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Use of Meso-Scale Catalysts for Bulk-Scale Processing of Natural Gas – A Case Study of Steam Reforming of Methane

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1. Introduction

1.1 Catalytic steam reforming

Catalytic steam reforming of hydrocarbons, alcohols and light oil fractions involves the reaction of steam with methane, ethane, natural gas, LPG, naphtha, gasoline, alcohols like methanol, ethanol, and propanol, over catalysts at elevated temperatures (473 to 1173 K) and pressures (1 to 30 atm) to produce a mixture of hydrogen, carbon monoxide and carbon dioxide (Rostrup−Neilsen, 1984) . The mixture of hydrogen and carbon monoxide is known commonly as syngas.

The technology has matured over the last 55 years. However the endothermic nature of the reactions makes the process energy–intensive. Coke formation which results in catalyst deactivation is also another major concern. Work is still in progress to use milder operating parameters, increase reactor through–put and minimise coke formation increasing catalyst life and thus reduce reformer down time.

It is reported that 90% hydrogen generated globally, is produced by the steam reforming of natural gas and light oil fractions. The major reason for this is the commercial viability of such plants by which hydrogen can be produced at $2.11/kg of H_2 (Momirlan & Veziroglu 2002, Harayanto et al. 2005). This is by far the most efficient process available in comparison to other processes like, carbon dioxide reforming, coal gasification, pyrolysis, water electrolysis and photobiochemical techniques.

1.2 Uses of hydrogen

Hydrogen has been termed as the "energy carrier of the future" (Das et al. 2001, Momirlan & Veziroglu 2002). It has the highest energy content of 120.7 kJ/gm (Harayanto et al. 2005). It burns producing no polluting emissions like SOx, NOx, CO, VOC etc. However it is available in nature only in the bound form. This makes it necessary to process the primary fuel to obtain H_2 and then use it in energy producing devices such as fuel cells or as fertiliser

feedstock. Industry generates some 48 million metric tons of hydrogen globally each year from fossil fuels (Navarro et al., 2007). Nearly 50% of this hydrogen goes into making ammonia which is used in the manufacture of bulk chemicals like urea, phosphates and other fertilisers. Refineries use the second largest amount of hydrogen for chemical processes such as removing sulfur from gasoline (hydro–desulphurisation), converting heavy hydrocarbons into gasoline or diesel fuel, hydro–alkylation, hydro–cracking etc. Apart from these, hydrogen is used in Fischer–Tropsch synthesis, hydrogenation of oils and fats, pharmaceutical manufacture, cryogenic applications, in nuclear reactors, radio isotopes, mineral ore processing, reduction processes, oil processing.

1.3 Production of hydrogen

Bulk manufacturing of hydrogen is done in steam reforming units which use packed bed tubular reactors in which the catalyst (in the form of small pellets, spheres or tablets) is randomly dumped to obtain the desired products (syngas) at elevated temperature and pressure. Steam reforming system for hydrogen production is composed of a steam reformer, a shift converter, and a hydrogen purifier based on the pressure swing adsorption (PSA) or membrane separation unit. A mixture of natural gas and steam is introduced into a catalyst bed in the steam reformer, where the steam reforming reaction proceeds on nickel−based catalyst at 973 to 1073 K The reformed gas is supplied to a shift converter, where carbon monoxide is converted into carbon dioxide to produce more hydrogen by the shift reaction. The reformed gas is passed to PSA unit to separate hydrogen.

A typical steam reformer unit consists of a reformer block containing 40 to 400 tubes of height 6 to 12 m having an inner diameter of 0.7 to 0.16 m and a thickness of 0.01 to 0.02 m (Rostrup−Neilsen, 1984). The tubes are generally made of high alloy nickel chromium steel. As the process is endothermic, the required heat needs to be supplied to the reformer unit. The tubes can be heated externally or internally. In external heating, part of the feed is combusted outside the reformer tube to reach the desired reaction temperature. In internal heating part of the feed is combusted inside the tube of the reformer. This latter process is known as partial oxidation or autothermal reforming depending on the energy supplied to the process.

1.4 Catalysts used

Conventional catalysts are available in the form of cylindrical pellets, tablets and spheres and are simply dumped in the reformer tube. This is called as a fixed bed or packed bed reformer. The catalyst pellets are randomly placed in the reformer tube and do not contribute to a defined structure to the bed. There is no structure to the bed as a whole and it can be imagined as a bed containing a large number of convoluted or tortuous paths through which the feed gas flows. As the gas flows through the path, there is an increased pressure drop (relative to the use of structured catalysts). The quantity of catalyst and its composition is determined on the basis of the feed quantity and quality or composition. The role of the catalyst is to achieve maximum possible conversion of the feed to syngas, a constant pressure drop and to have sufficient mechanical and thermal strength to provide a long process cycle (Rostrup−Neilsen, 1984). Many Indian fertiliser plants use supported nickel catalysts. The support is generally silica, alumina, and/or magnesia. The properties of

the catalyst are further modified by addition of components like, calcium oxide, aluminium, molybdenum, special carbides, zirconia, ceria, other alkali earth metals like potassium, etc. to make the catalyst coke resistant, and to increase its mechanical and thermal strength. Effect of promoters such as Cu, La, Mo, Ca, Ce, Y, K, Cr, Mg, Mn, Sn, V, Rh, Pd, and their combinations have been used for improving the stability of Ni catalysts supported on alumina for steam methane reforming. The use of platinum, rhodium, and palladium, along with nickel has also been reported (Harayanto et al. 2005). However, industrial catalysts are usually nickel based catalysts. The most commonly used catalysts are nickel−alumina, nickel−alumina−magnesia, nickel−magnesia, etc. The percentage of nickel varies from as low as 3 % to as high as 52% by weight. Nickel possesses hydrogenation activity but limited water gas shift activity. It is a low-cost but effective catalyst for cleavage of $O-H$, $-CH_2-$, $-C-C-$ and $-CH_3$ bonds. It is these properties that make nickel a favourable choice as a steam reforming catalyst. However, nickel alone cannot be used as a steam reforming catalyst due to its limited water gas shift activity. In order to exploit this secondary reaction, nickel or other metal catalysts are coupled (or supported on) with another metal oxide such as alumina or magnesia.

1.5 Micro and meso−scale reactors

Micro− and meso–scale reactors are a rapidly emerging technology field (Lowe, 2000, Hessel et al., 2005, Holladay et al., 2004). They differ in type / configuration and manufacturing procedures. The most widely used varieties include substrates such as silicon or silicon carbide on which channels are "etched" using well established lithography or deep reactive ion etching (DRIE) techniques. They consist of a stack of plates, onto which channels are introduced. The channels, which have width ranging from 50 to 500 μm, and depths up to 2000 μm, can be coated with active catalytic materials. This offers an advantage over traditional fixed bed reactors as higher transport rates and lower pressure drop can be achieved in a reduced volume. The large surface to volume ratio of these structures leads to effective heat dissipation making these systems suitable for highly exothermic / endothermic reactions with short contact times. There are very few papers that report the use of such micro and meso–scale reformers for the production of hydrogen from steam reforming of methane and ethanol (Pattekar & Kothare, 2004, Lowe, 2000, Hessel et al., 2005, Holladay et al., 2004).

1.6 Concept of the meso−scale, channel reactor

A novel way of developing micro or meso−scaled reactors which can be readily integrated in existing steam reformer plants for bulk manufacture of hydrogen is the use of wash−coated monoliths which can be fitted inside reformer tubes. The size of the monolith and the base material (ceramic or metal) can be selected as per the process requirements. The basic support monolith can be purchased from a number of suppliers like Corning, Degussa, and Emitec in the market and subsequently the wall coating can be modified to suit the feed stock. Monoliths or honeycomb reactors have been used as a support for catalytic converters for treatment of automobile exhaust gases and as filters for processing exhaust gas streams from industries. Monolith reactors act as multifunctional reactor systems having the advantages of low pressure, efficient contact of the reactants with (most

frequently) solid catalyst and hence avoiding the problems related to partial wetting of the catalyst with liquid/gas phase; the possible choice of combining reaction and separation processes; the controlled loading of reactants, product removal, etc. Thus in monolith reactors one can combine the advantages of conventional multiphase reactors such as fixed bed, slurry and trickle bed reactors (Vergunst, 1999). This increases process efficiency and its cost effectiveness. One disadvantage of monolith reactors is the poor distribution of liquid and/or gas along the reactor's cross-section. This makes their use difficult, especially under higher flow rates.

Ceramic monoliths are usually made of cordierite which has a composition of $2MgO.5SiO_2.2Al_2O_3$. There are hardly any references (in literature) to the use of meso−scale, cordierite, monolith channels for steam reforming of methane (heat provided external to the reformer tube). It was therefore decided to use ceramic based (cordierite) monoliths having meso−scale rectangular channels as the base material for the monolithic catalyst for steam reforming of methane.

1.7 Objectives of this work

The focus of this work was on the development of novel channel monolithic reactors with meso-scale dimensions which can be coated with suitable catalytic metal oxide and used for steam reforming of methane. The objective of this article is to present the performance characteristics of such a novel reactor and to identify possible strategies for use of novel small dimension reactors for the same process. These meso–scale structures can withstand extreme pressure and temperature conditions. These structures provide the advantages of meso−scale reactors such as high surface area, low pressure drop and can be used in bulk scale manufacture of syngas and hence hydrogen. This work includes a comparison of the performance of these developed reactors with commercial catalysts (used in fixed bed reactors).

The catalyst block (named as PS−CAT) consists of a cordierite meso−scale, channeled, monolithic structure which is wash coated (a specified number of times to achieve the desired catalyst loading) with a nickel−based salt solution (2M concentration), dried, calcined, and reduced with hydrogen. This procedure of wash coating the cordierite substrate and the subsequent processing (drying and calcining of the same) is critical for the durability and quality of the catalyst (Mathure, 2008, Mathure et al., 2007a, Vergunst, 1999). The structured catalyst consists of a number of thin−walled channels which exactly fit the reformer tube inner diameter. A number of such blocks can be stacked one above the other to fill the entire length of the reformer tube. Also, the diameter of such blocks can be as per the process requirements. In this study, separate experiments were conducted with 4 channels (figure 1) as well as for 49 channels, each part of a larger monolith consisting of 100 cpsi (cells per square inch). As the reactor has straight structured channels, the resulting pressure drop is much less than that for a tubular packed bed of catalyst. This reactor concept can be used in the existing reformer infrastructure without any major change in process equipment to significantly increase hydrocarbon feed throughput. With higher throughput, the same steam reformer unit can produce larger quantities of syngas. The main advantages are increased throughput, simplicity of the arrangement, and minimum plant modification. Figure 1a shows a 4−channel PS−CAT. Figure 1b shows a schematic of the a 49−channel PS−CAT

Fig. 1a. PS−CAT (4−channel): A meso−scale, channel, structured catalyst.

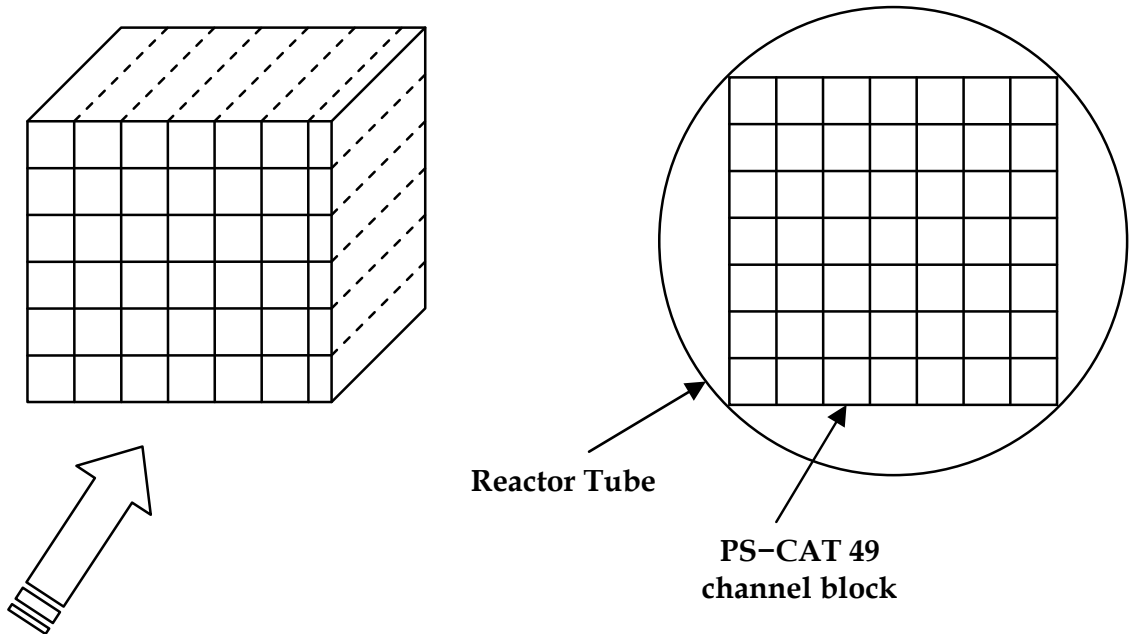**Reactor Tube**

**PS−CAT 49
channel block**

Fig. 1b. Typical schematic of a meso−scale, channeled monolith. The figure on right shows
the block placed in a reactor tube.

2. Literature review

The main focus of this section is review work on the use of monolithic, channel reactors for
steam reforming of methane for production of hydrogen. Tomasic and Jovic, 2006 have
published a state of the art review on the use of monolithic catalysts. According to the
authors development of monolithic catalysts and/or reactors has been one of major
achievements in the field of heterogeneous catalysis and chemical reaction engineering of
the recent years. The work highlights the advantages of monolithic catalysts and/or reactors
with respect to the conventional ones, with particular focus on the integral approach to the
catalyst and reactor design. The paper is detailed and gives basic definitions and
classification of monolithic catalysts, including basic features of the monoliths and factors
that have proceeded to the development and application of the monolith structures. The

paper also discusses the preparation of monolithic catalysts and their commercial application with particular emphasis on the less known applications, and those which are still under development. These applications include the use of monolithic catalysts for Fischer−Tropsch synthesis, selective hydrogenation, oxidation, catalytic fuel combustion units, and gas cleaning devices for industries and automobiles. The authors have concluded that futher research should be directed towards the development of new constructional designs by changing geometries to resolve the distribution problems at the entry of monolithic structures.

Hessel et al., 2005 have reviewed work on micro−structured devices (both etched channels and monoliths) developed for reforming of methane and other hydrocarbons. They have reported a number of devices which can have been used mainly for partial oxidation or autothermal reforming of methane, propane, isooctane and gasoline.

Meille, 2006 has discussed the methods used to deposit a catalyst on structured surfaces. The review outlines both physical methods such as physical vapour deposition and chemical methods (sol–gel, chemical vapour deposition, direct synthesis, etc.) The coating of catalysts based on oxide, zeolite or carbon support is detailed on various surfaces such as silicon or steel microstructured reactors, cordierite monoliths or foams, fibres, tubes, etc.

Zhou et al., 2006 have investigated alumina supported Pt group metal monolithic catalysts for selective oxidation of CO in hydrogen−rich methanol reforming gas for proton exchange membrane fuel cell (PEMFC) applications. The results show that Pt/Al_2O_3 was the most promising candidate to selectively oxidize CO from an amount of about 1 vol% to less than 100 ppm. They have investigated the effect of the O_2 to CO feed ratio, the feed concentration of CO, the presence of H_2O and/or CO_2, and the space velocity on the activity, selectivity and stability of Pt/Al_2O_3 monolithic catalysts. The Pt/Al_2O_3 catalyst was scaled up and applied in 5 kW hydrogen producing systems based on methanol steam reforming and autothermal reforming.

Giroux et al., 2005 have published a review paper for the technical and market potential of hydrogen for use in varied applications namely, stationary fuel cell power generation units, on-site generators of hydrogen for industrial uses, and hydrogen fueling stations for fuel powered automobiles. They have proposed the use of monolithic structures as alternatives to particulate catalysts for the reforming of hydrocarbons for hydrogen generation. They have further proposed that new process designs for fuel processing can take advantage of the successful experience of environmental catalysis in automotive and stationary applications using monolithic catalysts and other substrates such as heat exchangers.

Bobrova et al., 2005 have studied syngas formation by selective catalytic oxidation of liquid hydrocarbons in a short contact time adiabatic reactor. Their research involved pilot plant scale exploration of syngas formation from liquid fuels like isooctane and gasoline by selective catalytic oxidation at short contact times at nearly adiabatic reactor conditions. Monolithic catalysts with different supports (micro−channel ceramics and metallic honeycomb structure) have been used in the experiments. Their results demonstrated that over the range of the operational parameter O_2/C = 0.50–0.53 required for syngas generation, equilibrium syngas was produced over the catalysts employed, thus proving the evidence of their high activity and selectivity.

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Qia et al., 2005 have studied the performance of La–Ce–Ni–O monolithic perovskite catalysts for gasoline autothermal reforming system. Autothermal reforming of gasoline or its surrogates, n−octane with or without thiophene additive, was carried out on either bulk perovskite pellet or monolithic perovskite catalyst. During the 220−h long-term test, the pellet catalyst exhibited high thermal stability and activity with hydrogen yield approaching to the theoretical maximum value and only minor amount of CH_4 slipping through. It possessed fairly good sulfur tolerance (almost immune to 5 ppmw sulfur) although it could still be seriously poisoned when subjected to high concentration of sulfur. Their raw cordierite monolith could be an effective catalyst for autothermal reforming of gasoline, exhibiting superior performance to the catalyst of 0.3 weight % $Rh/CeO_2–ZrO_2/$cordierite at a temperature range of 923 to 1073 K.

Pasel et al., 2004 have studied different water−gas−shift catalysts for combined autothermal reforming with water−gas−shift (WGS) reaction. The autothermal reforming of liquid hydrocarbons using different conditions have been studied. In the first step, the dry reformate from autothermal reforming and a separate stream of steam was used to conduct the WGS reaction. Strong differences concerning the catalytic activity between the three investigated commercial monolithic catalysts could be observed. The most active one showed a very promising catalytic behaviour. At a gas hourly space velocity (GHSV) of 12,250 h^{-1}, CO conversion amounted to 85% at 553 K. CO concentration in the reformate reduced from 6.1 to about 0.9 vol. %. In another step, unconverted water from autothermal reforming was fed to the reactor for the WGS reaction together with additional components of the reformate. No catalyst deactivation was observed within almost 90 h under autothermal reforming conditions generating only traces of carbon dissolved in the water.

Lindstrom et al., 2003 have carried out an experimental investigation on hydrogen generation from methanol using monolithic catalysts. They have evaluated the activity and carbon dioxide selectivity for the reforming of methanol over various binary copper−based materials, Cu/Cr, Cu/Zn and Cu/Zr. The methanol reforming was performed using steam reforming and combined reforming (a combination of steam reforming and partial oxidation). This combined reforming process was carried out at two modes of operation: near autothermal and at slightly exothermal conditions. Their results show that the choice of catalytic material has a great influence on the methanol conversion and carbon dioxide selectivity of the reforming reaction. The zinc−containing catalyst showed the highest activity for the steam reforming process, whereas the copper/chromium catalyst had the highest activity for the combined reforming process. The copper/zirconium catalyst had the highest CO_2 selectivity for all the investigated process alternatives.

Apart from these there are a few patents which refer to the use of ceria–coated zirconia monoliths for catalytic partial oxidation process of hydrocarbons for syngas production and the use of platinum and palladium monoliths for autothermal reforming of hydrocarbons (Jiang et al, 2006, Hwang et al., 1985).

Vergunst, 1999 has published a detailed thesis on the preparation aspects of carbon−coated monolithic catalysts and three phase hydrogenation of cinnamaldehyde using the same [3]. The author has covered preparation of monolithic catalysts, testing of monolithic catalysts in the (selective) hydrogenation of benzaldehyde, cinnamaldehyde, methylstyrene, benzene, and γ−butyrolactone, testing of monolithic catalysts in solid acid catalyzed reactions

(acylation and esterification) and in the selective oxidation of cyclohexanol into adipic acid, development of internally finned monolithic structures, hydrodynamics, and scale up. The work is extremely important for any work related to monolithic catalysts. However the manufacture of these catalysts and their subsequent application is totally different from the current application (steam reforming) being discussed.

As can be observed from the above work, wash−coated monoliths with meso or micro−scaled channel sizes are a promising substitute for conventional large and small scale fixed bed reactors. Once the coating procedure and coating material is finalized, these monoliths provide cost-effective reactor geometries to retrofit existing reformer units. To the best of our knowledge, there are hardly any references (in literature) to the use of meso−scale, ceramic, monolith channels for steam reforming of methane (heat provided external to the reformer tube). It was therefore decided to use ceramic based (cordierite) monoliths having meso−scale rectangular channels as the base material for the monolithic catalyst for steam reforming of methane. As nickel possesses hydrogenation activity and is a low-cost but effective catalyst for cleavage of $O-H$, $-CH_2-$, $-C-C-$ and $-CH_3$ bonds, it was decided to exploit these properties and use nickel nitrate solution for the coating of the monoliths.

3. Development of the monolith structures

3.1 Coating of the monolith structures

The catalyst block (named as PS-CAT) developed in the course of our work consisted of a cordierite substrate with a square-channel, monolithic structure which was wash-coated with a nickel-based salt solution (2M concentration), dried at 393 K, calcined at 673 K, and reduced with hydrogen (Mathure, 2008). The catalyst block is shown in figure 1. The structured catalyst consisted of a number of thin-walled channels which exactly fitted the experimental reformer tube inner diameter (Mathure et al. 2007b). The average wall thickness was found to be about 270 μm. The channel dimensions were determined to be 1500 μm × 1500 μm (hence the term meso-scale). In this study, experiments were conducted with a block having 4 channels cut out from a larger monolith consisting of 100 cpsi (channels per square inch). Figure 1 shows a 4-channel PS-CAT. The performance of the developed catalyst was tested extensively using a multi-feed, multi-scale, fully instrumented experimental rig fabricated by M/s. Texol Engineering Private Limited, Pune, Maharashtra, India & M/s Dampf Kolben , Pune, India. The details of experimental rig and procedure have been reported elsewhere (Mathure et al., 2007b, Mathure, 2008). Figure 2 from shows the actual photograph of the experimental rig and its components such as the mass flow meter, HPLC pumps, reactors and Reactor furnace assembly. Figure 3 shows the schematic arrangement of the experimental rig. PS-CAT contained a nickel oxide loading of around 8.5% (weight% of the coated block). The elemental nickel loading was around 6.7% (weight% of the coated block) as determined by EDS –X-ray analysis.

Each block was weighed before being dipped into the coating solution, and after the calcination, to find out the amount of catalyst (nickel oxide) loading on the block. This weight was taken as W for calculation of W/F_{CH4} during the steam reforming experiment. The blocks were activated using a hydrogen stream of flow rate 40 N ml/minute in the steam reformer unit just before use in the experiment.
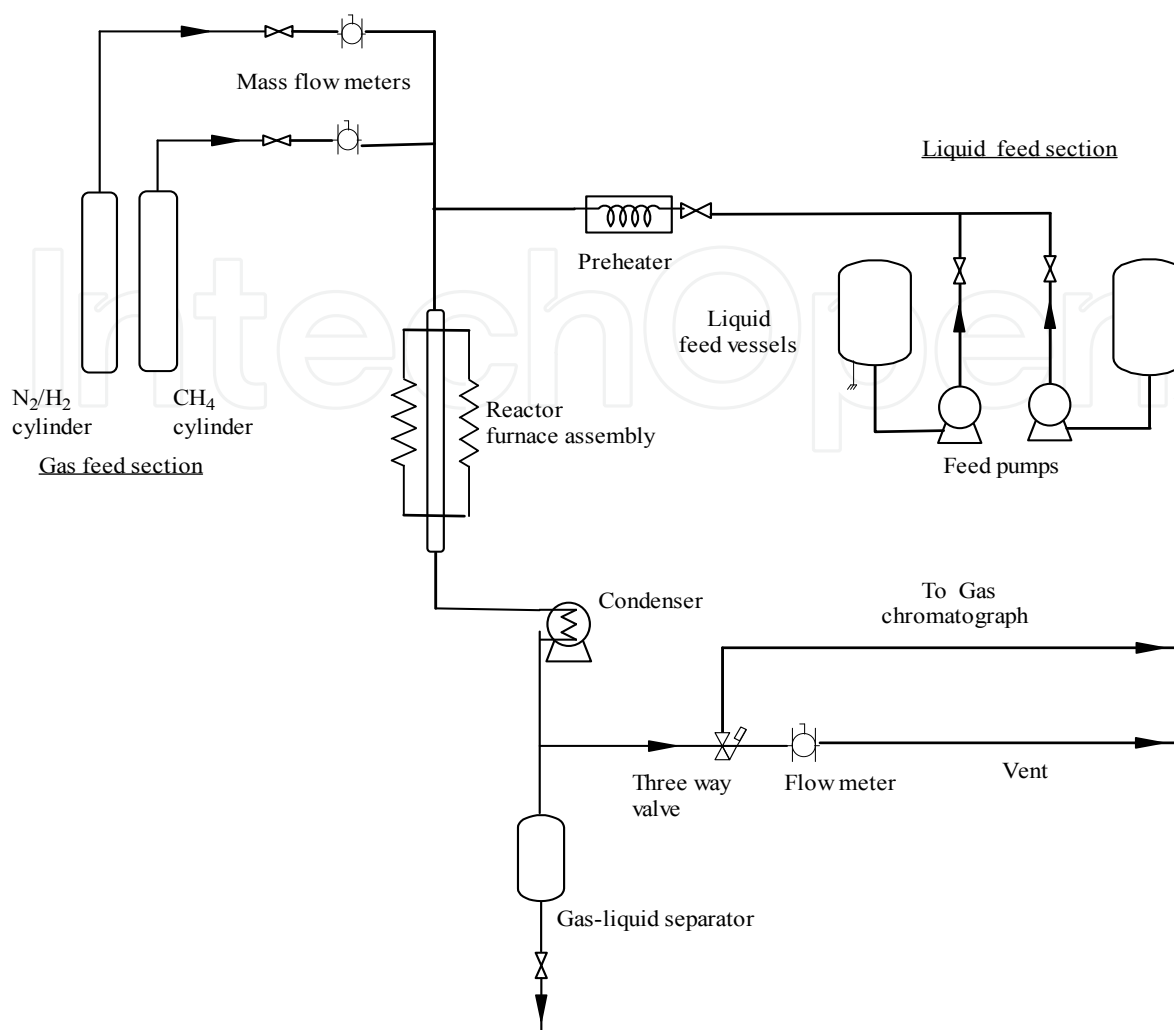
Fig. 2. Experimental rig and its components used for steam reforming of methane.

Fig. 3. Schematic of the experimental rig used for steam reforming of methane and ethanol.

3.2 Characterisation of the structures

The characterisation was done by EDS–X-ray analysis, BET surface area measurement and XRD analysis. A detailed discussion of the characterization can be found the work of Mathure, 2008.

3.2.1 X-ray diffraction study

The crystal phases in the uncoated cordierite substrates and the coated PS–CAT were identified by a X-ray powder diffraction study. XRD spectra were obtained with a Rigaku–Miniflex diffractometer using monochromatic Cu–Kα radiation. The 2θ scanning was performed from 10 to 80° at a rate of 2°/min. Figure 4 shows the XRD patterns for the uncoated cordierite substrate and Figure 5 shows the XRD pattern for the coated PS–CAT. The only active ingredient in the coated catalyst was the nickel oxide species. An observation of both XRD patterns shows that the extra peaks present in Figure 5 are of nickel oxide as verified using JCPDS database. These peaks are not seen in the uncoated raw substrate.

XRD data - Intensity vs 2theta
Uncoated cordierite substrate

Cordierite peaks

Cordierite peaks

Cordierite peak

Cordierite peaks
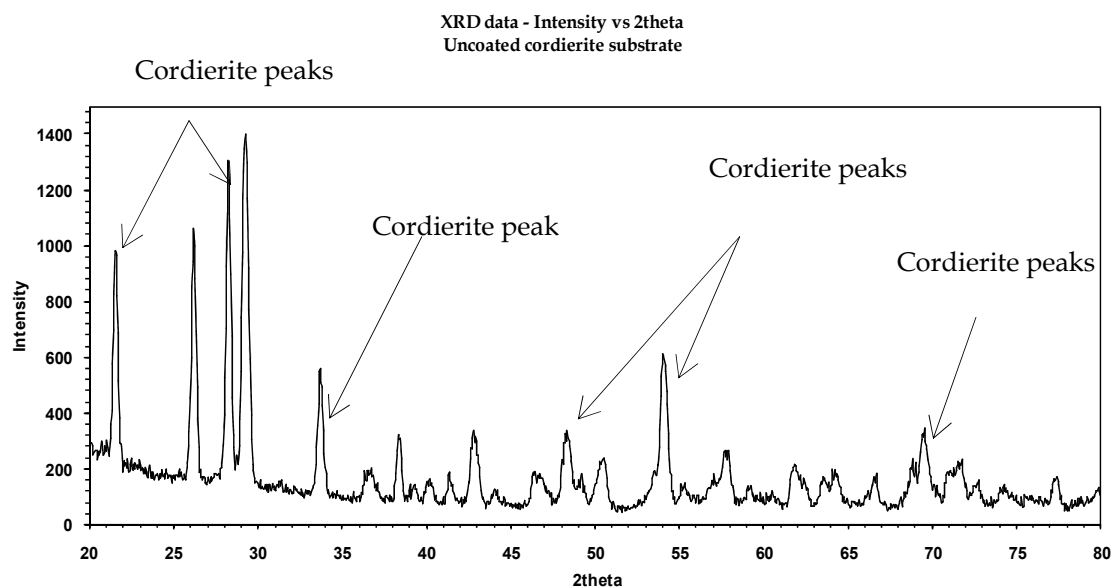
Fig. 4. X-ray diffraction spectra of the raw uncoated cordierite substrate.

XRD Intensity vs 2theta
PS CAT

Cordierite peaks
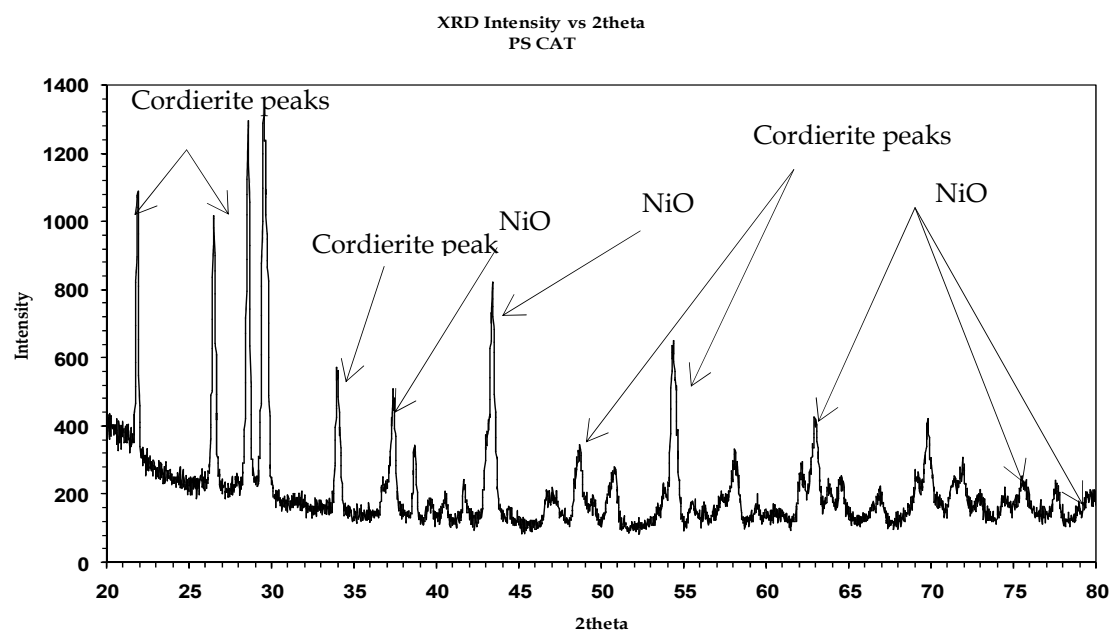
Cordierite peaks

NiO

Cordierite peak

NiO

NiO

Fig. 5. X-ray diffraction spectra of the coated catalyst block PS–CAT.

3.2.2 Energy dispersive spectroscopic X−ray analysis (EDS–X-ray)

The metal loading was estimated by EDS– X–Ray unit (Link ISIS 300, Japan). Nickel oxide which acts as the active ingredient content was found to be 8.5% (weight % of the coated block). The elemental nickel loading was found to be around 6.7% (weight % of the coated block).

3.2.3 BET surface area measurement

The Brunauer–Emmett–Teller (BET) specific surface area was measured using nitrogen as an adsorbent in a Quantachrome make AUTOSORB 1C machine. The samples were degassed for 12 hours at 573 K before analysis. The values obtained were as follows;

Uncoated (raw) cordierite substrate   : 3.14 m²/gm
Coated substrate, PS–CAT   : 1.59 m²/gm
Used (post–experimentation) PS–CAT   : 1.18 m²/gm

The extremely low values have been observed due to the use of cordierite ceramic blocks which have very low specific surface area in the first place. Subsequent and prolonged dip coating further decreases this value. It must be noted here that the blocks were directly coated with the metal salt solution. No binder or support material such as γ–Al_2O_3 sol was used to enhance the surface area.

4. Experimental study

The performance of the developed catalyst was tested extensively using the experimental set up described detail in Mathure, 2008 & Mathure et al., 2007a. The testing was carried out by varying the process parameters such as time–on–stream analysis (100 hours on stream), temperature (673 to 1048 K), space time (W/F_{CH4} = 10 to 55.0 gm–cat min/mol), and the number of channels (4 channels and 49 channels in parallel). However as the number of monoliths available to us were limited, the bulk of the experiments were performed using the 4 channel PS−CAT. Time−on−stream studies were carried out for both the blocks. The length of each block (both 4 channels and 49 channels) was 0.025 m. In case of experiments with the 4 channel PS−CAT, the tubular reactor housing with inner diameter 6 mm was used. Five blocks each having 4 channels were placed end to end within the tubular reactor housing such that the centre of the catalyst bed corresponded to the central heating zone of the furnace. Rest of the tubular reactor housing (both above and below the catalyst blocks) was filled up with inert particles. As 5 blocks were used in series, the total length of the meso−scale channel reactor was 0.125 m. In case of experiments with the 49 channel PS−CAT, the tubular reactor housing with inner diameter 22 mm was used. Two blocks each having 49 channels were placed end to end within the tubular reactor housing such the centre of the catalyst bed corresponded to the central heating zone of the furnace. Rest of the tubular reactor housing (both above and below the catalyst blocks) was filled up with inert particles. As 2 blocks were used in series, the total length of the meso scale channel reactor was 0.05 m. The reactor was mounted in the furnace assembly. Fresh catalyst was used for each experimental run.

The catalyst was activated in a hydrogen flow of 40 N ml/min with a steady increase of temperature. The catalyst was maintained at the desired reaction temperature for two hours. Methane gas (make: BOC, XL grade, purity: 99.9 %, specific gravity: 0.553, calorific value: 55530 kJ/kg) was fed to the reactor at the desired flow rate using a Bronkhorst make mass flow meter. The preheater temperature was maintained at 443 K to ensure complete vaporisation of the feed water even at high liquid flow rate.

A HPLC (high pressure liquid chromatography Make: SSI, USA) pump was used to feed water to the reactor at the desired flow rate (between 0 to 5 ml/min). The product stream

was condensed using the double pipe condenser at the outlet of the reactor. The liquid product (mostly water) was collected in a separator while the outlet gas stream flow rate was measured using a wet gas flow meter.

The gas was periodically sent to the GC (gas chromatograph) for analysis using a three-way valve. Gas analysis was done using a thermal conductivity detector (TCD) with Spherocarb column (1/8″ diameter and length 8′) to find the composition of the outlet gas stream. The product gas was found to contain methane, carbon monoxide, carbon dioxide and hydrogen. No other hydrocarbon species was detected. The results of the gas analysis of the product gases indicated whether steady state conditions had been achieved. The measurements for the study were done once similar gas compositions were obtained after the start of the experiment. As this is a fast reaction in general steady state conditions were observed within 15 to 20 minutes from the start of the experiment. The pressure for all experimental runs was maintained at 1 atmosphere.

The liquid product was weighed and analysed periodically in the GC using the TCD in a Porapak Q column (1/8″ diameter and length 6′). The liquid product was found to be only water. The reaction was stopped after 3 to 6 hours of steady state operation (except for time−on−stream studies which were conducted for 100 hours of operation).

Methane conversion was calculated using equation 1.

$$\frac{mols_{CH4}in - mols_{CH4}out}{mols_{CH4}in} \times 100 = X_{CH_4} \tag{1}$$

Reproducibility of the experiments was verified by conducting repeat runs for a few random reaction conditions. The results showed a maximum error of ±4.0%.

5. Results and discussion

5.1 Effect of temperature

Steam reforming of methane was carried using PS−CAT in a temperature range of 673 K to 1048 K keeping the molar ratio of feed to steam (MR) and the W/F_{CH4} constant. Figure 6 shows the effect of temperature on the conversion of methane. As temperature increases the conversion of methane gradually increases from 30% to nearly 100%. The catalyst exhibited a methane conversion of more than 90% for a temperature above 973 K. The catalyst showed nearly complete conversion (above 98 %) of methane at a temperature above 1048 K at a W/F_{CH4} close to 55.0 g–cat min/mol and a molar ratio (CH_4:H_2O) close to 3.0. With increase in temperature the carbon monoxide content in the product gas stream increase from as low as 0.21% to 22.43% (v/v). The carbon dioxide content decreases with increase in temperature. Thus the catalyst promotes the endothermic steam reforming reaction but does not promote the exothermic water−gas−shift reaction which is favoured at low temperature. This result is in accordance with the presence of nickel as the active ingredient of the catalyst which promotes bond cleavage in the steam reforming reaction but has limited water−gas−shift activity (Rostrup−Neilsen, 1984, Vaidya & Rodrigues, 2006).
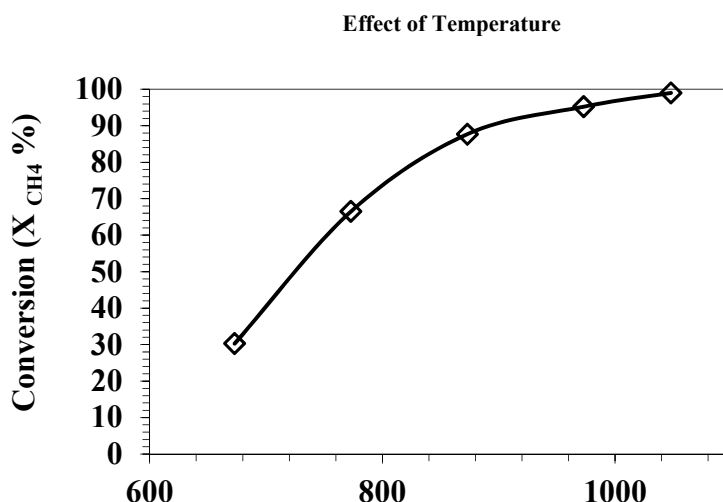
Fig. 6. Effect of temperature on methane conversion. Other conditions: PS−CAT 4 channel block, 5 blocks in series, W/F_{CH4} = 56 gm–cat min/mol, steam to methane molar ratio in feed = 3:1.

5.2 Time–on–stream study

The most important feature of industrial catalysts is their ability to perform steam reforming of methane for hundreds of hours of continuous operation without significant loss of activity (Rostrup−Neilsen, 1984). The study to test the performance of the catalyst for long duration of continuous operation is called as time–on–stream study.

PS–CAT was tested for steam reforming of methane at a steam to methane molar ratio of 3:1 at atmospheric pressure and temperature of 1048 K for a over 100 hours on stream. Both the 4 channel PS–CAT as well as the 49 channel PS–CAT were tested. The resulting exit gas was analysed and the results of the same for four channels is shown in figure 7 and figure 8. As can be seen a methane conversion of more than 98 % is obtained over the entire period (more than 100 hours) of operation. The product gas composition also shows steady formation of all species. In case of the 49 channel PS–CAT the temperature of operation was 1113 K. The higher temperature was necessary as due to increase in the number of channels, the time required to acquire steady state conditions increased by 60 minutes. The reason for this is the low thermal conductivity of the cordierite substrate (2.76 W/m K). Thus the 49 channel block required more time to "soak− up" heat and attain a uniform temperature. Once a uniform temperature was attained, the performance of this block was also very good and exhibited a steady methane conversion of more than 97%. Therefore the catalyst block can readily be used in industrial reformers simply by using a block of higher diameter to fit the inside of a reformer tube with minimum modification to the existing infrastructure of the plant. In both cases the amount of CO produced was around 20 % (v/v of the dry product gas). This shows that the catalyst exhibits limited water gas shift capability. This aspect has been included in the scope of future work wherein the catalyst composition can be varied to enhance water gas shift reaction also. The amount of hydrogen produced was nearly 70 % (v/v of the dry product gas) in both cases. Thus PS–CAT is a very promising substitute for packed bed reactors for production of syngas and hydrogen which can be used for manufacture of fertilisers.

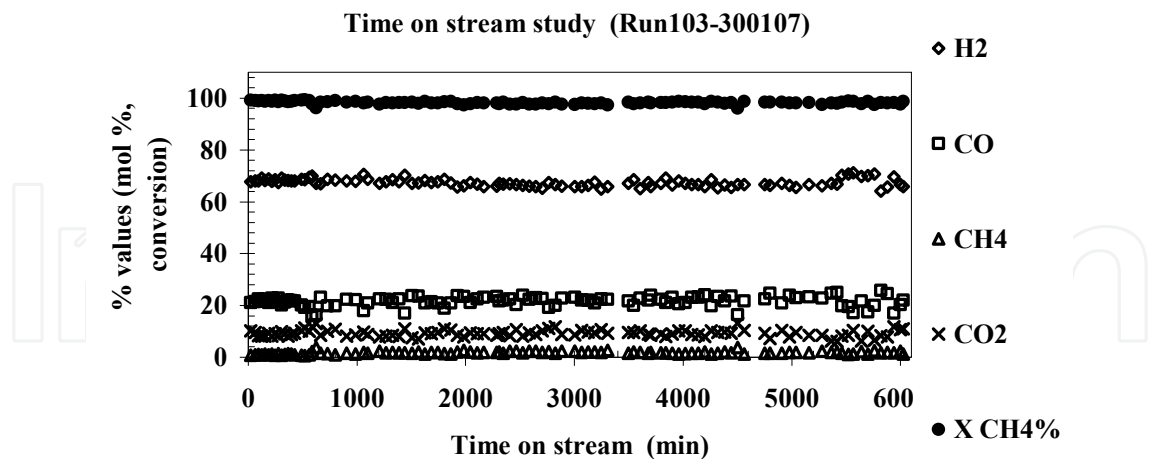**Time on stream study (Run103-300107)**

Fig. 7. Product gas composition of the exit gases. Other conditions PS−CAT 4 channels, 5 blocks in series, feed to steam molar ratio of 1:3, W/F = 56 gm−cat min/mol, pressure = 1 atm and temperature 1048 K, X_{CH4} = 98.27%, Yield 3.4 mol of H_2/mol of CH_4 reacted.
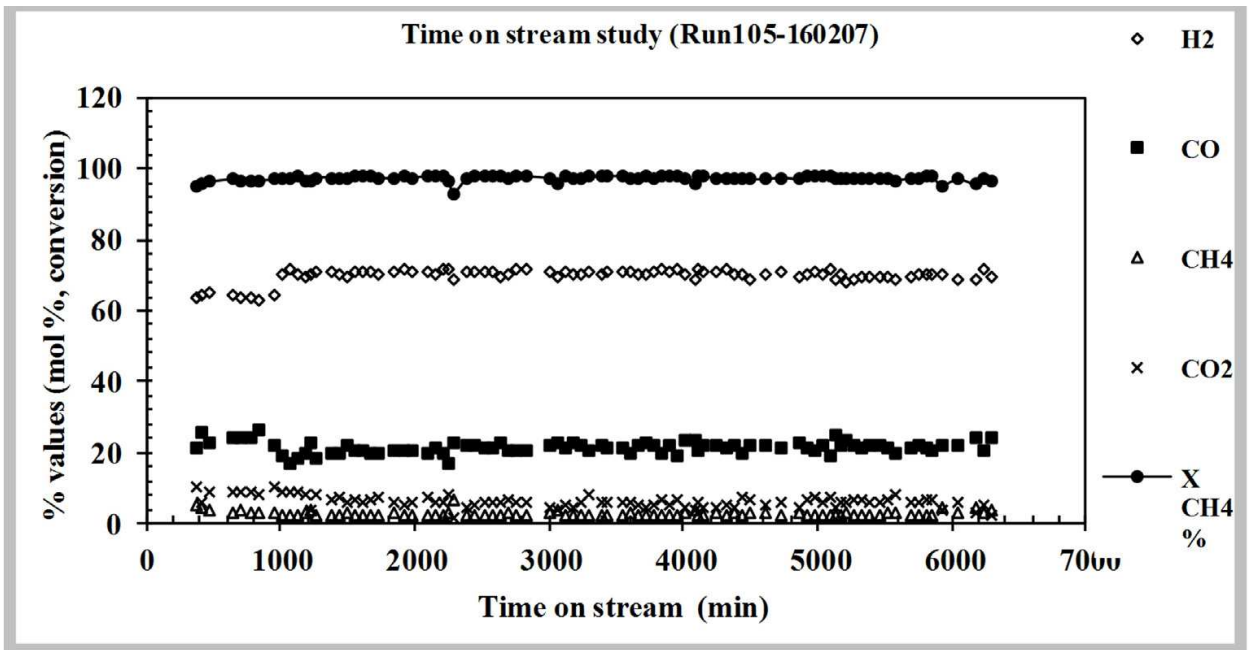

Fig. 8. Product gas composition of the exit gases. Other conditions PS−CAT 49 channels (7×7) channels, 2 blocks in series, feed to steam molar ratio of 1:3, W/F = 56 gm−cat min/mol, pressure = 1 atm, T =1113 K, X_{CH4} = 98.27%, Yield 3.14 mol of H_2/mol of CH_4 reacted.

5.3 Effect of space time

The effect of space time was studied by varying the W/F_{CH4} ratio from 10 to 55.0 gm−cat min/mol for three temperatures namely 873, 973 and 1048 K at a molar ratio of steam to methane of 3.0. Figure 9 shows the effect of space time on methane conversion. The

Effect of W/F CH4 and Temperature
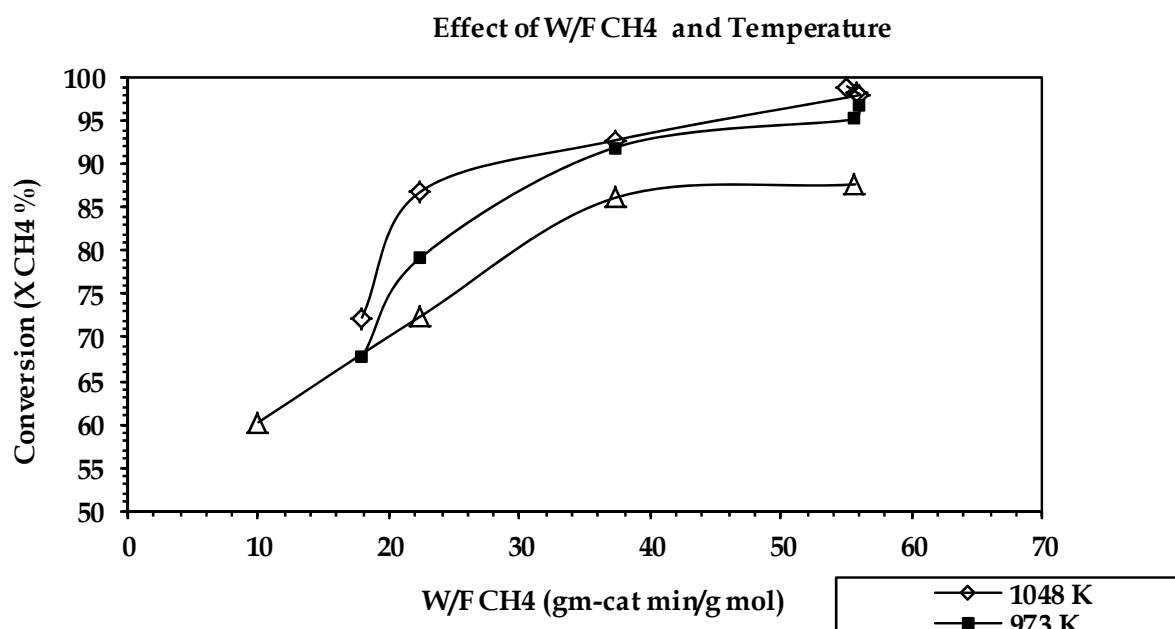
Fig. 9. Effect of space time on methane conversion. Other conditions: PS−CAT 4 channel block, 5 blocks in series, steam to hydrocarbon molar ratio in feed = 3.0.

conversion of methane increases with increase in W/F_{CH4} ratio. The catalyst exhibits a conversion of more than 90% for a W/F_{CH4} ratio above 37.3 gm−cat min/mol for temperature above 923 K.

5.4 Comparison of performance with a commercial catalyst

As mentioned in the literature review section, to the best of our knowledge there are hardly any references (in literature) to the use of meso−scale, ceramic, monolith channels specifically for steam reforming of methane (heat provided external to the reformer tube). Thus direct comparison with other data was not possible.

In order to compare the performance of the developed catalyst, experimental runs were conducted using a commercial nickel containing catalyst in a tubular fixed bed reactor of inner diameter 6 mm and 3 mm. In case of the 3 mm and 6 mm reactors the experiment was conducted maintaining the ratio of the length of the catalyst bed to the diameter of the reactor to enable a common basis of comparison between the two cases (Hoang and Chan, 2006). This ratio was maintained at 10. Table 1 gives the details of the process parameters used to compare the performance of PS−CAT with a commercial catalyst. The table also gives the composition of the catalyst determined using EDS–X-ray analysis. Swamy, 2007 has reported a detailed kinetic study of steam reforming of methane using the same catalyst. The commercial catalyst was crushed, sieved to obtain the required size of particles (approx 1.0 mm). The required weight of catalyst (0.1 gm) was filled in the tubular packed bed reactor of diameter 3 mm or 6 mm such that the centre of the catalyst bed corresponded to the central heating zone of the furnace. The remainder of the reactor was filled with inert ceramic material. The reactor was mounted in the furnace assembly. The catalyst was activated in a hydrogen flow of 40 N ml/min with a steady increase of temperature. The

Composition of active components		Structure	Weight	Residence Time	Molar Ratio	Temp.	Conversion of Methane
			gm	gm cat min / mol	Steam to Methane	K	(%)
Commercial Catalyst							
compound	wt− %	Particles of average size of 1 mm. Packed bed reactor used	0.1	56.00	3	1048	**79.73**
Ni	25						
Al$_2$O$_3$	15						
MgO	55						
PS-CAT							
compound	wt− %	Meso Scale Channel dimension 1.5 x 1.5 mm 100 cpsi 4 channels used, 5 blocks of 25 mm length used in series	0.1 (coating only)	56.00	3	1048	**98.27**
NiO	8.5						

Table 1. Process parameters used to compare the performance of PS−CAT with a commercial catalyst.

catalyst was maintained at the desired reaction temperature for two hours or till steady state conditions were achieved which can be determined from the temperature of the bed and the reactor skin temperature (outer wall of the reactor). At identical conditions (feed to steam molar ratio of 1:3 at a W/F = 56 gm−cat min/mol , pressure = 1 atm and temperature 1048 K), when a commercial nickel−based steam reforming catalyst was tested for steam reforming of methane in a 6 mm packed bed reactor the corresponding conversion obtained was 79.7 %. The conversion of methane using PS−CAT at identical conditions was found to be 98.27 % exhibiting a massive increase in the conversion of methane. Figure 10 shows the effect of temperature on methane conversion while comparing the performance of PS−CAT with commercial catalyst at identical process conditions. Figure 11 compares the performance of PS−CAT with commercial catalyst exhibiting the effect of W/F$_{CH4}$ on methane conversion. In both cases, PS−CAT outperforms the commercial catalyst.

The reactor exhibited a minimum increase of 10% and a maximum increase of 22% in the conversion of methane that directly translates into increased production of syngas and hydrogen with existing plant infrastructure. Thus PS–CAT is a very promising substitute for packed bed reactors for production of syngas and hydrogen which can be used for manufacture of fertilisers. The better contact between the reactants and the active catalytic ingredient in case of the use of the structured catalyst shows a substantial increase in the performance in comparison to a fixed bed catalyst consisting of randomly packed catalyst. In the case of the 3 mm and 6 mm diameter fixed bed reactors, the conversion of methane in the 3 mm reactor was higher than the 6 mm reactor. This is in agreement with principles of use micro or meso−scale devices (Lowe, 2000). Decreasing the linear dimensions, for a given

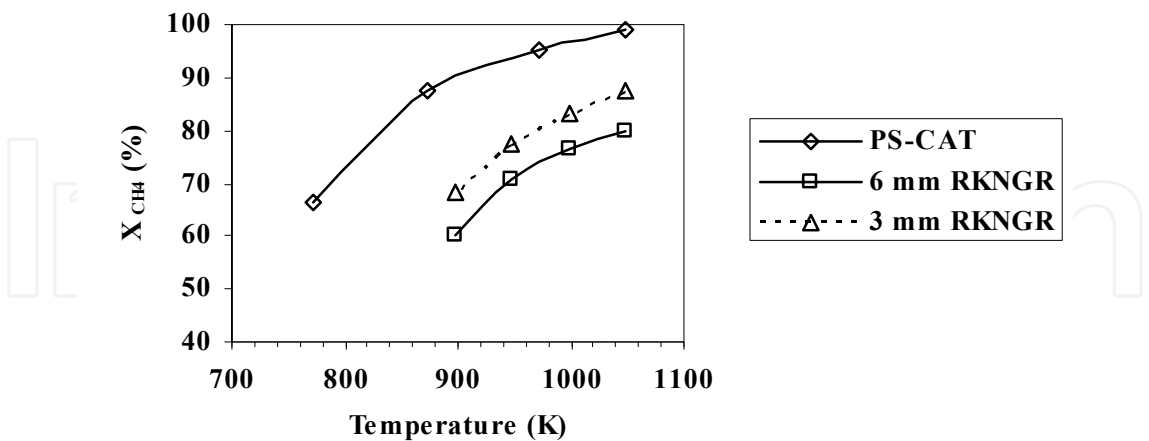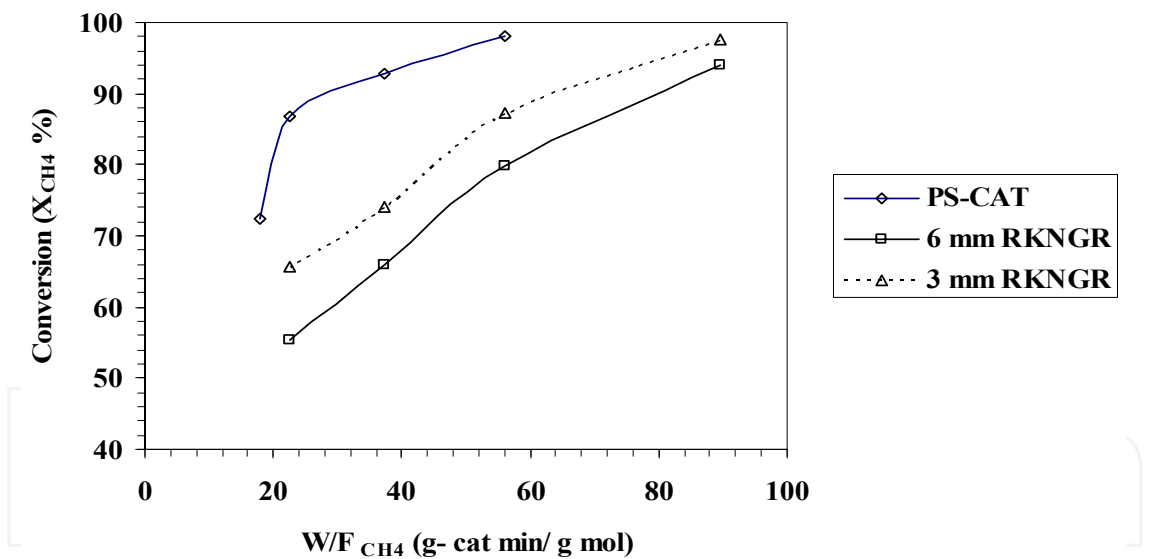**Comparison of performance with commercial catalyst**

Fig. 10. Comparison of performance of PS−CAT with commercial catalyst, effect of temperature on methane conversion. Other conditions: PS−CAT 4 channel block, 5 blocks in series, W/F_{CH4} = 56 gm−cat min/mol, steam to hydrocarbon molar ratio in feed = 3.0.

Conversion vs W/F $_{CH4}$, T= 1048 K, MR ~ 3

Fig. 11. Comparison of performance of PS−CAT with commercial catalyst, effect of W/F_{CH4} on methane conversion. Other conditions: PS−CAT 4 channel block, 5 blocks in series, T= 1048 K, steam to hydrocarbon molar ratio in feed = 3.0.

difference in a physical property (like temperature or concentration) increases the respective gradient. Consequently the driving forces for heat transfer, mass transport or diffusion flux per unit volume or unit area increase.

Literature reports the effect of changing diameter of a membrane reactor system on methane conversion for the partial oxidation process (Hoang and Chan, 2006). The authors have reported an increase in methane conversion with decrease in reactor diameter (at the same

length to diameter ratio). Even though the system reported is different from this study the reasoning for the increase in methane conversion for smaller reactor diameters has a similar basis and can explain the increase in conversion for the 3 mm reactor.

6. Conclusions

A novel, meso–scale, structured, channel reactor was developed and successfully tested for steam reforming of methane. The structured catalyst called PS-CAT is a cordierite based monolithic structure coated with nickel oxide. The coating procedure was finalised on the basis of a set trials. The characterisation was done by EDS–X-ray analysis, BET surface area measurement and XRD analysis. The testing was carried out by varying the process parameters such as time–on–stream analysis (100 hours on stream), temperature (673 to 1048 K, space time (W/F_{CH4} = 10 to 55.0 gm–cat min/mol), and the number of channels (4 channels and 49 channels *in parallel*). PS–CAT was tested for steam reforming of methane at a steam to methane molar ratio of 3:1 at atmospheric pressure and temperature of 1048 K for over 100 hours of operation.

The conversion of methane observed with the said conditions was above 97 %. The catalyst exhibited good conversion (above 90%) of methane for a molar ratio of steam to methane from 2.5 to 7. The catalyst showed a conversion of more than 90% for a W/F_{CH4} ratio above 37.3 gm–cat min/mol for temperature above 923 K. Maximum hydrogen yield of 3.8 mol of H_2/mol of CH_4 reacted was observed at a W/F_{CH4} of 55.1 gm–cat min/mol at a temperature of 1048 K and molar ratio of steam to methane of 3.0.

Finally the performance of this developed catalyst was compared with the performance of commercial nickel–based catalyst in small diameter (3 mm and 6 mm) fixed bed reactors. The catalyst exhibited a minimum increase of 10% and a maximum increase of 22% in the conversion of methane that directly translates into increased production of syngas and hydrogen with existing plant infrastructure.

The main advantages of use of PS–CAT are increased throughput, simplicity of the arrangement, and minimum plant modification. Thus PS–CAT is a very promising substitute for packed bed reactors for production of syngas and hydrogen which can be used for manufacture of fertilisers. This case study also emphatically demonstrates the application of meso-scale catalytic structures for bulk scale production of commodity gases such as syngas

7. Nomenclature

F_{CH4} = molar flow rate of methane, mol/min
F_{H2O} = molar flow rate of water, mol/min
Q_{CH4} = volumetric flow rate of methane, N ml/min
Q_{H2O} = volumetric flow rate of water, ml/min
T = temperature, K
v/v = composition of gas species expressed as volume percent of the total product gas %
W = weight of catalyst, gm
W/F = ratio of weight of catalyst to molar flow rate of feed (space time), gm–cat min/mol
X_{CH4} = fractional conversion of methane

8. Abbreviations

BET–SSA	=	Brunauer–Emmett–Teller specific surface area method
cpsi	=	cells per square inch
EDS X-ray	=	energy dispersive spectroscopic X–ray analysis
GC–TCD	=	thermal conductivity detector of gas chromatograph
MR	=	molar ratio of steam to feed hydrocarbon
XRD	=	X–ray powder diffraction
WGS	=	water–gas–shift
DRIE	=	deep reactive ion etching
LTS	=	low temperature shift
PSA	=	pressure swing adsorption

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10. References

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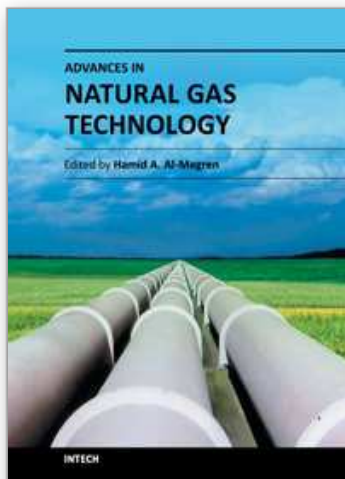
Advances in Natural Gas Technology

Edited by Dr. Hamid Al-Megren

Natural gas is a vital component of the world's supply of energy and an important source of many bulk chemicals and speciality chemicals. It is one of the cleanest, safest, and most useful of all energy sources, and helps to meet the world's rising demand for cleaner energy into the future. However, exploring, producing and bringing gas to the user or converting gas into desired chemicals is a systematical engineering project, and every step requires thorough understanding of gas and the surrounding environment. Any advances in the process link could make a step change in gas industry. There have been increasing efforts in gas industry in recent years. With state-of-the-art contributions by leading experts in the field, this book addressed the technology advances in natural gas industry.

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