CNMS Staff Science Highlight

Functionalized few-layer graphene as a metal-free catalyst

Scientific Achievement

Manipulation of the oxygen functionalities on the surface of few-layer graphene can help to identify the active sites for heterogeneous catalytic oxidative dehydrogenation. Activity is more closely related to the availability of edges sites where oxygen functional groups can be formed and exchanged than to the total quantity of oxygen in the catalyst.

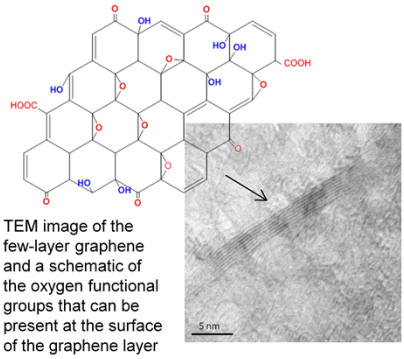
Significance

Carbon-based catalysts are ideal candidates to substitute for conventional metal-oxide catalysts since they can be easily disposed of, enabling greener, more sustainable catalytic processes. Identification of the most active oxygen sites in oxidative dehydrogenation will enable the engineering of active functionalities in nanostructured carbons.

Research Details

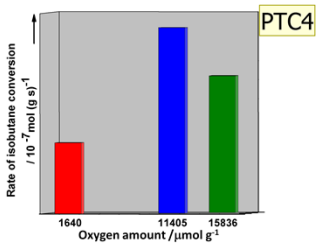
- Oxygen functionalization of synthetic few-layer graphene derived from the Hummers method was varied by systematic removal of the oxygen groups through high temperature or reducing conditions, but no clear correlation was found between oxidative dehydrogenation (ODH) of isobutane rate and the total amount of oxygen groups.
- Temperature programmed method and XPS provided information about the type of oxygen functional groups. Microscopy, Raman and surface area measurements were used to correlate edge and surface area and changes in carbon structure.
- The re-oxidation of the graphene surface occurs at the same rate as the ODH reaction suggesting a similar mechanism to that which takes place on oxide surfaces.

V. Schwartz, W. Fu, Y. Tsai, H. M. Meyer III, A. J. Rondinone, J. Chen, Z. Wu, S. H. Overbury and C. Liang, *ChemSusChem (2012)* **DOI:**



TEM image of the few-layer graphene and a schematic of the oxygen functional groups that can be present at the surface of the graphene layer

$$iC_4H_{10} + 1/2O_2 \longrightarrow iC_4H_8 + H_2O$$



Reaction rate of isobutane conversion (ODH reaction above) versus amount of oxygen on the surface of selected functionalized graphene samples.

U.S. DEPARTMENT OF ENERGY | Office of Science

Center for Nanophase Materials Sciences

OAK RIDGE National Laboratory

Highlight Narrative Text

The utilization of carbon-based materials for catalysis, both as a support or as an active phase, has been growing in importance as a variety of well-defined nanostructured carbons are being developed.[1] From an environmental standpoint, metal-free carbon based catalysts are ideal candidates to substitute the conventional metal oxide catalysts since they can be easily disposed of by combustion after achieving their life-time, enabling a more sustainable alkene production. The scientific challenge is to achieve a detailed mechanistic understanding of the structural or chemical sites of the carbon that are catalytically active especially because of the very heterogeneous nature of carbon surfaces. We have utilized oxygen functionalized, few-layer graphene and attempted to relate their catalytic function with their structural and chemical properties by systematic variation in the oxygen content. Activity is more closely related to the availability of edges sites than to the total quantity of oxygen in the catalyst as the figure shows no clear correlation between isobutane consumption rate and the oxygen content of the samples.

(1) a) B. F. Machado, P. Serp, Catal. Sci. Technol. 2012, 2, 54-75; b) F. Rodriguez-Reinoso, Carbon 1998, 36, 159-175.

References:

"Oxygen functionalized few-layer graphene as active catalysts for oxidative dehydrogenation reaction", V. Schwartz,[a] W. Fu,[a] Y. Tsai,[a] H. M. Meyer III,[b] A. J. Rondinone,[a] J. Chen,[a] Z. Wu,[a,c] S. H. Overbury,[a,c] and C. Liang[a]

[a] Center for Nanophase Materials Sciences, ORNL

[b] Material Science Division, ORNL

[c] Chemical Science Division, ORNL
ChemSusChem **DOI:**

Acknowledgements
This work was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, Office of Basic Energy Sciences, U. S. Department of Energy. The research was supported in part by an appointment to the ORNL Postdoctoral Research Associates Program administered jointly by Oak Ridge Institute for Science and Education (ORISE) and ORNL.