Microscale Simulations of Catalyst Deactivation During Gas-Phase Upgrading of Biomass Pyrolysis Vapors

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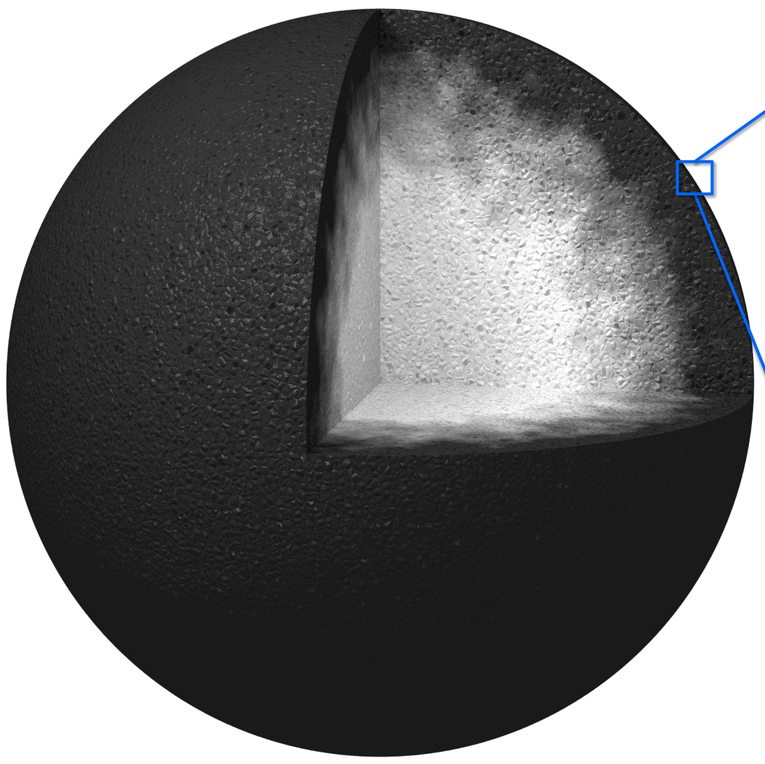
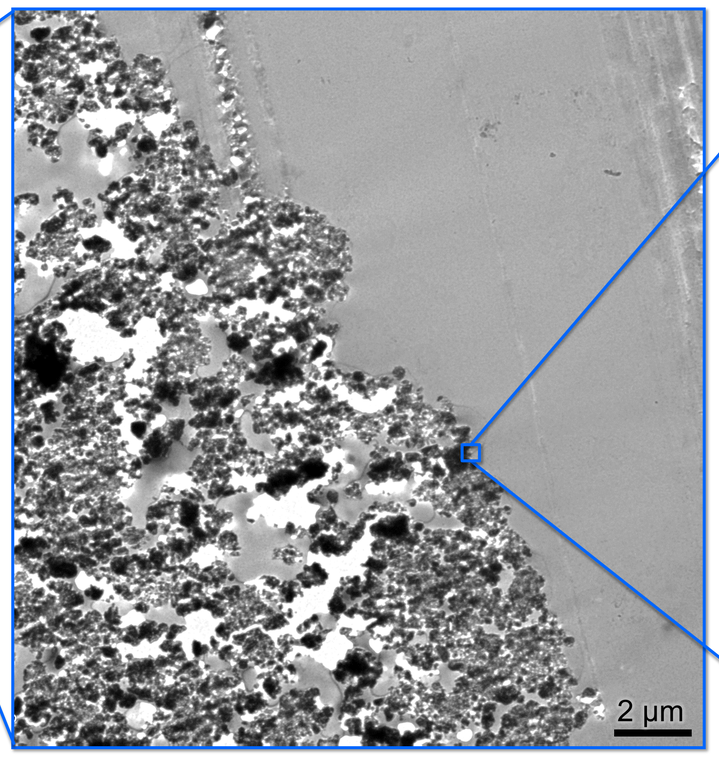
Background and Motivation

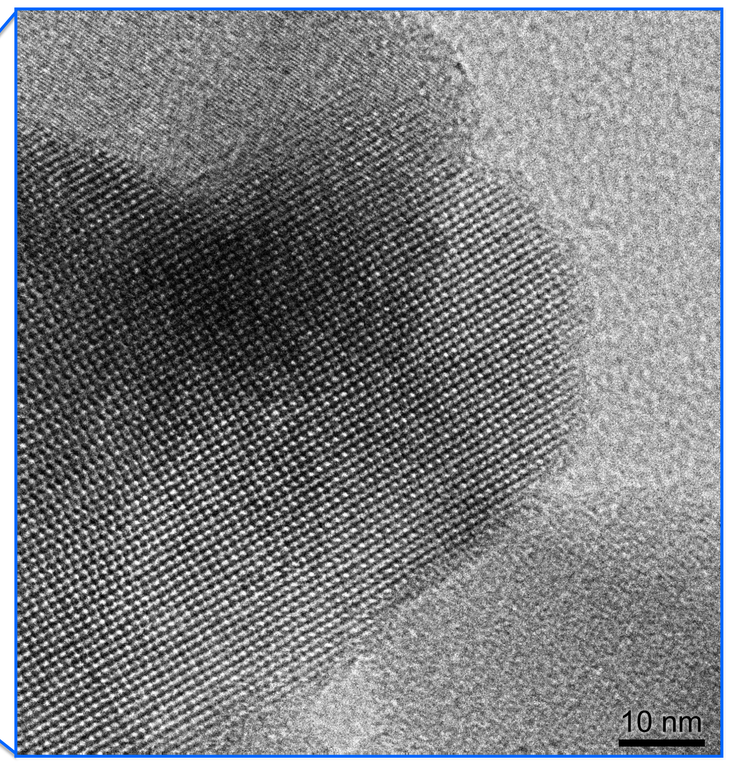
Renewable fuels and chemicals derived from biomass are a promising and sustainable means to displace large quantities of fossil fuels and petroleum-derived products. Catalytic fast pyrolysis is one process by which biomass may be directly converted into liquid hydrocarbon transportation fuels and chemical co-products. Chemical compounds in raw pyrolysis vapor have high oxygen content and therefore must be deoxygenated in order to meet specifications for hydrocarbon fuels. One strategy to accomplish this is to pass the vapors over a deoxygenation catalyst immediately after pyrolysis in a process called ex-situ catalytic fast pyrolysis. During catalytic upgrading, coke accumulates on the catalyst with increased exposure to pyrolysis vapors which deactivates catalytic sites. In order to accurately predict effective reaction rates, transport of products and reactants through the catalyst must be considered in tandem with chemical kinetics of product evolution and coke formation.



Partially deactivated zeolite catalyst particle



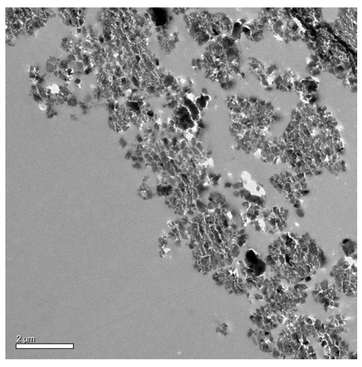
Low-magnification TEM image showing catalyst microstructure



High-magnification TEM image showing catalyst atomic structure

Approach

Obtaining Simulation Geometry from Electron Microscopy Image Data



TEM Micrograph

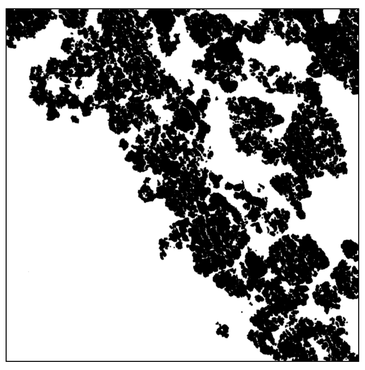
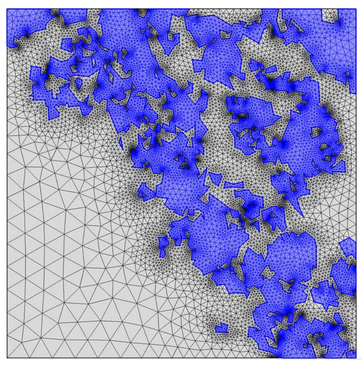


Image Binary



Meshed Geometry

In order to obtain realistic geometry that accounts for the intra-particle porosity of the catalyst particles, we used Transmission Electron Microscopy to map the geometry directly into Comsol. First, a TEM image was obtained of a thin section of a catalyst particle. The TEM image was used to generate an image binary. The image binary was converted to a vector image and imported into Comsol using the CAD Import module. The geometry was divided into two domains: a gas phase domain outside the particle and within the void spaces and solid phase domain (shown in blue).

Computational Approach: Reaction/Diffusion Kinetic Model with Catalyst Deactivation

Kinetic Model

$$R + S \xrightarrow{k_1} P + S \xrightarrow{k_2} C$$

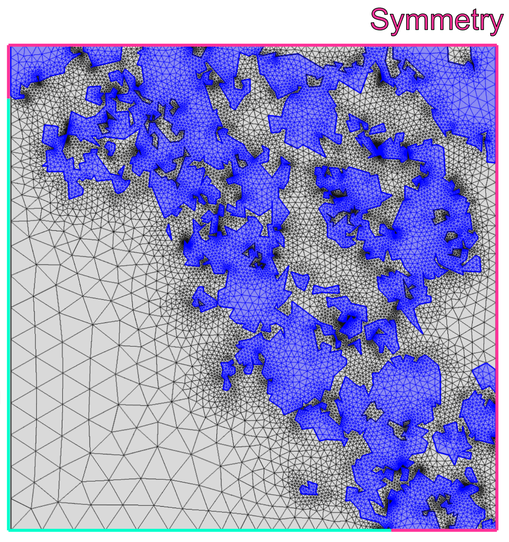
$$\frac{dC_R}{dt} = -k_1 C_R C_S$$

$$\frac{dC_P}{dt} = k_1 C_R C_S - k_2 C_P C_S$$

$$\frac{dC_S}{dt} = -k_2 C_P C_S$$

$$\frac{dC_C}{dt} = k_2 C_P C_S$$

Symmetry B.C.s



Concentration B.C.s

Transport Model

$$\frac{\partial C_R}{\partial t} = \nabla \cdot (\mathrm{D}_i \nabla C_i) + \sum R_i$$

$$\mathrm{D}_{\mathrm{R,solid}} = \mathrm{D}_{\mathrm{P,solid}} = 10^{-12} m^2 \cdot \mathrm{s}^{-1}$$

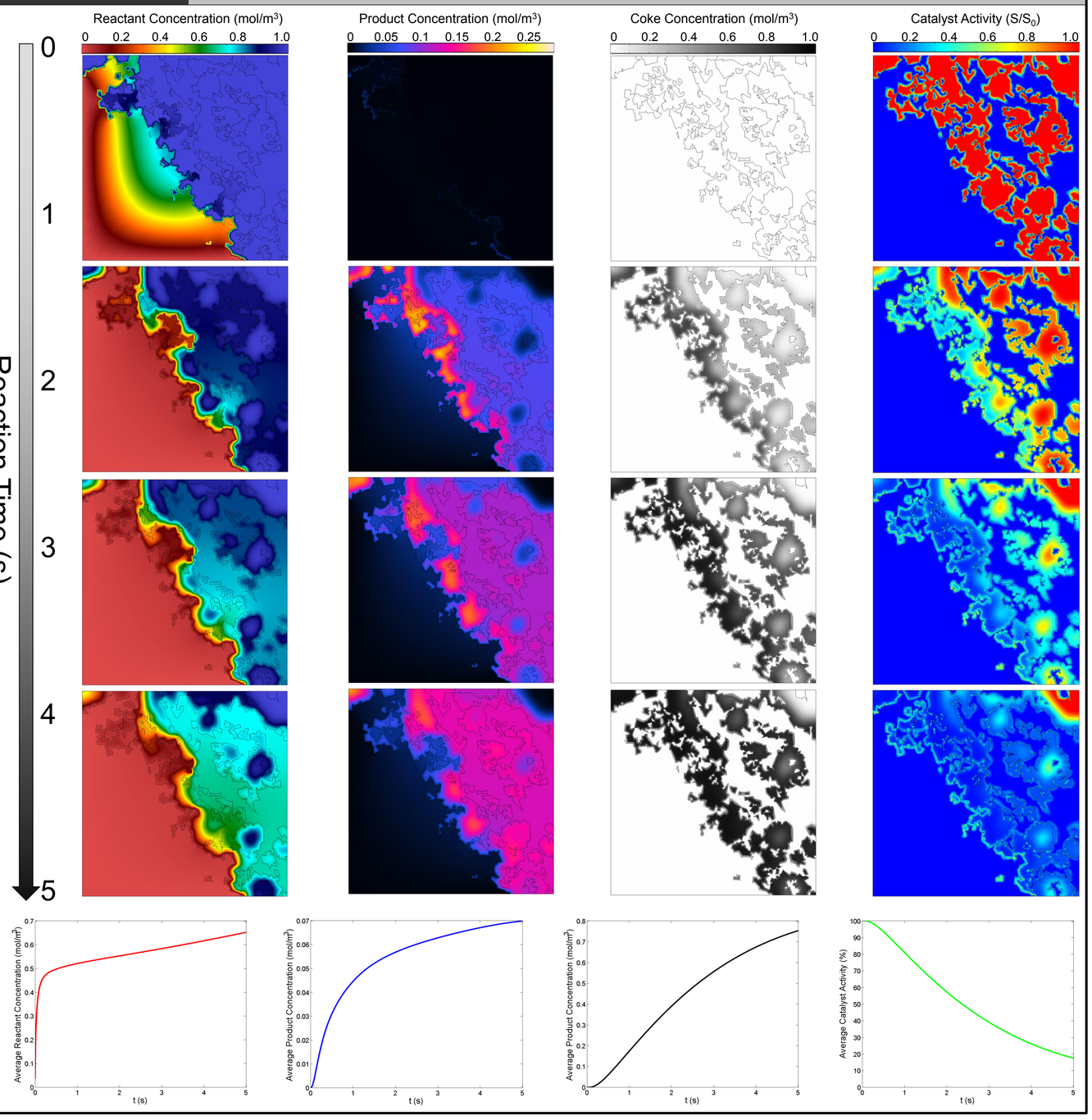
$$\mathrm{D}_{\mathrm{R,gas}} = \mathrm{D}_{\mathrm{P,gas}} = 10^{-6} m^2 \cdot \mathrm{s}^{-1}$$

$$\mathrm{D}_{\mathrm{S,solid}} = \mathrm{D}_{\mathrm{C,solid}} = \mathrm{D}_{\mathrm{S,gas}} = \mathrm{D}_{\mathrm{C,gas}} = 0$$

The Transport of Dilute Species interface was used to implement the reaction/diffusion model. Reaction kinetic parameters and diffusion coeficcients of reactant and product species in the gas and solid domains were estimated from literature values for similar systems. Diffusion coefficients of the chemical species representing catalyst sites and coke were set to zero to prevent diffusive migration of these stationary catalyst features.

Results

Solution to Transient Reaction/Diffusion Kinetic Model



Conclusions and Future Directions

In summary, we have demonstrated that Comsol simulations may be used to estimate the activity of catalysts during vapor phase upgrading of pyrolysis vapors. The system geometry is obtained directly from electron microscopy. These methods can be used to determine catalyst residence times that result in optimal upgrading of biofuel products. Future studies will coordinated closely with targeted experiments to determine reliable kinetic parameters for specific catalysts. Eventually, we aim to optimize catalyst geometric parameters, such as particle diameter and porosity, to design more effective catalysts.

Acknowledgements

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