A package for reacting flow simulations with surface chemistry in Open-source CFD platform

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Abstract

Catalytic surface reactions occur in numerous industrial processes such as hydrogen production, emission control, and chemical synthesis. Despite their importance, modeling these catalytic reactions remains challenging due to the complexity of surface chemistry and the limitations of the existing standard OpenFOAM libraries. This study introduces a novel OpenFOAM-based framework with newly developed libraries for surface chemistry. The framework incorporates flux-matching boundary conditions, enabling precise simulations of chemical species production, consumption, and reaction heat at gas-surface interfaces. The surface chemistry library is validated against hydrogen oxidation simulations on Rh/Al₂O₃ catalysts using experimental and numerical data. This validation demonstrates that the library shows reasonably good agreement with benchmark data, confirming the library's capability to reproduce both experimental and numerical results, confirming its reliability and robustness. Consequently, the developed framework provides a robust platform for advancing the understanding of catalytic surface reactions and supporting application in various industrial chemical processes.

Keywords: Catalytic combustion; Surface chemistry; Numerical combustion; OpenFOAM.

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Information for Colloquium Chairs and Cochairs, Editors, and Reviewers

1) Novelty and Significance Statement

The currently available standard OpenFOAM library has limitations in solving surface chemical reactions. To overcome this limitations, this study presents the development of a surface chemistry library integrated with Open-FOAM standard library. The developed surface chemistry library is designed to describe complex gas-surface interactions such as the chemical species generation and consumption at gas-surface interfaces. This development can offer significant advancements in modeling gas-surface interactions, providing researchers in heterogeneous reacting flow simulations with a robust computational tool.

2) Author Contributions

- Jae Hun Lee: investigation, methodology, software, visualization, writing original draft.
- Danh Nam Nguyen: investigation, methodology, software, validation, writing review & editing.
- Hae Won Seo: software, validation, writing review & editing.
- Hyung Jun Ahn: software, validation, writing review & editing.
- Chun Sang Yoo: Conceptualization, funding acquisition, methodology, project administration, resources, supervision, writing review & editing.

3) Manuscript Length

- Four-page paper √
- Eight-page paper

The four-page format was selected to highlight the key aspects of our research, delivering a concise presentation.

4) Colloquium Selection

- Colloquium topic 1: Numerical Combustion
- Colloquium topic 2: Heterogeneous Combustion

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1. Introduction

OpenFOAM [1], an open-source computational 2 fluid dynamics (CFD) platform, offers a robust and з extensive framework for simulating reactive flows. 4 Despite its capabilities, it remains unable to properly 5 address surface chemistry-a key aspect of numer-6 ous chemical processes such as hydrogen production, emission control, and chemical synthesis-due to its 8 limited libraries. These processes often involve reac-9 tions occurring at the gas-solid interface, known as 10 heterogeneous or surface reactions [2]. 11 12 In this study, we developed a surface chemistry platform and integrated it with the standard Open-13 FOAM library. This platform facilitates the model-14 ing of the production and consumption of chemical 15

62 species at gas-surface interfaces, allowing for more 16 63 accurate simulations of catalytic systems. The surface 17 64 chemistry platform was applied in the simulation of 65 18 hydrogen catalytic combustion on an Rh/Al2O3 cata-19

lyst, and the results were validated against the bench-20

21 mark data from Karakaya et al. [2].

2. Theoretical modeling 22

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The theoretical basis of the developed surface 23 chemistry solver is organized into two main pats: 24 the governing equations, which describe the trans-25 port processes within the fluid, and the flux-matching 26 boundary conditions, which account the surface reac-27 tions occurring at the gas-surface interface. 28

The governing equations for the gas phase are the 29 same as those in OpenFOAM's original reactingFoam 30 solver. These equations describe the conservation of 31 mass, momentum, species, and energy: 32

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \tag{1}$$

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ho \mathbf{v} \mathbf{v}) -
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$$\frac{\partial(\rho Y_i)}{\partial t} + \nabla \cdot (\rho \mathbf{v} Y_i) = \nabla \cdot (\mu_{\text{eff}} \nabla Y_i) + \dot{w}_i^{\text{gas}},$$
$$(i = 1, \dots, k_g) \quad (3)$$

$$\frac{\partial(\rho h_s)}{\partial t} + \nabla \cdot (\rho \mathbf{v} h_s) + \frac{\partial(\rho K)}{\partial t} + \nabla \cdot (\rho \mathbf{v} K)$$
$$= \frac{\partial p}{\partial t} + \nabla \cdot (\alpha_{\text{eff}} \nabla h_s) + \dot{Q}_r^{\text{gas}} \quad (4)$$

where t is the time, ρ the mixture density, v the ve-36 locity vector, p the pressure, $oldsymbol{ au}$ the viscous stress ten-37 sor, Y_i and \dot{w}_i^{gas} the mass fraction and the net reaction 84 38 rate in the gas phase of the *i*-th species in the mix-39 ture. h_s , K, and \dot{Q}_r^{gas} denote the sensible enthalpy, 40 the kinematic energy, and the net heat of reaction from 41 42 gas-phase reactions, respectively. μ_{eff} and α_{eff} are the effective viscosity and thermal diffusivity of the mix-85 43 ture, and k_g is the number of species in the gas pase. 44 Radiative heat transfer was neglected due to its 45 46 negligible effect under the conditions considered in

this study. To account for molecular and thermal diffusions, the standard kinetic theory transport model was implemented to address the limitations of the existing OpenFOAM transport model. This approach calculates species transport properties, including viscosity (μ), thermal conductivity (λ), and binary diffusion coefficients (D_{ij}) , based on the kinetic theory. Detailed formulations of the model can be found in CHEMKIN [3].

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Surface reactions, determined by the fraction of chemical species absorbed on the active sites on the catalyst surface and represented by the site fraction, θ_k [4], differ from gas-phase reactions, which depend on the concentration of gas phase species. As a result, modeling surface chemistry requires solving a system of governing equations, along with an additional equation for the conservation of adsorbed chemical species, which is expressed through the site coverage conservation:

$$\sum_{k=1}^{K} \theta_k = 1, \quad (k = 1, \dots, k_s)$$
(5)

Furthermore, the formation rate of the k-th site species on the catalytic surface, \dot{w}_k^{surf} , depends on the variation in the site fraction θ_k .

$$\rho_{\text{site}} \frac{\partial \theta_k}{\partial t} = \dot{w}_k^{\text{surf}}, \quad (k = 1, \dots, k_s) \tag{6}$$

where ρ_{site} is the site density, representing the number of moles of active sites on the catalyst surface per unit area.

The developed surface chemistry solver uses fluxmatching boundary conditions to handle species production, consumption, and heat of reactions at the gas-surface interface. These are expressed by the i^{th} gas-phase species production rate and heat of reactions as follows:

$$(\lambda \nabla T) \Big|_{\text{catalyticWall}} = F_{\text{cat/geo}} \dot{Q}_r^{\text{surf}} \tag{7}$$

$$\rho D_{im} \nabla Y_i) \Big|_{\text{catalyticWall}} = F_{\text{cat/geo}} \dot{w}_i^{\text{surf}},$$
$$(i = 1, \dots, k_g) \quad (8)$$

To enhance the surface reactivity, catalytic surfaces are designed to have large specific surface area, maximizing the availability of active sites and enhance reaction rates. This enhancement is accounted for using the term $F_{\text{cat/geo}}$, which represent the ratio of the catalytic area to the geometric area:

$$F_{\text{cat/geo}} = \frac{A_{\text{catalyst}}}{A_{\text{geometric}}} \tag{9}$$

where D_{im} is the individual species mixtureaveraged diffusion coefficient, and $\dot{Q}_{\tau}^{\text{surf}}$ represents the heat of reaction due to surface reactions on the catalytic surface.

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1 3. A new developed framework

Building upon the standard thermophysical OpenFOAM library, we developed a novel framework
for simulating heterogeneous reacting flows in
OpenFOAM-8. This framework incorporates the
surface chemistry libraries and implements fluxmatching conditions at the gas-surface interface, calculated based on site fraction.

9 4. Validation

The stagnation flow reactor configuration was cho-10 sen due to its effectiveness as a tool for kinetic mea-11 surements, providing a well-defined flow field that 12 enables the study of heterogeneous chemistry under 13 both steady-state and transient conditions [2]. A 14 hydrogen catalytic combustion simulation was con-15 ducted using this configuration to validate the imple-16 mentation of the surface chemistry library. Surface re-17 actions were facilitated by the stagnation disk, which 18 was coated with an Rh/Al₂O₃ catalyst [2]. 19

A 2-D axisymmetric stagnation flow reactor con-20 figuration, illustrated in Fig. 1, was adopted. The re-21 actor design features a 39 mm gap between the gas 22 inlet and the stagnation disk, with a disk radius of 78 23 mm to approximate an infinite flat plate. At the inlet, 24 a mixture of H₂, O₂, and Ar, of which mole fractions 25 are 0.0573, 0.0287, and 0.914, respectively, is intro-26 duced at a velocity of 0.51 m/s and a temperature of 27 313 K. The reactor pressure is maintained at 0.5 bar. 28 The flow impinges on the catalyst-coated stagnation 29 disk, which is heated to 673 K, where surface reac-30 31 tions convert H_2 into H_2O . $F_{cat/geo}$ is set to 30.



Fig. 1: Stagnation flow reactor configuration. r and z denote the radial and axial direction, respectively. δ represents the boundary layer thickness.

In this configuration, the boundary layer develop-32 ing near the disk significantly affects reactant trans-33 port, product emission, heat transfer, and reaction 34 rates. To accurately capture these effects, a high-35 resolution grid near the stagnation disk was generated 36 near the dist. The computational domain employed a 37 uniform grid with a resolution of 50 µm, ensuring ac-38 curacy in the results. A mesh sensitivity test was also 39

40 conducted to confirm the validity of the mesh.

The H₂ sub-mechanism from the surface reaction mechanism detailed in [5] was adopted to model hydrogen catalytic combustion on an Rh/Al₂O₃ catalyst. This mechanism was selected because it effectively reproduces experimental results for hydrogen reactions on Rh/Al₂O₃ surfaces [5]. It comprises six reversible elementary reactions involving three gasphase species and six site species, as outlined below:

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- R1: $H_2(g) + 2Rh(s) \rightarrow 2H_2(s)$ (r1)
- R2: $O_2(g) + 2Rh(s) \rightarrow 2O_2(s)$ (r2)
- $\label{eq:R3: H2O(g) + Rh(s) \to H_2O(s) } \qquad (r3)$
- R4: $2H(s) \rightarrow 2Rh(s) + H_2(g)$ (r4)
- R5: $2O(s) \rightarrow 2Rh(s) + O_2(g)$ (r5)
- R6: $H_2O(s) \rightarrow Rh(s) + H_2O(g)$ (r6)
- R7: $H(s) + O(s) \rightarrow OH(s) + Rh(s)$ (r7)
- R8: $OH(s) + Rh(s) \rightarrow H(s) + O(s)$ (r8)
- $\label{eq:R9:H} \begin{array}{ll} \text{R9:} & H(s) + \text{OH}(s) \rightarrow H_2\text{O}(s) + \text{Rh}(s) & (r9) \end{array}$
- $\mbox{R10:} \quad \mbox{H}_2 O(s) + \mbox{Rh}(s) \rightarrow \mbox{H}(s) + \mbox{OH}(s) \quad \ (r10) \label{eq:R10:}$
- R11: $2OH(s) \rightarrow H_2O(s) + O(s)$ (r11)
- R12: $H_2O(s) + O(s) \rightarrow 2OH(s)$ (r12)

where $Rh_{(s)}$ represents a vacant site. g and s denote a gaseous species and an adsorbed species on the catalyst surface, respectively.

Table 1: The rate constants in CHEMKIN format for Rh/Al_2O_3 catalyst

Reaction No.	A [cm,mol,s]	β	E_a [kJ/mol]
1	3.000×10^{-2}	Stick	-
2	1.000×10^{-2}	Stick	-
3	1.000×10^{-1}	Stick	-
4	5.574×10^{19}	0.239	59.69
5	5.329×10^{22}	-0.137	387.00
6	6.858×10^{14}	-0.280	44.99
7	8.826×10^{21}	-0.048	73.37
8	1.000×10^{21}	0.045	48.04
9	1.743×10^{22}	-0.127	41.73
10	5.408×10^{22}	0.129	98.22
11	$5.735 imes10^{20}$	-0.081	121.59
12	1.570×10^{22}	0.081	203.41

 $\rho_{\rm site} = 2.72 \times 10^{-7} \text{ kmol/m}^2.$

Based on Langmuir–Hinshelwood kinetics, the mechanism models adsorption, desorption, and surface reactions between adsorbed species using the mean-field approximation. This approximation assumes that the surface is uniform, with species randomly distributed across it.

The rates of reactions r_i (i = 1, ..., 12) are expressed in CHEMKIN format, with the reaction rate constant coefficients listed in Table 1. The formulation of r_i is as follows:

$$r_{i} = k_{i} \prod_{k=1}^{K} [X_{k}]^{\nu_{k}^{\prime i}}$$
(10)

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The rate constant k_i is calculated using Eq. 11 for 30 1

standard surface reactions and Eq. 12 for sticking co-2

3 efficient reactions:

$$k_{i} = \begin{cases} A_{i}T^{\beta_{i}} \exp\left(-\frac{E_{a,i}}{RT}\right) & (11) \\ \gamma_{i}\frac{\prod_{j=1}^{2}\sigma_{j}^{\prime_{i}}}{(\Gamma_{\text{tot}})^{m}}\sqrt{\frac{RT}{2\pi W_{k}}} & (12) \end{cases}$$

where γ_i is the sticking coefficient, representing the 4

- probability of a gas molecule adhering to the surface 5
- upon collision in a chemical reaction. σ_i denotes the 6
- number of sites occupied by the species j, and W_k 7
- represents the molecular weight of the species. 8



Fig. 2: 1-D profiles of mole fractions of H2, O2 and H2O as a function of distance from the catalytic disk. The symbol and dashed line represent the experimental data [2] and numerical prediction [2], respectively. The solid line denotes the numerical prediction from thisstudy.

Fig. 2 shows the 1-D species concentration profiles 9 of H₂, O₂ and H₂O obtained from the present simula-10 tion together with the benchmark data from Karakaya 11 et al. [2]. The simulation results show good agree-12 ment with the benchmark numerical data. However, 13 minor deviations are observed when compared to the 14 experimental data, particularly in the diffusion be-15 havior of H₂ near the stagnation disk. These differ-16 ences are attributed to uncertainties in transport prop-17 erties arising from the mixture-averaged approxima-18 tion, which introduces inaccuracies in predicting the 19 diffusion of light species like H₂ [6]. 20

It is worth noting that similar discrepancies also 21 exist in the benchmark numerical data when com-22 pared to their experimental data [2]. This consis-23 24 tency also confirms the reliability of the developed surface chemistry solver in reproducing trends ob-25 served from the benchmark study, demonstrating the 26 successful implementation of the OpenFOAM-based 27 surface chemistry library. 28

5. Conclusions 29

In this study, we successfully developed a novel framework that integrates a surface chemistry library with flux-matching boundary conditions at catalytic surfaces. This approach enables accurate prediction of species production and consumption, as well as the heat of reaction associated with heterogeneous reactions. The developed surface chemistry library was validated against hydrogen oxidation over Rh/Al₂O₃ catalysts, based on the data from Karakaya et al. [2]. The simulation results were compared with benchmark data, showing good agreement. While minor discrepancies were observed in the H₂ concentration profiles near the catalytic surface, the developed framework demonstrated its capability to reasonably reproduce the benchmark results. These findings confirm the validity and reliability of the developed code.

Declaration of competing interest 46

The authors declare that they have no known com-47 peting financial interests or personal relationships that 48 could have appeared to influence the work reported in 49 this paper. 50

Acknowledgments 51

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