

## FINAL REPORT

# Detailed Reaction Kinetics for CFD Modeling of Nuclear Fuel Pellet Coating for High Temperature Gas-Cooled Reactors

by

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## Executive Summary

The research project was related to the Advanced Fuel Cycle Initiative and was in direct alignment with advancing knowledge in the area of Nuclear Fuel Development related to the use of TRISO fuels for high-temperature reactors. The importance of properly coating nuclear fuel pellets received a renewed interest for the safe production of nuclear power to help meet the energy requirements of the United States. High-temperature gas-cooled nuclear reactors use fuel in the form of coated uranium particles, and it is the coating process that was of importance to this project. The coating process requires four coating layers to retain radioactive fission products from escaping into the environment. The first layer consists of porous carbon and serves as a buffer layer to attenuate the fission and accommodate the fuel kernel swelling. The second (inner) layer is of pyrocarbon and provides protection from fission products and supports the third layer, which is silicon carbide. The final (outer) layer is also pyrocarbon and provides a bonding surface and protective barrier for the entire pellet. The coating procedures for the silicon carbide and the outer pyrocarbon layers require knowledge of the detailed kinetics of the reaction processes in the gas phase and at the surfaces where the particles interact with the reactor walls.

The intent of this project was to acquire detailed information on the reaction kinetics for the chemical vapor deposition (CVD) of carbon and silicon carbide on uranium fuel pellets, including the location of transition state structures, evaluation of the associated activation energies, and the use of these activation energies in the prediction of reaction rate constants. After the detailed reaction kinetics were determined, the reactions were implemented and tested in a computational fluid dynamics model, MFIX. The intention was to find a reduced mechanism set to reduce the computational time for a simulation, while still providing accurate results. Furthermore, fast chemistry techniques would be coupled to MFIX to effectively treat the complex chemistry thus improve the computational efforts. Based on the reaction kinetics modeling, it was determined that the detailed set of chemical reactions for the thermal decomposition of a methyltrichlorosilane (MTS)/H<sub>2</sub> mixture consisted of 45 species and 114 gas-phase reactions. Further work identified a mechanism consisting of approximately 60 surface reactions for the surface chemistry of SiC chemical vapor deposition. A reduced mechanism for the MTS gas-phase pyrolysis was constructed using the scanning method based on optimization concepts, which consisted of only 28 species and 29 reactions.

The benefits of this project are that we have determined gas-phase species produced during and after the various decomposition reactions of MTS. The success of the computational approaches can now be used to predict the complex chemistry associated with the CVD process in producing nuclear fuel. It is expected that the knowledge we acquired can be easily transferred and that it will contribute to further experimental investigations. Furthermore, the computational techniques can now be used for reactor design and optimization for the next generation of nuclear reactors.

## Introduction

The objective of the proposed research was to conduct a state-of-the-art computational study of the chemical vapor deposition process in a spouting bed in order to validate and improve computational fluid dynamics (CFD) models for the reaction kinetics to coat uranium fuel pellets with carbon and silicon carbide. Two computational techniques were used: 1) computational chemistry for the development of kinetic models to represent the interactions between the gas-phase and surface molecules leading to deposition, and 2) the multi-fluid CFD code known as MFIX coupled with in-situ adaptive tabulation (ISAT) to efficiently treat complex chemistry. The ultimate goal was to predict the surface coating rates as a function of local species concentrations and temperature in the gas and solid phases.

At the conclusion of the project, we successfully determined the detailed set of chemical reactions for the thermal decomposition of methyltrichlorosilane (MTS) with the carrier gas  $H_2$  to consist of 45 species and 114 gas-phase reactions using computational chemistry. Further work identified a mechanism consisting of approximately 60 surface reactions for the surface chemistry of SiC chemical vapor deposition. However, in order to minimize the computational costs involved in the CFD modeling of the fluidized bed CVD process, a reduced chemistry set was needed. The reduced chemistry involved fewer species and reactions while preserving the important physics of the full reaction system. We found a reduced chemistry set using the scanning method based on optimization concepts, which consisted of only 28 species and 29 reactions. The full and reduced chemistry sets were implemented into MFIX and tested using ISAT.

## Accomplishments

The goals of this research were to improve MFIX capabilities to accurately model the complex reactions of the fluidized bed coating operation and validate the simulations with experiments. The tasks to accomplish the objective are 1) to determine the detailed gas- and surface-phase reaction kinetics, 2) to implement the reaction kinetics using in situ adaptive tabulation for complex chemistry, and 3) to implement a polydispersity model to account for particle size evolution. Based on the work accomplished, the first two tasks were successfully completed. As will be described in the next section, task 3 was not found to be of importance to the research at this stage.

## Project Activities

### Reaction Kinetics Modeling

*The homogeneous chemistry mechanism for the chemical vapor deposition of silicon carbide (SiC) was finalized to include 114 gas phase reactions and 45 species.* The decomposition reactions of methyltrichlorosilane (MTS)  $CH_3SiCl_3$  and consecutive gas phase reactions were studied at the UMP2/aug-cc-pVDZ level by using the GAMESS package. Single point energies for the local minima and transition states (TS) were calculated by applying the MP2/aug-cc-pVTZ and state-of-the-art CCSD(T)/aug-cc-pVDZ methods at the MP2/aug-cc-pVDZ geometries.

The CCSD(T)/aug-cc-pVTZ single point energies were estimated by combining the CCSD(T)/aug-cc-pVDZ energies and the basis set effects obtained at the MP2 level of theory,

which were then used to compute the reaction rate constants using the transition state theory. Comparisons of values for heat capacity ( $C_p$ ) and entropy ( $S$ ) were made between theoretical calculations and experiments for various gas phase species. The calculated  $C_p$  and  $S$  values matched well with the experimental values within a wide range of temperatures from 298.15 to 2000 K. Calculated reaction enthalpies at various temperatures were also satisfactorily close to available experimental data within 1-2 kcal/mol.

Constrained optimization calculations were performed to investigate detailed reaction paths of the association/dissociation reactions without a well-defined transition state, such as  $\text{CH}_3\text{SiCl}_3 \rightarrow \text{CH}_3 + \text{SiCl}_3$ , at the MP2/aug-cc-pVDZ level of theory. Hessian calculations were performed to obtain the partition functions for the structures along the reaction paths. A recently developed coupled cluster method, the left eigenstate completely renormalized coupled cluster method (CR-CCL), was used to obtain single point energies for every studied structure on the reaction path to locate the generalized transition state (i.e., the structure with the maximum free energy along the reaction path). However, this new coupled cluster method was implemented only for singlet species; hence doublet constrained reaction paths could not be examined presently by this method.

Due to the discrepancy between the potential energy surfaces (PES) of ethylene ( $\text{C}_2\text{H}_4$ ) predicted in the present work and previous studies, the more accurate CCSD(T)/aug-cc-pVDZ method was used to obtain the optimized structures of local minima and transition states on the  $\text{C}_2\text{H}_4$  potential energy surface. Hessian calculations were performed to obtain the zero point energies at the CCSD(T)/aug-cc-pVDZ level of theory. The CCSD(T) results agrees with Jensen et al. calculations at the MP2/6-31G(d,p) level of theory, but not with MP2/aug-cc-pVDZ calculations. This study completed the transition state search for all the gas phase reactions in this work.

Predicted reaction rate constants by POLYRATE, a code based on variational transition state theory, compared well with the available experimental values through the NIST database. CCSD(T) single point energies were obtained for 4 extra points used to obtain the partition functions along the reaction paths and MP2/aug-cc-pVTZ energies were calculated for estimating the basis set effect.

The surface integrated molecular orbital molecular mechanics (SIMOMM) method was carefully examined for properly modeling the highly conjugated pyrolytic C surface. Optimum choices of the quantum mechanics (QM) and molecular mechanics (MM) regions have been determined to balance the efficiency and accuracy of the SIMOMM method for effectively modeling the heterogeneous chemistry that takes place on the pyrolytic C surfaces. The molecular mechanics parameters for Si-Cl, C-Cl, and Cl-Cl bond stretching and Cl-Si-C, Cl-Si-Cl, Cl-Si-H, H-Si-C (sp<sup>2</sup> C), and H-Si-C (sp<sup>3</sup> C) bending were optimized by fitting MM energies with MP2/aug-cc-pVDZ energies of training molecules. These MM parameters were used in the SIMOMM calculations for the heterogeneous reactions between the gas phase species and the pyrolytic C and SiC solid surfaces.

Improvements were made to the accuracy of the rate constant calculations for the gas phase reactions in the SiC CVD process. The free energy profiles were studied along the reaction paths for the gas phase reactions. Association reactions between radicals were found to have nontrivial free energy barriers due to the significant entropic effect at high CVD temperatures. The energy profiles of the association/dissociation gas-phase reactions were obtained using the left eigenstate completely renormalized coupled-cluster singles, doubles and non-iterative triples (CR-CCSD(T)\_L) methods. The efficacy of the CR-CCSD(T)\_L method was compared with the

full configuration interaction (FCI) method for a modest basis set of 10 possible types of single bond breaking reactions between C, H, Si, and Cl and the Si=Si double bond breaking reaction. Comparisons were made to ensure that CR-CCSD(T)\_L agrees with FCI because the FCI method predicts the exact solution in the chosen basis set with the Born-Oppenheimer approximation. The comparisons were further motivated because many other coupled-cluster methods, such as the “gold standard” CCSD(T) method, fail when applied to bond-breaking reactions. Figure 1 illustrates an example of CR-CCSD(T)\_L agreeing with FCI for a C-Si bond breaking reaction  $\text{CH}_3\text{SiH}_3 \rightarrow \text{CH}_3 + \text{SiH}_3$ . It was found that the CR-CCSD(T)\_L method recovers FCI energies within 1 kcal/mol error for single bond reactions. The CR-CCSD(T)\_L method also predicts a reasonably accurate PES for the  $\text{H}_2\text{Si} = \text{SiH}_2$  double bond breaking reaction, despite the state crossing that originates from the mixing of occupied and virtual orbitals.

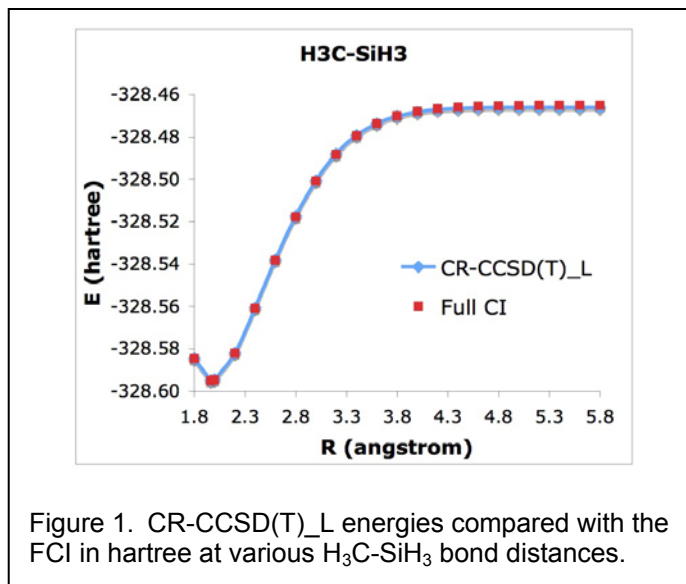


Figure 1. CR-CCSD(T)\_L energies compared with the FCI in hartree at various  $\text{H}_3\text{C-SiH}_3$  bond distances.

Comparisons were also made between the restricted open-shell left eigenstate completely renormalized coupled-cluster (RO-CCL) potential energy surfaces and the FCI method for the bond breaking reactions of several open shell species. The results show that the RO-CCL potential energy surfaces agree with the FCI method within an error of 2 mhartree (1 mhartree = 0.627 kcal/mol) for most of the studied bond breaking reactions. The largest error is 3.4 mhartree for the  $\text{H}_2\text{C-H} \rightarrow 3\text{H}_2\text{C} + \text{H}$  bond breaking reaction with a 6-31G(d) basis set being used. Figure 2 shows that the RO-CCL method predicts more accurate relative energies than the conventional unrestricted (U) coupled-cluster singles, doubles, and noniterative triples [CCSD(T)] method. It was determined that the characteristic coupled-cluster energy error humps appear at longer bond distances on the RO-CCL potential energy surfaces than with the UCCSD(T). Although RO-CCL does not provide a complete PES for several bond-breaking reactions with a minimal basis set due to Hartree-Fock convergence problems, it does so successfully with a more commonly used larger double- or triple- $\zeta$  basis set.

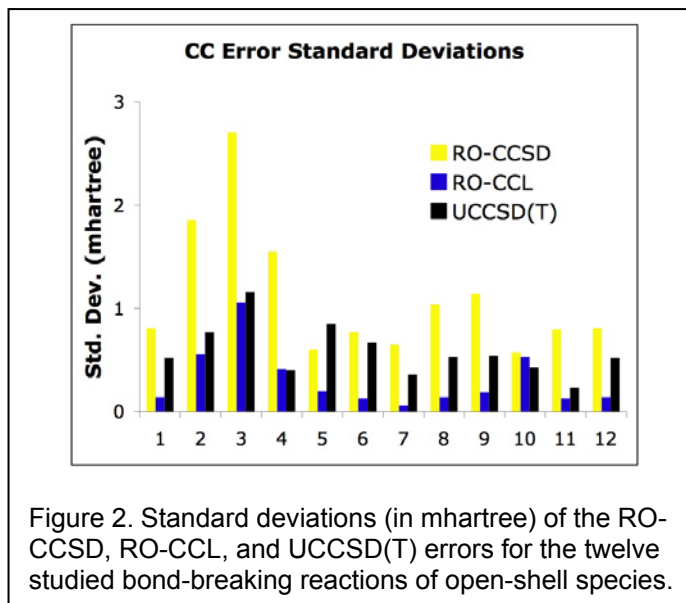


Figure 2. Standard deviations (in mhartree) of the RO-CCSD, RO-CCL, and UCCSD(T) errors for the twelve studied bond-breaking reactions of open-shell species.

We completed the comparisons between the restricted open-shell left eigenstate completely renormalized coupled-cluster (abbreviated as CCL for simplicity), the conventional unrestricted

coupled cluster singles, doubles, and noniterative triples [UCCSD(T)], and the multi-reference Moller-Plesset 2nd-order perturbation theory (MRMP2) potential energy errors for the bond-breaking reactions of eight C-H-Si-Cl open-shell species with five different basis sets: MINI, 6-31G, 6-31G(d), cc-pVDZ, and cc-pVTZ. The benchmark potential energy surfaces were obtained by using the full configuration interaction (FCI) method and the multi-reference configuration interaction (MRCI) method. FCI predicts the exact energy within a given basis set; the MRCI method reproduces the corresponding FCI energies with small errors. The comparisons show the CCL method is more accurate than the UCCSD(T) and MRMP2 methods in predicting the PES of the bond-breaking reactions of the eight C-H-Si-Cl open-shell species in the silicon carbide chemical vapor deposition.

*A mechanism consisting of 60 surface reactions involved in the silicon carbide CVD process was proposed.* The surface reactions were grouped into four categories: desired reactions that account for SiC growth, side reactions that account for Si growth and C growth, and diffusion reactions that take place on the SiC surface. The diffusion reactions play a less important role in the composition of the SiC coating than the other three types of reactions. However the diffusion reactions may alter the surface structure and reduce the overall deposition rate by competing with other heterogeneous reactions. The hybrid surface integrated molecular orbital/molecular mechanics (SIMOMM) method was used to study the properties of the surface species and the reaction paths of the surface reactions with a transition state.

*In summary, all of the tasks for the Reaction Kinetics Modeling were completed and resulted in two published manuscripts, one manuscript in preparation and two conference presentations.*

### Complex Chemistry Modeling

*The CFD code MFIX was successfully coupled with ISAT to efficiently use the detailed kinetic reactions and predict the CVD of silicon carbide.* Since the final goal is to conduct a CFD simulation of the CVD process in a spouting bed and the software to be used is MFIX, the challenge is to efficiently implement the detailed chemistry into MFIX. The reactions are formulated as a source term in the governing equations and a set of ordinary differential equations (ODEs) must be solved. The ISAT methodology to efficiently compute the chemistry was coupled with MFIX to obtain the species concentration and source terms at each time step.

In order to implement the chemical species compositions involved in the decomposition of MTS, a thermodynamic database was compiled for each species. For the coupling of MFIX with ISAT, whereby ISAT is based on CHEMKIN software libraries, an input file was created containing the required chemistry information in a format compatible with CHEMKIN. The CHEMKIN software requires thermodynamic data to be stored in the form of polynomial fits for specific heat, enthalpy and entropy, while the reaction rates are stored in the form of parameters characterizing the Arrhenius temperature dependence of the reaction rates. Based on data for forward rate constants for each of the MTS decomposition reactions obtained from ab initio calculations, the Arrhenius rate parameters were determined, viz. the pre-exponential factor, the temperature exponent and activation energy, using a least-squares procedure for parameter estimation.

Using the chemistry input, the evolution of the species concentrations was obtained by numerical solution of the corresponding ordinary differential equations (ODEs). For a test case of 1 mole of MTS and 4 moles of H<sub>2</sub> at 1000 K under constant pressure and adiabatic conditions, the dominant species at equilibrium include H<sub>2</sub>, CH<sub>4</sub>, SiHCl<sub>3</sub>, SiCl<sub>4</sub> and CH<sub>3</sub>SiCl<sub>3</sub>,

with mole fractions ranging from 0.1 to 0.7. Several species were found to have very low concentration values with mole fractions less than  $10^{-6}$ . In a preliminary effort, a reduced chemistry set was obtained by eliminating such low concentration species (and the reactions containing them) if they were not directly involved in the decomposition of MTS or if they were not important for surface reactions. By analyzing the ODEs corresponding to the reduced chemistry set, the evolution of the dominant species (and their equilibrium concentrations) in the reduced chemistry set were nearly the same as those in the full chemistry set. An alternative method was used to verify the equilibrium species concentrations obtained from integration of the corresponding ordinary differential equations. The alternative method is based on chemical element potentials, along with minimization of Gibb's free energy. In this alternative approach, the equilibrium composition of the mixture was obtained using CHEMKIN software (along with EQUIL and STANJAN). Based on the results, the two approaches (i.e., ODE integration and chemical element potential) gave the same species concentrations at equilibrium.

A procedure was developed to couple the solution of the ODEs for the reaction source terms with ADIFOR. The purpose of ADIFOR is to generate the analytical Jacobian, which is then used to calculate the mapping gradient in ISAT. It was determined that ISATAB is the appropriate FORTRAN library to use and requires supplementary information to perform the calculation, such as the right hand side of the set of ODEs, the Jacobian matrix, and the ODE solver. A benchmark case was studied for the simulation of a pairwise mixing stirred reactor (PMSR) to test and validate the implementation of the CFD driver that calls the sequence of ISAT libraries and routines. The implementation was successful and it was determined that 1) as the simulation runs longer, higher speed-up was obtained, 2) ISAT speed-up increased dramatically as the error tolerance increased, and 3) switching to ISAT from direct integration (DI) after the initial transit state increased speed-up thus reducing the size of the ISAT table.

Studies continued to elucidate the best means to determine an appropriate reduced mechanism set based on optimization methodology. The species reduction can be formulated as the following optimization problem:

$$\min_{\lambda} \sum_{k=1}^{KK} \lambda_k \quad (1)$$

subject to  $\chi(\lambda) \leq \varepsilon$ , where  $\chi$  is the measure of the discrepancy between the full and reduced mechanism,  $\varepsilon$  is the criterion,  $\lambda_k$  are binary variables used to denote the nonexistence ( $\lambda_k = 0$ ) or existence ( $\lambda_k = 1$ ) of a particular species,  $KK$  is the total number of species in the full mechanism, and  $k$  is the index of species.

The discrepancy function is defined as:

$$\chi(\lambda) = \sum_{i=1}^{Nstep} \sum_{k=1}^{KK} \lambda_k \text{abs} \left( \frac{y_k^{full} - y_k^{reduced}}{y_k^{full}} \right)_i / \left( \sum_{k=1}^{KK} \lambda_k / Nstep \right) \quad (2)$$

where  $y$  represents the value of a matched quantity, which can be temperature or species concentration, and the superscripts denote values for the full and reduced mechanisms, respectively. For the dynamic problem under consideration, the species concentration and temperature vary with time. The solution at each discrete time step  $i$  is computed, and  $Nstep$  is the total number of time steps during which the full mechanism and reduced mechanism are compared.

The test problem was the simulation of a constant-pressure reactor. At adiabatic conditions, the temperature and the mass fraction of species were solved based on the following equations:

$$\frac{dY_k}{dt} = \dot{\omega}_k \frac{W_k}{\rho} \quad (3)$$

$$\frac{dT}{dt} = -\frac{1}{\rho C_p} \sum_{k=1}^{KK} H_k \dot{\omega}_k \quad (4)$$

$$\dot{\omega}_k = \sum_{i=1}^I \nu_{ki} q_i \quad (k = 1, \dots, KK) \quad (5)$$

$$\nu_{ki} = (\nu_{ki}'' - \nu_{ki}') \quad (6)$$

$$q_i = k_{fi} \prod_{k=1}^{KK} [X_k]^{\nu_{ki}'} - k_{ri} \prod_{k=1}^{KK} [X_k]^{\nu_{ki}''} \quad (7)$$

$$k_{fi} = A_i T^{\beta_i} \exp\left(-\frac{E_i}{R_c T}\right) \quad (8)$$

$$k_{ri} = \frac{k_{fi}}{K_{ci}} \quad (9)$$

where  $Y_k$  is the mass fraction of species  $k$ ,  $t$  is time,  $\dot{\omega}_k$  is the production rate of species  $k$ ,  $\rho$  is the density,  $T$  is the temperature,  $C_p$  is the heat capacity,  $H_k$  is the specific enthalpy of species  $k$ ,  $\nu_{ki}$  is the stoichiometric coefficient of species  $k$  in reaction  $i$ ,  $q_i$  is the reaction rate for reaction  $i$ ,  $k_{fi}$  and  $k_{ri}$  are rate constants for forward and reverse of reaction  $i$ ,  $[X_k]$  is the concentration of species  $k$ ,  $A_i$ ,  $\beta_i$  and  $E_i$  are the pre-exponential factor, temperature exponent and activation energy of reaction  $i$ ,  $K_{ci}$  is the equilibrium constant in concentration units for reaction  $i$ . Equations (1)-(9) correspond to an integer nonlinear programming problem. Since it is a nonconvex problem, a general optimizer can not guarantee global optimality other than by enumerating all  $2^{KK}$  possible values of  $\lambda_k$ .

For the reaction reduction, an equation similar to (1) can be used:

$$\min_{\lambda} \sum_{r=1}^I \lambda_r \quad (10)$$

subject to  $\chi(\lambda) \leq \varepsilon$ , where  $r$  is the index for a reaction, and  $I$  is the total number of reactions.

The optimization began by first identifying which species have extremely low concentrations ( $< 10^{-24}$ ) and these species are removed. The remaining species were then used to develop the objective function and numerous simulations are performed to determine the effects of removing species. The same process is then used to eliminate reactions. Further details can be found in our manuscript under preparation.

Based on the original 45 species identified using Reaction Kinetics Modeling, 9 species were found to have low concentrations and were removed. The remaining 36 species and corresponding reactions were used as the chemistry set and multiple simulations were performed for a wide range of initial conditions: 3 temperatures (1500 K, 1773 K, and 2000 K) and 4 MTS mole fractions (20%, 10%, 5%, and 1%). Performing the species reduction



produced a new reduced mechanism set that included a total of 28 species with 83 reactions. After the reduced species set was obtained, the objective function was constructed based on these 28 species in order to perform the reaction reduction. It was determined that 54 reactions could be removed using the optimization methodology, and therefore, 28 species with 29 reactions remain in the final reduced mechanism set. Using the new reduced mechanism, a series of PMSR simulations were performed to test the speed-up of the reduced mechanism and the reduced mechanism and ISAT require approximately one-third of the CPU.

A comparison between the full and reduced mechanisms for the major species has been plotted in Figure 3. The six species that are important for the surface reaction and SiC deposition are a)  $\text{CH}_3\text{SiCl}_3$ , b)  $\text{CH}_3$ , c)  $\text{SiCl}_3$ , d)  $\text{CH}_2\text{SiCl}_2$ , e)  $\text{SiCl}_2$ , and f)  $^3\text{CH}_2$ . The solid lines are the results predicted using the reduced mechanism after species and reaction reduction, and dashed lines with symbols are the results calculated using the full mechanism. It can be seen that the discrepancy between the full mechanism and the reduced mechanism for the major species is so small that symbols must be used to help identify the full mechanism results.

Efforts to incorporate polydispersity modeling to represent the particle size distribution using the population balance equation was not pursued at this time. We determined that the finding a procedure to reduce the detailed mechanism set was more valuable and required time not anticipated at the onset of this research.

### Summary

Based on the detailed reaction chemistry determined from computational chemistry, a reduced mechanism has been proposed using the scanning method based on the idea of optimization for MTS decomposition at high temperatures. By first performing species reduction, the number of species and reactions was reduced to 28 and 83 from 45 and 114, respectively. Reaction reduction further reduced the number of reactions to 29 after species reduction. The overall accuracy of the final set of reactions for the reduced mechanism was examined by comparing it with the full mechanism for simulations of an adiabatic batch reactor at constant pressure. The species profiles of the reduced mechanism agreed well with the full mechanism, although a few species show some small discrepancies. The results also show that the scanning method based on optimization is very efficient for model reduction, thus removing reactions that are unimportant.

It should be noted that for a more complete description of MTS deposition, the surface chemistry should be considered, and this is the topic of a future manuscript based on this research. We anticipate that a different reduced gas phase mechanism may be realized with the inclusion of surface chemistry. However, the method proposed in this paper for mechanism reduction is still valid and it could be used in any complex chemistry. Finally, the test case of an adiabatic reactor used in this study models a closed system (e.g., a batch reactor); the implication is that the concentrations of MTS and  $\text{H}_2$  continuously decrease over time. Therefore a dynamic system is considered here by collecting errors for a period of time. In practice, the spouted bed reactors used to fluidize uranium pellets have a continuous stream of MTS and  $\text{H}_2$  entering the reactor, where the species concentration could reach equilibrium and make the situation much simpler than that addressed here. Theoretically the results should only depend on the operating parameters like pressure, temperature and concentration not the reactor model, so the reduced kinetic model should work in the real fluidized bed as long as the parameters are in the range of our tests. The validation of the reduced mechanism in fluidized bed will be addressed in future work.

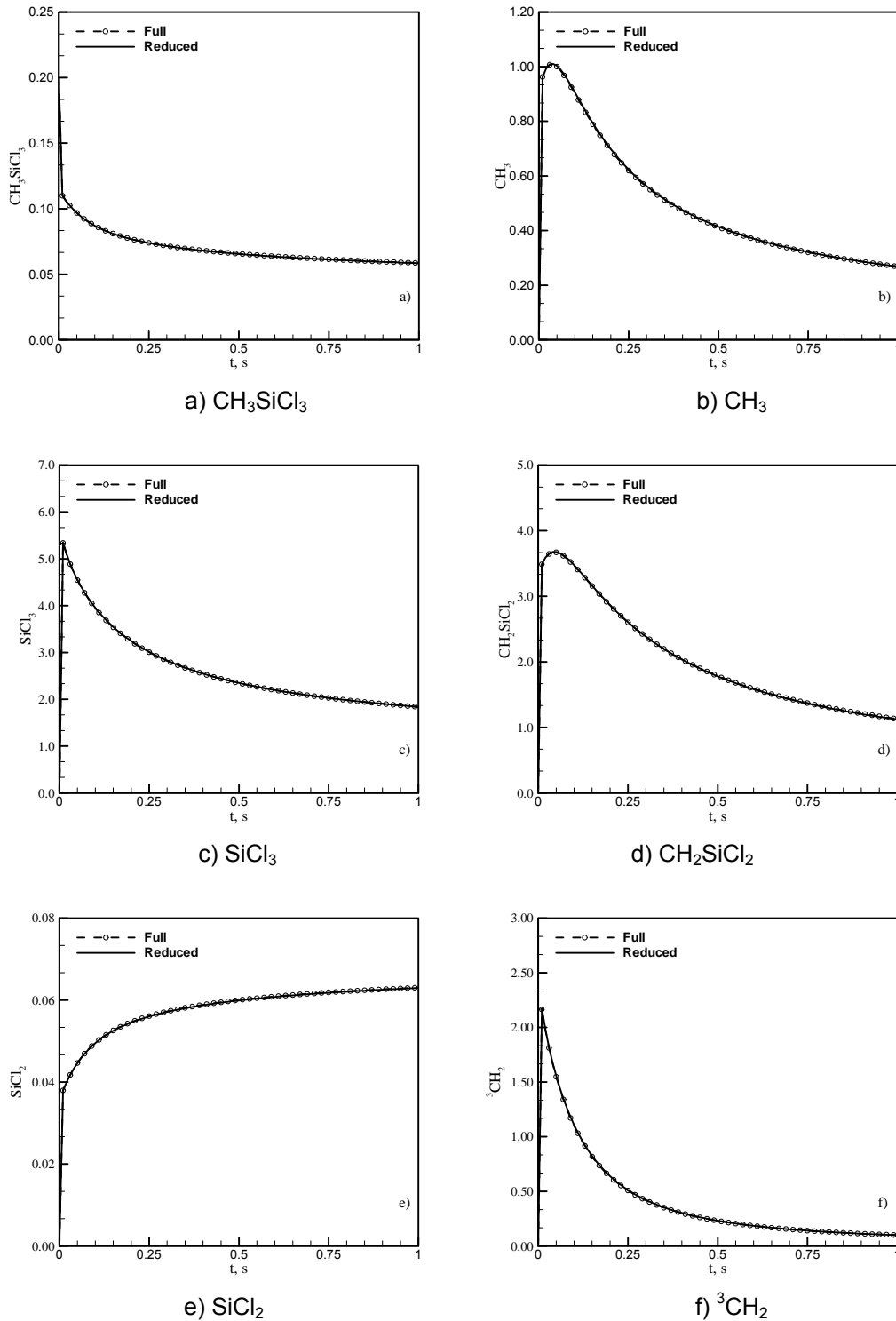


Figure 3. Mole fraction profiles of major species versus time using an initial temperature of 1773 K, 20% MTS and 80%  $\text{H}_2$  for a)  $\text{CH}_3\text{SiCl}_3$ , b)  $\text{CH}_3$ ,  $y \times 10^3$ , c)  $\text{SiCl}_3$ ,  $y \times 10^4$ , d)  $\text{CH}_2\text{SiCl}_2$ ,  $y \times 10^4$ , e)  $\text{SiCl}_2$  and f)  ${}^3\text{CH}_2$ ,  $y \times 10^8$ , where  $y$  is the mole fraction scale.

## Products Developed

### Publications

Ge, Y., Gordon, M.S., Battaglia, F., and Fox, R.O., "Theoretical study of the pyrolysis of methyltrichlorosilane in the gas phase. 2. Reaction paths and transition states". *Journal of Physical Chemistry*, **111**(8), 1475-1486, March (2007).

Ge, Y., Gordon, M.S., Battaglia, F., and Fox, R.O., "Theoretical study of the pyrolysis of methyltrichlorosilane in the gas phase. 1. Thermodynamics". *Journal of Physical Chemistry*, **111**(8), 1462-1474, March (2007).

### Manuscripts in Process

Ge, Y., Gordon, M.S., Battaglia, F., and Fox, R.O., "Theoretical study of the pyrolysis of methyltrichlorosilane in the gas phase. 4. Rate constant calculations".

Gao, Z., Battaglia, F., Fox, R.O., Ge, Y., and Gordon, M.S., "Theoretical study of the pyrolysis of methyltrichlorosilane in the gas phase. 4. Reduced Mechanism".

### Conference Presentations

Ge, Y., Gordon, M.S., Fox, R.O., and Battaglia, F., "Theoretical Study of the Pyrolysis of  $\text{CH}_3\text{SiCl}_3$  in the Gas Phase," presentation to the International Chemical Congress of Pacific Basin Societies, Honolulu, HI, December 17, 2005.

Battaglia, F., Fox, R. O., Gordon, M.S., and Ge, Y., "Coupling molecular and continuum modeling for detailed reaction kinetics of TRISO fuel coating", Presented at the Mini-symposium on Multiscale/Multiphysics Methods for Gas-Solid Reacting Flows, Society for Industrial and Applied Mathematics Meeting (SIAM), February 21, 2007.

Gao, Z., Battaglia, F., Fox, R.O., Gordon, M.S., Ge, Y., and Pope, S.B., "Implementation of Detailed Chemistry of Methyltrichlorosilane Decomposition into ISAT and Parametric Study", 2007 Annual Meeting of the American Institute of Chemical Engineers, (Salt Lake City, UT) November 4-9, 2007.

Battaglia, F., Gao, Z., Fox, R. O., Ge, Y., and Gordon, M.S., "Detailed Reaction Kinetics for CFD Modeling of Nuclear Fuel Pellet Coating for High-Temperature Gas-Cooled Reactors", 2007 ANS/ENS International Meeting and Nuclear Technology Expo, Washington, DC, November 11-15, 2007.