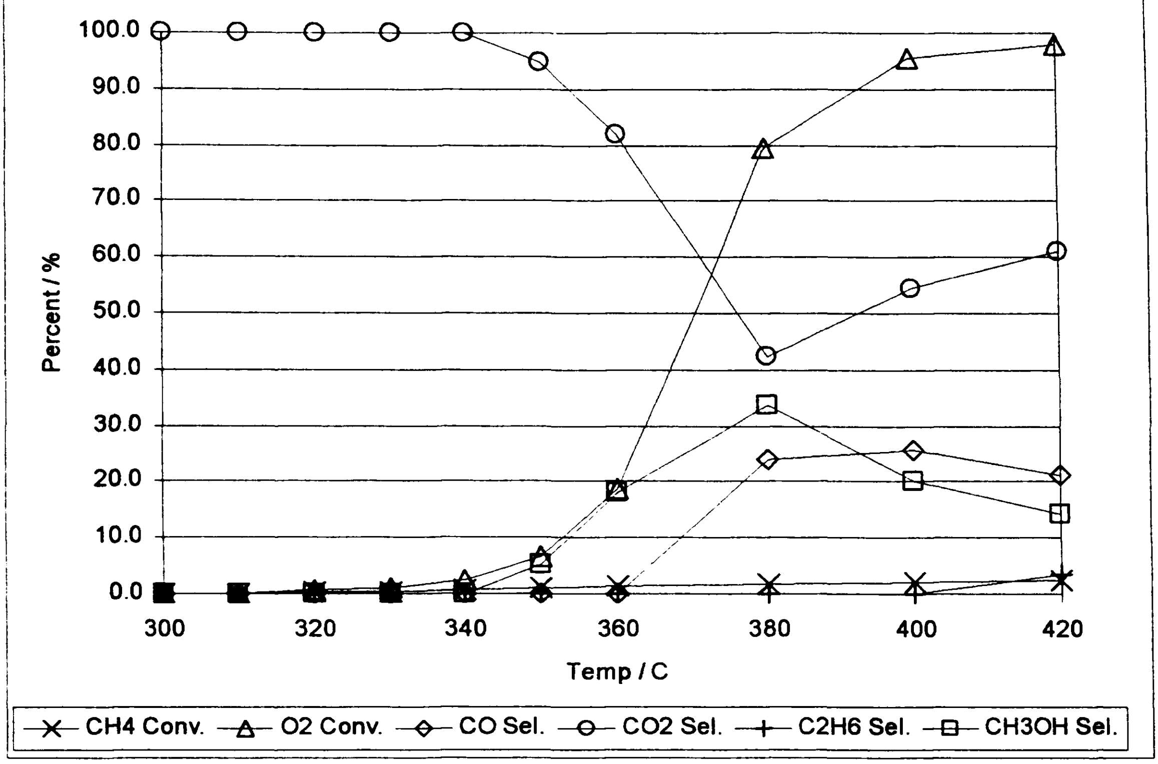
Initial activity for the 10%Ga ZnO coprecipitated catalyst was at 340°C, with CO_2 the only product initially detected. CO_2 selectivity then dramatically decreased with increased temperature, falling to a minimum of 35% at 360°C, then staying in the region of 27-35% region for the rest of the temperature range. Oxygen conversion was low until a level of 13.8% at 360°C, rising to 69.3% at 370°C. The maximum CH_3OH yield was 32% at 370°C, at low O_2 conversion, then falling steadily as the temperature was increased. Ethane selectivity was high, 36%, at 360°C, but at higher temperatures remained low. At higher temperatures CO was the most selective product. Oxygen conversion rose above 90% at 390°C.

Figure 5.5 Methane partial oxidation for 10%Ga ZnO



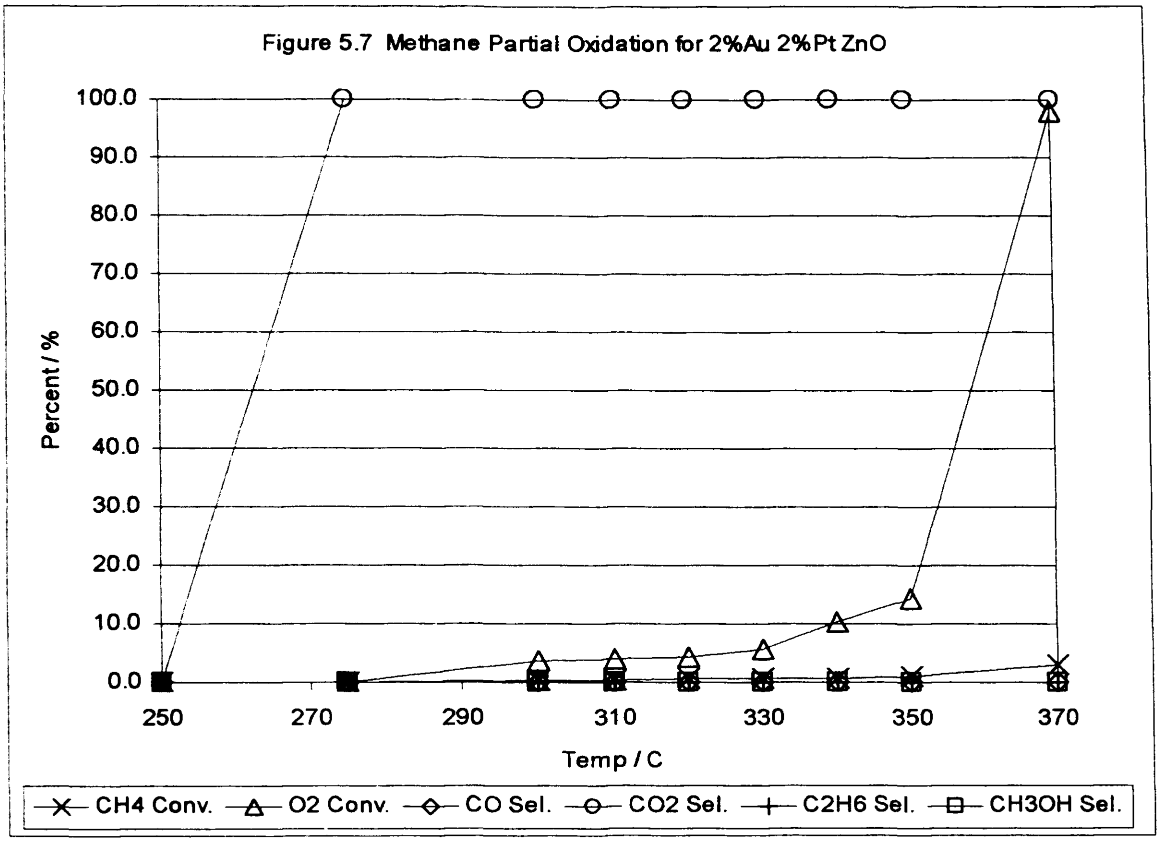
The results for the 2%Au modified ZnO catalyst are displayed in figure 5.6.

Figure 5.6 Methane partial Oxidation over 2% Au ZnO



Activity began at 300°C for the 2%Au ZnO catalyst, and until 350°C CO_2 was the only product detected. Throughout the whole temperature range, CO_2 was by far the dominant product, except at 380°C, where CO_2 selectivity was 42% and CH_3OH selectivity was 34%. Oxygen conversion was low until 360°C, where it rose to 18.7%, before rising again to 79.5% at 380°C. At higher temperatures, CO selectivity rose to a stable selectivity in the region of 25%. Ethane was only detected at 400°C, and 90% oxygen conversion was detected at the same temperature.

The most promising methane activation catalysts from chapter 4 were those modified with 2%Au and 2%Pt. The results for the 2%Au 2%Pt ZnO catalyst are displayed in figure 5.7. Activity began at low temperatures, but over the entire temperature range CO_2 was the only product detected, with total oxygen conversion by 370°C.



5.2.3 Other Catalysts

Initial activity for the iron oxide catalyst was seen at 300°C, with 100% selectivity for CO_2, and its selectivity stayed above 70% throughout the entire range except at 340°C, and was the most selective product at every temperature in the experiment. Oxygen conversion reached 90% at 390°C.

Activity was first seen for the Au modified iron oxide catalyst at 320°C, CO_2 being the only product, and CO_2 selectivity remained above 90% throughout the entire temperature range tested. O_2 conversion was low until rising to 23.2% at 340°C, and 73.2% at 350°C.

Figure 5.8 Methane Partial Oxidation over Fe2O3

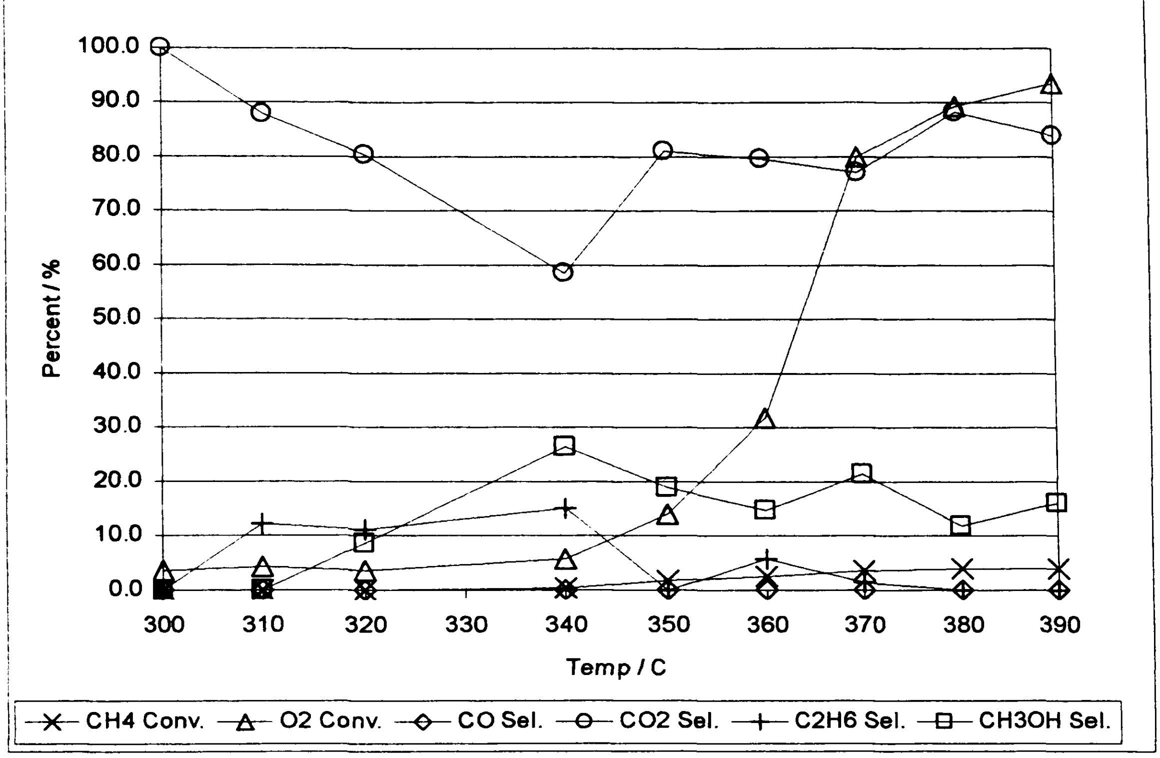
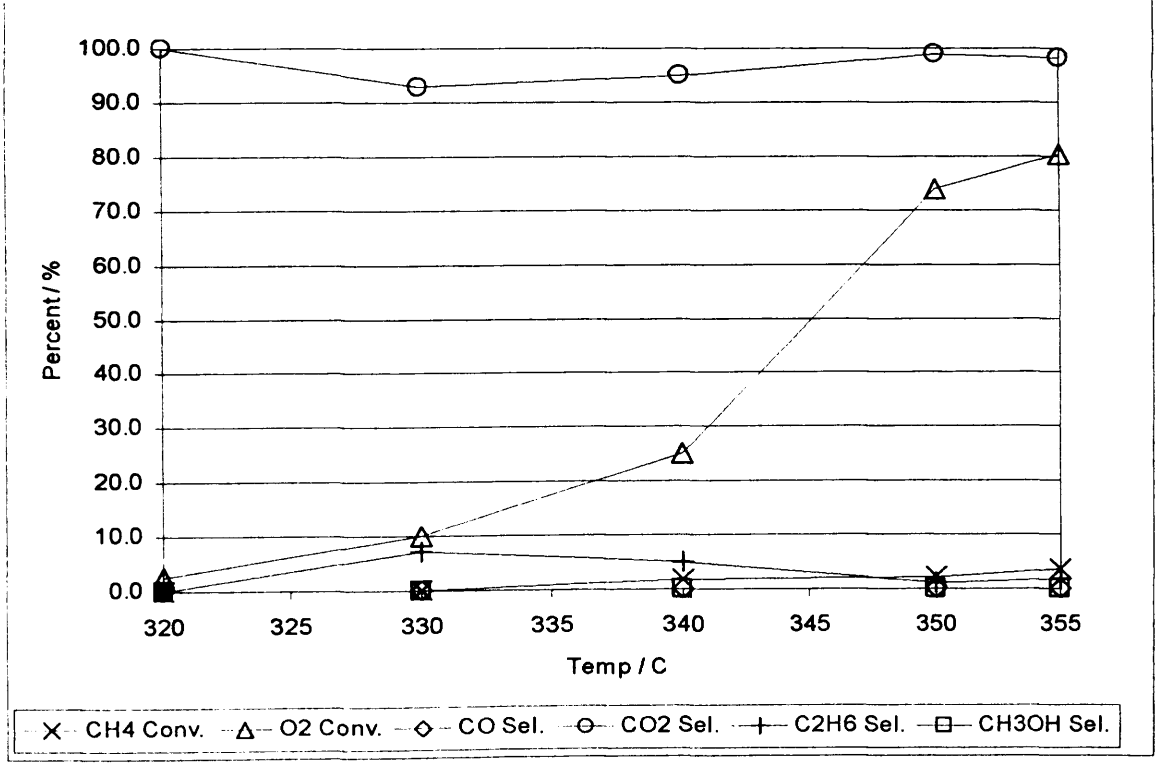
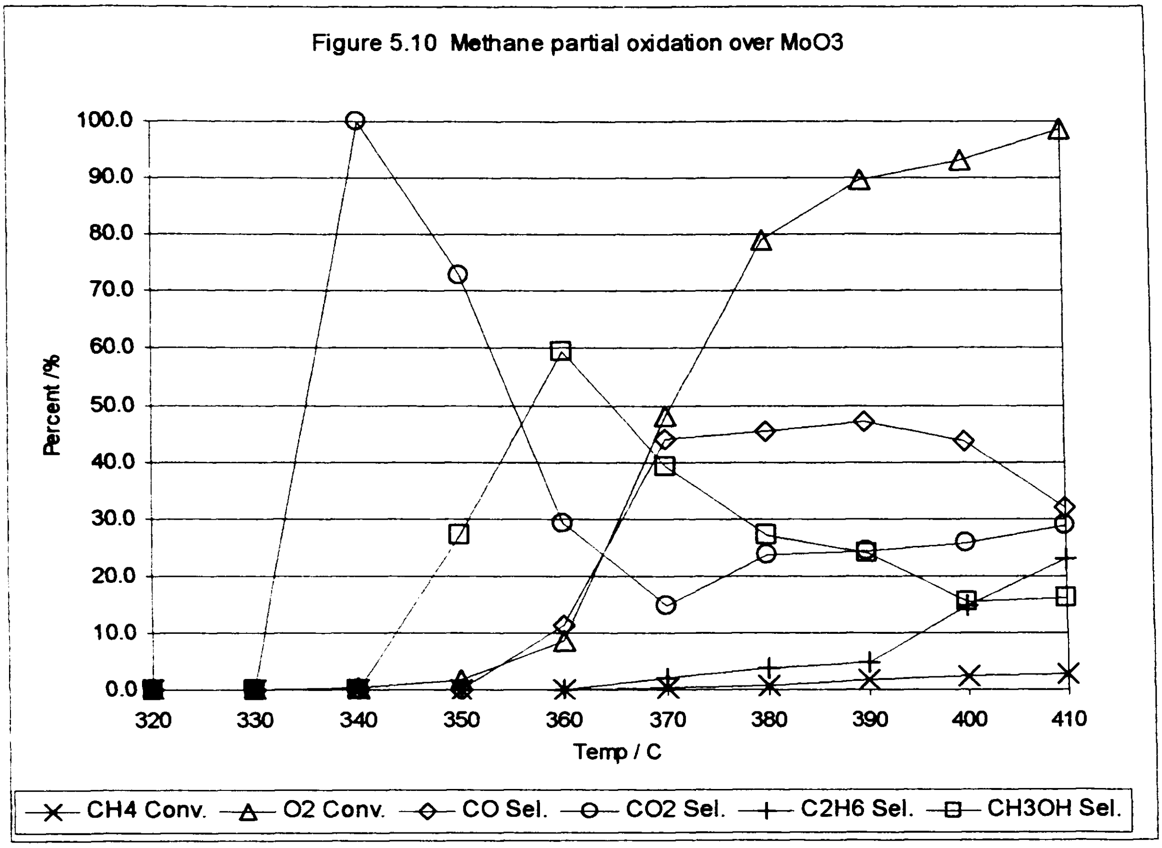


Figure 5.9 Methane Partial Oxidation over 1%Au Fe2O3





Initial activity for MoO_3 was detected at 340°C, CO_2 being the only product. There was low O_2 conversion until 360°C, where it was 8.7%, rising sharply to 48.1% at 370°C and 79.2% at 380°C. At lower temperatures and conversions, CH_3OH was highly selective, a maximum of 59% at 360°C but as the temperature rose its selectivity steadily dropped. From 370°C onwards the most selective product was CO, staying in the region of 40-45% selectivity up until 400°C.

5.2.4 Blank runs

In this section three experiments were carried out to investigate the methane oxidation behaviour when there was no catalyst present. The first experiment investigated the activity of an empty reactor tube. The second investigated the activity of pelleted quartz, and the third glass beads of 0.5mm diameter. These were chosen as they are inert materials. The quartz was sieved to uniform size, the same as the catalysts, and the quartz and glass beads were packed to the same volume as previously.

The results obtained for the CH_4 partial oxidation in the empty reactor tube are shown in figure 5.11. Conversion was first detected at 350°C, where methanol was the most selective product at 43%, with ethane selectivity at 38%. Oxygen conversion was low at 350°C, at a level of 3%, rising very sharply to 54.5% at 375°C and 95.5% at 400°C. CO_2 levels rose steadily with increased reaction temperature, reaching a maximum of 61% at 400°C. The maximum CH_3OH selectivity was 45% at 375°C, but this fell steadily as the temperature was raised. CO selectivity remained low throughout the temperature range, with a maximum of 10% at 400°C. 90% O_2 conversion first occurred at 400°C.

Figure 5.11 Methane Partial Oxidation for Empty Reactor Tube

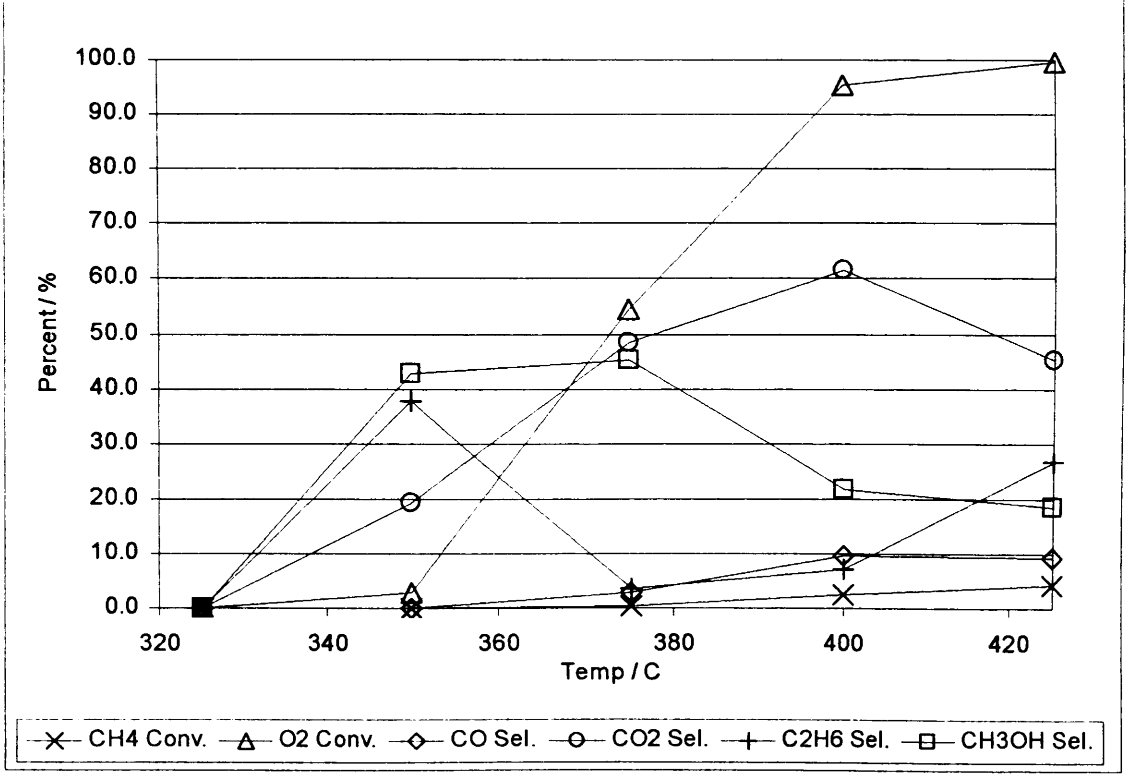
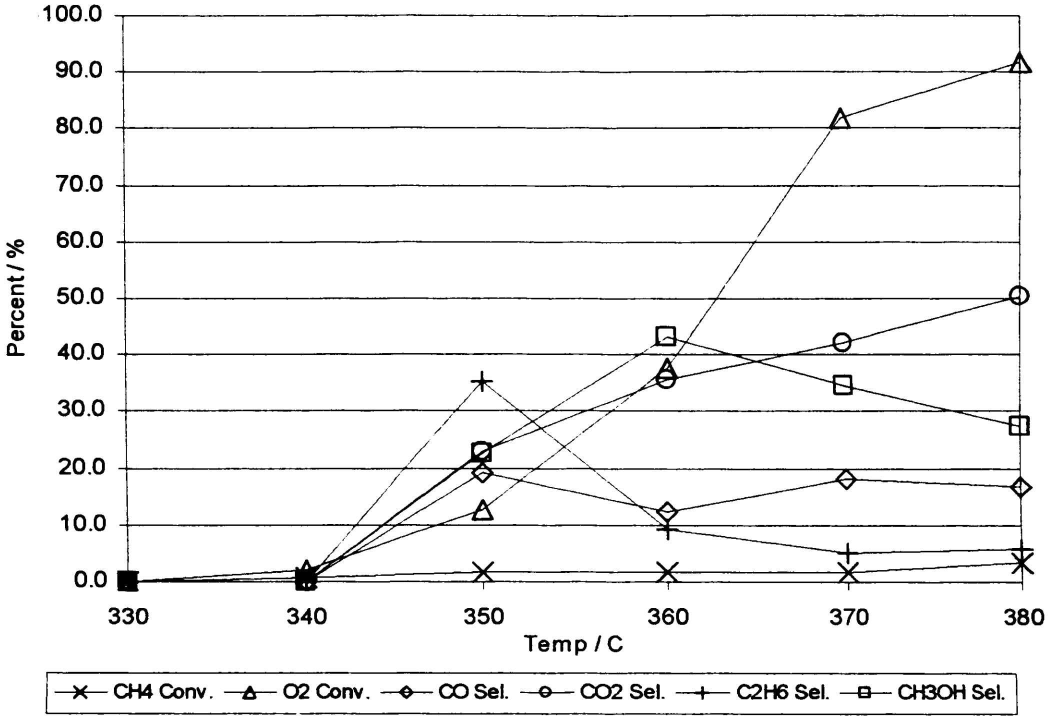
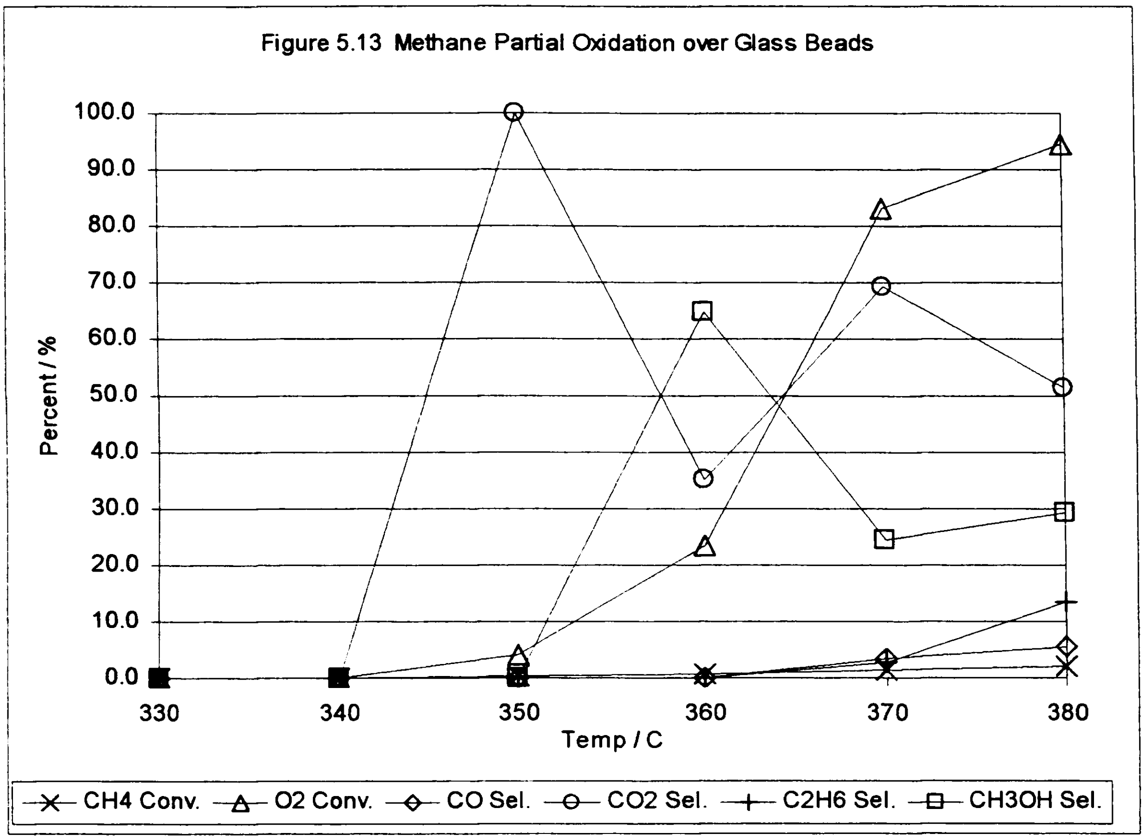


Figure 5.12 Methane Partial Oxidation over Quartz



The results obtained for the pelleted quartz are shown in figure 5.12. Initial activity was first detected at 350°C, with all four different products detected, with the highest selectivity at 35% for ethane. Oxygen conversion rose very sharply, from 10.7% at 350°C, to 36.1% at 360°C and then up to 81.5% at 370°C. CO_2 selectivity steadily rose all the way through the temperature range, reaching a maximum of 50% at 380°C. CH_3OH had its maximum selectivity at 360°C, with a level of 43%. 90% O_2 conversion was first detected at 380°C.

The results obtained for the glass beads are shown in figure 5.13. Like the quartz, initial activity was detected at 350°C. At this temperature the only product was CO_2, which fell from 100% selectivity to 35.17% at 360°C, before again rising to 69.4% at 370°C. The maximum selectivity for CH_3OH was 69.8% at 370°C, which then fell steadily as the temperature was raised. Low selectivities of CO and ethane were seen at 370°C and above. 90% O_2 conversion was detected at 380°C.

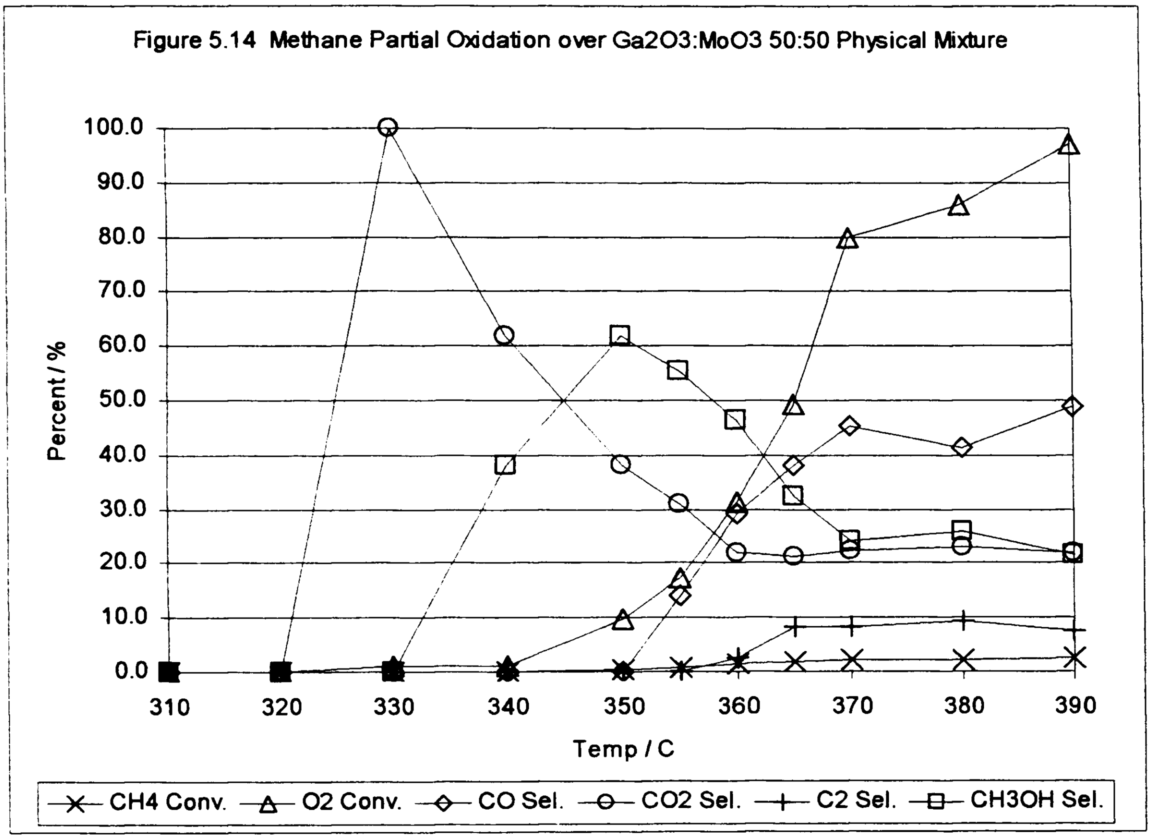


5.3 Methane Partial Oxidation over Physically Mixed Oxide catalysts.

The catalysts that have demonstrated impressive CH_4 activation properties in previous studies have been tested in conditions that are hoped would yield favourable CH_3OH selectivity in experiments. As tested in earlier studies [1] the physical mixing of these CH_4 activation catalysts with molybdenum oxide in a 50:50 mix produced better results than the two catalysts separately.

5.3.1 Chapter 3 Catalysts Physically Mixed with MoO_3

To begin with a recreation of the previous experiments with 50:50 gallium: molybdenum catalysts mixed was undertaken. The CH_4 partial oxidation results for the GaO(OH) : MoO_3 50:50 physical mix catalyst is shown in figure 5.14.



Initial activity is observed at 330°C, with only trace CO_2 detected. The CO_2 selectivity falls steadily as the temperature rises, to a level of approximately 20% from 360°C onwards. Maximum CH_3OH selectivity is observed at 350°C, at a level of 62%. Upon raising the temperature, this selectivity falls steadily until stabilising in the region of 20-30% in the 365-380°C temperature range. From 350°C, CO selectivity steadily rises, and from 365°C onwards is the most selective product, with a maximum of 49% at 390.°C. Oxygen conversion was low until 350°C, at 9.6%, which then rises steadily to levels of 79.8% at 370°C. Ethane was first detected at 360°C, and stayed at a selectivity below 10% from 360°C onwards.

The CH_4 partial oxidation results for the ZnO: MoO_3 50:50 physical mix catalyst is shown in figure 5.15.

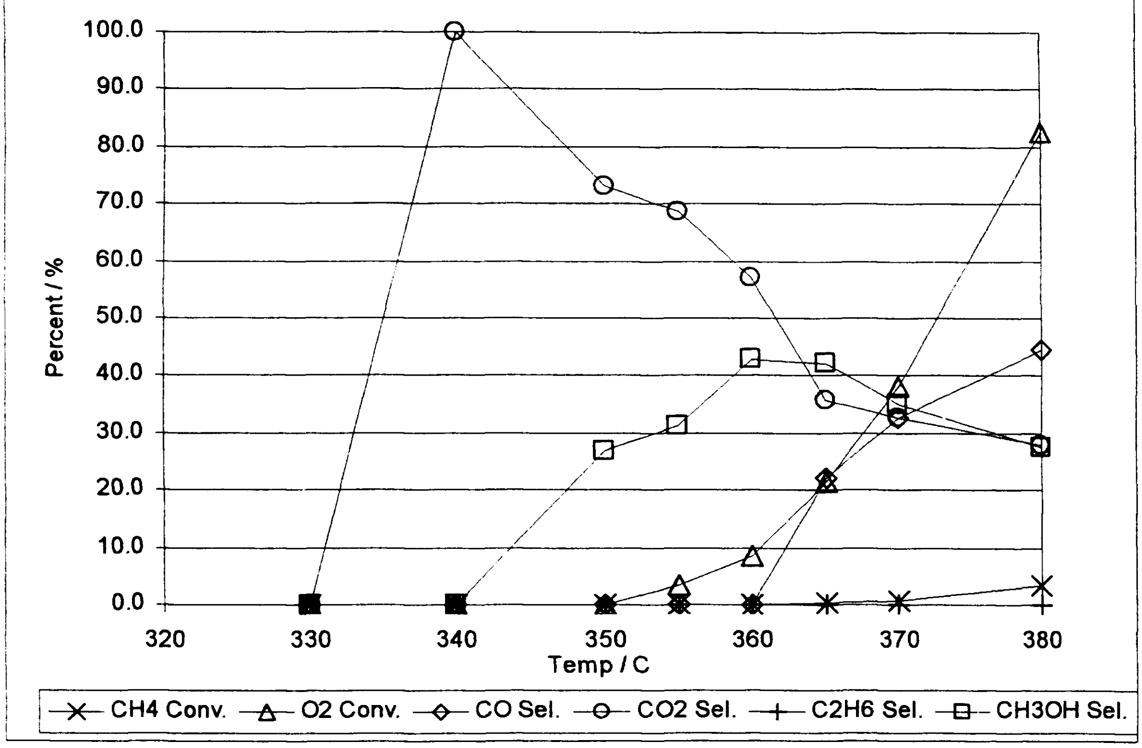
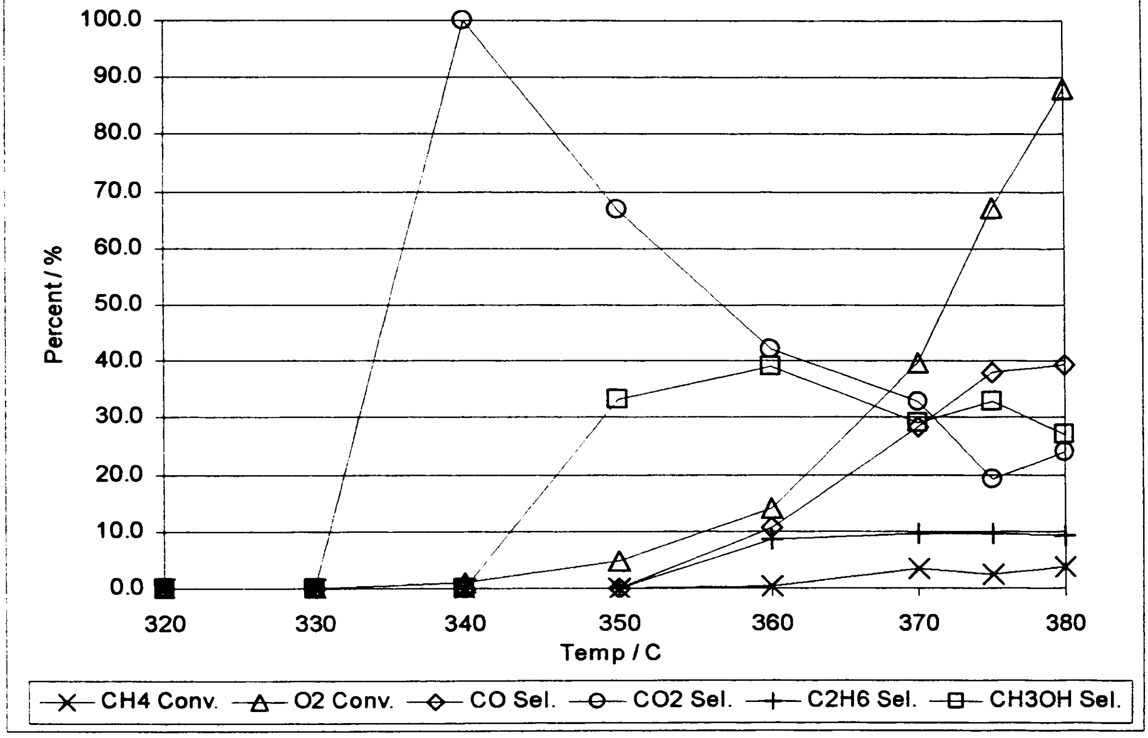


Figure 5.15 Methane Partial Oxidation over ZnO : MoO3, 50:50 Physical Mixture

Initial activity is observed with trace CO_2 at 340°C, with CO_2 selectivity then generally decreasing as the temperature is increased. However CO_2 is still the most selective product up until 365°C, when the most selective product is CH_3OH. CH_3OH selectivity increased steadily from 350°C onwards, reaching a maximum of 43% at 360°C and 42% at 365°C. Oxygen conversion was low until 365°C, at 21.3%, rising sharply to 38% at 370°C and 82.8% at 380°C. As the oxygen conversion rises sharply, so does CO selectivity, reaching a maximum of 45% as CH_3OH and CO_2 selectivities fall. No ethane was detected under these experimental conditions.

In chapter 3 it was seen that the addition of Ga by coprecipitation to ZnO lowered its light off temperature, so a 50:50 mix of this with MoO_3 was tested, and the results are displayed in figure 5.16.

Figure 5.16 Methane Partial Oxidation over 10%Ga ZnO : MoO3, 50:50 Physical Mixture



Initial activity began at 340°C, the same temperature as the unmodified ZnO catalyst, with CO_2 the only product. The selectivity for CO_2 then decreased as the temperature was raised, with CH_3OH having its maximum selectivity at a level of 39% at the temperature of 360°C. It can be seen that this catalyst exhibited similar trends and selectivities as the unmodified ZnO. Upon close scrutiny of the results, it can be seen that the modification of ZnO with Ga does not improve its CH_4 oxidation properties.

5.3.2 Chapter 4 Catalysts Physically Mixed with MoO_3

The most impressive Au modified gallium catalyst from chapter 4, the 2%Au GaO(OH) was mixed with MoO_3 in a 50:50 ratio, and the results are displayed in figure 5.17.

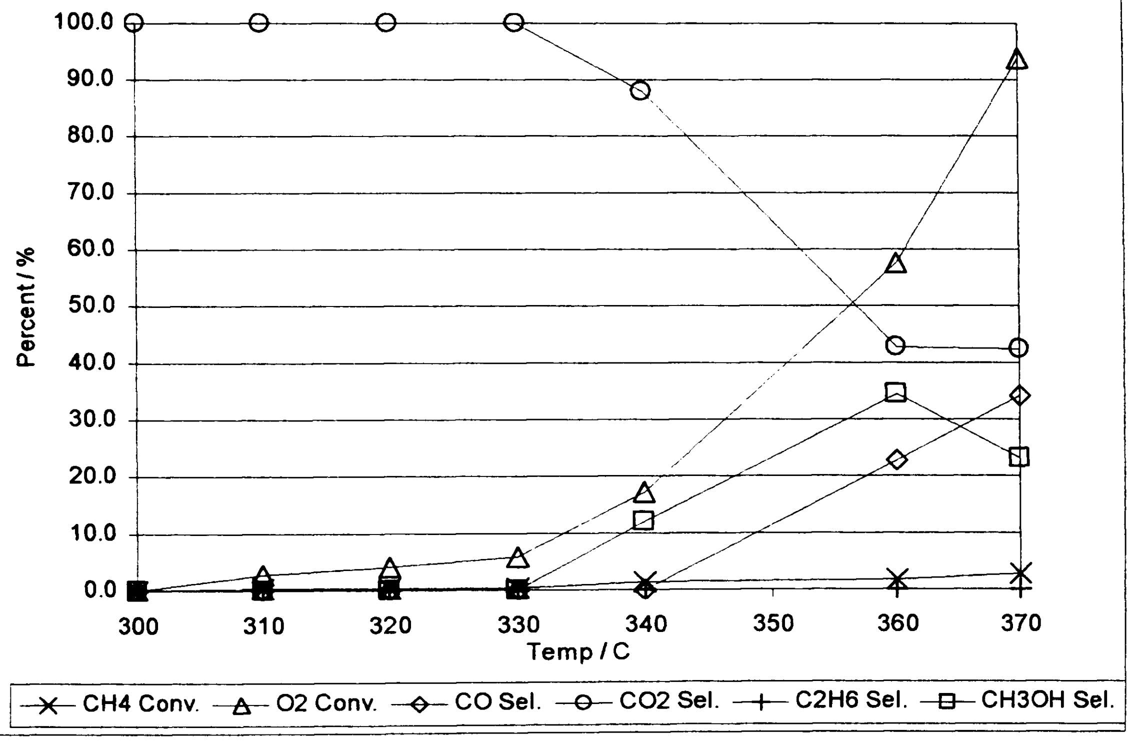
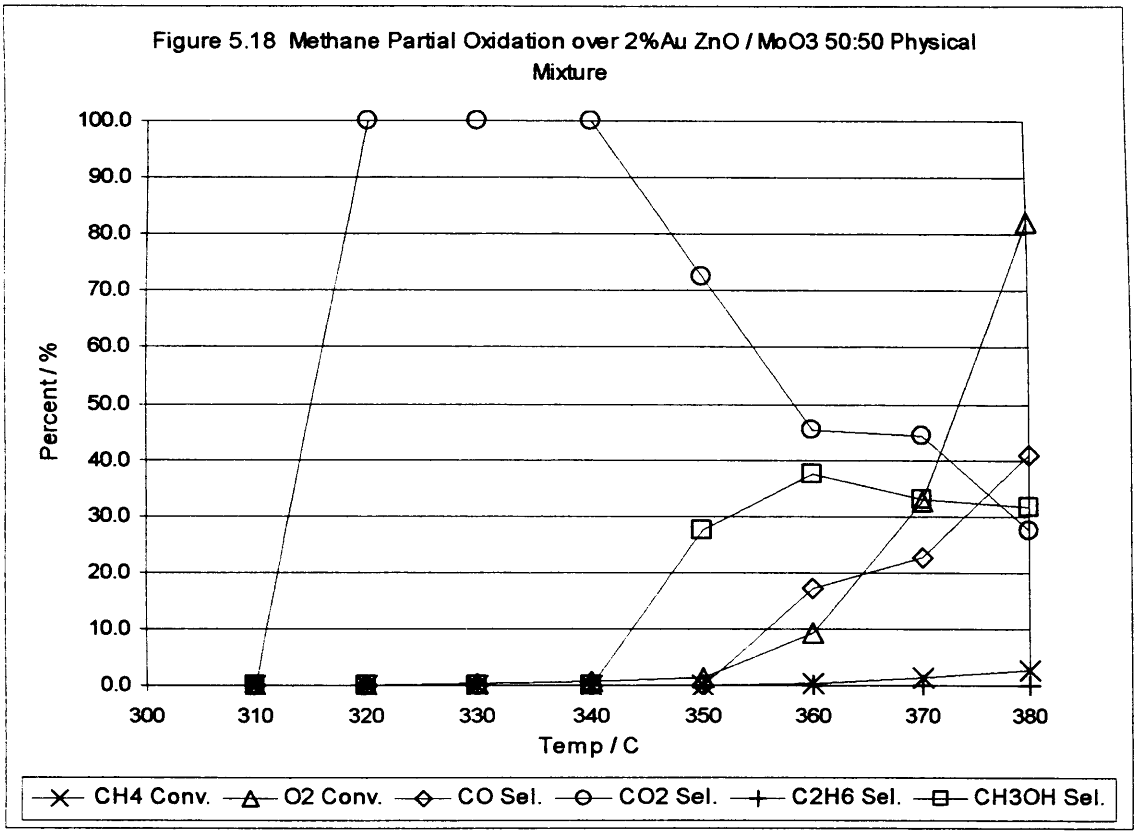


Figure 5.17 Methane Partial Oxidation over 2%Au GaO(OH) : MoO3 50:50 Physical Mixture

Initial activity is detected at 300°C, with trace CO_2 the only product, and this remained the same until 340°C, where methanol was first detected. Throughout the entire temperature range studied CO_2 was the most selective product, with a minimum value of 43%. At 360°C CH_3OH selectivity reached a maximum of 35%, and then decreased as the temperature was increased. Once oxygen conversion began to increase, from 17.2% at 340°C to 57.7% at 360°C, the selectivities of CO and CH_3OH both increased, and the selectivity of CO_2 fell. No ethane was detected.

The most impressive Au modified ZnO catalyst from chapter 4, the 2%Au ZnO was mixed with MoO_3 in a 50:50 ratio, and the results are displayed in figure 5.18.



Initial activity is detected at 320°C, with trace CO_2 the only product, and this remained the same until 350°C, where CH_3OH was first detected. After 350°C CH_3OH selectivity increased to a maximum of 37% at 360°C, before falling as the temperature increased. Once oxygen conversion began to increase, from 18.7% at 360°C to 79.5% at 380°C, the selectivity of CO_2 fell, finishing at a level of 27%. At higher temperatures and oxygen conversion CO became the most selective product. No ethane was detected.

For the 2%Au2%Pt ZnO, whose results are displayed in figure 5.19, initial activity was detected at 270°C, with trace levels of CO_2, which was the only product detected until 340°C, where CH_3OH was first detected. Throughout the entire temperature range, CO_2 was the most selective product. As oxygen conversion increased, CO and CH_3OH selectivity increased, as CO_2 selectivity fell. After the catalyst was heated to 380°C, even if the temperature was allowed to drop and stabilise at a lower temperature, total oxidation occurred. As before, the Pt portion of the catalyst was activated and selective partial oxidation ceased.

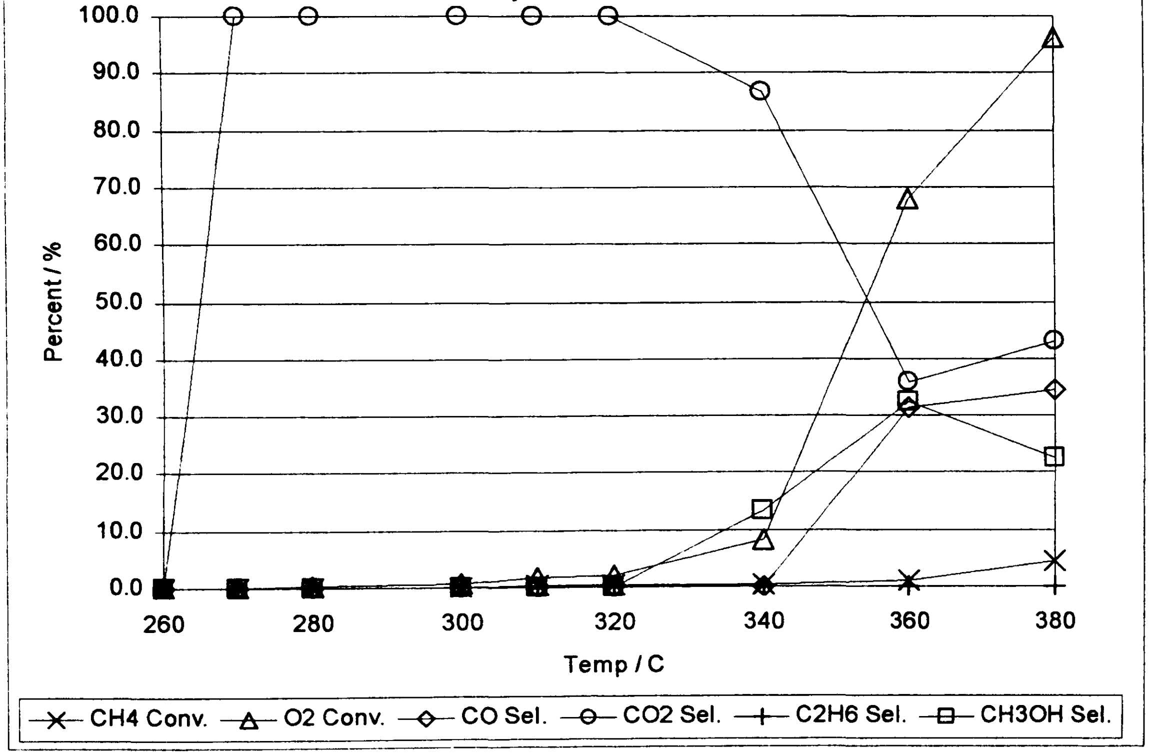
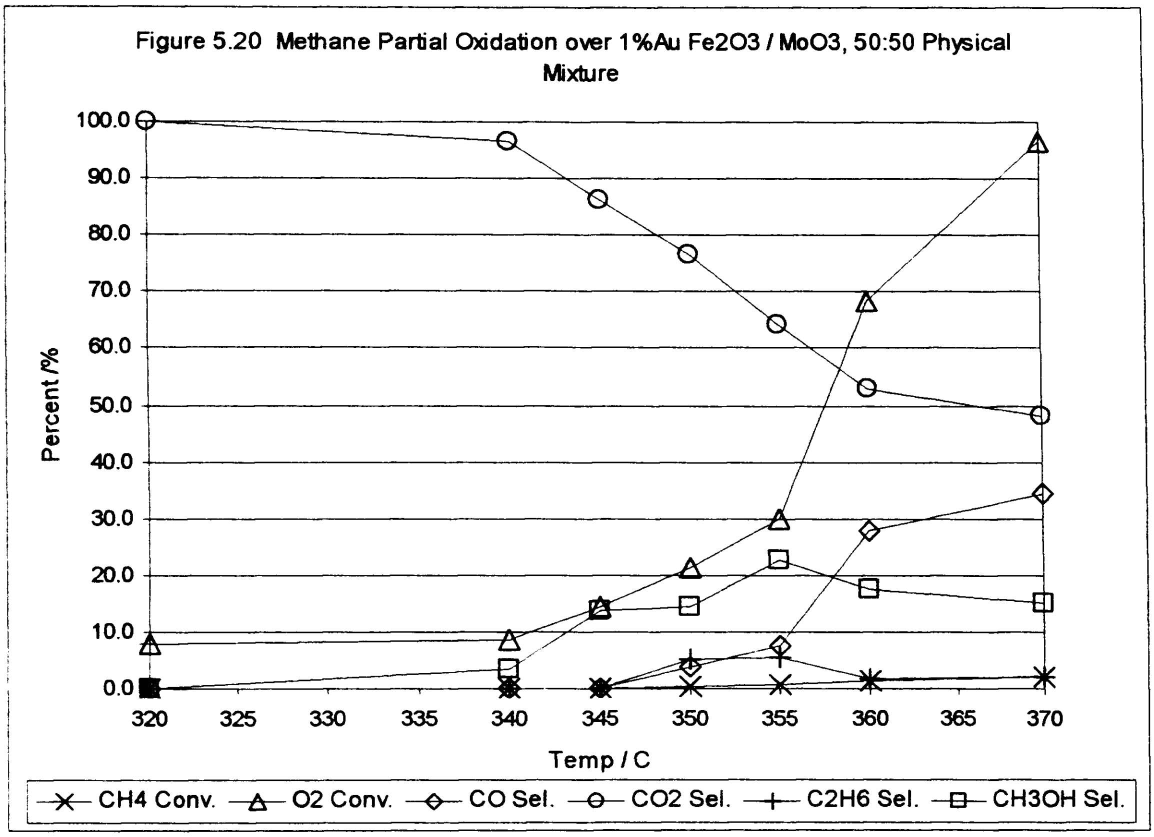


Figure 5.19 Methane Partial Oxidation over 2%Au 2%Pt ZnO / MoO3 50:50 Physical Mixture

For comparison, the 1%Au Fe_2O_3 from chapter 4 was mixed with MoO_3 in a 50:50 ratio, and the results are displayed in figure 5.20.



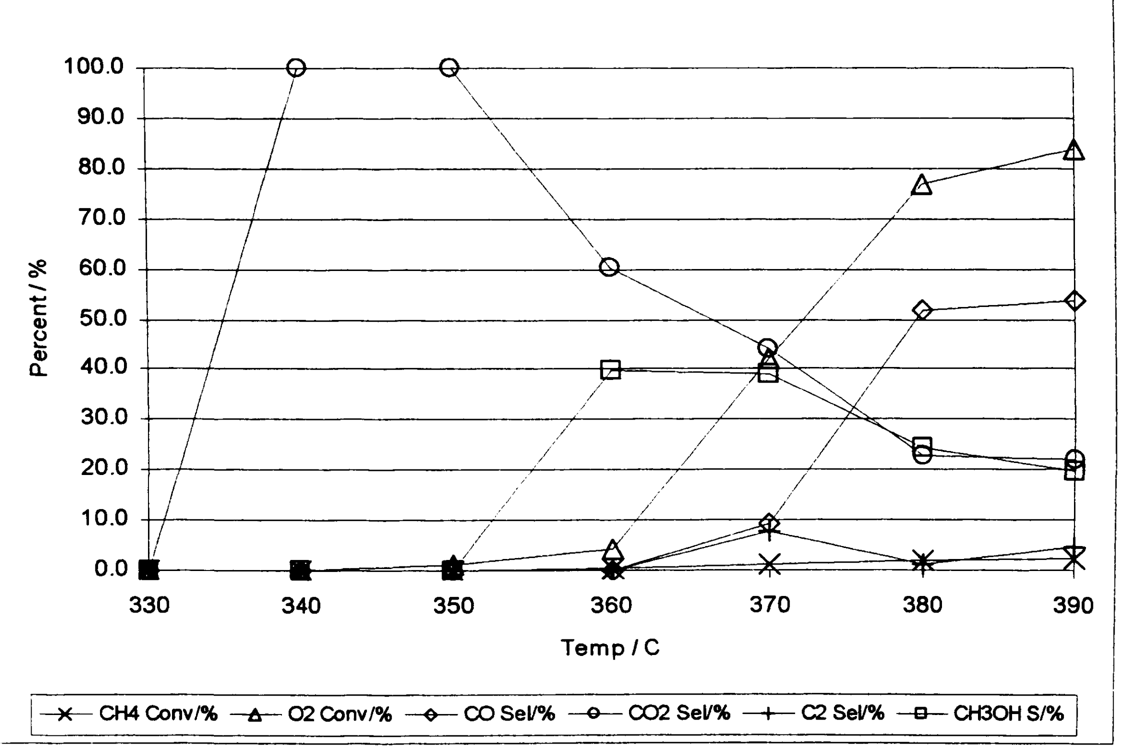
This catalyst had a very low initial activity temperature, but oxygen conversion remains very low until 340°C, when it rises sharply to 30% at 355°C and 68.2% at 360°C. CO_2 displayed the highest selectivity of all products throughout the temperature range investigated, with its selectivity dropping as oxygen conversion increased, falling to a minimum value of 49% at 370°C. The maximum CH_3OH selectivity was 24% at 355°C, but this value then fell as the temperature was raised. Also as the temperature and oxygen conversion increased, CO selectivity increased to a maximum of 35% selectivity at 370°C. There was a small amount of ethane detected at the higher temperatures.

5.3.3 Varying the Ratios in Physical Mixture Catalysts

All physical mixes tested both in these studies and previous work have involved mixtures of equal amounts of each oxide. In this section varying the GaO(OH):MoO_3 ratios was undertaken, with 25:75 and 75:25 tested, to compare with the 50:50 mix in section 6.2.1, displayed in figure 5.14.

To observe the effect of lowering the amount of GaO(OH) and raising the amount of MoO_3 in a physical mix catalyst, a GaO(OH) : MoO_3 catalyst with a ratio of 25:75 was tested, and the results are displayed in figure 5.21.

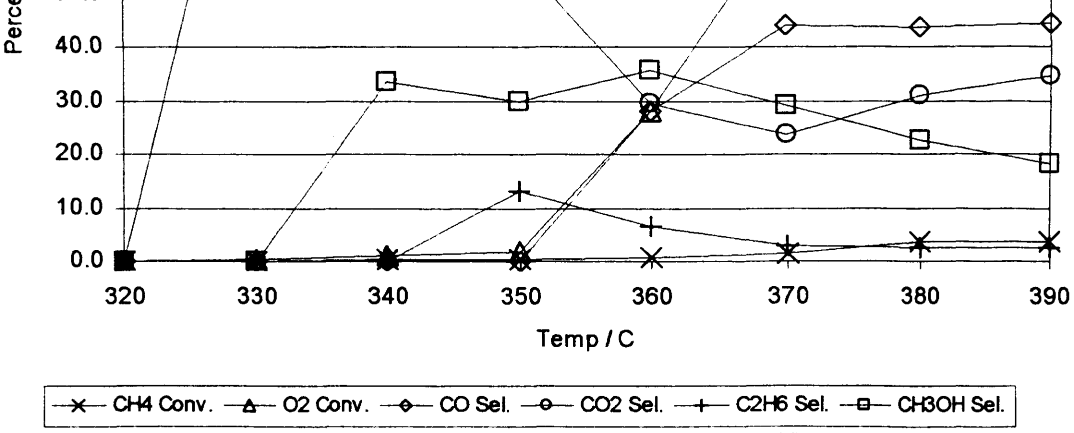
Figure 5.21 Methane partial Oxidation Over GaO(OH) : MoO3, 25:75 Physical Mixture



Initial activity was observed at 340°C, and CO_2 was the only product detected, at trace levels. As the temperature was raised, CO_2 selectivity fell dramatically, with CH_3OH selectivity rising to a maximum of 40% at 360°C and 39% at 370°C. Oxygen conversion was low until levels of 42% at 370°C, rising sharply to 76.7% at 380°C. As oxygen conversion levels increase, so did CO selectivity, rising above 50% at 380°C and above, becoming the most selective product at higher temperatures. Low levels of ethane were detected at temperatures of 370°C upwards.

Conversely, to observe the effect of increasing the amount of GaO(OH) and decreasing the amount of MoO_3 in a physical mix catalyst, a GaO(OH) : MoO_3 catalyst with a ratio of 75:25 was tested, and the results are displayed in figure 5.22.

Figure 5.22 Methane Partial Oxidation over GaO(OH):MoO3, 75:25 Physical Mixture



Initial activity was observed at 340°C, with trace amounts of CO_2. As the temperature is then increased, CO_2 selectivity falls and CH_3OH selectivity increases, to a maximum of 36% at 360°C, which then fell as the temperature was increased. Oxygen conversion was low until 370°C, 27.9%, rising to 64.6% at 380°C, and 93.9% at 390°C. As the oxygen conversion level increased, so did CO selectivity, to levels of 44-45% in the 380-400°C temperature range. From temperatures of 350°C upwards low levels of ethane were detected.

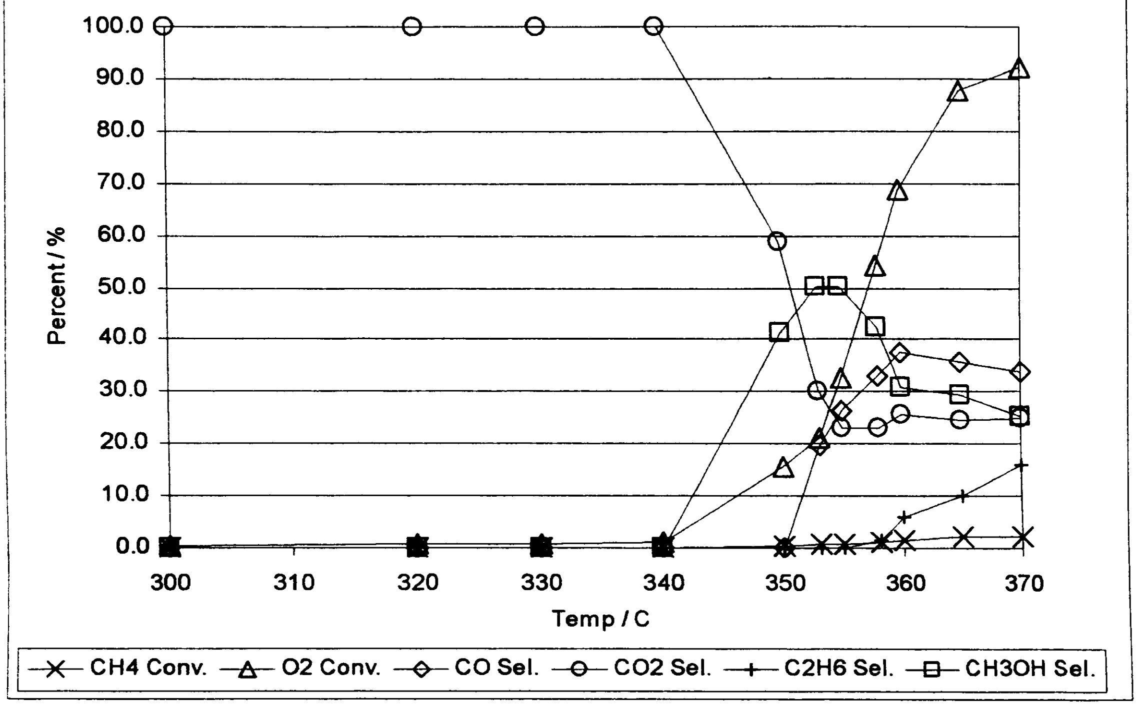
5.4 Methane Partial Oxidation over Separate Layer Catalysts.

In section 5.3 the most impressive CH_4 activation catalysts were tested in a physical mixture with MoO_3. In these experiments the relevant catalysts responsible for CH_4 activation and MoO_3 were pelleted, then placed in the reactor tube in separate layers. The activation catalyst was the bottom layer, and MoO_3 on the top. Therefore the feed gases had to pass through the activation catalyst before reaching the MoO_3. The ratio of the catalysts used were varied, but keeping the same overall volume of catalyst. The layers were separated by a thin layer of silica wool, 1-2mm thick, thus giving the same GHSV as previous experiments.

5.4.1 Methane Partial Oxidation over Separate Layers of 2%Au GaO(OH) and MoO_3

Data representative of the experiment with a 50:50 ratio of the two catalysts is displayed in figure 5.23.

Figure 5.23 Methane Partial Oxidation over 2%Au GaO(OH) : MoO3, 50:50, separate layers



Trace CO_2 was detected at 300°C, and this remained the only product until 350°C. Due to the large amount of activity in the 350-370°C region for the physical mixture catalyst of the same ratio, much smaller steps in temperature were taken to observe the changes in selectivities and conversions more closely. This was especially of interest as oxygen conversion rose sharply over these temperatures. From 350°C upwards, as oxygen conversion began to rise, CO_2 selectivity decreased rapidly, before stabilising at a level of 23-26% in the 355-370°C range. Between 350°C and 360°C with oxygen conversion in the 15.6% to 68.8% range, CH_3OH selectivity rose from 41% at 350°C to a maximum selectivity of 50% at 353-355°C, before decreasing as the temperature was increased further. At higher temperatures, CH_3OH and CO_2 selectivity fell, and CO selectivity increased to a maximum of 45% at 370°C. From 358°C ethane was detected at low levels, with its maximum selectivity of 16% occurring at 370°C

In the next experiment, the ratio of catalysts was altered. In order to try and promote selective partial oxidation, the amount of 2%Au GaO(OH) was decreased to 25% of the catalyst volume, and MoO_3 increased to 75%. The results for this experiment are displayed in figure 5.24. Initial activity was detected at 340°C with trace CO_2, with oxygen conversion rising to 7.2% at 350°C. Between the temperatures of 350°C and 360°C oxygen conversion rose from 7.2% to 39.8%. In this temperature region CH_3OH selectivity rose to a maximum of 69% at 353°C, and then decreased steadily to 57% at 360°C, before falling to 36% at 370°C. Above 350°C CH_3OH was the most selective product for the entire temperature range tested. CO_2 selectivity stayed between the levels of 16-24% above 353°C, and as oxygen conversion increased with higher temperatures, so did CO selectivity, rising to a maximum of 33% at 370°C. Ethane was detected from 358°C, reaching a maximum selectivity of 12% at 370°C.

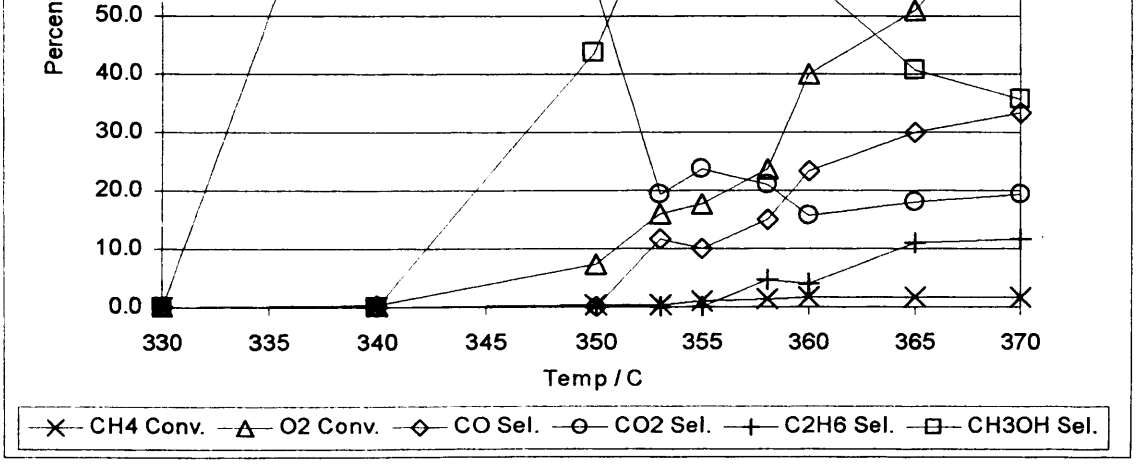
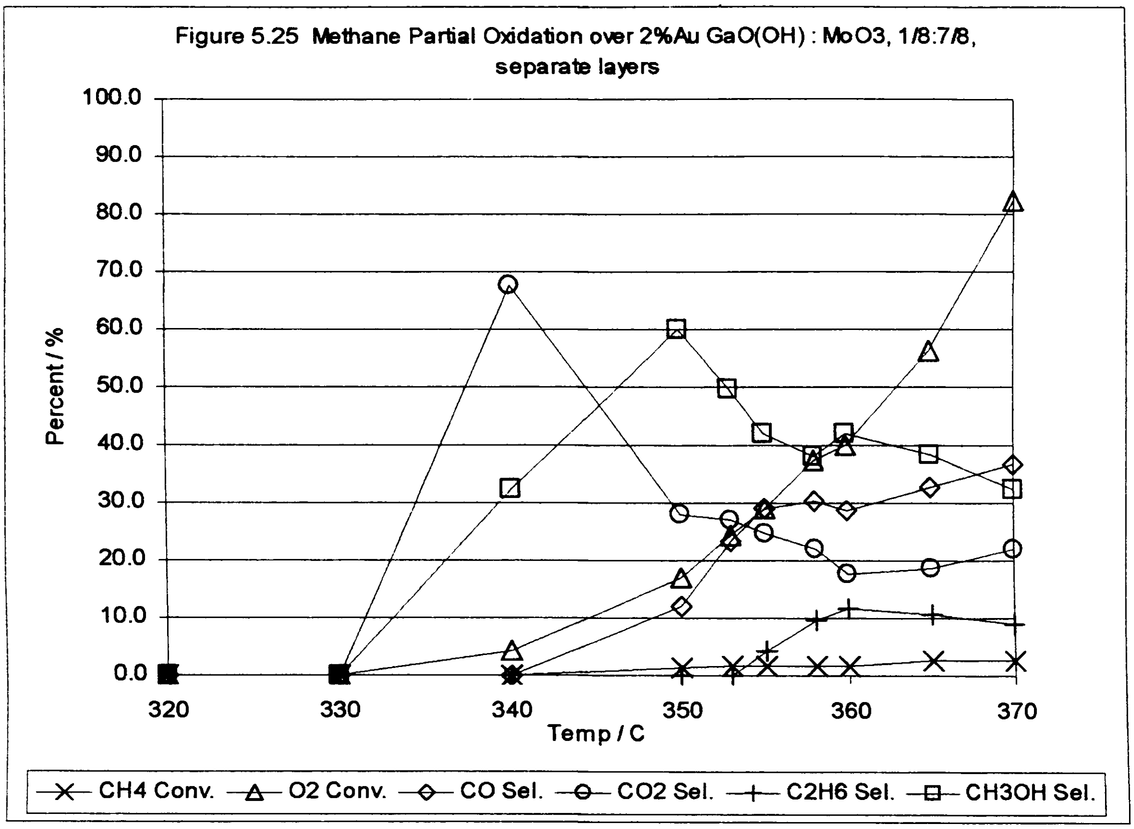
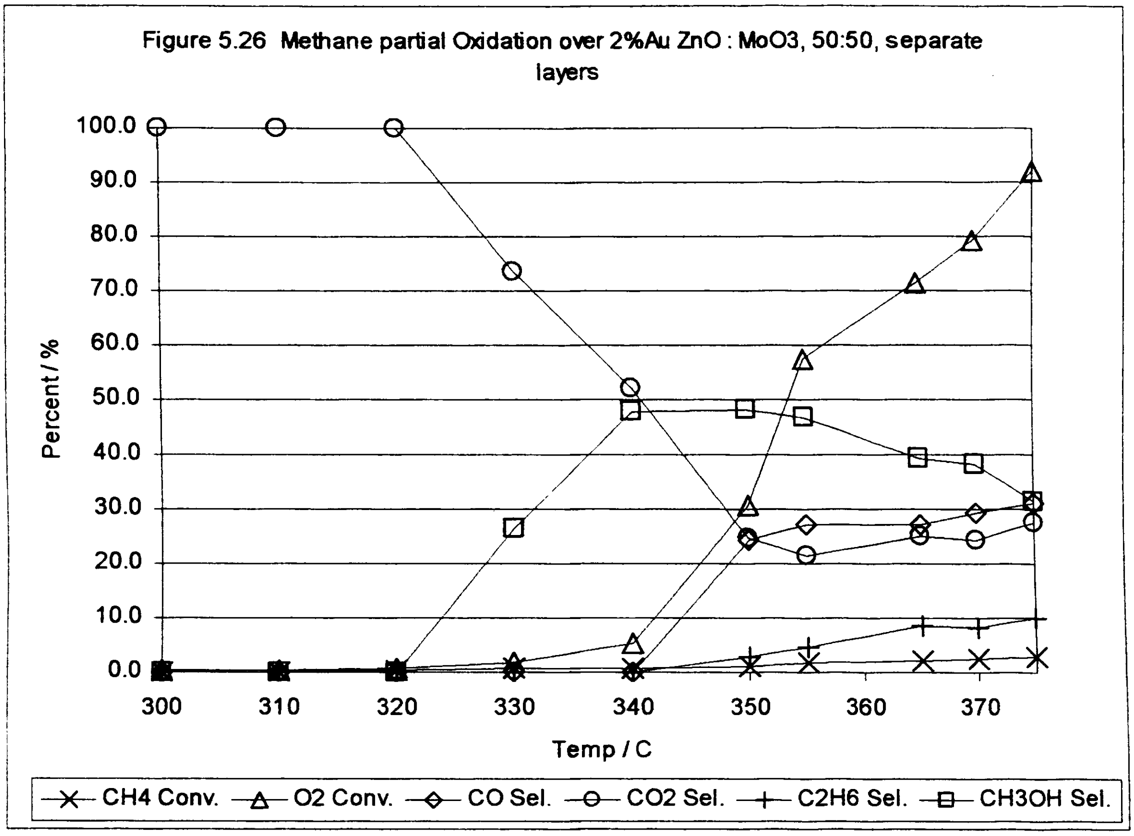


Figure 5.24 Methane Partial Oxidation over 2%Au GaO(OH) : MoO3, 25:75, separate layers



Again the ratio of catalysts was altered, with the amount of 2%Au GaO(OH) decreased to ⅛ of the catalyst volume, and MoO_3 increased to ⅞. The results for this experiment are displayed in figure 5.25. Trace amounts of CO_2 and methanol were detected at 340°C, with selectivities of 68% and 32% respectively. After this temperature, CO_2 selectivity then fell, staying in the 18-28% region for the 350-370°C temperature range. In this same temperature range, CH_3OH selectivity had its maximum value of 60% at 350°C, before decreasing as the temperature was raised. However CH_3OH remained the most selective product in the 350-365°C temperature range. At high oxygen conversion levels CO selectivity increased to its maximum at 40%. From 355°C ethane was detected, rising to a selectivity of 12% at 360°C.

5.4.2 Methane Partial Oxidation over Separate Layers of 2%Au ZnO and MoO$_3$



Data representative of the experiment with a 50:50 ratio of the catalysts is displayed in figure 5.26. Trace CO$_2$ was detected at 300°C, and this remained the only product until 330°C. Due to the large amount of activity above 350°C for the physical mixture catalyst of the same ratio, 5°C steps in temperature were taken to observe the changes in selectivities and conversions more closely. This was especially of interest as oxygen conversion rose sharply over these temperatures, with oxygen conversion rising from 30.6% to 71.4% in the 350-365°C range. From 340°C upwards, as oxygen conversion began to rise, CO$_2$ selectivity decreased rapidly, before stabilising in the region 22-28% in the 350-375°C range. Maximum CH$_3$OH selectivity was 48% at 340-350°C, before decreasing as the temperature was increased further. At higher temperatures, CH_3OH and CO_2 selectivity fell, and CO selectivity increased to a maximum of 31% at 370°C. There were low levels of ethane detected from 350°C.

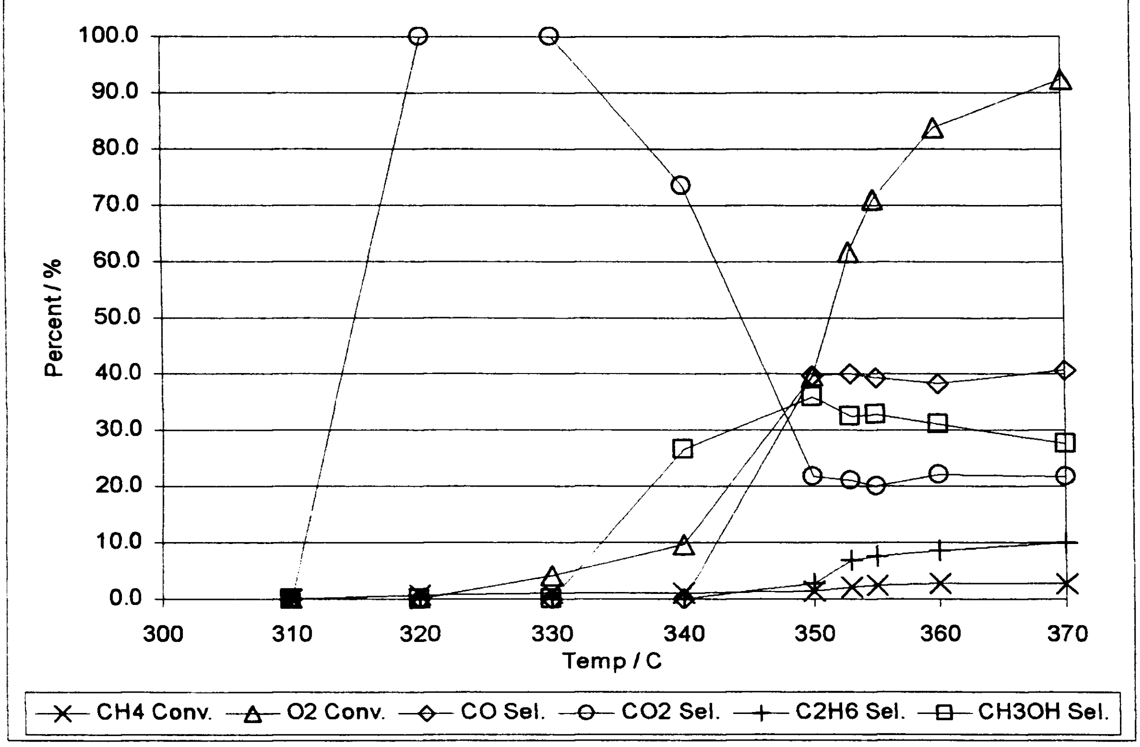
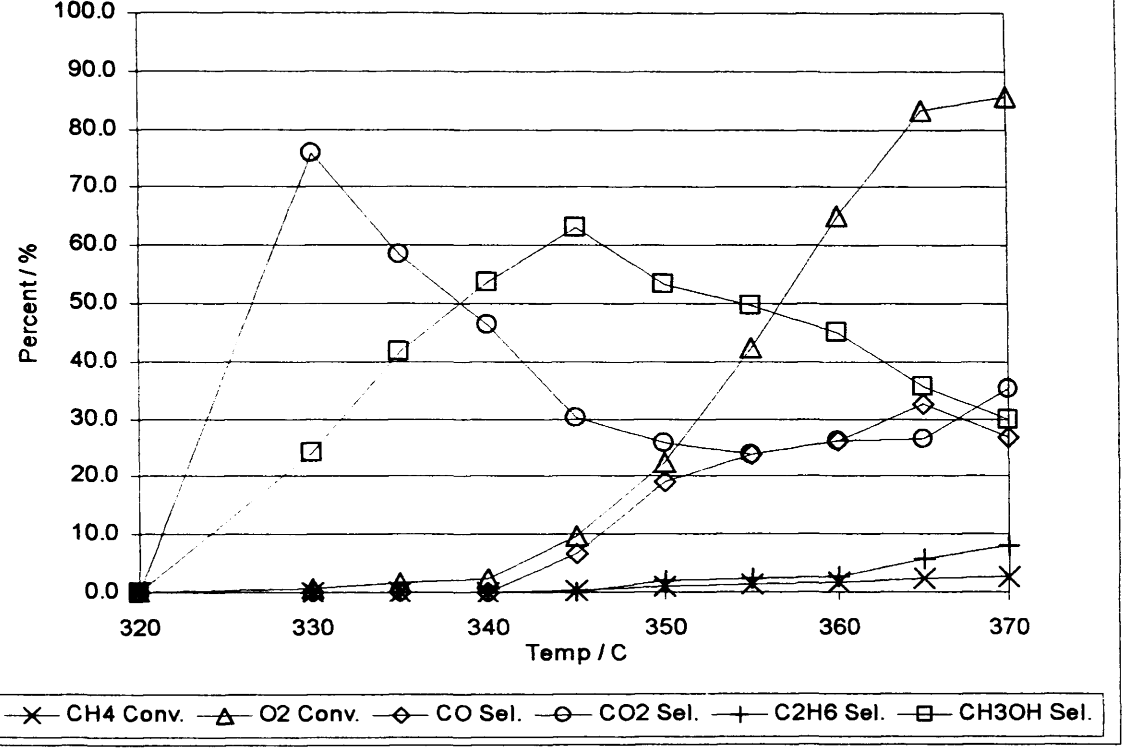


Figure 5.27 Methane partial Oxidation over 2%Au ZnO : MoO3, 25:75, separate layers

As before, the ratio of catalysts was altered. In order to try and promote selective partial oxidation, the amount of 2%Au ZnO was decreased to 25% of the catalyst volume, and MoO_3 increased to 75%. The results for this experiment are displayed in figure 5.27. Initial activity was detected at 320°C with trace CO_2, with oxygen conversion rising to 9.8% at 340°C, before rising to 39.8% at 350°C. In this temperature region CO_2 selectivity decreased rapidly from 73% to 22%, then staying in the 21-23% region for all higher temperatures. CH_3OH selectivity increased until reaching a maximum of 36% at 350°C, before falling very steadily until a reading of 28% at 370°C. As oxygen conversion increased with higher temperatures, so did CO selectivity, being the most selective product at 350°C and above, rising to a maximum of 41% at 370°C. There were low levels of ethane detected from 350°C

The amount of 2%Au ZnO was decreased again, to ⅛ of the catalyst volume, and MoO_3 increased to ⅞. The results for this experiment are displayed in figure 5.28.

Figure 5.28 Methane Partial Oxidation over 2%Au ZnO : MoO3, 1/8:7/8, separate layers

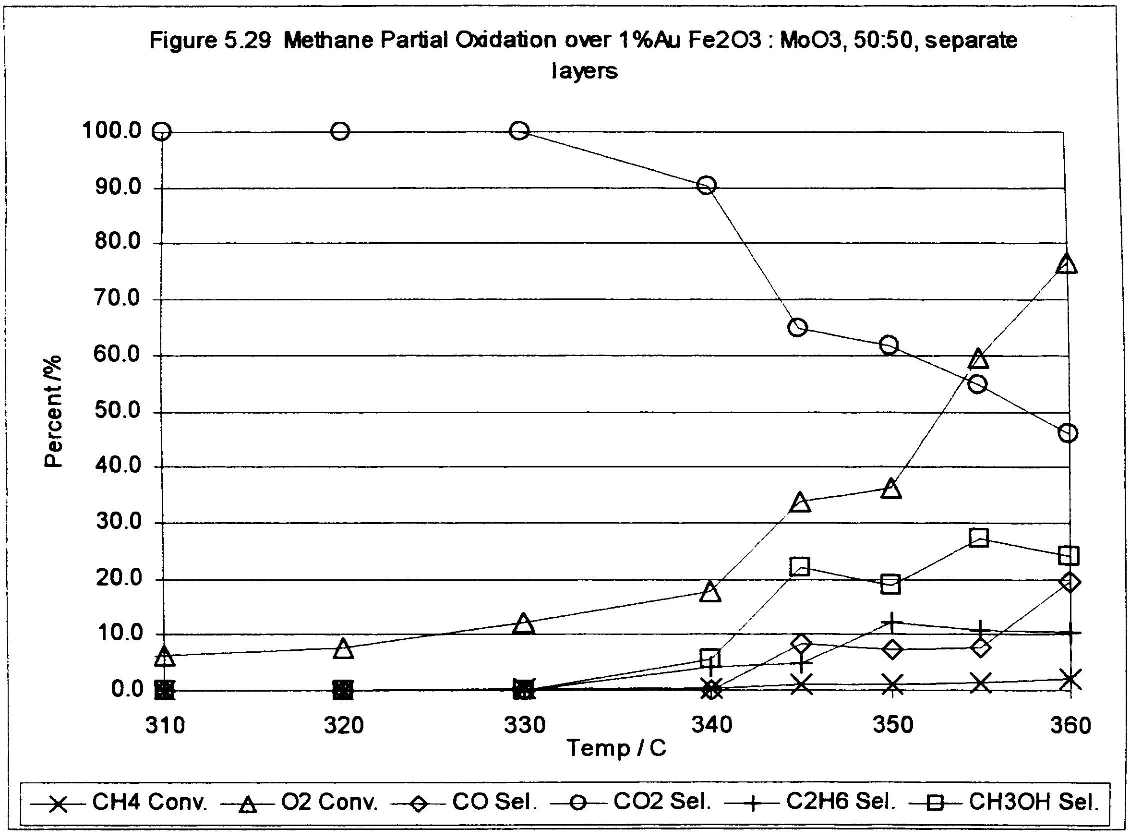


Trace amounts of CO_2 and methanol were detected at 330°C, with selectivities of 76% and 24% respectively. After this temperature, CO_2 selectivity then fell, to a minimum level of 24% at 355°C. As the CO_2 selectivity fell, CH_3OH selectivity increased rapidly, reaching a maximum value of 63% at 345°C, before decreasing steadily as the temperature was raised. However CH_3OH remained the most selective product in the 340-365°C temperature range. As the oxygen conversion levels rose, so did CO and

CO_2 selectivity the maximum selectivity of ethane was 8% at 370°C, with it first being detected at 350°C.

5.4.3 Methane Partial Oxidation over Separate Layers of 1%Au Fe_2O_3 and MoO_3

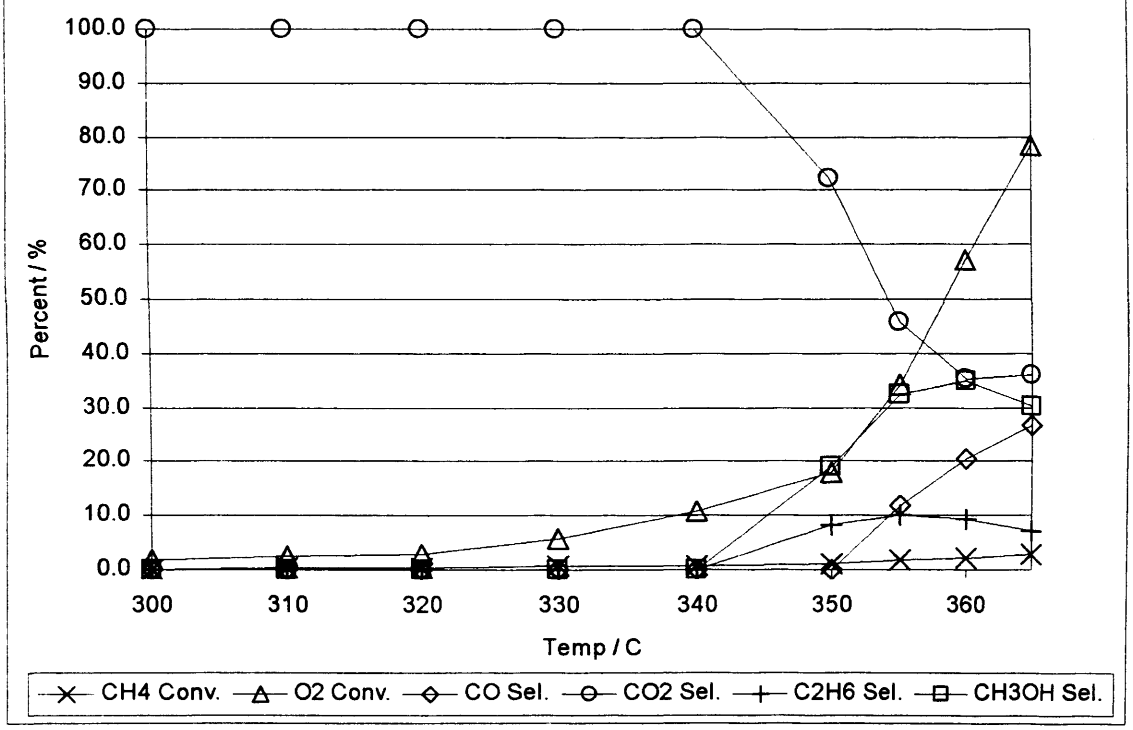
Data representative of the experiment with 1%Au Fe_2O_3 from chapter 4 in a 50:50 ratio with MoO_3 is displayed in figure 5.29.



This catalyst had a very low initial activity temperature, and oxygen conversion rose very steadily until 340°C, when it began to rise more sharply, especially between 350°C and 370°C, rising from 33.8% to 76.5%. CO_2 displayed the highest selectivity of all products throughout the temperature range investigated, with its selectivity dropping as oxygen conversion increased, falling to a minimum value of 46% at 360°C. The maximum CH_3OH selectivity was 27% at 355°C, but this value then fell as the temperature was raised. Also as the temperature and oxygen conversion increased, CO selectivity remained constant, at a level of 7-8%, before increasing to a maximum of 19% selectivity at 360°C. Ethane was first detected at 345°C, with a maximum selectivity of 12%, which then decreased with higher temperatures.

In the next experiment the amount of 1%Au Fe_2O_3 was decreased to 25% of the catalyst volume, and MoO_3 increased to 75%. The results are displayed in figure 5.30.

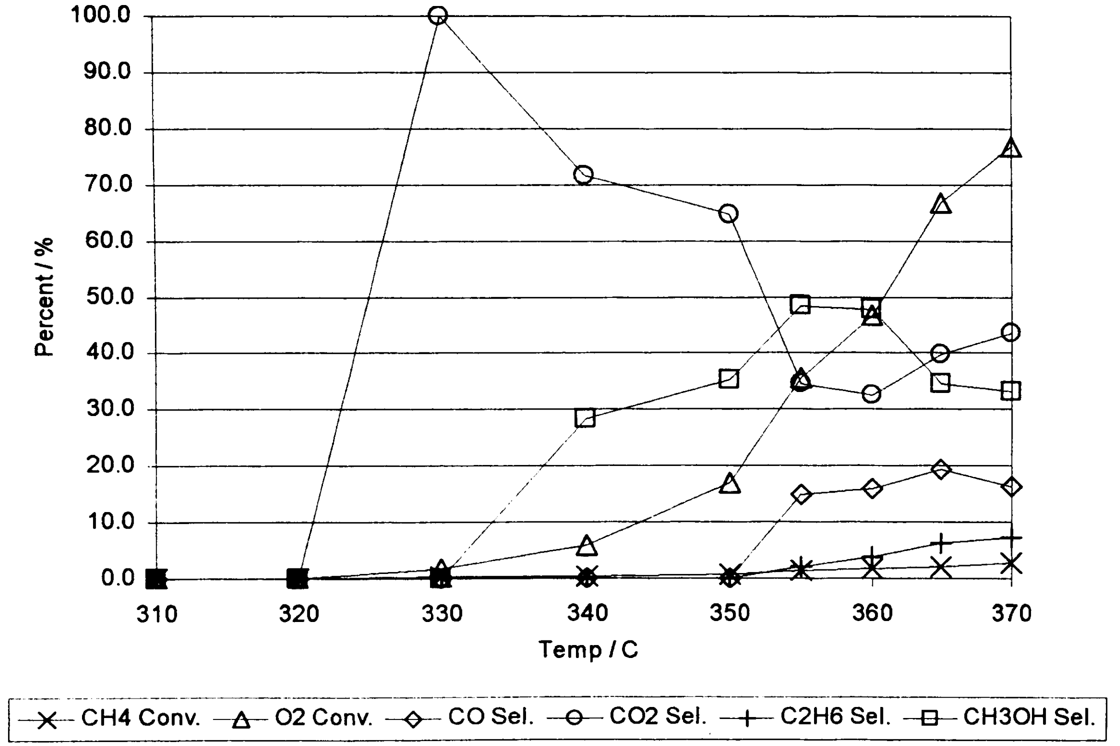
Figure 5.30 Methane Partial Oxidation over 1%Au Fe2O3 : MoO3, 25:75, separate layers



Initial activity was seen at lower temperatures, but the oxygen conversion level remained low until reaching 10.7% at 340°C, and at this temperature and below, CO_2 was the only product detected. At 350°C, as oxygen conversion began to increase, and was at a level of 18.1%, CH_3OH was first detected at a selectivity of 19%. Upon further increase of the temperature CO_2 selectivity decreased and CH_3OH selectivity increased, reaching a maximum of 35% at 360°C, with CO_2 selectivity also at 35%. Also above 350°C CO was detected, and at higher oxygen conversions CO selectivity rose, to a maximum level of 27% at 365°C. Low levels of ethane were detected from 350°C onwards.

The amount of 1%Au Fe_2O_3 was decreased again, to ⅛ of the catalyst volume, and MoO_3 increased to ⅞. The results for this experiment are displayed in figure 5.31.

Figure 5.31 Methane Partial Oxidation over 1%Au Fe2O3 : MoO3, 1/8:7/8, separate layers



Trace amounts of CO_2 were detected at 330°C, where it was the only product detected. At 340°C CH_3OH was first detected, at a selectivity of 28%, and there were only two products detected until 355°C. At this temperature CO was first detected, CO_2 selectivity fell and CH_3OH selectivity rose to its maximum selectivity of 49%, falling slightly to 48% at 360°C. Above 360°C CH_3OH selectivity fell, CO_2 selectivity rose and CO selectivity rose to its maximum selectivity, 19% at 365°C. Low levels of ethane were detected from 355°C onwards.

5.5 Discussion

5.5.1 Discussion for Catalysts in Section 5.2

Due to the large excess of CH_4 compared to O_2 in the feed supply in this study, CH_4 conversion was limited by the extent of the O_2 supply. As explained in chapter 1, previous studies have mostly concentrated on the homogeneous gas phase oxidation of CH_4 to CH_3OH. In this study the heterogeneous reaction has been investigated, with no attempt made to modify reaction conditions in order to maximise CH_3OH selectivity. Based on the hydrogen balance, current kinetic models predict a limiting selectivity of 67% for methanol [7]. Hydroxyl radicals, produced in the gas phase, are highly efficient in forming H_2O by hydrogen abstraction. As the CH_4 is in excess, it is therefore the major source for hydrogen atom abstraction. Since both CH_4 and CH_3OH contain four hydrogen atoms, the loss of hydrogen to form H_2O suggests that not all the available carbon from CH_4 can react to produce CH_3OH. Therefore from the appropriate stoichiometric reactions the limiting selectivity was derived.

In order to gauge the extent of effect a catalyst has on a reaction, it must be compared to the reaction where there is nothing in the reactor tube, and when there is an inert substance in place of the catalyst. A major effect of the addition of a catalyst bed to a reactor tube is the residence time of the gas in the heated zone of the reactor. The residence time, t_r in the heated zone can be summarised in the following equation:-

$$t_r = \frac{1}{S_v} \times \frac{273}{T} \times P$$

$$\text{Where } S_v = \frac{\text{Flow rate at 273K, 1 bar pressure}}{\text{Void volume of reactor heated zone}}$$

T = Reaction Temperature (K)

P = Reaction Pressure (bar)

As the quartz was pelleted, and was of uniform size, a maximum packing efficiency of 74% would be possible. If this were true, the void volume would be 26% for the quartz. Therefore the empty tube would have a higher residence time by a factor of 3.8 (100/26=3.8), resulting in the higher conversions of CH_4 and O_2. The residence time for the empty tube at 400°C was approximately $5.07s^{-1}$, and this is reduced to approximately $1.31s^{-1}$ upon the addition of a catalyst bed. An influence on CH_4 conversion may be due to the presence of pelleted quartz itself. Baldwin et al [8] concluded that the use of SiC or quartz considerably decreased the rate of CH_4 oxidation, through influencing radical reactions, by promoting quenching reactions. However this study did not take the residence time in the heated reactor zone into consideration. Another study, by Chun and Anthony [9], has taken residence time into consideration, and has concluded that radical reaction inhibition did not become significant until the surface area to volume ratio was at a value of 300cm^{-1} or higher, and therefore under the conditions used in this study would not be considered relevant.

The distribution of products for both quartz and the empty tube were not dissimilar, and this suggests that homogeneous gas phase reactions in the void space of the quartz were responsible for the product selectivities. Due to the much lower residence time for quartz, at higher temperatures (over 380°C), CH_3OH selectivity is much higher for quartz than for the empty tube, as it seems the increased residence time has led to further oxidation of the CH_3OH, to CO_2. For the quartz, further oxidation of the CH_3OH was also to CO, though not to as high a level as CO_2. However at temperatures below 380°C, it seems the residence time is not a factor as CH_3OH selectivity is higher for the empty tube than over quartz. Previous studies by Burch et al [10] suggest that CH_3OH is stable in the presence of O_2 in a blank tube in the pressure range 1-50 bar at 475°C. When CH_4 is then added to the gas feed, CH_3OH is less stable, and under the same conditions a significant proportion of CH_3OH is further oxidised to carbon oxides. There are several possible explanations for the decrease in CH_3OH selectivity and increase of CO_2 at higher temperatures, including; the effect of the much larger surface area of the quartz, the more efficient heat transfer properties of the quartz, and the disturbance of the flow pattern of the gases by the quartz. One or all of these may affect the reaction products.

The results have been quantified in an attempt to assess which catalyst has the best results. When CH_3OH yields are usually calculated, the CH_4 conversion is used.

However, as the CH_4 counts recorded in this study are so large, up to 700,000, the difference between these large numbers are not deemed reliable enough to calculate the yield. Therefore for these results the conversion by products values have been used to calculate the CH_3OH per pass % yield. The following equation was used to calculate the yield:-

$$\frac{\text{Conversion by Products x } CH_3OH \text{ Selectivity}}{100} = CH_3OH \text{ per pass \% yield}$$

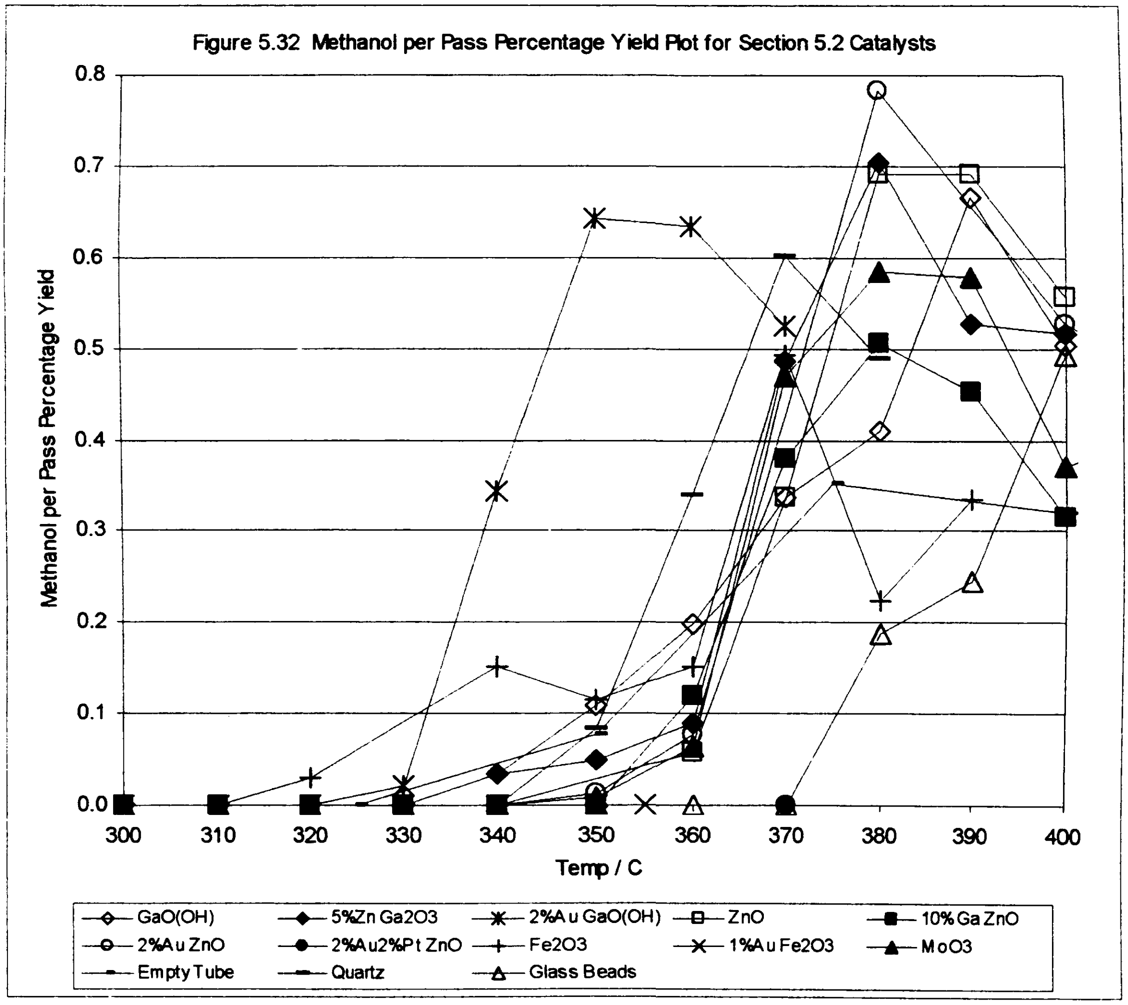


Figure 5.32 Methanol per Pass Percentage Yield Plot for Section 5.2 Catalysts

The figures for the catalysts tested in section 5.2 are displayed in figure 5.32. Until higher temperatures, GaO(OH) produced only carbon oxides. CH_4 and O_2 conversion were much higher than that of quartz at the same temperatures. This would imply that the reactions leading to the products detected were not completely homogeneous. Upon the addition of 5%Zn by coprecipitation to gallium oxide, very similar selectivity of products is seen throughout the temperature range. However, ethane was detected over this catalyst at much lower temperatures, and at a higher selectivity, than for the unmodified gallium catalyst. The zinc was added to gallium oxide in an attempt to create defects within the catalyst, and it may be that this could be a result of defects within the Ga_2O_3 catalyst. This is also true for the ZnO catalyst with 10%Ga by coprecipitation, as there was no ethane detected for ZnO, but there was ethane detected over the zinc catalyst modified with Ga. Unfortunately, as it has not been determined whether or not defects are present by characterisation within these catalysts, this cannot be proven.

As in chapter 4, the addition of Au by coprecipitation resulted in a higher activity for the catalyst, with a lower activation temperature, higher O_2 and CH_4 conversions at lower temperatures. At these lower temperatures, CO_2 was the only product. For the GaO(OH) and 10%Zn Ga_2O_3 catalysts CO_2 was the only product until 340°C, with CO_2 selectivity over the Au modified catalyst at 92% until this temperature. Therefore it can be deduced that until this temperature all gallium catalysts have similar selectivities, and the modification of the gallium catalysts with Zn and Au alters its oxidative properties. The Au modified catalyst produced no ethane, only oxidising CH_4 to carbon oxides and CH_3OH. At lower temperatures, especially at 350°C, the CH_3OH per pass yield is much higher than any other catalyst, by a factor of three. At this temperature the CH_3OH selectivity was 34%, O_2 conversion was 73.1% and the conversion by products at a value of 1.92%. As the temperature is increased for the gallium catalysts, CH_3OH selectivity falls as it is further oxidised to carbon oxides.

For all the ZnO based catalysts tested, CO_2 was the only product detected at lower temperatures, with its selectivity falling as O_2 and CH_4 conversion increases. The conversion of O_2 and CH_4 over the quartz was higher than over the zinc based catalysts. For ZnO CO_2 was the main product, followed by CH_3OH and then CO at higher temperatures and conversions. Upon the addition of gallium, the carbon oxide and CH_3OH levels are all similar, with low levels of ethane. Thus it can be assumed that while the addition of gallium by coprecipitation to ZnO lowers the light off temperature of the catalyst, it does not increase its oxidation properties. The addition of Au lowered the light off temperature of ZnO, with all ZnO catalysts producing only CO_2 at lower temperatures and conversions. Similarly to the gallium oxide catalysts, the production of only CO_2 ends at a certain temperature; the ZnO and Ga modified ZnO had 100% CO_2 selectivity until 360°C, with the Au modified catalyst having 95% selectivity at this temperature. At 380°C the CH_3OH per pass percentage yield was 0.72%, the highest yield for any of the catalysts tested in section 5.2. The respective conversions and selectivities at this temperature was CH_3OH selectivity at 34%, O_2 conversion 79.5% and conversion by products at a value of 2.31%. This may be due to the production of methyl peroxy radicals, which is discussed more fully later, which then may react in the gas phase to produce CH_3OH.

The gallium and zinc catalysts modified with 2%Au and 2%Pt had almost exactly the same activity, with only the zinc catalyst displayed in the results section. They displayed very low light off temperatures, with total conversion to CO_2 over the whole temperature range. This is consistent with previous studies [11], where modification of catalysts with these precious metals produce CH_4 combustion catalysts.

As has been explained in chapter 4, Fe_2O_3, both unmodified and modified with Au, have been tested, to appraise the feasibility of using a weak CH_4 combustion catalyst [12] as the CH_4 activation component of a successful CH_4 partial oxidation catalyst. The main product for the unmodified Fe_2O_3 was CO_2, with the selectivity for this product remaining high throughout the entire temperature range. Ethane was seen at lower temperatures and higher selectivities over the unmodified Fe_2O_3 than for the catalyst modified with Au. Both CH_4 and O_2 conversion are higher for the Au modified Fe_2O_3 catalyst, with O_2 conversion at levels of over 70% at 350°C for the Au catalyst, whilst the unmodified Fe_2O_3 catalyst is at a level of 13.9%. The 1%Au Fe_2O_3 catalyst is such a strong oxidant that if there were any CH_3OH produced in the reaction, it was then further oxidised to CO_2, with no CO detected.

The conversion of CH_4 and O_2 was higher over pelleted quartz than over MoO_3 throughout the entire temperature range. The CH_3OH selectivity pattern for MoO_3 was similar to that of quartz, with a maximum selectivity at 360°C, with selectivity then falling as the temperature was raised, implying that the CH_3OH produced is then further oxidised to CO_2. Except at 380°C, where the selectivities for both were 27%, CH_3OH selectivity was higher for MoO_3 than quartz for all temperatures tested

At certain temperatures, the conversion of CH_4 and O_2 was lower over the catalysts in comparison to the inert quartz. Unlike as previously discussed in this section, the residence times are identical and so this effect can be discounted. The decrease in conversion may be due to the ability of the oxide to quench gas phase reactions, in relation to the quartz. However, the catalysts modified with Au do not fit into this theory, and have much higher O_2 and CH_4 conversions at similar temperatures than the quartz. This is to be expected, as the results in chapter 4 proved, whereby the addition of Au lowered the light off temperature of the catalyst, and increased the rate of O_2 and CH_4 conversion. For the 2%Au GaO(OH) catalyst, the O_2 and CH_4 conversion was higher, but interestingly so was its CH_3OH selectivity at similar temperatures. This was not true for the 2%Au ZnO catalyst, its CH_3OH selectivity is lower, but with higher O_2 and CH_4 conversion at lower temperatures, with similar conversion properties at higher temperatures. The 1%Au Fe_2O_3 had much higher O_2 and CH_4 conversion, as would be expected from making a CH_4 combustion catalyst more active, CH_4 was oxidised almost completely to CO_2.

Another factor that has to be considered is the reaction of $CH_3\cdot$ radicals with the surface of the oxide catalyst. This reaction proceeds according to the equation put forward by Tong and Lunsford [13], shown below:-

$$M^{(n+1)+}O^{2-} \quad + \quad CH_3\cdot_{(g)} \quad \rightarrow \quad M^{n+}(OCH_3)^-$$

The radical reaction rate is greater the easier the oxide is to reduce. The formation of surface methoxide and formate species were confirmed using IR spectroscopy, and these were suggested to be intermediates for the production of carbon oxides. This route for the formation of carbon oxides would be more pronounced at higher temperatures, where the effect of radical reactions are more prevalent. When the results for this section are considered, it would seem that if this were the route of the reaction, then it was more likely to form CO_2 than CO. At lower temperatures, rather than via the interaction of $CH_3\cdot$ with the surface, the production of carbon oxides would more likely be from the oxidation of CH_3OH.

For the reaction with the empty tube, and with some of the catalysts, the selectivity of ethane increased as the temperature was increased. Examples include GaO(OH) and MoO_3, and this usually coincided with a decrease in the selectivity for CH_3OH. This effect can be explained when the following equilibrium is considered:-

$$CH_3\cdot \quad + \quad O_2 \quad \leftrightarrow \quad CH_3O_2\cdot$$

Below 500°C, the equilibrium lies to the right hand side of the equation, in favour of the methyl peroxy radical, increasing the probability of gas phase CH_3OH production, possibly through the reactions:-

$$CH_3O_2\cdot \quad + \quad CH_4 \quad \rightarrow \quad CH_3OOH \quad + \quad CH_3\cdot$$

$$CH_3OOH \quad \rightarrow \quad CH_3O\cdot \quad + \quad HO\cdot$$

$$CH_3O\cdot \quad + \quad CH_4 \quad \rightarrow \quad CH_3OH \quad + \quad CH_3\cdot$$

This could also explain why, at higher pressures, that CH_3OH not HCHO is produced, with HCHO more often produced at atmospheric pressure. Above 500°C, the equilibrium lies to the left hand side, with $CH_3\cdot$ production favoured. Since the oxidative coupling of CH_4 to form ethane is generally accepted to occur via the dimerisation of $CH_3\cdot$ radicals, with increased temperature the selectivity towards coupling products increased.

5.5.2 Discussion for Physical Mixture Catalysts in Section 5.3.

As explained earlier in chapter 1, the theory behind the physical mixture catalyst is that one constituent part is responsible for the activation of CH_4, with these catalysts tested earlier in chapters 3 and 4. The other constituent part of the mixed oxide system is responsible for oxygen activation and insertion. The oxide chosen for this was MoO_3, as it has extremely high oxygen exchange activity, where the mechanism of exchange occurs across the whole of the lattice oxygen [14], not just on the surface layer, meaning the mobility of lattice oxygen is very easy. In other studies, other oxides that have shown similar oxygen exchange properties, V_2O_5 and WO_3 have found many applications as selective oxidation catalysts [15].

The presence of the catalyst is postulated to provide the CH_4 activation by producing an activated surface methyl species. The migration of the activated methyl species to an M=O site on the MoO_3 could lead to the formation of a surface OCH_3 species. The activation catalyst and MoO_3 is physically mixed to provide many phase boundaries, leading to the formation of CH_3OH via a migration process, outlined later. The rapid regeneration of the M=O site due to the lattice oxygen, suggested by Smith and Ozkan [16], will make OCH_3 desorption to the gas phase relatively easy. M=O sites on the surface of MoO_3 have been proposed as the active sites for CH_4 partial oxidation to

HCHO at atmospheric pressure. Also, the loss of oxygen on the surface would quickly be replaced by oxygen from the lattice, meaning no deactivation of the MoO_3.

It is hypothesised that the surface OCH_3 species can lead to CH_3OH by two possible routes. The first is via the reaction in the gas phase with CH_4:-

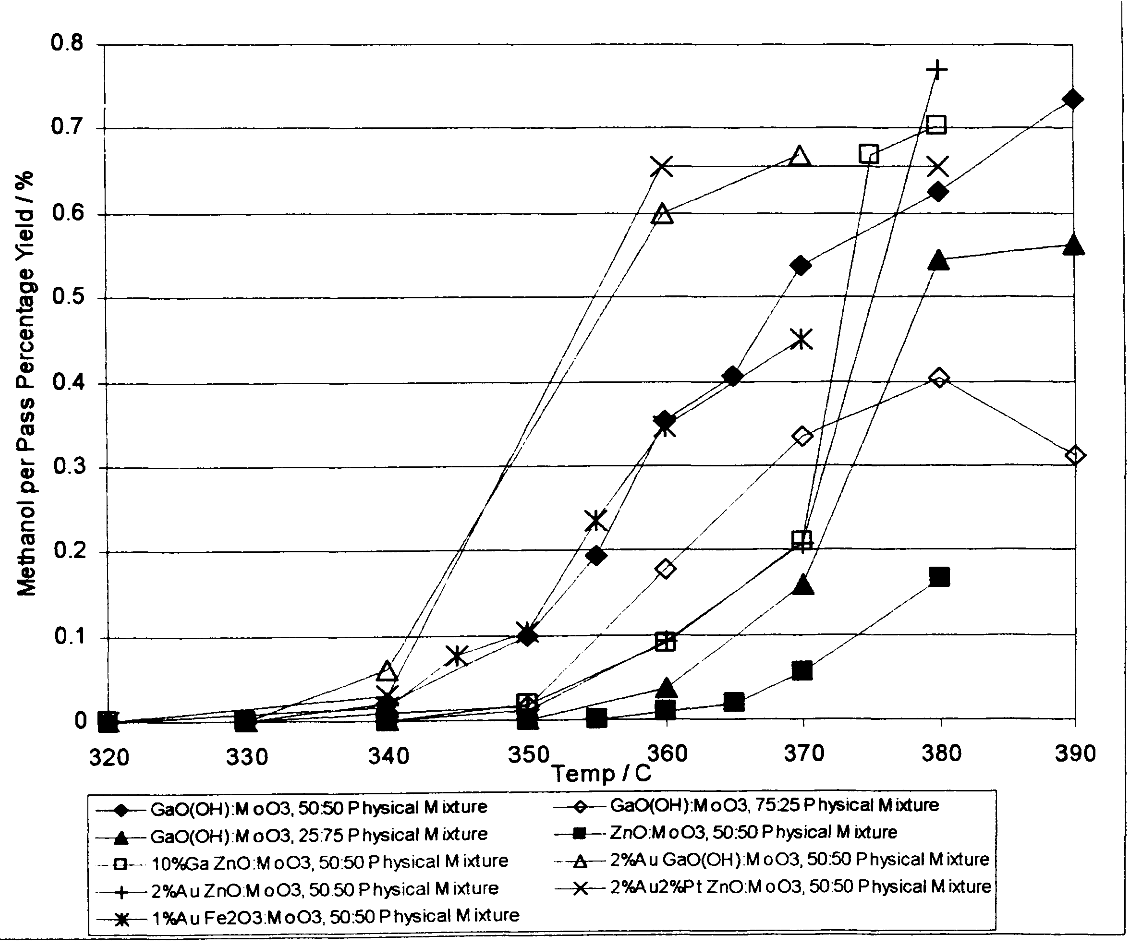
$$CH_3O\cdot + CH_4 \xrightarrow{\cdot} CH_3OH + CH_3\cdot$$

The second is via the surface reaction with a supply of hydrogen, possibly from OH groups, forming CH_3OH, which would then desorb from the surface. However, the formation of CH_3OH could occur in the opposite manner to above, with the migration of oxygen to the adsorbed species on the activation catalyst. This occurs for the $MoO_3/\alpha\text{-}Sb_2O_4$ catalyst used for the oxidation of isobutene to methacrolein (C_4H_6O) [17]. Due to the differences in the reacting species (the radical in this reaction is much larger than the methyl radical necessitating the oxygen spillover), and the oxygen species migrating to the activation catalyst could promote further oxidation, which is not observed. Therefore this reverse process is thought not to occur.

As has been previously reported by Taylor et al. [18], the combination of MoO_3 and Ga_2O_3 combined the beneficial aspects of the two oxides to create a better CH_4 partial oxidation catalyst. Even though GaO(OH) was used in these experiments instead of Ga_2O_3, at first glance this is also the case in these experiments. The 50:50 physical mixture has the same light off temperature as GaO(OH), with increased CH_3OH selectivity, with CO_2 selectivity decreased. Between the temperatures of 320-360°C, the catalyst has similar conversions to the GaO(OH) catalyst tested in section 5.2.

From 370°C upwards the selectivities are similar to those of the MoO_3 tested, also in section 5.2, with the highest selectivity to CO, with CO_2 and CH_3OH at a similar level in the 10-30% range. When the ratio of GaO(OH):MoO_3 is varied, O_2 conversion is higher for the 75:25 and 50:50 catalysts than for the 25:75 physical mixture at the temperatures of 360-370°C, and at 370°C a selectivity of 39% towards CH_3OH was recorded. The selectivity at this temperature for the other physically mixed GaO(OH) catalysts and MoO_3 was much lower. The 75:25 mixture had similar CH_3OH selectivity over the whole range as GaO(OH). The addition of MoO_3, even at levels of 25%, makes the selectivity for CO_2 drop to the same levels as MoO_3, with CO selectivity rising to the same level as MoO_3 accordingly.

Figure 5.33 Methanol per Pass Percentage Yield for Section 5.3 Physically Mixed Catalysts

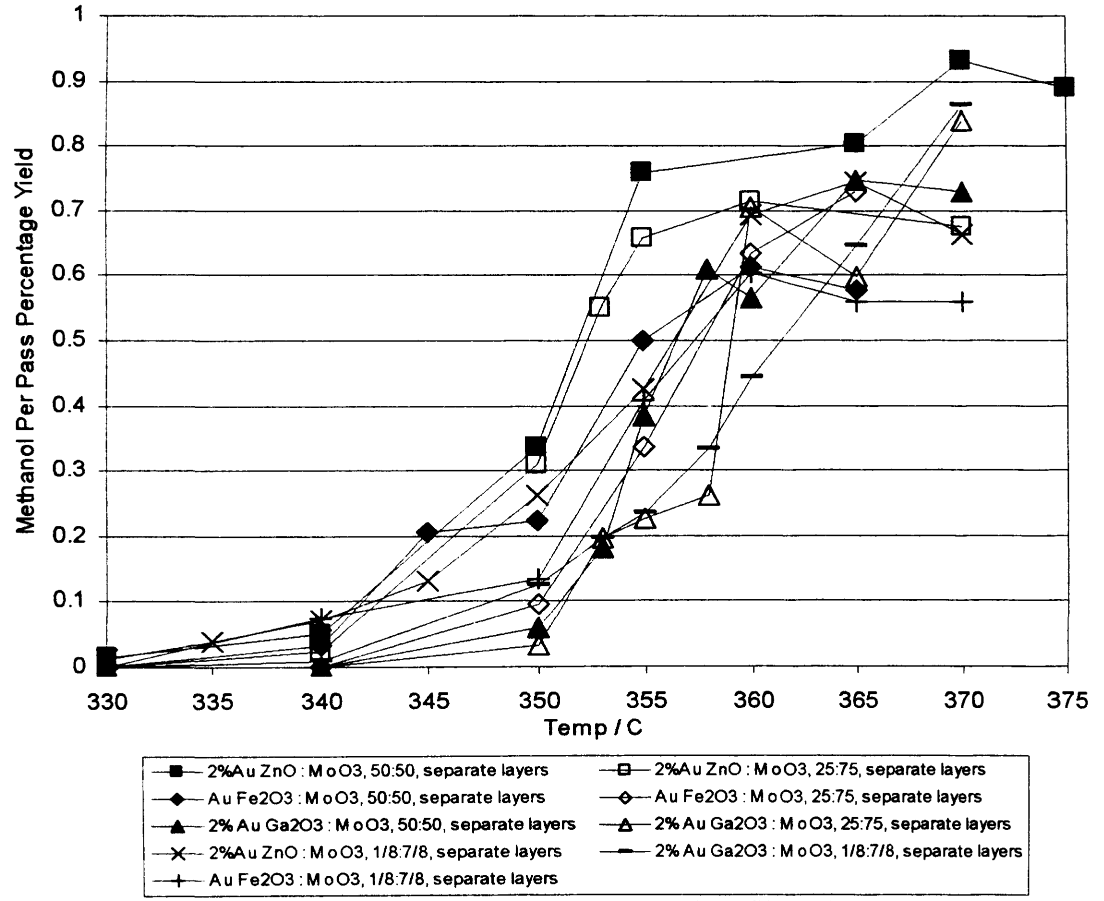


The CH_3OH per pass percentage yield for these physical mixture catalysts were calculated according to the equation in section 5.5.1., and are displayed in figure 5.33. The effect of physically mixing GaO(OH) and MoO_3 previously reported by Taylor were repeated here. The GaO(OH):MoO_3 50:50 physical mixture had a higher yield than its two constituent parts. At 370°C the yield of the mixture was 0.537%, GaO(OH) 0.337% and MoO_3 0.47%. At 380°C the yields were 0.624%, 0.401% and 0.583% respectively. The maximum yield for the GaO(OH):MoO_3 50:50 physical mixture was 0.7537% at 390°C. The highest yield for any of the physically mixed catalysts is 0.769% at 380°C for the 2%Au ZnO:MoO_3 catalyst. This is a higher yield than for the 2%Au ZnO tested in section 5.2. The mixture of the Au modified ZnO with MoO_3 produced a higher yield, but the addition of MoO_3 to unmodified ZnO is not as beneficial, giving a lower CH_3OH yield. While the 10%Ga ZnO catalyst had a lower CH_3OH per pass percentage yield than ZnO, when these are combined with MoO_3 the Ga modified catalyst had a far superior CH_3OH yield. At lower temperatures, the highest values for the physically mixed catalysts were for the 2%Au2%Pt ZnO:MoO_3 50:50 mix with a maximum yield of 0.655% at 360°C , and the 2%Au GaO(OH):MoO_3 50:50 mix with a maximum yield of 0.668% at 370°C. These values were high as these were effectively combustion catalysts with higher O_2 conversion at lower temperatures, not necessarily with high CH_3OH selectivities. None of the physical mixtures in this section demonstrated outstanding performance in relation to the catalysts tested in section 5.3. The higher yields for the physical mixtures that Taylor et al. reported were not repeated, with a possible reason for this being the influence of the reactor walls. In Taylor's study the reactor was lined with silica, and in this study the reactor wall was stainless steel.

5.5.3 Discussion for Separate Layer Catalysts in Section 5.4

As previously described in Chapter 1, Sun et al. [19] have developed the use of a double layered bed for CH_4 partial oxidation, consisting of two separate layers of 1%Sr La_2O_3 and MoO_3/SiO_2. The first layer of 1%Sr La_2O_3 was chosen to provide a flux of methyl radicals to the molybdenum bed, which converted the radicals to HCHO. The overall result of these changes in selectivity and conversion was an increase in the space time yield of HCHO by a factor of 3.4.

Figure 5.34 Methanol Per Pass Percentage Yield for Section 5.4 Separate Layer Experiments



When the double layered bed was replaced with a single physically mixed bed of the same catalyst composition its HCHO yield was reduced by nearly a factor of two, and the CH_4 conversion was increased. The study concluded that the formation of formaldehyde occurred on the surface of the MoO_3/SiO_2 catalyst surface rather than in the gas phase.

For the separate layer experiments carried out in this study no HCHO was detected, due to the reasons highlighted in the discussion section earlier. The lower layer catalyst that had the highest CH_3OH per pass percentage yield, displayed in figure 5.34, were those containing 2%Au ZnO. From 350-370°C the 50:50 ratio 2%Au ZnO had the highest yield. All three experiments using this catalyst, using the different ratios of 50:50, 25:75 and ⅛:⅞ had some of the highest yields. The maximum yield was 0.931% at 370°C for the 50:50 2%Au ZnO:MoO_3 experiment. This is a much higher yield than for MoO_3 at this temperature, 0.47%, and that for 2%Au ZnO, while there is no reading at this temperature, by extrapolation from the graph would have a yield in the region of 0.4-0.5%. At 355°C, the 50:50 2%Au ZnO separate layer yield was 0.76%, and at 365°C it was 0.805%. In comparison, at 360°C, the MoO_3 yield was 0.063%, and the yield for 2%Au ZnO was 0.077%, a huge difference.

The 2%Au GaO(OH) separate layer experiments all produced results with high CH_3OH selectivities at lower temperatures, and when O_2 conversion was low. As the ratio of 2%Au GaO(OH) is lowered, the selectivities of CO_2 decrease, CH_3OH selectivity increases and is detected at lower temperatures. For all three experiments with 2%Au GaO(OH), at higher temperatures, the selectivities of the products tend to follow the same pattern, with CO_2 in the 20-30% region, CO selectivity rising,

CH_3OH selectivity decreasing, and ethane selectivity rising to levels of around 10%. The maximum CH_3OH per pass percentage yields for 2%Au GaO(OH) in the separate layer experiments were as follows; the 50:50 ratio maximum yield was 0.744% at 365°C, the 25:75 maximum was 0.838% at 370°C, and the ⅛:⅞ maximum was 0.8617%, also at 370°C.

The results of the 2%Au ZnO experiments have some of the same trends as the 2%Au GaO(OH) reviewed in the previous paragraph. As the ratio of 2%Au ZnO is decreased, O_2 and CH_4 conversions decrease at equivalent temperatures, but the light off temperature remains lower than for MoO_3. When the ratio is ⅛:⅞ CH_3OH is detected at the lowest temperature, at 330°C. At the lower temperatures, when the 2%Au ZnO ratio is decreased, the selectivity for CO_2 also decreases; when the ratio is 50:50 CO_2 selectivity is 100% from 300-330°C, for the 25:75 ratio CO_2 selectivity is 100% from 320-330°C, and for the ⅛:⅞ ratio the maximum CO_2 selectivity is 76% at 330°C, with selectivity falling steadily as the temperature is increased. Another feature of increasing temperature is the increasing selectivity of CO, with CO_2 selectivity stabilising in the region of 20-30%. The highest CH_3OH selectivity is detected over the ⅛:⅞ ratio, with a value of 63% at 345°C. The highest yield over all the separate layer catalysts was over the 50:50 ratio 2%Au ZnO catalyst, with a yield of 0.931% at 370°C, corresponding to a CH_3OH selectivity of 38%, with conversion by products at 2.43% and an O_2 conversion of 79.4%

When the ratio of 1%Au Fe_2O_3 is decreased in the separate layer experiments, the O_2 conversion also decreases at lower temperatures. For example, at 330°C, the O_2 conversion for the 50:50 ratio experiment was 12.3%, for the 25:75 ratio it was 5.7%

and the value for the ⅛:⅞ ratio was 1.7%. The light off temperature for the ⅛:⅞ ratio was only at 320°C, with the other ratios being active at much lower temperatures. CH_3OH selectivity increased as the amount of 1%Au Fe_2O_3 was decreased, with the maximum selectivities reading 27% for the 50:50, 35% for the 25:75 and 49% for the ⅛:⅞ ratio. Conversely, as the amount of 1%Au Fe_2O_3 was decreased, the selectivity towards CO_2 decreased, as at higher temperatures the ratio of 1%Au Fe_2O_3 seemed to directly influence the CO_2 selectivity. The highest yield was for the 25:75 ratio, with 0.728% at 365°C.

In a review by Haruta et al [20], for gold modified CO oxidation catalysts, it was proposed that the adsorption of CO on oxidic Au sites are inhibited by moisture because of the stronger adsorption of H_2O. This then suggested that metallic Au particles are responsible for adsorption. Results were inconclusive for the adsorption of O_2 on the Au surface. It was postulated that the adsorption occurred on the step, edge and corner sites of metallic Au particles, with the adsorbed species then interacting with the oxygen molecules at the perimeter sites on the oxide support surfaces. Therefore it is possible that in this study a methyl species could be adsorbed onto the Au species, and could migrate to the boundary with the oxide to form an OCH_3 species on the surface of the catalyst. This could then desorb to form CH_3OH in the gas phase in the manner described earlier. The interaction of the $OCH_3\cdot$ with MoO_3 could then react with the M=O to produce $CH_3O_2\cdot$, the methyl peroxy radical, which after desorbing could then react in the gas phase to create CH_3OH, as described earlier in this discussion section.

The reasoning behind this approach by Sun et al. was to create a flux of methyl radicals that would then be partially oxidised by the MoO_3 to CH_3OH. To an extent, this may be true in this case, as at higher temperatures ethane is detected with increasing selectivity. It may be that at these higher temperatures such a large amount of methyl radicals are produced that not all can be trapped on the MoO_3 surface, resulting in ethane formation via the dimerisation of methyl radicals. Mehandru et al [21] have suggested that methyl radicals can be trapped on the surface of MoO_3. Once the methyl radicals are adsorbed on the surface of the MoO_3 they then form an OCH_3 species on the surface. As described earlier this can relatively easily desorb due to the lattice oxygen, allowing the $OCH_3\cdot$ species to react in the gas phase to form CH_3OH. However, as the catalysts used were not calcined, there may be hydroxyl species present, as was discussed in chapter 4, that may also produce CH_3OH on the surface of the lower layer catalyst.

5.6 Conclusions

In section 5.2, where the CH_4 activation catalysts were tested under high pressure, none demonstrated outstanding performance. When the CH_3OH per pass percentage yields were compared, the only catalyst to give any significantly different results to the rest was the 2%Au GaO(OH), and this was due to the higher conversions at lower temperatures rather than high CH_3OH selectivity. The quantified results for all of the catalysts were in the same region as the inert quartz packing, and at 370°C quartz had the highest yield, but at 380°C and above the majority of catalysts had higher yields. The modification of the catalysts with Au had a tendency to lower light off temperature, with higher O_2 and CH_4 conversion at lower temperatures, however this was usually to the detriment of the CH_3OH selectivity. The modification of Ga_2O_3 and ZnO to create defects, outlined in chapter 3, did not change the activity and selectivities of the gallium based catalysts. While the 10%Ga ZnO gave an inferior yield to ZnO, when this was physically mixed with MoO_3 there was a marked increase in yield.

The reasoning behind the approach for the physically mixed catalysts, tested in section 5.3, was the proposed cooperative effect of two mixed catalysts, one for CH_4 activation, tested in chapters 3 and 4, and MoO_3 for oxygen insertion. The proposed mechanism for this reaction was the activation of CH_4 to form a CH_3 species on the surface of the one catalyst, with the methyl species then migrating to a phase boundary where the MoO_3 was responsible for oxygen insertion. The work carried out in this study attempted to build upon this previous work by looking at more improved CH_4 activation catalysts, either through the creation of defects or modification with precious metals, or through the use of known CH_4 combustion catalysts, and combining this with MoO_3. The end product of this was to hopefully create a mixed oxide catalyst with similar if not better CH_3OH selectivities to MoO_3, at lower temperatures due to the CH_4 activation catalyst. The previous results by Taylor et al. were repeated, with the physical mixture of GaO(OH) and MoO_3 in equal measures producing a higher yield than of its constituent parts. The CH_4 combustion catalysts, apart from 1%Au Fe_2O_3, when combined with MoO_3, produced yields higher than that of MoO_3, but at lower temperatures due to the increased CH_4 activation properties of the combustion catalysts.

The use of separate layers of catalysts reported by Sun et al. was investigated in section 5.4. The testing of the Au modified Ga, Zn and Fe catalysts in separate layers to MoO_3, with differing ratios of the two layers, gave very encouraging results. As the ratio of the CH_4 activation, and in the case of the Fe, CH_4 combustion catalyst is reduced, the selectivities toward CH_3OH increase. The separate layer experiments seem to combine both the lower light off temperature, and higher O_2 and CH_4 conversion properties of the CH_4 activation catalysts, together with the high CH_3OH selectivity and stability over MoO_3. Sun et al. concluded that the use of the first layer was to supply a flux of methyl radicals to the second MoO_3 layer, producing $CH_3O\cdot$ radicals which then react in the gas phase to create CH_3OH. This may be the mechanism of CH_3OH formation, but judging by the low amount of coupling products, namely ethane, until higher temperatures, another method of formation is more likely. A possible pathway is the reaction of desorbed $CH_3O\cdot$ with MoO_3 to create $CH_3OO\cdot$, which may then desorb to react in the gas phase. As the chemistry of Au catalysts is still not certain, other mechanisms of CH_3OH formation are possible.

The highest yield for all the experiments conducted for this study was for the 50:50 2%Au ZnO:MoO_3 separate layer experiment, with a CH_3OH selectivity of 38%, with conversion by products at a value of 2.43%, at an O_2 conversion of 79.4% at 370°C, then falling to a CH_3OH selectivity of 32%, conversion by products at 2.83%, and O_2 conversion at 92%, at 375°C.

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Chapter 6

Conclusions

In a design approach proposed by this group, it was considered a successful partial oxidation catalyst must activate CH_4, activate oxygen and not destroy the desired product, CH_3OH. All these properties could not be found in a single catalyst, so a bi-component catalyst system was proposed, one responsible for CH_4 activation and the other for oxygen activation/insertion. In previous work, two metal oxides demonstrated appreciable activity for the activation of CH_4, these being Ga_2O_3 and ZnO. These oxides were then modified in an attempt to improve their CH_4 activation properties, by lowering the temperature of CH_4 activation, so that the reaction occurs at lower temperatures before gas phase reactions become dominant.

Initial work to increase the activation of Ga_2O_3 through the creation of defects was not successful, though the surface area was greatly increased. The addition of gallium to ZnO by coprecipitation improves its CH_4 activation properties, as well as increasing the surface area of the catalyst.

In later studies the activation of CH_4 was probed by studying CH_4 oxidation at ambient pressure over gallium and zinc based catalysts prepared by precipitation and modified with Au and Pt. The addition of Au to ZnO and GaO(OH) catalysts markedly increased its activity when compared to the unmodified ZnO and GaO(OH) catalysts, with the optimum Au loading for both the Ga and ZnO catalysts being 2%. However, when these catalysts were calcined before use, the 2%Au Ga_2O_3 had the lowest light off temperature, and the Au modified ZnO catalyst with the highest activity was the 5% loading. The addition of Pt at levels of 1% decreased the light off temperature when compared to the unmodified catalysts. The greatest decrease in light off temperature over the ZnO and GaO(OH) catalysts was observed on the addition of both Au and Pt together, at levels of 1% and 2% each respectively.

When the CH_4 activation catalysts were tested under high pressure, none demonstrated outstanding performance, with the only catalyst to give any significantly different results was due to higher conversions at lower temperatures rather than high CH_3OH selectivity. The quantified results for all of the catalysts were in the same region as the inert quartz packing. The modification of the catalysts with Au had a tendency to lower light off temperatures, with higher O_2 and CH_4 conversion at lower temperatures, however this was usually to the detriment of the CH_3OH selectivity. The modification of Ga_2O_3 and ZnO to create defects, outlined in chapter 3, did not change the activity and selectivities of the gallium based catalysts. While the 10%Ga ZnO gave an inferior yield to ZnO, when this was physically mixed with MoO_3 there was a marked increase in yield.

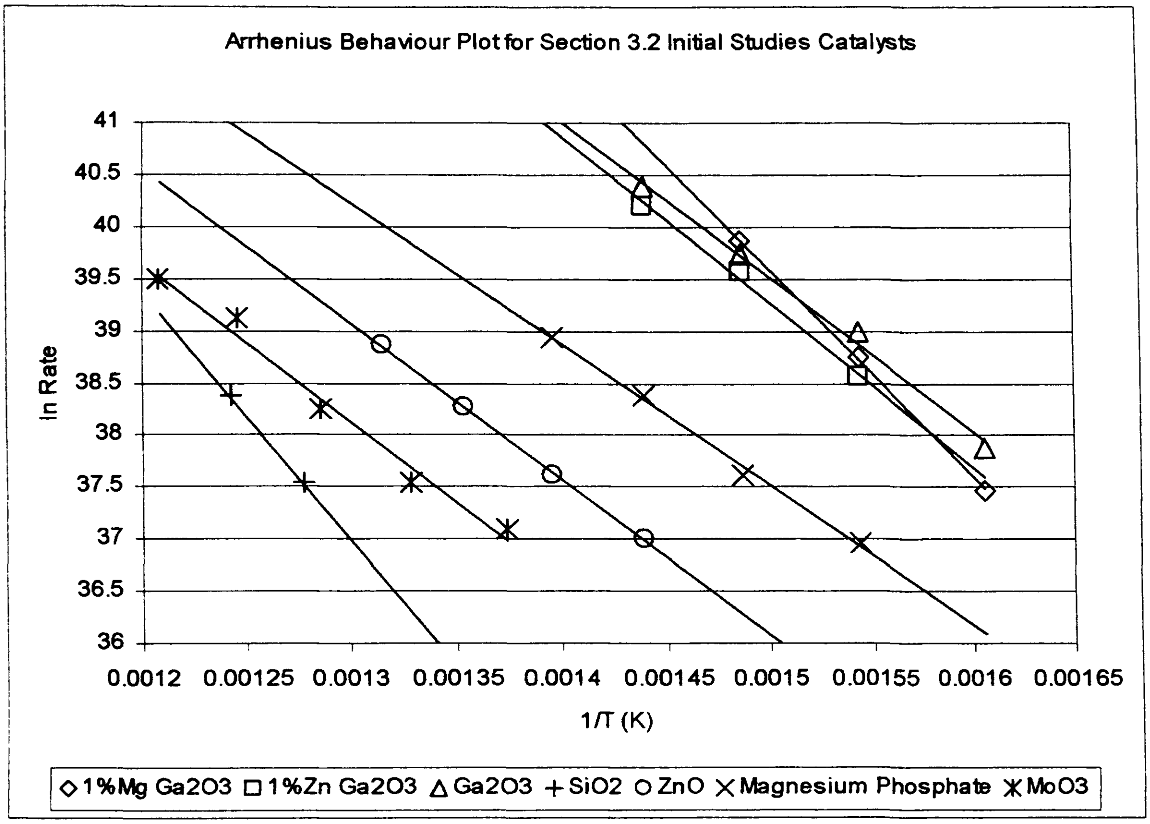
The reasoning behind the approach for the physically mixed catalysts, tested in section 5.3, was the proposed cooperative effect of two mixed catalysts, one for CH_4 activation, tested in chapters 3 and 4, and MoO_3 for oxygen insertion. The previous results by Taylor et al. were repeated, with the physical mixture of GaO(OH) and MoO_3 in equal measures producing a higher yield than of its constituent parts. Other physical mixture catalysts that gave higher CH_3OH per pass yields than that of its constituent parts were the 2%Au 2%Pt ZnO and 2%Au GaO(OH) mixtures, with the addition of MoO_3 not significantly affecting the yield for 2%Au ZnO. However, none gave significantly high yields.

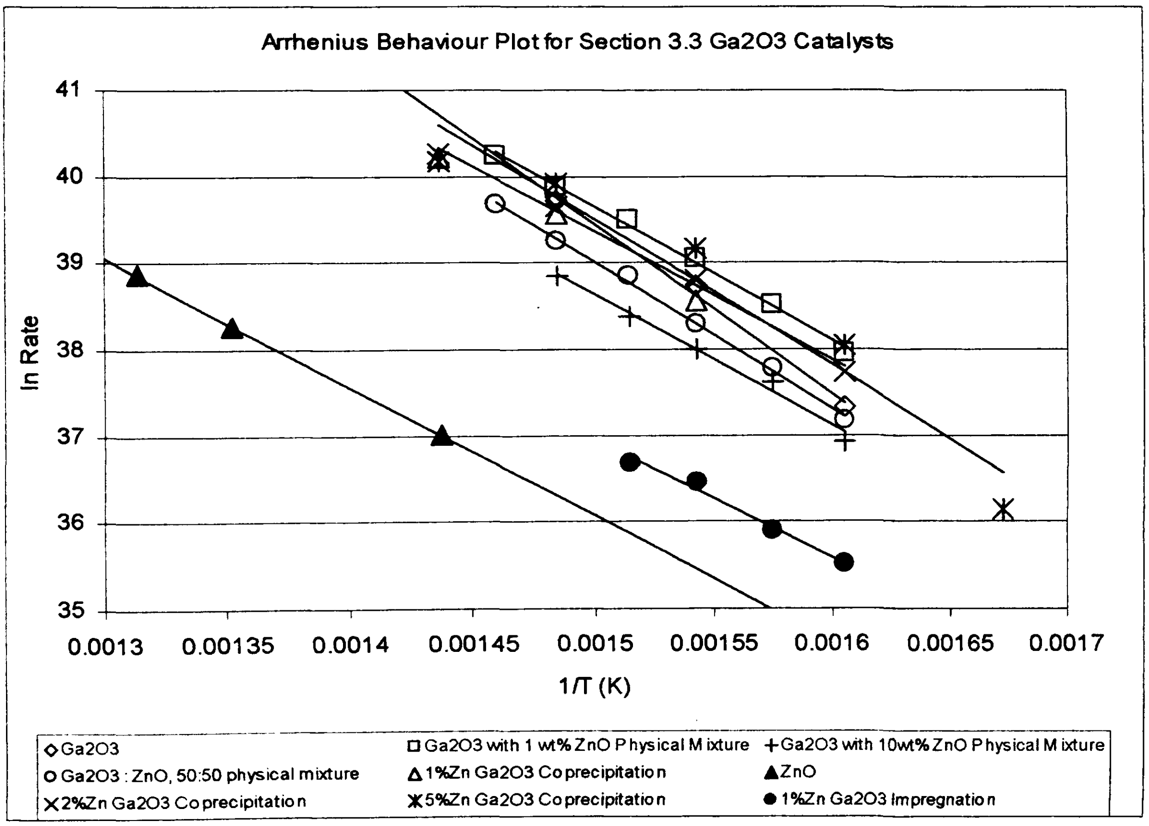
The highest CH_3OH per pass yields recorded in this study were for the separate layer experiments, with the 50:50 ratio 2%Au ZnO:MoO_3 giving the highest yield. In general for the separate layers experiments, as the ratio of the CH_4 activation catalyst is reduced, the selectivities toward CH_3OH increase. The separate layer experiments combine both the lower light off temperature, and higher O_2 and CH_4 conversion properties of the CH_4 activation catalysts, together with the high CH_3OH selectivity and stability over MoO_3. As the chemistry of Au catalysts is still not certain, the method of CH_3OH formation is still uncertain.

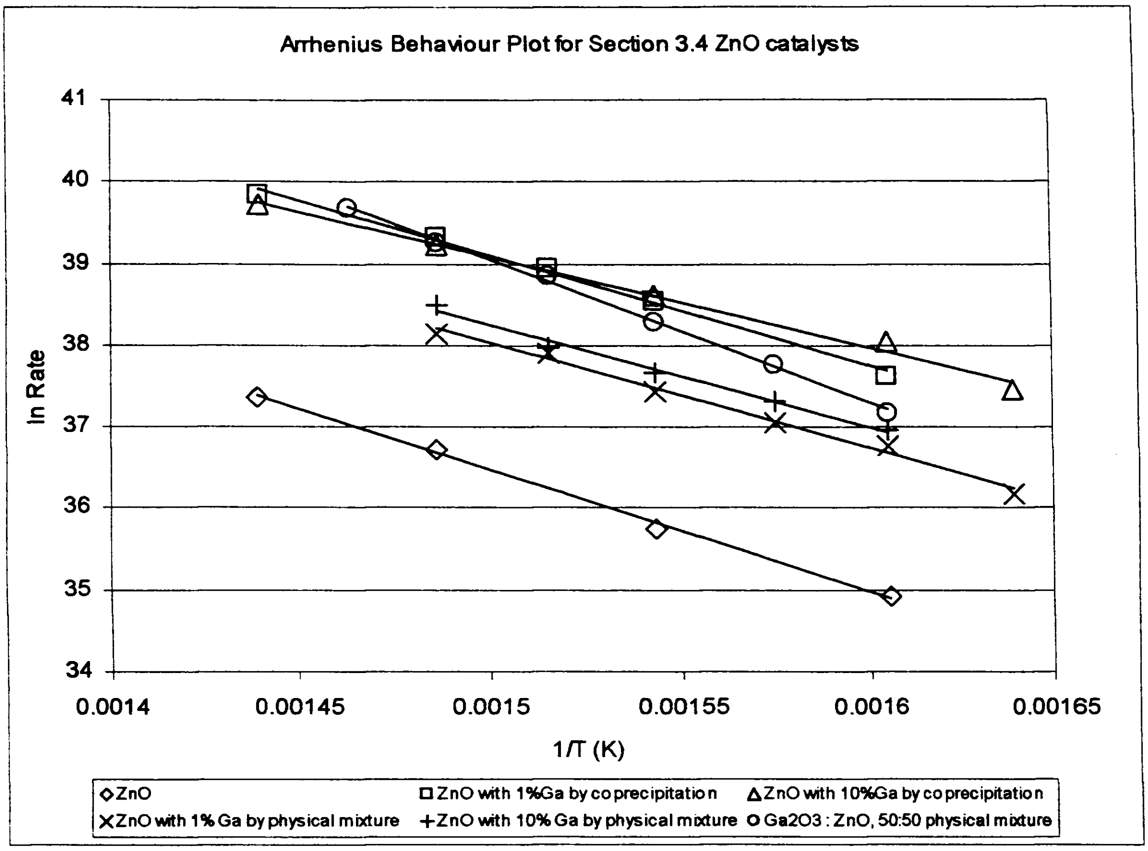
Further work in this area may involve the development of the MoO_3 catalyst used in this study. Heat treatments of MoO_3 have shown that crystals can be synthesised to beneficially favour the ratio of side to basal planes, with the side planes mainly consisting of Mo=O. The oxygen insertion catalyst can also be investigated, with high oxygen exchange properties, instead of MoO_3. Other effects that have not been investigated are the thickness of the inert material separating the two layers of catalyst, and the composition of the separating material.

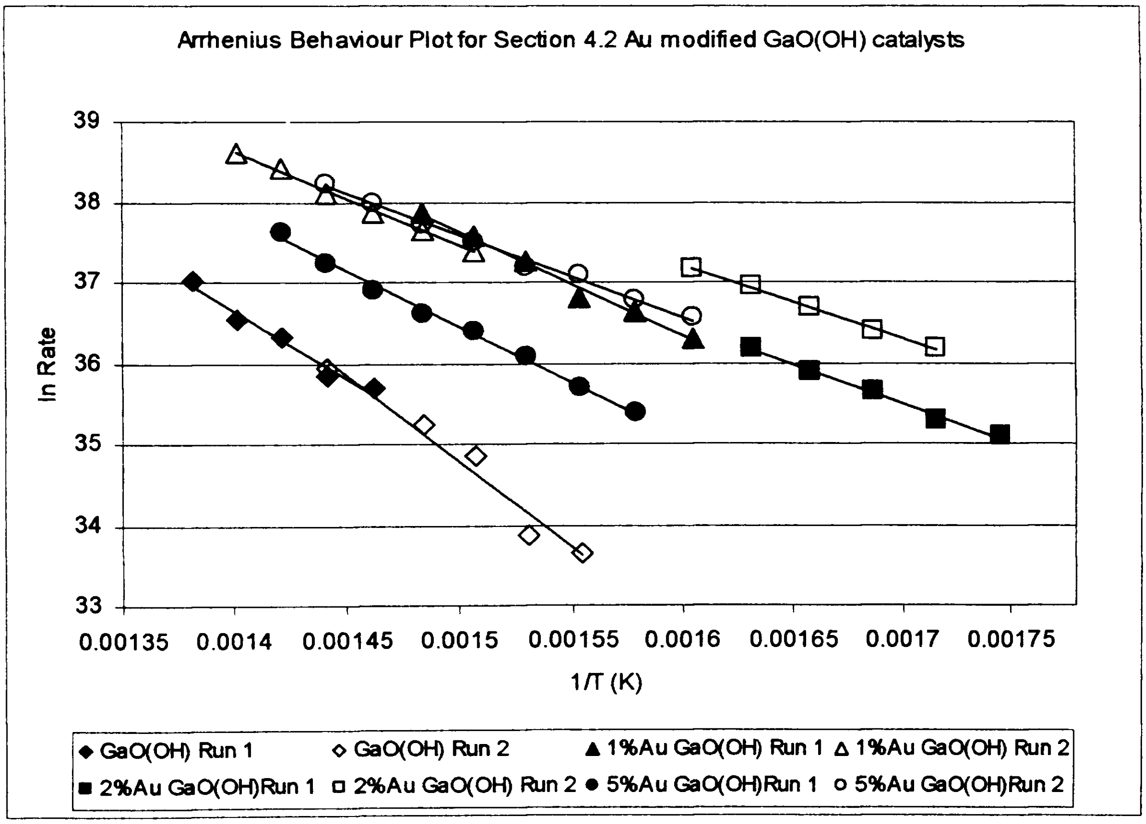
Appendix A

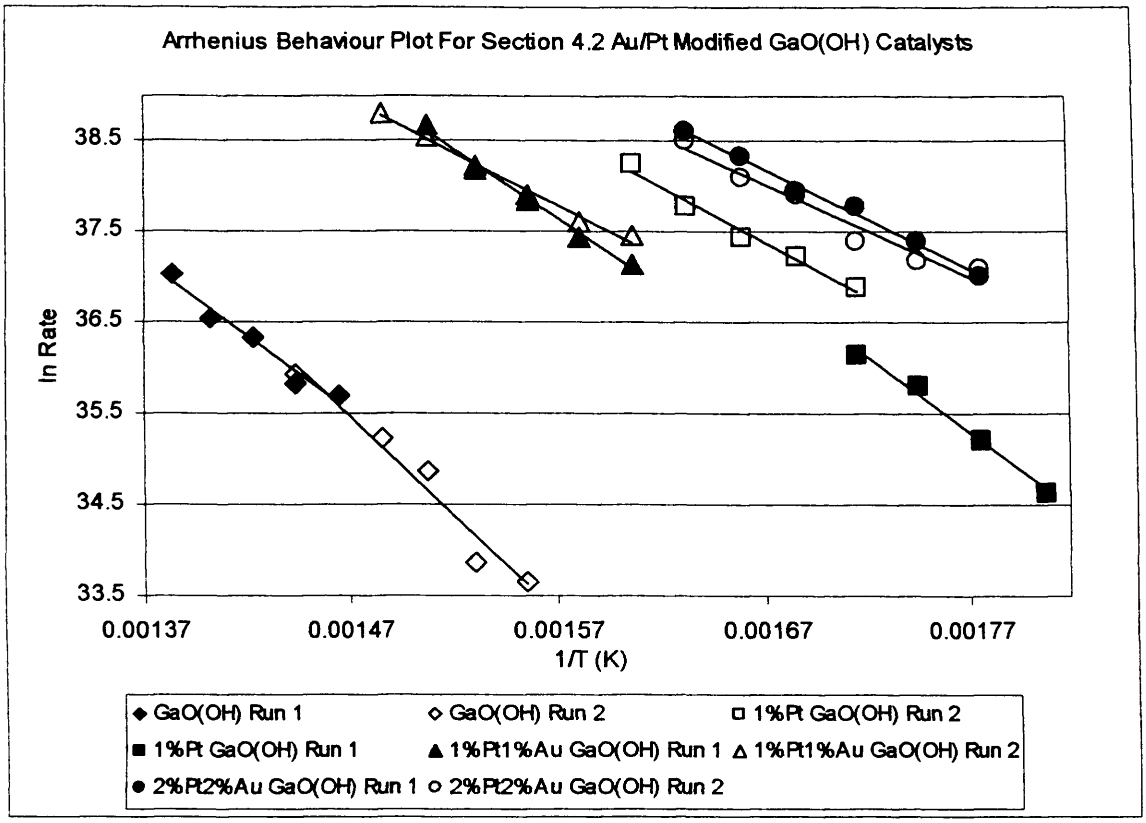
Arrhenius Behaviour Plots

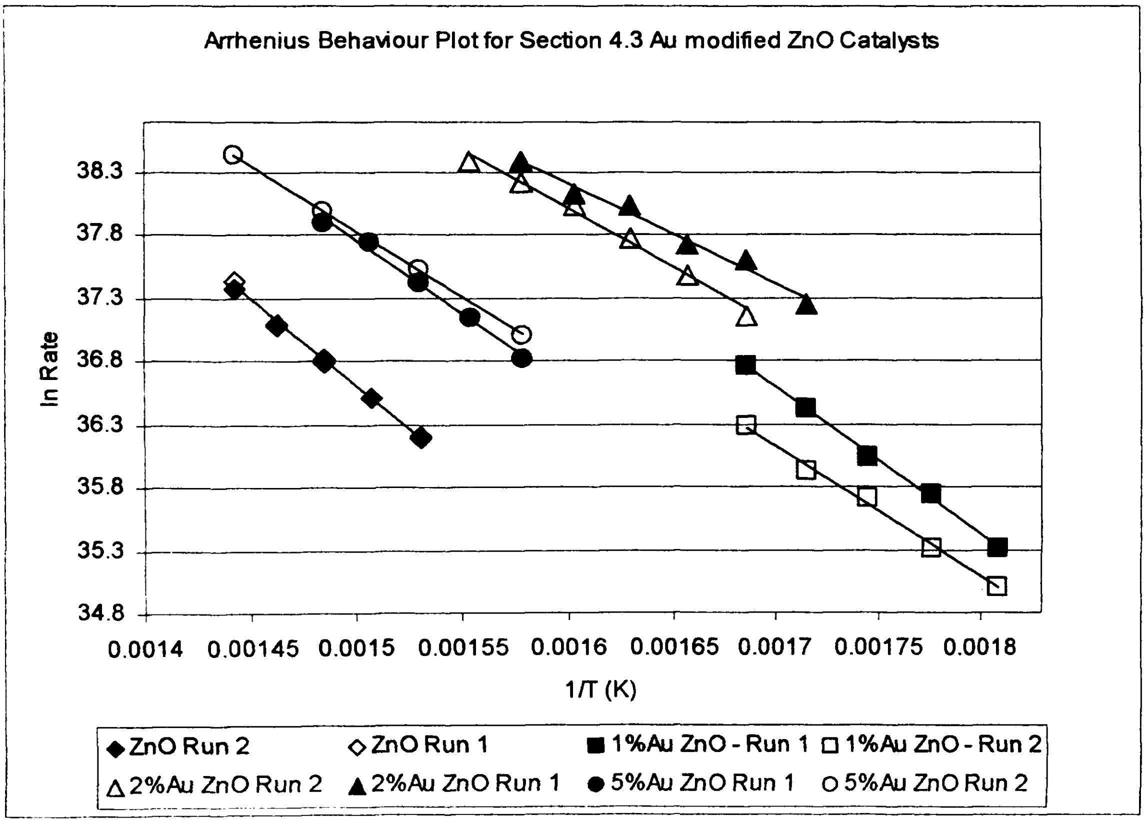


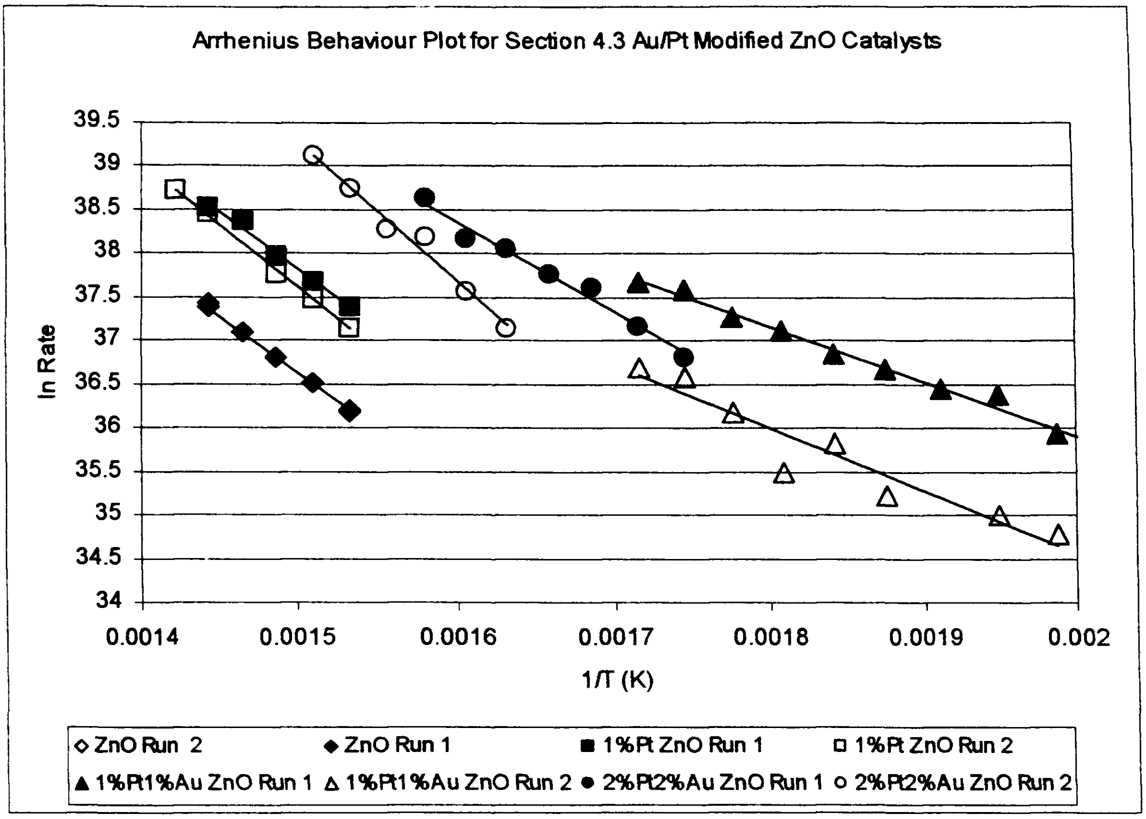


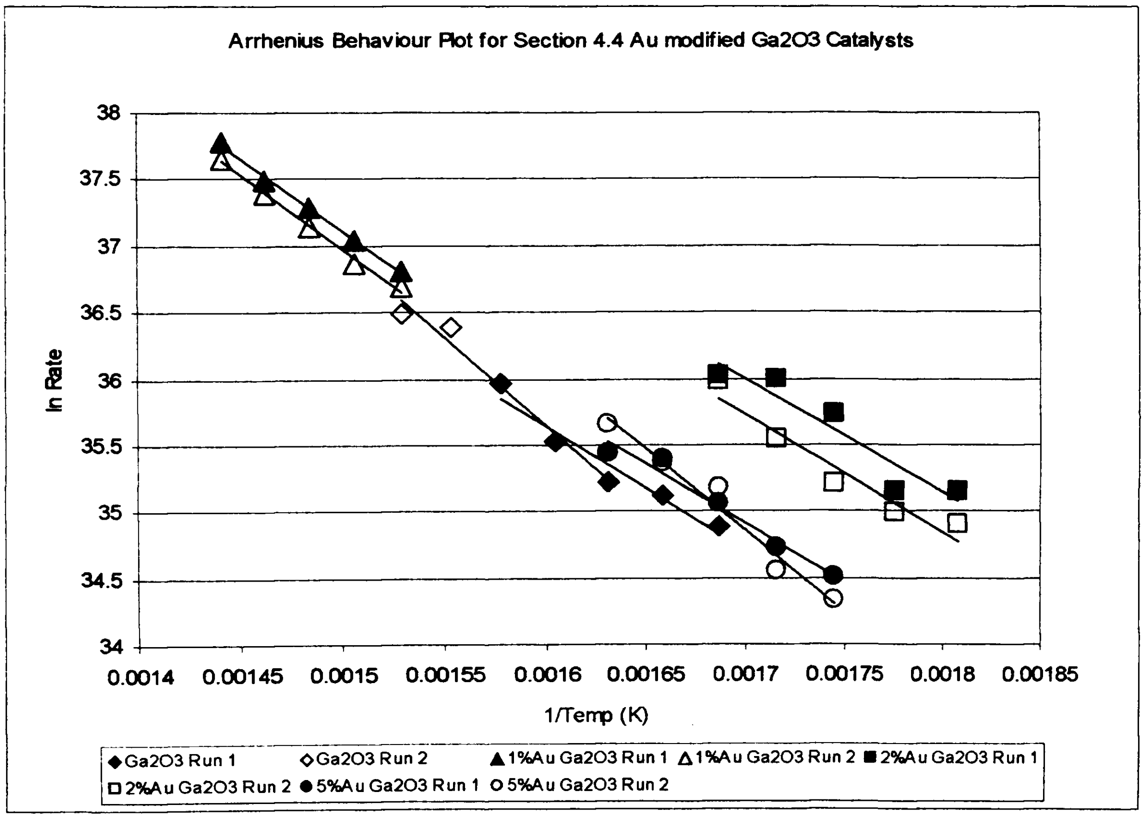

Arrhenius Behaviour Plot for Section 3.4 ZnO catalysts
ln Rate
41
40
39
38
37
36
35
34
0.0014
0.00145
0.0015
0.00155
0.0016
0.00165
1/T (K)
◇ZnO
□ZnO with 1%Ga by coprecipitation
△ZnO with 10%Ga by coprecipitation
×ZnO with 1% Ga by physical mixture
+ZnO with 10% Ga by physical mixture
○Ga2O3 : ZnO, 50:50 physical mixture

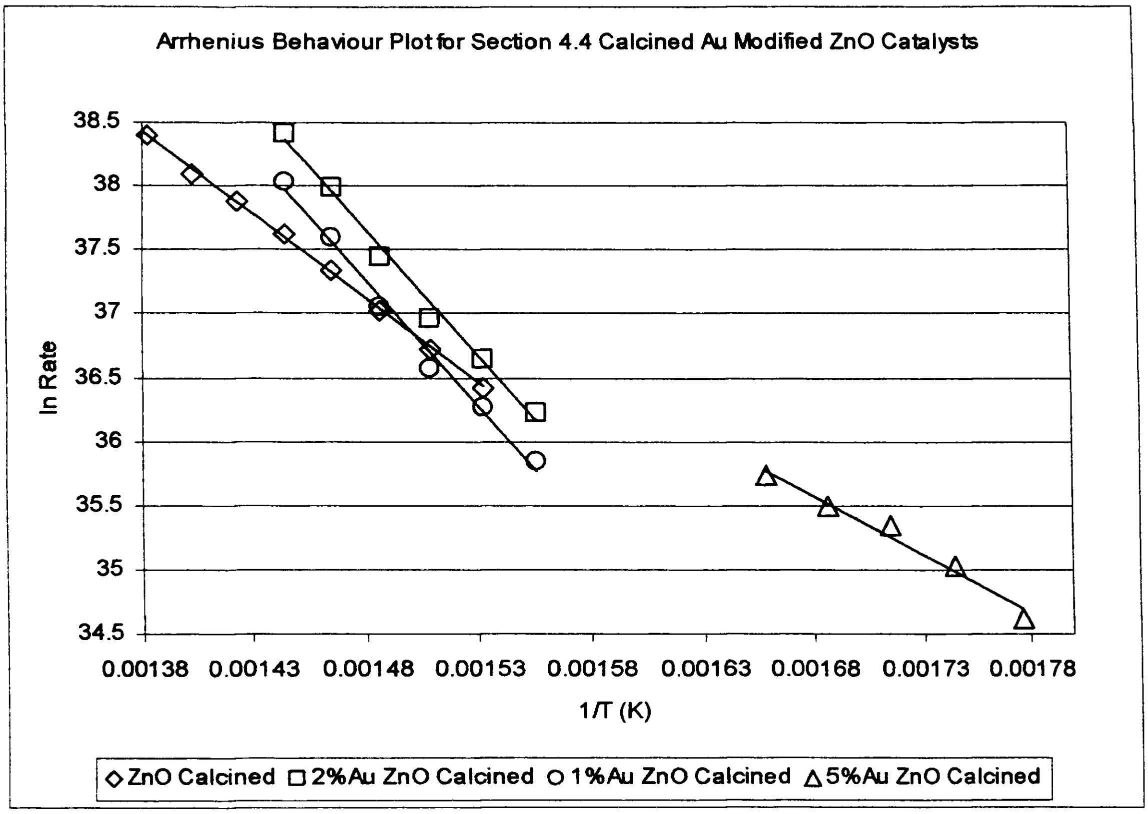

Arrhenius Behaviour Plot for Section 4.2 Au modified GaO(OH) catalysts
ln Rate
39
38
37
36
35
34
33
0.00135
0.0014
0.00145
0.0015
0.00155
0.0016
0.00165
0.0017
0.00175
1/T (K)
◆ GaO(OH) Run 1
◇ GaO(OH) Run 2
▲ 1%Au GaO(OH) Run 1
△ 1%Au GaO(OH) Run 2
■ 2%Au GaO(OH)Run 1
□ 2%Au GaO(OH) Run 2
● 5%Au GaO(OH)Run 1
○ 5%Au GaO(OH)Run 2

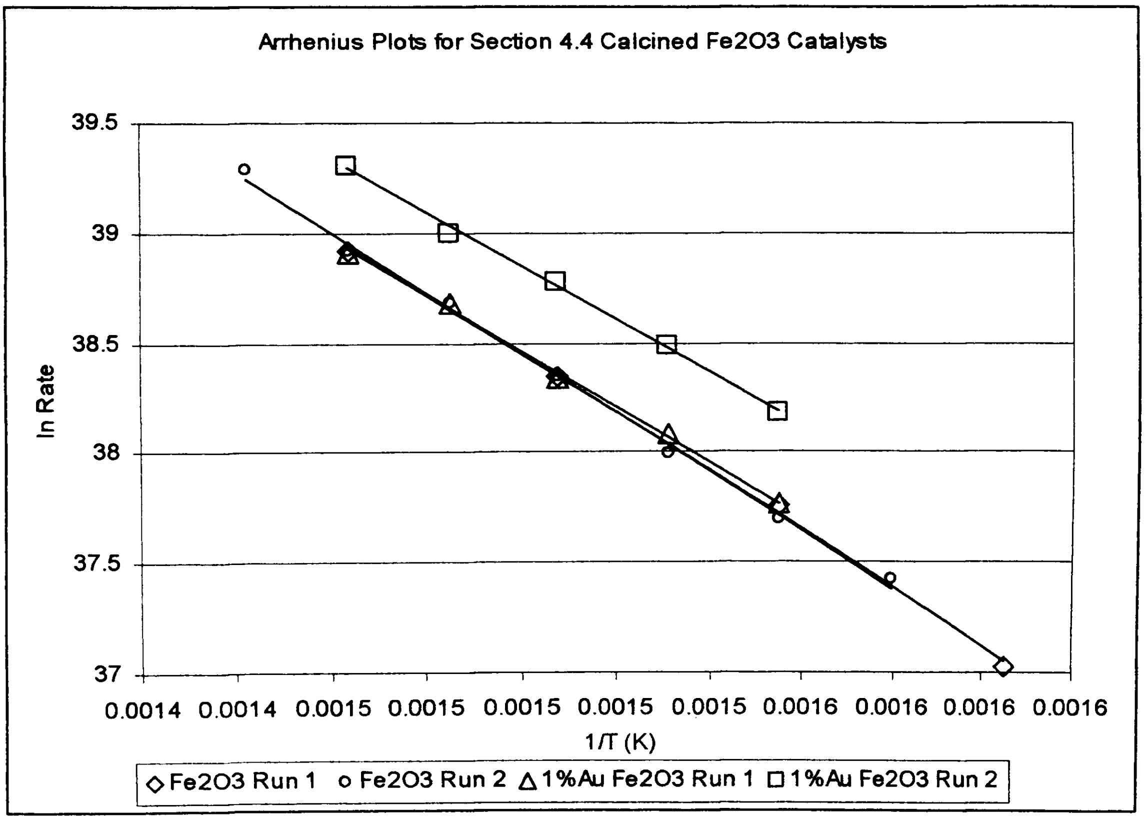

Arrhenius Behaviour Plot For Section 4.2 Au/Pt Modified GaO(OH) Catalysts
ln Rate
38.5
37.5
36.5
35.5
34.5
33.5
0.00137
0.00147
0.00157
0.00167
0.00177
1/T (K)
◆ GaO(OH) Run 1
◇ GaO(OH) Run 2
□ 1%Pt GaO(OH) Run 2
■ 1%Pt GaO(OH) Run 1
▲ 1%Pt1%Au GaO(OH) Run 1
△ 1%Pt1%Au GaO(OH) Run 2
● 2%Pt2%Au GaO(OH) Run 1
○ 2%Pt2%Au GaO(OH) Run 2


Arrhenius Behaviour Plot for Section 4.3 Au modified ZnO Catalysts
ln Rate
38.3
37.8
37.3
36.8
36.3
35.8
35.3
34.8
0.0014
0.00145
0.0015
0.00155
0.0016
0.00165
0.0017
0.00175
0.0018
1/T (K)
◆ ZnO Run 2
◇ ZnO Run 1
■ 1%Au ZnO - Run 1
□ 1%Au ZnO - Run 2
△ 2%Au ZnO Run 2
▲ 2%Au ZnO Run 1
● 5%Au ZnO Run 1
○ 5%Au ZnO Run 2


Arrhenius Behaviour Plot for Section 4.3 Au/Pt Modified ZnO Catalysts
ln Rate
39.5
39
38.5
38
37.5
37
36.5
36
35.5
35
34.5
34
0.0014
0.0015
0.0016
0.0017
0.0018
0.0019
0.002
1/T (K)
◇ ZnO Run 2
◆ ZnO Run 1
■ 1%Pt ZnO Run 1
□ 1%Pt ZnO Run 2
▲ 1%Pt1%Au ZnO Run 1
△ 1%Pt1%Au ZnO Run 2
● 2%Pt2%Au ZnO Run 1
○ 2%Pt2%Au ZnO Run 2


Arrhenius Behaviour Plot for Section 4.4 Au modified Ga2O3 Catalysts
ln Rate
38
37.5
37
36.5
36
35.5
35
34.5
34
0.0014
0.00145
0.0015
0.00155
0.0016
0.00165
0.0017
0.00175
0.0018
0.00185
1/Temp (K)
◆ Ga2O3 Run 1
◇ Ga2O3 Run 2
▲ 1%Au Ga2O3 Run 1
△ 1%Au Ga2O3 Run 2
■ 2%Au Ga2O3 Run 1
□ 2%Au Ga2O3 Run 2
● 5%Au Ga2O3 Run 1
○ 5%Au Ga2O3 Run 2


Arrhenius Behaviour Plot for Section 4.4 Calcined Au Modified ZnO Catalysts
ln Rate
38.5
38
37.5
37
36.5
36
35.5
35
34.5
0.00138
0.00143
0.00148
0.00153
0.00158
0.00163
0.00168
0.00173
0.00178
1/T (K)
◇ZnO Calcined
□2%Au ZnO Calcined
○1%Au ZnO Calcined
△5%Au ZnO Calcined


Arrhenius Plots for Section 4.4 Calcined Fe2O3 Catalysts
ln Rate
39.5
39
38.5
38
37.5
37
0.0014
0.0014
0.0015
0.0015
0.0015
0.0015
0.0015
0.0016
0.0016
0.0016
0.0016
1/T (K)
◇Fe2O3 Run 1
○ Fe2O3 Run 2
△1%Au Fe2O3 Run 1
□1%Au Fe2O3 Run 2

Appendix B

Results Tables For Methane Partial Oxidation : Section 5.2 Experiments

Partial Oxidation results over GaO(OH)

Temp / °C	Conversion / %			Selectivity / %			
	CH_4	Products	O_2	CO	CO_2	C_2H_6	CH_3OH
320	0.0	0.00	0.0	0	0	0	0
330	0.1	0.02	0.6	0	100	0	0
340	0.4	0.10	5.8	0	66	0	34
350	0.6	0.35	26.1	0	69	0	31
360	0.9	0.67	43.1	14	56	0	30
370	1.0	1.60	71.6	18	57	4	21
380	1.1	1.72	87.4	6	57	14	24
390	2.3	2.48	94.9	13	52	8	27
400	2.6	2.88	97.9	20	52	10	17

Partial Oxidation results over 5%Zn Ga_2O_3

Temp / °C	Conversion / %			Selectivity / %			
	CH_4	Products	O_2	CO	CO_2	C_2H_6	CH_3OH
320	0.0	0.00	0.0	0	0	0	0
330	0.0	0.03	0.0	0	100	0	0
340	0.2	0.09	0.5	0	62	0	38
350	0.5	0.22	3.0	0	49	29	22
360	0.9	0.40	9.5	24	36	18	22
370	1.2	1.26	46.2	27	29	5	39
380	2.0	2.14	63.6	28	37	2	33
390	2.3	2.86	98.8	20	47	14	18
400	2.6	3.36	99.1	17	50	18	15

Partial Oxidation results over 2%Au GaO(OH)

Temp / °C	Conversion / %			Selectivity / %			
	CH_4	Products	O_2	CO	CO_2	C_2H_6	CH_3OH
300	0.0	0.00	0.0	0	0	0	0
310	0.0	0.03	0.0	0	100	0	0
320	0.2	0.06	4.3	0	100	0	0
330	0.4	0.27	7.2	0	92	0	8
340	0.7	0.92	38.5	11	51	0	37
350	1.3	1.92	73.1	19	48	0	34
360	1.9	2.49	90.4	26	49	0	25
370	2.4	2.66	95.9	23	57	0	20

Partial Oxidation results over ZnO

Temp / °C	Conversion / %			Selectivity / %			
	CH_4	Products	O_2	CO	CO_2	C_2H_6	CH_3OH
320	0.0	0.00	0.0	0	0	0	0
340	0.0	0.02	0.0	0	100	0	0
360	0.3	0.12	6.4	0	54	0	46
370	1.8	0.86	40.1	0	61	0	39
380	2.2	2.12	78.9	32	35	0	33
390	2.4	2.55	95.0	33	40	0	27
400	2.7	2.39	96.8	30	46	0	23

Partial Oxidation results over 10%Ga ZnO

Temp / °C	Conversion / %			Selectivity / %			
	CH_4	Products	O_2	CO	CO_2	C_2H_6	CH_3OH
330	0.0	0.00	0.0	0	0	0	0
340	0.0	0.01	0.0	0	100	0	0
350	0.8	0.02	4.0	0	100	0	0
360	0.4	0.42	13.8	0	35	36	29
370	1.6	1.19	69.3	32	33	4	32
380	1.6	1.83	82.8	36	27	10	28
390	2.1	1.98	94.0	41	32	5	23
400	2.5	1.92	96.7	36	33	15	16

Partial Oxidation results over 2%Au ZnO

Temp / oC	Conversion / %			Selectivity / %			
	CH_4	Products	O_2	CO	CO_2	C_2H_6	CH_3OH
300	0.0	0.02	0.0	0	100	0	0
310	0.2	0.05	0.0	0	100	0	0
320	0.2	0.05	0.6	0	100	0	0
330	0.5	0.08	0.9	0	100	0	0
340	0.8	0.14	2.6	0	100	0	0
350	1.1	0.24	6.5	0	95	0	5
360	1.3	0.42	18.7	0	82	0	18
380	1.7	2.31	79.5	24	42	0	34
400	2.1	2.63	95.5	26	54	0	20
420	2.6	2.93	97.8	21	61	4	14

Partial Oxidation results over 2%Au2%Pt ZnO

Temp / °C	Conversion / %			Selectivity / %			
	CH_4	Products	O_2	CO	CO_2	C_2H_6	CH_3OH
250	0.0	0.00	0.0	0	0	0	0
275	0.2	0.03	0.0	0	100	0	0
300	0.2	0.04	3.8	0	100	0	0
310	0.5	0.05	4.1	0	100	0	0
320	0.5	0.07	4.2	0	100	0	0
330	0.6	0.15	5.7	0	100	0	0
340	0.7	0.24	10.2	0	100	0	0
350	1.1	0.45	14.2	0	100	0	0
370	3.2	4.14	98.1	0	100	0	0

Partial Oxidation results over Fe_2O_3

Temp / °C	Conversion / %			Selectivity / %			
	CH_4	Products	O_2	CO	CO_2	C_2H_6	CH_3OH
300	0.0	0.21	3.4	0	100	0	0
310	0.0	0.28	4.2	0	88	12	0
320	0.1	0.34	3.4	0	80	11	9
340	0.2	0.57	5.7	0	59	15	26
350	1.8	0.60	13.9	0	81	0	19
360	2.4	1.05	31.8	0	80	6	14
370	3.7	2.30	79.9	0	77	1	22
380	3.8	1.91	89.2	0	88	0	12
390	3.8	2.10	93.4	0	84	0	16

Partial Oxidation results over 1%Au Fe_2O_3

Temp / °C	Conversion / %			Selectivity / %			
	CH_4	Products	O_2	CO	CO_2	C_2H_6	CH_3OH
320	0.0	0.14	2.3	0	100	0	0
330	0.1	0.52	10.1	0	93	7	0
340	1.7	1.17	25.0	0	95	5	0
350	2.3	3.18	73.8	0	99	1	0
355	3.6	3.47	80.2	0	98	2	0

Partial Oxidation results over MoO_3

Temp / °C	Conversion / %			Selectivity / %			
	CH_4	Products	O_2	CO	CO_2	C_2H_6	CH_3OH
340	0.0	0.00	0.0	0	0	0	0
350	0.0	0.03	1.6	0	100	0	0
360	0.0	0.11	8.5	11	29	0	59
370	0.0	1.20	48.0	44	15	2	39
380	0.1	2.22	93.0	44	23	4	29
390	0.1	2.42	98.6	47	24	5	24
400	0.4	2.39	98.4	44	26	15	16
410	0.5	2.55	99.0	32	29	23	16

Partial Oxidation results for Empty Reactor Tube

Temp / °C	Conversion / %			Selectivity / %			
	CH_4	Products	O_2	CO	CO_2	C_2H_6	CH_3OH
325	0.0	0.00	0.0	0	0	0	0
350	0.2	0.18	3.0	0	19	38	43
375	0.4	0.78	54.5	3	48	4	45
400	2.4	1.47	95.5	10	61	7	22
425	3.3	1.88	99.5	9	45	27	19

Partial Oxidation results over Quartz

Temp / °C	Conversion / %			Selectivity / %			
	CH_4	Products	O_2	CO	CO_2	C_2H_6	CH_3OH
330	0.0	0.00	0.0	0	0	0	0
340	0.6	0.00	2.2	0	0	0	0
350	1.8	0.37	12.6	19	23	35	23
360	1.8	0.79	37.5	12	35	9	43
370	1.8	1.74	81.9	18	42	5	35
380	3.3	1.78	91.9	17	50	6	27

Partial Oxidation results over Glass Beads

Temp / °C	Conversion / %			Selectivity / %			
	CH_4	Products	O_2	CO	CO_2	C_2H_6	CH_3OH
340	0.0	0.00	0.0	0	0	0	0
350	0.4	0.03	4.3	0	100	0	0
360	0.7	0.29	23.5	0	35	0	65
370	1.4	1.00	83.1	3	69	3	25
380	2.2	1.68	94.4	6	51	13	29

Section 5.3 Experiments

Partial Oxidation Results over the GaO(OH) : MoO_3 50:50 physical mix catalyst

Temp / °C	Conversion / %			Selectivity / %			
	CH_4	Products	O_2	CO	CO_2	C_2H_6	CH_3OH
320	0.0	0.0	0.0	0	0	0	0
330	0.1	0.0	1.0	0	100	0	0
340	0.1	0.1	1.1	0	62	0	38
350	0.4	0.2	9.6	0	38	0	62
355	0.7	0.3	17.4	14	31	0	55
360	1.3	0.8	31.1	29	22	2	46
365	1.8	1.3	49.3	38	21	8	32
370	2.1	2.2	79.8	45	22	8	24
380	2.3	2.4	85.9	41	23	9	26
390	2.5	3.4	97.1	49	22	7	22

Partial Oxidation Results over ZnO: MoO_3 50:50 physical mix catalyst

Temp / °C	Conversion / %			Selectivity / %			
	CH_4	Products	O_2	CO	CO_2	C_2H_6	CH_3OH
330	0.0	0.00	0.0	0	0	0	0
340	0.0	0.01	0.0	0	100	0	0
350	0.0	0.03	0.0	0	73	0	27
355	0.1	0.06	3.5	0	69	0	31
360	0.1	0.13	8.4	0	57	0	43
365	0.3	0.39	21.3	22	36	0	42
370	1.1	0.89	38.1	33	32	0	35
380	2.9	2.20	82.8	45	28	0	27

Partial Oxidation Results over 10%Ga ZnO : MoO3, 50:50 Physical Mix Catalyst

Temp / °C	Conversion / %			Selectivity / %			
	CH_4	Products	O_2	CO	CO_2	C_2H_6	CH_3OH
330	0.0	0.00	0.0	0	0	0	0
340	0.0	0.02	1.1	0	100	0	0
350	0.2	0.06	5.0	0	67	0	33
360	0.4	0.23	14.2	11	42	9	39
370	0.8	0.72	39.6	29	33	10	29
375	2.1	2.04	67.0	38	19	10	33
380	2.6	2.60	87.9	39	24	9	27

Partial Oxidation Results over 2%Au GaO(OH) : MoO_3, 50:50 physical mixture

Temp / °C	Conversion / %			Selectivity / %			
	CH_4	Products	O_2	CO	CO_2	C_2H_6	CH_3OH
290	0.0	0.03	0.0	0	100	0	0
300	0.1	0.06	0.0	0	100	0	0
310	0.3	0.11	2.8	0	100	0	0
320	0.3	0.15	4.2	0	100	0	0
330	0.5	0.22	5.8	0	100	0	0
340	1.5	0.50	17.2	0	88	0	12
360	1.8	1.73	57.7	23	43	0	35
370	2.7	2.88	93.8	34	43	0	23

Partial Oxidation Results over 2%Au ZnO : MoO_3, 50:50 physical mixture

Temp / °C	Conversion / %			Selectivity / %			
	CH_4	Products	O_2	CO	CO_2	C_2H_6	CH_3OH
310	0.0	0.00	0.0	0	0	0	0
320	0.0	0.00	0.0	0	100	0	0
330	0.0	0.01	0.3	0	100	0	0
340	0.1	0.02	1.6	0	100	0	0
350	0.1	0.04	1.5	0	72	0	28
360	0.2	0.25	9.2	17	46	0	37
370	1.4	0.63	32.6	23	44	0	33
380	2.9	2.43	82.1	41	27	0	32

Partial Oxidation Results over 2%Au2%Pt ZnO: MoO_3, 50:50 physical mixture

Temp / °C	Conversion / %			Selectivity / %			
	CH_4	Products	O_2	CO	CO_2	C_2H_6	CH_3OH
260	0.0	0.00	0.0	0	0	0	0
270	0.1	0.04	0.0	0	100	0	0
280	0.1	0.05	0.4	0	100	0	0
300	0.2	0.08	0.5	0	100	0	0
310	0.4	0.10	1.7	0	100	0	0
320	0.9	0.11	2.0	0	100	0	0
340	1.1	0.23	8.1	0	87	0	13
360	1.9	2.01	67.8	32	36	0	33
380	3.2	2.92	96.3	35	43	0	22

Partial Oxidation Results over 1%Au Fe_2O_3 : MoO_3, 50:50 physical mixture

Temp / °C	Conversion / %			Selectivity / %			
	CH_4	Products	O_2	CO	CO_2	C_2H_6	CH_3OH
200	0.0	0.02	0.0	0	100	0	0
250	0.1	0.12	0.0	0	100	0	0
300	0.1	0.46	7.5	0	100	0	0
310	0.1	0.56	7.8	0	100	0	0
320	0.1	0.53	8.0	0	100	0	0
340	0.1	0.44	8.7	0	97	0	3
345	0.1	0.56	14.6	0	86	0	14
350	0.3	0.72	21.2	4	77	5	14
355	0.4	1.04	30.0	7	64	6	23
360	0.8	1.96	68.2	28	53	2	18
370	2.0	2.95	96.7	34	48	2	15

Partial Oxidation Results over GaO(OH) : MoO_3, 25:75 physical mixture

Temp / °C	Conversion / %			Selectivity / %			
	CH_4	Products	O_2	CO	CO_2	C_2H_6	CH_3OH
330	0.0	0.00	0.0	0	0	0	0
340	0.0	0.01	0.0	0	100	0	0
350	0.2	0.01	1.3	0	100	0	0
360	0.3	0.10	4.1	0	60	0	40
370	1.2	0.41	42.0	9	44	8	39
380	1.8	2.19	76.7	52	23	1	24
390	2.3	2.44	83.9	54	22	4	20

Partial Oxidation Results over GaO(OH) : MoO_3, 75:25 physical mixture

Temp / °C	Conversion / %			Selectivity / %			
	CH_4	Products	O_2	CO	CO_2	C_2H_6	CH_3OH
320	0.0	0.00	0.0	0	0	0	0
330	0.0	0.01	0.2	0	100	0	0
340	0.3	0.03	1.0	0	67	0	33
350	0.4	0.05	1.8	0	57	13	30
360	0.6	0.50	27.9	28	30	7	36
370	1.5	1.15	64.6	44	24	3	29
380	2.3	1.77	93.9	44	31	3	22
390	2.5	1.67	97.8	45	35	2	18

Section 5.4 Experiments

Methane partial oxidation over separate layers of 2%Au GaO(OH) : MoO_3, 50:50

Temp / °C	Conversion / %			Selectivity / %			
	CH_4	Products	O_2	CO	CO_2	C_2H_6	CH_3OH
300	0.0	0.02	0.4	0	100	0	0
320	0.0	0.02	0.6	0	100	0	0
330	0.0	0.04	0.7	0	100	0	0
340	0.1	0.08	1.1	0	100	0	0
350	0.2	0.15	15.6	0	59	0	41
353	0.6	0.36	21.3	20	30	0	50
355	0.9	0.76	32.6	26	23	0	50
358	1.3	1.44	54.4	33	23	2	42
360	1.3	1.83	68.8	37	26	6	31
365	2.1	2.54	87.7	36	25	10	29
370	2.2	2.89	92.2	34	25	16	25

Methane partial oxidation over separate layers of 2%Au GaO(OH) : MoO_3, 27:75

Temp / °C	Conversion / %			Selectivity / %			
	CH_4	Products	O_2	CO	CO_2	C_2H_6	CH_3OH
330	0.0	0.00	0.0	0	0	0	0
340	0.0	0.02	0.3	0	100	0	0
350	0.1	0.08	7.2	0	56	0	44
353	0.4	0.29	16.2	12	19	0	69
355	0.9	0.34	17.6	10	24	0	66
358	1.3	0.44	23.6	15	21	5	60
360	1.6	1.24	39.8	23	16	4	57
365	1.7	1.46	51.0	30	18	11	41
370	1.8	2.35	71.7	33	19	12	36

Methane partial oxidation over separate layers of 2%Au GaO(OH) : MoO_3, ⅛:⅞

Temp / °C	Conversion / %			Selectivity / %			
	CH_4	Products	O_2	CO	CO_2	C_2H_6	CH_3OH
330	0.0	0.00	0.0	0	0	0	0
340	0.1	0.03	4.4	0	68	0	32
350	1.2	0.21	17.1	12	28	0	60
353	1.6	0.40	24.4	23	27	0	50
355	1.6	0.56	29.1	29	25	4	42
358	1.8	0.88	37.5	30	22	10	38
360	2.0	1.05	40.0	29	18	12	42
365	2.6	1.69	56.2	33	19	11	38
370	2.8	2.66	82.4	37	22	9	32

Methane partial oxidation over separate layers of 2%Au ZnO : MoO_3, 50:50

Temp / °C	Conversion / %			Selectivity / %			
	CH_4	Products	O_2	CO	CO_2	C_2H_6	CH_3OH
300	0.0	0.02	0.4	0	100	0	0
310	0.1	0.02	0.5	0	100	0	0
320	0.5	0.04	0.7	0	100	0	0
330	0.6	0.06	1.6	0	74	0	26
340	0.7	0.10	5.5	0	52	0	48
350	1.1	0.69	30.6	24	25	3	48
355	1.9	1.63	57.3	27	22	5	47
365	2.1	2.05	71.4	27	25	9	39
370	2.5	2.43	79.4	29	24	8	38
375	2.8	2.83	92.0	31	28	10	32

Methane partial oxidation over separate layers of 2%Au ZnO : MoO_3, 25:75

Temp / °C	Conversion / %			Selectivity / %			
	CH_4	Products	O_2	CO	CO_2	C_2H_6	CH_3OH
310	0.0	0.00	0.0	0	0	0	0
320	0.6	0.03	0.0	0	100	0	0
330	0.9	0.04	4.3	0	100	0	0
340	1.1	0.09	9.8	0	73	0	27
350	1.4	0.86	39.8	40	22	3	36
353	2.0	1.71	61.9	40	21	7	32
355	2.3	2.00	71.1	39	20	8	33
360	2.6	2.31	83.8	38	22	9	31
370	2.8	2.41	92.5	41	22	9	28

Methane partial oxidation over separate layers of 2%Au ZnO : MoO_3, ⅛:⅞

Temp / °C	Conversion / %			Selectivity / %			
	CH_4	Products	O_2	CO	CO_2	C_2H_6	CH_3OH
320	0.0	0.00	0.0	0	0	0	0
330	0.0	0.05	0.5	0	76	0	24
335	0.1	0.09	1.5	0	58	0	42
340	0.1	0.13	2.3	0	46	0	54
345	0.4	0.21	9.7	7	30	0	63
350	1.0	0.49	22.6	19	26	2	53
355	1.3	0.85	42.4	24	24	2	50
360	1.6	1.54	65.2	26	26	3	45
365	2.3	2.10	83.1	32	26	6	35
370	2.7	2.22	85.7	27	35	8	30

Methane partial oxidation over separate layers of 1%Au Fe_2O_3 : MoO_3, 50:50

Temp / °C	Conversion / %			Selectivity / %			
	CH_4	Products	O_2	CO	CO_2	C_2H_6	CH_3OH
300	0.0	0.22	3.9	0	100	0	0
310	0.0	0.30	6.3	0	100	0	0
320	0.1	0.37	7.5	0	100	0	0
330	0.2	0.52	12.3	0	100	0	0
340	0.2	0.58	17.7	0	90	4	6
345	1.0	0.92	33.8	8	65	5	22
350	1.2	1.18	36.2	7	62	12	19
355	1.2	1.84	59.5	8	55	11	27
360	2.1	2.57	76.5	19	46	11	24

Methane partial oxidation over separate layers of 1%Au Fe_2O_3 : MoO_3, 25:75

Temp / °C	Conversion / %			Selectivity / %			
	CH_4	Products	O_2	CO	CO_2	C_2H_6	CH_3OH
300	0.0	0.10	1.7	0	100	0	0
310	0.3	0.11	2.4	0	100	0	0
320	0.5	0.16	2.7	0	100	0	0
330	0.6	0.20	5.7	0	100	0	0
340	0.8	0.27	10.7	0	100	0	0
350	1.2	0.49	18.1	0	72	8	19
355	1.6	1.04	34.2	12	46	10	32
360	2.2	1.81	57.3	21	35	9	35
365	3.0	2.41	78.5	27	36	7	30

Methane partial oxidation over separate layers of 1%Au Fe_2O_3 : MoO_3, ⅛:⅞

Temp / °C	Conversion / %			Selectivity / %			
	CH_4	Products	O_2	CO	CO_2	C_2H_6	CH_3OH
320	0	0	0	0	0	0	0
330	0.2	0.13	1.7	0	100	0	0
340	0.4	0.26	5.8	0	72	0	28
350	0.7	0.38	17.0	0	65	0	35
355	1.5	0.84	35.8	15	35	2	49
360	1.7	1.26	46.7	16	33	4	48
365	2.2	1.62	66.7	19	40	6	35
370	2.9	1.69	76.7	16	44	7	33