古河電工グループの
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Chemical Reaction Mechanisms in Synthesis Burner for Silica Glass Optical Fiber

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〈概要〉
石英ガラス光ファイバ母材を合成するバーナーの効率的な開発には，火炎挙動やシリカ堆積を予測できる詳細な化学モデリングが有用である。本研究では，量子化学計算に基づくオクタメチルシクロテトラシロキサン（OMCTS）の分解機構とメタン燃焼反応速度論を統合することにより，包括的な予測シミュレーションモデルを開発した。拡散および熱泳動による粒子輸送を考慮した堆積モデルを，数値流体力学（CFD）フレームワーク内に実装した。この統合的アプローチにより，様々なバーナー構成に対して「スート」と呼ばれる微小シリカ粒子の粒径分布および表面堆積速度の予測が可能となる。予測された火炎構造は実験観察と良く一致し，またOMCTS分解反応速度予測も実験炉での測定により検証された。得られたモデルは，前駆体利用効率の向上および材料損失の最小化を実現し，運用中のバーナー設計を最適化するための有用なツールとなる。

1. INTRODUCTION

Optical fiber manufacturing is a complex process that begins with the synthesis of the glass preform using chemical vapor deposition (CVD) techniques[1]. This critical step involves the deposition of silica onto a substrate through several chemical reactions occurring both in the gas phase and on the substrate surface, ultimately yielding a well-formed preform with precisely tuned optical properties.

Conventional glass preform manufacturing utilizes $SiCl_4$ as the silica precursor, which is introduced into an H_2/O_2 flame[2]. The essential chemical processes are:

$$2\ H_2 + O_2 \rightarrow 2\ H_2O$$
$$SiCl_4 + O_2 + 2\ H_2 \rightarrow SiO_2 + 4\ HCl$$

The corrosive nature of the precursor $SiCl_4$, the product HCl, and the byproduct Cl_2, combined with the environmental impact of the hydrogen production and the unfavorable transmission losses due to chlorine doping of silica glass[3], has motivated the development of alternative precursors.

Octamethylcyclotetrasiloxane (OMCTS) – $[(CH_3)_2SiO]_4$ is an attractive alternative precursor because it is non-toxic, non-corrosive, readily available, and its combustion yields SiO_2[4), 5)]. Combustion in a methane flame eliminates the need for hydrogen production:

$$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$$
$$[(CH_3)_2SiO]_4 + 16\ O_2 \rightarrow 4\ SiO_2 + 8\ CO_2 + 12\ H_2O$$

However, efficient and clean preform production requires complete OMCTS combustion to prevent carbon deposition, while achieving adequate deposition rates requires an appropriate mixing of fuel and precursor gases and a proper positioning of the preform. Consequently, changing the precursor and fuel necessitates complete burner redesign.

Simulations offer a versatile and economical means to accelerate the development by providing detailed insights into the processes and allowing an efficient evaluation of multiple burner configurations[2), 4), 6)]. Advanced burner design requires an integrated multidisciplinary approach combining chemical reaction kinetics, particle synthesis, surface deposition phenomena and Computational Fluid Dynamics (CFD). We combine elements of molecular-level mechanism development — including quantum chemistry computations for precursor decomposition pathways and also thermodynamic and transport property estimation — with advanced computational modeling range from molecular dynamics simulations to coupled CFD-particle transport analysis.

We demonstrate the integration of a theoretical rigor in materials chemistry, practical computational expertise, and direct industrial experience in complex fiber optic production systems through chemical mechanism developments.

2. OVERVIEW OF REACTION MECHANISM

The chemical reactions in optical fiber preform synthesis are shown in Figure 1. Methane fuel and evaporated OMCTS precursor are introduced into the burner along with oxygen for complete combustion and also nitrogen

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dilution gas. A series of complex chemical reactions then occurs. Methane combustion generates the high temperature necessary for OMCTS decomposition, which proceeds via pyrolysis in oxygen-lean regions or oxidation in oxygen-rich regions of the flame.

OMCTS decomposition is a multi-step process involving the elimination of small molecular fragments from the precursor or oxidation of organic groups. The final decomposition products are small gas-phase molecules, ideally SiO_2, which initiate the complex particle growth process. The resulting silica particles (termed as "silica soot") are deposited on the preform, which is continuously rotated and translated to ensure uniform deposition both in axial and lateral directions.

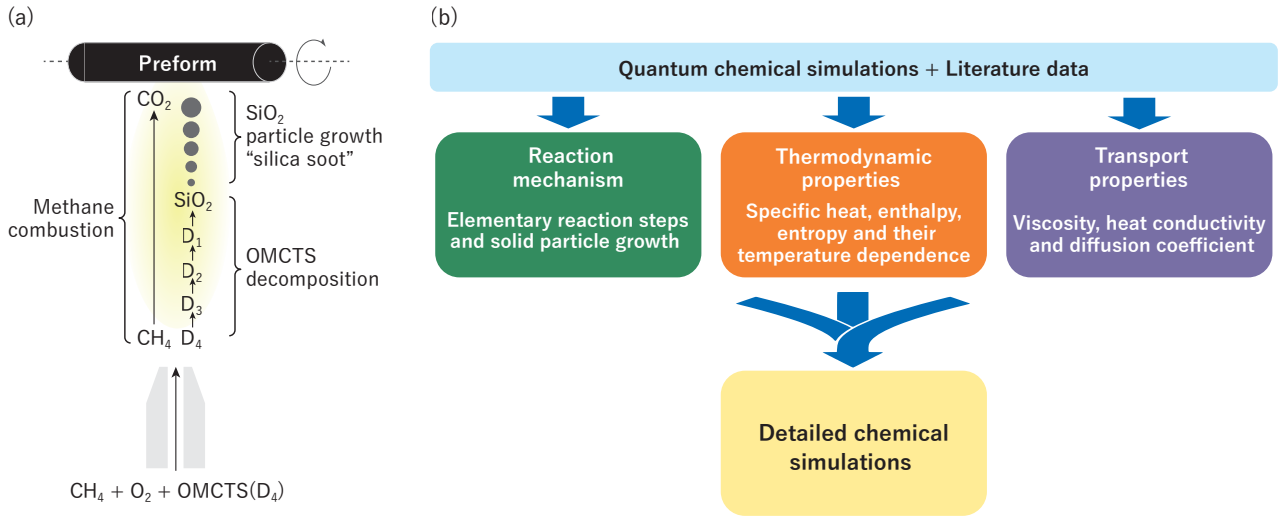

Figure 1　Optical fiber preform synthesis mechanism from OMCTS. (a) Chemical reactions (b) Mechanism setup

3. DETAILED CHEMICAL MECHANISM-BASED REACTOR SIMULATIONS

The primary goal of detailed chemical mechanism-based reactor simulations is to predict silica soot particle deposition by simulating the thermal structure and the chemical composition of the flame. Detailed chemical reaction mechanisms coupled with CFD enable flexible, accurate reactor simulations targeting good transferability to different conditions and designs. By coupling these mechanisms with quantum chemically derived thermodynamic and kinetic parameters, we aim to model the complex interplay between methane combustion, OMCTS decomposition, particle nucleation, growth and deposition. This enables us to explore how variations in burner geometry, fuel-to-precursor ratios, flame temperature, and oxygen distribution can affect silica deposition quality and uniformity on the optical fiber preform.

Several physical and chemical parameters are required for this model (Figure 1), including reaction rates and thermal and transport properties. We provide a brief overview of the modeling approach.

Detailed chemical simulations are constructed from chemical species (different chemical structures, like molecules, or radicals participating in the reactions) and their elementary reactions, which collectively form comprehensive reaction mechanisms describing precursor decomposition, intermediate transformations, and product formation. The reaction rates of these elementary steps constitute the most critical parameters, and they are commonly expressed using the extended Arrhenius equation due to their strong temperature-dependence. Accurate kinetic data are available from high-precision experiments[6] or advanced quantum chemistry computations[7]. In cases where direct measurements are not feasible, reaction rates may be estimated through fitting to experimental observations or inferred by analogy with similar systems.

The temperature profile of the flame depends on both the heats of the elementary reaction steps and the local composition-dependent specific heat of the gas mixture. The mixture-dependent specific heat is computed from the gas composition and the thermal properties — specific heat, enthalpy, and entropy — of each chemical species involved in the reaction mechanism. While thermal properties of reactants and several products are available from experiments, data for intermediates are often scarce and, in several cases, must be derived using statistical thermodynamics from molecular geometry and vibrational levels obtained through quantum chemistry computations. These temperature-dependent thermal properties are typically expressed in NASA polynomial format (standardized polynomial expressions representing specific heat, enthalpy, and entropy of gas-phase chemical species).

Viscosity and heat conductivity of the gas mixture are computed from the contributions of each chemical species, while diffusion and thermal diffusion coefficients are calculated for individual chemical species. The transport properties needed for this calculation — derived from intermolecular potentials using Chapman-Enskog theory — describe van der Waals interactions in

Lennard-Jones form and include dipole moments. In our workflow, we use well-tested reaction mechanisms when available and augment them with quantum chemistry-based reaction, thermal, and transport data.

Reaction data from literature and quantum chemistry studies using Q-Chem[8] and xTB[9] programs connect to the CFD problem of the reacting CH_4-OMCTS flame through a systematic workflow that translates molecular-level calculations into parameters required by ANSYS Fluent. NASA polynomial coefficients derived from quantum chemistry frequency calculations using our in-house Python code provide temperature-dependent thermodynamic properties (heat capacity, enthalpy, and entropy) for each chemical species, feeding directly into the CFD energy equation for accurate temperature field and flame structure prediction. Lennard-Jones parameters (calculated from quantum chemical geometry and polarizability data) and dipole moments, determine transport properties — viscosity and diffusion coefficients — that control chemical species transport in the CFD momentum and conservation equations. Activation energies and pre-exponential factors extracted from transition state calculations define Arrhenius reaction rate constants, which govern local chemical source terms and determine the decomposition rate of the OMCTS and the formation of SiO_2 at different flame locations. An energy reference correction applied to the NASA polynomial a_6 coefficient reconciles differences between experimental and quantum chemistry-based heats of formation, ensuring thermodynamic consistency when coupling the OMCTS mechanism with the methane combustion mechanism in the combined CFD simulation. The entire mechanism underwent iterative validation: first through 1D flame calculations in Cantera to verify convergence and chemical feasibility, then through 2D axisymmetric Fluent simulations that demonstrated how mechanism optimization yields more reliable temperature and chemical species concentration fields.

4. METHANE COMBUSTION

Combustion of methane has been extensively investigated, and several validated reaction mechanisms are available[10]. These mechanisms contain the reaction rates of elementary reaction steps, specific heat, enthalpy, and entropy values for each chemical species in a NASA polynomial form, as well as Lennard-Jones parameters and dipole moments for transport properties. The primary challenge is that these mechanisms are computationally expensive for CFD simulations due to their size. However, reaction mechanism reduction — the selective removal of elementary reactions and chemical species that do not significantly impact accuracy under given conditions — can substantially decrease computational cost. Additionally, the coefficients of the retained reactions can be optimized to achieve a high accuracy. The Optima++ code was employed for reaction mechanism reduction and optimization[6),11)].

5. OMCTS DECOMPOSITION

Detailed reaction mechanisms have been reported for the thermal decomposition of silicon-containing precursors, including $SiCl_4$ in H_2/O_2 flames (Hannebauer et al.)[7], tetramethylsilane in H_2/O_2 flames (Janbazi et al.)[12], and OMCTS in H_2/O_2 flames (Chen et al.)[4], covering oxidation, pyrolysis, and hydrolysis pathways. Additionally, the OMCTS decomposition has been investigated in shock tube experiments (Peukert et al.)[13], and hydroxyl radical reactions with D_3 and D_4 chemical species have been characterized experimentally (Xiao et al.)[14]. Building on this foundation, and through refinement and extension using quantum chemistry computations and with meta-dynamics and kinetic simulations, we developed a thermodynamically consistent mechanism that retains only the most significant elementary reactions across four sub-mechanisms: methane reactions, precursor oxidation, pyrolysis, and hydrolysis (Figure 2). Using our

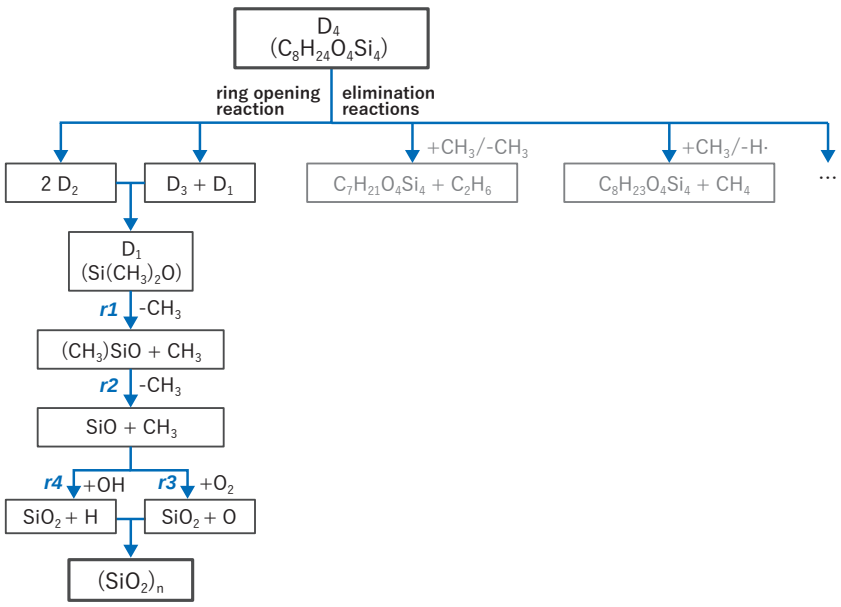

Figure 2　OMCTS decomposition mechanism.

quantum chemical computations, we systematically generated comprehensive transport parameters for all chemical species and calculated NASA polynomials covering 300-3500 K, providing accurate thermodynamic representations for practical applications.

The ring opening mechanism tracing the pathway $D_4 \rightarrow D_1 \rightarrow SiO_2$ was investigated through meta-dynamics simulations and quantum chemistry computations and was compared to mass-spectra experimental data (Figure 3). During pyrolysis, meta-dynamics simulations using GFN-xTB[15] identified ring opening as a key pathway, with hydrogen and methyl radical eliminations as important processes. We found that Si-O bond fission had a high energy barrier, and that the linear form of OMCTS (l-D_4) could easily re-close or cleave into D_1 and D_3. We proposed that intramolecular hydrogen atom transfer from a CH_3 group to oxygen could provide the driving force for ring opening, followed by CH_3OH elimination and cyclization. Once D_1 formed, quantum chemistry computations revealed that methyl group eliminations were barrierless, leading to sequential decomposition through intermediates like CH_3SiO to ultimately SiO, which is oxidized to SiO_2 with only small energy barriers.

For validation of the simulation results at clean and well-defined conditions, we also studied the temperature dependence of the OMCTS (D_4) decomposition using in-house experiments. Experiments were conducted in a tube furnace equipped with operando quadrupole mass-spectrometry analysis at the outlet, enabling in situ characterization of decomposition products (Figure 4). Measurements were performed under vacuum (3.1 mbar) in an inert argon atmosphere at temperatures ranging from 550–800°C.

We identified characteristic peaks for the OMCTS and its decomposition products (D_3, D_2, and D_1) on the mass spectrum based on previous experimental data. To investigate temperature dependence, we calculated the intensity of characteristic peaks relative to their total amount at each temperature (Figure 5 (a)).

The OMCTS thermolysis begins above 600°C, as evidenced by exponential growth of the D_3 peak (the primary decomposition product) with increasing temperature, accompanied by a simultaneous decrease of the D_4 peak. This exponential trend continues to approximately 700°C, where further temperature increase causes a deviation, indicating that D_3 dissociates into smaller fragments at elevated temperatures. Notably, D_2 intensity remains low across the entire temperature range, suggesting low thermal stability of this molecule.

The temperature dependence of the first thermolysis step (D_4 decomposition to D_3 and D_1) was analyzed using our reaction mechanism and compared with experimental results (Figure 5 (b)). Simulations indicate that the reaction proceeds at 550–600°C and generates D_3. The simulated conversions follow the same exponential trend as observed experimentally (600–700°C), demonstrating that our kinetic parameters accurately describe the temperature dependency of the chemical process.

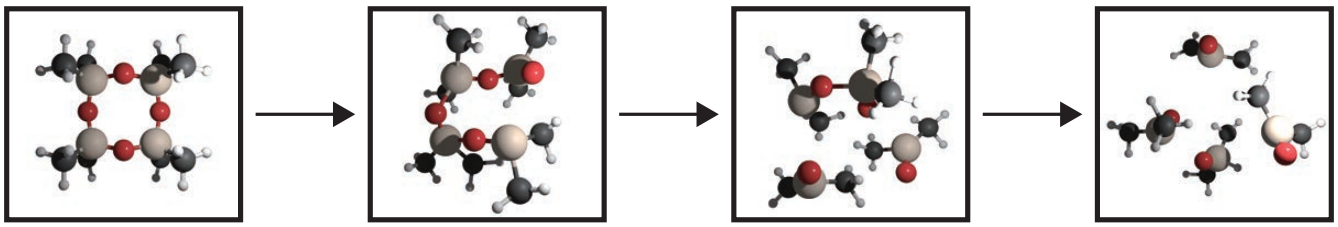

Figure 3　**OMCTS ring opening reactions, as computed using metadynamics simulations. Color coding: dark grey – carbon, beige – silicon, red – oxygen, light gray - hydrogen**

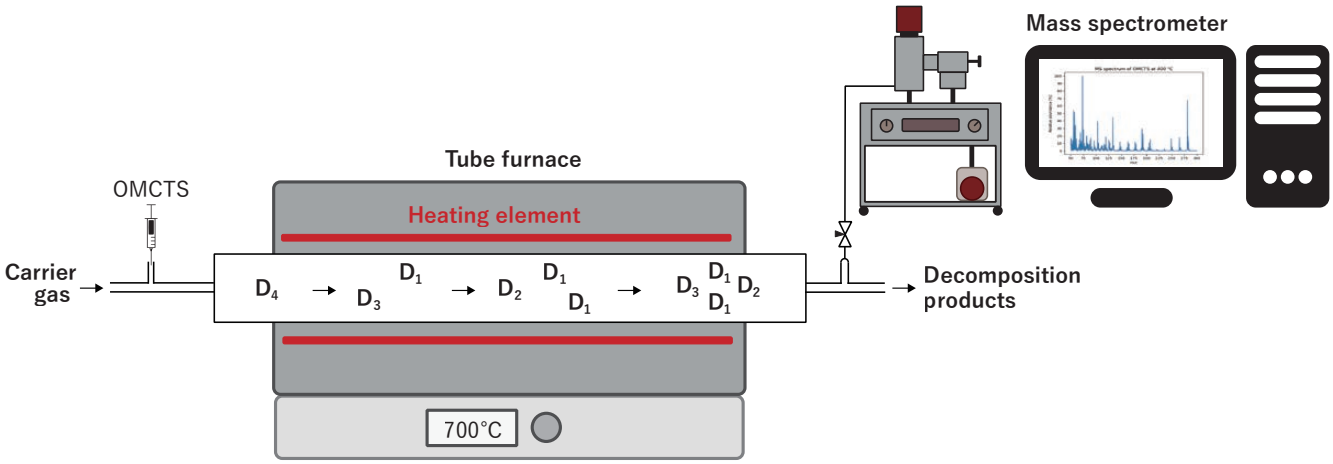

Figure 4　**Experimental setup at FETI used to study the temperature dependency of the OMCTS decomposition.**

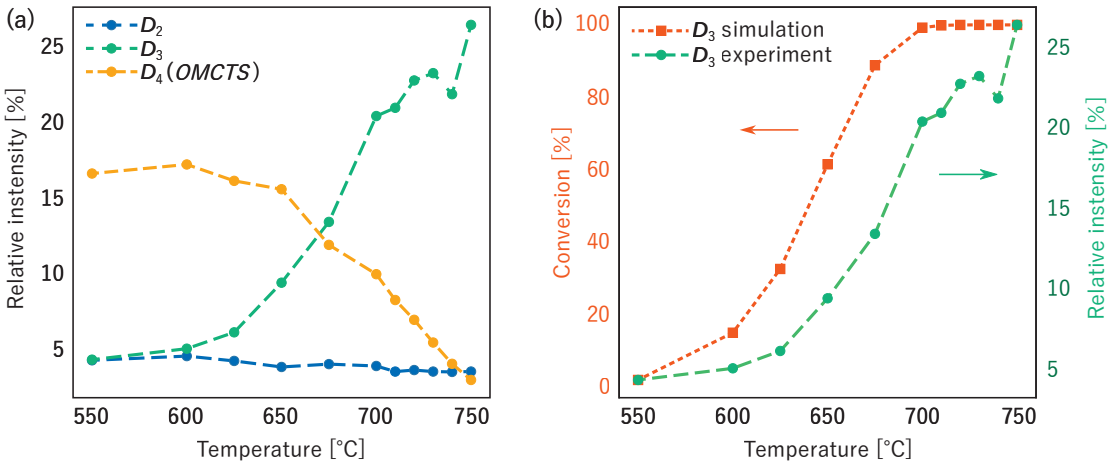

Figure 5　**Temperature dependency of the OMCTS and its decomposition products measured by mass spectrometer (a), and comparison of D_4 to D_3 decomposition between experimental measurements and simulations (b).**

At 800°C, the tube reactor walls became white due to SiO_2 powder deposition, the final OMCTS decomposition product. SiO_2 appeared only downstream of the heated zone, indicating that OMCTS decomposition occurred entirely in the gas phase.

6. PARTICLE GROWTH MECHANISM AND DEPOSITION ON THE PREFORM

Detailed chemical reaction mechanisms rapidly become unwieldy if all reactions relevant to SiO_2 particle growth are treated individually. To address this, we applied the Population Balance Model (PBM), which focuses on the evolution of the SiO_2 particle size distribution rather than tracking individual particle concentrations. PBM has been shown to provide accurate predictions for SiO_2 particle growth and has been integrated into CFD simulations and has been validated against experimental data[16), 17)]. We solved the population balance equations using the sectional method, where particles of different sizes are grouped into bins that participate in formal reactions. We accounted for both particle growth through addition of small gas-phase molecules (such as SiO, SiO_2 and $Si(OH)_4$) and particle agglomeration.

Particle transport in the fluid significantly influences size distribution and deposition. Diffusion and thermophoretic forces act on particles suspended in the gas. Thermophoresis is particularly important because it directs particles from hotter to colder regions, thereby promoting deposition on the preform.

7. FULL MECHANISM AND REACTOR SIMULATIONS

The complete assembled mechanism — encompassing methane combustion, OMCTS decomposition, and SiO_2 particle growth — was implemented in a multiphase reactive flow simulation that properly accounts for SiO_2 soot formation. We employed the volume fraction method and accounted for drag forces exerted by the gas flow on particles, and a turbulence model has also been applied. Representative results are shown in Figure 6, which clearly demonstrates that the predicted flame structure agrees with experimental observations.

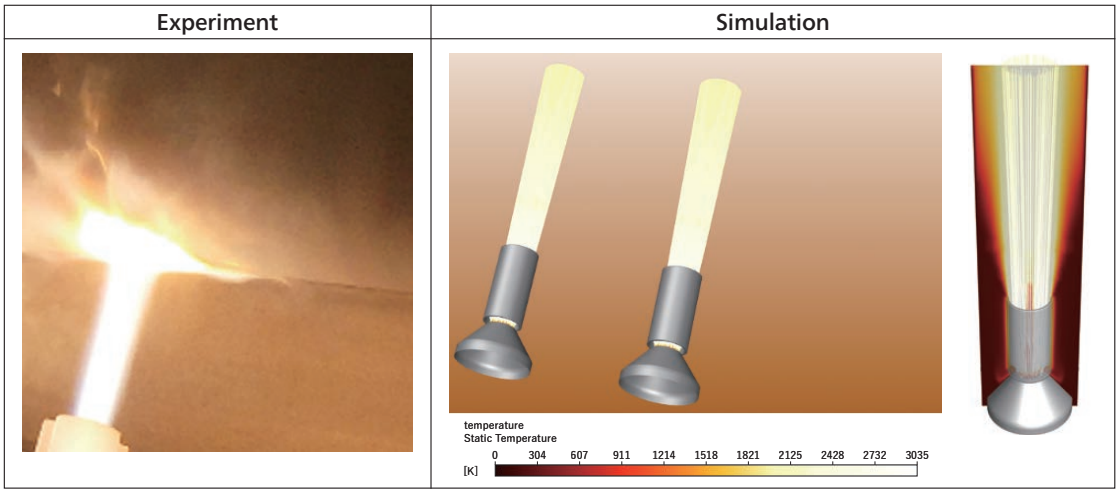

Figure 6　**Illustrative results of the CFD simulation for optical fiber preform manufacturing.**

8. CONCLUSIONS

We have presented a comprehensive overview of chemical reaction mechanism development for the OMCTS decomposition to facilitate burner development for optical fiber preform manufacturing. The systematic development of detailed reaction mechanisms, combined with a carefully assembled fluid dynamics model validated against experiments, contributed to improved understanding and provided a predictive capability. The reactive model served as a conceptual "Digital Twin Prototype", enabling evaluation of various burner configurations and supporting the identification of the most promising design.

Our work demonstrates that integration of quantum chemistry computations, molecular dynamics simulations, and computational fluid dynamics creates a robust framework for understanding and supporting optimization of a complex industrial process. By translating molecular-level chemistry into reactor-scale predictions, we help bridge a critical gap between fundamental science and practical engineering. The OMCTS decomposition mechanism represents a validated approach for predicting particle formation and deposition under relevant operating conditions. This level of mechanistic detail supports improved control over silica particle characteristics, including size distribution, morphology, and deposition uniformity on the optical fiber preform.

The development methodology itself is expected to be broadly applicable. Rather than relying solely on empirical data or simplified engineering correlations, this approach combines literature data with validation experiments and quantum chemical computations. This aims to maintain the accuracy of simulation predictions across the broad temperature range (300–3500 K) and diverse chemical environments encountered in the burner. The systematic correction of thermodynamic parameters through energy reference adjustments to the NASA polynomial coefficients ensures consistency with experimental observations while maintaining theoretical soundness.

Beyond the immediate application to OMCTS-based fiber manufacturing, this integrated computational approach offers significant potential for other precursor systems and industrial CVD processes. The workflow — encompassing quantum chemical geometry optimization, frequency calculations, polarizability assessment, reaction kinetics determination, and CFD implementation — is potentially generalizable to a broad range of volatile organic or organometallic precursor. Industries ranging from semiconductor coating to advanced material synthesis could benefit from similar approaches, as they enable rapid exploration of process alternatives without extensive experimental campaigns. Furthermore, the capability to predict particle size distribution and surface deposition rates supports improved control over final product quality, reducing waste and improving manufacturing efficiency.

Such models are expected to play an important role in enabling Digital Twin-based operations and control systems in the future. As computational power advances and machine learning techniques become integrated with physics-based simulations, more sophisticated process optimization and real-time adaptive control could become feasible. The framework demonstrated here provides a solid foundation for such future developments.

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REFERENCES

1) MacChesney, J. B., O'Connor, P. B., & DiMarcello, F. V.: "Preparation of low loss optical fibers using simultaneous vapor deposition and fusion", Proceedings of the 10th International Congress on Glass, 6-40 (1974).
2) Huang, Y., Zheng, L., Zhang, H., Zhang, G., & Jiang, L.: "Design and optimization of substrate placement for large-sized and high-quality fused silica glass by $SiCl_4$ flame hydrolysis deposition", International Journal of Heat and Mass Transfer, 111, 917-932 (2017).
3) Grishchenko, A. B., et al.: "Effect of the preform fabrication process on the properties of all-silica optical fibers and their resistance to UV and gamma radiation", Journal of Non-Crystalline Solids, 612, 122387 (2023).
4) Chen, J., Huang, Z., & Zheng, L.: "Detailed OMCTS/H_2/O_2 chemical kinetics mechanism and its application in the fused silica glass synthesis", Journal of Non-Crystalline Solids, 481, 33-40 (2018).
5) Lee, T. K., Choi, J., Lee, G. H., Jeon, H. J., & An, S. J.: "The dependence of N_2 carrier gas flow rate on deposition rate and density changes of porous silica preform synthesized by eco-friendly octamethylcyclotetrasiloxane", Physical Status Solidi (a), 216(16), 1900289 (2019).
6) Turányi, T., Nagy, T., Zsély, I. G., Cserháti, M., Varga, T., Szabó, B. T., ... & Curran, H. J.: "Determination of rate parameters based on both direct and indirect measurements", International Journal of Chemical Kinetics, 44(5), 284-302 (2012).
7) Hannebauer, B., & Menzel, F.: "The combustion of $SiCl_4$ in hot O_2/H_2 flames", Zeitschrift für anorganische und allgemeine Chemie, 629(9), 1485-1490 (2023).
8) E. Epifanovsky, et al.: "Software for the frontiers of quantum chemistry", An overview of developments in the Q-Chem 5 package J. Chem. Phys. 155, 084801 (2021).
9) Bannwarth, C., Ehlert, S., & Grimme, S.: "GFN2-xTB—An accurate and broadly parametrized self-consistent tight-binding quantum chemical method with multipole electrostatics and density-dependent dispersion contributions", Journal of chemical theory and computation, 15(3), 1652-1671 (2019).
10) Zhang, P., Zsély, I. G., Papp, M., Nagy, T., & Turányi, T.: "Comparison of methane combustion mechanisms using laminar burning velocity measurements", Combustion and Flame, 238, 111867 (2022).

11) Papp, M., Varga, T., Busai, A., Zsély, I.G., Nagy, T., Turányi, T.: Optima++ v2.5: A general C++ framework for performing combustion simulations and mechanism optimization (2024); available at http://respecth.hu/
12) Janbazi, H., Karakaya, Y., Kasper, T., Schulz, C. Wlokas, I., Peukert, S.: “Development and evaluation of a chemical kinetics reaction mechanism for tetramethylsilane-doped flames”, Chemical Engineering Science, 209, 115209 (2019).
13) Sela, P., Peukert, S., Herzler, J., Schulz, C., & Fikri, M.: “Shock-tube study of the decomposition of octamethylcyclotetrasiloxane and hexamethylcyclotrisiloxane”, Zeitschrift für Physikalische Chemie, 234(7-9), 1395-1426 2020).
14) Xiao, R., Zammit, I., Wei, Z., Hu, W-P., MacLeod, M., Spinney, R.: “Kinetics and Mechanism of the Oxidation of Cyclic Methylsiloxanes by Hydroxyl Radical in the Gas Phase: An Experimental and Theoretical Study”, Environmental Science & Technology, 49(22), 13322-13330 (2015).
15) Grimme, S.: “Exploration of chemical compound, conformer, and reaction space with meta-dynamics simulations based on tight-binding quantum chemical calculations”, Journal of chemical theory and computation, 15(5), 2847-2862 (2019).
16) Shekar, S., Smith, A. J., Menz, W. J., Sander, M., & Kraft, M.: “A multidimensional population balance model to describe the aerosol synthesis of silica nanoparticles”, Journal of Aerosol Science, 44, 83-98 (2012).
17) Tsagkaridis, M., Rigopoulos, S., & Papadakis, G.: “Modeling of silica synthesis in a laminar flame by coupling an extended population balance model with computational fluid dynamics”, Aerosol Science and Technology, 57(4), 296-317 (2023).