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1. EXECUSIVE SUMMARY

This is the final report of the one-year R&D project, titled “Methyl Chloride from Direct Methane Partial Oxidation: A High-Temperature Shilov-Like Catalytic System” under the award agreement number DE-EE0003461 from United States Department of Energy. The intension of this study is to demonstrate and evaluate the scientific and economic feasibility of using special solvents to improve the thermal stability of Pt-catalyst in the Shilov system, such that a high reaction temperature could be achieved. The higher conversion rate (near 100%) of methyl chloride from partial oxidation of methane under the high temperature (~ 200 °C) without significant Pt⁰ precipitation has been achieved. High concentration of the Cl⁻ ion has been identified as the key for the stabilization of the Pt-catalysts. H/D exchange measurements indicated that the over oxidation will occur at the elevated temperature, developments of the effective product separation processes will be necessary in order to rationalize the industry-visible CH₄ to CH₃Cl conversion.

2. PROJECT OVERALL OBJECTIVE

This project aims at developing a high-temperature Shilov-like catalytic system (HT-Shilov-Like System) which can directly and efficiently convert methane (CH_4) to methyl chloride (CH_3Cl). The ultimate target of the developing technology is to cost-effectively as well as environmental-friendly utilize the abundant yet mostly untapped natural gas reservoirs providing low-cost chemical feedstock and energy resources while greatly reducing greenhouse gas (GHG) emission (methane is the largest non- CO_2 GHG).

3. BACKGROUND

Methyl Chloride (CH_3Cl), also known as chloromethane, is a very important chemical intermediate in the production of silicone polymers. It is also used as a solvent in pharmaceutical manufacturing, metal cleaning/degreasing, petroleum refining and other chemical processing applications. Currently, most of industrial CH_3Cl are produced through the reaction of methanol (CH_3OH) and hydrogen chloride (HCl). Because the methanol production itself is a multiple-step, high temperature and energy intensive process from methane (CH_4), CH_3Cl is considered as the end product in chemical hydrocarbon conversion processing. On the other hand, the CH_3Cl hydrolysis to form CH_3OH is a well-established process, which makes the CH_3Cl equally important as CH_3OH to be the raw materials for many hydrocarbon conversions. Therefore, development of high-efficient and cost-effective CH_4 to CH_3Cl conversion process belongs to the next generation manufacturing concept that could be significantly improve the energy efficiency as well as reduce the production cost.

Although CH_4 can be directly chlorinated by chlorine gas at temperature above $400\text{ }^\circ\text{C}$, the reaction is a free radical reaction suffering from the poor selectivity. As a matter of fact, direct utilizations of CH_4 as feedstock to important commodity chemicals, such as CH_3Cl , CH_3OH , $(\text{CH}_3)_2\text{O}$, HCOOH and HCOH etc, through selective oxidation processes, have been regarded as a 'Holy Grail' in the chemical industry. The main hurdle is originated from the extreme stable C-H bonds and high symmetric molecular structure of the CH_4 molecule. Since 1970s, extensive R&D efforts have been taken on the development of low-temperature, high-selectivity, direct CH_4 oxidation chemistry, yet

there are not commercially visible processes available. The developed catalytic processes suffer from several weaknesses such as (1) poor catalytic efficiency such that the CH₄ conversion rates are low at mild temperature/pressure conditions; (2) poor product selectivity such that additional separation processes are demanded; and (3) over-oxidation to form carbon dioxide (CO₂) since the formation of CO₂ is thermodynamically more favorable than other desired products.

The first successful attempt was made by Alexandra Shilov in 1972, who discovered a low temperature (80 ~ 150 °C) aqueous catalytic system, the so-called Shilov system. The original system developed by Shilov consisted of Pt^{II}Cl₂ as catalyst with [Pt^{IV}Cl₆]⁻² acting as the oxidant in the aqueous solution. The over Shilov process consists of three key reaction steps, namely (1) the electrophilic C-H activation; (2) the oxidation of the intermediate complex; and (3) the catalyst regeneration through the nucleophilic replacement.

The key hindrance of the original Shilov system is the poor thermal stability of the Pt^{II}Cl₂ catalyst, which forms the Pt⁰ precipitation at the elevated temperature. As a result, only relatively low reaction temperature could be used such that the conversion rate was very low. Also the stoichiometric consumption of Pt^{IV}-oxidant is cost-prohibitive for the practical application of the Shilov system in the industrial scale.

Significant efforts have been taken to stabilize the Pt-catalyst by using different organic ligand molecules. The one of the most successful attempts came from the work of Dr. Roy Perianan at Catalylica in 1990s. The Pt-based catalyst system, (bpym)PtCl₂, has been developed to partially oxidize CH₄ to CH₃OH at relatively low temperature (~ 250 °C) in high-concentrated sulfuric acid solution. The high one-pass conversion rate (> 70%) of CH₄ and high selectivity (> 80%) of methyl-bisulfate product (could be further converted to CH₃OH through hydrolysis reaction) had been achieved. This Catalylica process also suffered from several technical shortness including insufficient reaction rate, water-poison effect of catalyst, high product separation cost, high cost for the regeneration of the highly concentrated sulfuric acid, and the environmental concerns for using the strong sulfuric acid, etc.

The further improvements have been made by us, when we added ionic liquids to form Pt-catalyst/Ionic Liquid/Sulfuric Acid ternary systems for the partial CH₄ oxidation. Several classes of task-specifically designed ionic liquids have been identified and synthesized to rationalize the CH₄-to-CH₃OH conversion. These PEER catalytic systems have super reactivity (3-fold enhanced than the Catalytica system), elongated catalyst lifetimes, and greatly improved water-resistance. The key of these successes is to use special ionic liquids which are stable under the harsh reaction conditions (high-temperature, strong acidity, powerful catalyst and strong oxidants).

Ionic liquids are special salts with the low melting points (~ 100 °C). Among of many special characteristics of ionic liquids such as excellent thermal stability (up to 400 °C), virtually not detectable vapor pressure, large electrochemical windows, special ionic liquids could also dissolve a wide variety of organic and inorganic compounds. By addition of selected ionic liquids to the Shilov system, we anticipate to reverse the Pt⁰ precipitation reaction by maintaining significant amount of Pt-catalyst in solution, such that a higher reaction temperature (120 ~ 250 °C) could be achieved. At the elevated reaction temperature conditions, the methane conversion rate and the catalytic efficiency could be increased.

4. TASKS AND SCHEDULES

Task 1: To develop an optimized HT-Shilov-Like Catalytic System for CH₄-CH₃Cl Conversion (months 1-9)

Task 1.1 to search for appropriate stabilizing agent

Task 1.2 to search for effective yet cheap oxidants

Task 1.3 to search for powerful catalysts

Task 1.4 to investigate the mechanisms involved in HT-Shilov-Like System

Task 2: To build up a novel bench-scale reactor for catalytic methane conversion experiments (Months 5-10)

Task 3: To conduct bench-scale tests and preliminary economic analysis (Months 10-12)

Task 4: Potential benefits assessment (Months 10-12)

Task 5: Project management and reports (Months 1-12)

Table 1 Gantt Chart of Task/Milestones Information

| Task | Description | Duration (Months) | | | | | | | | | | | | |
|-------------------------------|---------------------------------|-------------------|---|---|---|---|---|---|---|---|----|----|----|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | |
| 1 | HT-Shilov-Like Catalytic System | █ | █ | █ | █ | █ | █ | █ | █ | █ | █ | | | |
| 2 | Bench-Scale Reactor | | | | | █ | █ | █ | █ | █ | █ | █ | | |
| 3 | Bench-Scale Tests | | | | | | | | | | | █ | █ | █ |
| 4 | Potential Benefits Assessment | | | | | | | | | | | █ | █ | █ |
| 5 | Project Report | █ | █ | █ | █ | █ | █ | █ | █ | █ | █ | █ | █ | █ |
| Milestone 1: Optimized System | | | | | | | | | | | | | | |
| Milestone 2: Bench-scale Test | | | | | | | | | | | | | | |

5. RESULTS AND DISCUSSIONS

5.1 To search for appropriate stabilizing Agents (Task 1.1)

5.1.1 The Pt⁰ precipitation of the High-Temperature Shilov System

At temperature higher than 120 °C, the original Shilov system (K₂PtCl₄) suffered from the Pt⁰ precipitation. It had been suggested by Shilov himself that addition of the CH₃COOH might significantly accelerate the conversion rate (~ 30 times) at low temperature and low conversion rate. He attributed this observation to the enhanced CH₄ solubility and chelate formation of the carboxylic anions of Pt-catalyst. To examine the effects of CH₃COOH addition at the higher reaction temperature, we had carried out several probe experiments and the results are summarized in Table 2. The H/D exchange between the methane (CH₄) with deuterium water (D₂O) and the deuterium isomer of Acetic acid (CD₃COOD) is determined as the indicator of the methane conversion. All experiments without additions of ionic liquids and/or other stabilizers resulted in the precipitation of the Pt catalyst, although substantial enhancements of the conversion rates had been observed. These results suggested that the addition of the acetic acid might enhance the methane solubility, but their chelation strengths on Pt-catalyst are not strong

enough to prevent the precipitation. Changing of the catalytic system from the K_2PtCl_4 to H_2PtCl_6 and their mixtures, or fluorination of the acetic acid did not improve the Pt stability.

Table 2 Effect on the Pt^0 precipitation by the addition of CH_3COOH . Experimental conditions: Gold tube experiments were conducted at 140 °C with 3700 psi external hydraulic pressure. Turn-Over Numbers (TON) shaded indicated the formation of Pt^0 (Coating).

| Rxn No. | Catalyst | Reaction Media | Ionic Liquid | Reaction Time (hr) | H/D Exchange Ratio | | TON |
|---------|-------------------------|-------------------------|--------------|--------------------|--------------------|---------|-----|
| | | | | | CD_xH_{4-x} | CDH_3 | C-H |
| 1 | K_2PtCl_4 | D_2O | --- | 4 | 7.2 | 3.3 | 0.5 |
| 2 | K_2PtCl_4 | $D_2O + CD_3COOD$ (30%) | --- | 4 | 13.0 | 5.1 | 2.1 |
| 3 | K_2PtCl_4 | $D_2O + CD_3COOD$ (30%) | --- | 12 | 13.1 | 5.0 | 2.1 |
| 4 | H_2PtCl_6 | $D_2O + CD_3COOD$ (30%) | --- | 12 | 19.4 | 7.3 | 3.2 |
| 5 | K_2PtCl_4 | $D_2O + F_3COOD$ (20%) | --- | 5 | 18.0 | 9.9 | 2.6 |
| 6 | $K_2PtCl_4 + H_2PtCl_6$ | $D_2O + CD_3COOD$ (30%) | --- | 12 | 31.4 | 8.3 | 0.8 |

5.1.2 Effects of the additional Ionic Liquids

When selected ionic liquids to the original Shilov system, there are virtually not Pt^0 precipitation occurring at the reaction temperature of 140 °C (Table 3). However, the observed H/D exchange rates also decrease. One possibility is that the added ionic liquids do form chelation with the Pt-catalyst to prevent the precipitation, but do not improve the CH_4 solubility or might weaken the reactivity of catalyst. Nevertheless, since our reaction temperature was set at the 140 °C, which is exceed the shilov's low-temperature experiments (80 ~ 120 °C), the effect of adding selected ionic liquids to stabilize Pt catalyst is important. However, the Pt^0 precipitation occurred again with the further increases of the reaction temperature to 185 °C (Table 4). Higher reaction temperature (exceed to 220 °C) conditions were forbidden in our experimental setting, due to the thermal stability of selected ionic liquids under the strong Pt-catalytic and high pressure conditions.

Table 3 Effects of addition Ionic Liquids on the Pt⁰. Gold tube experiments were conducted at 140 °C with 3700 psi external hydraulic pressure.

| Rxn No. | Catalyst | Reaction Media | Ionic Liquid | Reaction Time (hr) | H/D Exchange Ratio | | TON C-H |
|---------|----------------------------------|---|--|--------------------|----------------------------------|------------------|---------|
| | | | | | CD _x H _{4-x} | CDH ₃ | |
| 7 | K ₂ PtCl ₄ | D ₂ O | [pyrz][HSO ₄] ^a | 4 | 1.9 | 1.8 | 0.1 |
| 8 | K ₂ PtCl ₄ | D ₂ O | [pyrz][HSO ₄] ^b | 4 | 2.0 | 1.7 | 0.1 |
| 9 | K ₂ PtCl ₄ | D ₂ O + CD ₃ COOD (30%) | [1mim]Cl ^a | 4 | 2.2 | 1.7 | 0.4 |
| 10 | K ₂ PtCl ₄ | D ₂ O + CD ₃ COOD (30%) | [1mim][HSO ₄] ^a | 4 | 2.2 | 1.8 | 0.4 |
| 11 | K ₂ PtCl ₄ | D ₂ O + CD ₃ COOD (30%) | [1mim]Cl ^b | 4 | 3.1 | 2.2 | 0.5 |
| 12 | H ₂ PtCl ₆ | D ₂ O + CD ₃ COOD (30%) | [1mim]Cl ^b | 12 | 6.2 | 3.5 | 1.0 |

Notes:

^a: the ionic liquid and the catalyst were heated at 150 °C for 30 min, and added into the CD₃COOD solution after cooling down.

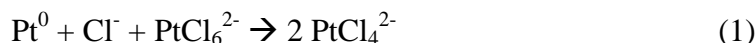
^b: the ionic liquid, the catalyst and the CD₃COOD solution were mixed together at room temperature.

Table 4 H/D exchange experiments at 185 °C in ionic liquid modified Shilov system

| Rxn No. | Catalyst | Reaction Media | Ionic Liquid | Reaction Time (hr) | H/D Exchange Ratio | | TON C-H |
|---------|----------------------------------|---|-----------------------|--------------------|----------------------------------|------------------|---------|
| | | | | | CD _x H _{4-x} | CDH ₃ | |
| 13 | K ₂ PtCl ₄ | D ₂ O + CD ₃ COOD (30%) | [1mim]Cl ^b | 4 | 9.5 | 5 | 1.6 |
| 14 | H ₂ PtCl ₆ | D ₂ O + CD ₃ COOD (30%) | [1mim]Cl ^b | 4 | 15.9 | 8.8 | 2.7 |

5.1.3 Effects of Acid Stabilizers

The addition of the excess hydrogen chloride (HCl) and sulfuric acid (H₂SO₄) could effectively prevent the coating formation at temperature 140 °C (Table 5). Importantly, at the reaction temperature of 185 °C, HCl did prevent the Pt⁰ precipitation, while H₂SO₄ did not (Table 6). The stabilization effect of adding acids can be attributed to the concentrated Cl⁻ ions through the reaction:



which is the reverse reaction of the Pt⁰ precipitation. Importantly, it seems that the acidity does not have significant effects on the Pt⁰ stabilization, since the sulfuric acid does not prevent the precipitation at the elevated temperature of 185 °C. This offers the opportunity to replace high concentrated proton ion (H⁺) with more eco-friendly cations such as those in the ionic liquids including [1mim][Cl] etc.

Table 5 H/D experiments at 140 °C with the additions of excess amount of strong acids (HCl and H₂SO₄)

| Rxn No. | Catalyst | Reaction Media | Ionic Liquid | Reaction Time (hr) | H/D Exchange Ratio | | TON C-H |
|---------|----------------------------------|--|--------------|--------------------|----------------------------------|------------------|---------|
| | | | | | CD _x H _{4-x} | CDH ₃ | |
| 15 | K ₂ PtCl ₄ | CD ₃ COOD (30%) + HCl (8.4M) | --- | 4 | 2.8 | 2.0 | 0.5 |
| 16 | K ₂ PtCl ₄ | CD ₃ COOD (30%) + D ₂ SO ₄ (1M) | --- | 4 | 2.9 | 1.0 | 0.5 |

Table 6 H/D experiments at 185 °C with the additions of excess amount of strong acids (HCl and H₂SO₄)

| Rxn No. | Catalyst | Reaction Media | Ionic Liquid | Reaction Time (hr) | H/D Exchange Ratio | | TON C-H |
|---------|----------------------------------|--|--------------|--------------------|----------------------------------|------------------|---------|
| | | | | | CD _x H _{4-x} | CDH ₃ | |
| 18 | K ₂ PtCl ₄ | D ₂ O(30%) + DCl (8.4M) | --- | 24 | 54.1 | 11.8 | 30.6 |
| 19 | K ₂ PtCl ₄ | CD ₃ COOD (30%) + DCl (8.4M) | --- | 4 | 22.6 | 11.2 | 3.8 |
| 20 | K ₂ PtCl ₄ | CD ₃ COOD (30%) + DCl (8.4M) | --- | 24 | 66.5 | 22.5 | 37.7 |
| 21 | K ₂ PtCl ₄ | CD ₃ COOD (30%) + D ₂ SO ₄ (4.2M) | --- | 4 | 35.5 | 18 | 5.9 |

5.1.4 Effects of the Cl⁻ Concentration

To examine the concentration of the Cl⁻ on the Pt stabilization, we carried out the H/D exchange experiments under different Cl⁻ concentrations. From the results listed in Table 7, it clearly indicated that the stabilization is mainly due to the high concentration of the Cl⁻ ion in the system.

Table 7 H/D exchange experiments at 185 °C with various Cl⁻ concentrations for the system of K₂PtCl₄ (20mM) + CD₃COOD (30%)

| Stabilizer | [Cl ⁻] (M) | H/D Exchange Ratio (%) | | Coating |
|--|---------------------------|----------------------------------|------------------|----------|
| | | CD _x H _{4-x} | CDH ₃ | |
| DCl | 0.7 | 61 | 29 | Yes |
| DCl | 2.8 | 60.7 | 33.7 | Yes |
| DCl | 4.2 | 61.1 | 22.5 | Yes |
| DCl | 4.9 | 65.5 | 22.6 | Slightly |
| DCl | 5.6 | 58.8 | 22 | No |
| DCl | 6.3 | 43.3 | 18.8 | No |
| DCl | 8.4 | 22.6 | 11.2 | No |
| KCl | 4 | 8.6 | 5.2 | Yes |
| KCl + CF ₃ SO ₃ D (30%) | 4 | 20.7 | 10.6 | Yes |

5.1.5 Summary and Discussions

The originally proposed by Shilov of using carboxylic acids to form the chelation of the Pt complexes did not work at the elevated temperature. The key to stabilize the Pt-catalyst is the excess amount of the Cl^- ion in the aqueous solution. And the source of the Cl^- could be from the hydrogen chloride or Cl-based ionic liquids.

5.2 To search for effective yet cheap oxidants (Task 1.2)

The original Shilov system used $[\text{Pt}^{\text{IV}}\text{Cl}_6]^{2-}$ as the oxidant, which is consumed during the reaction. Regeneration of the expensive Pt oxidant is economically forbidden for the industry-scale applications. Therefore, identifications of the proper oxidants, such as FeCl_3 and CuCl_2 which are effective and economically feasible, are important to rationalize CH_4 - CH_3Cl conversion cycle. One of the key issues in the investigation of the alternate oxidant is the over-oxidation to form carbon dioxide (CO_2). Detailed analysis of the reaction products both in gas and liquid phases are essential.

Gas Chromatograph (GC) (HP 6890) with a Gas Pro column is used to analyze the gas products (Figure 1). A customized gas transfer system attached to the GC system is able to provide the total amount of gaseous compounds in the reaction gas mixtures. The standard CH_4 with 15% of Helium (He) is used as the internal standard to quantify the CH_4 conversion. All produced gas compounds including CH_3Cl and CO_2 from the over-oxidation will be analyzed using this system.



Figure 1 Series of GC/LC equipped with FID, TCD, and ECE detectors to analyze the full-spectrum of the gas products

The formic acid (HCOOH) is the major liquid oxidation product in solution. Both GC-MS and HPLC-UV techniques were applied to quantify the amount HCOOH. Due to the strong acidity (pH \sim 1) of the formation solution, direct injection for the GC-MS analysis is not tolerable. Additional dilution process (5 \sim 10 times) will be required to neutralize to pH \sim 3 before injection. To test the efficiency of the GC-MS detection, we carried out methane conversion reaction using FeCl₃ as oxidant in HT-Shilov-Like system (0.3 mL D₂O + 8.4 M DCl + 5 mM K₂PtCl₄ + 300 mM FeCl₃) in gold tube reactor (T \sim 320 °C, P \sim 3700 psi) for 4 hours. Significant amount of HCOOH product had been detected in the aqueous solution (Figure 2).

For the HPLC-UV method, two additional cartridges will be required to remove the Cl⁻ and Fe³⁺/Cu²⁺ ions. Possible HCOOH loss when passing these cartridges needed to be calibrated. Consequently, the HPLC-UV method can be applied to analyze the larger volume of the reaction liquid with proper calibration.

A series of the oxidation reactions using CuCl₂ as oxidant were performed. The system had been tested includes K₂PtCl₄ (5 mM) as catalyst, CuCl₂ (300 mM) as Oxidant, and HCl (8.4) as stabilizer, with CH₄ pressure at \sim 50 psi and the external hydraulic pressure at 3400 psi. The detected gas products and selectivity are listed in Table 8. The

main oxidation products are CH₃Cl and CO₂ (due to over-oxidation). The over-oxidation to produce CO₂ seems to be inevitable considering the C-H bond strength of CH₄ is considerably stronger than any of its partially oxidized products.

Table 8 Gold-tube experiments to investigate the effects of reaction temperature and duration on the selectivity of the HT-Shilov-Like System with CuCl₂ as oxidant.

| Temperature (°C) | Time (min) | CH ₄ (%) | CO ₂ (%) | CH ₃ Cl(%) | Selectivity(%) |
|------------------|------------|---------------------|---------------------|-----------------------|----------------|
| 310 | 5 | 10 | 2 | 8 | 80 |
| 310 | 10 | 20 | 15 | 5 | 25 |
| 310 | 20 | 37 | 29 | 8 | 22 |
| 280 | 20 | 11 | 4 | 7 | 64 |
| 280 | 30 | 17 | 6 | 11 | 65 |
| 280 | 65 | 38 | 20 | 18 | 47 |

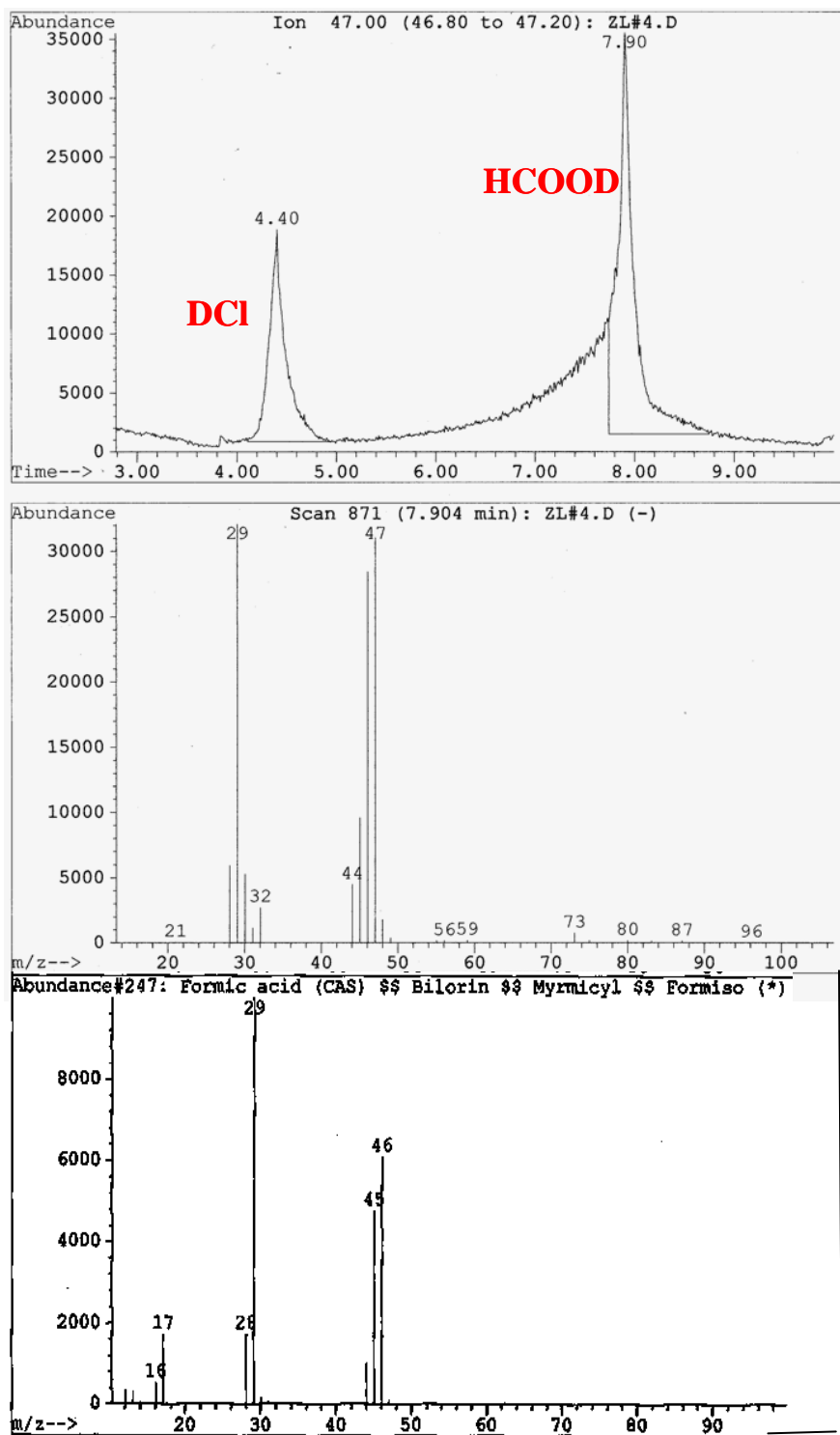


Figure 2 GC-MS for liquid compound analyses (a) Chromatograph; (b) Spectrum of the HCOOH peak; and (c) standard spectrum of HCOOH.

Discussions: Searching for the effective yet cheap oxidants as replacements of $[\text{Pt}^{\text{IV}}\text{Cl}_6]^{2-}$ should be a continuous effort to develop the HT-Shilov-Like system. When FeCl_3 and CuCl_2 were used as oxidants, the reaction temperature will be higher at ~ 300 °C. This indicated that oxidation and functionalization steps become the rate-limiting step with higher activation barriers than that of the C-H activation. Over-oxidation to generation CO_2 seems to be evitable under such reaction conditions.

5.3 To search for powerful catalysts (Task 1.3)

The super solubility of ionic liquids allows us to achieve homogeneous systems with many other metal-based catalysts. We have tested the solubility, stability and reactivity of several non-Pt catalyst systems, including $\text{Pd}(\text{CH}_3\text{OO})_2$, $(\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_3)\text{PdCl}_2$, AuCl_3 , RuCl_3 , ReCl_3 , IrCl_5 and some Os^{III} and Os^{V} -compounds. It has been found that the high valence Osmium compounds also exhibited the C-H activation reactivity. Table 9 lists some of these test results. Os-01, Os-02 and Os-03 compounds are in high valence states, and Os-04 and Os-05 are in the low valence states. Unlike the Shilov-system, all tested Os-compounds do not have any reactivity in the aqueous solution (basic or neutral). While in the sulfuric acid (even in the dilute 85 w.t.%), significant C-H activation capacity of the Os-based catalysts had been found.

Table 9 Methane C-H activation in selected Os-based systems

| Catalyst | Reaction Media | Temp (°C) | H/D Exchange Rate (%) | |
|----------|---|-----------|---|-----|
| | | | $\text{CD}_x\text{H}_{4-x}/\text{CH}_4$ | D/H |
| Os-01 | KOH(10 wt%) + D_2O | 220 | 0 | 0 |
| Os-02 | D_2O | 220 | 0 | 0 |
| Os-03 | KOH(2.5 wt%) + D_2O | 250 | 0 | 0 |
| Os-03 | D_2SO_4 (98%) | 220 | 75 | 31 |
| Os-03 | D_2SO_4 (98%) | 250 | 61 | 37 |
| Os-04 | D_2SO_4 (98%) + IL-007(6:1) | 250 | 53 | 28 |
| Os-04 | D_2SO_4 (98%) + IL-007(6:1) | 250 | 34 | 12 |
| Os-05 | D_2SO_4 (85%) + IL-048(6:1) | 250 | 101 | 79 |
| Os-05 | D_2SO_4 (85%) + IL-007(6:1) | 250 | 15 | 5 |

5.4 To investigate the reaction mechanism involved in HT-Shilov-Like System (Task 1.4)

Theoretical studies based on the Quantum Mechanics had been conducted to provide fundamental insights on the HT-Shilov-Like system mediated by ionic liquids. For the C-H activation step, the calculated energy profile is illustrated in Figure 3. The transition state **TS1** with the activation energy of 26.5 kcal/mol, which is related to the uptake of CH₄ molecule on the Pt-center, is even higher than that of the C-H activation barrier (**TS2** with an activation energy 21.2 kcal/mol). This partially explains our experimental observations that the solubility of methane in into the solution greatly affects the conversion rate; and the additions of the ionic liquids or the HCl solution could enhance the C-H activation reaction. From these studies, we have found several important differences between IL-mediated systems with original Shilov's chemistry. (1) We have found a strong interaction between the dissociated Cl⁻ ions with the hydride in configuration **D** ($R_{\text{H-Cl}} = 2.07 \text{ \AA}$), which facilitates the H/D exchange in the configuration **E**. (2) We have also observed a strong coordination of the acidic H to the Pt^{II} d_{z²} orbital, which disappears in the C-H cleavage transition state **TS2** but returns in **E**.

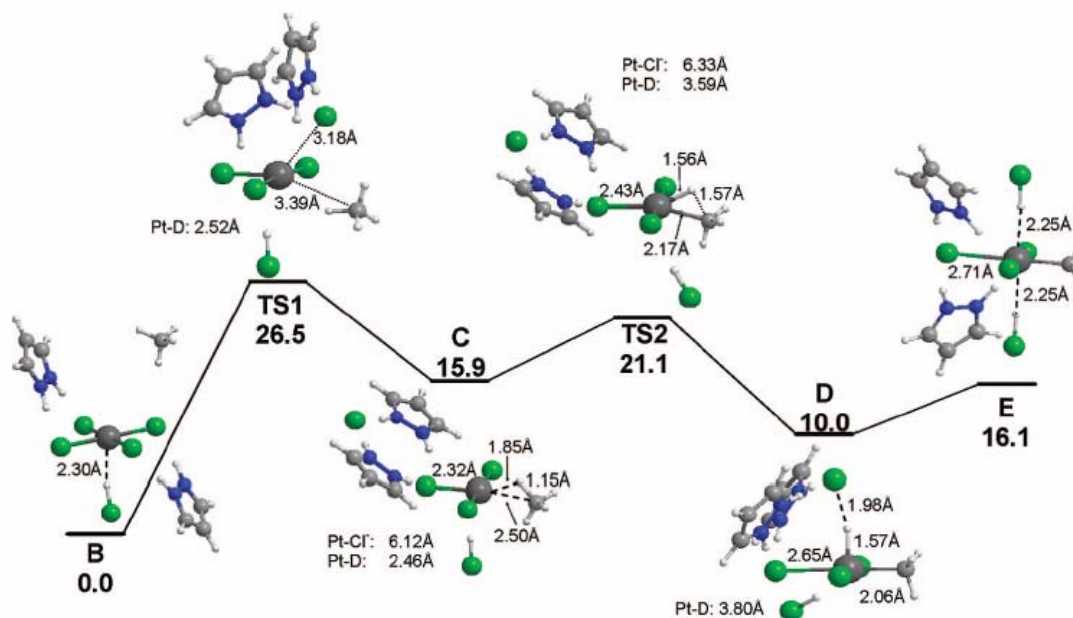
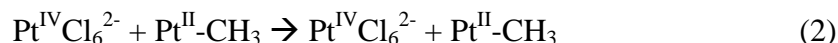


Figure 3 Calculated energy pathway and associated molecular structures for the methane C-H activation catalyzed by PtCl₄²⁻ in ionic liquid. All energies are solvated in unit of kcal/mol.

For the oxidation step along with the Shilov reaction pathway, the calculated energy profile is depicted in Figure 4. This reaction pathway features the rate-determining step in the class of reactions in which the $\text{Pt}^{\text{II}}\text{-CH}_3$ intermediate to be oxidized to $\text{Pt}^{\text{IV}}\text{-CH}_3$ by a metal halide:



The oxidation reactions in aqueous solution could occur in several possible ways such as (1) the ligand substitution (between water and chloride); (2) association of $\text{Pt}^{\text{II}}\text{-CH}_3$ with a $\text{Pt}^{\text{IV}}\text{-Cl}$ monomer. Faster oxidation of $\text{Pt}^{\text{II}}\text{-CH}_3$ intermediate may be achieved if the oxidant is more positively charged at high chloride concentration. This suggests the exploration of neutral chelating ligands on metals intended as oxidants. Such ligands are expected to inhibit the C-H activation, but they could possibly be chosen to preferentially bind to Cu or Fe centers.

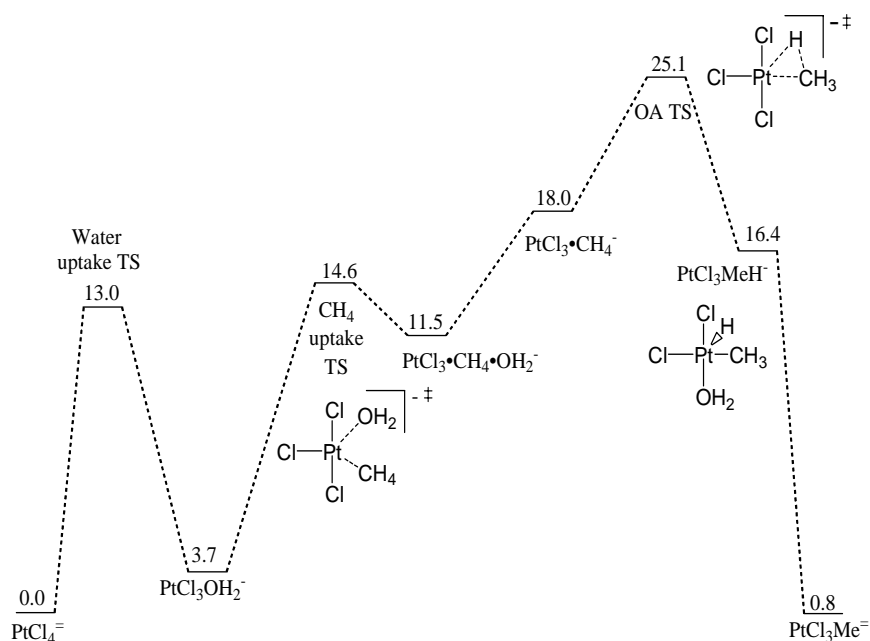


Figure 4 Schematic diagram of the energy profile of oxidation reaction pathway to form the activated $\text{Pt}^{\text{II}}\text{-CH}_3$ species. All energies are in unit of kcal/mol.

6. Bench-scale reactor for the catalytic methane conversion reactions (Task 2)

Initially, a home-made stainless steel high-pressure reactor was used. This type of reactor suffers from several technical drawbacks. (1) Large dead volume. The overall capacity of the reactor is in the range of ~ 70 mL. There is a large portion of empty space when only ~ 1 mL of reaction liquid was loaded; resulting in the low conversion rate and low yields. (2) Poor temperature control for the reaction region. The lower portion of the cylindrical reactor is submerged in conductive oil bath in where the reaction temperature is controllable. But the gas/liquid phases inside the reaction are difficult to reach the stable thermal equilibrium; resulting in the longer reaction time. (3) Low mixing speed for gas/liquid phases. Even when a magnetic stirring bar was used, the main reaction region remains in the gas/liquid phases; resulting in the low yield.

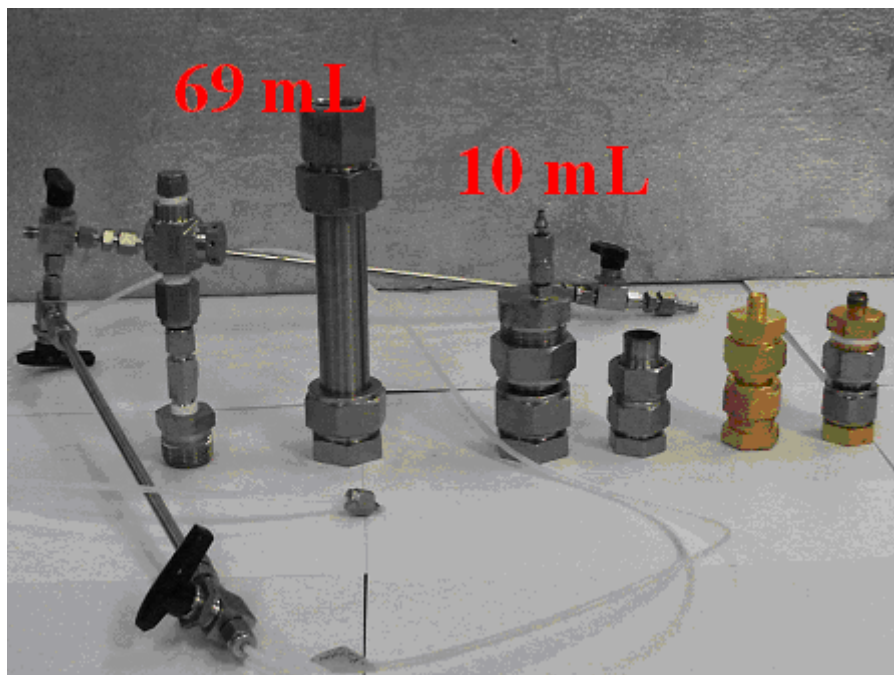


Figure 5 Improved high-pressure stainless reactors

The improved stainless steel high-pressure reactor with smaller-size (Figure 5) was used. A shorter reactor is designed and built. This smaller-size reactor reduces the total amount of methane loaded to ensure the observed yield. The reaction liquids loaded into the reactor is in the milliliter range and the gas/liquid mixing is carried out by a magnetic stir bar spinning. Such a shorter reactor design bears several disadvantages

associated with the original big reactor, functionalizes well for our preliminarily screening tests.

In order to identify and optimize reaction performance, we used special sealed gold tube mini-reactor to quantify the mass and atomic balances of reaction products (liquids, gas and solid). Gold was chosen as one of the most chemically inert materials and can give really good mass balance, uniform temperature and external high pressure control. Our sealed-gold tube reactor has a total volume in the range of 1 mL, with ~ 30% of which loaded with the reaction liquids and the rest of it filled with the methane gas (50~ 100 psi). Arc welding is used to seal the gold-tube at both ends. Sealed-gold tubes are then placed in an autoclave, which is placed into a box furnace at desired temperature with an external hydraulic pressure up to 3700 psi applied.

The advantages of this sealed-gold tube design include (1) completed mass balance; (2) well-controllable temperature/pressure conditions; (3) parallel experimental setting for the high-throughput screening. One disadvantage of the original seal-gold tube reactor is the poor heat conductivity, therefore the time required to reach fully equilibrium inside gold tube could take as long as a couple hours.

We have redesigned the autoclave system by (1) changing the steel material to aluminum (Al6061T), which could still hold liquids at high pressure (~ 3000 psi) at high temperature (up to 350 °C); (2) reducing the size of the autoclave from 1.5" hexagonal cross-section and 14" long to 1" hexagonal cross-section and 5" long, such that to reduce the heat capacity; and (3) changing the heating system from original large hot-air oven to a flux solder tin pot (Model C161). The materials of this tin pot are made from the Tin(70%)-Cu(30%) which significantly enhances the heat transport capability. Upon making these changes, we are able to conduct the seal-gold tube experiments in a much fast pace (to reach 300 °C equilibrium in less than 5 minutes).

- A modified bench-scale reactor (Figure 6) has also been constructed as proposed. This reactor is modified from the commercially purchased Parr reactor, which is superior in providing high pressure (up to 1000 psi), high gas-liquid mixing (rotating

baffles at 3000 rpm), and in-situ temperature and pressure controlling. However, the commercially available Parr reactor cannot be directly used in our experiments because of its poor corrosive resistance, at our strong oxidation and highly active catalytic conditions. Several modifications have been made on this reactor system such as using gold to coat the inner surface of the Parr reactor to increase its corrosion resistance. We also inserted a liner inside of the reaction vessel to avoid damage/precipitates on the wall of the reaction vessel.

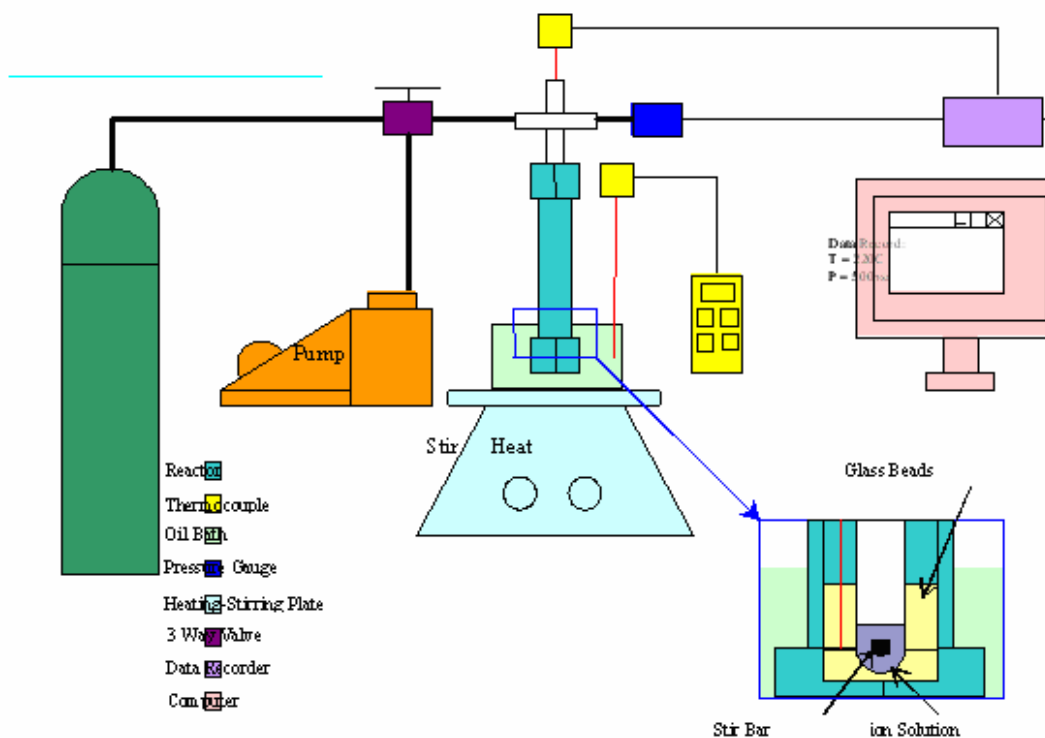


Figure 6 Schematic diagram of the bench-scale flow reactor design

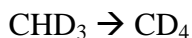
7. Bench-scale tests and preliminary economic analysis (Task 3)

H/D exchange has been used to test our developing HT-Shilov-Like system. Previous investigations reported on H/D exchange were mostly limited at reaction temperature below 120 °C due to the poor stability of the Pt-catalyst. At this temperature, only very low conversion ratio could be detected, and there are not any reaction kinetics had been established.

Our improved reactor design enables excellent controls of the gas/liquid/solid product characterizations to reach 100% mass/atomic balances. Also, operating at much higher temperature (~ 200 °C) has potentials to achieve near 100% conversion rate. We were able to generate sufficient H/D exchange ratio data for detailed kinetic studies.

The reaction system consists of K₂PtCl₄ (5mM) as catalyst, DCl (9M with D₂O solution) as solvent; and CD₃COOD (30%) as stabilizer, with CH₄ as the reactant at isotherm reaction temperature of 200 °C. The reaction time runs from 0 to 120 hours with measurements taken at different time intervals. Total methane conversion rates as well as the isotopic distributions among methane isomers are determined (Figure 7).

The reaction network for the methane H/D exchanges could be expressed as:



The kinetic fitting was conducted using the PMod program to find out all associated activation energies (Table 10) and the optimized coefficient factors a_{xy} (Table 11).

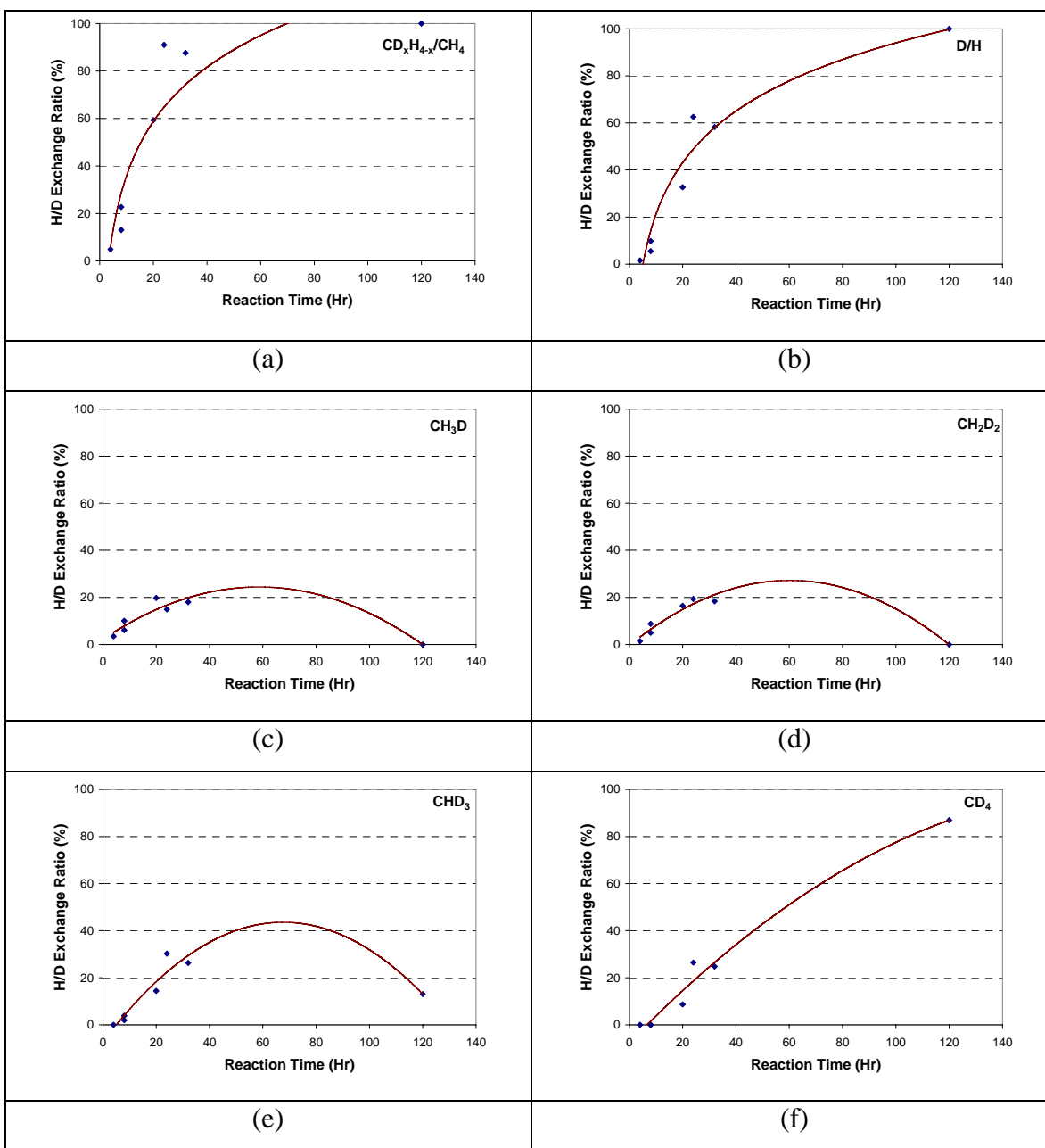


Figure 7 Experimental data of the H/D exchange ratios of methane in the HT-Shilov-Like system. (a) total ratio of methane isotopic isomers CD_xH_{4-x} to methane CH_4 ; (b) total deuterium D to hydrogen H ratio; (c) ratio of the D-isomer CH_3D ; (d) ratio of the D-isomer CH_2D_2 ; (e) ratio of the D-isomer CHD_3 and (f) ratio of the D-isomer CD_4 .

Table 10 Optimized activation energies for the H/D exchanged reactions in the HT-Shilov-Like system

| Reaction | Activation Energy (kcal/mol) |
|---|---|
| CH ₄ -> CH ₃ D | 29.9 |
| CH ₄ -> CH ₂ D ₂ | 30.0 |
| CH ₄ -> CHD ₃ | 30.1 |
| CH ₄ -> CD ₄ | 37.2 |
| CH ₃ D -> CH ₂ D ₂ | 31.9 |
| CH ₃ D -> CHD ₃ | 28.2 |
| CH ₃ D -> CD ₄ | 30.3 |
| C ₂ H ₂ -> CHD ₃ | 26.5 |
| C ₂ H ₂ -> CD ₄ | 30.4 |
| CHD ₃ -> CD ₄ | 25.7 |

Table 11 Optimized coefficient factors

| Coefficient | Optimized Result |
|--------------------|-------------------------|
| a ₁₁ | 0.506 |
| a ₁₂ | 0.492 |
| a ₁₃ | 0.002 |
| a ₁₄ | 0.000 |
| a ₂₁ | 0.414 |
| a ₂₂ | 0.567 |
| a ₂₃ | 0.019 |
| a ₃₁ | 0.735 |
| a ₃₂ | 0.265 |

Preliminary engineering and economic analyses were conducted. There are at least three key issues related to the optimized processing of the developing HT-Shilov-Like system. (1) Reactor design: one of the key problems in our bench-scale research for the HT-Shilov-Like system is the strong corrosive of Pt-based catalysts on the reactor, it is unavoidable that this question needs to be taken care in the scale-up production stage. (2) Side products: when operating at relatively low conversion rate, the possible side reactions such as the generations of the CH₂Cl₂, CHCl₃, and CCl₄, become noticeable. This will certainly increase the technical difficulty since additional separation processes will be required. (3) The stability (thermal and chemical) of the Pt-based catalysts should be taken into account.

8. Potential Benefit Assessments (Task 4)

8.1 Market assessments

Chlorine chemistry is central to the production of the highly purified silicon that is required for the manufacture of the silicon-based integrated circuits, solar cells, silicone-based products, glass optical fibers and high purity fumed silica. In US and Canada, these industries account for over \$50 billion in sale at the wholesale level and much more at the consumer level. Over 90% of CH_3Cl produced in U.S. is consumed as feedstock in the manufacture of the chemical intermediate methyl chlorosilanes (Figure 8). Methyl chlorosilanes are used in the production of silicone fluids, elastomers, and resins. The largest volume goes into silicone fluids, which are used in a wide range of production including processing aids such as antifoaming agents, release agents, and light-duty lubricants. It's also used in the specialty chemicals for consumer products such as cosmetics, auto polishes, furniture polishes, and paper coatings.

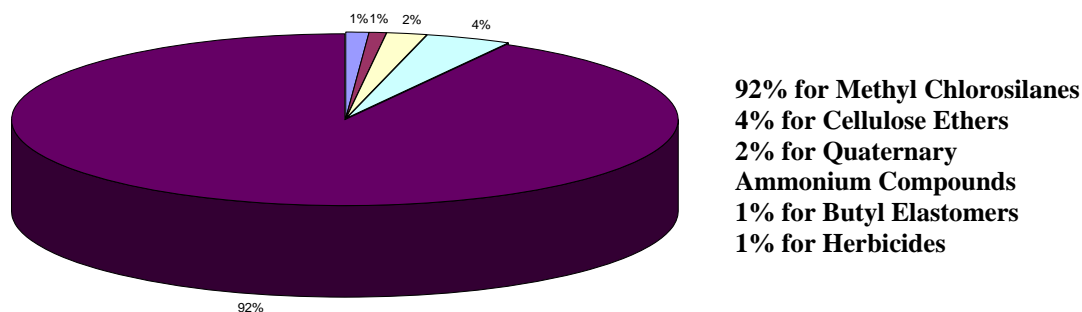
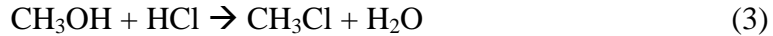


Figure 8: Current End-Uses of Methyl Chloride (CH_3Cl)

Production of CH_3Cl is mainly domestically, with three manufacturers with 5 plants producing CH_3Cl in the United States: Dow Chemical, Occidental Chemical, and Vulcan Chemicals, with an average annual capacity in about 500 million pounds in 90s', but declining gradually. The average sale price of the bulk CH_3Cl as in 2010s' is in the range of \$600/ton, moderately higher than its precursor CH_3OH (\$400/ton).

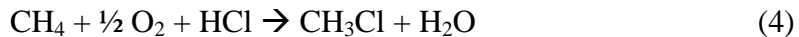
8.2 Economic Assessments

Currently, the CH₃Cl production is prepared by reacting methanol with hydrogen chloride with a catalyst, such as ZnCl₂ as in the OxyChem's process, or gas-solid heterogeneously catalytic process over an alumina catalyst at 350 °C. The basic chemical equation is:



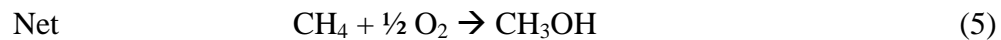
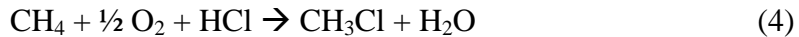
Therefore, the cost for the CH₃Cl production is greatly dependent to the methanol supply. In U.S. the demand for methanol is usually higher than domestic production capacity, and the price is fluctuating from importers.

The developing HT-Shilov system, if fully optimized, will take methane as feedstock to produce CH₃Cl, according to the chemical equation,



Therefore, if CH₄ can be used as the feedstock to replace methanol in the CH₃Cl production, the overall cost for the raw materials could be significantly reduced.

Furthermore, if the process (4) could be highly efficient and cost comparative, we can even reverse the process (3) by using CH₃Cl to produce CH₃OH. This will give rise to an improve process for the production of CH₃OH by:



Therefore, our economic assessments are based on the two-stage method. First, we target at the engineering and economic feasibility to use our developing HT-Shilov's process as a replacement to the current industrial processes for the CH₃Cl production from CH₃OH, because those are relatively mature. Secondly, we will also aim at the eventual potentials to produce CH₃OH from CH₄ using our HT-Shilov's process to replace current syngas routes.

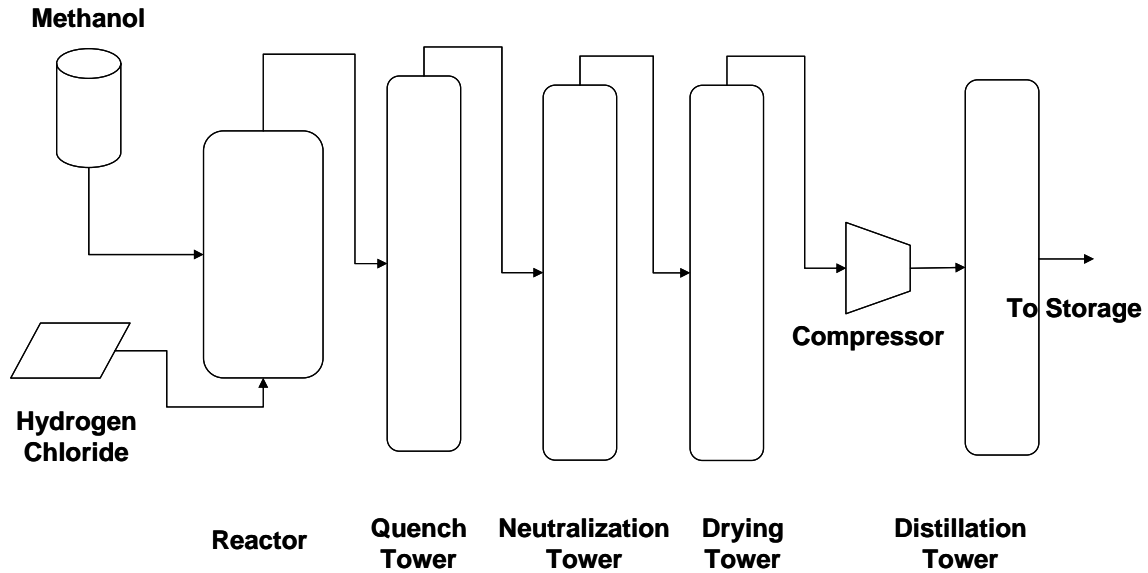


Figure 9: Typical Process of the CH_3Cl production from CH_3OH

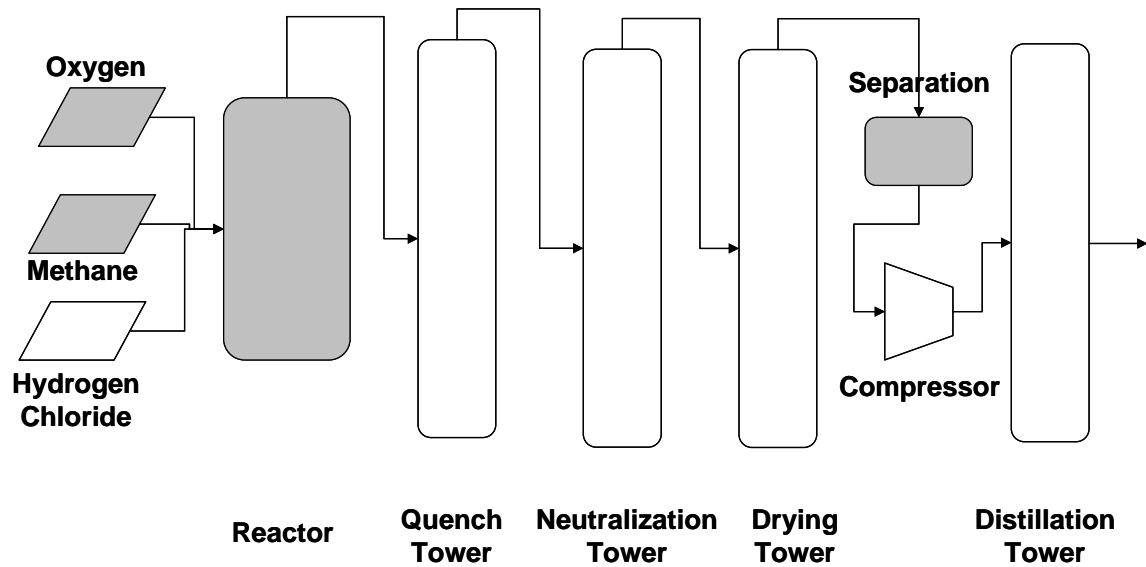


Figure 10: Diagram of the Developing HT-Shilov Process Derived from the Commercial Process. Changes of units are displayed in filled.

The methanol made from natural gas (methane) remains at ~ 47 cents per gallon, the basic cost for the production of 1 mole of CH_3Cl (by consuming 1 mole of methanol assuming 100% conversion) will be around 2.08 USD. On the other hand, the price of natural gas delivered at the Henry Hub remains arrange \$2.0 ~ 4.0 per cubic feet, which reflects to an average 1.01 USD/mole of methane to produce 1 mole of CH_3Cl , if the

process could be fully optimized. Furthermore, oxygen as oxidant (or other types of oxidants) will be consumed. Although oxygen can be obtained from air, separation or purification processes will normally required. In here, we take the price of bulk oxygen at \$35/1000 m³ (\$1.10/1000 ft³), and also notice that only one-half of oxygen molecule is required to oxidize one methane molecule. This gives rise to an additional 0.18 USD/mole feedstock for oxidant. This brings about a potential saving of \$0.89/mol of the CH₃Cl production, or \$0.04/kg or **\$40/ton saving**.

Table 12: Comparison of the Feedstock Prices of Conventional and HT-Shilov Systems

| | Conventional | | HT-Shilov | |
|-----------|----------------|----------------------|----------------|----------------------|
| | Chemicals | Unit Price (\$/mole) | Chemicals | Unit Price (\$/mole) |
| Feedstock | Methanol | 2.08 | Methane | 1.01 |
| | | | Oxygen (1/2) | 0.18 |
| Product | Methylchloride | 2.08 | Methylchloride | 1.19 |

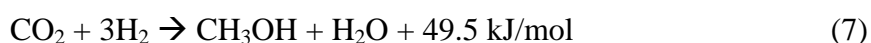
The above comparison is only for the feedstock price by assuming the exact same operation cost and capital investment. It reflects a baseline comparison of the potential economic assessment of the developing HT-Shilov process. Several factors need to be taken into accounts:

- Catalyst Technology – The current HT-Shilov system uses the Pt-based catalyst which is much more expensive than the well commercialized alumina catalysts in the OxyChem’s process. Catalyst scale-up will be one of the most important issues for the eventual commercialization.
- Reactor Technology – Higher acidic and stronger catalytic system requires improved reactor design. On the positive side is that the required operation temperature (< 250°C) is lower than the conventional system (~ 350°C). This is not only an important energy saving, but also can reduce the heat management requirement for the reactor design. Heat transfer is the most important issue in most of previous attempts for the CH₃Cl production from CH₄, especially for those processes based on the radical reaction. The exceed heat generated from the extremely exothermic synthesis reactions might initiate combustion of both reactants and products that are even more exothermic, resulting in the runaway situation.

- Product Purification Technology – Products from the current process include various distributions of the CH₃Cl, CH₂Cl₂, CHCl₃, and CCl₄. This is not the critical issue if we focus on the production of CH₃Cl from CH₄, and the other byproducts can be separated for other uses. But it could be an additional factor needed to be considered if we are going to use CH₄ to produce CH₃OH *via* the CH₃Cl pathway.

8.3 Energy Savings

The methanol production from natural gas is a well-established industrial process. Currently, there are six companies provide proprietary processes for the methanol synthesis: ICI, Lurgi, Tops oe, Mitsubishi, M.W. Kellogg, and Uhde. The syngas route is the predominating commercialized process and the syngas preparation and compression typically accounts for about 60% of the investment and almost all energy is consumed in this process section, while the methanol synthesis from syngas is highly exothermic.



On the other hand, the conversion of CO/CO₂ to methanol is limited by the pertinent chemical equilibrium (Table 13), which is favored under low temperature and high pressure conditions. Today’s methanol plants are mainly based on Cu/ZnO/Al₂O₃ catalyst that must be operated at 50 bar pressure and temperature exceeding 210 °C to ensure sufficient catalyst activity. Because of the high temperature, only a low fraction (< 30%) of syngas is converted per pass. Recycling the un-reacted syngas increases the energy costs for the recycling and the re-compression.

Table 13: The conversion of CO and CO₂ at equilibrium conditions (syngas: 3 vol.% CO₂, 27 vol.% CO, 64 vol.% H₂, 6 vol.% CH₄ + N₂)

| Pressure (bar) | 25 | | 50 | | 70 | | 150 | | 300 | |
|------------------|------|-----------------|------|-----------------|------|-----------------|------|-----------------|------|-----------------|
| Temperature (°C) | CO | CO ₂ | CO | CO ₂ | CO | CO ₂ | CO | CO ₂ | CO | CO ₂ |
| 275 | 14.4 | 3.91 | 39.1 | 4.18 | 53.9 | 4.47 | 81.9 | 6.23 | 95.8 | 13.5 |
| 300 | 5.94 | 5.55 | 21.7 | 5.68 | 35.1 | 5.88 | 69.2 | 7.13 | 90.1 | 11.6 |
| 325 | | | 10.4 | 7.63 | 19.5 | 7.76 | 53.2 | 8.64 | 81.8 | 11.7 |
| 350 | | | | | 9.41 | 10.1 | 36.4 | 10.7 | 70.1 | 12.8 |

Recycling the syngas reactant has more strait demands for the purity of oxidant, i.e., the oxygen has to be separated from air before entering the reaction system. Otherwise, the nitrogen will be accumulated during the recycling.

Our developing process has potentials to overcome these drawbacks in the currently commercialized processes, thus offers the energy cost reductions in the following aspects.

(1) Oxygen Separation – Considering the reaction of partial oxidation of methane to produce syngas from:



For each mole of methane conversion, 0.5 mole of oxygen will be consumed. The typical energy consumption for oxygen separation is about 600 kWh/t O₂, we estimate the additional energy cost for the production of 1 ton of methanol, resulting from the oxygen separation is ~ 1.1 GJ.

(2) Syngas Recompression – Considering one-pass CO conversion in traditional methanol synthesis at 250 °C and 50 bar is about 20%, in order to reach 96% conversion,

at least 15 cycles will be needed (e.g., $\sum_{i=1}^{15} 0.2 * (1 - 0.2)^{i-1} = 0.96$). Therefore, at least

4.82x of compression energies will be needed (e.g., $\sum_{i=1}^{15} (1 - 0.2)^{i-1} = 4.82$). Which means

for the production of 1 mole of methanol, 4.82 moles of CO and 9.64 moles of H₂ will need to be compressed from 10 bars (pressure before compressor) to 50 bars. Assuming the efficiency of a compressor of 75%, then the power for the compression is over 6.0 GJ/t methanol. For our developing process which only requires one pass of compression of methane, the estimated energy consumption is only 2.7 GJ/t methanol.

By combining above energy savings, our process offers the potential of reducing energy consumption of 4.4 GJ for each ton of methanol production. Compared to the Lurgi MegaMethanol technology, which supplies 60~70% of the world methanol production capacity and has the lowest specific energy consumption of methanol at ~ 30 GJ/ton methanol. Our process offers the potential to save energy for at least **15%**. Considering

the annual methanol production of 2.6 billion gallons (or 7.8 million metric tonne) in the United States alone, the energy saving could be significant at the level of over 30 Trillion Btu per year. Or according to DOE data that the CO₂ emission is 1.3 lb/kWh for the electric power in the U.S., we estimate the annual greenhouse emission reduction is over 5 million metric tonne of CO₂.

8.4 Discussions

Development of the HT-Shilov methane conversion process can be taken in two steps. First step is the produce CH₃Cl by using CH₄ for feedstock as replacement of the currently used CH₃OH which is produced from CH₄ *via* high-temperature syngas route. Even through the CH₃OH production is a well-developed commercialization process, the CH₄ to CH₃Cl conversion offers moderate economic advantages with the potential saving of \$40/ton and 15% energy savings over the traditional CH₃OH to CH₃Cl conversion, assuming other processing factors remain the same. However, certain technical hurdles needed to be overcome for the developing HT-Shilov system.

The CH₄ to CH₃OH conversion by taking CH₃Cl as an intermediate, rather than as a final product, offers another great commercialization potential for the HT-Shilov system. Methanol (CH₃OH) is no double one of the most important commodities worldwide. Over 90 methanol plants have a combined production capacity of about 75 million metric tons (almost 90 billion liters), and each day more than 100,000 tons of methanol is used as a chemical feedstock or as a transportation fuel. In 2010, global methanol demand totaled about 45.6 million metric tons. Methanol is one of the top 5 chemical commodities shipped around the world each year. Therefore, development of the alternate industrial processes to replace or to improve could have significant economic, energy and environmental impacts. In order to fully utilize the HT-Shilov process as a replacement for the syngas route widely used in the commercial process, improvements of the CH₄ conversion and high CH₃Cl selectivity are important technical issues.