

METHYL CHLORIDE VIA OXYHYDROCHLORINATION OF METHANE

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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 ¹⁰. An additional review by Kenney ¹¹ is helpful on the subject of catalytic melts.

There are several key technology challenges associated with the development of a CH_4 oxyhydrochlorination process. Among these are the chemistry problems associated with development of a selective CH_3Cl catalyst, and in addition, the chemical engineering challenges associated with the operation of a process containing HCl and CH_3Cl . 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 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 CCl_4 as well as heavily oxidized byproducts. In addition, kinetic measurements, done both as part of our research and published previously, ¹² 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 CH_3Cl .

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 CH_4 , the reaction to form CH_3Cl has an activation energy of 121 kJ/mol, this compares with 225 and 240 to form CO and 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 CO and 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 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 CH_3Cl . 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 Cl chlorocarbons, resistance to $\text{HCl}(\text{aq})$, insolubility with H_2O , 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 CH_3Cl 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^{13,14,15,16} regarding selective catalysis of the OHC reaction to CH_3Cl . The primary catalytic metals reported to be useful for the OHC reaction of CH_4 are Cu and Fe , with the PETC group also reporting the use of Co as a selectivity enhancing catalyst¹⁶. 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% CH_4 conversion and 80% CH_3Cl selectivity represents the desired range of operation for this technology. As is shown, only the single point represented by the British Petroleum patent¹⁴ 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 Al_2O_3 catalyst was evaluated with a feed stoichiometry of $4.4/1/1.2$ $\text{CH}_4/\text{O}_2/\text{HCl}$. The CH_3Cl and CH_2Cl_2 selectivities as well as the CO_x (oxygenated products) selectivity and 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 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 CO_x products dropped from 18% to 8%. This was accompanied by a rise in the CH_3Cl selectivity from 68% to 78%. This is a fairly clear indication that the excess heat was serving only to further react product CH_3Cl via combustion to CO and 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 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 CH_4 conversion of about 5%. Clearly this catalyst, with about 2% Cu loading, did not possess adequate activity to provide the targeted 20% 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% CH₃ 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 CH₃Cl 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 CH₃Cl 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.

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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

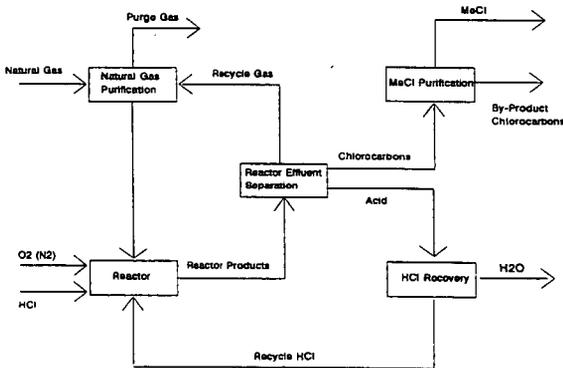


Figure 3

OHC Catalyst Evaluations

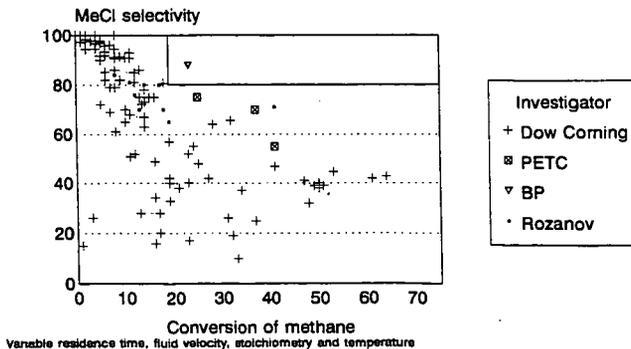
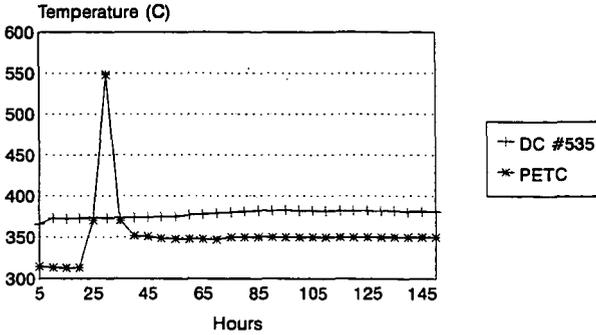


Figure 4

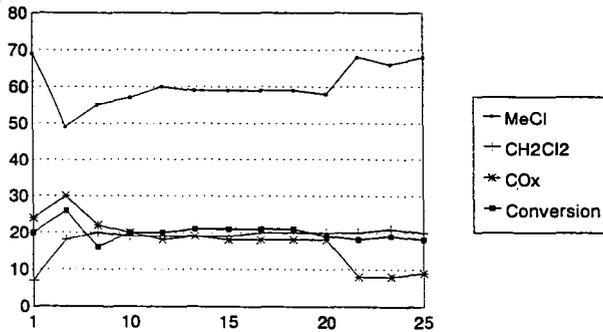
Comparison of Internal Packed Bed Temperatures



Catalyst Comparison

Figure 5

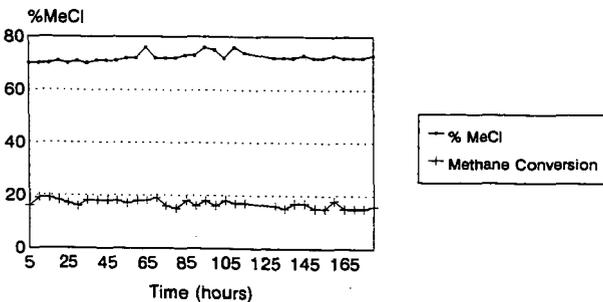
Impact of Reaction Temperature upon Selectivity



Stoichiometry 4.4/1/1.2 CH₄/O₂/HCl

Figure 6

Promoted OHC Catalyst with Increased Stability



Catalyst #538D, Temperature 340 C
Stoichiometry CH₄/O₂/HCl 4:1:1.3
Experiment 11046009