PRESSURE EFFECTS ON THE OXYHYDROCHLORINATION OF METHANE

Mark A. McDonald and Michael F. Zarochak
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[1]. In the first step, methane is oxyhydrochlorinated to chloromethane:

$$CH_4 + HCl + \frac{1}{2} O_2 = CH_3Cl + H_2O \quad (1)$$

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

$$CH_3Cl = -CH_2- + HCl \quad (2)$$

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[2].

Several publications have described work done at atmospheric pressure on the two steps in this process[3,4]. 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[2].

EXPERIMENTAL METHODS

Flow rates of CH_4, HCl, O_2, and N_2 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[5,6]. Analysis of this dried catalyst precursor yielded a composition that can be expressed as 41.7% CuCl, 11.5% KCl, 9.4% $LaCl_3$, and 37.5% SiO_2[4]. 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[7].

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_2, O_2, N_2, CH_4, and CO) were analyzed with a 3A molecular sieve column and an argon carrier gas. Chloromethanes and CO_2 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_2 at 543 K for 0.5 h. Catalyst tests were typically carried out for a maximum of five days.

The N_2 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 $1 \cdot 10^{19}$ catalyst surface atoms per m^2 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^2g^{-1}, in contrast to the value of 325 $m^2\ g^{-1}$ for the pure Cab-O-Sil. Table 1 shows catalyst yield and selectivity data for relative compositions of 5:2:1 CH_4:HCl:O_2. 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^{-1}.

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 $(WHSV)^{-1}$, 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:

$$r \propto [CH_4]^{0.8}\,[HCl]^{0.4}\,[O_2]^{0.2} \qquad (3)$$

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.*[4] reported CH_4 conversion at 604 K that converts to a STY value of $0.18 \cdot 10^{-3}\ s^{-1}$. 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_4 concentration in the feed (a stoichiometric 2:2:1 CH_4:HCl:O_2 was used) and at generally higher CH_4 conversions. When

adjusted for the higher concentrations of 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 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 HCOOH at intermediate conversion levels and mainly CO_2 at highest conversions and saw no CO. In contrast to their work and also to results of Conner *et al.*[8], we saw no 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 HCOOH decomposition and the differences in the reaction systems involved. The HCOOH molecule is known to decompose on reduced nickel surfaces at *ca.* 400 K [9], 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 CH_4, side reactions of any product HCOOH could have occurred. In contrast, Taylor *et al.* used a quartz reactor and PTFE tubing, which do not catalyze HCOOH decomposition.

CONCLUSION

The oxyhydrochlorination yield of a 5:2:1 ratio of CH_4:HCl:O_2 increased over threefold as pressure increased from 130 to 930 kPa. This increase was accompanied by a decrease in selectivity to CH_3Cl, 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 HCOOH was observed, likely due to 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., Zarochak, 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
Inlet concentration (%)							
N_2	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_4	55.6	58.8	58.8	55.6	58.8	57.1	58.8
O_2	11.1	11.8	11.8	11.1	11.8	11.4	11.8
Nominal Site-Time Yield CH_4 (10^{-3} s^{-1})	0.15	0.56	1.79	0.45	1.14	2.55	0.51
Apparent activation energy (kJ mol^{-1})	171			186			-----
Conversions (%)							
CH_4	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_2	14	24	69	22	30	69	8.9
Selectivities (%)							
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

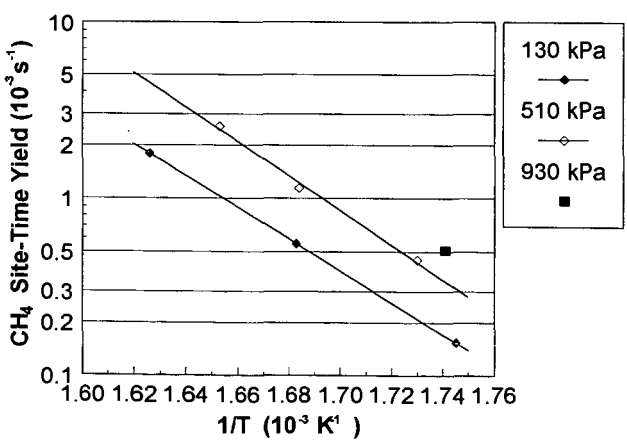

Figure 1. Arrhenius Plot

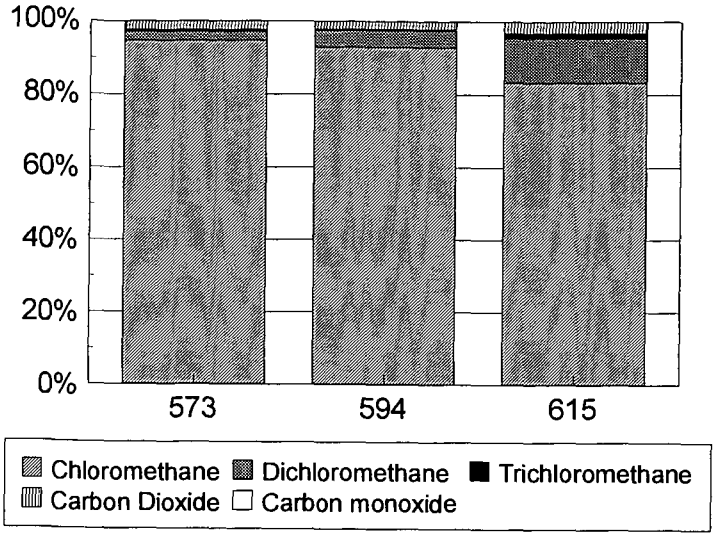

Figure 2 Selectivities at 130 kPa

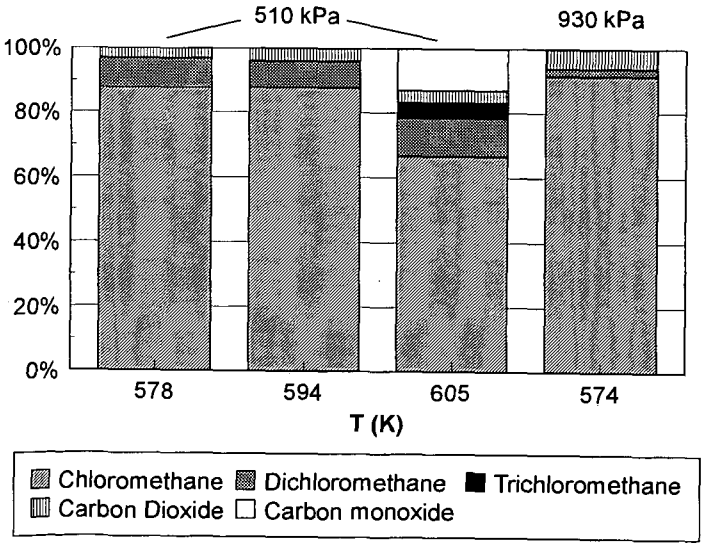

Figure 3 Selectivities at 510 and 930 kPa