The Catalytic Conversion of Methane to Methanol and Formaldehyde under Mild Conditions

By

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"I declare that The Catalytic Conversion of Methane to Methanol and Formaldehyde under Mild Conditions is my own work and that all the sources I have used or quoted have been indicated and acknowledged by means of complete references."

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Summary

The oxidation of methane to produce methanol and formaldehyde is an important process since methanol is used directly as a fuel or can be converted to valuable products such as other transportable fuels, fuel additives, or chemicals. Methane oxidation will continue to receive attention because of the large amount of methane available to be upgraded and the demand, worldwide, for low cost transportation fuel. There are many ways to activate methane; Hunter and Gesser [1] discussed photochemical and electrochemical activation, laser-induced activation, and radiolysis, as well as catalytic activation. The right combination has yet to be discovered. The key to any further improvement in this process may lie in the design of the reactor and the catalyst.

In this study a catalyst that works at low temperature and at atmospheric pressure for the oxidation of methane to methanol and formaldehyde was developed. Catalyst preparation was based on the fact that the higher activity and selectivity to the desired products obtained over supported catalysts, compared to bulk oxides, can be attributed to the formation of easily reducible supported metal oxide phases, as reported by McCormick et al [2].

Inorganic ceramic membranes were used as supports for the catalysts. Various sources of silica (tetraethoxysilane and fumed silica) were used to modify the membrane support for the introduction of silanol groups that participate in the chemical reaction to form different bonds. Silica is known to stabilise the membrane support and it was found that it also increased the surface area of the membrane support. Tetraethoxysilane (TEOS) was incorporated through the sol-gel technique and was found to be the best method for the introduction of silica upon the membrane support. The BET surface area of the membrane support increased from 2.4 to 12.6 and 4.5 m^2/g upon modification with TEOS and fumed silica respectively. The surface of the silica modified membrane support was grafted with chlorodimethylsilane (CDMS) and γ-aminopropyltriethoxysilane (APTS) for the introduction of hydrolytically and thermally stable Si-O-Si bonds. This modification was followed by the deposition of the active metal centre.

The metals deposited were silver, platinum and iron (in the form of hemin). For the silver-based catalyst an increase in porosity was observed due to the formation of clusters of silver on the surface. The void volume between the particles may thus have been measured as part of the pore volume. The platinum-based catalyst introduced small mesopores (between 100-300 Å). There was a significant reduction of large mesopores upon modification in the case of the hemin-based catalyst. During characterisation by temperature-programmed oxidation, the hemin-based catalyst consumed more oxygen than the silver and the platinum-based catalysts. This suggest that the hemin catalyst may have more reducible species than silver and platinum catalysts thus can activate oxygen, which in turn activates methane to produce the desired products, methanol and formaldehyde. A suitable catalytic device for testing the activity of tubular ceramic membrane catalysts was designed and constructed. Preliminary activity of the potential catalysts for the oxidation of methane to methanol and formaldehyde was studied under mild conditions with the aid of the constructed catalytic device. The synthesised membrane catalysts were active at low temperature.

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APTS	: γ-aminopropyltriethoxysilane
BET	: Brunauer, Emmet and Teller
BJH	: Barett, Joyner and Halenda model
CDMS	: chlorodimethylsilane
DMF	: N,N-dimethylformamide
EDX	: Energy dispersive X-ray spectroscopy
FID	: flame ionization detector
fv(rp)	: pore size distribution based on pore volume
fA(rp)	: pore size distribution based on pore area
GC	: gas chromatography
M-85	: a mixture of gasoline (15%) and methanol (100%)
M-100	: pure methanol
SEM	: scanning electron microscopy
TCD	: thermal conductivity detector
TEOS	: tetraethoxysilane
TPD	: temperature programmed desorption
t-plot	: the volume of gas adsorbed versus the statistical thickness of the adsorbed film (t)
TPO	: temperature programmed oxidation
TPR	: temperature programmed reduction
U.S.	: United States
UV	: ultraviolet

W% : weight percent

CHAPTER 1 Literature Review

1.1 Methane conversion

In the future, natural gas is likely to become increasingly important as a feedstock for the chemical industry. Methane is the principal constituent of natural gas (either lean natural gas or associated gas from crude oil production), landfill gas, or coal-bed methane. It is also a by-product of oil refining and chemicals processing.

Partial oxidation of methane to methanol is important as methanol can be used as an energy source (fuel cells), and starting material for various chemical synthesis, such as the production of chloroform, methyl chloride. Methanol is also used as a solvent in paint strippers, paints, carburettor cleaners, and automobile windshield washer solutions. Since 1965, methanol has been used in the U.S. as fuel in certain vehicles (e.g. race cars) either as pure methanol (M-100) or as mixtures of gasoline (15%) and methanol (85%) i.e. (M-85). Due to the liquid properties of methanol at room temperature, ambient pressure, the high hydrogen to carbon ratio, and the relatively low combustion temperature, methanol is considered an ideal hydrogen carrier for fuel cell vehicles [3]

Methane conversion follows two routes [4] i.e. indirect and direct conversion as shown in equation (1).

$$\begin{tikzcd} CH_4 \arrow[r, Rightarrow, "1"] \arrow[rr, bend right, "4"'] & CO / H_2 \arrow[r, Rightarrow, "2"] & CH_3OH \arrow[r, Rightarrow, "3"] & CH_2O \end{tikzcd} \qquad (1)$$

The commercial indirect conversion includes the production of methanol from methane via high temperature catalytic steam reforming to form synthesis gas ($CO + H_2$) in step 1. This energy-intensive, endothermic reaction is followed by catalytic conversion of the synthesis gas to CH_3OH [5, 6]. Direct partial oxidation of CH_4 to CH_3OH (step 4) has been studied because it is a one-step, exothermic process. This conversion eliminates the need for synthesis gas (step 1). If this can be done efficiently, the goal of achieving a cost-effective route to methane oxidation might be within reach. Direct conversion technologies can be classified into four groups i.e. direct partial oxidation (to methanol, methyl halides or others), oxidative coupling (to ethylene), reductive couplings and other direct conversion processes [7].

There are many ways to activate methane yet the problem is that methane is a very stable molecule. Its reactions generally have high activation energy and, once activated, it is difficult to stop the reaction from going further than desired [5]. Both methanol and formaldehyde are unstable toward decomposition [8]. The attempt to reach a high degree of methane conversion into methanol or formaldehyde leads to a sharp decrease in selectivity.

Methane can be partially oxidized by oxygen to methanol by several methods, which include:

- gas phase oxidation [9],
- catalytic oxidation and
- biological oxidation.

Methane can be oxidized even at lower temperature than 100°C. Ogura et al [10] showed that methane could be oxidized to partially oxidized products at around 100°C by UV irradiation of a CH_4, O_2 and steam mixture. In the system water was activated by photolysis to free radicals, then the free radicals activated methane to initiate the reaction [11].

1.2 Mechanisms for partial oxidation reactions

1.2.1 Molecular approach

The Mars and van Krevelen mechanism proposed in 1953 usually occurs for partial oxidation reactions [12]. It involves both a redox function of the solid catalyst surface and oxygen insertion of the reagent molecule from lattice oxygen ions. The reaction conditions are demanding since the reaction involves abstraction of the substrate H atom, insertion of O atom and electron transfer. This occurs on active sites with a certain size from several atoms up to a complete crystalline face.

Since the early eighties a molecular approach concept was developed that promotes the view of surface atoms, which cause the complex reaction mechanism to take place at the catalyst surface. Several cations and oxygen ions are considered to constitute the active site [13]. Oxygen species on an oxide surface exhibits different properties. Monoatomic species with the electrophilic or nucleophilic character (O^-, O^{2-}) may exist or diatomic species (O_2^-, O2). The electrophilic character of the oxygen species is important since it favours the deprotonation of the nucleophilic hydrocarbon molecule or the weak allylic attack and the electrophilic aromatic ring. Electrophilic oxygen species correspond to O^-, superoxo (M-O-O) or peroxo (O2) species while nucleophilic species are rather metal oxo species (M = O).

1.2.2 Theoretical analysis of the process

The kinetic analysis of the high pressure partial methane oxidation has shown that: [1].

1. The process has two phases differing by their time scales.

The very short initial stage involves the chain-branched mechanism, which is very similar to the mechanism of H_2 oxidation. It is very sensitive to initial conditions, especially pressure. This stage (auto-accelerating phase) is completed by a subsequent quasi-stationary phase, which is characterised by the approximate equality of the rates of branching and radical recombination.

The second phase is considered as a degenerate chain-branched mechanism. Chain branching is connected with intermediate products. The most important branching reactions in this phase are interaction of methyl peroxide and hydrogen peroxide radicals with methane, methanol, formaldehyde and H_2O_2.

2. Formation of the main products (CH_3OH and HCHO) proceeds simultaneously and independently. Only a relatively small part of formaldehyde forms from the oxidative and thermal decomposition of methanol. The difference in their concentration is only due to the difference in their stability to further oxidation. The large amount of methanol forms at the end of the reaction just, before total oxygen consumption. It explains the very high sensitivity of methanol yield to residence time and temperature at incomplete oxygen conversion.

3. The increase in O_2 concentration decreases the selectivity of methanol formation and reduces the whole rate of the process.

4. Two stationary regimes of the process exist, differing in radical concentrations and in the process velocities of over 4 orders of magnitude. There also exists a critical pressure for the transition between these two regimes.

5. A high-pressure region above the critical pressure of the initial chain-branched phase provides a very high velocity of radical generation, so any catalyst, promoter, or other source of radicals can hardly compete with it.[11] Usually their influence on the process is negligible. It also explains the failure of numerous attempts to improve the high-pressure process by means of a catalyst.

1.3 Gas phase oxidation reactions

The chemistry that occurs in partial oxidation of methane is similar to that of most general combustion processes. The conversion process involves an initiation step, propagation and termination (or removal of active species) step. Previous research concentrated on optimisation of the high-pressure conversion, effect of additives, use of modelling to determine the overall reaction mechanism, use of novel reactor design and photochemical initiation [14].

1.3.1 Effect of variables on the reaction

1.3.1.1 Effect of pressure

Early studies found that high pressures encouraged the formation of methanol, or reduced the reaction time and the reaction temperature [14]. However, the cost of gas compression is one of the most prominent factors in the total product cost [15]. There are no advantages in using catalysts at high pressures. Recent work has tried to find optimum conditions for this conversion which study still continues. [16] Sexton et al studied the effect of pressure on the behaviour of 7Mo-2Na-cabosil in the range 101-1520 kPa using O_2 as an oxidant. At lower pressures the conversion was very small. A very small conversion was noted on increasing the pressure from 101 (0.3 %) to 506 kPa (0.5 %). On increasing the pressure from 506 to 1520 kPa a large increase in methane conversion from 0.45 % to 13.5 % was obtained which was accompanied by a decrease in formaldehyde selectivity.

1.3.1.2 Influence of temperature

Once a high enough temperature for complete oxygen conversion is reached, further temperature increases are undesirable because they may cause a decrease in methanol and formaldehyde selectivities [15]. Sexton et al [16] investigated the performance of different catalysts at various temperatures (500-600 °C) with N_2O as oxidant. They found that the homogenous oxidation of methane by nitrous oxide does not occur to a significant extent below 600 °C. 5Mo-cabosil gave the poorest methane conversion at all temperatures. 7Mo-2Na-cabosil and 10Mo-2Cu-aerosil gave comparable conversions at each temperature examined. The best conversion, at 550 °C was obtained using 2V-cabosil. With 7Mo-2Na-cabosil the selectivity to formaldehyde decreased with increasing temperature. The selectivity to methanol, however, increased with temperature. The combined selectivity to the partial oxidation products was approximately constant (4.5-5 %) at all temperatures examined.

1.3.1.3 Influence of the composition of the reacting mixture on the process

The partial oxidation is very sensitive to the methane/oxygen ratio. Methanol selectivity decreases with the reduction of this ratio. In the absence of methane-oxygen mixing volume or radical initiators no gas phase activation of methane is expected [17]. Hence the catalyst alone cannot activate methane since the void volume between the particles is too small to allow a significant activation of methane. Dilution of the reacting mixture by N_2 and, apparently other non-reactive compounds did not influence the process while the methane/oxygen ratio remained constant. In some cases the use of cheaper air instead of pure oxygen in the process is possible. The influence of small impurities of higher hydrocarbons on the process is well established. Their presence in natural gas lowers the necessary reaction temperature without producing changes in product yield. High methane to oxygen ratios was used to prevent full oxidation.

1.3.1.4 Influence of an oxidant

In terms of oxidants, dioxygen (O_2) is clearly the most desirable oxidant due to its ready availability and high reduction potential [18]. Molecular oxygen gave higher formaldehyde selectivity with decreased CO_x selectivity relative to N_2O [9]. The catalytic differences have been ascribed to the differing oxidizing power of N_2O and O_2. In accordance with the Mars-Krevelen mechanism (in section 1.2) the re-oxidation of the catalyst will be less effective with N_2O, compared to O_2. The role of the dioxygen is to regenerate or to maintain the oxidized state of the catalyst [12]. The oxygen atom incorporated into the substrate stems from the lattice and is in a (–2) oxidation state. The catalyst does not activate methane. Oxygen is the key to methane activation [17]. It can be expected that oxygen get activated on the surface of the catalyst, thus enabling methane activation. Up to 30 % savings may be achieved if air is used instead of pure oxygen [15].

1.4 Catalyst Preparation

A key to direct conversion of CH_4 to CH_3OH is the development of catalysts that will activate the relatively inert C-H bond in CH_4. Metal-based catalysts have been a source of interest since the early 1970s. For the catalyst to be successful one oxide must be capable of catalysing the oxidation of hydrocarbons and the other of catalysing the hydration of alkanes. It was found that supported catalysts work better than unsupported catalysts [9].

1.4.1 Support materials

In the oxidation of hydrocarbons, supported metal oxide catalysts exhibit different activity and selectivity to the desired oxygenated hydrocarbon products, depending on the support material. Compared to bulk oxides, higher activity and selectivity to the desired products over supported catalysts can in part be attributed to the formation of easily reducible supported metal oxide phases [2].

Available partial oxidation catalysts can be supported on a ceramic membrane to increase their selectivity to CH_3OH [19]. This will have several advantages for CH_3OH formation:

- Combining two processes, reaction and separation, that are normally carried out separately may lower capital equipment costs. Separations can account for 70% of a chemical plant's cost.

- Higher selectivities can be obtained by preferentially removing the partial oxidation products before they are further oxidized to CO_2 and H_2O.
- Reaction rates and selectivities can be controlled by controlled permeation of oxygen.

Most porous ceramic membranes are composites or graded structures. A thick layer (few mm) of a porous and mechanically strong support is coated with a thin layer of a selective membrane (a few microns thick). The pore size distribution is rather narrow compared to porous polymeric membranes; this results in a good separation performance. Ceramics with Angstrom pore size are currently available. The ceramics are also well suited for the catalytic membranes since Al_2O_3, is normally used as a catalyst support and thus the same impregnation procedures can be used for catalytic ceramic membranes as used for supported catalysts [19, 20].

It is often necessary to introduce appropriate properties in order to use ceramic membranes in gas separation and catalytically active membrane reactors. This can be done by modification of γ-alumina thin films. The purpose is two fold. Firstly, it is desirable to reduce the pore size in order to enhance gas separation. Secondly, the chemical characteristics of the membrane surface should be controllable, in order to optimise its gas separation and catalytic properties. The reservoir method, which is especially effective for supported membranes, may be used to prepare such supports. The method was based on the urea method, a well-known impregnation technology to deposit a finely dispersed material in a catalyst. The urea decomposes at 90 °C, thereby hydrolysing the metal salts present. The much larger volume of the support compared to the catalytic layer was employed to create a high load in the catalytic layer only. The support acts as a reservoir containing material, which under favourable conditions, precipitates only in the surface layer [20].

Among the different support materials, silica appears to be the most effective for the selective oxidation of methane to formaldehyde [17]. Silica samples with different surface areas have been prepared by calcining microspheroidal silica at 1200 °C for different lengths of time [21]. Other preparation methods developed include preparation of a 'SiO_2/ceramic' microporous membrane using the sol-gel method. Silica gel was supported on a porous ceramic substrate (the average pore size is ca. 1-15 μm, $\phi=12\times1.5$ mm) and then dried and calcined in air. Furthermore, a 'catalyst/SiO_2/ceramic' catalytic function membrane was prepared by coating catalyst components onto the 'SiO_2/ceramic' membrane by impregnation or smearing. Catalyst loading on the membrane was controlled by repeated catalyst coating step [15].

Silica supported $FePO_4$ exhibits relatively high activity and selectivity for oxidation of methane to methanol and formaldehyde. Supported $FePO_4$ catalysts were prepared by impregnation of alumina (Alfa Aesar, 182 m^2/g), titania (Degussa, 61 m^2/g), and zirconia (Degussa, 47 m^2/g), with aqueous solutions of ferric nitrate and ortho-phosphoric acid. Prior to impregnation the supports were dried at 673 K in air. For each material, the iron nitrate solution with a concentration that ensured the desired loading was added to the dried support. These materials were dried overnight to give a free-flowing powder, to which was then added a stoichiometric ortho-phosphoric acid solution to provide a P/Fe ratio of unity. Impregnation was followed by evaporation at 363 K with continuous stirring, and calcining in air for 24 h at 973 K. All catalysts were compressed at 20 000 kPa and, subsequently crushed and sieved to obtain pellets of 0.2-0.3 mm particle size range [2].

Other supports, such as Al_2O_3, TiO_2, ZnO, MgO, and SnO_2 have also been studied [22, 23, 24]. It has been reported that zirconium oxide does not catalyse methane conversion to formaldehyde but no detailed investigation has been done for ZrO_2 as a support for metal oxide catalyst in methane oxidation [2].

It was shown that metal oxide-support interaction controls both the reducibility and dispersion of the active phase and in some cases lead to dramatic enhancement in catalytic activity and selectivity relative to unsupported oxides. SiO_2 and Al_2O_3 are both well known as acid-base catalysts and as supports for hydrogenation and oxidation reactions. [21]. The catalytic activity of SiO_2 and Al_2O_3 in oxidation reaction is due to their weak acidity. Cairati and Trifiro′ concluded that the oxidation of methanol to formaldehyde occurs through the elimination of protons from the surface methoxy group by adjacent oxygen ions upon SiO_2 and Al_2O_3 supports.

1.4.1.1 The effect of additives on a support

A variety of metal ions have been investigated as additives on silica supports and may result in a promoting or a poisoning effect. The role attributed to these promoters is to provide redox centres, which accelerate the activation of oxygen. This enhances the activity of silica, which exhibits high selectivity but poor catalytic activity for formaldehyde formation [2]. The addition of Na^+ and Mg^{2+} to SiO_2 and Al_2O_3 destroys the centres that are responsible for the formation of methyl formate, formaldehyde and CO_2 [21].

1.4.1.2 Chemical modification

Chemical modification of membrane surfaces also provides a way in which catalytically active membranes can be prepared [25, 26, 27]. Complexes of 1,3-diazoles with cations of transition metals are active in the oxidation, reduction, dehydration and hydroxylation reactions of organic compounds. Therefore, the conversion of 1,3-diazoles into heterogeneous catalytic forms is of interest from two points of view, namely, for the synthesis of adsorptive and catalytic phases and for the modelling of active centres of biocatalysts [28].

The simplest method of imidazole immobilization is by adsorption on the surface of oxide materials [29, 30, 32]. The main shortcomings of the method are the weak retention on the surface of carrier and a significant decrease in catalytic activity compared with homogeneous analogues. Despite these shortcomings, imidazole and its metal complexes adsorbed on the surface of oxides have stable catalytic activity in reduction-oxidation reactions. An increase in the bonding durability of imidazole and its metal complexes with the carrier is possible by incorporation of functional groups, for example amino groups, in the surface layer of oxide materials. An effective and comparatively simple method of imidazole heterogeneity is the encapsulation of catalytically active metal complexes with imidazole into a gel. Carriers that can form stable sols and gels are suitable for such imidazole immobilisation. Among the inorganic carriers, silica has such properties. A possible shortcoming of this method is a decrease in catalytic activity due to diffusion factors.

Sidorchuk et al [33] investigated the factors involved in the modification of aerosilogel (prepared from silica). They found that:

- The effect of the substance used for modifying the surface properties of the silica depended on the method whereby the process was conducted (liquid, vapour or solution; temperature, pressure) and on the mechanism of its interaction with the surface.
- The analysis of the kinetic data indicated that 4-5 h were sufficient for the completion of the surface modification.
- The initial thermal treatment of the adsorbent in vacuum was often not necessary due to the fact that the pressure of the modifying substance

considerably exceeded that of the water vapour desorbed from the silica surface.

- An increase in temperature favoured a greater extent of modification. Temperatures of the order of 200-300 °C were usually sufficient to attain a maximum degree of surface coverage with bound organic radicals.
- For modifications proceeding under high reagent pressures chemical modification was most likely as well as immobilisation of the organic phase on the surface by adsorption forces. In order to determine the type of interactions involved in such cases careful washing of the silica with an appropriate solvent was necessary for removing the adsorbed organic phase followed by checking the sample using various techniques. When physical or chemical immobilisation occurs geometrical modification of the adsorbent, i.e. a change in the parameters of its porous structure, takes place.

Modification can also be done with silicon compounds. Organosilanes are used for modification but aminoorganosilanes are more reactive since they carry the catalysing amine function, required for chemical bonding with the silica surface, inside the molecule [34]. This reduces the complexity of the liquid phase reaction system to be studied. The electron rich amine centre can enter into hydrogen bonding interactions with hydrogen donating groups, such as hydroxyls or other amines. Because of its basic character ($pK_a = 10.8$ for a terminal primary amine), the amine is easily protonated.

1.4.2 Metal oxides

For the conventional catalysts Slagtern, Swaan et al [35] investigated the partial oxidation of methane to synthesis gas over Fe/La/Al_2O_3, Co/La/Al_2O_3 and Ni/La/Al_2O_3 in a fixed bed quartz reactor at 500-950 °C. Fe-based catalyst showed a higher activity for total oxidation than the Co- and Ni-based solids. Fe-based catalyst may be a possible catalytic partial oxidation of methane in fluidised bed reactors at 1100°C.

Metal oxide catalysts have been used as catalysts for the selective oxidation of methane to methanol and formaldehyde [36]. Anderson and Tsai [37] have reported that a Cu^{2+} -exchanged Fe-ZSM-5 catalyst is active for the production of methanol by oxidation of methane with nitrous oxide at 230-350 °C. However methanol was not formed over copper free H-Fe-ZSM-5. Copper played a more significant role in the formation of methanol than iron. Doping of small amount of iron into ZnO and silica enhanced the formation of formaldehyde (< 1 % yield). The conversion of methane was accelerated by co-feeding hydrogen (as a reductant) with oxygen over several iron containing catalysts. Particularly co-feeding of hydrogen induced the formation of methanol over $FePO_4$, $FeAsO_4$ and FAPO-5 (Fe:Al:P = 0.1:0.9:1.0) catalysts at atmospheric pressure and rather low temperatures (623-723 K) [37]. The promotional effect of these dopants was due to the fact that they possessed both redox ($Cu^{I/II}$ /$Fe^{II/III}$) and Lewis acid (Fe^{III}) functions, which facilitated the surface oxidation of intermediate methyl radicals by a redox process of the methoxide species formation and subsequent transfer of a hydride ion to the dopant redox couple [9]. Thus, it appears that iron-copper species may possess a true synergy for the selective oxidation of methane.

In an investigation of the reaction mechanism of formaldehyde formation over silica catalyst in the temperature range 630-780 °C [2] it was proposed that formaldehyde was formed by a surface reaction rather than by gas-phase radical reactions. Residence time experiments indicated that both formaldehyde and C_2 hydrocarbons were primary products and apparent activation energies determined for total methane conversion, formaldehyde and ethane production, indicated that different pathways were operative. The proposed mechanism is shown in figure 1.1

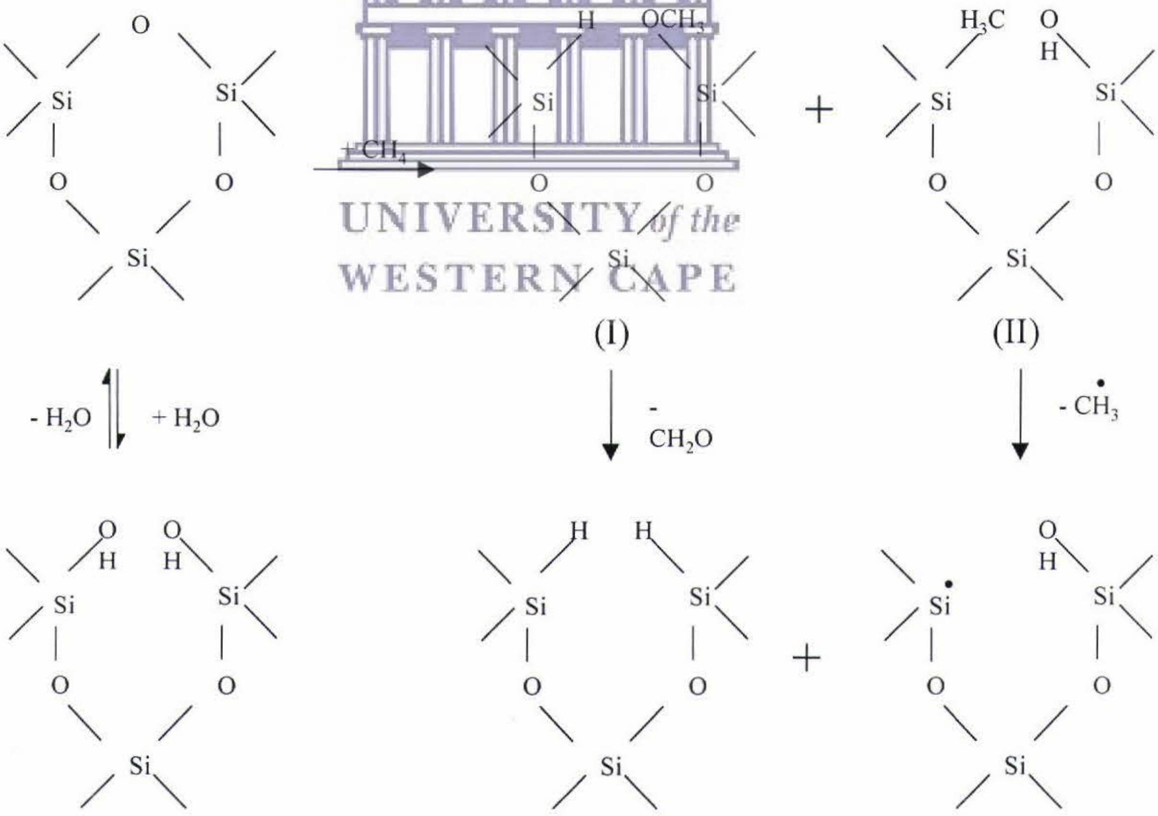


Fig. 1.1: Schematic mechanism for methane oxidation over SiO_2 catalyst [9]

Methane is suggested to dissociate on a siloxane bridge and be chemisorbed as two possible intermediates, one of which decomposes to generate the observed formaldehyde, whilst the other releases methyl radicals which couple in the gas phase to form ethane. The siloxane bridges may be more accessible in the silica gel than those generated upon the fumed silica [9].

Some types of metal complexes have been known to activate methane to form metal complexes that co-ordinate both methyl species and hydrogen [11]. The metals that are active for the oxidative addition of methane to a metal complex include Ir, Rh, Re and Pt. The electrophilic substitution to form new methane complexes (equation 2) may be an intermediate of the oxidation reaction where M is a metal.

$$M + CH_4 \Rightarrow M\text{-}R^- + H^+ \tag{2}$$

Methane partial oxidation has been carried out [9] using molecular oxygen over a MoO_3 silica supported catalyst at 560 °C. The major reaction products were HCHO, CO, and CO_2, with only traces of CH_3OH and H_2 at low conversions. HCHO was produced with 71 % selectivity. The best catalyst was MoO_3 Cab-O-Sil prepared by physical milling of the components. Catalysts prepared by impregnation also proved to be active but were less selective. The effect of dopants was investigated by impregnating the Cab-O-Sil support with solutions of chromium, cobalt, iron, silver, sodium and vanadium, to produce a series of catalysts with 2 wt % loadings. These materials showed low activity at 500-600 °C for methane conversion when N_2O was used as the oxidant, and only the vanadium impregnated catalyst exhibited selectivity towards HCHO. Under the same conditions the addition of Mo to the majority of the supports induced the production of HCHO. In the case of the 2 wt % vanadium catalysts, the addition of Mo increased conversion while depressing the HCHO selectivity, consequently rates of HCHO production were increased.

Catalysts based on vanadium have also been extensively used for this reaction [9]. V_2O_5 supported on silica formed HCHO when O_2 was used at 500-600 °C. At low conversions high HCHO selectivities were observed with trace quantities of CH_3OH under some conditions. Formaldehyde decomposition studies showed that CO was the product at the onset of conversion. At higher conversions CO_2 was also formed indicating a sequential oxidation mechanism. Comparison with the Mo-based catalyst showed that the vanadium material was more active. [11]. H_2PtCl_5/Na_2PtCl_4 in aqueous solution can oxidize methane at 120°C and 60 atm to give a mixture of methanol and methyl chloride, which system can be catalytically operated in the presence of oxygen.

Zhu et al [23] tested many metal oxide catalysts, such as single-component (V_2O_5/SiO_2, Cr_2O_3/SiO_2, MoO_3/SiO_2), binary- and multi-component catalysts consisting of Cr, Mo, V, BiO_x/SiO_2. The reaction was run at 450 °C, 5 Mpa, 7200/h and O_2: CH_4: N_2 = 1:10.6: 4.1. The results showed that Cr, Mo, V, BiO_x/SiO_2 are the most effective catalysts.

Taylor et al. found that methanol was most stable over the oxides MoO_3, WO_3, Nb_2O_5, Ta_2O_5 and SbO_3 whilst it was destroyed readily by CuO and Cr_2O_3 [36]. With the exception of Sb_2O_3 the conversion of methanol over these catalysts was relatively high, however, high selectivity to the partially oxidised products formaldehyde and dimethyl ether were observed. The reaction was carried out at 15 bar pressure and between 450-500 °C. Palladium has been reported to absorb methane at room temperature and produce only methyl radicals above 130°C [38].

1.5 The Catalytic Reactor

The design of the reactor is of the critical nature since it can alter the selectivity to oxygenates [14]. The majority of small-scale experimental work has used either static or flow-tube reactors. Hunter et.al [1] looked at the influence of the reactor wall in the production of methanol. They concluded that metals are, in general, undesirable because they lead to some degree of over-oxidation. However some researchers [1] claimed that for pressures of more than 40 bar, there was little difference between Pyrex and stainless steel. Nonetheless, the agreement was reached that a relatively inert non-metallic surface, like quartz or Pyrex, is necessary to obtain the best yield.

G. Lu et al. used a catalytic membrane reactor consisting of an inner tube (ceramic membrane, $\phi = 12 \times 1.5$ mm) and a shell tube (stainless steel, $\phi = 16 \times 2$ mm) [20]. Air or oxygen was passed through the inner tube and methane was passed through the shell layer simultaneously. Quenching of the reactor was used. Taylor et al. [36] studied the catalytic activity for methane partial oxidation in a fused silica lined stainless steel micro-reactor operator at 15 bar pressure.

Two approaches can be used to demonstrate the effectiveness of a catalytic membrane reactor to selectively form methanol by partial oxidation of methane [19]. The inside of a ceramic membrane tube can be coated with an oxide catalyst. The CH_3OH product formed by partial oxidation can be selectively removed through the ceramic pores before further oxidation to CO_2 and H_2O occurs. This selective removal can occur if the methanol coverage on the surface of the membrane is higher than that of the reactants (CH_4 and O_2). Some of the complete oxidation products (CO_2, H_2O) will also adsorb on the oxide surface, but this will not affect selectivity, and these products can be easily separated from the methanol afterwards. Movement of methanol through the membrane can occur by surface diffusion along the pore surface, and products will be removed from the outside of the tube. Methoxy species can surface diffuse on alumina. The second approach for partial oxidation in a catalytic membrane reactor is to feed CH_4 to the centre of the membrane tube and O_2 through the membrane walls in order to control oxidation. [19].

The approach that [8] Sokolovskii et al used to remove product from the reaction mixture was to condense the formaldehyde in a cooled trap (-15 °C) with re-circulation of the reaction mixture. In the case of oxidation of methane to methanol, the product was extracted from the reaction mixture by special adsorbents (the trap was filled with silica treated with boric acid), from which methanol was recovered by substitution with water. The latter procedure allows methanol recovery with high efficiency as a concentrated solution.

Movement of methanol through the membrane can occur by surface diffusion along the pore surface, and products may be removed from the outside of the tube [19]. Methoxy species can surface diffuse on alumina and thus surface diffusion is expected to be important in membrane separation with ceramic membranes. The short length of the small pores in the membrane means that high fluxes are possible. In the absence of selective removal, methanol will desorb from the surface, and as it moves down the reactor, will be completely oxidised to CO_2, and H_2O.

Banares, Alemany et al measured the activity of silica-supported transition metal oxide catalysts at atmospheric pressure in a fixed bed quartz micro-catalytic reactor by feeding CH_4 (99.95 volume %) and O_2 (99.98 volume %) without diluent [17]. The CH_4: O_2 molar ratio was adjusted to 2 gh/mol. Catalyst loading was 50 mg and it was sieved to the particle size range of 0.12-0.25 mm. They found that formaldehyde, C_2H_n, and CO_2 are primary products in this reaction, while CO originates from further oxidation of formaldehyde and hydrocarbons.

1.6 Alternative approaches to partial oxidation of methane

An alternative route to partial oxidation of methane is the non-radical intermediate route for the activation of methane [9]. For an example the use of hydrogen peroxide as oxidant in liquid superacidic conditions at low temperature has produced methanol with the selectivity high than 95 %. Whilst the use of ozone instead of H_2O_2 generated formaldehyde. Protonation of the resultant products was suggested to prevent their further oxidation and the reaction was stated to occur via an electrophilic insertion mechanism. This approach possesses the advantage of high selectivity, but suffers from the disadvantage of being homogenous thus separation of the product may present difficulties.

Another example of electrophilic activation of methane involves the reaction of methane with hydrogen peroxide and trifluoroacetic anhydride catalysed by Pd(II) species at 90 °C. The reaction produces methyltrifluoroacetate, which could then be hydrolyzed to produce methanol [39]. The substitution of $Pd(O_2CCH_5)_2$ by either $Pb(O_2CCH_3)_4$, $Fe(O_2CCH_3)_2$ or $Co(O_2CCF_3)_2$ resulted in a yield of $CF_3CO_2CH_3$ that was either similar to or only marginally higher than that observed with peroxytrifluoroacetic acid alone.

A double-layered catalytic bed was shown to enhance the yield of formaldehyde [9]. 1 wt % Sr/La_2O_3 was used to provide a methyl radical flux to a MoO_3/SiO_2

catalyst. Ultra-violet radiation was used to enhance the selectivity of methane oxidation to formaldehyde using MoO_3/SiO_2 catalyst at 190-220 °C. Experiments using optical filters demonstrated that wavelengths higher 300 nm were able to induce reaction with ZnO-based catalysts in contrast to the MoO_3/SiO_2 which required less than 300 nm. In neither case was reaction observed to occur in the absence of irradiation. This type of approach although using fairly conventional catalysts offers the possibility of minimising undesirable gas-phase contributions because of the low temperatures involved. The economic feasibility of running the photocatalytic reaction on a large scale is not clear.

1.7 Conclusion

For direct partial oxidation of methane to methanol to compete with the conventional route via syngas formation, it is desirable to enhance the product yield. The high selectivities (higher than 60 %) to methanol and formaldehyde that have already been reached open a wide area for practical use of the direct partial oxidation process. Designing a catalyst for methane partial oxidation to methanol is one of the ways to enhance the yield of methanol. The majority of catalysts used are metal oxides. The approach to catalyst design involves identifying metal oxide catalyst components that activate methane and oxygen, but do not readily destroy methanol.

CHAPTER 2 Objectives of research

The research work was done in collaboration with The Institute of General and Inorganic Chemistry of Ukraine Academy of Sciences. The objective of the collaboration was the development of a new technology and the transfer of technology to South Africa and entailed different methods of catalyst preparation, characterisation and testing the activity of the prepared catalysts.

The other objectives of the study are:

(ii) the preparation of a variety of catalysts followed by a comparative study of their physical properties

(iii) the design and construction of a suitable reactor for testing the reactivity of the catalysts, and as principal objective, the development of a low temperature and pressure catalyst for the oxidation of methane to methanol and formaldehyde.

3.1 CATALYST PREPARATION

3.1.1 Introduction

The support material used for the synthesis of the catalysts in this study is inorganic ceramic membrane. [19] Inorganic ceramic membranes are formed by a combination of a metal with a non-metal in the form of an oxide, nitride or carbide.

Alumina (α-Al_2O_3) and zirconia (ZrO_2) are the most important representatives of the ceramic membrane supports. They are usually prepared by sintering of micro particles. Their specific properties originate from their electronic behaviour. The non-metal atoms resulting in a highly stable bond retain the metal valence electrons and consequently these materials are highly thermally and chemically resistant [40]. The melting points are very high and can reach values above 4000 ^{o}C. The high temperature resistance make these materials very attractive for gas separation at high temperatures, especially in combination with a chemical reaction where the membrane is used as catalyst support as well as a selective barrier to remove one of the components that has been formed. They can generally be applied at a wide range of pH and in any organic solvent. All kinds of cleaning agents can be used, allowing strong acid and alkali treatment.

As discussed in chapter 1, silica has proved to be the most suitable inorganic carrier of the desired catalysts [24]. Silica is an amorphous material of the general formula SiO_2. In bulk silica, the Si and O atoms are connected in tetrahedra of SiO_4^{4-} units linked through siloxane bonds (≡Si-O-Si≡) to form the silica network [34]. In ambient environments containing water vapour, the surface reacts with water and becomes covered with silanol (≡Si-OH) groups, which possess excellent hydrogen bonding characteristics [34]. Amorphous silica is highly porous. Porosity introduces large surface area inside the silica particles. Therefore the introduction of silica on the membrane support will maintain and increase the surface area of the membrane support [22] and enhance its thermal stability. Surface area, pore volume, pore size and particle size can be controlled independently by changing the method and specific parameters of the silica preparation. These are the four variables governing the chemical and physical behaviour of silica [34, 41, 42].

The activity of the silica-based catalysts has been found to increase when the metal centres are deposited on modified silica. The silica surface can be chemically modified with silicon compounds, boron, titanium, aluminium compounds etc [34]. In the present study silicon compounds such as amino-organosilanes and chlorosilanes are used.

The improvement of the catalyst activity for the oxidation of methane to methanol and formaldehyde was attempted by modifying the membrane support surface, consisting of alumina, with various types of silica (Fumed and TEOS). Grafting a simple silane for example CDMS or APTS on the deposited silica surface followed this. The final step was to deposit a molecule holding the chosen reactive centre. The reactive centres chosen were Ag, Pt, and hemin.

The selection of hemin for the preparation of catalytically active support materials for methane oxidation was based on the high activity of porphyrin compounds in different oxidation processes [29, 30]. Hemin heterogenisation can be carried out by adsorption, co-ordinated immobilisation with amino groups upon the carrier's surface or by the chemical reaction of functional side groups of hemin. Hemin is a metal complex compound of a tetraazamacrocyclic ligand and the $Fe^{3+[31021]}$ ion. Hemin is present as a biocatalyst in oxidation reactions, which take place in live organisms at low temperature and atmospheric pressure. Figure 3.1 represents the structure of hemin [31].

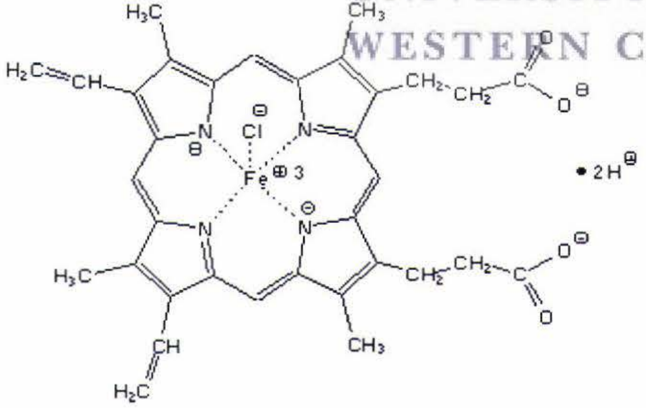


Fig. 3.1: The structure of hemin

Silver was selected as an active centre for catalysing the oxidation of methane because it is used in the oxidation of hydrogen by molecular oxygen to form H_2O. Platinum was chosen since it is used in the oxidation of CO by molecular oxygen to CO_2 [43, 44, 45].

3.1.2 EXPERIMENTAL PROCEDURE

3.1.2.1 Reagents used

Table 3.1 shows the source and the purity of the reagents used for catalyst preparation.

Table 3.1: Reagents used in the preparation of catalysts

Reagents	Source	Purity
Fumed silica, surface area 380m^2/g	Aldrich	99.8%
Tetraethoxysilane	Aldrich	98%
Chlorodimethylsilane	Aldrich	98%
γ-Aminopropyltriethoxysilane	Aldrich	99%
N,N-dimethylformamide	Aldrich	99.8%
Silver nitrate	Saarchem	99.8%
Hexachloro Platinic Acid	Next Chimica	99.95%
Hemin, bovine	Aldrich	

3.1.2.2 Tubular ceramic membranes as supports

According to Belyakova et al. the ceramic membrane support used in this research work have the following properties as presented in table 3.2 [28].

Table 3.2: Properties and dimensions of membrane used

Membrane type	Tubular
Chemical composition	α-Al_2O_3 70%, ZrO_2 30%, Y_2O_3 <1%
S_{sp} (m^2/g)	2-5
Total porosity (%)	45
Average pore diameter (μm)	0.2
Length used (cm)	13.2, 3.0, 5.0
Inner diameter (mm)	10.2
Outer diameter (mm)	11.6

3.1.2.3 Silica modified membranes

Two methods were used for modifying the ceramic membrane supports with silica based on the sol-gel technique.

(i) Method one

The ceramic membranes were cut to the desired length according to the size of the reactor, rinsed with water and dried at room temperature. The membranes were heated in a furnace at 120 °C for 2 h to remove adsorbed water. Before coating with silica the membranes were cooled and weighed. 40 g of fumed silica powder was fired in a furnace at 900 °C for 2 h to remove organic impurities and then cooled in a dessicator (in the presence of molecular sieve 3 A beads heated at 250 °C) for 3 h. 1000 ml distilled water was added to the cooled silica powder and stirred for 2 h. The dry membrane tubes were immersed in the sol for 1 h while shaking after which the membranes were dried on a Petri dish in an upright position. Once dry they were heated in a furnace for 1 h at 120 °C and then cooled in air.

(ii) Alternative method

Figure 3.2 is a schematic representation of the sol-gel method for the preparation of SiO_2 and the deposition upon the substrate (ceramic membrane support).

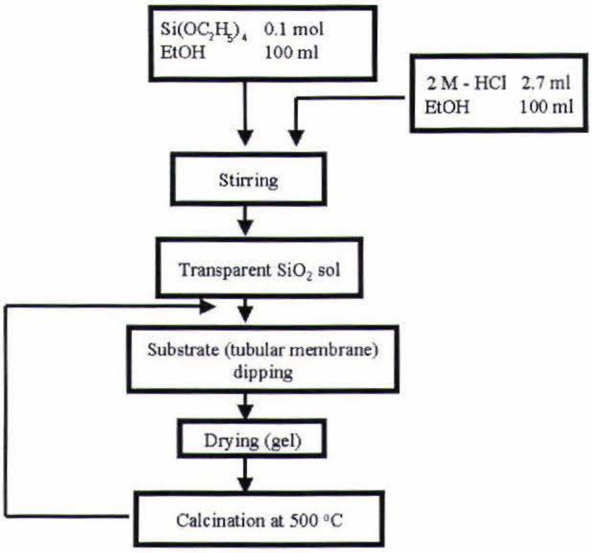


Fig. Schematic diagram of sol-gel process to prepare the SiO_2 thin films

Fig. 3.2: Schematic representation of the sol-gel technique for the preparation of SiO_2

Ethanol and hydrochloric acid, were measured as shown in figure 3.2, and mixed with a magnetic stirrer bar, after which $Si(OC_2H_5)_4$ was added to the mixture. It was stirred until the transparent SiO_2 sol was formed (about 1 h). The ceramic membrane tubes were dipped in the sol for 1 h, after which membranes were dried on a Petri dish in an upright position. Once dry they were calcined at 500 °C for 1 h and then cooled in air. To obtain more than one layer on the ceramic membrane the last three steps were repeated according to the desired number of layers.

3.1.2.4 Silver-containing membrane catalyst

(i) Deposition of silver on the surface of the blank ceramic membrane supports

The blank ceramic membrane tubes were placed in a 0.1M silver nitrate solution for 4 h at room temperature, which was stirred after every 30 min. The membranes were removed from the solution and air dried overnight. They were then placed in an oven at 120 °C for 1 h in order to promote the reduction of silver.

(ii) Silver deposition on ceramic membrane modified with SiO_2

After SiO_2 modification as described in section 3.1.2.3 the tubes were placed in the silver nitrate solution as explained above.

(iii) The interaction of silica modified membranes with chlorodimethylsilane

The silica-modified tubes were refluxed in 20 ml of CDMS for 3 days at room temperature. After removing and draining the tubes they were dried at room temperature and then weighed.

(iv) The interaction of silica-chlorodimethylsilane modified membranes with silver nitrate

The membranes were dipped in a 0.1M $AgNO_3$ solution for 4 h at room temperature. To promote the reduction of silver the tubes were subsequently heated at 120 °C for 1 h. The membranes were then cooled in air and the weight gain was recorded.

3.1.2.5 Platinum-containing membrane catalysts

The procedure described above in section 3.1.2.4 was followed to modify the blank ceramic tubes but using 0.05M hexachloroplatinic acid [$H_2PtCl_6.6H_2O$] instead of silver nitrate

3.1.2.6 Hemin-containing membrane catalysts

N,N-Dimethylformamide (DMF) was stored using molecular sieves for drying. 1 % hemin in DMF was prepared by dissolving 1 g hemin in 100.6 ml of DMF.

(i) Hemin on the surface of initial ceramic membrane

Ceramic membrane tubes were placed in 1 % solution of hemin in DMF as prepared in 3.1.2.6 at room temperature for 4 h. The solution was stirred after every 30 min. The tubes were removed from the solution and the excess solution was shaken off. The samples were dried in air and then in an oven at 120°C for 1 h, after which they were cooled and weighed.

(ii) Hemin on silica modified membranes

After SiO_2 modification, ceramic membrane tubes were placed in a 1% hemin solution as prepared in 3.1.2.6 at room temperature for 4 h, which was then stirred after every 30 min. The ceramic membrane tubes were dried in air where after they were placed in an oven at 120 °C for 1 h and then cooled.

(iii) The interaction of silica modified membranes with γ-aminopropyltriethoxysilane (APTS) followed by hemin coating

The silica modified membrane tubes were treated (by dipping) with undiluted APTS for 5 min at room temperature and then dried in air. The tubes were heated in at 120°C for 1 h and then cooled. The samples were placed in hemin solution as described previously.

3.1.2.7 Unsupported catalysts [without membrane]

In order to compare catalytic activity with characteristics of the catalyst such as their reducibility and oxidative behaviour it was necessary to prepare unsupported catalyst. A different source of silica having a low surface area to that of the fumed silica was used.

The samples used were obtained in Ukraine. They were prepared using Aerosil A-300 as a source of silica that was modified with trichlorosilane or dichloromethylsilane in the case of platinum and γ-aminopropyltriethoxysilane for hemin. It was necessary to modify silica with silanes for the introduction of Si-O-Si bonds.

(i) Platinum containing catalyst

1 g of the sample was dissolved in 25 ml of 0.05M hexachloroplatinic acid while stirring for 4 h. For samples that were hydrophobic 1 ml of isopropanol was added to the mixture until the silica-silane powder dissolved in platinic acid solution. The samples were filtered by gravimetric filtration and then washed with 50 ml water three times, followed by drying at room temperature.

(ii) Hemin containing catalyst

0.4mmol hemin was prepared in 25 ml of DMF. 1 g of APTS treated SiO_2 sample was mixed with the hemin solution for 4 h after which it was filtered and then washed with DMF [25 ml x3] and then dried at room temperature.

3.2 CHARATERISATION PROCEDURE

The catalysts were characterized using several techniques and the experimental details are outlined as follows:

3.2.1 Scanning electron microscopy (SEM)

A Leo S440 analytical scanning electron microscopy was used to take micrographs of the catalyst samples in order to determine the distribution of the catalysts over the membrane. The samples were mounted on aluminium stubs and coated with gold or silver paste for conduction. The operating parameters are detailed below:

Accelerating voltage	15keV
Beam current	2000.0 picoAmps
Tilt angle	0°
Resolution	>-9
Working distance	25.0 mm
Solid Angle Beam Current	12.2

3.2.2 Energy dispersive X-ray spectroscopy (EDX)

EDX allows qualitative and quantitative elemental analysis of the sample, and it gives the elements relative abundance as a weight percentage. The EDX instrument was attached to ADDA Hitachi X650 SEM.

Accelerating voltage	25kV
Tilt angle	0°
Take off	34.7
Res	145
Tc	40
Lsec	100

3.2.3 Nitrogen adsorption porosimetry [BET]

Changes in catalyst surface area, pore volume and pore size distribution were determined using a Micromeritics ASAP 2010. The catalysts were degassed in flowing helium at 110 °C for 16 h and at 260 °C for 1 h before characterising. The characterisation was based on the physical adsorption of nitrogen at liquid nitrogen temperature (77 K). The specific surface area was calculated from a multi-point using BJH nitrogen adsorption isotherm.

3.2.4 Thermal analysis

The catalyst's thermal stability was determined with a Rheometric Scientific STA 1500: RSI Orchestrator. The samples were heated from room temperature to 700 °C at a rate of 5 to 10 °C/min under nitrogen.

3.2.5 Temperature programmed techniques

The degree of reduction, and subsequent oxygen uptake and release by the synthesised catalyst were measured. The experiments were performed on Micromeritics AutoChem 2910. A thermal conductive detector was used.

3.2.5.1 Temperature programmed reduction (TPR)

In temperature programmed reduction, a reducible catalyst is treated with a flow of reducing gas mixture (normally a few volume % of H_2 in argon) while the temperature is ramped linearly. The rate of reduction is monitored continuously by measuring the H_2 content at the outlet of the reactor using a TCD detector in comparison to a reference gas. The total amount of hydrogen adsorbed is used to calculate the degree of reduction. The reducibility determines how reduced the catalyst will be during the reaction conditions. The experimental conditions are as follows:

Mass of sample	0.5 - 1.00 g
Temperature range	25 – 110 / 25 – 700 °C
Temperature gradient	5 – 10 °C/min
Flow rate	50 ml/min
Reactant gas	10 % H_2 in Ar

3.2.5.2 Temperature programmed oxidation (TPO)

Temperature programmed oxidation can be applied to determine the redox behaviour of catalysts. TPO determines the amount of the reduced species. The experimental conditions are as follows:

Mass of sample	0.5 - 1.00 g
Temperature range	25 – 110 / 25 – 700 °C
Temperature gradient	5 – 10 °C/min
Flow rate	50 ml/min
Oxidant gas	10.2 % O_2 in He

3.2.5.3 Temperature programmed desorption (TPD)

In temperature programmed desorption, a catalyst is pre-treated and equilibrated with an adsorbing gas or vapour under controlled conditions and then subjected to a linear temperature ramp. This experiment was performed directly sequentially to the TPO and the desorbing oxygen was measured. The experimental conditions are as follows:

Mass of sample	0.5 - 1.00 g
Temperature range	25 – 110 / 25 – 700 °C
Temperature gradient	5 – 10 °C/min
Flow rate	50 ml/min

3.2.6 Potentiometric titration

Potentiometric titration was used to determine aluminol groups in initial ceramic samples and the concentrations of silanol and amino groups in modified ceramic membranes [26]. Mettler Delta 350 INGOLD HA405-EQ-57/120 combination pH electrode, pH 0-14; 0-100 °C was used to measure the pH of the solutions.

For the aluminol, 1 g of the unmodified membrane was mixed with water for 24 h and then the pH was recorded as pH1. pH2 was obtained by saturating 1 g of the unmodified membrane with 10 ml of 0.1M NaOH for 24 h while stirring. Following the previous procedure using silica-modified membranes instead of the initial support the concentration of the silanol groups was determined. Whereas for the concentration of the aminopropyl groups, APTS modified samples were saturated with 0.01M HCl. The following formulae were used for calculations.

$[NH_2] = ((10^{-pH1} - 10^{-pH2})\ v)/1000m \qquad mol/g$

where v is the volume of equilibrium solution and m is the mass of the weighed sample

$pOH = 14 - pH$

3.3 REACTION STUDIES

The catalytic activity of the samples was tested using the oxidation of methane with oxygen as an oxidant. This reaction was used as a probe reaction.

3.3.1 Reactor design

Reaction studies were performed using a tubular membrane reactor shown below in fig.3.3. The reactor was made of stainless steel. The reactor structure was based on the module of a tubular ceramic membrane (1). The membrane was supported in the reactor by means of O-rings (2). The hermetic sealing of the membrane was accomplished by means of the upper and lower inlet/outlet (3) for the introduction of reagents and the outlet of reaction products. The proposed reactor design provides for the separation of internal (4) and external (5) catalytic reactor volumes. The additional inlet/outlet (6) provide for the introduction and output of reagents in the external volume. The reactor used was based on the unit size of the ceramic tubular membrane used as a support, with the length of 15.0 cm and the internal diameter of 12.2 mm.

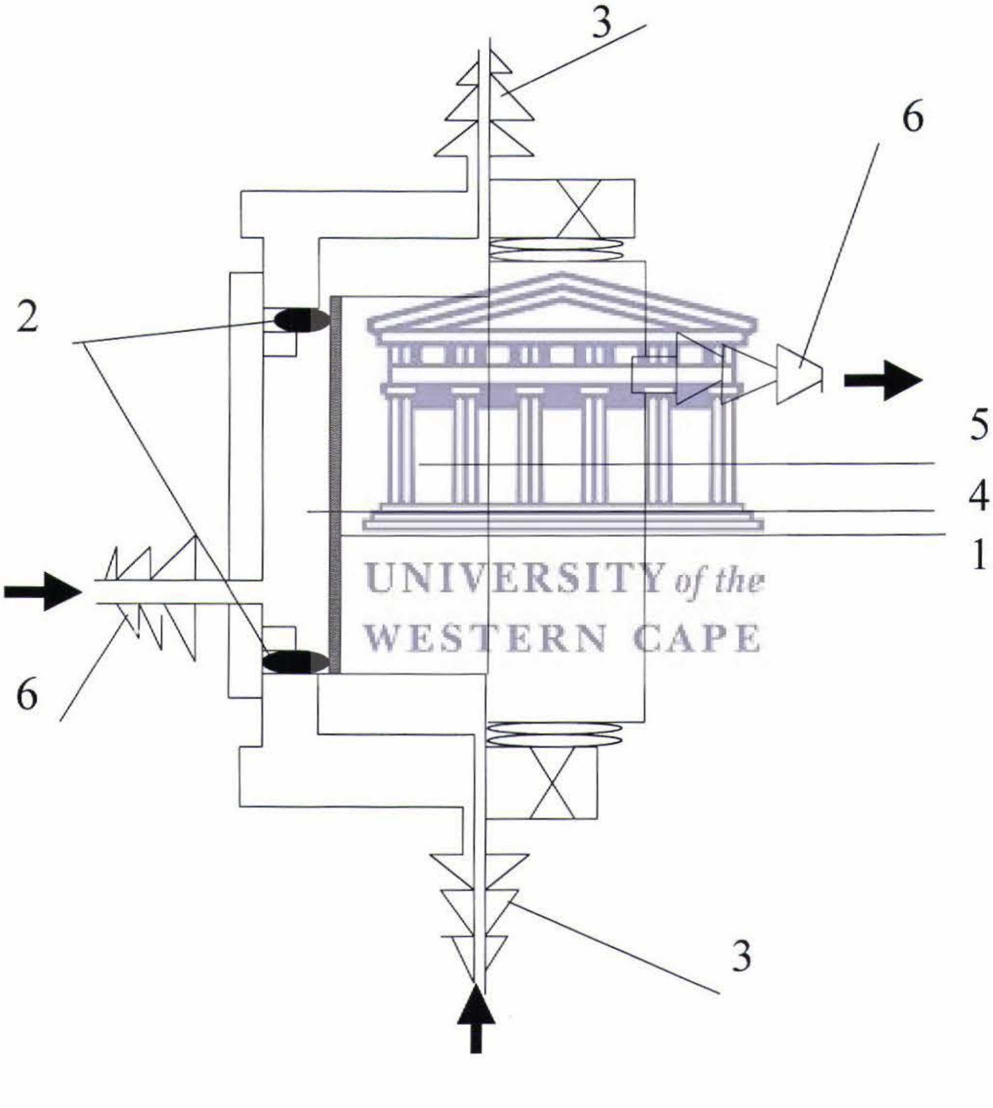


Fig. 3.3: Schematic representation of the cross section of catalytic membrane reactor.

According to the design of the reactor different methods can be used for the introduction of gaseous reagents into the reactor and for the output of the reaction products from the reactor. Figure 3.4 illustrates the method employed in the current study.

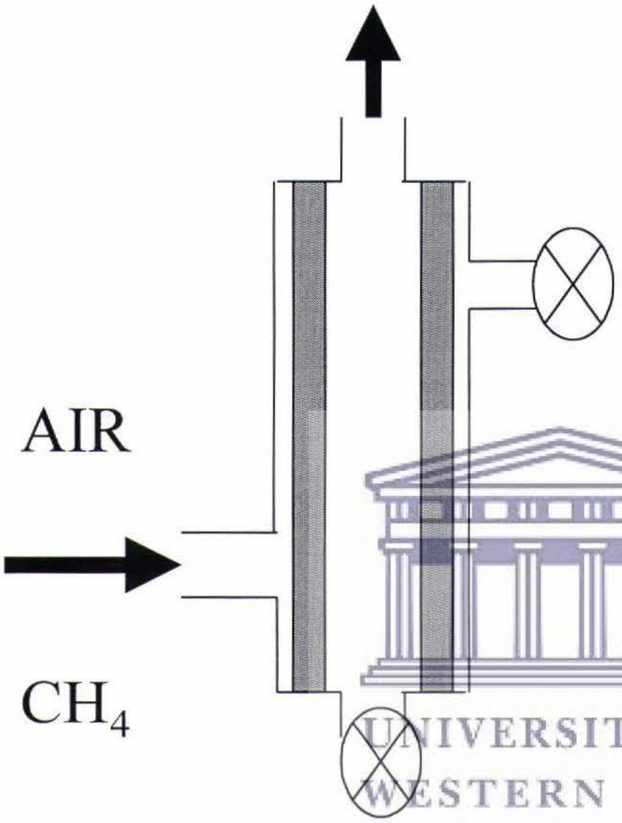


Fig. 3.4: Schematic representation of the method of introduction of reagents and removal of the products of the reaction (the exterior view).

A mixture of methane and air or pure oxygen was introduced into the external reactor volume, passed through the catalyst-containing ceramic membrane and then exited through the internal reactor volume.

3.3.2 Reactor set-up

Figure 3.5 represent the device used to estimate the catalytic activity of different catalysts supported on ceramic membranes. Flash back arrestors were installed just after the regulator to prevent explosion. Stainless steel tubing was used for the connections. Pure oxygen or air was used as oxidant. Mass flow controllers metered the methane and oxygen feeds, which were mixed and preheated (indicated by the shaded area), in coiled tubing (500 cm), before being introduced into the reactor.

The experiments were run at atmospheric pressure. Membranes coated with catalyst were inserted into the reactor. A thermocouple was inserted into the lumen of the membrane to measure the temperature of the catalyst bed and the membrane wall. The second thermocouple was used to measure the temperature of the outer wall of the reactor and the connection lines before and after the reactor.

The reactor and the connection lines were covered with heating tapes and heat insulators. The pressure transducers were used to measure the pressure of the internal and external output. Needle valves controlled the pressure. The product stream was heated to 100 °C using heating tapes downstream of the reactor to prevent condensation, and it was then analysed by an on-line gas chromatography. The loading and injection were done automatically.

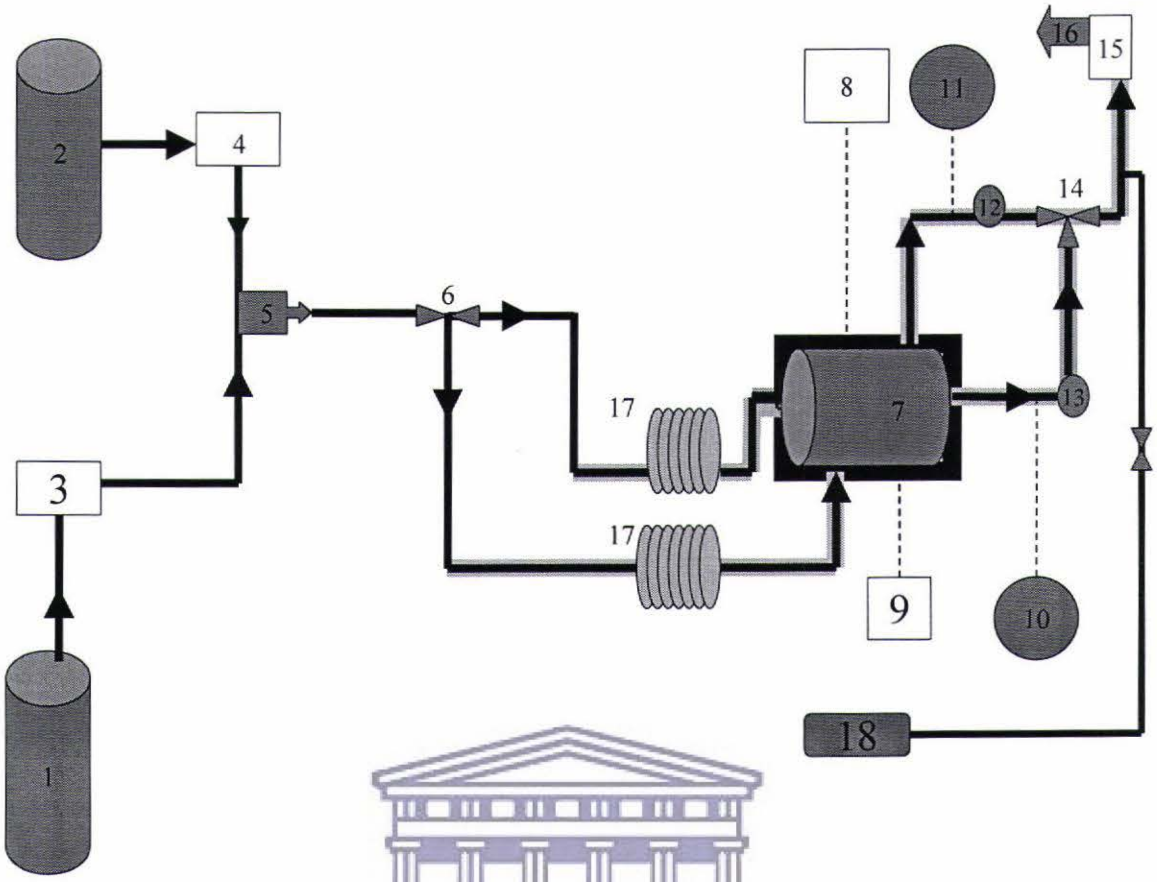


Fig. 3.5: Flow system used for the partial oxidation of methane

(1)air/O_2 cylinder, (2) methane cylinder, (3) and (4) mass flow controllers, (5) mixing chamber, (6) switch valve, (7) membrane reactor, (8) and (9) temperature controllers + indicators for inside the reactor and outside the reactor respectively, (10) and (11) pressure transducers for the internal output and the external output respectively, (12) and (13) needle valves for the external and internal outputs respectively, (14) 3 port valve, (15) gas chromatography connected to the computer, (16) vent, (17) coiled tubing and (18) internal standard.

3.3.3 Run procedure

The catalytic activity testing of the catalysts for methane oxidation was carried out at atmospheric pressure. The catalysts were placed in the reactor and heated under a flow of helium of 20 ml/min, 30 ml/min at the reaction temperature for 1 h. After an hour, the heated reactant mixture (CH_4 + O_2) was fed into the reactor at the required flow rate and reaction temperature.

Table 3.3: Experimental conditions

Variable	Condition
CH_4 : O_2 ratios	15:1, 10:1, 5:1, 3:1, 2:1, 1:1
Flow rates	20 ml/min, 30 ml/min
Reaction temperatures	30 °C, 60 °C, 90 °C
Pressure	atmospheric pressure

3.3.4 Gas chromatography (GC)

The product gases were analysed with an on-line Varian 3300 GC using a flame ionisation detector (FID). A 1.7 m x 3 mm HAYESEP T 100/120 MESH 75CC packed column was used to separate the compounds. GC settings and flow rates are shown in table 3.4

Table 3.4: Varian 3300 GC parameters

GC Parameter	Setting
Helium flow rate	30 ml/min
Hydrogen flow rate	30 ml/min
Air flow rate	300 ml/min
Column temperature	132 °C
Injector temperature	165 °C
Detector temperature	180 °C
Sampling loop volume	100 μl

4.1 CATALYST PREPARATION

4.1.1 Supported catalysts

The support was modified firstly with various silica sources followed by the deposition of the active centre on the membrane support. Various changes of the support surface were obtained after support modification. These changes were characterised by gravimetric analysis, N_2 adsorption, SEM/EDX, thermal stability and by testing for catalytic activity using temperature programmed techniques.

4.1.1.1 Sources of silica

Different sources of silica were introduced on the surface of the support (refer to section 3.1.2.3) in order to produce a suitable surface area for supporting the catalysts. The presence of silanol groups may allow the interaction of the adsorbed catalytic species with the surface of the support, usually through hydrogen bonding or dipole-dipole interaction [34]. The support modified by silica, prepared through the sol-gel technique (TEOS) (section 3.1.2.3), resulted in more silica being deposited than in the case of the support modified with fumed silica. Table 4.1 gives the mass increase of the support after modification with silica.

Table 4.1: Mass before and after modification with various silicas

Silica Sources	Fumed silica	TEOS
Mass % of silica deposited on the support*	2.09	8.45

The surface area and the pore volume of supports modified with various silica sources are shown in table 4.2.

Table 4.2: Surface area of supports modified with different silica sources

Physical properties obtained from N_2 adsorption	Support	SiO_2 [TEOS] on support	SiO_2 [fumed] on support
Surface area (BET) (m^2/g)	2.4	12.6	4.5
Single point surface area (m^2/g)	2.3	12.4	4.4

The support modified with TEOS has larger pore volume and surface area that can be used for further modification or grafting with inorganic and organic complex compounds. Large pore area distribution in region 1 were observed for the TEOS modified support, refer to appendix B1.

The pore size values reported in this study, using the t-plot method, are statistical average values and not the actual pore size, as was discussed by Vansant et al. [34]. Detailed analysis of the pore volume data was done in order to observe the changes that occur during the modification of the support by the desired catalyst. From 300 Å the pore size distribution becomes very broad especially in the case of TEOS.

Figure 4.1 presents the pore size distribution of supports modified with either TEOS or fumed silica, based on the pore volume. According to fig.4.1 there are three regions of porosity i.e. region 1 at 20-100 Å, region 2 at 100-300 Å and region 3 at 300-500 Å. In region 1 smaller mesopores started to appear upon modification with silica. In region 2 medium mesopores disappeared upon modification. The large mesopore volume was reduced upon modification in region 3. Therefore modification of the support with silica reduced the mesoporosity.

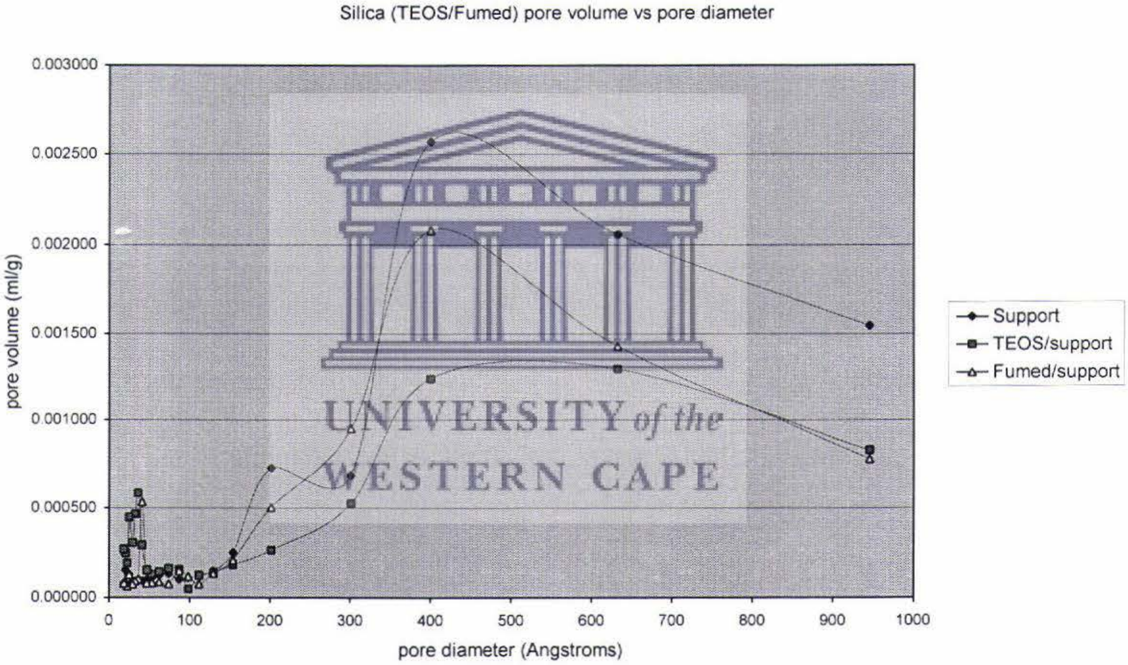


Fig. 4.1: Pore size distributions of supports modified with either TEOS or Fumed silica, based on the pore volume ($f_v(r_p)$)

The TEOS pore volume was less than that of the fumed silica and hence for the preparation of catalysts TEOS was used more often as the source of silica.

The morphology of the various silica sources was studied by using SEM micrographs. Large deposits of silica in both the inner and outer area of the tubular support were clearly visible. No silica deposits were observed in the edges exposed by breaking the tubular membranes. The fumed silica deposited on the support upon modification did not adhere sufficiently and was not uniformly dispersed on the membrane support in some of the samples studied. Cracks were also observed in the deposited layer of silica as shown in figure 4.2, which might affect the durability of the catalyst as well as the contact time of the feed during testing due to greater residence time. This is the reason for not using fumed silica more often in this study for catalyst preparation.

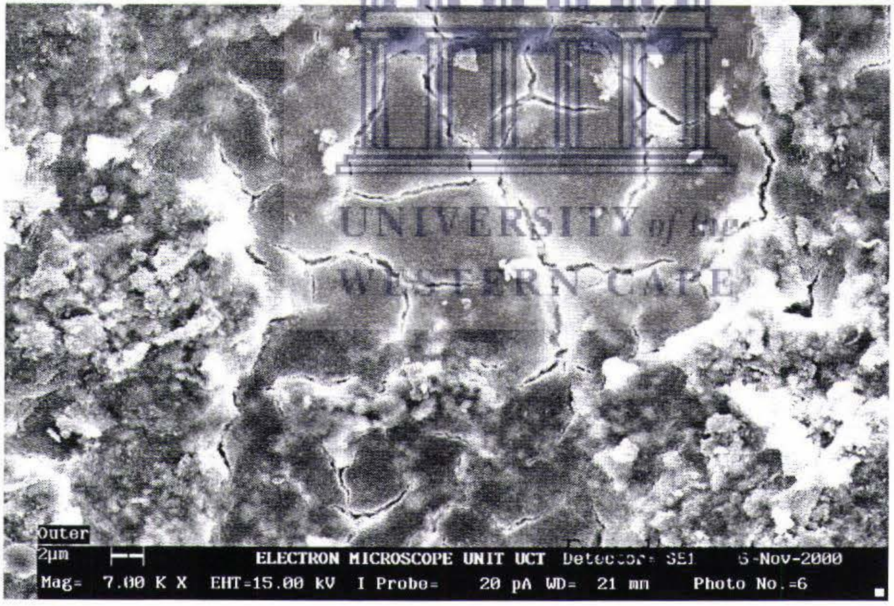


Fig. 4.2: SEM image of silica modified membrane support

4.1.2 Metal-containing supported catalysts

This section will cover the modification of the silica-modified support with the active metal species followed by the characterisation techniques. The deposition of active metal species on membrane support without silica modification will be reported for comparison.

4.1.2.1 Mass changes

After modification of the tubular and powder supports with metal species as described in section 3.1.2.4 - 7 the gain in mass was determined. Table 4.3 shows the mass percentage increase after deposition of various catalysts on modified and unmodified supports. Column three gives the mass percent of silica on the support prior to addition of the silane and the active metal species. Catalysts 1,4 and 9 were not modified with silica. Column 4 shows the mass percent of the deposited metal on the support modified or unmodified with silica. The catalysts produced after modification with fumed silica were not of high quality. Since the colour of the catalyst was not uniform throughout the support and black spots were observed on the surface. This was due to the silica layer that was not homogeneously dispersed on the surface of the membrane. During the modification process the silica was not properly stirred and hence some areas had more silica than other areas. To solve this problem the silica solution was stirred continuously when coating to ensure homogenous dispersion on the support.

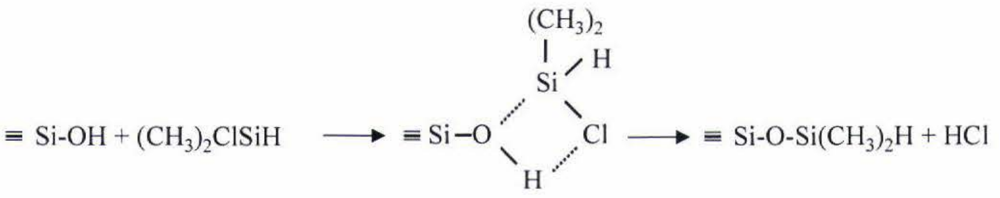
Table 4.3: Mass % of various supported catalysts

Catalyst No.	Description	Mass % of SiO_2 on support prior to addition of metal species	Mass % increase of metal on support modified with or without silica
1	Ag/support	———	0.165
2	Ag/fumed/support	0.368	0.041
3	Ag/CDMS/fumed/support	0.283	0.379
4	Pt/support	———	0.319
5	Pt/fumed/support	0.386	0.158
6	Pt/CDMS/fumed/support	0.162	-0.019
7	Pt/TEOS/support	1.433	0.238
8	Pt/CDMS/TEOS/support	1.481	0.009
9	Hemin/support	———	0.161
10	Hemin/fumed/support	0.068	0.127
11	Hemin/APTS/support	7.135	-0.532
12	Hemin/APTS/fumed/support	0.150	0.448
13	Hemin/TEOS/support	1.415	0.297
14	Hemin/APTS/TEOS/support	0.321	6.474

Table 4.3 will be discussed separately according to the active metal species impregnated on the membrane support.

(i) Silver impregnation

Grey coloured silver-based catalysts were synthesised after dipping unmodified and silica modified supports in silver nitrate solution as described in section 3.1.2.4. Catalyst 3 turned grey immediately after immersing it in the solution, while the other samples did not change colour immediately. According to Samuneva et al. [46] the active silver catalyst needs to be dark grey or black, which indicates that Ag^+ was reduced to Ag^0. Hence the grey colour of the synthesised silver-based catalysts may indicate that silver ions were reduced to silver metal after the impregnation process. Catalyst 3 has more silver deposition than the other two silver-based catalysts. This was due to the properties of amorphous silica discussed in section 3.1.1 [47]. Dimethylchlorosilane was used to activate the silica for further modification with metal or organic compounds. The hydrolytically and thermally stable Si-O-Si bonds were formed between the surface of silica and silane as reported by Varvarin et al [48, 49, 50]. In the case of catalyst 1 the Al-OH functional groups of the porous support interacted with the metal atoms. The Al-O-Si bonds, which are weaker than the Si-O-Si bond, may have formed in catalyst 2 and hence less silver loading may have resulted. Tertykh et al. reported that the chemical reaction for the formation of Si-O-Si bond follows the mechanism of electrophilic proton substitution in isolated silanol groups as shown below [25, 26].



$$\equiv Si\text{-}OH + (CH_3)_2ClSiH \longrightarrow \equiv Si-\underset{H}{O}\cdots\overset{(CH_3)_2\,,\,H}{Si}\cdots Cl \longrightarrow \equiv Si\text{-}O\text{-}Si(CH_3)_2H + HCl \qquad (3)$$

$$\equiv Si\text{-}O\text{-}Si(CH_3)_2H + AgNO_3 + H_2O \longrightarrow \equiv Si\text{-}O\text{-}Si(CH_3)_2OH + Ag^0 + H_2 \qquad (4)$$

(ii) Platinum impregnation

Platinum-based catalysts changed colour from yellow and light grey (obtained only for catalyst 8) to dark grey after heat treatment. This was in agreement with the results obtained by Samuneva et al. [46, 44]. There was more platinum on the unmodified support than on the sample prepared with silica followed by platinum deposition. This was due to the loss of some of the silica layer from the support when in contact with the platinic acid solution. This was confirmed by the presence of a powder at the bottom of the Pt reservoir beaker. The disadvantage of this was that the catalyst was not uniformly dispersed on the support. The reaction on the silica surface is as follows:

$$\equiv \mathrm{Si\text{-}O\text{-}Si(CH_3)_2H} + \mathrm{H_2PtCl_6} + \mathrm{H_2O} \rightarrow \equiv \mathrm{Si\text{-}O\text{-}Si(CH_3)_2OH} + \mathrm{Pt^{2+}/Pt^0} + \mathrm{H_2} \qquad (5)$$

(iii) Hemin impregnation

For the hemin-based catalysts there was no colour change after hemin impregnation on the support and the same colour as the initial hemin solution was observed. As the modification continued the colour turned to dark brown and black for the fumed and TEOS respectively and both were green colour in the lumen of the tube support. More hemin was deposited on the TEOS modified support (catalyst 13) than the fumed modified support (catalyst 10) since the TEOS modified support had a large surface area and pore volume as discussed in section 4.1.1. However the hemin deposits on these catalysts (13 and 10) was less than the hemin deposited on catalysts prepared by modifying the support with silica followed by immobilisation with APTS (catalysts 12 and 14). The type of bonds that form during the interaction between the support surface and the silica as well as the silane as was highlighted above in the case of silver and platinum may account for the difference. The reaction between the silica surface and γ-APTS is as follows:

$$\equiv\text{Si-OH} + (C_2H_5O)_3Si(CH_2)_3NH_2 \longrightarrow \text{Si-O-Si}(C_2H_5O)_2(CH_2)_3NH_2 + C_2H_5OH \qquad (6)$$

This reaction shows the presence of both the Si-O-Si and the aminopropyl groups in the catalyst. γ-Aminopropyltriethoxysilane can form strong metal complexes with the cations of d-metals e.g. Fe^{3+} also found in hemin (refer to 3.1.1 for the structure of hemin). APTS has a high reactivity due to the three ethoxy groups and the catalysing amine function, required for chemical bonding with the silica surface, inside the molecule $\equiv\text{Si-O-H-NH}_2(CH_2)_3\text{Si-}(C_2H_5O)_3$. Upon addition of the aminosilane to the silica substrate, the amine group may form hydrogen bonds or proton transfer complexes with the surface silanols. Figure 4.3 shows the mechanism for APTS reaction with the silica substrate in dry conditions [34], where (a) hydrogen bonding, (b) proton transfer, (c) condensation to siloxane.

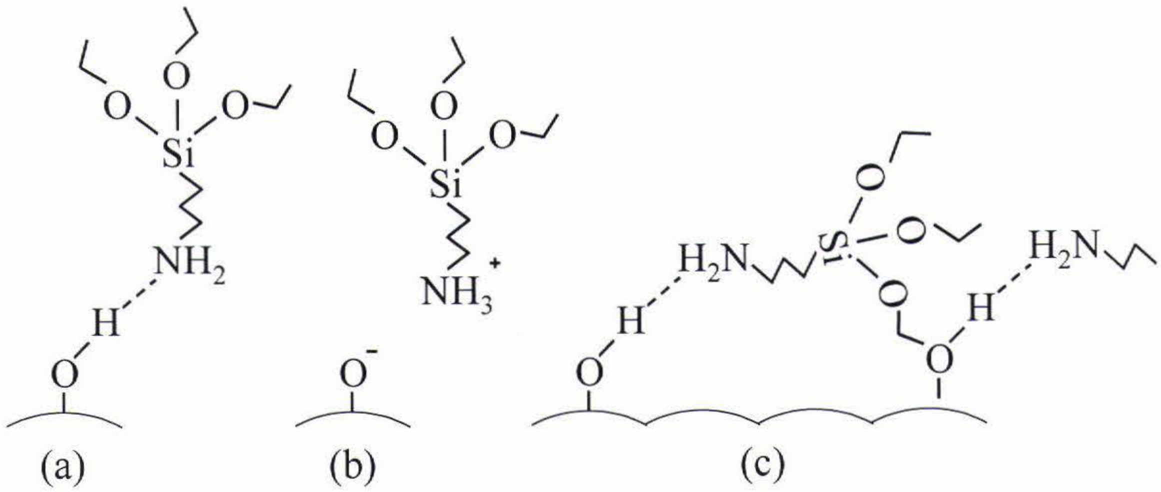


Fig. 4.3: Silica surface and aminosilane interactions in the loading step,

The following reaction between APTS and the support shows the bonding involved in catalyst 11

$$\equiv Al\text{-}OH + (C_2H_5O)_3Si(CH_2)_3NH_2 \longrightarrow \equiv Al\text{-}O\text{-}Si(C_2H_5O)_2(CH_2)_3NH_2 + C_2H_5OH \qquad (7)$$

Some roughness was observed on the surface of the porous membrane after drying. With time, the modified surface became glassy and the modification layer flaked off as Vansant et al. [34] reported. This was due to the silane polymer that forms especially in the liquid form. A significant increase in weight of the support in the process of surface immobilisation due to the polymeric silane fragments was obtained. The coating was not uniformly dispersed and thus unstable since the grafting was by adsorption and not by the formation of a chemical bond. This explains why catalyst 11 had a negative mass increase and hence a negligible sorption of hemin on the surface.

4.1.3 Unsupported catalysts [without membrane]

Metal containing unsupported catalysts were prepared as discussed in section 3.1.2.6. Table 4.4 shows the mass percentage of the unsupported catalysts. The colour changes of these catalysts were almost similar to those of the supported catalysts. The platinum catalyst was grey and the hemin catalyst turned black [32].

Table 4.4: Mass % of various unsupported catalysts

Catalyst No.	Description	Mass increase of metal on silica (%)
15	Ag/DCMS/Aerosil	8.70
16	Pt/DCMS/Aerosil	-15.1
17	Hemin/APTS/Aerosil	5.48

The platinum-based catalyst gave a negative mass percent as was observed for the platinum deposited on the support modified with fumed silica (catalyst 6) in section 4.1.2. There was more silver deposited on the unsupported catalyst (8.7 %) than on the membrane-supported catalyst (0.38 %) due to the large surface area of the powder catalyst (unsupported). In the case of hemin catalyst there was a small difference in the mass percentage of deposited hemin between the unsupported and the supported catalysts.

4.2 Catalyst Characterisation

This section will discuss the characterisation of the catalysts prepared previously (refer to table 4.3).

4.2.1 Concentration of aluminol, silanol and amino groups

Attempts were made as described in section 3.2.6 to determine the concentration of Al-OH groups on unmodified support, Si-OH groups on silica modified support and NH_2 groups on supports modified with APTS. Table 4.5 give the concentration of the H^+ or HO^- ions after dissociation.

Table 4.5 Concentration of H^+ and HO^- in the solution

Sample	pH(water)	pH(solution)	Conc.of H^+ or HO^- in the solution*
Al-OH (support)	6.5	5.4	0.018 µmol/g
Si-OH (silica on support)	6.5	4.2	0.313 µmol/g
Aminopropyl (APTS/silica/support)	6.5	9.7	0.250 µmol/g

* refer to appendix A for calculations

The addition of water to the silica coated membrane released protons into the solution. Therefore the solution was expected to be acidic. Similar dissociation was expected for the support (Al-OH). The concentration of H+ is higher in the silica-modified support than in the unmodified support. Silica gives off protons faster than alumina. The aminopropyl group accepts protons from the solution and hence a high pH was observed.

4.2.2 Porosity (N_2 Adsorption)

Surface areas and pore size distribution were determined as discussed in 3 in experimental section.

4.2.2.1 Surface area

As observed in section 4.1 the surface area of the TEOS modified support was larger than the support modified with fumed silica. The changes in surface area obtained after further modification of the support are shown in table 4.6, which presents the surface area and pore volume of the prepared catalysts.

Table 4.6 Surface area of the prepared catalysts

Catalyst No.	Description	Surface area (BET) (m^2/g)	Single point surface area (m^2/g)
A	Support	2.4	2.3
B	Fumed/support	4.5	4.4
C	TEOS/support	12.6	12.4
D	Ag/CDMS/TEOS/support	2.3	2.1
3	Ag/CDMS/fumed/support	2.0	1.9
4	Pt/support	1.9	1.8
7	Pt/TEOS/support	10.8	10.5
8	Pt/CDMS/TEOS/support	6.6	6.5
9	Hemin/support	2.0	1.9
13	Hemin/TEOS/support	10.1	9.8
14	Hemin/APTS/ TEOS/support	0.8	0.7

Further modification of the silica modified support resulted in a decrease in the surface area. This decrease in surface area may be explained by the blockage of the pores of the support modified with different silica sources by the deposited CDMS, APTS, silver, platinum and hemin. For platinum-based catalysts the surface area was reduced from 12.6 to 6.6 m^2/g showing that the pores were less filled compared to the silver-based catalyst where the surface area decreased from 12.6 to 2.3 m^2/g. In the case of the hemin-based catalysts as presented in table 4.7 the BET surface area of the support modified with TEOS decreased upon impregnation with hemin but the pores were not completely filled. However the introduction of APTS and hemin on the TEOS modified support reduced the surface area significantly to 0.8 m^2/g. APTS blocked the pores of the silica and support.

Table 4.7 BET surface area of hemin-based catalysts

Description	BET Surface area (m^2/g)
TEOS/support	12.6
Hemin/TEOS/support	10.1
Hemin/APTS/TEOS/support	0.8

4.2.2.2 Pore size distribution

The modification of the support with silica reduced the mesoporosity of the support as discussed previously in section 4.1.1. Introduction of silver on the silica-modified support had an opposite effect on the pores that is the volume of the large mesopores was increased. Figure 4.4 presents the pore size distribution of the silver-based catalysts.

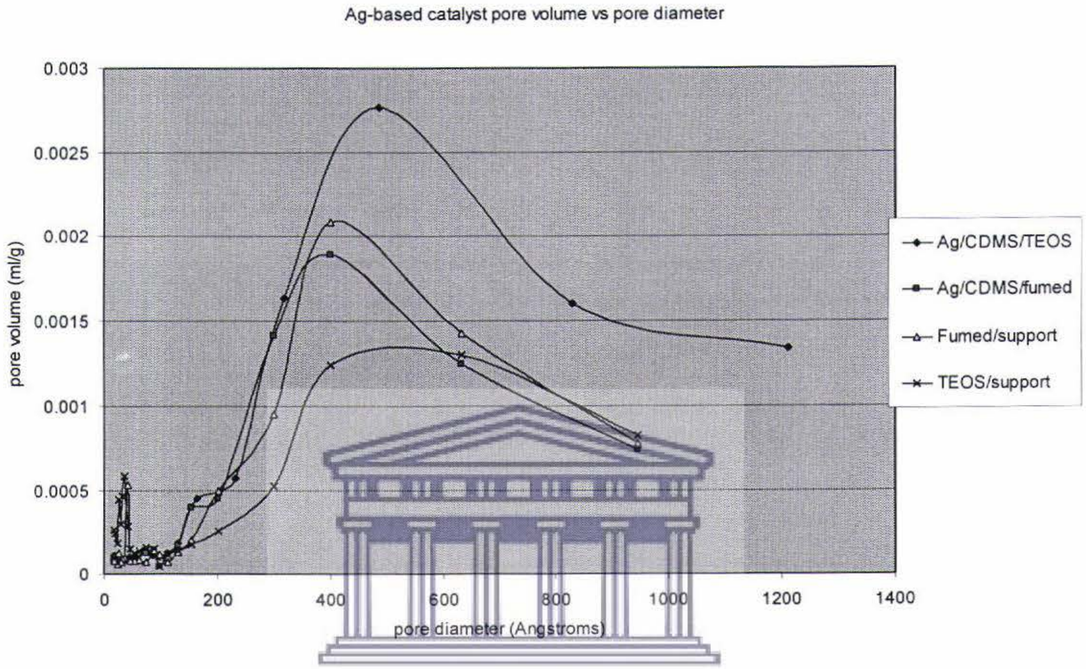


Fig. 4.4: Pore size distributions of the supported silver catalysts, based on the pore volume ($f_v(r_p)$)

The increase in porosity may be due to the formation of clusters of silver particles. The void volume may thus have been included as part of the pore volume. Silver on TEOS modified support showed large pore volume hence large void volume suggesting that there were more clusters formed by silver on the TEOS modified support than on fumed modified support. Therefore the TEOS sample retained its mesoporosity to a greater extent than the fumed silica sample.

Unlike the silver-based catalyst the pore size distribution for platinum-based catalysts exhibited the three regions of porosity more clearly. However the pore volume in region 20-100 Å was insignificant therefore the other two regions (i.e. 100-300 Å is region 2 and region 3 is 300-500 Å) will be discussed. Figure 4.5 presents the pore size distribution based on the pore volume for platinum-based catalysts.

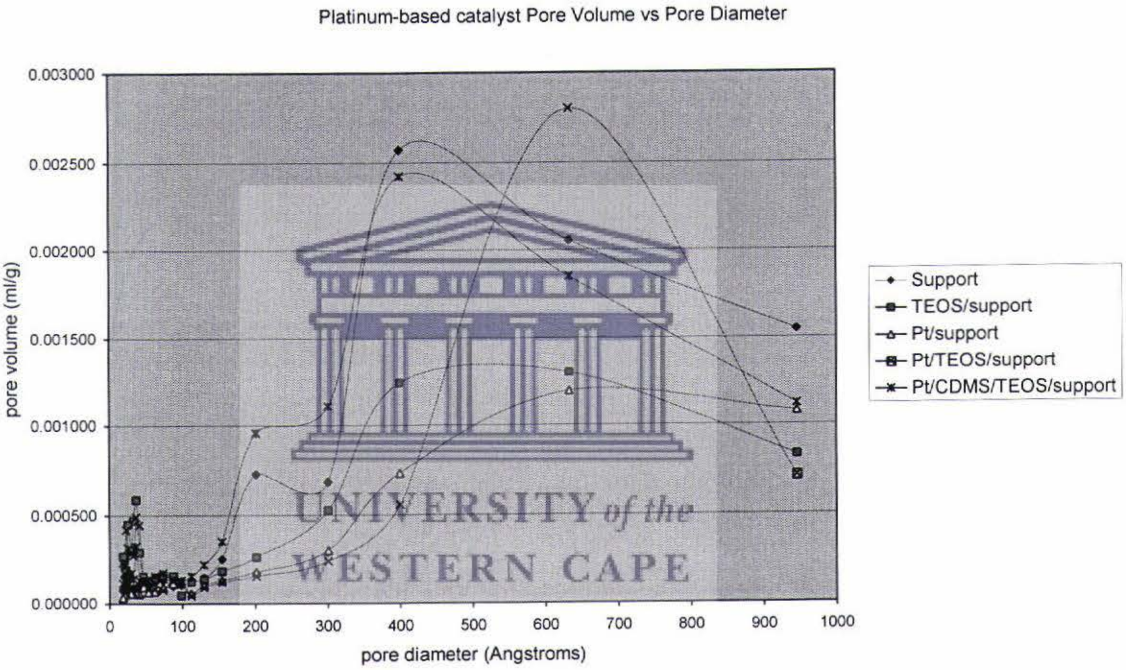


Fig. 4.5: Pore size distributions of the supported platinum catalysts, based on the pore volume ($f_v(r_p)$). The source of silica is TEOS.

Impregnation of platinum on the unmodified support showed a huge reduction in the volume of the large mesopores and this was due to the blocking of the support pores with platinum. This pore blockage was more than that observed upon modification of the support with TEOS. A very broad pore distribution of these two catalysts was observed. Platinum clusters were formed by the introduction of platinum on TEOS modified support since there was an increase in the pore volume due to the void volume. The pores that were blocked by the TEOS were opened by the preparation method for impregnation of platinum suggesting that the silica (TEOS) was washed off. Macropores (500-800 Å) were created between the Pt clusters. The presence of CDMS in the catalyst increased the pore volume of the small mesopores and opened the large mesopores that were blocked by the TEOS. Table 4.8 gives the summary of the changes observed upon modification of the support with the platinum-based catalysts.

Table 4.8 Summary of the pore size distribution results for platinum-based catalysts

Sample description	100-300 Å	300-500 Å
Support	Small mesopores low volume	Large mesopores larger volume
TEOS/support	Small mesopores disappear	Large mesopore volume reduced and pores blocked up
Pt/support	Small mesopores disappear	Large mesopore volume huge reduction and pores blocked up
Pt/TEOS/support	Small mesopores disappear	Large mesopores opened up and macropores formation
Pt/CDMS/TEOS/ support	Small mesopores increase in volume	Large mesopores volume decreases

In the case of the hemin-based catalysts there was a reduction in the pore volume and then further modification of the support blocked the pores of the support. The

APTS on the surface blocked the support/TEOS pores and hence resulted in the huge reduction in the volume. Table 4.9

Table 4.9 Summary of the pore size distribution results for hemin-based catalysts

Sample description	100-300 Å	300-500 Å
Support	Small mesopores low volume	Large mesopores larger volume
TEOS/support	Small mesopores volume reduced	Large mesopore volume reduced and pores blocked up
Hemin/support	Small mesopores disappear	Large mesopore volume huge reduction and pores blocked up
Hemin/TEOS/support	Small mesopores disappear	Large mesopores volume huge reduction
Hemin/APTS/TEOS/ support	Small mesopores completely blocked, huge reduction	Large mesopores volume huge reduction, blocked

The three catalysts, support modified with TEOS, hemin on support, and hemin on TEOS modified support showed the same shape of pore size distribution and the latter catalyst had a smaller pore volume. The pore size distribution based on pore volume for the hemin catalysts is presented in figure 4.6.

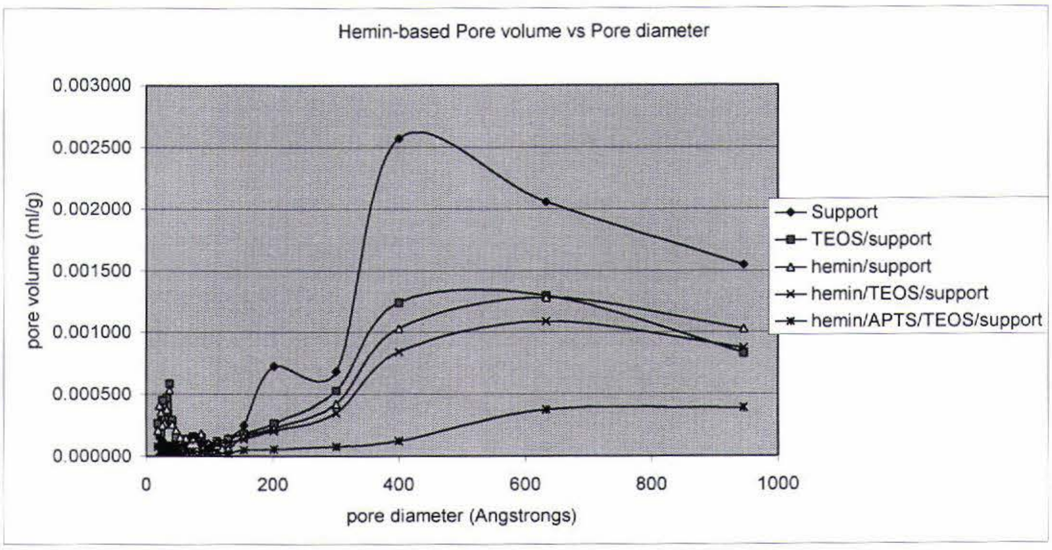


Fig. 4.6: Pore size distributions of the supported hemin catalysts, based on the pore volume ($f_v(r_p)$). The source of silica is TEOS

Fig 4.7 gives the comparison of the pore size distribution based on pore volume ($f_v(r_p)$) for Ag/CDMS/TEOS/support, Pt/CDMS/TEOS/support and hemin/APTS/TEOS/support catalysts. An increase in the pore volume of large mesopores for the silver and platinum catalysts was observed due to the metal clusters formed on the surface of the support membrane. The small mesopores appeared between 100-200 Å. Hemin catalyst showed opposite results to that of silver and platinum catalysts. A huge decrease in pore volume is observed. The pores were blocked with the APTS and hemin.

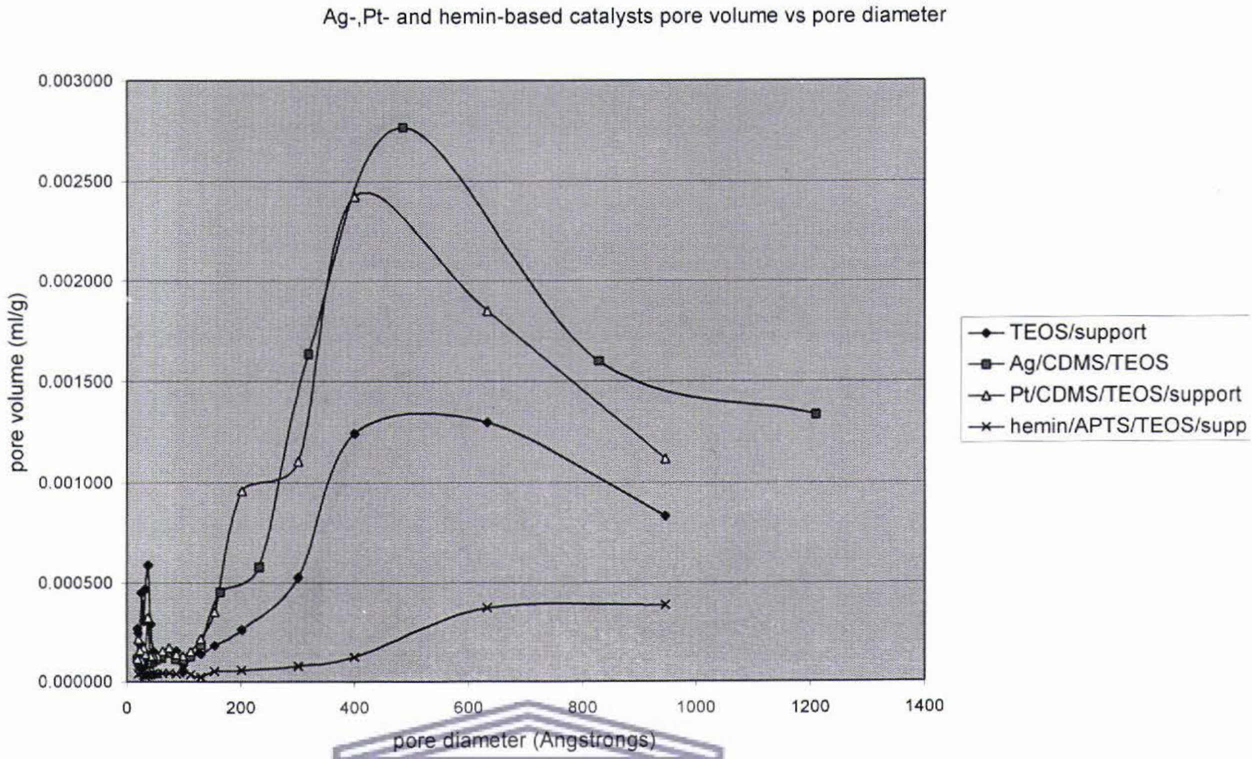


Fig. 4.7: Comparison of the pore size distribution based on pore volume ($f_v(r_p)$) of Ag-, Pt- and hemin catalysts. TEOS as source of silica.

4.2.3 Catalyst morphology and elemental composition

The dispersion of the active metal centre deposited on modified membrane support can be explained by using figure 4.8 and 4.9. Platinum-based catalyst was chosen since good resolution was obtained. Similar results were obtained for the silver-based and hemin-based catalysts. The outer surface (in figure 4.8) of the membrane support for the platinum-based catalyst was compared to the edges (in figure 4.9) which were exposed by breaking the tubular membrane On the outer surface platinum was more easily noticeable than in the edges. There was a large amount of platinum clusters on the outer surface than in the edges.

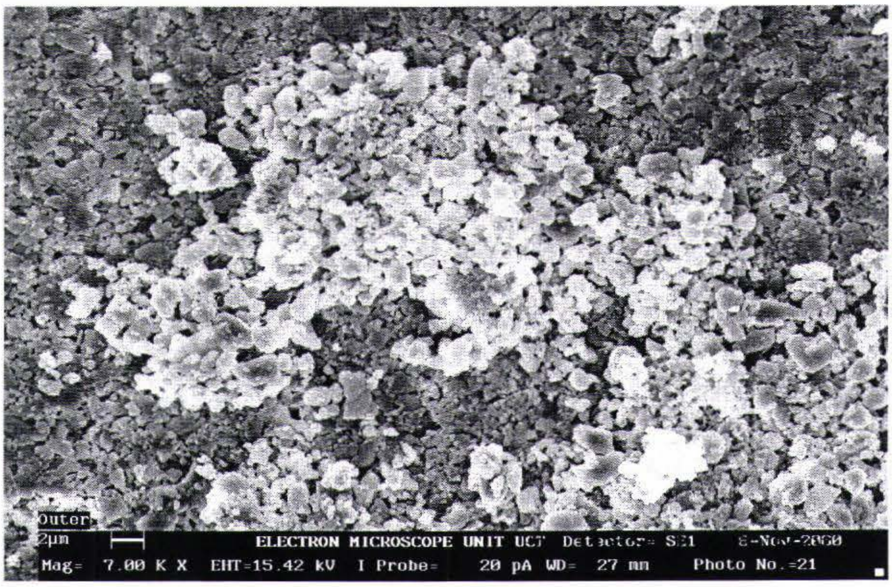


Fig. 4.8: SEM image of platinum deposited on silica modified membrane support (outer surface)

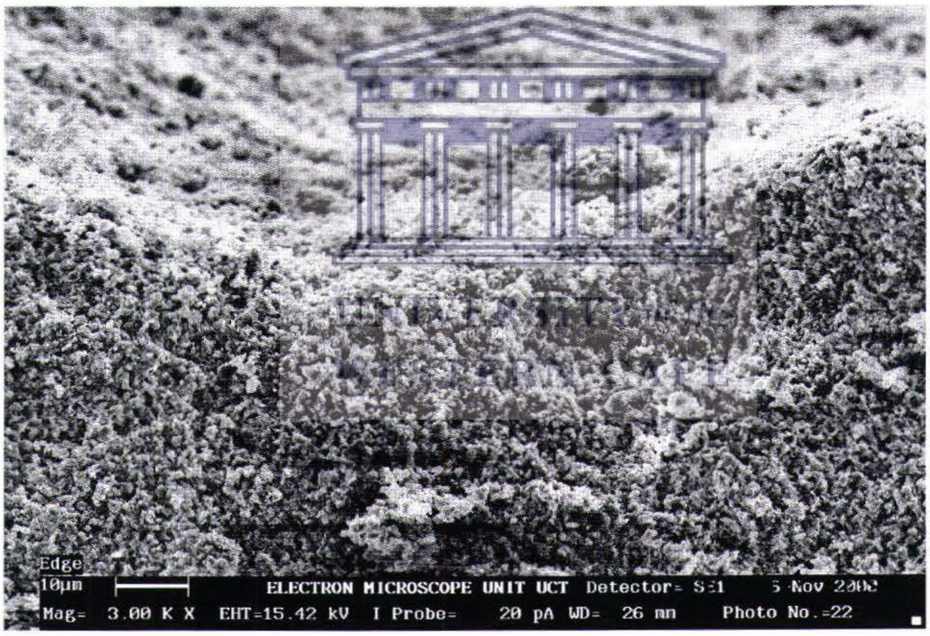


Fig. 4.9: SEM image of platinum deposited on silica modified membrane support (edge)

4.2.4 Elemental composition

Elemental composition of prepared membrane catalysts was determined by EDX. The results obtained for the Ag/CDMS/silica/support, Pt/CDMS/silica/support and hemin/APTS/silica/support are summarized in table 4.10. Silver deposited on the silica-modified membrane was less when compared to the platinum and hemin deposited on the same membrane support. There was no silver observed in the edges. In the case of the platinum and hemin there was higher loading of the elements Pt and Fe respectively on the outer surface than in the edges exposed by breaking the support membrane.

Table 4.10 Elemental composition of the prepared membrane catalysts

Catalyst	W % of element Outer (top) surface	W % of element Inner (lumen) surface	W % of element Edge surface
Ag/CDMS/silica/support	1.89	1.42	0.00
Pt/CDMS/silica/support	10.46	15.90	2.08
hemin/APTS/silica/support	17.44	12.85	5.74

The higher loads of metal (silver, platinum, iron from hemin) in the top layer of the support can be explained using figure 4.10. Since the membrane support pore volume is larger than that of the top layer, capillary forces develop in both the support and the top layer when drying. The top layer experiences larger capillary forces and then a pressure drop is created inside the system causing the liquid to flow from the support to the top layer. Therefore the support acts as reservoir. The concentration of the metal reactant increases on the top layer and results in higher loads of metal in the top layer than in the edges [20].

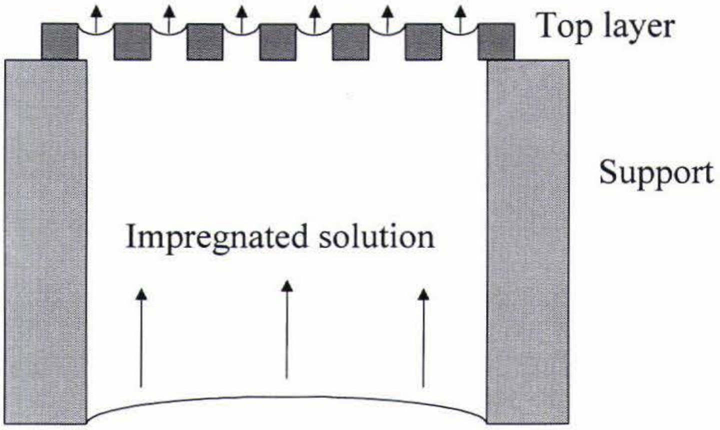


Fig. 4.10: Schematic and idealised representation of a support pore and top layer pores, filled with impregnation solution

4.2.5 Thermal analysis

The stability of the catalysts prepared was determined by thermal analysis method.

Table 4.11 Thermal analysis results for the unsupported catalyst

	Ag/CDMS/Aerosil	Pt/CDMS/Aerosil	Hemin/APTS/Aerosil
Mass loss (mass %) Between 25-700 °C	2.53	4.95	7.41
Onset of decomposition (°C)	220	150	120

Powder samples with no support were used for this analysis to ensure the maximum amount of the catalyst in the sample holder. Silver catalyst started to decompose at a higher temperature than the platinum and the hemin (Fe complex) catalysts and lost less mass between 25-700 °C, thus were more stable and less prone to thermal degradation. Figure 4.11, 12 and 13, present the mass lost by the silver, platinum and hemin catalysts respectively.

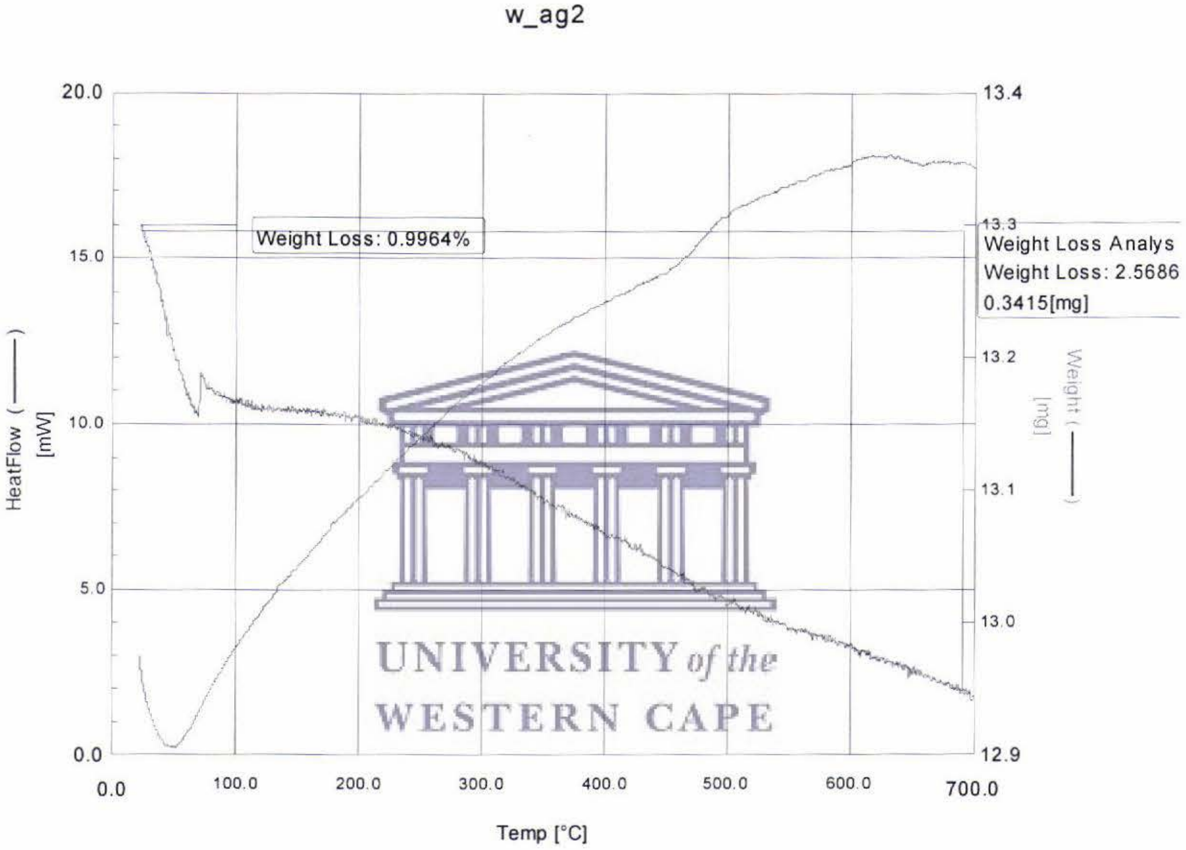


Fig. 4.11: Graph of weight loss or heat flow as a function of temperature for the silver-based catalyst.

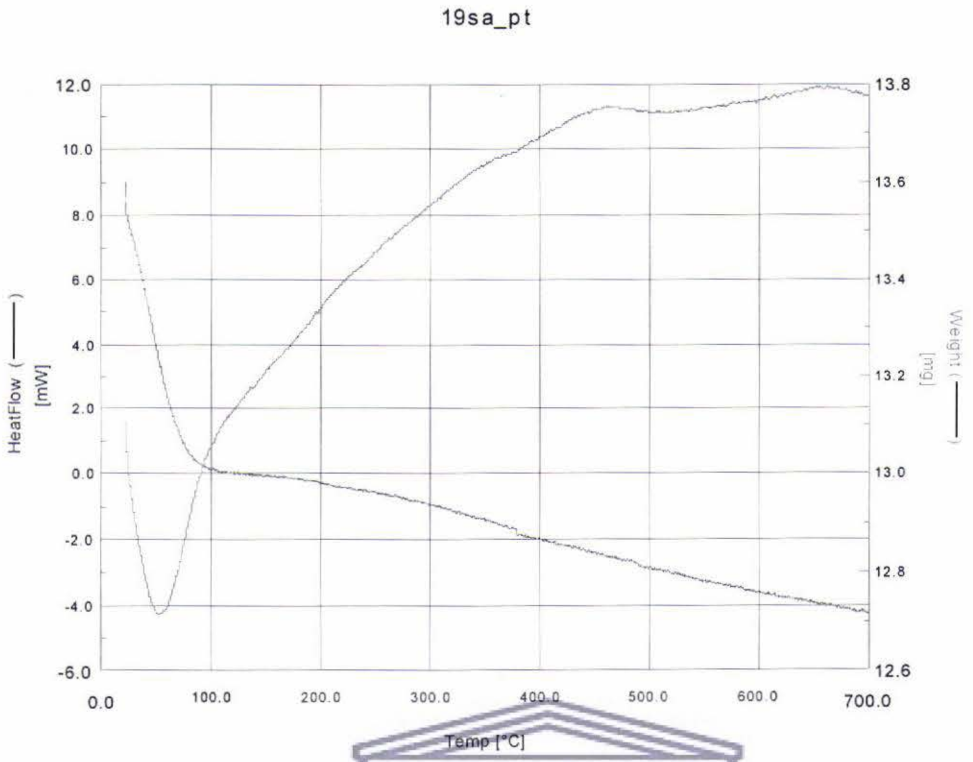


Fig. 4.12: Graph of weight loss or heat flow verses temperature for the platinum-based catalyst.

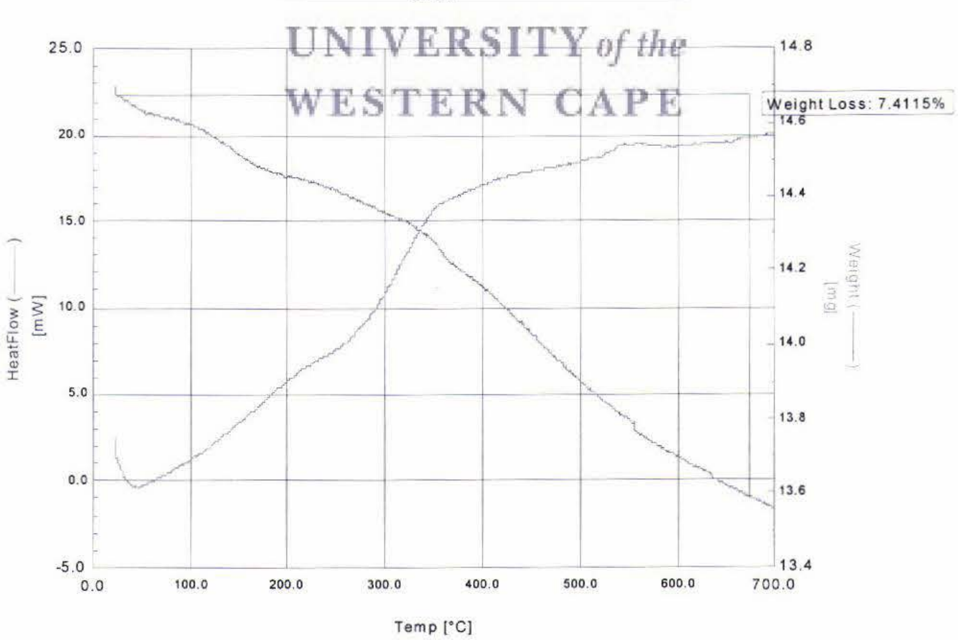


Fig. 4.13: Graph of weight loss verses temperature for the hemin catalyst

4.2.6 Temperature programmed techniques

Temperature programmed techniques were performed in order to determine the amount of the reducible species in the catalysts prepared.

4.2.6.1 Temperature programmed reduction (TPR)

(i) Supported catalysts

The major and minor peaks of the hydrogen consumed as well as the reduction temperatures are presented in table 4.12 for the supported catalysts. For the blank membrane support there was almost no hydrogen consumption with only a small amount consumed at a lower temperature (42 °C). Upon modification of the support with TEOS there was an increase in the amount of hydrogen consumed (10 times higher) at a lower temperature of 34 °C. In the case of metals deposited on the silica modified support the silver-based catalyst consumed more hydrogen than the Pt-and Fe-based catalysts.

Table 4.12 TPR reduction temperature of maximum peak area for the supported catalysts

Catalyst No.	Metal	Catalyst description	Reduction temperature (°C)	Peak area of H_2 consumed
A	—	Membrane (support)	41.8	Minor
C	—	TEOS/support	33.6	Minor
D	Ag	Ag/CDMS/TEOS/support	240.6	Major
8	Pt	Pt/CDMS/TEOS/support	42.9	Minor
14	Fe	Hemin/APTS/TEOS/support	798.7	Minor

The platinum-based catalyst (catalyst 8) was resistant towards reduction and this decreases the number of sites that can activate oxygen, and therefore activate methane to produce desired products. The presence of the reduced species especially on the silver-based catalyst will provide sites for adsorption of oxygen thus will increase reactivity. As pointed out by Webb et al.[10] the reduction temperature of the hemin-based catalyst was very high (799 °C), showing that there exists a strong interaction between the hemin and the silica modified support surface and hence giving less reducible species. The hemin peak at 799 °C corresponds to the transition of Fe^{2+} to Fe as reported by Webb and Orr for the hematite [10]. The reducibility determines how reduced the catalyst will be during the reaction conditions. From the obtained results it can be deduced that the metals are not completely reduced to metallic species (that is the oxidation state of zero), suggesting that no metal clusters will be formed on the catalysts after the activity test in the reactor. This will contribute to the longer lifetime of the catalyst, as the catalysts will be less prone to sintering and thus more stable. Metal species may be dispersed mono-atomically rather than in small clusters and prevented from migrating by the bonds formed.

(ii) Unsupported catalysts

The unsupported silver and platinum catalysts showed no reduction peaks. They were highly resistant towards reduction. Therefore there will be no or less sites to activate oxygen. Table 4.13 shows the major and minor peaks of the hydrogen consumed as well as the reduction temperature for unsupported catalysts.

Table 4.13 TPR reduction peaks of the H_2 consumed for the unsupported catalysts

Catalyst No.	Metal	Catalyst description	Reduction temperature (°C)	Peak area of H_2 consumed
15	Ag	Ag/CDMS/Aerosil	—	—
16	Pt	Pt/CDMS/Aerosil	—	—
17	Fe	Hemin/APTS/Aerosil	199.5	Major

The reduction temperature of the unsupported hemin catalyst (199.5 °C) was lower than that of the supported hemin catalyst (799 °C), showing that interaction between the hemin and the silica modified surface is weak and hence will give more reducible species than the supported catalyst. This catalyst showed a cyclic behaviour in the presence of H_2. It adsorbed and desorbed hydrogen continuously from 49.6 until 199.9 °C.

4.2.6.2 Temperature programmed oxidation (TPO)

Temperature programmed oxidation was studied in order to determine the quantity of reduced species.

(i) Supported catalysts

The amount of oxygen consumed is related to the amount of reducible species on the surface. Table 4.14 gives the major and minor oxidation peaks at the maximum temperature for the supported catalysts. For silver-based catalysts the catalyst supported on fumed silica membrane consumed more oxygen at a higher temperature than the TEOS catalyst. Platinum deposited on TEOS modified support was resistant towards oxidation.

Table 4.14 TPO oxidation peaks of the O_2 consumed for the supported catalysts

Catalyst No.	Metal	Catalyst description	Max. temperature (°C)	Peak area of the O_2 consumed
D	Ag	Ag/CDMS/TEOS/support	80.4	Minor
3	Ag	Ag/CDMS/fumed/support	119.7	Minor
8	Pt	Pt/CDMS/TEOS/support	80.1	Minor
12	Fe	Hemin/APTS/fumed/support	94.0	Major
14	Fe	Hemin/APTS/TEOS/support	107.2	Major

Unlike the silver-based catalyst the hemin deposited on the membrane modified with TEOS consumed oxygen very easily at a higher temperature than the hemin deposited on the membrane modified with fumed silica. Therefore more reducible species are expected on the surface of the hemin supported on fumed silica membrane. Figure 4.14 shows the oxidation peak of the hemin/APTS/TEOS /support, catalyst 14.

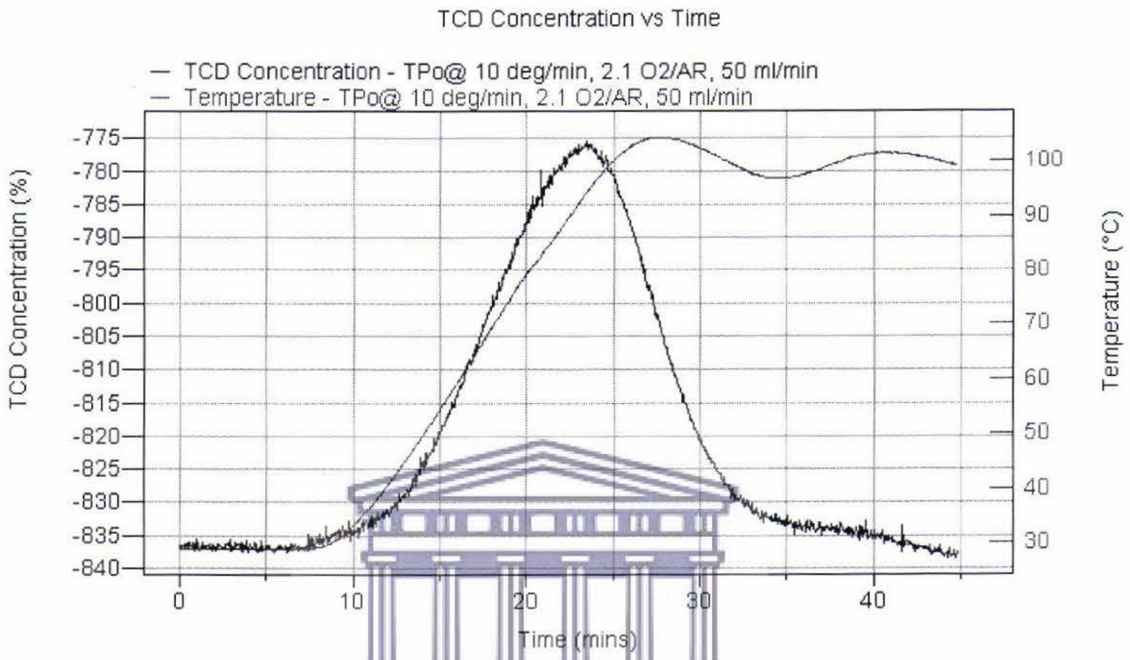


Fig. 4.14: Temperature- programmed oxidation profile of hemin/APTS/TEOS-/support

Oxygen consumption started at very low temperature for hemin deposited on TEOS modified membrane support (30 °C) reaching a maximum at about 107 °C as illustrated in the figure. TPO profile of Pt showed a constant rising signal. The silver-based catalyst showed two oxygen consumption peaks. The second peak was very broad and is illustrated in figure 4.15.

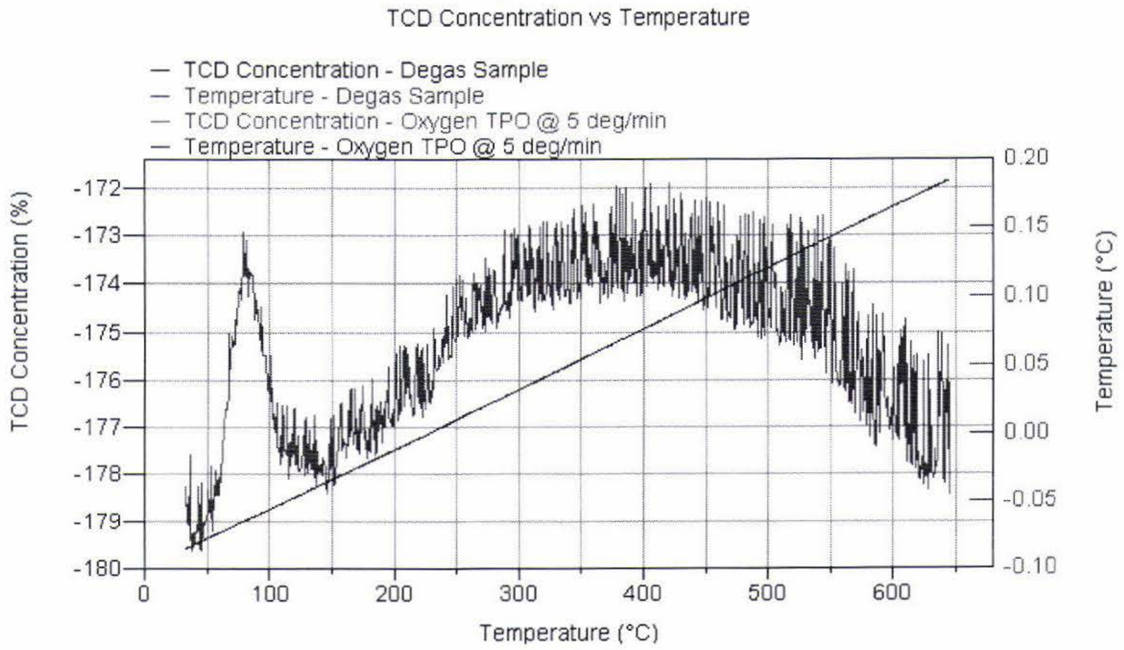


Fig. 4.15: Temperature-programmed oxidation profile of Ag/CDMS/TEOS-support

(ii) Unsupported catalysts

Platinum and hemin based catalysts consumed oxygen at lower temperatures than the supported catalysts. A constant uptake of O_2 with no peak was observed for silver-based catalyst. Table 4.15 gives the summary of the TPO oxidation peaks for the unsupported catalysts.

Table 4.15 TPO oxidation peaks and the amount of O_2 consumed for the catalysts

Catalyst No.	Metal	Catalyst description	Max. temperature (°C)	Peak area of the consumed O_2
15	Ag	Ag/DCMS/Aerosil	52.5	—
16	Pt	Pt/DCMS/Aerosil	61.9	Minor
17	Fe	Hemin/APTS/Aerosil	112.4	Major

The hemin catalyst consumed large quantities of oxygen, since a major peak was observed, thus more reducible species are expected for the activation of oxygen and hence the reactivity will be increased. Figure 4.16 shows the TPO profile of Pt/DCMS/Aerosil catalyst.

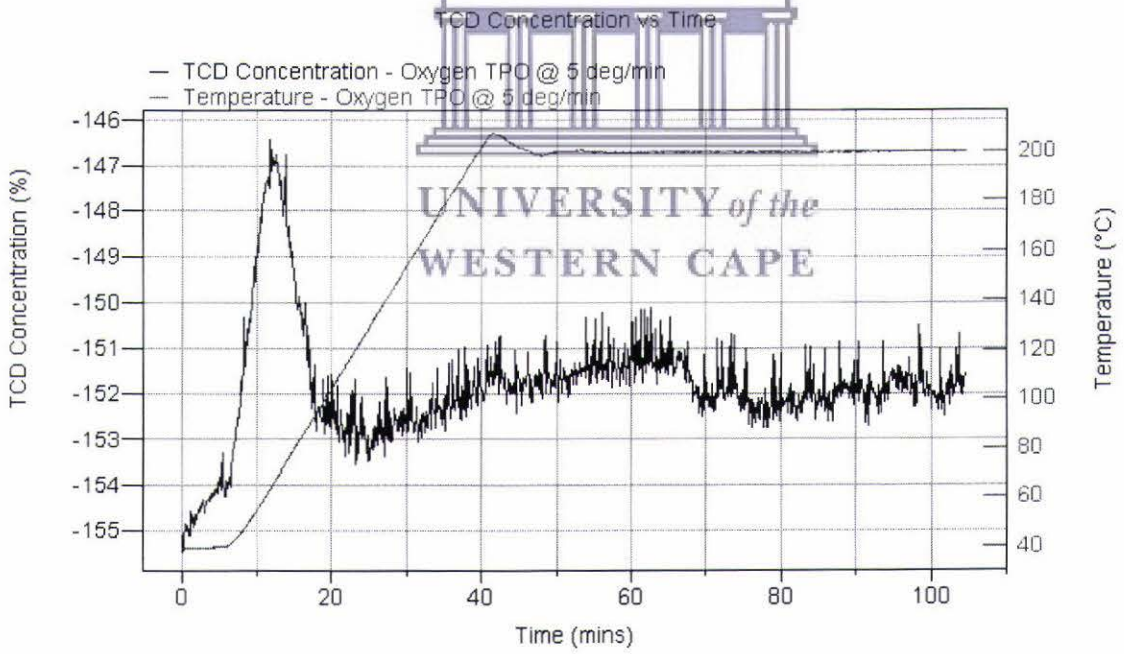


Fig. 4.16: TPO profile of Pt/DCMS/Aerosil catalyst

Figure 4.17 present the TPO profile of hemin/APTS/Aerosil catalyst.

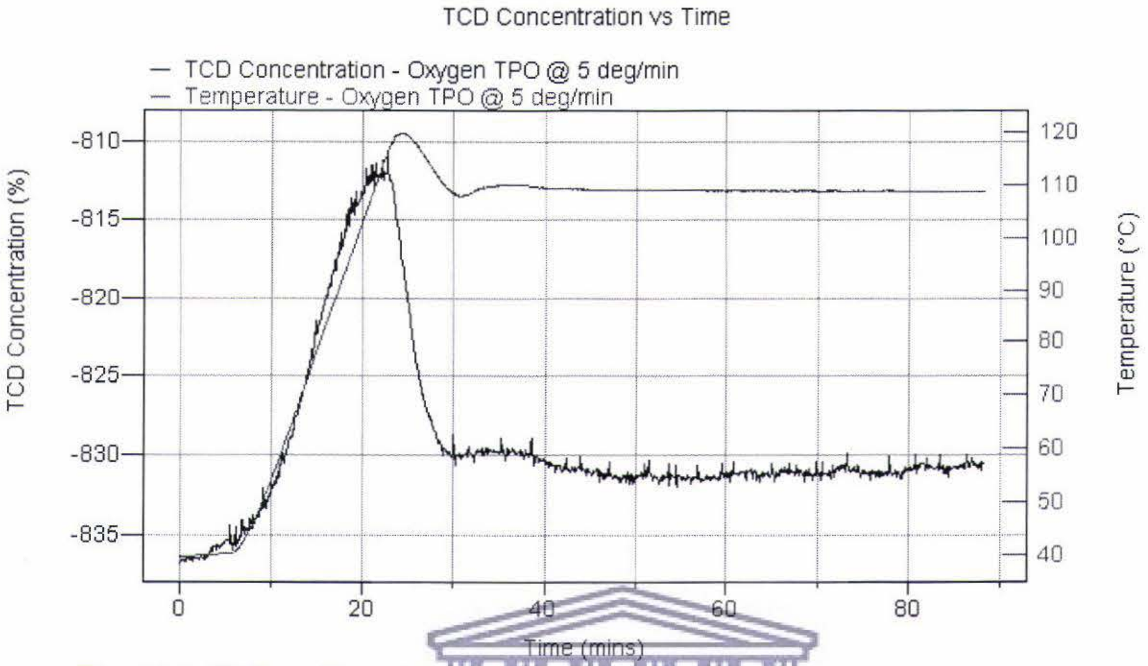


Fig. 4.17: TPO profile of hemin/APTS/Aerosil catalyst

A similar TPO profile was observed for the unsupported hemin and supported hemin catalysts as can be seen in figure 4.17. Oxygen consumption started at a very low temperature (40 °C) reaching a maximum at 110 °C. Oxygen was consumed at the one temperature irrespective of the presence of the support for the hemin-based catalysts.

4.2.6.3 Temperature programmed desorption (TPD)

(i) Supported catalyst

It was observed that only the silver-based catalyst (catalyst 3) showed a desorption peak at a lower temperature of 72°C for the supported catalysts, suggesting that for the hemin and platinum catalysts it was difficult to desorb the consumed oxygen. The reaction conditions used (refer to section 3.2.5) might be too mild for these catalysts since there was a strong interaction of hemin with the support surface.

(ii) Unsupported catalyst

TPD results for the platinum and hemin based catalysts are presented in table 4.15. Many TPD peaks were observed for the platinum (2 peaks) and hemin (5 peaks) based catalysts. The first peak corresponds to a weak adsorption of oxygen that may have arisen from weak chemisorption. Catalyst 17 (hemin/APTS/Aerosil) was allowed to under go reduction, followed by oxidation and then desorption. The results obtained are represented in table 4.16. Four peaks were observed compared to the five peaks obtained for the same catalyst without undergoing TPR before oxidation. The temperature of these peaks corresponds to the temperatures for catalyst 17 with no TPR. The peak at 259.6 °C disappeared, suggesting that this peak represent the reducible species on the hemin catalyst.

Table 4.16 TPD results for catalyst 17 Hemin/APTS/Aerosil and catalyst 16 Pt/DCMS/Aerosil

Catalyst No.	Temperature-programmed reactions	Max. Temperature (°C)	Peak area of desorbed H_2
16	TPO followed by TPD	75.4 348.3	Minor Major
17	TPR followed by TPO and then TPD	56.4 203.5 344.9 434.7	Minor Minor Major Minor
17	TPO followed by TPD	67.8 203.3 259.6 351.7 393.1	Minor Minor Minor Major Minor

According to temperature programmed techniques the hemin-based catalyst is the most promising catalyst for the oxidation of methane to methanol and formaldehyde under mild conditions, followed by the platinum-based catalysts. Silver-based catalysts showed promising results under TPD and TPO experiment.

4.3 CATALYTIC ACTIVITY

The Ukrainian research group who developed these catalysts were successful in producing methanol and formaldehyde under mild conditions employing the catalysts prepared using procedures similar to those discussed in this report. In order to determine whether the catalysts prepared in this study were as active as the catalysts developed and prepared in the Ukraine, catalytic testing was done according to the method described in section 3.3.

Table 4.17 presents the methane peak area obtained after the methane oxidation reaction performed at different reaction temperatures for Ag/CDMS/Fumed/support catalyst. Similar trends of the methane peak area were observed for the platinum- and hemin-based catalysts. Therefore the results are not presented in this report.

Methanol or formaldehyde peaks were not observed as expected products, instead only methane peak was observed. The methane peak decreased as the reaction temperature increased as can be seen in the table below, which indicates that there was a reaction occurring at 90°C. At the moment no conclusions can be reached regarding the type of reaction taking place, whether complete or partial oxidation, as a carbon balance could not be obtained.

Table 4.17 Results of methane oxidation on the silver-based catalyst (Ag/CDMS/Fumed/support)

Ratio of Methane :oxygen	Flow rate (ml/min)	Methane peak area at reaction temperature 70 °C	Methane peak area at reaction temperature 90 °C
15:1	20	359028	286217
10:1	20	347233	285222
5:1	20	315695	261484
3:1	20	279953	252447
2:1	20	248698	230138
1:1	20	188277	162627

The reasons for not observing methanol and formaldehyde in our reaction system are discussed below.

The flame ionization detector (FID) used in our GC cannot detect H_2O and CO, which require that the thermal conductive detector (TCD) must be used for analysis. Hence it should be possible to determine the carbon balance. Thereafter a conclusion may be reached that the reaction resulted in the formation of the desired products (methanol and formaldehyde) or into CO_2 and H_2O. Moreover the sample loop for introducing the post reactor gas stream to the GC is small (100 μl) for gas samples. The % conversion to the products might not be high enough for detection. Furthermore the reactor was not leak-free. Methanol may be produced in small amounts and hence may be difficult to detect. It is difficult to make the reactor leak-free due to cracks on the membrane support. Several attempts were made but the membrane support tended to break when pressure was applied in order to seal the membrane into the reactor to make it leak-free.

CHAPTER 5 Conclusions

The membrane supports were modified with silica from various sources followed by silanization. Thereafter active metal species were introduced on the surface of silica modified support.

Deposition of silica, from various sources, on the membrane support was successful since there was a mass increase of the membrane support upon silica modification. An increase in the BET surface area was also observed for both silicas (fumed and TEOS). This was confirmed by the presence of silanol groups on silica modified membranes that allowed the interaction of the adsorbents with the surface of the membrane support. As seen from the cracks visible by SEM results modification with fumed silica did not give good results. The fumed silica sol used during preparation seemed to be too concentrated thus excess amounts of silica deposited on the support membrane brought about the loss of silica from membrane surfaces during the deposition of the active centre. TEOS was observed to be the best introduction method of silica on the membrane support. Large surface areas were obtained for the TEOS sample (five times more than the blank membrane support) and it also retained its mesoporosity.

Silanization of the silica surface with CDMS and the APTS was necessary for the introduction of the thermally stable Si-O-Si bond. Introduction of these silanes reduced the pore volume of the catalysts after deposition of the active centre as shown by the porosity results. The morphology of the silica surface changed completely after silanization and the change was homogeneous on the membrane support surface. When comparing the mass increase of the unsupported catalysts and the supported catalysts a similar trend was observed. For the platinum-based catalyst a negative mass increase was obtained and this was accounted by the type of silica source used during catalyst preparation. In the case of the hemin-based catalyst there was a small difference in mass increase while silver deposition was higher on the unsupported than on supported silver-based catalyst since there was a large surface area for the unsupported catalyst than the supported catalysts.

The silver-based catalysts decomposed at a higher temperature than the platinum- and hemin-based catalysts thus were more stable and less prone to thermal degradation. The unsupported and supported hemin-based catalysts prepared using Aerosil, TEOS and fumed silica consumed more oxygen between temperatures of 94 to 112 °C during temperature programmed oxidation. This shows that the hemin-based catalysts were easily oxidised. The amount of the oxygen consumed is related to the amount of reducible species. Thus the larger the amount of reducible species the more active oxygen will be and therefore activate methane to form desired products (methanol and formaldehyde). Hence the hemin-based catalyst is a potential catalyst to increase the yield of methanol with high selectivity.

The catalytic device for the oxidation of methane to methanol and formaldehyde under mild conditions was designed and constructed for tubular ceramic membrane catalysts. The catalytic activity of the synthesised membrane catalysts was performed at temperatures between 30 and 90°C and atmospheric pressure. Methane and air or pure oxygen were introduced into the catalytic reactor as a mixture. Methane/oxygen mixture was fed into the external volume of the reactor, passed through the ceramic membrane catalyst and then exited through the internal reactor volume. The synthesised supported catalysts were active for the production of methanol and formaldehyde.

In the future, the study will be directed at improving the yield of methanol and formaldehyde as well as the selectivity towards methanol. These can be achieved by improving the catalysts for methane oxidation under mild conditions. The conditions for the synthesis of the catalysts need to be optimised. Once the catalysts activate methane to produce high yields of methanol in a catalytic device already constructed then the conditions for the partial oxidation of methane to methanol will be optimised. The catalytic device will be up-scaled to the pilot plant.

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Appendix A

1. Actual % of Ag on the support

$$\%\text{ Ag} = \frac{\text{mass of Ag coated membranes - mass of CDMS modified}}{\text{mass of Ag coated membranes (final mass)}} \text{ X } 100$$

2. Actual % of Pt on the support

$$\%\text{ Pt in the membrane} = \frac{\text{mass Pt coated membranes - mass CDMS modified membrane}}{\text{mass Pt coated membranes (final mass)}} \text{ X } 100$$

3. Actual % of hemin on the support

$$\%\text{ hemin in the membrane} = \frac{\text{mass hemin coated membranes - mass APTS modified membrane}}{\text{mass hemin coated membranes (final mass)}} \text{ X } 100$$

4. Potentiometric titration calculations

- Acidic samples i.e.[Si-OH] and [Al-OH]

$$\text{Concentration of } H^{+} \text{ in the solution} = \frac{[(10^{-pH})\text{solution} - (10^{-pH})\text{water}]V}{1000m}$$

mol/g

- Basic samples i.e. aminopropyl group

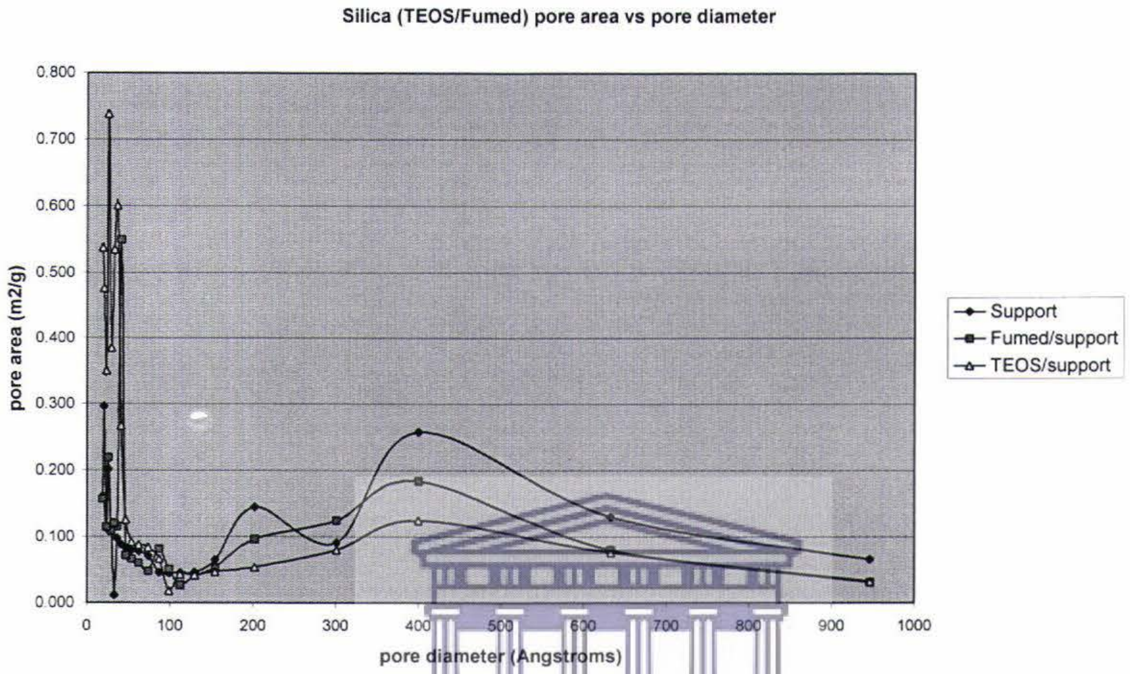
$$\text{Concentration of } HO^{-} \text{ in the solution} = \frac{[(10^{-pOH})\text{solution} - (10^{-pOH})\text{water}]V}{1000m}$$

where V is the final volume of the solution
and m is the mass of the weighed sample

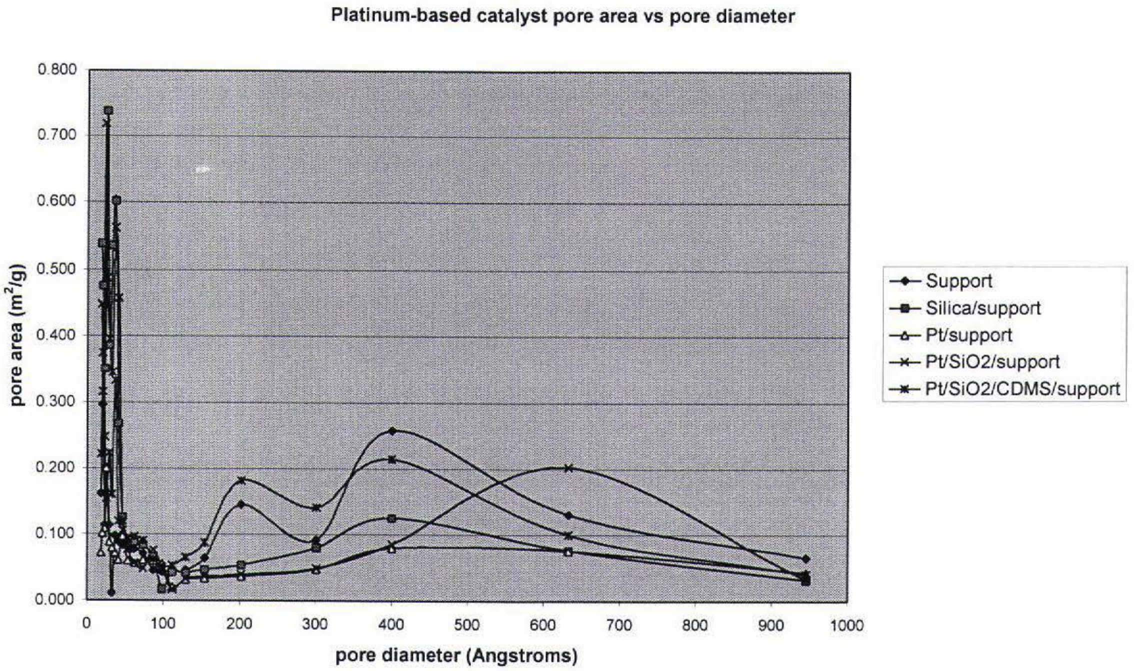
Appendix B

B.1 N_2 Adsorption

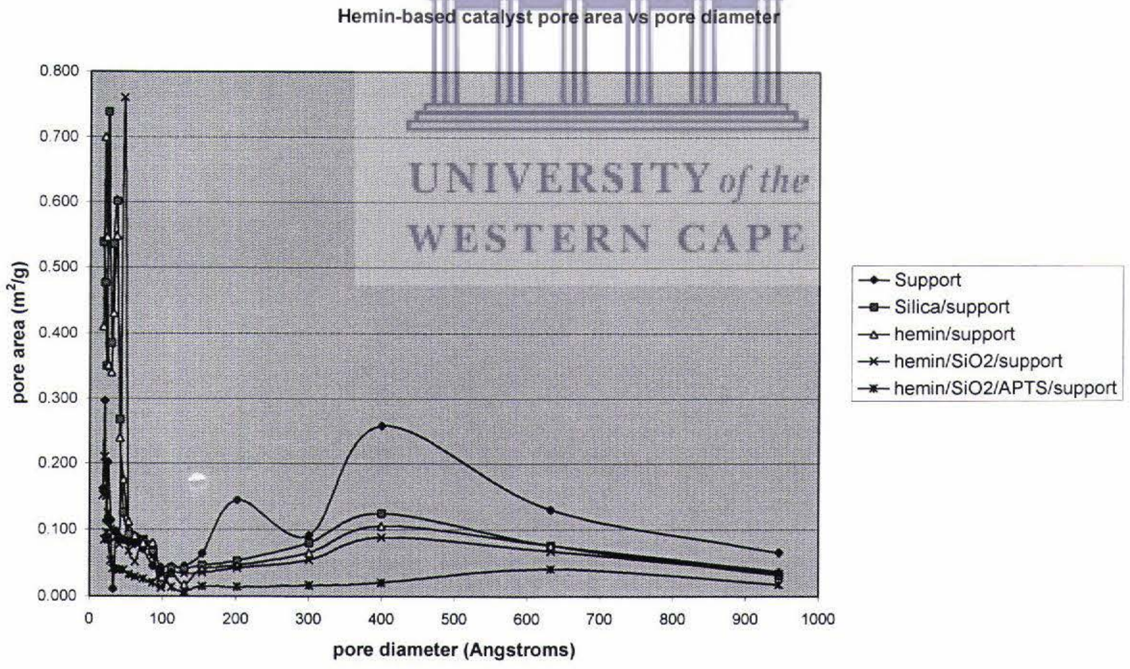
1. Fig. Pore size distributions of silica made from TEOS and Fumed silica, based on the pore area ($f_A(r_p)$)



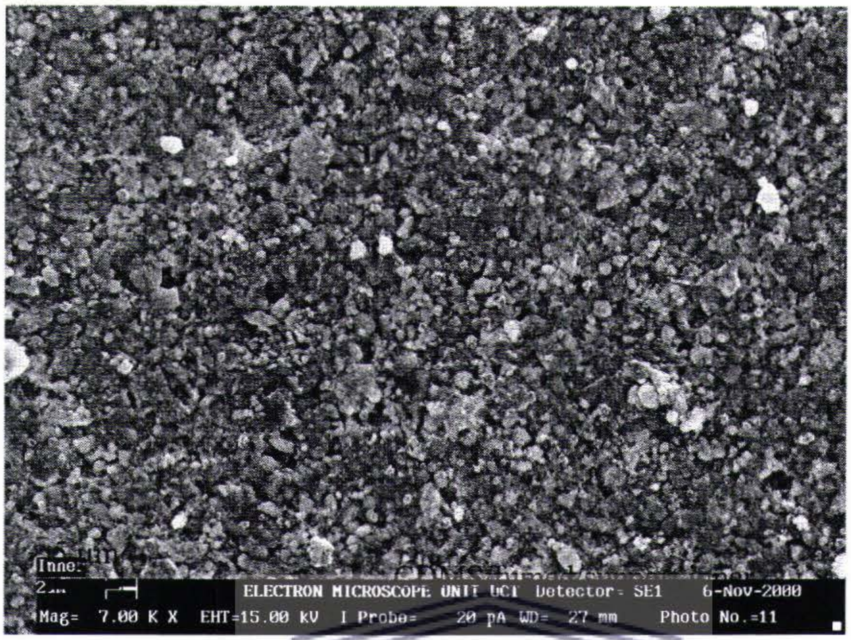
2. Fig Pore size distributions of platinum-based catalysts on a support based on the pore area ($f_A(r_p)$)



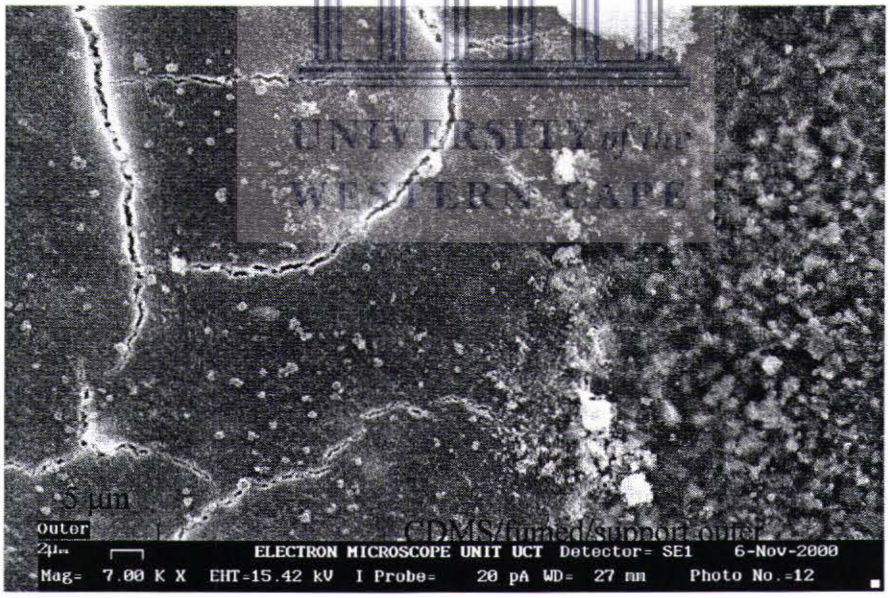
3. Fig Pore size distributions of hemin-based catalysts on a support based on the pore area ($f_A(r_p)$)



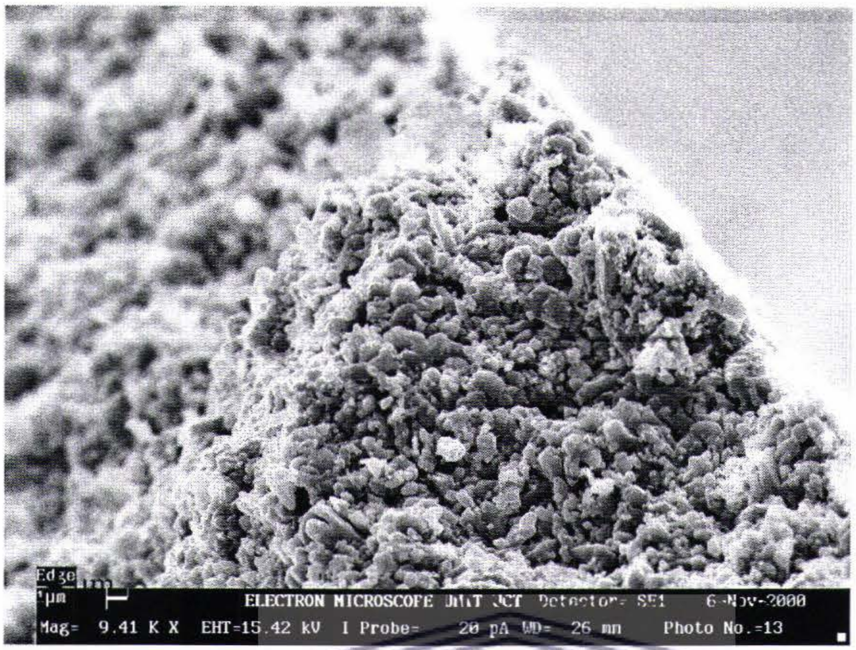
SEM image of CDMS/fumed/support on the inner surface



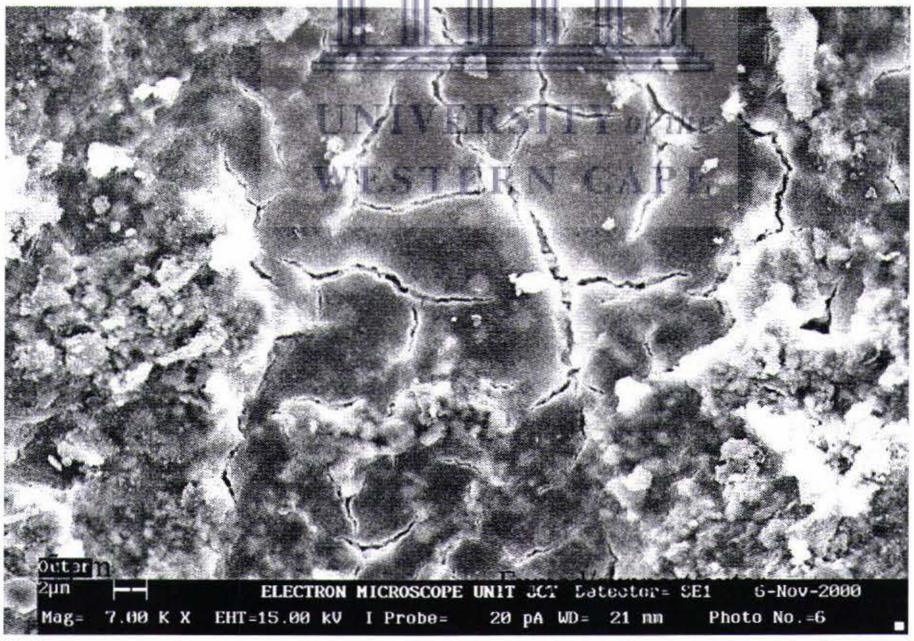
SEM image of CDMS/fumed/support on the outer surface



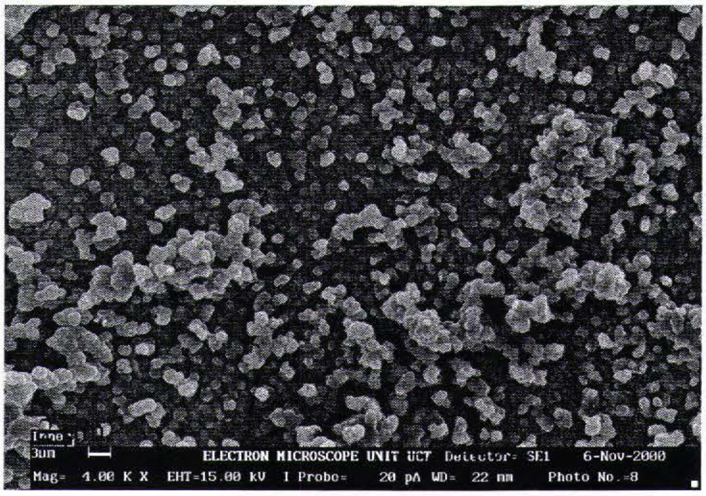
SEM image of CDMS/fumed/support on the edge



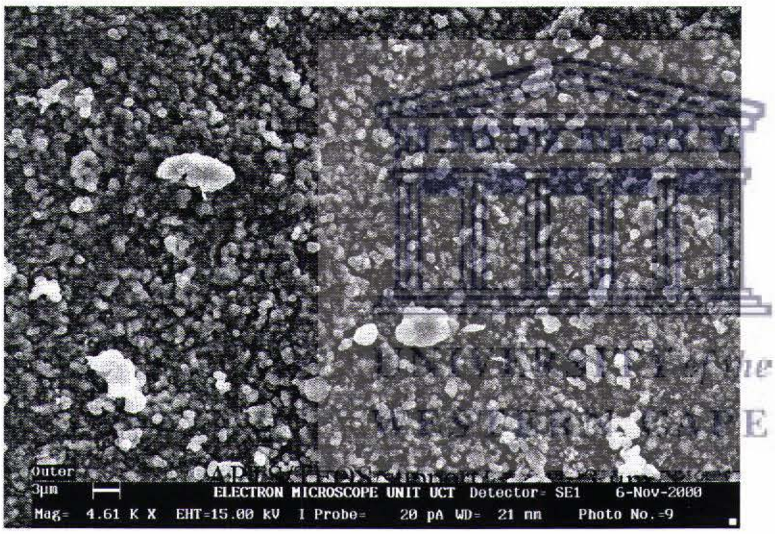
SEM image of silica modified membrane support on the outer surface



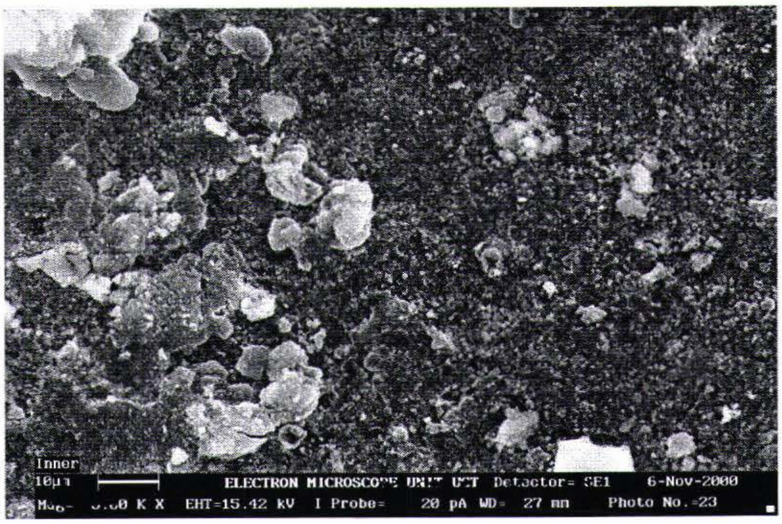
SEM image of APTS/TEOS/support on the inner surface



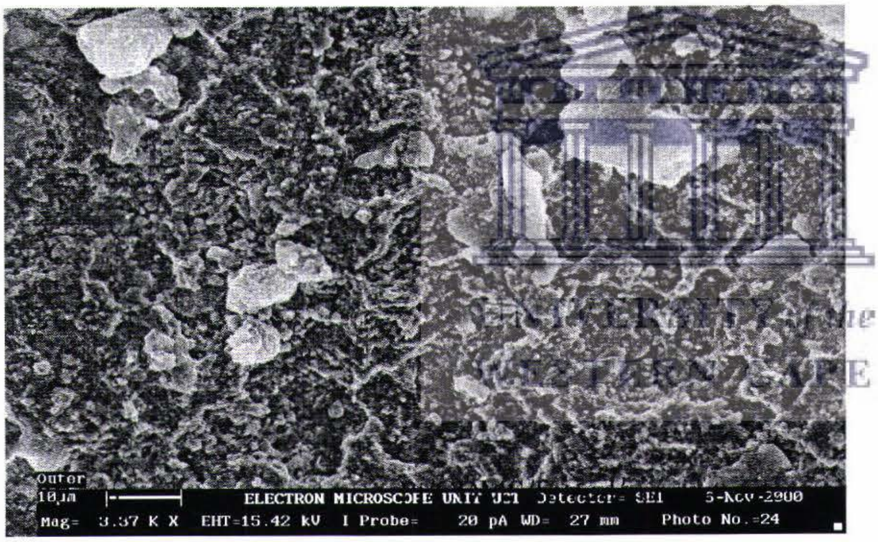
SEM image of APTES/TEOS/support on the outer surface



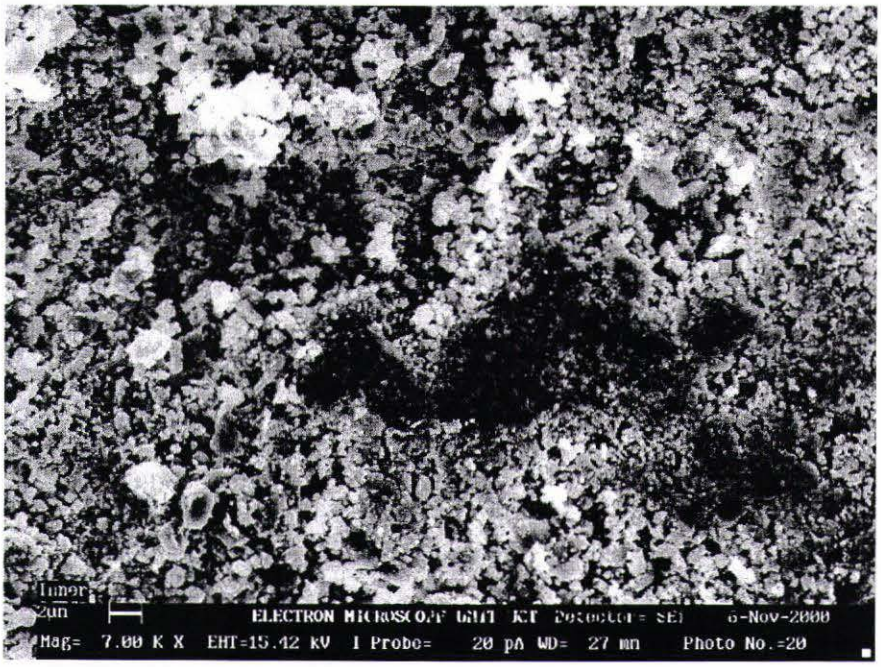
SEM image of Pt/CDMS/fumed/support on the inner surface



SEM image of Pt/CDMS/fumed/support on the outer surface

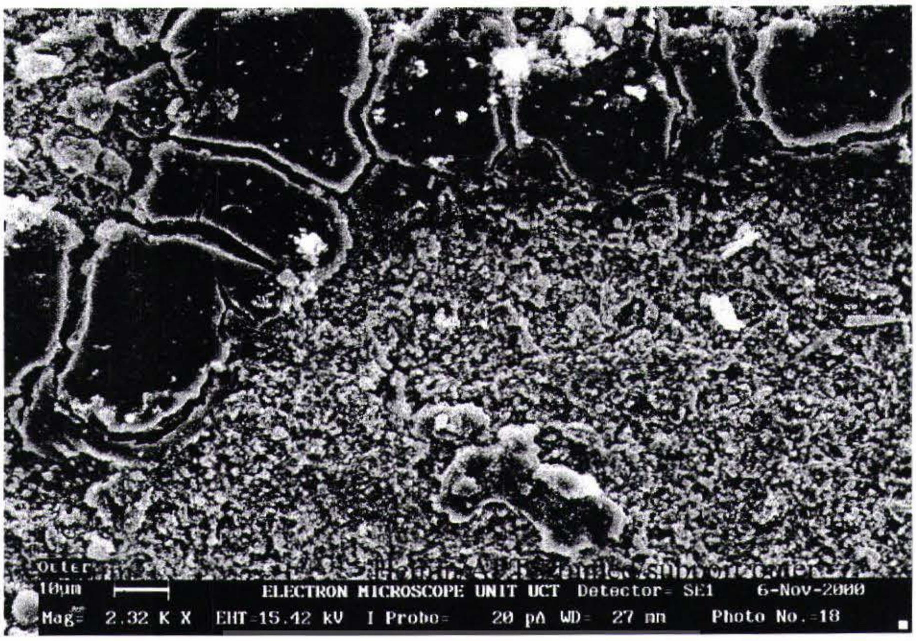


SEM image of Pt/CDMS/TEOS/support on the inner surface

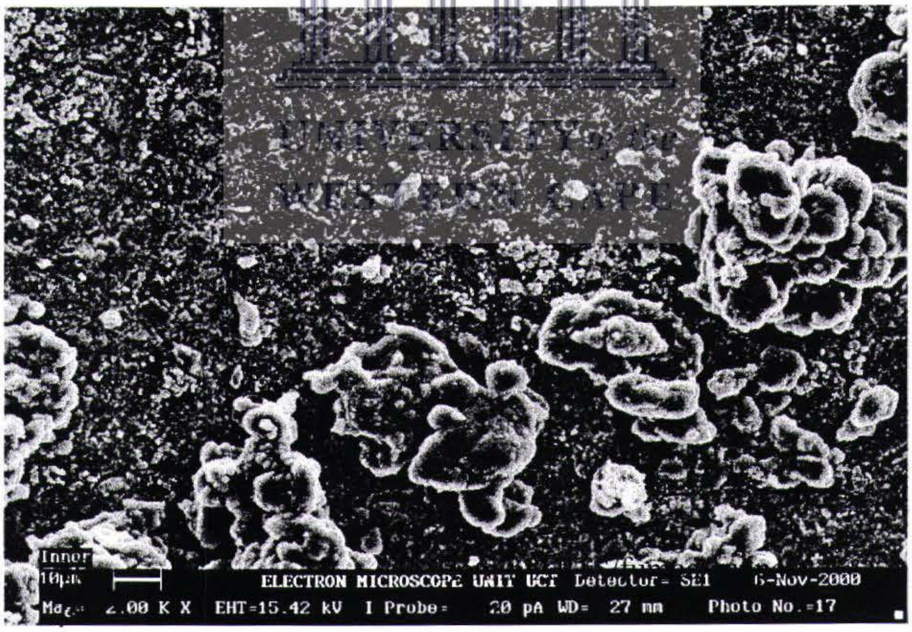


SEM image of Pt/CDMS/TEOS/support on the outer surface

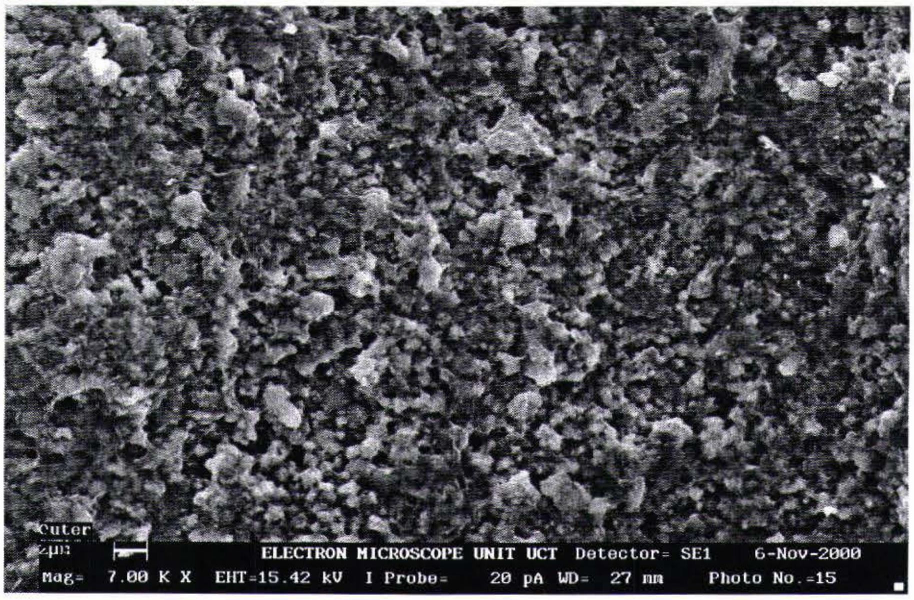
SEM image of hemin/APTS/fumed/support on the outer surface



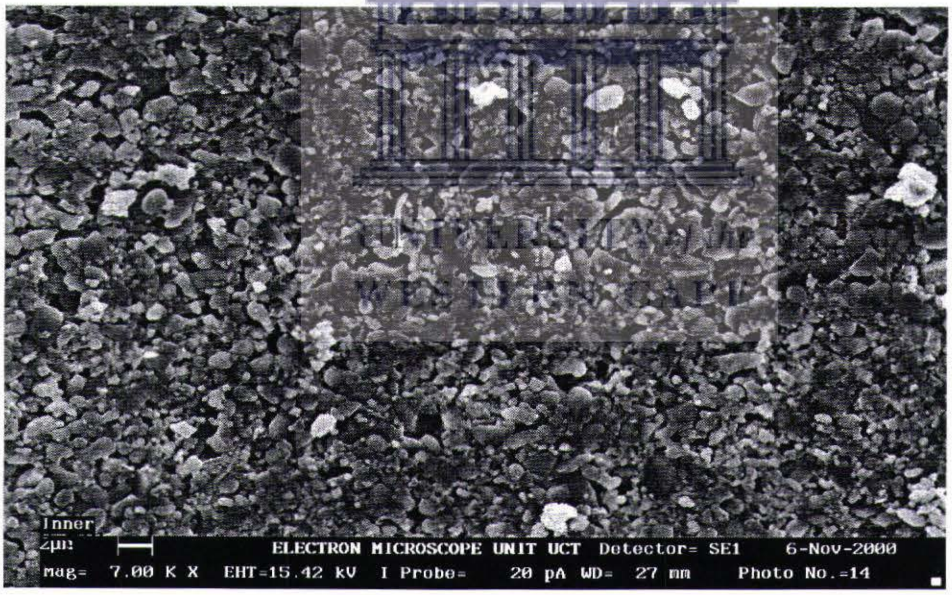
SEM image of hemin/APTS/fumed/support on the inner surface



SEM image of hemin/APTS/TEOS/support on the outer surface



SEM image of hemin/APTS/TEOS/support on the inner surface



Hemin/APTS/TEOS/support inner