

# CO<sub>2</sub> Reforming of Methane in a Probe Reactor with a Thin Catalyst Layer

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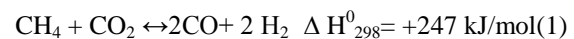
**Abstract** - Probe (annular) and channel reactors with thin catalyst layers are considered to be much more effective than conventional reactors and can offer several advantages such as excellent heat transfer characteristics and negligible intra-catalyst diffusion resistance. A probe reactor and a channel reactor were designed, fabricated and coated with thin layers of Ni/Al<sub>2</sub>O<sub>3</sub> catalysts and tested for dry reforming of methane. The catalysts were initially prepared by the Sol-Gel method and calcined at different conditions. Several catalyst coats with different catalyst loading were tested at different operating conditions. High conversions were achieved on thin layer of Ni/Al<sub>2</sub>O<sub>3</sub> catalysts and high coking resistance was obtained by addition of Cr, Ba and La<sub>2</sub>O<sub>3</sub>. The experimental results also showed that as CO<sub>2</sub>/CH<sub>4</sub> ratio increased the coking rate decreased. Low pressure drop and low temperature gradient along the length of the reactor were attained. The catalyst effectiveness factor was about 1 and the values of activation energy indicated the reactions did not have any diffusion limitations.

**Keywords:** CO<sub>2</sub> Utilization; Probe Reactor; Channel Reactor; Thin Layers; Sol-gel; Process Intensification.

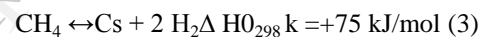
## 1. INTRODUCTION

Intensified catalytic reactors (ICR) have several advantages compared to conventional packed bed, slurry, or tubular reactors. Besides the reduction in size, ICR have negligible mass and heat transfer resistances, due to the use of a thin catalyst layer coated on the reactor surface, which reduces mass and heat transfer restrictions compared with pellet catalysts and can improve the effectiveness factor. It is reported that the "functioning layer" of catalyst pellets in a conventional reforming tube is only about 50 μm thick [1]. The vital advantage of catalytic plate reactor concept would be that thin catalyst films would have much less resistance to transport processes than traditional catalyst pellets. Hence catalyst effectiveness factors would be near unity. There have been several recent studies of the application of plate reactors [2-4]; CO<sub>2</sub> reforming of CH<sub>4</sub> has attracted interest from both industrial and environmental perspectives [5,6]. The CO<sub>2</sub> reforming of methane has two major advantages over steam reforming of methane or partial oxidation of methane. Firstly, from an environmental point view, the two most abundant carbon containing greenhouse gases, methane and carbon dioxide, can be utilized effectively in this reaction and converted into useful chemical products. This is an important area of

recent catalytic research. Secondly, from an industrial perspective, the reaction produces syngas with a higher purity and a lower H<sub>2</sub>/CO ratio than steam reforming. The CO<sub>2</sub> and CH<sub>4</sub> are convertible to synthesis gas with H<sub>2</sub>/CO ratio about 1, which is suitable for specific synthesis processes such as alcohols by carbonylation [7,8]:



The great challenge in the industrial application of CO<sub>2</sub> reforming of methane is deactivation and shattering of catalysts from carbon deposition via CO disproportionation, Reaction 2 and methane decomposition, Reaction 3.



Relatively speaking, Reaction 2 is favored at low temperature and low pressure, while Reaction 3 is favored at high temperature and low pressure. Therefore, substantial number of publications were produced on different strategies implemented to minimize the amount of coke [5-7, 9-13]; optimizing the operating conditions (feed ratio), use of alternative catalysts (additives), control of surface reactions and take advantage of catalyst characterizations to optimize the preparation method and reduction temperature.

Preparation techniques are crucial in developing an active, selective, stable and durable catalyst. Although the sol-gel technique has been adopted for stainless steel substrate and micro-channel reactors coatings [2,3], there have been limited studies on the characterization and testing of this catalyst coats prepared by the Sol-Gel method. Li and Wang [7] investigated the preparation and characterization of Sol-gel catalysts. However, their study focused on using catalyst powder in a fixed bed reactor for CO<sub>2</sub> reforming reactions. To the best of the authors' knowledge, there have been no reports in the open literature on the testing of Sol-Gel coats for important potential applications such as dry reforming of methane. The objective of the present study, therefore, is to examine the performance of dry reforming of methane reaction onto a probe and channel reactor coated by thin layers of catalyst via a sol gel method. The activity and stability of

the CO<sub>2</sub> reforming over Ni/Al<sub>2</sub>O<sub>3</sub> and Ni-Cr-Ba/La<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts were investigated.

## 2. EXPERIMENTAL SETUP

### 2.1 Annular or Probe Reactor

The probe reactor used in the study was fabricated from 316 stainless steel tubing (12.7 mm OD, 9.5 mm ID) with a length of 500 mm. An inner steel tube (6.4 mm OD), sealed at one end, was centrally installed via the exit tee fitting, inside the outer tube which formed a narrow (1.55 mm) annulus with 9.5 mm OD and 6.4 mm ID. The inner tube had small spot welds along its length which protruded from the tube and were a sliding fit inside the outer tube. This ensured that the inner tube was positioned centrally inside the outer tube. Approximately 150 mm of the outside of the inner tube was coated with catalyst to give a coated area of approximately 30 cm<sup>2</sup> and an annulus volume of 5.88 cm<sup>3</sup> around the catalyst. Thermocouples were placed inside the inner tube to measure the temperature inside the reactor. The main body of the reactor was held axially within a three zone furnace such that the middle of the coated area was approximately mid-way along the furnace length. The entrance and exit tee fittings were held outside the furnace and lagged with insulation.

### 2.2 Catalysts

Catalysts were prepared by dispersing 'Disperal' alumina supplied by Sasol, Germany [14] in 1% nitric acid and adding the appropriate nickel and other additives as nitrates to give composition of calcined catalysts in wt%; Ni(49%)/Al<sub>2</sub>O<sub>3</sub>(51%) (Catalyst A) and Ni(33%)-Cr(5.6%)-Ba(11%)/ La<sub>2</sub>O<sub>3</sub>(19%)-Al<sub>2</sub>O<sub>3</sub>(31.4) (Catalyst B), respectively. The inner tube of the reactor described in Section 2.1 was pre-treated before coating to improve adhesion. Approximately 150 mm from the sealed end of the tube was roughened using coarse emery paper and then degreased by dipping in a measuring cylinder containing acetone. The tube then weighed using 4-decimal place analytical balance. This 150 mm roughened part of the tube was coated by dipping into a measuring cylinder containing the sol-gel. The coated area was 150 mm long and marked with a PTFE tape, which was also used to prevent the coating of the seals tip end. The probe was submerged in the sol gel for couple of seconds, lifted out and dried at 100 °C. Multiple dips were used to build up the desired catalyst weight and finally calcined at 400 °C. The reactor described in Section 2.1 was coated with catalyst by forcing the sol-gel through the channel, blowing out the surplus and air-drying at 100 °C. Multiple coats were used to build up the desired catalyst weight and the catalyst then calcined at 400 °C. The reactor's blocks were light enough to be weighed to +/- 1 mg, giving accuracy in the mass of catalyst of +/- 1% or better.

### 2.3 Experimental Procedure

After calcination, the reforming catalysts were reduced in situ in a stream of hydrogen at 600°C for at least 2 hours and a small flow of hydrogen was maintained throughout the experiments to reduce carbon lay down, Reactions 3.

The reactants were preheated in the furnace before entering the reactor.

## 3. RESULTS AND DISCUSSION

### 3.1 Thermodynamic analysis

Dry reforming of methane (Reaction 1) is an important reaction that produces syngas with a higher purity and a lower H<sub>2</sub>/CO ratio than steam reforming. It also utilizes CO<sub>2</sub> as a gaseous pollutant that is well known to contribute to global warming.

A thermodynamic analysis was carried out for Reaction (1) to determine the equilibrium composition at different temperatures and to estimate the heat of reaction as a function of temperature. The analysis was conducted using HSC Chemistry, a chemical reaction and equilibrium software. For a fixed temperature and pressure, the number of moles present at equilibrium for any species can be determined using the Gibbs free energy minimization method.

Reaction (1) is highly endothermic and becomes spontaneous for temperatures beyond 640 °C as shown in Figure 1. The catalytic reaction is usually carried out in the temperature range of 600 to 800 °C, where the heat of reaction is almost constant with temperature as shown in the figure. The equilibrium composition of the two reactants (CH<sub>4</sub> and CO<sub>2</sub>) and two products (CO and H<sub>2</sub>) is presented in Figure 2 at a pressure of 1 Bar. The figure shows that the reaction commences at about 400 °C and reaches completion at about 1000 °C. It is worth noting here that both reactants and both products appear on the same line as shown in the figure and as indicated by the initial equimolar stoichiometry of the reaction.

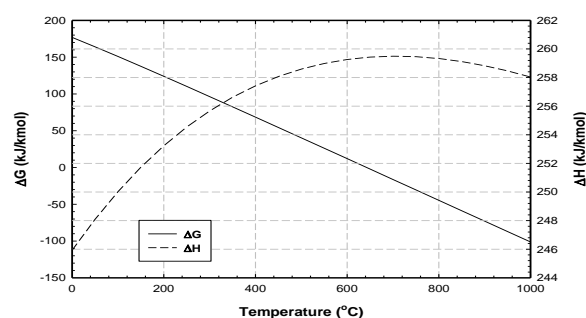


Figure 1. Heat of reaction and Gibbs free energy for Reaction (1) at different temperatures at 1 Bar .

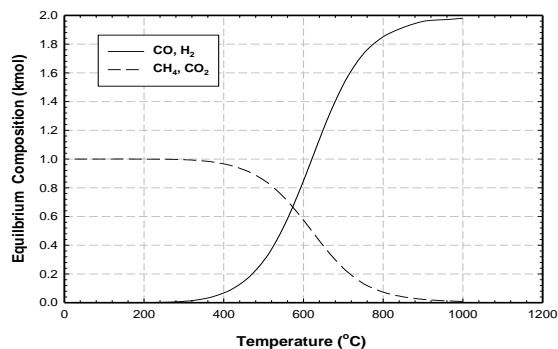


Figure 2. Equilibrium composition for Reaction (1) at different temperature and 1 Bar.

Since the dry reforming reaction is a gaseous reaction with volume increase, it is highly affected by the operating pressure. High pressure tends to hamper the progress of the reaction. On the other hand, low pressure favors the forward reaction and leads to reaction completion at a much lower temperature as shown in Figure 3. Although the probe reactor was not tested at pressures lower than atmospheric, the thermodynamic analysis shown in Figure 3 suggests that low pressure may be more suitable for dry reforming and may favor Reaction 1 over Reaction 2 and hence lead to less carbon deposition.

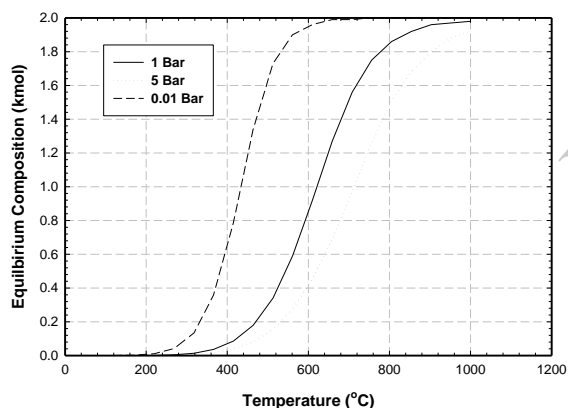


Figure 3. Equilibrium compositions for CO and H<sub>2</sub> of Reaction (1) at different temperatures and different pressures.

### 3.2 Catalyst Activity and Feed Ratios

The catalyst film gave about 80% methane and carbon dioxide conversion at atmospheric pressure as shown in Figure 4. The methane flow rate was 0.58 mol/hr with 1:1 molar CH<sub>4</sub>:CO<sub>2</sub> ratio. From Reaction 1, it can be seen that the stoichiometric requirement for CO<sub>2</sub>/CH<sub>4</sub> ratio is 1 and from an industrial point view, it may be desirable to operate with CO<sub>2</sub>/CH<sub>4</sub> ratios near unity. Previous studies [9, 10] recommended that CO<sub>2</sub>/CH<sub>4</sub> ratio be above unity to prevent carbon deposition. However, the results showed that as CO<sub>2</sub>/CH<sub>4</sub> ratio increased the coking rate decreased as well as H<sub>2</sub>/CO product ratio  $\leq 1$ . The results of each test over Catalyst B were summarized in Table 1.

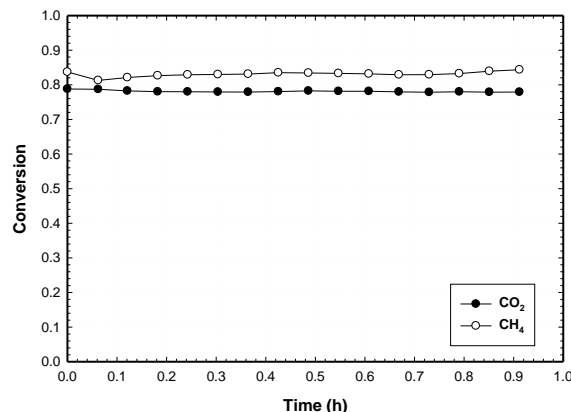


Figure 4. Methane and CO<sub>2</sub> conversion vs. time over Catalyst A; catalyst loading 15.23 mg/cm<sup>2</sup> in Probe reactor at 700 °C furnace temperature

Table 1. Effect of Feed Ratio on the Rate of Carbon Deposition and Product Ratio for Catalyst B

CO <sub>2</sub> /CH <sub>4</sub> Feed ratio	Mole carbon deposited/ mole carbon converted	Coking rate [g- carbon/h]	H <sub>2</sub> /CO Product ratio	CH <sub>4</sub> Conversion %
1	0.022	1.05	0.81	89-93
1.17	0.0084	0.4297	0.79	87
1.34	0.0041	0.22761	0.74	80-90

### 3.3 Reaction Kinetics

A previous study [15] confirmed that replacing steam with CO<sub>2</sub> in the reforming reaction has no drastic influence on the mechanism. However, the experimental results over Catalyst B suggested that the reaction order with respect to methane is approaching first order and the reaction order with respect to CO<sub>2</sub> being closer to zero order. These results are in agreement with those of [15, 16] who reported a zero order dependence with respect to CO<sub>2</sub>, as well as first-order dependence with respect to methane, in CO<sub>2</sub> reforming over Ni-based catalyst. The rate of CO<sub>2</sub> reforming was described by applying Langmuir-Hinshelwood rate equations [17].

### 3.4 Diffusion Limitations

In catalytic plate reactors, small channels coated with a thin catalyst film offer short diffusion and conduction path lengths for rapid mass, and heat transfer. This results in minimal intra-catalyst diffusion limitations and thus high catalyst utilization (effectiveness factor  $\approx 1$ ). However, results showed that increase of the catalyst loading in the plate reactors results in enhancement of methane and carbon dioxide conversion under the same reaction conditions, see Figure 5. The catalyst thickness is estimated to be up to 50  $\mu\text{m}$ , assuming that the layer is uniformly deposited and has a porosity of 35%. At such thickness, internal mass and heat transfer resistances are considered to

be negligible. The apparent activation energy was varied from 110 to 85 kJ/mol when catalyst loading increased from 2 mg/cm<sup>2</sup> (7.7 μm) to 6 mg/cm<sup>2</sup> (23.1 μm), based on the density of Catalyst B estimated at 2.6 g/cc. These activation energy values are within the range reported by other researchers [16, 18, 19] who used Ni-based catalysts. It can be seen that the presence of promoters in Ni/Al<sub>2</sub>O<sub>3</sub> catalyst film have minor effects on activation energy magnitudes. As a rule of thumb, chemical reaction is rate limiting if the apparent activation energy is greater than 40 kJ/mol. If it is in the range of 12-15 kJ/mol or lower, then the transport processes are assuming a greater degree of control over the reaction [20]. This means that for the range of catalyst loadings examined, the reaction apparent activation energy values are too high for any diffusion limitation.

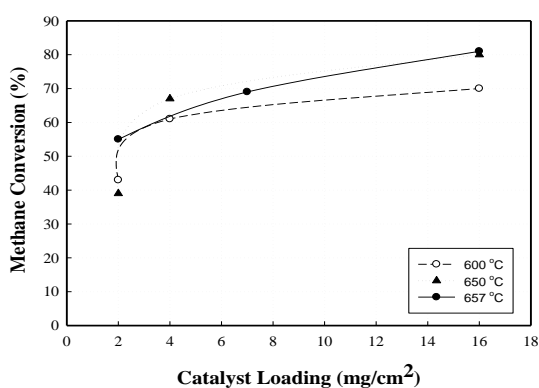


Figure 5. Methane conversion as a function of catalyst loading for different reactor temperatures.

## CONCLUSIONS

- It has been demonstrated that sol gel method facilitates catalyst preparation. The sol-gels can be prepared to have good rheological properties for coating onto stainless steel substrate which after calcining form an adherent thin catalyst layer with good metal dispersion.
- The catalyst film gave about 80% methane and carbon dioxide conversion.
- Carbon deposition rate was high on Ni/Al<sub>2</sub>O<sub>3</sub> (Catalyst A) and reduced by the addition of Ba, Cr and La<sub>2</sub>O<sub>3</sub> as well as CO<sub>2</sub>/CH<sub>4</sub> ratio increased the coking rate decreased.
- Probe (annular) reactor is more convenient for rapid activity tests.
- Low temperature gradient along the length of the channel reactor was attained compared to probe reactor.
- Low pressure drop along the length of the reactors were achieved.
- The values of activation energy indicate the reaction is free from any diffusion limitation effect.

## ACKNOWLEDGEMENT

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