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Accurate Microkinetic Mechanisms for Homogeneous/Heterogeneous Coupled Systems: A Case Study of Catalytic Combustion Using RMG-Cat

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Abstract

RMG-Cat has been updated extensively. Density functional theory calculations were performed for 69 adsorbates on Pt(111), and the resulting thermodynamic properties were added to RMG-Cat. The thermo database is significantly more accurate; it includes nitrogen-containing adsorbates for the first time, as well as better capabilities for predicting the thermochemistry of novel adsorbates. Additionally, RMG-Cat can now simultaneously pursue mechanism expansion on both the surface and in the gas-phase. This coupled capability is tested on the catalytic combustion of methane on platinum. The results confirm that under some conditions, the catalyst is capable of inducing thermal ignition in the gas-phase.[1]

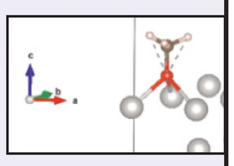
What is RMG-Cat?

It is an open source software which automatically generates complete kinetic mechanisms for heterogeneous catalysis systems[2]. RMG-Cat is an offshoot of the gas-phase RMG of Green and West[3].

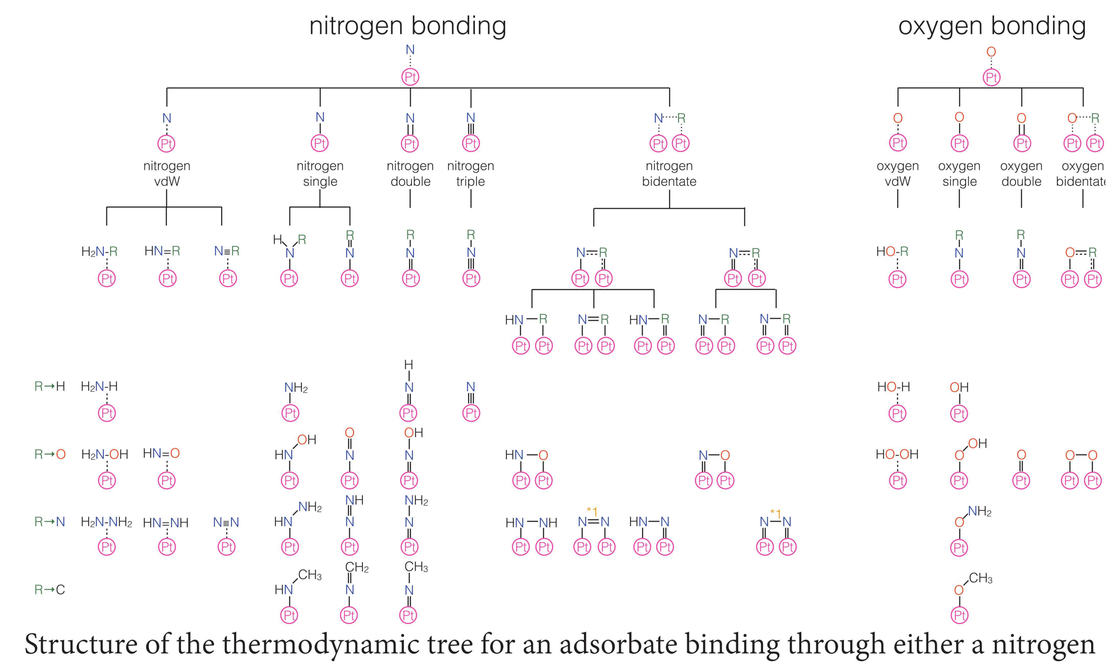
How does it work? RMG-Cat has a database of thermodynamic properties, as well as the ability to estimate the thermodynamic properties of novel species. Similarly, the code has a database of predetermined rate constants for new reactions. Finally, RMG-Cat uses a flux-based approach for mechanism expansion.

What's new? RMG-Cat can now explore kinetic pathways simultaneously on the surface and in the gas phase. Additionally, the new thermo database is a notable improvement from the original release of RMG-Cat in three key respects:

1. Nitrogen was added to the system.
2. The thermodynamic database was restructured to include all major adsorbates that consist of up to two heavy atoms.
3. The electronic structure properties were computed using more accurate electronic structure methods: VASP through ASE was used with the BEEF-vdW functional[4].



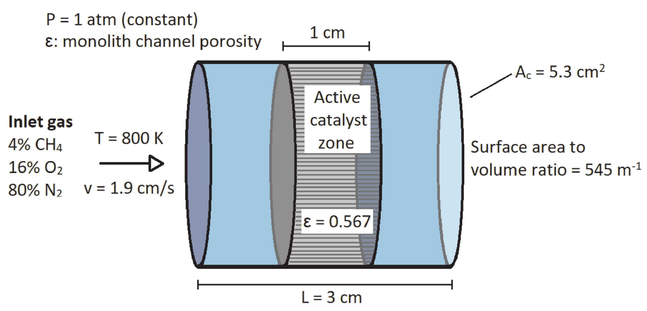
Finally, the inclusion of platinum in addition to nickel as a catalyst adds new versatility to the software.



Structure of the thermodynamic tree for an adsorbate binding through either a nitrogen or an oxygen atom.

The new features were tested on CH_4 catalytic combustion

RMG-Cat was used to generate a mechanism for the catalytic combustion process at a temperature range of 800-1750K. It was then simulated using a catalytic plug flow reactor (PFR) model in Cantera[5], an open source library of subroutines for reactive flow simulations.

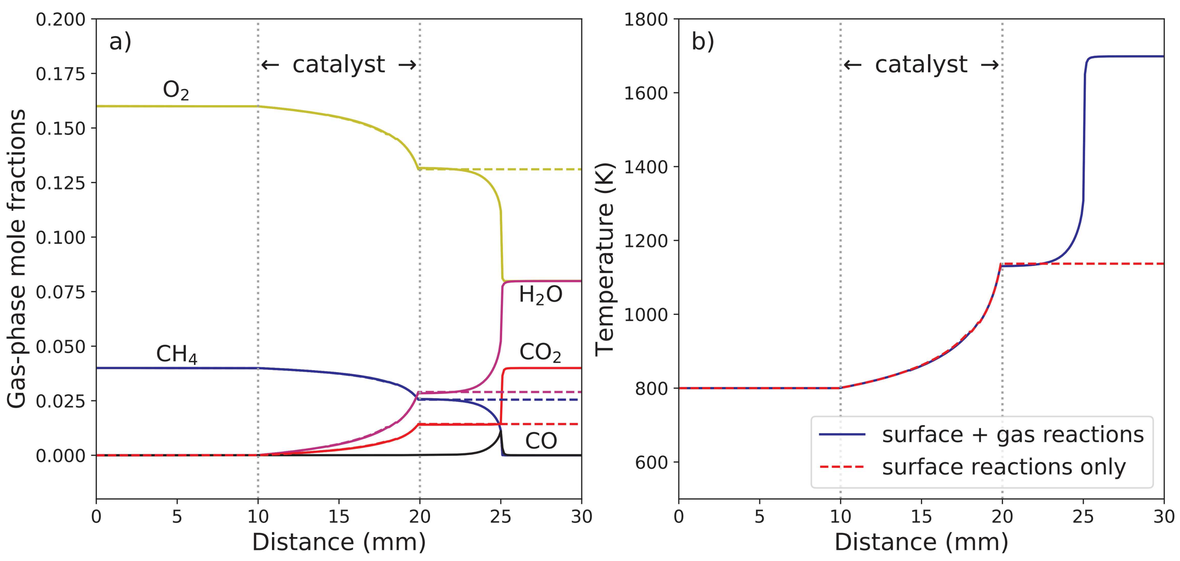


Results

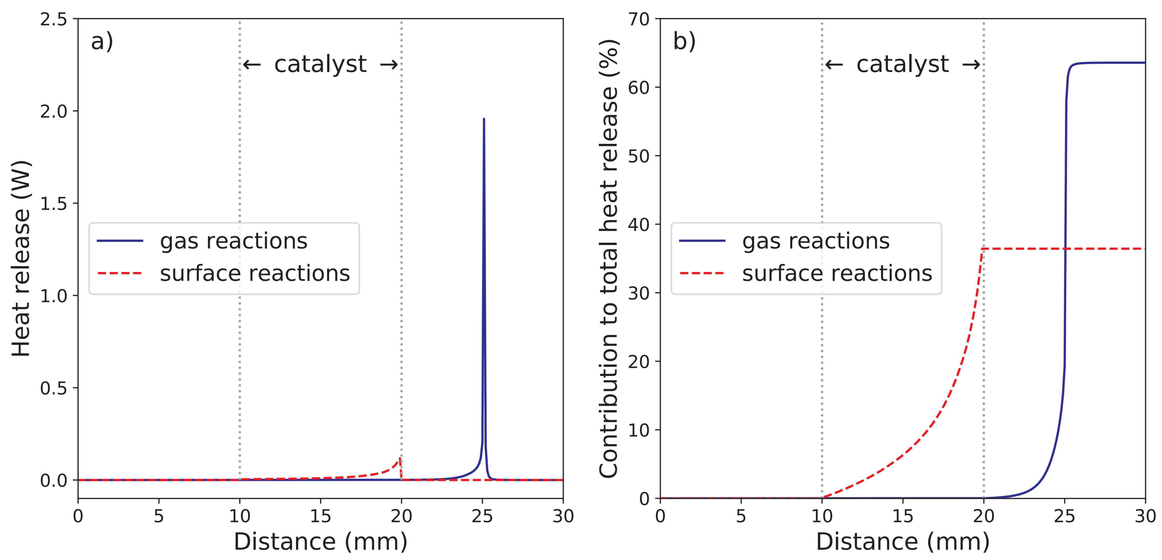
The final mechanism generated by RMG-Cat includes 21 adsorbates and 55 surface reactions with 38 gas-phase intermediates and 340 gas-phase reactions. The model "edge" contained an additional 196 species and 298 reactions.

The Cantera simulation results indicate that the contribution of gas-phase chemistry to the total fuel conversion is negligible during the 10 mm section that includes the catalyst. However, once the catalyst zone ends, the concentration of fuel and oxidizer is still sufficiently high that thermal ignition occurs.

The effect of gas-phase chemistry can be seen from the heat release rates. The sharp heat release rate at 25 mm is effectively a standing flame within the reactor, which would pose a severe operational hazard.



PFR results for catalytic combustion of natural gas over Pt: (a) the major gas-phase species, and (b) the temperature. The catalyst is located in the region between 10-20 mm from the inlet. The solid lines include both surface and gas-phase reactions; the dashed lines do not include gas-phase chemistry.



Heat release rates for catalytic combustion in a PFR: (a) net rate of heat release, (b) contribution of each reactive phase towards the total heat release.

Conclusions

The simulation results, obtained using the recently improved RMG-Cat, confirm that the rapid temperature rise associated with the surface oxidation chemistry can lead to thermal ignition. This case study demonstrates the capability of the software to provide accurate and thermodynamically consistent microkinetic mechanisms for homogeneous/heterogeneously coupled systems.

Acknowledgements

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References

[1] Blondal, Jelic, Mazeau, Studt, West, Goldsmith. (2019). *Ind. Eng. Chem. Res.* (under review).
[2] Goldsmith, C. F., West, R. H. (2017). *J. Phys. Chem. C, 121*, 9970-9981.
[3] Gao, C. W. Allen, J. W. Green, W. H. West, R. H. (2016). *Comput. Phys. Commun., 203*, 212–225.
[4] Wellendorff, J. et al. (2012). *Phys. Rev. B 85*.
[5] Goodwin, D. G., Moffat, H. K., Speth, R. L. (2017). http://www.cantera.org, Version 2.3.0

RMG-Cat has now been merged into the master branch of RMG 2.4, and all the features described are now available as part of the RMG software suite.
To download the latest version of RMG, please go to https://rmg.mit.edu/

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