

Steam Reforming of Methane over Ni/Al₂O₃ Catalysts in a Probe Reactor

Mohamed Al Nakoua ⁺

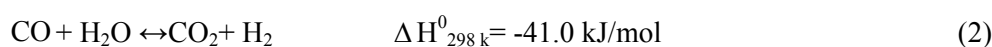
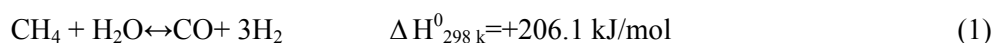
Department of Chemical and Petroleum Engineering, United Arab Emirates University, Al Ain, UAE

Abstract. Probe (annular) reactor with thin catalyst layers has numerous advantages over conventional ones including excellent heat transfer and negligible intra-catalyst diffusion resistance. Another important advantage of this reactor is the flexibility in selecting the desired catalyst loading. A probe reactor was designed, fabricated and coated with thin layers of catalysts. The catalysts were initially prepared by the Sol-Gel method and calcined at different temperatures. The thin layers ($\leq 50 \mu\text{m}$) were homogeneous with a good adherence onto the stainless steel reactor surface. Ni/Al₂O₃, Ru/La₂O₃-Al₂O₃ and Co/Al₂O₃ catalysts, as thin layers have been tested for steam reforming of methane. Several catalyst coats with different catalyst loading were tested at different operating conditions. The Ni/Al₂O₃ catalyst exhibited high stability and allowed methane conversion of 100% to be achieved. The experimental evidence suggests that the main reason for the catalyst deactivation was sintering of the nickel particles. 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: probe reactor, thin layers, sol-gel, steam reforming of methane.

1. Introduction

Probe (Annular) reactor has several advantages compared with fixed bed reactor. Firstly, the absence of pressure drop due to the laminar regime and the absence of tortuosity which characterize the gas flow along the annular duct. Secondly, the reduction of temperature gradients due to the presence of additional routes of heat dispersion mainly radiation from the oven wall. In addition, the annular reactor has a much higher void volume than a fixed bed reactor and the gas stream contacts the catalyst-coated probe longitudinally, achieving very high space velocities without pressure drop along the reactor. Furthermore high flow rates may be used for probe reactor compared to packed beds, where the high pressure gradients prevent the use of high flow rates [1, 2]. Finally, employing the catalyst as a thin layer ($<50 \mu\text{m}$) coated on the probe surface reduces mass and heat transfer restrictions compared with pellet catalysts and can improve the effectiveness factor. It has been reported that the “functioning layer” of catalyst pellets in a conventional reforming tube is only about $50 \mu\text{m}$ thick [3]. One of the most important potential applications of thin catalyst coats is methane-steam reforming in a probe reactor according to the following reactions:



This is a particularly attractive target for the application of probe reactors as there is a huge potential application in the distributed production of small quantities of hydrogen for fuel cells. Hydrogen is a clean

⁺ Corresponding author. Tel.: + (971 50 5639737); fax: + (971 3 7624262).
E-mail address: (mnakoua@uaeu.ac.ae).

burning fuel and can be directly burnt in an internal combustion engine or electrochemically transformed to electricity in a fuel cell. Neither of these methods produces carbon dioxide nor monoxide [4].

For many years nickel has been regarded as the most suitable metal for steam reforming of methane. Other metals can be employed; for example cobalt, platinum, palladium, iridium, ruthenium and rhodium. Some of these precious metals are more active per unit mass than nickel but are more expensive and nickel is effectively active to enable suitable catalysts to be produced economically. Therefore, various metals that modify the active phase can be added to increase the practical life and the stability of the nickel supported catalysts.

Preparation techniques are crucial in developing an active, selective, stable and durable catalyst. The sol-gel technique has been adopted for stainless steel substrate and micro-channel reactors coatings [5-9]. The objective of the present study is to examine the performance of steam reforming of methane reaction onto a probe coated by thin layers of catalyst via a sol gel method. The activity and stability of the steam reforming over Ni/Al₂O₃, Ru/La₂O₃-Al₂O₃ and Co/Al₂O₃ catalysts were investigated.

2. Experimental

2.1. Synthesis of Sol-Gel

Catalysts were prepared by dispersing 'Disperal' alumina supplied by Sasol, Germany [10] in a solution of dilute nitric acid (1 wt%, 0.11 M) to give 5 wt. % alumina sol-gel. Since the powder contains 78% of alumina this was taken into account when making up the sol-gel. The alumina was poured into a 100 ml measuring beaker containing the acid then the sol gel was mixed for 10 to 15 min. A glass propeller, with a spinning speed of approximately 200 rpm provided by rotating motor, was used for mixing. Nickel, ruthenium, lanthana and cobalt as nitrates, were added to the alumina sol-gel to give composition of calcined catalysts in wt%; Ni(50%)/Al₂O₃(50%) (Catalyst A), Ru(1.4%)/ La₂O₃(46%)-Al₂O₃(52.6%) (Catalyst B), Co(50%)/Al₂O₃(50%) (Catalyst C), respectively. After vigorous stirring at room temperature for about 30 minutes, the sol-gel was ready for coating.

2.2. Annular or Probe Reactor

The general design of the probe reactor used is shown schematically in Fig. 1. The reactor was made from a 500 mm length of 316 stainless steel tubing (12.7 mm OD, 9.5 mm ID) and two tee fittings. 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 cm² and an annulus volume of 5.88 cm³ around the catalyst. Thermocouples were placed inside the inner tube to measure the temperature inside the reactor.

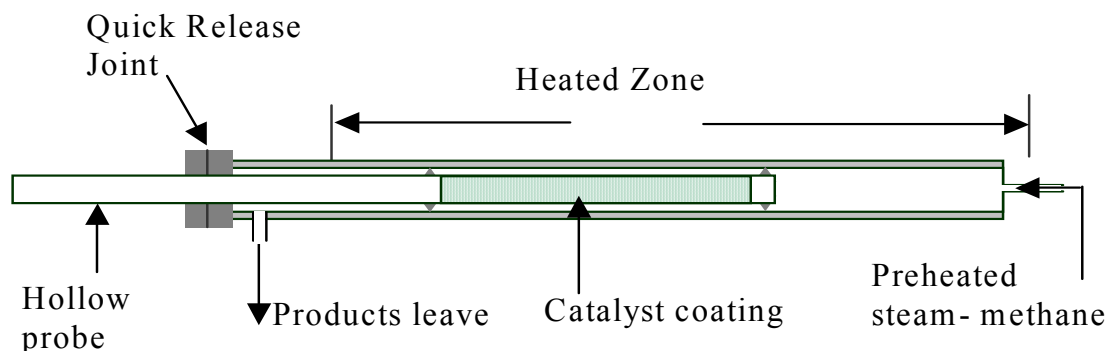


Fig. 1: Annular or Probe Reactor

2.3. Apparatus and Experimental Procedure

The inner tube of the reactor described in Section 2.2 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 (gave highest surface area,[11]). 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. 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 prevent the metals from re-oxidation and reduce carbon lay down. Mixing of feed gases and steam was promoted in a 1 litre stainless steel pot placed vertically in circular ceramic fibre heater. The temperature of generated steam in the mixer with feed gases was maintained by heating tape up to the furnace entrance. The reactants were preheated in the furnace before entering the reactor.

3. Results and Discussion

3.1. Catalyst Activity and Stability

The catalyst preparation method outlined above produced catalysts that adhered well to stainless steel (type 316). The methane flow rate was 0.54 mol/hr with a 4.2:1 molar steam:methane ratio. Five coats of sol-gel with intermediate drying gave a catalyst loading of 32.2 mg/cm² after calcination. The results showed that the formulation with 50 % of nickel supported on alumina (Catalyst A) was the most active catalyst. Thus, the methane conversion rose from 33 at 500 °C to 100 % at 720 °C and remained stable; after 16 hour on stream, the conversion dropped drastically to 48 % due to absence of steam (water pump failure) for half an hour and carbon deposition took place. The carbon was removed by treatment with a CO₂ stream at 650 °C for one hour, then catalyst was reduced with H₂. After regeneration the catalyst restored its activity. The results of the Ni/Al₂O₃ catalyst activity tests are shown in Fig. 2. At the same flow rate; two coats of the sol-gel gave a loading of 3.71 mg/cm² (Catalyst B) and the methane conversion was 34% at 900 °C. On the other hand, the methane conversion was higher at the same temperature 900 °C about 55 % when three coats was used (8.8 mg/cm²). Six coats (22.64 mg/cm²) of (Catalyst C) showed good activity 90% at 720 °C but catalyst was ineffective to stabilize the conversion at steady temperature. Conversion has dropped consistently despite the temperature increase.

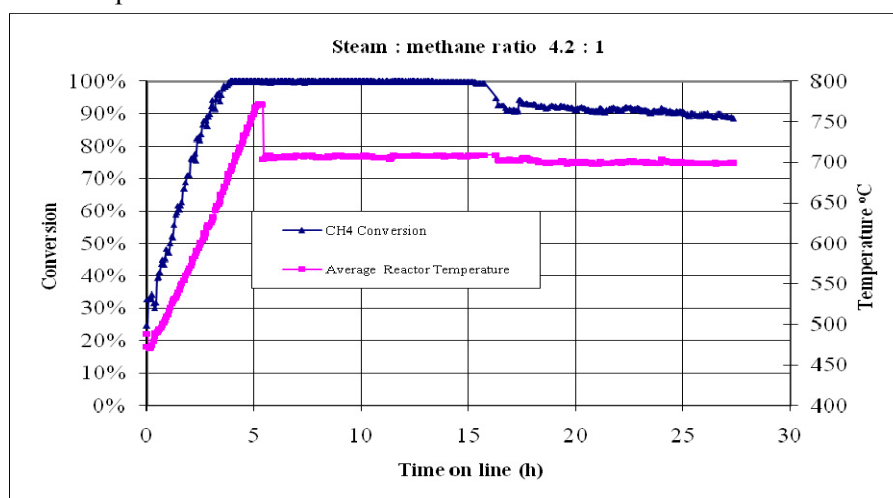


Fig. 2: Conversion, temperature vs. time on line over Catalyst A, catalyst loading 32.2 mg/cm² at atmospheric pressure

3.2. Effect of Steam:Methane Ratio

From Reaction 1 it can be seen that the stoichiometric requirement for steam per carbon atom is 1 if only reforming occurs. Steam reforming produces a syngas with H₂:CO ratio of 3:1. This ratio is increased to 4:1

by the ‘shift reaction’ (Reaction 2). Reaction 2 is beneficial if the aim is to maximize hydrogen for fuel cells. Many reforming catalysts take this reaction to equilibrium and at reforming temperatures this gives CO₂:CO ratios to 1:1. This requires a minimum H₂O/CH₄ ratio of 1.5. This was not practicable because the coking rates at this ratio were high compared to 3-4 feed ratios. Consequently the H₂O/CH₄ ratio was maintained above 3 to avoid carbon deposition. The results of each test were summarized in Table 1. It is obvious that carbon deposition rate increases as H₂O/CH₄ ratio decreases.

Table 1. Effect of feed ratio on carbon deposition rate and product ratios

H ₂ O/CH ₄ Feed ratio	Mole carbon deposited/ mole carbon converted	Coking rate [g- carbon/h]	H ₂ /CO Product ratio	CH ₄ Conversion %
4-3	0.00165 - 0.002	0.007038	5.2	54-76
2	0.004	0.020803	4.3	86
1.5	0.01	0.032555	4.1	53-59
1	0.03-0.06	0.139835	3.3	36-70

3.3. Diffusion Limitation

The effect of catalyst loading in mg catalyst per cm² of coated reactor area versus activation energy was investigated onto the probe using different catalysts. The published kinetic results suggested that the steam reforming reaction was first and zero order with respect to methane and steam, respectively. The data from the thermal cycling experiments was used to construct Arrhenius plots. The catalyst thickness is estimated to be up to 50 μm, assuming that the layer is uniformly deposited and has a porosity of 35%, based on the density of the catalyst estimated at 2 g/cc. At such thickness, internal mass and heat transfer resistances are considered to be negligible. The activation energy decreases as catalyst loading increase regardless the of catalyst composition. The activation energy of Catalyst A were 87 and 77 kJ/mol for 2 and 5 coats, respectively, Catalyst B for 3 coats was 99 kJ/mol, Catalyst C for 6 coats was 82 kJ/mol and, as shown in Fig. 3. These activation energy values represent the apparent activation energy, assuming that the methane reaction is first order. As a rule of thumb, chemical reaction will be 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 [12]. This clearly indicates that in the range of catalyst loadings examined in this study, the steam reforming reaction apparent activation energy values are too high for any diffusion limitation.

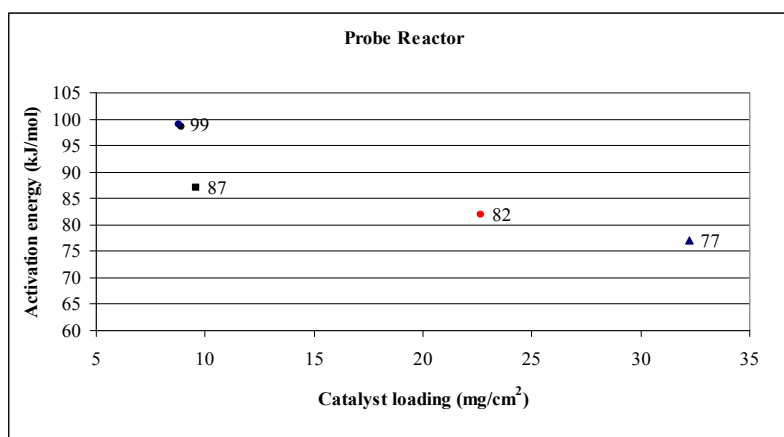


Fig. 3: Activation energy vs. catalyst loading over Catalyst A (87 & 77), Catalyst B (99) and Catalyst C (82)

4. Conclusion

- It has been demonstrated that sol gel method facilitates catalyst preparation. The sol-gels can be prepared to have readily rheological properties for coating onto stainless steel substrate which after calcining form an adherent thin catalyst layer.
- Methane-steam mixtures can efficiently be converted into synthesis gas at temperatures higher than 700 °C. Ni-based catalysts exhibit highest activity and stability compared to Ru/La₂O₃-Al₂O₃ and Co/Al₂O₃ catalyst.

- The experimental evidence suggests that the main reason for the catalyst deactivation was sintering of the nickel particles.
- The pressure drop and temperature gradient along the whole length of the reactor was negligible.
- The catalyst effectiveness factor was about 1 and the values of activation energy indicate the reaction is free from any diffusion limitation effect.

5. Acknowledgements

The author would like to acknowledge the financial support provided by the Research Affairs at the UAE University.

6. References

- [1] A. Beretta, et al. Development of a catalytic reactor with annular configuration. *Studies in Surface Science and Catalysis*. 1998, **118**, pp. 541-548.
- [2] D. Papadias, et al. Design and characterization of a close-concentric annular reactor for kinetic studies at high temperatures. *Chemical Engineering Science*. 2002, (**57**): pp. 749-762.
- [3] M. Twigg. *Catalyst Handbook*. Wolfe Publishing. London 1989.
- [4] Y. Seo, A. Shirley and S. Kolaczkowski. Evaluation of thermodynamically favorable operating conditions for production of hydrogen in three different reforming technologies. *Journal of Power Sources*. 2002, (**108**): 213-225.
- [5] D. Truyen, et al. Catalytic coatings on stainless steel prepared by sol-gel route. *Thin Solid Films*. 2006, (**495**): 257-261.
- [6] R. Charlesworth. The steam reforming and combustion of methane on micro-thin catalyst for use in a catalytic plate reactor. *Ph D thesis*, Newcastle University, UK, 1996.
- [7] M. Babovic. Enhanced heat transfer to endothermic reactions by catalytic combustion in small channels. *Ph D thesis*, Newcastle University, UK, 2003.
- [8] M. Nakoua. Syngas production processes on thin film catalysts for use in catalytic plate reactors, *Ph D thesis*, Newcastle University, UK, 2004.
- [9] A. A Mirzaei, et al. A silica supported Fe–Co bimetallic catalyst prepared by the sol/gel technique: Operating conditions, catalytic properties and characterization. *Fuel Processing Technology*. 2010, (**91**):pp. 335-347.
- [10] Sasol, “High purity dispersible aluminas-Disperal/Dispala” Accessed April 2010, http://www.sasoltechdata.com/tds/DISPERAL_DISPALA.pdf
- [11] M. Al Nakoua, M. El-Naas, and B. Abu-Jdayil. Preparation and Testing of Sol-Gel Catalysts in a Plate Reactor. *Fuel Processing Technology*. 2011, (**92**):pp. 1836-1841.
- [12] R. Augustine. *Heterogeneous catalysis for the synthetic chemist*. Marcel Dekker, INC. New York, 1996.