

## METHYL CHLORIDE VIA OXYHYDROCHLORINATION OF METHANE

B.M. Naasz, J.S. Smith, A.I. Toupadakis, C.G. Knutson, R.F. Jarvis, and B.R. Crum  
Dow Corning Corporation  
U.S. Hwy 42  
Carrollton, KY 41008

Keywords: oxyhydrochlorination, methyl chloride, selective chlorination

### INTRODUCTION

The historical aspects of oxyhydrochlorination of hydrocarbons began in the 1920's. Roka in 1923 first achieved the oxyhydrochlorination of methane with chlorine in the presence of oxygen. The bulk of the original work in oxyhydrochlorination was published in the 1940's and 1950's. A collection of papers and patents by Gorin, Hirschkind, Randall, Fontana, Joseph, and Pye are listed in references 1-9. An excellent review of oxyhydrochlorination catalysis through the end of the 1960's was written by Allen and Clark<sup>10</sup>. An additional review by Kenney<sup>11</sup> is helpful on the subject of catalytic melts.

There are several key technology challenges associated with the development of a  $\text{CH}_4$  oxyhydrochlorination process. Among these are the chemistry problems associated with development of a selective  $\text{CH}_3\text{Cl}$  catalyst, and in addition, the chemical engineering challenges associated with the operation of a process containing  $\text{HCl}$  and  $\text{CH}_3\text{Cl}$ . This paper describes effort toward the goal of developing this technology by working on both the chemical and the engineering challenges in a parallel and linked effort.

### RESULTS

Figure 1 shows the process chemistry that is operative in the oxyhydrochlorination (OHC) of  $\text{CH}_4$ . As is shown, this complex system is a mixture of chlorination and combustion reactions that are particularly challenging to control due to the consecutive nature of the reaction kinetics. The thermodynamics of these chemistries dictate the formation of the equilibrium favored  $\text{CCl}_4$  as well as heavily oxidized byproducts. In addition, kinetic measurements, done both as part of our research and published previously,<sup>12</sup> show that the kinetics of chlorination also favor a fast succession of chlorination steps to the deeply chlorinated chloromethanes. Because of these facts, neither the kinetics or the thermodynamics of this chemical reaction system are driving this system to selective formation of  $\text{CH}_3\text{Cl}$ .

In addition to the kinetic and thermodynamic factors disfavoring monochlorination reactions, another thermodynamic problem exists. The measured apparent activation energies for combustion reactions of methane are significantly higher than those for the chlorination reactions. For reactant  $\text{CH}_4$ , the reaction to form  $\text{CH}_3\text{Cl}$  has an activation energy of 121 kJ/mol, this compares with 225 and 240 to form  $\text{CO}$  and  $\text{CO}_2$  respectively. Clearly this dictates that the selectivity can be expected to be a function of temperature to a fairly significant extent, with higher temperatures favoring  $\text{CO}$  and  $\text{CO}_2$  as a product. To compound this situation the heats of reaction for the combustion chemistries are significantly higher and as such any increase in temperature without an associated increase in heat transfer capability will likely add to the non-isothermal reactor profile that is common in laboratory experiments.

This rather straightforward analysis shows that the ideal condition for limiting the combustion side reaction will be one with adequate heat transfer capability to remove the heat of reaction. Thus, the ideal system will likely be an isothermal reactor. This key fact has been central in determining both our reactor design, and accordingly, our catalyst activity.

Figure 2 depicts the overall OHC process schematic for the oxyhydrochlorination of  $\text{CH}_4$ . Without question the two most challenging unit operations are the reactor and the reactor effluent separation system. As such, it is these two unit operations that will be evaluated in the process development unit that is currently under construction.

Definition of the separation unit operation was a key technical challenge in this project effort. Many different methods of product separation were evaluated. All indirect cooling methods looked both technically and economically non-feasible. The large amount of non-condensable gas simply made the separation impossible. Pressure Swing Adsorption was evaluated on paper as a possible alternative method for use in this application. While technically feasible, the economics of this method were unacceptable. It became clear that a

direct contact absorption followed by a steam stripping operation was the only acceptable route to recover the product  $\text{CH}_3\text{Cl}$ . The potential of this approach was highly dependent on the identification of an appropriate process solvent.

The key requirements for the OHC process solvent are low volatility, strong absorption characteristics for  $\text{C1}$  chlorocarbons, resistance to  $\text{HCl}(\text{aq})$ , insolubility with  $\text{H}_2\text{O}$ , stability over temperature range of  $-20$  C to  $180$  C, and preferably a low viscosity.

The approach used to identify this solvent was fairly empirical. A great deal of information was gathered on potential process solvents. Once this database was put together a list of potential solvents was identified and procured. A series of  $\text{CH}_3\text{Cl}$  single component saturation experiments was performed. Solvents that showed some promise were then evaluated for stability in acid. Finally, multicomponent absorption studies were performed on several potential candidates. An appropriate solvent has been identified.

The development of a highly selective OHC catalyst is a parallel objective to the process development described above. Several key catalysts have been described in the recent literature<sup>13,14,15,16</sup> regarding selective catalysis of the OHC reaction to  $\text{CH}_3\text{Cl}$ . The primary catalytic metals reported to be useful for the OHC reaction of  $\text{CH}_4$  are Cu and Fe, with the PETC group also reporting the use of Co as a selectivity enhancing catalyst<sup>16</sup>. Our work has primarily focused on the optimization of a Cu based catalyst.

Figure 3 shows an overview of the published results as well as previously unpublished Dow Corning results for Cu oxyhydrochlorination catalysts. This data represents a wide range of residence times, fluid velocities, stoichiometries and temperatures. The box with a lower left corner at 20%  $\text{CH}_4$  conversion and 80%  $\text{CH}_3\text{Cl}$  selectivity represents the desired range of operation for this technology. As is shown, only the single point represented by the British Petroleum patent<sup>14</sup> is currently in this desired range. However, all three other groups have data that is very close to this range.

Two key elements of catalyst development have been the focus of recent effort in this project. The first is to establish the deleterious impact of excess heat upon the product distribution. As shown earlier, the ability to control the combustion side reactions should be a key area in increasing the selectivity of the reaction. Figure 4 shows the internal bed temperature for two different Cu on silica catalysts. These data, taken under identical conditions by a thermocouple inserted directly into the catalyst bed, show quite clearly the extent of exotherm possible if a catalyst with too high of an activity is used without adequate heat transfer capability to remove the large heat of reaction. Note that Dow Corning catalyst #535 gives a nominally flat profile over 145 hours of reaction. By comparison, a PETC catalyst with very high Cu loading gives an exotherm of about 200 C over baseline conditions. A correlating degradation of selectivity was noted.

An additional verification of the impact of temperature upon selectivity is shown in Figure 5. In this case a Cu on  $\text{Al}_2\text{O}_3$  catalyst was evaluated with a feed stoichiometry of 4.4/1/1.2  $\text{CH}_4/\text{O}_2/\text{HCl}$ . The  $\text{CH}_3\text{Cl}$  and  $\text{CH}_2\text{Cl}_2$  selectivities as well as the  $\text{CO}_x$  (oxygenated products) selectivity and  $\text{CH}_4$  conversions are given by the Y axis. The X axis denotes reaction time. This reaction was conducted at a constant temperature of 340 C for 20 hours. At this point the temperature was lowered 5 C to 335 C. Note that the  $\text{CH}_4$  conversion changed only very slightly, indicating that for this system a reactor temperature of 340 C was not necessary to obtain the target 20% conversion. The very interesting result however is that the  $\text{CO}_x$  products dropped from 18% to 8%. This was accompanied by a rise in the  $\text{CH}_3\text{Cl}$  selectivity from 68% to 78%. This is a fairly clear indication that the excess heat was serving only to further react product  $\text{CH}_3\text{Cl}$  via combustion to CO and  $\text{CO}_2$ .

The second key catalyst development issue is stability. A key reason for the use of very high metal loadings for some of the published catalysts is the fact that these catalysts deactivate, primarily via Cu loss. The technical approach followed in the current catalyst development was to establish the minimum amount of Cu necessary to maintain adequate activity and develop a mechanism to stabilize the catalyst. A series of experiments were performed to establish the impacts of several promoters that might be used to enhance the stability of these Cu catalysts. A simple Cu on  $\text{SiO}_2$  catalyst that was not promoted in any way was first evaluated. The conditions used were a reaction temperature of 340 C, stoichiometry of  $\text{CH}_4/\text{O}_2/\text{HCl}$  4/1/1.3. The overall activity of this catalyst was very low with a  $\text{CH}_4$  conversion of about 5%. Clearly this catalyst, with about 2% Cu loading, did not possess adequate activity to provide the targeted 20%  $\text{CH}_4$  under these reaction conditions.

In a subsequent experiment, a promoter was added to the this Cu catalyst system. The activity increased to an initial value of about 20%, but declined over a period of 180 hours to less than half of the original activity. The reaction conditions were identical. The catalyst was the same with the promoter added by sequential impregnation. The Cu loading on the catalyst remained the same. This is a strong indication that large loadings of Cu are not necessary to yield an active OHC catalyst.

Figure 6 shows the impact of adding another promoter sequentially. In this case the activity again started at about 20% CH<sub>3</sub> conversion, but declined very slightly and was still about 17% after 180 hours of experimentation. This series of sequential impregnations shows the apparent strong impact that key promoters can have on the stability of Cu oxyhydrochlorination catalysts. The data indicates that a relatively low loading Cu OHC catalyst may be able to be modified by the appropriate promoters to have sufficient long term stability.

## CONCLUSIONS

Recent effort on the development of a commercially feasible oxyhydrochlorination route to CH<sub>3</sub>Cl has dealt with a variety of technical challenges. Work has proceeded on the engineering development of a process demonstration unit to evaluate the process. Several technical development issues have been associated with this development. The results from our work on these issues over the past year have been two fold. First, a laboratory scale demonstration was initiated of a product recovery system that has the potential to solve the engineering challenge of removing the product CH<sub>3</sub>Cl from the large amount of non-condensable gases that are in the reactor effluent. This is an unavoidable situation in this relatively low conversion process. This recovery process is the key economic driver in process capital expenditure. This system will be demonstrated at the process demonstration unit scale.

Second, a promoted Cu based catalyst system with sufficient metal loading to achieve the desired activity was demonstrated. The technical advance with this catalyst is that it is a low metal loading catalyst. This has the impact of restricting the catalyst activity to the desired amount is to limit the selectivity and deactivation problems associated with the large exotherms found while using high metal loading catalysts under the conditions necessary for realistic process operation. It is of clear benefit to use the lower metal loading as long as necessary activity can be demonstrated and sustained. Future work will focus on long term stability improvements for this new catalyst.

## ACKNOWLEDGEMENTS

The authors would like to acknowledge the following individuals for their valuable assistance in this work: Steve Freeburne, Bob Smith, Wayne Ellegood, and David Miller. In addition the a special thanks to Bruce Crum who performed a significant portion of the laboratory work cited in this paper.

This work was supported by the Pittsburgh Energy Technology Center under DOE contract #DE-AC22-91PC91030 and by the Gas Research Institute under contract #5091-222-2300. The author's would like to also thank Texas Gas Transmission Company for their contributions supporting this effort.

## REFERENCES

1. E. Gorin et. al., *Ind. Eng. Chem.*, **40**(11), (1948), 2128.
2. W. Hirschkind, *Ind. Eng. Chem.*, **41**(12), (1949), 2749.
3. C.M. Fontana, et. al. , *Ind. Eng. Chem.*, **44**(2), (1952), 395.
4. U.S. Patent 2,488,083 to E. Gorin, et.al., Socony Vacuum Oil, Nov.15, 1949.
5. U.S. Patent 2,493,546 to E. Gorin, Socony Vacuum Oil, Feb. 21, 1950.
6. U.S. Patent 2,547,139 to M. Randall, Apr. 3, 1951.
7. U.S. Patent 2,575,167 to C.M. Fontana, et.al., Socony-Vacuum Oil, Nov.13, 1951.
8. U.S. Patent 2,752,401. To W.J. Joseph, Dow Chemical, June 26, 1956.
9. U.S. Patent 2,752,402 to D.J. Pye, Dow Chemical, June 26, 1956.
10. J.A. Allen and A.J. Clark, *Rev. Pure and Appl. Chem.*, **21**(1971)145.
11. C.N. Kenney, *Catal-Rev. - Sci. Eng.* **11**(2), (1975) 197.
12. Y.A. Treger and V.N. Rozanov, *Uspekhi Khimii*, Vol. 58 (1), (1989), pp. 138-164.
13. U.S. Patent 4,769,504. To R.D. Noceti, et.al., 06 Sept. 1988.
14. Int. Patent WO 84/ 03277. To J. Bromhead, Aug. 30, 1984.
15. V.N. Rozanov, *Khim. Prom.-st.*, **2**, (1989) , 495.
16. Taylor, C.E. and Noceti, R.P., *Proc. Int. Cong. Cat.*, **2**, 990, (1988).

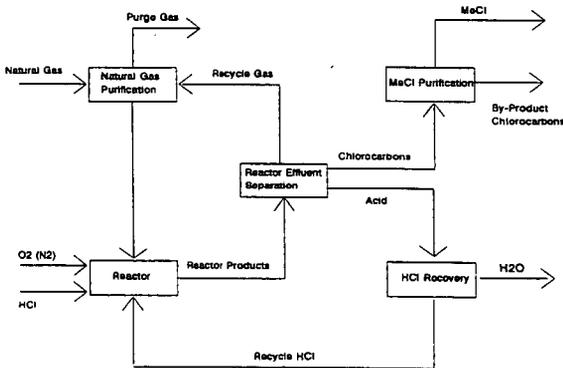
# Figure 1

## Major Reaction Pathways

- Chlorination Reactions
  - $\text{CH}_4 + 1/2 \text{O}_2 + \text{HCl} \longrightarrow \text{CH}_3\text{Cl} + \text{H}_2\text{O}$
  - $\text{CH}_3\text{Cl} + 1/2 \text{O}_2 + \text{HCl} \longrightarrow \text{CH}_2\text{Cl}_2 + \text{H}_2\text{O}$
  - $\text{CH}_2\text{Cl}_2 + 1/2 \text{O}_2 + \text{HCl} \longrightarrow \text{CHCl}_3 + \text{H}_2\text{O}$
- Combustion Reactions
  - $\text{CH}_4 + 3/2 \text{O}_2 \longrightarrow \text{CO} + 2 \text{H}_2\text{O}$
  - $\text{CH}_4 + 2 \text{O}_2 \longrightarrow \text{CO}_2 + 2 \text{H}_2\text{O}$
  - $\text{CH}_3\text{Cl} + \text{O}_2 \longrightarrow \text{CO} + \text{H}_2\text{O} + \text{HCl}$
  - $\text{CH}_3\text{Cl} + 3/2 \text{O}_2 \longrightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{HCl}$
- Deacon Chemistry
  - $2 \text{HCl} + 1/2 \text{O}_2 \longrightarrow \text{Cl}_2 + \text{H}_2\text{O}$

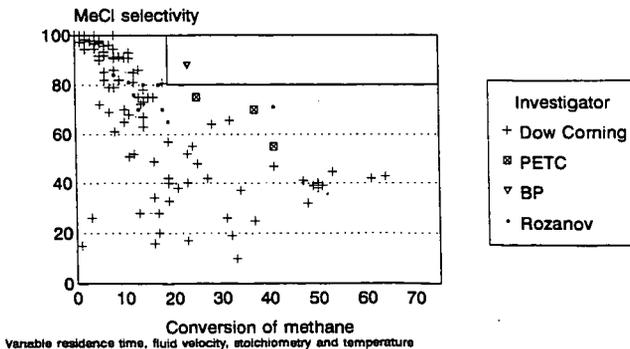
# Figure 2

## OHC PROCESS BLOCK FLOW DIAGRAM



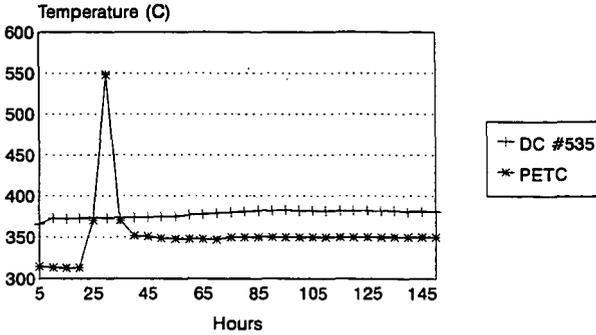
# Figure 3

## OHC Catalyst Evaluations



# Figure 4

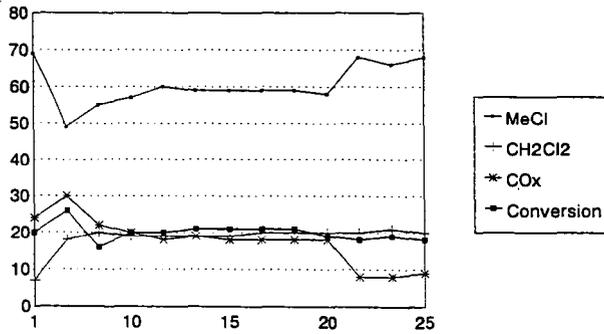
Comparison of Internal Packed Bed Temperatures



Catalyst Comparison

# Figure 5

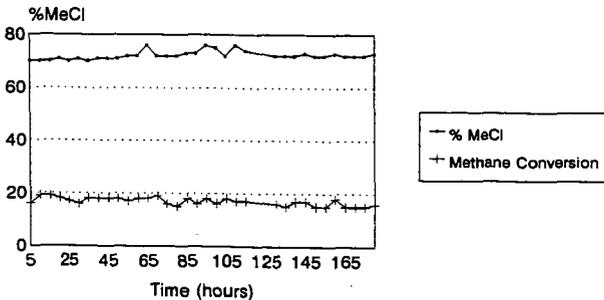
Impact of Reaction Temperature upon Selectivity



Stoichiometry 4.4/1/1.2 CH<sub>4</sub>/O<sub>2</sub>/HCl

# Figure 6

Promoted OHC Catalyst with Increased Stability



Catalyst #538D, Temperature 340 C  
 Stoichiometry CH<sub>4</sub>/O<sub>2</sub>/HCl 4:1:1.3  
 Experiment 11046009

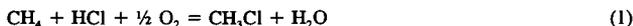
## PRESSURE EFFECTS ON THE OXYHYDROCHLORINATION OF METHANE

Mark A. McDonald and Michael F. Zaroachak  
Pittsburgh Energy Technology Center  
U. S. Department of Energy, P. O. Box 10940  
Pittsburgh, PA 15236  
and  
William J. Graham  
Gilbert Commonwealth  
P. O. Box 618  
Library, PA 15129

**KEYWORDS :** Methane, Natural gas, liquid fuels, chlorination

### INTRODUCTION

A process, developed at PETC, uses a two-step approach for converting methane to liquid fuels<sup>1</sup>. In the first step, methane is oxyhydrochlorinated to chloromethane:



In the second step, the chloromethane is oligomerized on a zeolite catalyst such as ZSM-5, producing hydrocarbons and regenerating the HCl:



The net result of these two process steps is similar to that of oxidative coupling/oligomerization processes, the oxidation of methane to heavier hydrocarbons and water<sup>2</sup>.

Several publications have described work done at atmospheric pressure on the two steps in this process<sup>3,4</sup>. We report oxyhydrochlorination activity and selectivity data for the copper catalyst used in the previous work, but at higher pressures. These data provide a firmer basis for feasibility studies of various technologies for methane conversion<sup>2</sup>.

### EXPERIMENTAL METHODS

Flow rates of CH<sub>4</sub>, HCl, O<sub>2</sub>, and N<sub>2</sub> were controlled by means of Tylan mass flow controllers. Gases were mixed and passed over a bed of powdered catalyst in a tubular reactor. The method of catalyst preparation has been described in detail elsewhere<sup>5,6</sup>. Analysis of this dried catalyst precursor yielded a composition that can be expressed as 41.7% CuCl, 11.5% KCl, 9.4% LaCl<sub>3</sub>, and 37.5% SiO<sub>2</sub><sup>4</sup>. Pressure was regulated by means of a Badger research control valve downstream of the reactor. All lines between the reactor entrance and the scrubber were heat-traced. The system required special materials; the considerations required to construct and operate the reactor are discussed elsewhere<sup>7</sup>.

The primary method of product analysis was gas chromatography. The Hewlett-Packard 5730 gas chromatograph was equipped with dual packed columns and thermal conductivity detectors. Light gases (H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, and CO) were analyzed with a 3A molecular sieve column and an argon carrier gas. Chloromethanes and CO<sub>2</sub> were analyzed with a Chromosorb 102 column and a helium carrier gas. Water and HCl were analyzed with an Extrel C60 mass spectrometer fitted with a fused-silica inlet.

Fresh catalyst samples were pretreated for 0.5 h in 50 sccm of HCl at 573 K. A typical day's operation gave results at three different experimental conditions, after which the catalyst was regenerated for use the following day in 100 sccm of flowing H<sub>2</sub> at 543 K for 0.5 h. Catalyst tests were typically carried out for a maximum of five days.

The N<sub>2</sub> BET surface area of a pretreated catalyst was determined with a Coulter Omnisorp 100 CX unit. Catalyst activity is reported as nominal site-time yield (STY), molecules of methane converted per catalyst surface atom per second, based on the total surface area determined from this BET area and assuming 1·10<sup>19</sup> catalyst surface atoms per m<sup>2</sup> BET area. Active catalyst surface atoms were not titrated, so the site-time yield values reported are likely to be lower limits to the values based on measurement of a specific surface area.

## RESULTS

The BET surface area of the pretreated catalyst was 88 m<sup>2</sup>g<sup>-1</sup>, in contrast to the value of 325 m<sup>2</sup>g<sup>-1</sup> for the pure Cab-O-Sil. Table 1 shows catalyst yield and selectivity data for relative compositions of 5:2:1 CH<sub>4</sub>:HCl:O<sub>2</sub>. The sevenfold increase in overall pressure increased the site-time yield values by less than a factor of four. An Arrhenius plot of nominal site-time yield values is shown in Figure 1. The slopes for the data in Figure 1 yield apparent activation energies of 171 to 186 kJ mol<sup>-1</sup>.

Figures 2 and 3 show selectivity to carbon-containing products as a function of temperature. At low pressure (Figure 2), selectivity to carbon dioxide and to chloromethanes, defined as the sum of selectivities to chloromethane, dichloromethane, and trichloromethane, was unaffected by temperature. (No tetrachloromethane was detected in any experiment.) However, the overall selectivity to chloromethane decreased with increasing temperature, as conversion to dichloromethane and trichloromethane increased. The intermediate pressure data in Figure 3 show more complex behavior; as temperature increased, conversion to carbon dioxide was constant within experimental error, overall conversion to chloromethanes decreased, and conversion to carbon monoxide jumped above 600 K. This drop in selectivity to chloromethane was apparently the result of the increase in conversions that accompanied the temperature increase; higher conversion clearly favors continued oxyhydrochlorination of chloromethane to dichloromethane and then to trichloromethane.

Although the tubular reactor was not appropriate for determination of detailed kinetic parameters, reaction orders were estimated at 510 kPa and 593 K. This was done by measuring site-time yield values for a given reaction composition at several different WHSV, plotting these values versus (WHSV)<sup>-1</sup>, then taking the y-intercept of each of these plots as the initial rate. This process was repeated for several different compositions and a power-law fit was obtained. The reaction orders obtained for methane conversion are described by the following expression:

$$r \propto [\text{CH}_4]^{0.8} [\text{HCl}]^{0.4} [\text{O}_2]^{0.2} \quad (3)$$

This approach does not account for dependence on product or other species.

## DISCUSSION

The yields reported here are consistent with previous work done at atmospheric pressure with this catalyst. Taylor *et al.*<sup>4</sup> reported CH<sub>4</sub> conversion at 604 K that converts to a STY value of 0.18 · 10<sup>-3</sup> s<sup>-1</sup>. Although this value is at least a factor of four lower than the values reported in Table 1, their results were obtained with a lower CH<sub>4</sub> concentration in the feed (a stoichiometric 2:2:1 CH<sub>4</sub>:HCl:O<sub>2</sub> was used) and at generally higher CH<sub>4</sub> conversions. When

adjusted for the higher concentrations of  $\text{CH}_4$  present in our work, the STY values differ by less than a factor of two.

The selectivity trends do not agree nearly as well. Taylor *et al.* did find the same trends in chloromethane yield, and  $\text{CH}_4$  conversion to oxygen-containing products increased as temperature and conversion increased. However, the nature of these oxygen-containing products differed; Taylor *et al.* observed mainly  $\text{HCOOH}$  at intermediate conversion levels and mainly  $\text{CO}_2$  at highest conversions and saw no  $\text{CO}$ . In contrast to their work and also to results of Conner *et al.*<sup>8</sup>, we saw no  $\text{HCOOH}$  in any experiment, even with the same mass spectrometric analysis of reaction products.

This discrepancy may be explained by noting the relative ease of  $\text{HCOOH}$  decomposition and the differences in the reaction systems involved. The  $\text{HCOOH}$  molecule is known to decompose on reduced nickel surfaces at ca. 400 K<sup>9</sup>, roughly the same temperatures used in heat tracing the reactor exit lines and substantially below temperatures in the reactor. Very little exposed metal surface in the coated nickel alloy tubing and fittings in the reactor would be required to decompose formic acid produced by the catalyst. Although blank tests showed no significant activity for reactions of  $\text{CH}_4$ , side reactions of any product  $\text{HCOOH}$  could have occurred. In contrast, Taylor *et al.* used a quartz reactor and PTFE tubing, which do not catalyze  $\text{HCOOH}$  decomposition.

## CONCLUSION

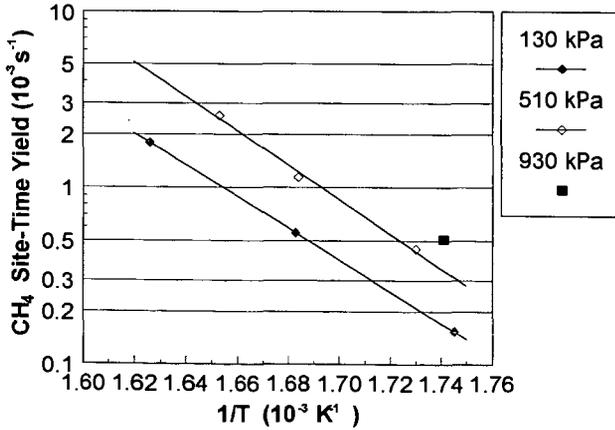
The oxyhydrochlorination yield of a 5:2:1 ratio of  $\text{CH}_4$ : $\text{HCl}$ : $\text{O}_2$  increased over threefold as pressure increased from 130 to 930 kPa. This increase was accompanied by a decrease in selectivity to  $\text{CH}_2\text{Cl}$ , and an increase in dichloromethane and trichloromethane. Oxidation was not favored and never accounted for more than 20% of the methane converted. Carbon dioxide was the major oxidation product, accounting for 2-6% of methane converted. No product  $\text{HCOOH}$  was observed, likely due to  $\text{HCOOH}$  decomposition on the walls of the reactor upstream of the product analysis.

## REFERENCES

1. Noceti, R.N. & Taylor, C.E., U. S. Patent 4,769,504, 1987.
2. Fox, J.M., Chen, T.P., & Degen, B.D. *Chem. Engr. Prog.* **86**, 42 (1990).
3. Taylor, C.E. & Noceti, R.N. *Preprints, Am. Chem. Soc., Div. Fuel Chem.* **32**, 307 (1987).
4. Taylor, C.E., Noceti, R.N. & Schehl, R.R. in *Methane Conversion* (eds. Bibby, D.M., Chang, C.D., Howe, R.F. & Yurchak, S.) 483 (Elsevier, Amsterdam, 1988).
5. Pieters, W.J.M., Carlson, E.J., Gates, W.E. & Conner, W.C., Jr., U. S. Patent 4,123,389, 1978.
6. Pieters, W.J.M., Conner, W.C., Jr. & Carlson, E.C. *Appl. Catal.* **11**, 35 (1984).
7. McDonald, M.A., Zaroachak, M.F. & Graham, W.J. *Chem. Eng. Sci.*, in preparation.
8. Conner, W.C., Jr., Pieters, W.J.M., Gates, W. & Wilkalis, J.E. *Appl. Catal.* **11**, 49 (1984).
9. Iglesia, E. & Boudart, M. *J. Catal.* **81**, 224-238 (1983).

**Table 1. Catalyst Activity and Selectivity**

|   |      |      |      |      |      |      |      |
|---|------|------|------|------|------|------|------|
| T (K)   | 573  | 594  | 615  | 578  | 594  | 605  | 574  |
| P (kPa)   | 130  | 130  | 130  | 510  | 510  | 510  | 930  |
| WHSV  | 1.76 | 3.29 | 3.29 | 2.72 | 5.07 | 5.25 | 7.01 |
| <b>Inlet concentration (%)</b>  |      |      |      |      |      |      |      |
| N <sub>2</sub>  | 11.1 | 5.9  | 5.9  | 11.1 | 5.9  | 8.6  | 5.9  |
| HCl   | 22.2 | 23.5 | 23.5 | 22.2 | 23.5 | 22.9 | 23.5 |
| CH <sub>4</sub>   | 55.6 | 58.8 | 58.8 | 55.6 | 58.8 | 57.1 | 58.8 |
| O <sub>2</sub>  | 11.1 | 11.8 | 11.8 | 11.1 | 11.8 | 11.4 | 11.8 |
| Nominal Site-Time Yield CH <sub>4</sub> (10 <sup>-3</sup> s <sup>-1</sup> ) | 0.15 | 0.56 | 1.79 | 0.45 | 1.14 | 2.55 | 0.51 |
| Apparent activation energy (kJ mol <sup>-1</sup> )                          | 171  |      |      | 186  |      |      | ---- |
| <b>Conversions (%)</b>  |      |      |      |      |      |      |      |
| CH <sub>4</sub>   | 2    | 3.8  | 11   | 3.8  | 4.6  | 9.5  | 1.5  |
| HCl   | 2    | 3.6  | 13   | 3.9  | 4.9  | 11   | 1.5  |
| O <sub>2</sub>  | 14   | 24   | 69   | 22   | 30   | 69   | 8.9  |
| <b>Selectivities (%)</b>  |      |      |      |      |      |      |      |
| Chloromethane   | 95   | 93   | 83   | 88   | 88   | 66   | 92   |
| Dichloromethane   | 3    | 5    | 12   | 9    | 8    | 12   | 2    |
| Trichloromethane  | 0    | 0    | 1    | 0    | 0    | 5    | 0    |
| Carbon dioxide  | 2    | 2    | 3    | 3    | 4    | 4    | 6    |
| Carbon monoxide   | 0    | 0    | 0    | 0    | 0    | 13   | 0    |



**Figure 1. Arrhenius Plot**

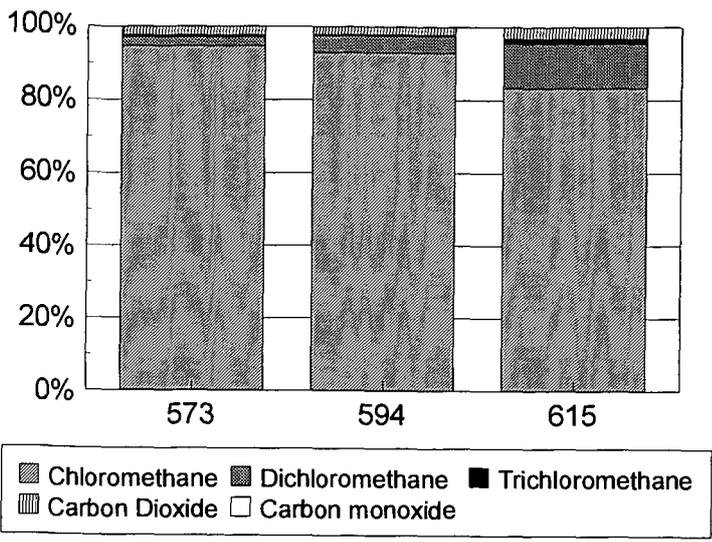


Figure 2 Selectivities at 130 kPa

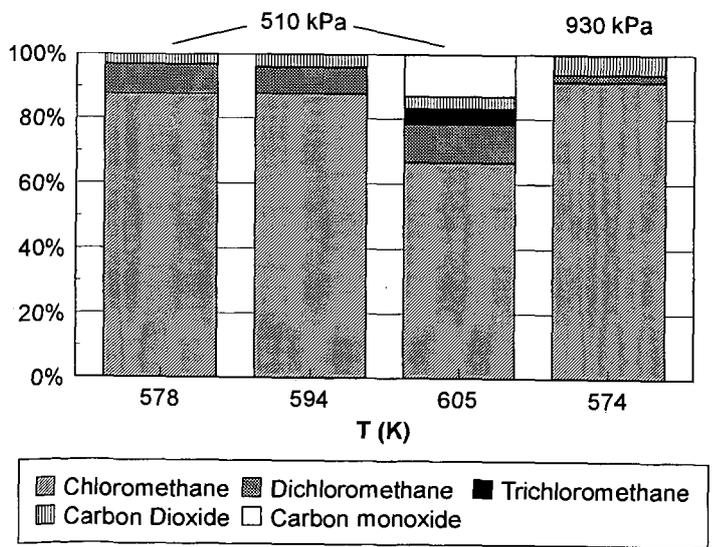


Figure 3 Selectivities at 510 and 930 kPa

## BIOMIMETIC CATALYST DEVELOPMENT FOR NATURAL GAS CONVERSION

Margaret C. Showalter, John A. Shelnett  
Fuel Science Department, Sandia National Laboratories  
P.O. Box 5800  
Albuquerque, NM 87185-0710

Craig J. Medforth  
Department of Chemistry  
University of California  
Davis, CA 95616

J. Martin E. Quirke  
Department of Chemistry  
Florida International University  
Miami, FL 33199

**Keywords:** alkane oxidation, metalloporphyrins, computer aided molecular design (CAMD)

### INTRODUCTION

Enzymes such as cytochrome P<sub>450</sub> are known to catalyze difficult reactions including the partial oxidation of unactivated alkanes to alcohols. We are using computer aided molecular design (CAMD) in conjunction with activity testing to develop biomimetic catalysts for the oxidation of light alkanes. Our stepwise approach to catalyst development involves first using CAMD to design and model potential metalloporphyrin catalysts, followed by synthesis and characterization of promising catalysts, and finally utilizing our catalysts in bench scale oxidation reactions. The information gained in laboratory testing enables us to evaluate and refine our models, and thus continue to design catalysts which are incrementally better. We anticipate that this iterative approach will lead to the development of biomimetic catalysts which are active enough to use air for the conversion of natural gas to oxygenated products.

Metalloporphyrins have been shown to catalyze the oxidation of light alkanes with air or oxygen as the oxidant under mild conditions with no added co-reductant.<sup>1</sup> Prior work has indicated three beneficial properties of the metalloporphyrin catalysts. These activity-enhancing features are: (1) the presence of strongly electron-withdrawing substituent groups at the periphery of the porphyrin ring, (2) an axial ligand complex favoring the most negative Fe(III)/Fe(II) redox potential, and (3) steric restraints on close bimolecular face-to-face approach of catalyst molecules.<sup>1,2</sup> We have designed and synthesized, and are currently testing a series of catalysts, the fluorinated iron dodecaphenylporphyrins (FeF<sub>x</sub>DPP where x=0,20,28,36), with enhanced features (1) and (3), and with an additional feature -- a rigid cavity that promotes the binding of the substrate alkane molecule. Figure 1 shows the dodecaphenylporphyrin catalysts which are the subject of the current investigation.

### EXPERIMENTAL

Molecular mechanics calculations were carried out on Silicon Graphics workstations using POLYGRAF software and a metalloporphyrin forcefield developed previously.<sup>3</sup> The forcefield has been extensively validated for predicting metalloporphyrin structures and relative energies.<sup>3,4</sup> Iron(III) parameters were the same as those used previously<sup>4</sup>, and fluorine and oxygen parameters were taken from the DREIDING force field.<sup>5</sup>

Catalysts were tested for activity in the oxidation of isopentane with both iodobenzene (PhIO) and oxygen as the oxidants. Catalyst concentration is 1-100µM. In the PhIO reactions, substrate, catalyst, and oxidant are mixed in an organic solvent, usually benzene, at room temperature. In a typical experiment, substrate concentration is 2M and PhIO concentration is 50mM. For the oxygen reactions, a solution of substrate and catalyst in solvent is sealed into a bomb reactor in which all internal surfaces are coated in teflon. The bomb is then pressurized with oxygen and heated while stirring. In a typical experiment, substrate concentration is

2M, oxygen pressure is 100-200psi, and temperature is 100°C. Reaction products were analyzed by gas chromatography after 2-15 hours.

## RESULTS AND DISCUSSION

**Catalyst Design.** Electron withdrawing substituents at the periphery of an iron porphyrin oxidation catalyst have at least two beneficial effects.<sup>2</sup> First, such substituents may activate the high oxidation state metal-oxo intermediate thus increasing catalyst reactivity. Second, by removing electron density from the porphyrin ring, the substituents make the porphyrin macrocycle less susceptible to self-destruction by electrophilic attack by the oxo intermediate of the catalyst. Iron dodecaphenylporphyrin can be systematically fluorinated to give the catalyst series shown in Figure 1. An interesting feature of this catalyst series is that it allows us to study the effect of electron withdrawing groups in the absence of significant structural changes of the macrocycle. Computer modelling and spectroscopic characterization indicate that the series of FeF<sub>x</sub>DPP catalysts, where x=0,20,28,36, have essentially the same structure, thus any difference in activity should be due to electronic factors alone.

Molecular modeling studies show that the FeDPP catalysts have a rigid cavity formed by the porphyrin ring and the quasi-axial CH's and CF's of the phenyl substituents. The cavity is of the size and shape of small linear alkanes. Figure 2 shows the shape of FeF<sub>20</sub>DPP. This rigid cavity is predicted to improve catalyst activity and selectivity by providing a "microreactor" environment for the oxidation reaction. In addition, these bulky catalysts should be more stable than typical planar porphyrin catalysts.

Energy minimization and molecular dynamics calculations show that methane will bind to the cavity and remain for significant times even in a vacuum at temperatures up to and above room temperature. Substrate binding is partly a consequence of the rigidity of the binding cavity and the favorable electrostatic interaction between the light hydrocarbon and the fluorocarbon groups of the cavity. The presence of this light hydrocarbon binding cavity should enhance catalytic activity by increasing the residence time of the substrate at the active metal site. Radical trapping of the intermediates R· and ·OH in the cavity may also promote recombination to form the alcohol product, thus enhancing selectivity. Finally, ejection of the product upon formation is expected as a result of the repulsion of the alcohol oxygen atom by the fluorine atoms lining the pocket. This repulsive interaction between the product and the substrate binding cavity serves two purposes. First, it clears the cavity after the reaction has occurred for the next alkane molecule to enter; and second, it prevents further oxidation of the alcohol molecule. The former effect is expected to improve catalytic rates; the latter is expected to improve selectivity for alcohol versus other oxidation products (ketones, aldehydes).

Past work has shown that bulky substituents attached to the porphyrin which prevent close face-to-face approach of two porphyrin molecules increase the resistance of the porphyrin to bimolecular destruction.<sup>2</sup> In our highly substituted FeDPP catalysts, there is considerable steric hinderance to the face-to-face approach of two porphyrin macrocycles. The steric constraints on face-to-face interactions of the porphyrin molecules may also play a beneficial role in the reaction mechanism proposed by researchers at Sun Marketing and Refining Company.<sup>1</sup> In the proposed mechanism, adventitious impurity or the alkane itself reduces Fe to start the catalytic cycle. A peroxo-bridged dimer is formed and splits to give the reactive Fe(IV)=O intermediate. This ferryl intermediate subsequently reacts with the alkane (RH) to form the alcohol (ROH). A competing reaction of the ferryl intermediate is the formation of  $\mu$ -oxo porphyrin dimer, Fe(III)-O-Fe(III), which is less reactive with the alkane. Thus, steric hinderance of the formation of face-to-face  $\mu$ -oxo dimer is desirable, but formation of the peroxo dimer must still be favorable. Molecular modeling indicates that this is the case for the FeDPP catalysts as shown in Figure 3. The peroxo dimer, which should be able to form with the DPP catalysts, may however, be strained which could aid in the formation of the active ferryl (oxo) intermediate thus further enhancing catalytic activity.

**Catalyst Testing.** Initial experiments for testing our catalysts have been performed using either oxygen or iodossylbenzene (PhIO) as the oxidant and isopentane as the substrate. We have observed the predicted trend that as the number of fluorine substituents increases, so does the catalyst activity for the FeF<sub>x</sub>DPP series.

Figure 4 shows the correlation between catalyst activity and overall electron depletion of the porphyrin measured by  $\Sigma\sigma$ , the sum of the Hammett substituent constants. However, all of the designed catalysts were significantly less active than the commercial planar catalyst  $\text{FeF}_{20}\text{TPP}$  (TPP = tetraphenylporphyrin), despite the built in cavity or "microreactor" of the  $\text{FeDPP}$  catalysts. We are trying to develop a better understanding of this apparent low activity on the part of our designed catalysts.

We have observed that the number of catalyst turnovers in our partial oxidation test reactions is dependent upon a number of experimental parameters, including initial catalyst concentration, solvent, and temperature. We are currently determining optimum experimental conditions so that more meaningful catalyst activity comparisons can be made. In a related experiment, solutions of substrate and solvent with no catalyst,  $\text{FeF}_{20}\text{TPP}$ , or  $\text{FeF}_{20}\text{DPP}$ , were prepared and allowed to stand in the laboratory with air in the headspace. After 4 months, GC analysis showed that essentially no reaction had occurred in the control and  $\text{FeF}_{20}\text{TPP}$  vials. However, the  $\text{FeF}_{20}\text{DPP}$  had catalyzed the oxidation of isopentane to alcohols. This experiment indicates that under certain conditions, the  $\text{FeF}_{20}\text{DPP}$  catalyst may be more reactive than its planar  $\text{FeF}_{20}\text{TPP}$  counterpart. Work is in progress to further our understanding of these results.

Because the ultimate goal of this research is to develop catalysts for natural gas conversion, we have begun testing our catalysts with gaseous substrates. We have attempted the oxidation of isobutane by both oxygen and  $\text{PhIO}$  using our catalysts. Results indicate the same trends observed with isopentane. That is, as the number of fluorines in the DPP series increases so does the catalytic activity. Again  $\text{FeF}_{20}\text{TPP}$  is more active than all of the  $\text{FeDPP}$ 's toward the production of alcohols under the reaction conditions employed. However, unlike the isopentane experiments which were "clean" (the only significant products were alcohols), additional products were produced in the isobutane experiments. We are currently working to identify and quantitate these additional reaction products so that we can more accurately evaluate and compare our catalysts. We are also working on modified reactor configurations and sample handling techniques so that we may also test our catalysts with the  $\text{C}_1\text{-C}_3$  hydrocarbons.

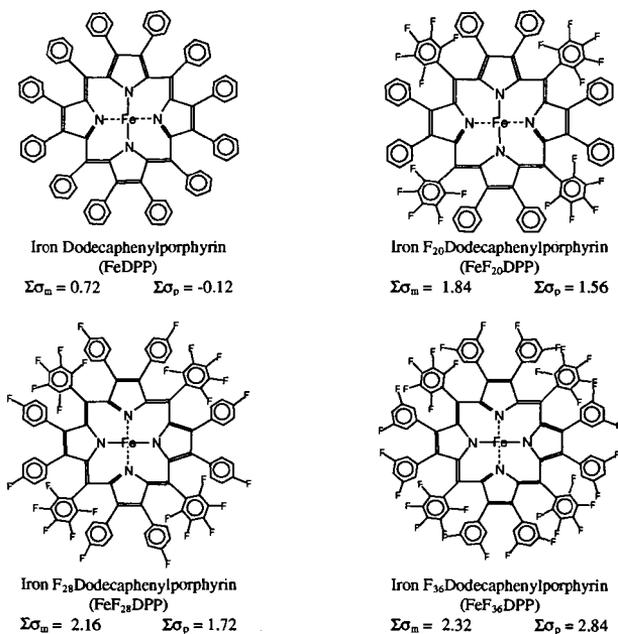
*Future Work.* In addition to continuing our catalyst testing to more adequately characterize and understand the current series of  $\text{FeDPP}$  catalysts, we are designing and synthesizing other highly substituted porphyrin catalysts. Synthesis of the fully fluorinated  $\text{FeF}_{20}\text{DPP}$  is in progress. This catalyst will complete the fluorinated DPP series and is expected to be more active than all those tested so far. In addition, we are developing other dodecaphenyl substituted porphyrin catalysts in which groups such as Cl or  $\text{NO}_2$  are substituted on the phenyl rings. We are also developing a new class of catalysts, the substituted octaphenylporphyrins ( $\text{FeOPP}$ ). These catalysts will allow us to substitute electron withdrawing groups directly on the porphyrin macrocycle at the meso positions. An example of this type of catalyst is iron octaphenyl *meso*-tetranitro porphyrin. However, while some of the substituted OPP catalysts are nonplanar, they do not have the deep, rigid binding cavity of the DPP catalysts.

## CONCLUSIONS

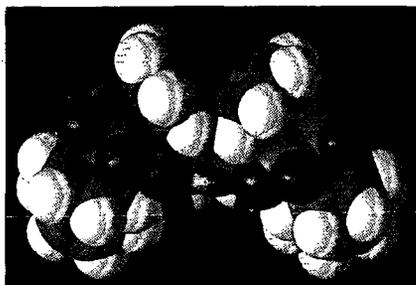
CAMD has been used to design a novel series of alkane oxidation catalysts, the fluorinated iron dodecaphenylporphyrins. Designed features in these catalysts include the systematic variation of the number of fluorine substituent across the series and a rigid binding cavity common to all catalysts in the series. Catalyst activity testing is underway for this series of catalysts. Results thus far indicate that catalytic activity does increase as the degree of fluorination increases. However, under the experimental conditions utilized, the overall activity of the catalysts is lower than expected. Further work is in progress to more adequately characterize the activity of this novel series of catalysts.

LITERATURE CITED

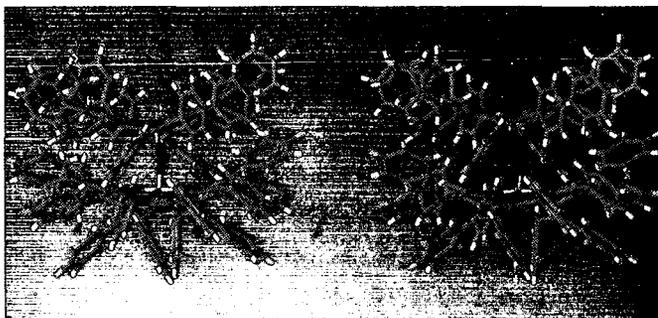
- (a) Paulson, D.R.; Ulman, R.; Soane, R.B.; Closs, G.L. *J. Chem. Soc. Chem. Comm.* **1974**, 186. (b) Ellis, Jr., P. E.; Lyons, J. E., *Symp. Oxygen Activation in Catalysis*, ACS, April 22-27, 1990. (c) Ellis, Jr., P. E.; Lyons, J. E. *Coord. Chem. Rev.* **1990**, *105*, 181-193.
- Nappa, M. J.; Tolman, C. A. *Inorg. Chem.* **1985**, *24*, 4711-4719.
- Shelnutt, J.A.; Medforth, C.J.; Berber, M.D.; Barkigia, K.M.; Smith, K.M. *J. Am. Chem. Soc.* **1991**, *113*, 4077-4087.
- Sparks, L.D.; Medforth, C.J.; Park, M.S.; Chamberlain, J.R.; Ondrias, M.R.; Senge, M.O.; Smith, K.M.; Shelnutt, J.A. *J. Am. Chem. Soc.* **1993**, *115*, 581-592.
- Mayo, S.L.; Olafson, B.D.; Goddard, W.A., III *J. Phys. Chem.* **1990**, *94*, 8897-8909.



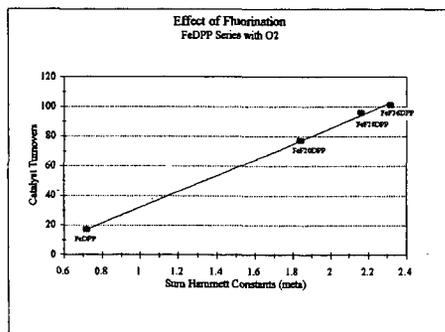
**Figure 1.** Structures of the catalysts in the fluorinated iron dodecaphenylporphyrin series.  $\Sigma\sigma$  is the sum of the Hammett substituent constants (shown for both meta and para), which is used as a measure of the overall electron depletion of the metal center.



**Figure 2.** Energy minimized structure of FeF<sub>20</sub>DPP showing the rigid binding cavity.



**Figure 3.** Calculated structures of the  $\mu$ -oxo (left) and peroxy- (right) dimers of a fluorinated dodecaphenylporphyrin. Calculated energies predict that the active peroxy-dimer is energetically favored, but the inactive  $\mu$ -oxo-dimer is unfavored by greater than 50kcal/mol.



**Figure 4.** Plot showing the correlation between catalyst activity and electron depletion of the metal center, measured by  $\Sigma\sigma$ , for the FeDPP catalyst series.

GAS-TO-LIQUIDS RESEARCH PROGRAM OF THE U.S. DEPARTMENT OF ENERGY  
A PROGRAMMATIC OVERVIEW

Arun C. Bose and Gary J. Stiegel  
U.S. Department of Energy  
Pittsburgh Energy Technology Center  
Pittsburgh, PA 15236

and

Rameshwar D. Srivastava  
Burns and Roe Services Corporation  
Pittsburgh Energy Technology Center  
Pittsburgh, PA 15236

Keywords: Methane: Partial Oxidation: Oxidative Coupling:  
Pyrolysis: Derivatization

ABSTRACT

Commercially viable technology development for converting light hydrocarbon gases to value-added fuel forms and chemicals is of strategic and scientific importance for responding to the growing needs for energy security, environmentally superior liquid fuels, and economic stimulation from introducing new technologies in the market place. To assist the development of technologies, the United States Department of Energy (USDOE) established the Gas-to-Liquids Research Program. This paper describes the Gas-to-Liquids technology development projects sponsored by the Pittsburgh Energy Technology Center (PETC) of the USDOE.

INTRODUCTION

Current proven world reserves of natural gas are estimated at around 4500 trillion cubic feet (TCF), approximately half of which is in remote areas (1, 2). Additionally, 400 TCF are occluded as coal bed methane in the U.S.(3). A potentially huge source of natural gas as gas hydrates has also been reported in the literature (4). Flaring of associated (oil field) gas in some regions of the world and venting of coal bed methane contribute to greenhouse effects. In energy equivalence terms, natural gas production has been predicted to grow faster than oil, but technology growth areas are not yet identified except for the electric utility sector (5). However, at identical capacity factors, it costs more to generate electricity by burning natural gas than coal. Monetization of natural gas by upgrading to value-added products, such as environmentally superior transportation fuels that will exceed requirements of the 1990 Clean Air Act Amendments (CAAA), is an attractive option. For effective utilization, natural gas reserves in remote areas will have to be converted to liquid hydrocarbon products on site and then transported to the marketplace. The increase in the Federal Energy Resources budget over the fiscal year 1994 appropriation shows government encouragement to develop natural gas utilization technologies.

In 1991, the Pittsburgh Energy Technology Center (PETC) of the United States Department of Energy (USDOE) issued a Program Research and Development Announcement (PRDA) inviting proposals for the development and demonstration of technologies for economical conversion of methane and other light hydrocarbon gases to transportation fuels and chemicals. The seven selected awards represented an optimal mix of projects believed to maximize the probability of achieving USDOE's overall objectives.

Methane conversion technologies will allow efficient utilization of our Nation's abundant supply of natural gas to manufacture the cleanest burning fuels, and the new technologies can be easily integrated into the existing refinery and distribution system. USDOE supported gas-to-liquids program to conserve natural gas will help the agency deliver its role in implementing the Climate Change Action Plan aimed at reducing carbon dioxide emissions.

HISTORY

Natural gas was first used as a fuel by the Chinese for lighting, circa 250 A.D., by piping it through bamboo tubes. In the United States, natural gas was first discovered in Fredonia, New York, in 1821 but was not considered a fuel source (4). After World War II, natural gas was recognized as a fuel commodity.

During the 1950s, natural gas dominated the market of fuel-gas industries. Gas pipelines were installed countrywide, reaching from gas fields to homes and factories. Natural gas not only became a predominating fuel gas, it also qualified as an important feedstock for synthesis of various liquid fuels, chemicals, and intermediates.

In the early 1950s, a commercial natural gas-to-liquid fuels plant was built by the Carthage Hydrocol Company in Brownsville, Texas. However, due to the availability of cheap Middle Eastern petroleum, the operation was not economical, and thus the plant was shut down. A 14,500 barrel-per-day natural gas-to-gasoline plant started operating in New Zealand in 1985 and was on stream producing 87 octane unleaded gasoline until recently. In this process, natural gas was first converted to methanol via synthesis gas, followed by conversion of methanol to gasoline using a novel catalyst developed by Mobil in the 1970s. A portion of Mobil's development efforts was funded by the Fossil Energy Program of the USDOE. In April 1993, Exxon announced its AGC-21 Advanced Gas Conversion Technology for converting natural gas to high quality refinery feedstock (6). Olefin-based transportation fuels from natural gas is produced in the Mossgas plant in South Africa (7). Recently, Shell Gas B.V. built a 12,000 barrels per day natural gas-to-middle distillate plant in Malaysia (8).

#### GAS-TO-LIQUIDS CONVERSION TECHNOLOGIES

Coupling of two methane molecules to higher hydrocarbons is not thermodynamically feasible because the energy of formation is not favorable. However, in the presence of a co-reactant, such as oxygen, the reaction path can be altered, and methane conversion reactions can be successfully carried out. Natural gas (primarily methane) can be upgraded to higher hydrocarbons either by direct conversion routes (single-step or staged), or via synthesis gas (a mixture of carbon monoxide and hydrogen). In this paper, the synthesis gas based process is termed the indirect process. A discussion of terminology classifying methane conversion processes can be found in the literature (9). The important process considerations for commercially viable natural gas upgrading operations are methane conversion rate and selectivity to preferred products.

Based on chemistry, the processes for natural gas upgrading include 1) partial oxidation to oxygenates, such as methanol, 2) oxidative coupling to higher hydrocarbons, such as ethylene, 3) derivatization, such as oxyhydrochlorination to chlorinated hydrocarbons, which are subsequently converted to higher hydrocarbons, and 4) pyrolysis to aromatic and/or higher hydrocarbons.

In the indirect process, natural gas is first converted to synthesis gas, followed by catalytic hydrogenation of the carbon monoxide in a synthesis reactor to a variety of higher hydrocarbon fuels. Fischer-Tropsch (FT) synthesis and its variants are important synthesis reactions, involving low-pressure conversion of synthesis gas to gasoline, diesel fuel, wax, and oxygenates. The products of reaction depend on the temperature, pressure, and catalyst used in the synthesis reactor.

#### PETC'S GAS-TO-LIQUIDS PROGRAM

The goals of PETC's Gas-to-Liquids program can be summarized as follows:

- Discover new chemistry and catalysts for the conversion of methane and other light hydrocarbon gases to value-added, easily transportable fuels and chemicals.
- Obtain necessary design and engineering information to develop prototype technologies for demonstration and commercial deployment.
- Pursue cost-shared, risk-shared, industry-driven R&D, demonstration, and technology transfer to ensure pay-off of Federal R&D investments.
- Contribute to energy policy goals by selecting investments consistent with the four major policy thrusts:
  - Energy security

- Economic growth
- Environmental quality improvement
- Enhancing scientific foundations.

PETC's program consists of R&D activities in several natural gas conversion chemistries. They will be discussed in the following groups (10):

- Partial Oxidation
- Oxidative Coupling
- Pyrolysis
- Derivatization

#### PARTIAL OXIDATION

Partial oxidation of methane refers to the selective oxidation of methane to oxygenates, such as methanol, or to synthesis gas. In either technology, control of the extent of gas phase oxidation to prevent the formation of complete oxidation products is extremely important. For both technologies, oxygen must be separated from air, which is capital and energy intensive. PETC is managing three projects in this area of technology.

1) PETC is sponsoring a Cooperative Research and Development Agreement (CRADA) between Amoco Chemical Company and USDOE's Argonne National Laboratory (ANL). The research is focusing on the development of oxygen-specific, dense-phase ceramic membranes for the conversion of methane to synthesis gas or methanol. These oxygen specific membranes permit the transport of oxygen through the membrane while totally excluding nitrogen. Research and development efforts are focused on producing membranes that have sufficient strength and mechanical integrity to withstand the harsh reaction environment of a commercial reactor. Such membranes will permit the use of air instead of purified oxygen for the oxidation reactions, thereby substantially improving the economics of both existing synthesis gas production technologies, as well as direct conversion technologies for methanol. Also, by using the ceramic membranes as a means of regulating the contact between oxygen and methane, and as a support for catalytic materials, achieving highly selective yields of tailored products may be possible. The project is examining the applicability of the membranes for partial oxidation of methane to both synthesis gas and methanol.

The Amoco/ANL team has developed novel, non-perovskite membrane materials for separation of oxygen from air, and conversion of methane into value-added, easily transportable liquid hydrocarbons. These proprietary membrane materials exhibited more than adequate oxygen separation capacity and thermal stability during a demonstration run. A pilot-scale demonstration is under active study, and the Amoco/ANL team has proposed several unique, conceptual process designs for the development of a commercial process.

2) Sandia National Laboratory (SNL) is developing catalysts for the low-temperature conversion of methane to methanol by simulating biological mechanisms using computer-aided molecular design techniques. SNL has tested several halogenated iron porphyrin catalysts for isopentane oxidation, and have gleaned mechanistic information for developing methane oxidation catalysts.

3) AMAX Research and Development has developed techniques for the synthesis and activation of vanadium phosphate catalysts from precursors to form the required active phase for the conversion of methane to methanol. The Colorado School of Mines will continue this activity.

#### OXIDATIVE COUPLING

Oxidative coupling refers to the chemistry of reacting methane with oxygen to form C<sub>2</sub> hydrocarbons as intermediate reactive feedstocks for subsequent conversion to preferred products.

Worcester Polytechnic Institute (WPI) is investigating the use of high-temperature inorganic membranes that are specific for oxygen diffusion to achieve the oxidative coupling of methane. By incorporating a suitable oxidative coupling catalyst into the membrane system and controlling the flow of oxygen across the membrane, the coupling reaction may be favored over other methane

oxidation reactions, thereby minimizing the production of carbon dioxide.

WPI is currently working to select suitable membrane material that will not undergo phase change at reaction conditions while providing optimal oxygen flux. Various perovskite type catalysts are being tested in suitable membrane reactors of various configurations.

#### PYROLYSIS

Pyrolysis refers to thermal decomposition of methane in the absence of any oxidant. Theoretically methane can be pyrolyzed to higher hydrocarbons by successive dehydrogenation and radical recombination, and to aromatics by cyclization of radical fragments. However, the pyrolysis must be controlled at a certain time-temperature condition to maximize yields of low molecular weight products and prevent coke formation. SRI International and Altamira Instruments are the two participants in this category of research.

1) SRI International is attempting to develop a process for the direct conversion of methane to higher hydrocarbons under controlled thermal and catalytic conditions using Fullerene-based catalysts. SRI has prepared metallized Fullerene catalysts and these catalysts have been shown to be effective in stabilizing methyl radicals. Preliminary methane conversion tests using Fullerene containing soot in the presence of an inert diluent gave high selectivity to preferred higher hydrocarbons at lower activation temperature.

2) Altamira Instruments is investigating a catalytic and/or free radical-induced pyrolysis route for converting methane to higher unsaturated hydrocarbons or aromatics.

The thermal decomposition of methane shows potential as a process for the production of higher unsaturated and aromatic hydrocarbons when the extent of reaction is limited. Preliminary experiments have shown that cooling the products and reacting gases as the reaction proceeds can significantly reduce or eliminate the formation of solid carbon and  $C_{10}+$  products. Optimizing the quenching process is one of the goals of the program. Another objective is to reduce the temperature of the pyrolysis reaction by using free-radical generators and catalysts.

Altamira has completed construction of a rapid-quench reactor to limit the extent of reaction and minimize coke formation. A thermodynamic simulation was used to determine yields of various pyrolysis products as a function of the time-temperature history in the reaction environment. Baseline runs in the absence of quench gave 31-48 mol% methane conversion, with the major detectable product being benzene. In the rapid-quenched mode operation, a conversion of 33 mol% was obtained with over 15 mol% selectivity to benzene, and at least a 20 mol% selectivity to  $C_6$  hydrocarbons. Product distribution shifted to lower hydrocarbon products as a result of quenching. Operating temperature was 900-1100 °C at ambient pressures. A 1100 °C quenched-mode run at a specific operating condition and methane feed rate gave 38 mol% methane conversion with 45 mol% selectivity to benzene.

The project was selected for economic and engineering analysis. The purpose of the analysis was to determine product and yield targets for commercial viability of the process and to estimate capital requirements. It is believed that systematic feedback of information from engineering analysis to the researchers would result in a parallel evolution of both an engineering and a scientific knowledge base for advancing the state-of-the-art needed for commercial demonstration.

#### DERIVATIZATION

Derivatization, in this paper, refers to a two-step process where methane is first converted to a reactive, but stable, intermediate followed by subsequent conversion of the intermediate product to desired higher hydrocarbons or value-added chemicals. The participants in this category of research are Dow Corning Corporation, Massachusetts Institute of Technology (MIT), Institute of Gas Technology (IGT), and the USDOE's Pittsburgh Energy Technology Center.

1) A multi-step approach involving oxyhydrochlorination was developed by in-house researchers at PETC for converting methane to gasoline using several new and better catalyst formulations. Dow Corning Corporation, the largest manufacturer of silicone products in the United States, is attempting to improve the PETC process by developing a direct methane to methyl chloride conversion route. Because large quantities of methanol for methyl chloride production are imported, replacing it with domestic natural gas will ensure a stable source and price. The cost of a methyl group from methane is significantly lower than that of a methanol-derived methyl group at current pricing.

Dow Corning successfully developed a highly selective Cu-based catalyst and a separation unit to recover methyl chloride from unreacted non-condensable effluent streams. Construction of a bench-scale reactor for optimization of catalyst and process condition studies is nearing completion. This project is an example of government-industry collaboration on technology development. PETC will provide catalyst expertise, while Dow will provide engineering experience in commercialization of technology. Dow will have a cost-effective process for producing methyl chloride for its silicone business, and PETC will have an improved first step in its methane to gasoline process. Such industrial cost participation promotes technology or technical know-how transfer to target segments of industry and enhances U.S. competitiveness.

2) The objective of the MIT project is to develop a process for converting methane to solid metal carbides that can be easily stored, transported, and hydrolyzed to acetylene or methyl acetylene, which are reactive precursors to higher hydrocarbons. MIT researchers are investigating the use of a thermal plasma reactor to cause decomposition of methane into an ionized, electrically conducting plasma followed by energetic reaction with alkaline metal oxides, such as calcium or magnesium oxides, to form corresponding carbides. Stoichiometrically, these reactions are net hydrogen producers.

MIT performed a thermodynamic simulation study to determine equilibrium compositions for the Ca-C-H-O and Mg-C-H-O systems. It was observed that a significant driving force exists for converting methane to carbides at 2100 K. Although energy intensive, such a process will be useful for on-site upgrading of remote natural gas.

3) IGT is investigating the catalytic reaction of methane with hydrogen sulfide to carbon disulfide, followed by subsequent conversion of the carbon disulfide to gasoline range hydrocarbons. The second step is the MOBIL process. Reaction of methane with sulfur to make carbon disulfide is known. The novelty of this process, however, is the reaction with hydrogen sulfide (instead of sulfur), which results in the net production of hydrogen for use in the second step. In the second step, carbon disulfide is reacted with hydrogen, regenerating hydrogen sulfide for recycle to the first step.

IGT prepared several proprietary transition metal sulfide catalysts for the methane/hydrogen sulfide reaction. These catalysts have been used to investigate the decomposition of hydrogen sulfide. Hydrogen sulfide decomposition is one of the mechanisms postulated to occur in the first step of the proposed process. At 600-1100 °C, and ambient pressure, one catalyst gave hydrogen sulfide decomposition close to values predicted by equilibrium. However, the thermal background, if any, has not yet been determined for this reaction.

4) PETC in-house methane conversion research has evolved from chemical to photochemical reaction systems. Currently, the researchers are investigating the production of methanol from the photochemical reaction of methane and water. This project combines interesting chemistries from several different technology areas and could result in a commercially viable process.

#### CONCLUSION

The USDOE Gas-to-Liquids R&D portfolio considers technical and policy objectives, and identifies key energy policy goals in the implementation of the program. The energy policy goals are based on balancing the economic, environmental, and energy security

objectives. The major policy thrusts for evaluating investments in the natural gas conversion/upgrading technology projects are energy security, economic growth, environmental quality improvement, and fortifying scientific foundations. The criteria for evaluating investments are based on how potential R&D activities can assure a secure, fuel-diverse, and environmentally sensitive energy sector.

Technological advances are critical to achieving the Nation's energy, economic, and environmental objectives and maintaining U.S. competitiveness in a rapidly advancing global economy. Growth in economic productivity arises principally from the introduction of new technology into the market place. The PETC Gas-to-Liquids conversion R&D program is based upon these convictions.

#### REFERENCES

1. Energy Information Administration, U.S. Crude Oil, Natural Gas, and Natural Gas Liquid Reserves, p 25, 1991 Annual Report.
2. Energy Statistics, vol 15, No. 3, p 25, Third Quarter 1992. A publication of the Institute of Gas Technology, Chicago, Illinois.
3. Quarterly Review of Methane from Coal Seams Technology, vol 11, No. 1, p 2, August 1993. A publication of the Gas Research Institute.
4. Speight, J. G., Fuel Science and Technology Handbook, Marcel Dekker, Inc., 1990.
5. Oil & Gas Journal, Nov 29, 1993, p 80.
6. Octane Week, vol IX, No. 10, p 1, March 7, 1994. A Hart Publication. Also presented at the Alternate Energy '93, Council on Alternate Fuels, Colorado springs, Colorado, April 27-30, 1993.
7. Eisenberg, B., "Advanced Natural Gas Conversion Technology For Remote Natural Gas Utilization," preprint, International Symposium on Gas Conversion and Utilization, The Catalysis Society of Metropolitan New York, May 9-11, 1994.
8. The Oil Daily, Wednesday, August 23, 1989, p 3.
9. Anderson, J. R., Applied Catalysis, vol. 47, p 177-196, 1989. Elsevier Science Publishers B.V., Amsterdam.
10. Proceedings of Liquefaction and Gas Conversion Contractors' Review Conference, Eds. Rogers, S and P. Zhou. U.S. Department of Energy, Pittsburgh, Pennsylvania, September 27-29, 1993.

# METHYLATION OF ETHYLENE OVER LEWIS-ACID CATALYSTS

M.V.C. Sekhar

Energy Research Laboratories, CANMET, Natural Resources Canada, 555 Booth Street,  
Ottawa, Canada, K1A 0G1  
email:sekhar@emr.ca

Keywords: Alkylation, Lewis-acids, Methane conversion

## INTRODUCTION

As a major constituent of natural gas, methane is abundant and is a relatively inexpensive feedstock for a variety of chemicals. The use of methane as a fuel is straightforward. Consequently, over the years, considerable research has been conducted to develop technologies for its efficient utilization. Work<sup>1</sup> on adsorbents for storing natural gas on-board automotive vehicles promises to expand its use considerably. Conversely, the use of methane as a chemical feedstock requires either the energy- and capital-intensive production of intermediate synthesis gas or its thermal cracking to a range of hydrocarbons. In recent years there has been a great deal of interest in processes<sup>2,4</sup> that convert methane directly to olefins, methanol and other functionalized methane derivatives.

Among the various conversion processes currently under development, the Oxidative Coupling (OC) route is the most promising. With increased attention being given to OC process, engineers have also begun outlining the corresponding reaction engineering aspects. The OC of methane rich natural gas yields a dilute olefin stream. At 25% hydrocarbon conversion, the ethylene in the dry reactor effluent is about 5%, with some propylene and other hydrocarbons. Because of the presence of large amounts of unconverted methane in the effluent, product separation is one of the main points of optimization in the existing oxidative coupling technology. Consequently, a processing scheme which does not require further separation of the product of the OC reactor would be of considerable advantage. Reactions between methane and ethylene using a number of solid acids have also been reported by a number of authors<sup>5-7</sup> in the past. However, some of these experiments were conducted at temperatures higher than ambient. In this paper we report some of the results obtained at ambient temperature as part of a screening program for developing catalyst systems for co-reacting methane with ethylene to produce higher hydrocarbons.

## PROCEDURES

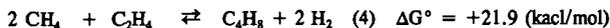
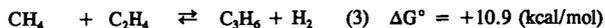
*Catalyst preparation.* The catalyst that was most extensively tested was a mixture of NbF<sub>5</sub> and AlF<sub>3</sub>. The catalysts were prepared using anhydrous hydrogen fluoride as a solvent. The metal fluorides were first physically mixed and then dissolved in anhydrous hydrogen fluoride. The mixture was stirred for about an hour, then the excess HF was allowed to evaporate by heating the mixture to about 100°C for several hours.

*Experimental conditions.* All experiments were carried out in a continuous flow fixed bed micro-reactor with a catalyst volume of between 5 and 10 mL. Experiments were conducted at two pressures, ambient and 10 atm. On line chromatography was used for product analysis. Samples were also collected and analyzed by off-line GC-MS. Experiments were performed with two different ratios of methane and ethylene. Nitrogen was used a tracer in several experiments in order to obtain a quantitative measure of the conversions. The catalysts were used in the form of fine powders and was diluted with dried sand or teflon chips.

## RESULTS AND DISCUSSION

A number of reactions between methane and ethylene and other olefins are thermodynamically favoured even at ambient temperature, provided the products are alkanes, viz., (reactions 1 and 2)





The formation of unsaturates (reactions 3 and 4) are associated with positive free energy change at ambient temperature. Self-oligomerization of ethylene to alkenes, however, is thermodynamically feasible:

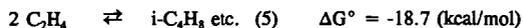
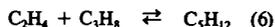


Table 1 compares the ethylene conversions obtained for reaction between ethylene and methane for two different methane/ethylene feed ratios. The corresponding product distributions, excluding unreacted methane and ethylene are shown in Table 2. Using a 7:1 molar ratio of methane to ethylene, almost complete conversion of ethylene is obtained, whereas at a higher ethylene content in the feed, conversions are reduced by half. The ethylene conversions continue to remain higher when the feedstream is richer with respect to methane. The presence of  $\text{C}_5$  hydrocarbons, n-pentane and 2-methyl butane, along with traces of propane suggests the participation of methane in the reaction sequence, since oligomerization of ethylene alone should yield even numbered unsaturated hydrocarbons. However, the methane conversions in these experiments were less than what would be expected based on the primary alkylation reaction (reaction 1), suggesting a larger contribution from oligomerization. The absence of olefins in the product spectrum resulting from such oligomerization is probably due to secondary reactions.

When ethylene alone was used as a reactant, the conversions of ethylene are much lower than when methane was also present in the feed mixture (Table 3). The product spectrum in the case of ethylene only experiments, is qualitatively similar to the case where methane was also present, however, the product is relatively richer in heavier hydrocarbons (Table 4). Small amounts of methane was also detected when ethylene alone was used as a feed, indicating that cracking of heavier hydrocarbons had occurred under these experimental conditions. The cracking also could explain the observation of negative methane conversions in some experiments. The absence of propane and butenes could be explained by the following reaction sequences. Propane which is formed by the primary alkylation reaction (reaction 1), undergoes ethylation with ethylene to produce a  $\text{C}_5$  alkane (reaction 6).



Oligomerization of ethylene produces butenes (reaction 5) as intermediates, which are alkylated by methane, also producing  $\text{C}_5$  hydrocarbons (reaction 7). A similar reaction involving the alkylation of isobutane by ethylene was recently reported<sup>8</sup>, producing mainly hexanes in addition to a variety of other alkanes and alkenes formed by secondary reactions.



By far the most abundant  $\text{C}_5$  hydrocarbon detected was isopentane and its formation can be explained by both of the above reactions. The formation of isobutane as the most abundant hydrocarbon product suggests extensive cracking of the  $\text{C}_5$  and  $\text{C}_6$  species (reaction 8).



The  $\text{CH}_4$  species could then be hydrogenated to methane by abstracting hydrogen from residual HF that was used in the preparation of the catalyst. Such cracking followed by hydrogenation could also explain the negative conversions of methane that was observed in a number of instances.

In order to discern the extent of the incorporation of methane in the reaction product, an experiment was performed using  $^{13}\text{CH}_4$  and unlabelled ethylene. The products were collected and analyzed off-line using a Porapak Q column and a mass selective detector. The mass spectrum of isobutane from reactions using labelled and unlabelled methane were then compared.

By measuring the abundance of the parent ions it was possible to quantify the amount of labelled isobutane present in the sample. From these data it was concluded that there was incorporation of at least one labelled carbon in the C<sub>4</sub> skeleton and it was estimated that 5% of the total isobutane formed contained the labelled <sup>13</sup>C. By comparison, the methane conversion for the same set of experiments was about 9%. This discrepancy can arise due to the fact that the formation of isobutane probably involves several alkylation and cracking steps. In such a scenario, the labelled carbon could be lost as either methane or some other hydrocarbon. The presence of labelled carbon in the other products such as 2,2-dimethyl butane or 2,3-dimethyl butane could not be established unambiguously due to the complex mass spectral fragmentation pattern of these compounds. The GC-MS analysis also revealed the formation of traces (about 50 ppm) of two fluorinated hydrocarbons, fluoroethane and 1,1-difluoroethane.

#### SUMMARY

The catalytic activity of metal fluoride based Lewis acid catalysts for the coreaction between methane and ethylene was studied. It was found that whereas substantial conversion of ethylene could be obtained even at ambient temperatures, methane conversions were much lower. Experiments using labelled methane confirmed the participation of the methane in the reaction sequences. The primary products were branched C<sub>4</sub> and C<sub>5</sub> saturates, with smaller amounts of straight chain hydrocarbons. The activity of the catalyst was found to decrease sharply with time, with the product spectrum shifting towards C<sub>6</sub> and higher hydrocarbons.

#### ACKNOWLEDGEMENTS

This research was supported in part by the federal Panel on Energy Research and Development (PERD) and by the Consortium on Natural Gas Conversion, sponsored by Amoco Corporation, Canadian Occidental Petroleum Limited, Centre des technologies du gaz naturel and Shell Canada Limited. I would like to express my thanks to N. Horvat for performing some of the preliminary experiments and M. Coffin for assistance with data analysis.

#### REFERENCES

1. R. Chahine and T.K. Bose, Twentieth Biennial Conference on Carbon, Santa Barbara, June 23-28, 1991.
2. Preprints Amer. Chem. Soc. Division of Petr. Chem., Symposium on Methane and Alkane conversion, 39(2), 1994.
3. C. Mirodatos, J.M. Basset, G.A. Martin and J. Saint-Just, Eds., Catalytic Methane Conversion, Proceedings of the Third European Workshop on Catalytic Methane Conversion, Villeurbanne, France, May 27-29, 1991, Catalysis Today, 13(2-3), 1992.
4. Preprints Amer. Chem. Soc. Division of Petr. Chem., Symposium on Natural gas Upgrading II, 37(1), 1992.
5. G.A. Olah, J.D. Felberg and K. Lammertsma, J. Am. Chem. Soc., 105, 6529 (1983).
6. M.S. Scurrall, Appl. Catal., 34, 109 (1987).
7. F.T.T. Ng, C.R. Rourke and J. Lynn, Progress in Catalysis, K.J. Smith and E.C. Sanford (Eds.) Elsevier, 1992, p.31.
8. J-M. Goupil, J-L. Poirier and D. Cornet, Ind. Eng. Chem. Res., 33, 712 (1994).

Table 1. Comparison of Ethylene Conversions (mol%) for different feed compositions

Experimental conditions: Catalyst: 1g; Temperature: ambient; Pressure: 10 atm; Total flow: 40 mL/min.

| Time(min)              | 15   | 45   | 73   | 102  | 158  | 189  | 217  |
|------------------------|------|------|------|------|------|------|------|
| Methane/ethylene (3:1) | 55.6 | 13.3 | 7.17 | 3.83 | 2.92 | 2.01 | 1.38 |
| Methane/ethylene (7:1) | 94.6 | 71.5 | 36.7 | 11.5 | 4.49 | 3.35 | 3.18 |

Table 2. Product composition (mol%) excluding unconverted methane and ethylene.

Experimental conditions: same as in Table 1.

Methane/ Ethylene Mol Ratio: 3:1 (upright data); 7:1 (italics data)

| Component / Time(min)              | 15          | 45          | 73         | 102        | 158         | 189         | 217         |
|------------------------------------|-------------|-------------|------------|------------|-------------|-------------|-------------|
| Propane                            | 0.39        |             |            |            |             |             |             |
| <i>Propane</i>                     | <i>0.03</i> | <i>0.15</i> |            |            |             |             |             |
| isobutane                          | 60.8        | 74.3        | 69.4       | 64.1       | 61.4        | 60.3        | 22.4        |
| <i>isobutane</i>                   | <i>76.6</i> | <i>61.9</i> | <i>58</i>  | <i>43</i>  | <i>65.3</i> | <i>63.8</i> | <i>63</i>   |
| n-butane                           | 2.79        | 3.6         | 4.06       | 6.5        | 8.12        | 8.81        | 3.49        |
| <i>n-butane</i>                    | <i>2.13</i> | <i>1.76</i> | <i>1.5</i> | <i>1.2</i> | <i>2.59</i> | <i>2.89</i> | <i>3.14</i> |
| isopentane                         | 16.1        | 21.8        | 25.9       | 28.9       | 30.5        | 30.9        | 11.5        |
| <i>isopentane</i>                  | <i>19.2</i> | <i>15.6</i> | <i>15</i>  | <i>16</i>  | <i>32.2</i> | <i>33.3</i> | <i>33.8</i> |
| n-pentane                          | 0.24        | 0.37        | 0.67       | 0.47       |             |             |             |
| <i>n-pentane</i>                   | <i>0.1</i>  | <i>0.13</i> | <i>0.1</i> | <i>0</i>   |             |             |             |
| C <sub>6+</sub> hydrocarbons       | 19.8        |             |            |            |             |             | 62.6        |
| <i>C<sub>6+</sub> hydrocarbons</i> | <i>1.88</i> | <i>20.4</i> | <i>26</i>  | <i>41</i>  |             |             |             |

Table 3. Ethylene conversions for ethylene oligomerization vs methane/ethylene coupling

Experimental conditions: Catalyst: 1g; Temperature: ambient; Pressure: 10 atm; Total flow: 120 mL/min.

| Time(min)                   | 5           | 33          | 62          | 90          | 119         | 219         | 251         |
|-----------------------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Methane/ethylene (7:1)      | 93.8        | 5.34        | 1.00        | 1.07        | 0.71        |             |             |
| <i>Argon/ethylene (7:1)</i> | <i>76.7</i> | <i>23.5</i> | <i>5.25</i> | <i>3.70</i> | <i>3.70</i> | <i>2.92</i> | <i>2.72</i> |

Table 4. Product composition (mol%) excluding unconverted methane and ethylene.

Experimental conditions: same as in Table 3. With ethylene alone as feed, argon was added to balance the total flow. Methane/ Ethylene Mol Ratio: 7:1 (upright data); Ethylene alone (italics data)

| Component / Time(min)              | 5           | 33          | 62          | 90          | 119  | 219         | 251         |
|------------------------------------|-------------|-------------|-------------|-------------|------|-------------|-------------|
| <i>Ethane</i>                      | 3.25        |             |             |             |      |             |             |
| Propane                            | 0.02        |             |             |             |      |             |             |
| <i>Propane</i>                     | <i>0.02</i> |             |             |             |      |             |             |
| isobutane                          | 63.1        | 26.3        | 21.0        | 19.6        | 18.7 |             |             |
| <i>isobutane</i>                   | <i>57.7</i> | <i>50.4</i> | <i>21.6</i> | <i>19.0</i> |      | <i>15.8</i> | <i>15.4</i> |
| n-butane                           | 2.00        | 3.44        | 2.44        | 2.29        | 2.36 |             |             |
| <i>n-butane</i>                    | <i>4.04</i> | <i>2.73</i> | <i>2.86</i> | <i>2.85</i> |      | <i>3.35</i> | <i>3.46</i> |
| isopentane                         | 17.4        | 15.3        | 13.7        | 13.4        | 12.9 |             |             |
| <i>isopentane</i>                  | <i>16.2</i> | <i>15.6</i> | <i>13.4</i> | <i>12.7</i> |      | <i>11.6</i> | <i>11.6</i> |
| n-pentane                          | 0.04        | 0.80        | 1.99        | 0.70        | 0.60 |             |             |
| <i>n-pentane</i>                   | <i>0.04</i> | <i>0.06</i> |             |             |      |             |             |
| C <sub>6+</sub> hydrocarbons       | 17.4        | 54.2        | 60.9        | 64.0        | 65.4 |             |             |
| <i>C<sub>6+</sub> hydrocarbons</i> | <i>18.8</i> | <i>31.2</i> | <i>62.9</i> | <i>65.5</i> |      | <i>69.2</i> | <i>69.6</i> |

## GASOLINE FROM NATURAL GAS BY SULFUR PROCESSING

Erek J. Erekson and Frank Q. Miao  
Institute of Gas Technology  
Chicago, IL 60616

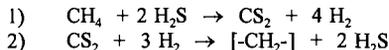
KEY WORDS: Sulfur Catalysts, Methane conversion, CS<sub>2</sub>

### ABSTRACT

The conversion of natural gas to transportable liquids continues to be an area of research interest. New processes for the direct oxidation of methane either to ethylene or to methanol, are hampered by apparent yield barriers due to CO<sub>x</sub> production. In addition new processes for fuel production from non-petroleum sources such coal, shale oil, tar sands are often hampered by the need for hydrogen. The subject process circumvents these difficulties in fuel production. The process consists of two steps that each utilize catalysts and sulfur containing intermediates:

- 1) to convert natural gas to CS<sub>2</sub>, and
- 2) to convert CS<sub>2</sub> to liquid hydrocarbons.

The general equations for the two steps are:



H<sub>2</sub>S is recycled, and the overall process is a net hydrogen producer.

A catalyst is being developed for the first step. The second step has been studied by others<sup>1</sup>. Initial results are reported. Engineering aspects and economic implications of the overall process will be discussed.

### INTRODUCTION

Natural gas is an abundant resource in various parts of the world. The major component of natural gas is methane, often comprising over 90% of the hydrocarbon fraction of the gas. The expanded use of natural gas as fuel is often hampered because of difficulties in storage and handling a gaseous fuel. This is especially true for natural gas in remote areas such as the north slope of Alaska. It is desirable to convert natural gas to more valuable liquids. The successful implementation of this process would decrease dependence on imported oil for transportation fuels.

There are two commercialized methods for converting natural gas to gasoline range liquids:

- 1) Fischer-Tropsch synthesis
- 2) Mobil's MTG process.

Each has two basic steps:

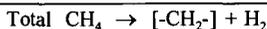
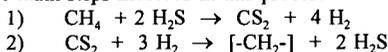
1. Removal of sulfur compounds (H<sub>2</sub>S, COS and mercaptans with sulfur adsorbing guard beds to prevent breakthrough of sulfur to the catalysts).
2. Steam reforming to make synthesis gas which requires 2 moles of superheated steam for every mole of methane.

In Fischer-Tropsch synthesis, the third step is the conversion of synthesis

gas to hydrocarbons. A fourth step consisting of mild hydrocracking is necessary in high wax producing Fischer-Tropsch synthesis such as Shell's Middle Distillate Synthesis Process. In Mobil's MTG process, the third step is methanol synthesis, and the fourth step is methanol conversion to gasoline liquids is required. The commercial steps listed above; i.e., steam reforming, methanol synthesis, or Fischer Tropsch synthesis, require the removal of sulfur compounds present in natural gas down to less than 0.1 ppm. This gas clean-up step adds cost, but it is necessary because the catalysts are quickly poisoned by sulfur compounds.

IGT has begun investigating a two-step process that uses H<sub>2</sub>S as a reactant to convert natural gas to gasoline-range liquids. Sulfur, which has been considered as a poison, is used as a reactant in the proposed process. This method of methane conversion utilizes H<sub>2</sub>S to catalytically convert methane to CS<sub>2</sub>. Then CS<sub>2</sub> plus hydrogen can be catalytically converted to gasoline range hydrocarbons. All of the H<sub>2</sub>S generated during the CS<sub>2</sub> to gasoline reaction is recycled. This process does not require steam reforming nor the manufacture of hydrogen.

There are two main steps involved in this process:



H<sub>2</sub>S is recycled, and the overall process is a net hydrogen producer.

Catalysts are being developed for the first step. The second step which has been demonstrated by researchers at Mobil<sup>1</sup> will be studied later in this project to try to improve yields of gasoline range hydrocarbons. In this paper, we will discuss the ASPEN simulation as well as experimental results for step 1.

## EXPERIMENTAL

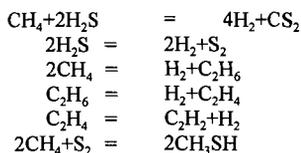
Figure 1. shows the schematic diagram of catalysis reactor system for step 1. Feed gas flows of hydrogen sulfide, nitrogen and methane are controlled by mass flow controllers (Brooks Instruments 5850). Gas flow rates are calibrated by a dry test meter (SINGER, American Meter Company). The feed gas flows through the adapter into 42 inch long, 22 mm I.D. and 25 mm O.D. quartz reactor. The joint which connects with adapter and quartz reactor were sealed by TFE sleeve. There are three indents around quartz reactor at 26 inch from the top. The catalyst is held above the indents by a plug of quartz wool. The temperature of catalyst reactor were measured by a type R high temperature thermocouple which is protected by 1/4 inch O.D. ceramic thermowell. The heat was provided by a 2 inch I.D. 32 inch long split tube high temperature furnace with maximum temperature 1540°C. (Series 3420, APPLIED TEST SYSTEMS, Inc). There is a sample point just after the reactor. The product gas is sampled before it flows into condenser. The gases were analyzed by GC. The product gas from the catalyst reactor flows into a liquid condenser which is put into an ice bath. The sulfur was cooled and condensed in condenser. After the condenser product gases flow into a 30% Hydrogen peroxide and 6M Sodium hydroxide solution to scrub hydrogen sulfide. The composition of gas from the scrubber was also analyzed by GC. The gas flow rate was measured by a wet test meter (PRECISION WET TEST METER, Precision Scientific Co) before it is released into the vent system.

Gas samples are analyzed by Gas Chromatograph (HP5890) with a thermal conductivity detector (TCD) and a flame photometric sulfur detector (FPD). A 1/8-inch diameter 10-ft long HayeSep C 80/100 column(SUPELCO Inc.) was used for gas separation. In order to measure hydrogen in the TCD detector, Argon was used as the carrier gas.

## RESULTS AND DISCUSSION

### 1) Equilibrium calculations

Equilibrium calculations were performed with ASPEN PLUS process simulator. The Gibbs Energy Minimization method was used for the simulation of equilibrium conditions. Six independent reactions have been taken into account for the chemical equilibrium study:



Equilibrium for three feed gas compositions at 700 to 1200°C was calculated using the following feed gas compositions:

|        | <u>CH<sub>4</sub></u> | <u>H<sub>2</sub>S</u> | <u>N<sub>2</sub></u> | <u>H<sub>2</sub>S/CH<sub>4</sub> Ratio</u> |
|--------|-----------------------|-----------------------|----------------------|--|
| Case 1 | 3.33 %                | 6.67 %                | 90 %                 | 2  |
| Case 2 | 2.00                  | 8.00                  | 90                   | 4  |
| Case 3 | 1.11                  | 8.89                  | 90                   | 8  |

Nitrogen was added as a diluent for all cases studied. Carbon graphite formation was not included in these calculations. At the temperatures of these equilibrium calculations, carbon graphite is so much more stable thermodynamically than methane or the other carbon compounds that including it would result in all the carbon going to graphite.

At equilibrium significant amounts of CS<sub>2</sub> and H<sub>2</sub> are predicted. In Figures 2, 3 and 4 equilibrium concentrations of CS<sub>2</sub> and CH<sub>4</sub> as well as experimental results are shown. The concentration of CS<sub>2</sub> at equilibrium increases with temperature. At 1100°C nearly all of CH<sub>4</sub> was converted in all three cases. There was very little of C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub> as well as CH<sub>3</sub>SH calculated in the products. The amount of C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub> as well as CH<sub>3</sub>SH was less than 10<sup>-6</sup>. In comparing the equilibrium calculations in Figures 2, 3 and 4 it appears that increasing the temperature as well as increasing H<sub>2</sub>S/CH<sub>4</sub> ratio will increase CS<sub>2</sub> concentration and decrease the CH<sub>4</sub> concentration at equilibrium.

### 2) Experimental Results

Reactor tests of IGT-MS-105, a sulfide catalyst, were performed using the same feed compositions as cases 1, 2 and 3 above. The experiments were performed at atmospheric pressure and in the range from 700 to 1200°C. The residence times were 1 to 5 seconds. 40 g. catalyst was put into the reactor. Only H<sub>2</sub>, CS<sub>2</sub>, S<sub>2</sub> as well as small amount of carbon soot were found in product steam. Figure 2, 3 and 4 show the concentration of the CS<sub>2</sub> in the product steams for these experiments as well as equilibrium concentrations calculated for cases 1 through 3. Hydrogen was

formed, but is not shown in these figures. As indicated from Figure 2. at 700°C CS<sub>2</sub> concentration is low compared to the equilibrium line. Catalyst activity increases until at 1100°C, CS<sub>2</sub> concentration is approaches close to equilibrium. The yield of CS<sub>2</sub> from methane at 1100°C for all three cases was above 90%. Methane concentration drops off as temperatures increases. In Figure 2. at 1100°C the concentration of methane for the 5 second residence time experiments falls below the equilibrium line. This may be attributed to the formation of some carbon solids in the reactor. As mentioned above carbon solids were not included in the equilibrium calculations. Carbon balances for these runs were in the range of 90 to 95%.

The results in this paper indicate that a catalyst for the first step, the conversion of CH<sub>4</sub> and H<sub>2</sub>S to CS<sub>2</sub> and hydrogen, has been found. We are continuing to develop catalysts from this beginning.

#### ACKNOWLEDGMENT

This work was supported by the U.S.Department of Energy, Pittsburgh Energy Technology Center, Pittsburgh, Pennsylvania under Contact No. DE-AC22-93PC92114.

#### REFERENCES

1. C.D.Chang, US patent #4,543,434, Sep.24, 1985

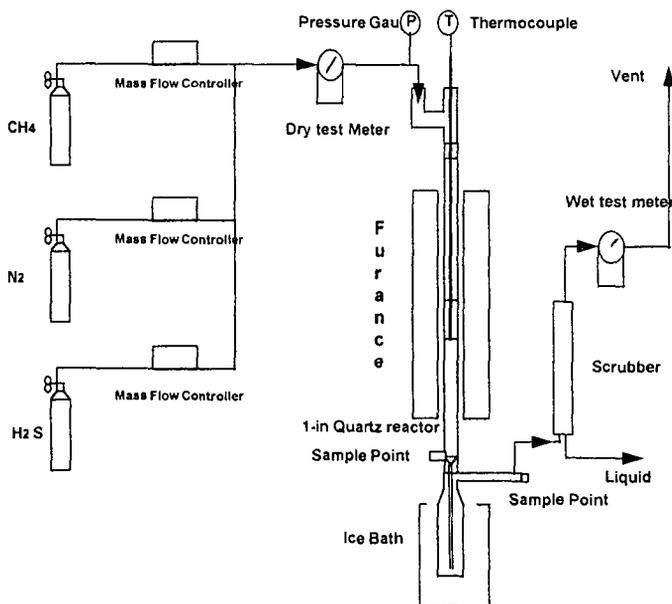


Figure 1. Schematic diagram of flow reactor system

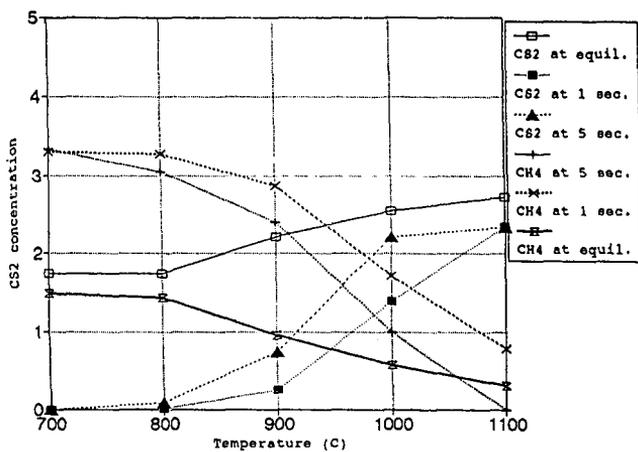


Figure 2. CS<sub>2</sub> production at H<sub>2</sub>S/CH<sub>4</sub>=2. for catalyst 1.

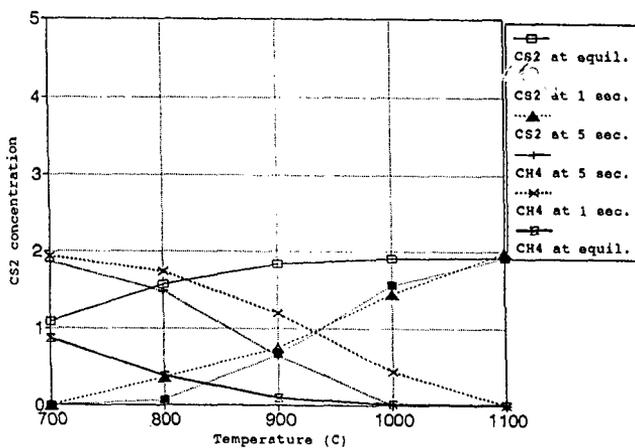


Figure 3. CS<sub>2</sub> production at H<sub>2</sub>S/CH<sub>4</sub>=4. for IGT-MS-105 catalyst.

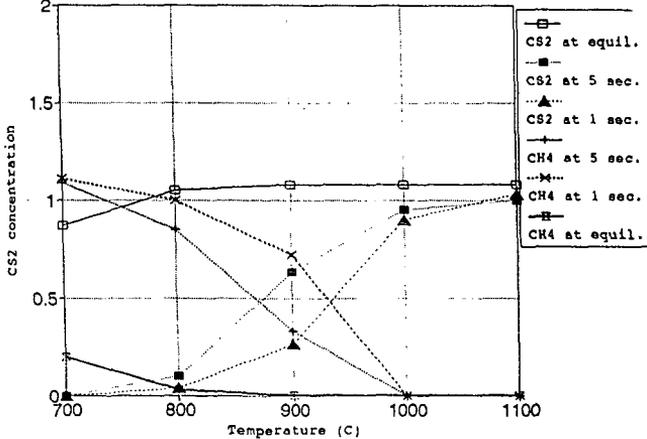


Figure 4. CS<sub>2</sub> production at H<sub>2</sub>S/CH<sub>4</sub>=8. for IGT-MS-105 catalyst.

# CERAMIC MEMBRANES FOR GENERATION OF PARTIAL-OXIDATION PRODUCTS FROM METHANE

U. Balachandran, J. T. Dusek, S. M. Sweeney,  
R. L. Mievile, and P. S. Maiya  
Argonne National Laboratory, Argonne, IL 60439

M. S. Kleefisch, S. Pei, and T. P. Kobylinski  
Amoco Research Center, Naperville, IL 60566

A. C. Bose  
U.S. Department of Energy  
Pittsburgh Energy Technology Center, Pittsburgh, PA 15236

**Keywords:** Dense membrane, mixed conductor, syngas

## INTRODUCTION

The most significant cost associated with partial oxidation of methane to syngas is that of the oxygen plant. In this paper, we offer a technology that is based on dense ceramic membranes and that uses air as the oxidant for methane-conversion reactions, and eliminating the need for an oxygen plant. Certain ceramic materials exhibit both electronic and ionic conductivities (of particular interest is oxygen-ion conductivity). These materials transport not only oxygen ions (functioning as selective oxygen separators), but also electrons, back from the reactor side to the oxygen/reduction interface. No external electrodes are required and if the driving potential of transport is sufficient, the partial oxidation reactions should be spontaneous. Such a system will operate without an externally applied potential. Oxygen is transported across the ceramic material in the form of oxygen anions, not oxygen molecules.

Recent reports in the literature suggest that ceramic membranes made of these mixed conductors can successfully separate oxygen from air at flux rates that could be considered commercially feasible, and thus can have potential applications for improving the economics for methane conversion processes [1-11].

## EXPERIMENTAL

Two ceramic powders of the La-Sr-Fe-Co-O system with differing stoichiometries, designated SFC-1 and SFC-2, were made by solid-state reaction of the constituent cation salts. The stoichiometry of SFC-1 is the same as that of  $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.6}\text{Co}_{0.4}\text{O}_x$ , which was used by Teraoka et al. [1,2]. SFC-2 is an improved version of SFC-1. Appropriate amounts of  $\text{La}(\text{NO}_3)_3$ ,  $\text{SrCO}_3$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{Fe}_2\text{O}_3$  were mixed and milled in isopropanol with  $\text{ZrO}_2$  media for  $\approx 15$  h. When dry, the mixtures were calcined in air at  $\approx 850^\circ\text{C}$  for  $\approx 16$  h, with intermittent grinding. After final calcination, with an agate mortar and pestle, we ground the powder to an average particle size of  $\approx 7 \mu\text{m}$ . The resulting powders were

characterized by X-ray diffraction (XRD), scanning electron microscopy, and thermal analysis, and analyzed for particle-size distribution.

The powder was made into a slip containing a solvent, dispersant, binder, and plasticizer. Membrane tubes were fabricated by extrusion of the slip to an outside diameter of  $\approx 6.5$  mm, lengths up to  $\approx 30$  cm, and wall thicknesses of 0.25–1.20 mm. The tubes were sintered at  $\approx 1200^\circ\text{C}$  for 5–10 h in stagnant air.

An Rh-based reforming catalyst was used inside the tubes. In addition to 80% methane, the feed gas contained 20% argon, which was used as an internal calibration standard for gas analysis. Both the feed gas and the effluents were analyzed with a gas chromatograph. Outside the tube, air was the source of oxygen.

#### RESULTS AND DISCUSSION

Tubes of SFC-1 lasted only a few minutes as a conversion reactor operating at  $850^\circ\text{C}$ ; they then broke into several pieces. XRD patterns of the original samples of SFC-1 were recorded at  $850^\circ\text{C}$  in Ar-O<sub>2</sub> gas mixtures. The phase behavior of SFC-1 in 1 and 20% O<sub>2</sub> is shown in Fig. 1. In an oxygen-rich (20% O<sub>2</sub>) atmosphere, the material was a cubic perovskite. However, once the oxygen partial pressure was lowered below 5%, the cubic phase transformed to an oxygen-vacancy-ordered phase. New peaks appeared in the XRD pattern, as seen in Fig. 1 (1% O<sub>2</sub>). It is important to note that this material expanded substantially after the phase transition; this can be seen from the change in the position of the Bragg peak near  $32^\circ$ . Evidently, this peak in the oxygen-vacancy-ordered phase (in 1% O<sub>2</sub>) was shifted to the low-angle (larger d-spacing) side of the corresponding peak in the cubic perovskite phase (in 20% O<sub>2</sub>).

Detailed thermogravimetric analysis (TGA) [12] showed that the oxygen content  $x$  of the sample in 1% O<sub>2</sub> was  $\approx 0.1$  lower than that in a sample in 20% O<sub>2</sub>. Dependence of the unit cell volume on the oxygen content of the sample has been established by comparing lattice parameters. For example, the volume of the primitive perovskite cell  $V_p$  is  $57.51 \text{ \AA}^3$  for  $x = 2.67$  and  $59.70 \text{ \AA}^3$  for  $x = 2.48$ . These results show that this material expands as oxygen is removed. Such behavior suggests that an electronic effect is predominant in influencing the specific volume; otherwise, a simple size effect would cause the lattice to shrink. By linear interpolation of the above results, we predict that a decrease in  $x$  of 0.1 will result in an increase in  $V_p$  by  $\approx 2\%$ .

Both XRD results and TGA data [12] give a clear picture of the state of SCF-1 under reaction conditions. When the membrane tube is operating, high oxygen pressure is maintained outside the tube and low oxygen pressure is maintained inside the tube. Before the tube is brought up to high temperature, the distribution of oxygen is uniform. Upon heating, the tube begins to lose oxygen that was incorporated during the fabrication process. Moreover, the material on the inner wall loses more oxygen

than that on the outer wall. As a result, a stable oxygen gradient is generated between the outer and inner walls. It follows that the material, depending on its location in the tube, may contain different phase constituents. It is probable that the inner zone of lower oxygen content contains more ordered oxygen vacancies and hence less oxygen permeability.

The most remarkable factor, which can cause tube fracture, appears to be the lattice mismatch between the materials on the inner and outer walls of the tube. The difference in composition between the inner and outer zones leads to an expansion of 2%, which is equivalent to thermal expansion caused by a 333°C temperature increase.

In comparison, SFC-2 exhibited a remarkable structural stability at high temperature, as shown in Fig. 2. No phase transition was observed in this material as oxygen partial pressure was changed. Furthermore, the Bragg peaks stayed at the same position regardless of the oxygen partial pressure of the atmosphere. The mechanical properties of the SFC-2 were measured by conventional methods, i.e., bulk density was measured by the Archimedes' principle; flexural strength, in a four-point bending mode; fracture toughness, by a single-edge notch method [13]; and Young's modulus, shear modulus, and Poisson's ratio, by ultrasonic methods [14]. The thermal expansion coefficient was measured in a dilatometer. The results are shown in Table I.

Table I. Physical and mechanical properties of SFC-2

| Property   | Value       |
|--|-------------|
| Bulk density, g.cm <sup>-3</sup>                                       | 4.81 ± 0.04 |
| Percent of theoretical density   | 93          |
| Coefficient of thermal expansion x<br>10 <sup>-6</sup> /°C (200-800°C) | 14.0        |
| Flexural strength, MPa   | 120.4 ± 6.8 |
| Fracture toughness, MPa√m  | 2.04 ± 0.06 |
| Young's modulus, GPa   | 124 ± 3     |
| Shear modulus, GPa   | 48 ± 2      |
| Poisson's ratio  | 0.30 ± 0.01 |

Figure 3 shows the probability of failure vs. flexural strength (Weibull statistics) for SFC-2 [15]. The Weibull modulus was observed to be 15, indicating only moderate scatter in the strength data. Measured room-temperature properties were used to develop failure criteria for the membranes under actual reaction conditions in a plant where methane is expected to be at higher pressures. Figure 4 shows the computed allowable external pressure on SFC-2 as a function of tube wall thickness. These calculations were based on the assumptions that the tensile strength is ≈0.67 times the flexural stress and that the compressive strength of SFC-2 is greater than its tensile strength by a factor of 8.

These results suggest an ability of this ceramic material to undergo reasonable stresses that might occur in a commercial reactor. Tubes made of this material, unlike those made of SFC-1, should not fracture under reactor conditions. Figure 5 shows the conversion data obtained with a membrane tube made of SFC-2 and operated at 850°C for ~70 h. As seen from Fig. 5, methane conversion efficiency is >98%, and CO selectivity is 90%. As expected, measured H<sub>2</sub> yield is about twice that of CO.

The role of the catalyst in the transport of oxygen across the membrane of an SFC-2 tube was tested without the reforming catalyst. The results from a run of ~350 h are shown in Fig. 6. The feed gases are the same as before. In the absence of a catalyst, the oxygen that was transported through the membrane reacted with methane and formed CO<sub>2</sub> and H<sub>2</sub>O. As seen in Fig. 6, methane conversion efficiency was ~35% and CO<sub>2</sub> selectivity was ~90%. Under our operating conditions, the measured oxygen flux was ~0.3 std cm<sup>3</sup>/cm<sup>2</sup>/min. Figure 7 shows the result of a reactor run made under more severe conditions and in the presence of a catalyst for >500 h. Conversion and selectivities are similar to those of the 350-h run but the oxygen flux was one order of magnitude greater. Some small deactivation in oxygen permeation rate was observed.

#### CONCLUSIONS

Long tubes of La-Sr-Fe-Co-O (SFC) membrane have been fabricated by plastic extrusion. Thermodynamic stability of the tubes was studied as a function of oxygen partial pressure by high-temperature XRD. Mechanical properties were measured and found to be adequate for a reactor material. Performance of the membrane strongly depended on the stoichiometry of the material. Fracture of certain SFC tubes was the consequence of an oxygen gradient that introduced a volumetric lattice difference between the inner and outer walls. However, tubes made with a particular stoichiometry (SFC-2) provided methane conversion efficiencies of >99% in a reactor. Some of the reactor tubes have operated for up to ~500 h.

#### ACKNOWLEDGMENTS

Work at Argonne National Laboratory is supported by the U.S. Department of Energy, Pittsburgh Energy Technology Center, under Contract W-31-109-Eng-38.

#### REFERENCES

1. Teraoka, Y., Zhang, H. M., Furukawa, S., and Yamoze, N., *Chem. Lett.*, 1743, 1985.
2. Teraoka, Y., Nobunaga, T., and Yamazoe, N., *Chem. Lett.*, 503, 1988.
3. E. A. Hazbun, U.S. Patent 4,791,079, Dec. 13, 1988.
4. Omata, K., Hashimoto, S., Tominaga, H., and Fujimoto, K., *Appl. Catal.*, L1, 52, 1989.
5. Balachandran, U., Morissette, S. L., Picciolo, J. J., Dusek, J. T., Poeppel, R. B., Pei, S., Kleefisch, M. S., Mieville, R. L., Kobylnski, T. P., and Udovich, C. A., *Proc. Int. Gas Research Conf.*, ed. by H. A.

- Thompson (Government Institutes, Inc., Rockville, MD 1992), pp. 565-573.
6. Mazanec, T. J., Cable, T. L., and Frye, Jr., J. G., *Solid State Ionics*, 111, 53-56, 1992.
  7. Gur, T. M., Belzner, A., and Huggins, R. A., *J. Membrane Sci.* 151, 75, 1992.
  8. Cable, T. L., European Patent EP 0399 833 A1, Nov. 28, 1990.
  9. Cable, T. L., European Patent EP 0438 902 A2, July 31, 1991.
  10. Bose, A. C., Stigel, G. J., and Srivastava, R. D., "Gas to Liquids Research Program of the U.S. Department of Energy: Programmatic Overview," paper to be presented at the Symposium on Alternative Routes for the Production of Fuels, American Chemical Society National Meeting, Washington, DC, August 21-26, 1994.
  11. Proceedings of Coal Liquefaction and Gas Conversion Contractors Review Conference, Eds. S. Rogers et al., U.S. Department of Energy, Pittsburgh Energy Technology Center, Pittsburgh, PA, September 27-29, 1993.
  12. Pei, S., Zajak, G. W., Faber, J., Mieville, R. L., Udovich, C. A., and Kleefisch, M. S., to be published.
  13. Brown, Jr., W. F., and Strawley, J. E., ASTM STP 410, Philadelphia, PA, 1967.
  14. Kraüt Kramer, J., and Kraüt Kramer, H., *Ultrasonic Testing of Materials*, (Springer-Verlag, New York, 1983).
  15. Weibull, W., *J. Appl. Mech.*, 293, 18, 1951.

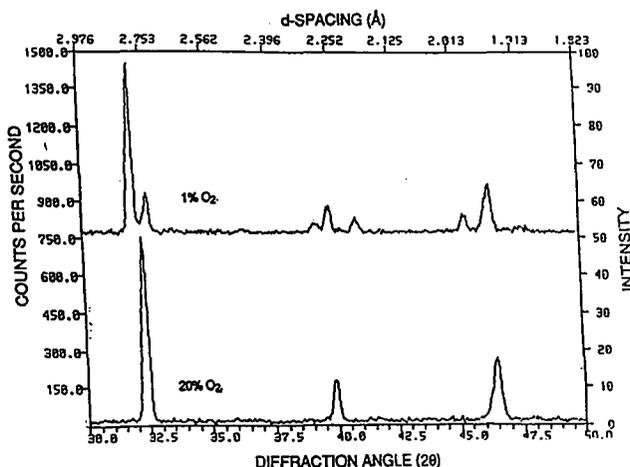


Figure 1. XRD of SFC-1 at 850°C in 1 and 20% O<sub>2</sub>.

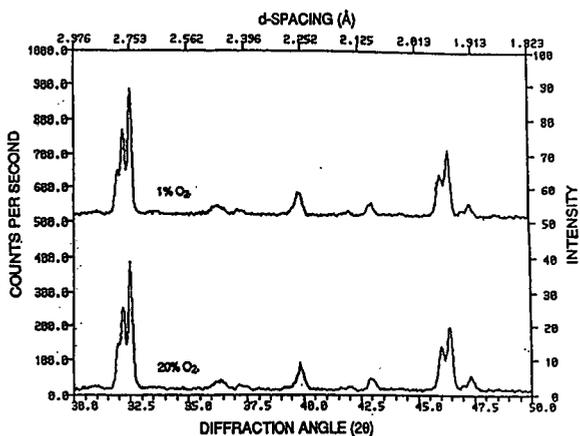


Figure 2. XRD of SFC-2 at 550°C in 1 and 20% O<sub>2</sub>.

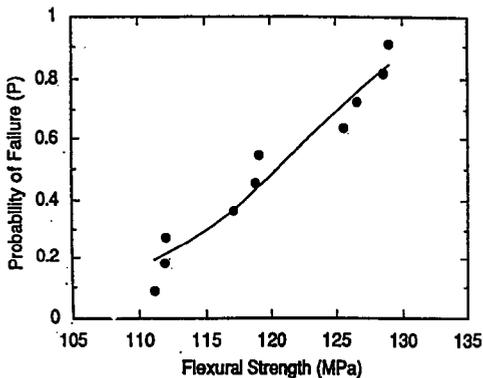


Figure 3. Probability of Failure vs Flexural Strength for SFC-2 (Weibull modulus = 14.5).

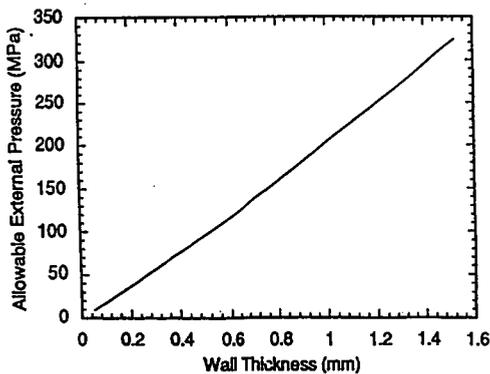


Figure 4. Allowable External Pressure on SFC-2 Tubes as a Function of Wall Thickness (outside diameter = 6.46 mm).

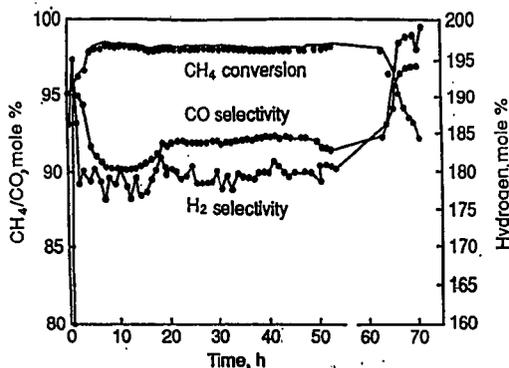


Figure 5. Methane Conversion and CO and H<sub>2</sub> Selectivities in SFC-2 Membrane Reactor with Reforming Catalyst.  
 Conditions: Feed (80% Methane, 20% Argon) Flow, 1.5cc/min, T<sub>exp</sub>, 850°C, P<sub>res</sub>, 1atm, Membrane SA, 10cm<sup>2</sup>.

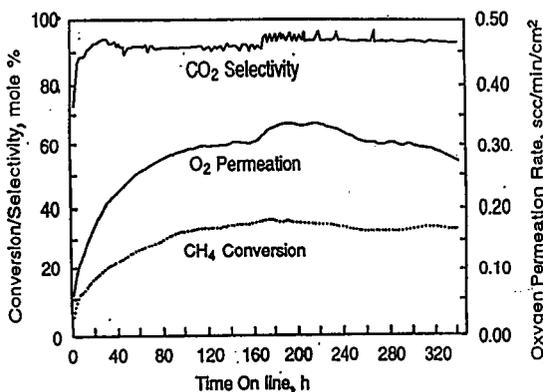


Figure 6. Methane Conversion and CO<sub>2</sub> Selectivity and O<sub>2</sub> permeation in SFC-2 Membrane Reactor without Reforming Catalyst.  
 Conditions: Same as in Fig 5

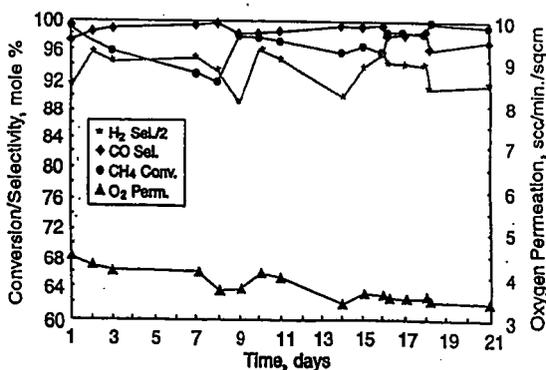


Figure 7. Methane Conversion and CO and H<sub>2</sub> Selectivities and O<sub>2</sub> permeation in SFC-2 Membrane Reactor with Reforming Catalyst.  
 Conditions: Feed (80% Methane, 20% Argon) Flow, 1.0cc/min, T<sub>exp</sub>, 900°C, P<sub>res</sub>, 1atm, Membrane SA, 8cm<sup>2</sup>.