This Week at NETL

May 13, 2013

NETL Catalyst Produces Winner in Shale Gas Innovation Contest

The Shale Gas Innovation & Commercialization Center selected Pittsburgh-based Pyrochem Catalyst Company (PCC) as one of three winners of this year's Innovation Contest. Winners receive $25,000 in seed capital to accelerate the commercialization of shale-gas-related technologies. In 2011, PCC licensed two NETL-developed technologies: (1) pyrochlore-type catalysts for reforming hydrocarbon fuels, including natural gas, into synthesis gas for fuel cell operation, and (2) a method for designing a reforming and/or combustion catalyst system. The licensing agreement marked the first time that an NETL-licensed technology was used as the basis for the creation of a start-up company. Pyrochlore-type oxide compounds can be customized to increase selectivity and conversion by partial substitutions of catalytically active metals into the oxide lattice. With these metals well dispersed and locked into place in the crystal structure, metal sintering, which typically occurs on supported catalysts used in reforming reactions, and deactivation by sulfur and carbon are greatly reduced. The NETL collaboration that developed novel pyrochlore catalysts for reforming hydrocarbon fuels was previously recognized with the 2012 Research Collaboration Award from the Council for Chemical Research, a nonprofit organization dedicated to advancing research in chemistry, chemical engineering, and related disciplines.

NETL-RUA Collaboration Investigates Quantum Alloys for Catalytic CO_2 Utilization

In collaboration with scientists at NETL-Regional University Alliance (RUA) partner Carnegie Mellon University, NETL researchers employed experimental and computational techniques to study a new class of small (~1 nanometer) "quantum alloys" of gold (Au) and silver (Ag). Earlier, the team demonstrated that Au_{25} nanoclusters—ligand-stabilized metal clusters consisting of exactly 25 gold atoms—were among the most efficient CO_2 catalysts ever synthesized. Au_{25} clusters have precisely determined atomic structures, with nearly every atom accessible for catalytic interactions. Quantum mechanical effects become significant at this size, so that even small changes in composition, such as replacing a few gold atoms with silver, have a unique impact on catalytic reactivity. Using density functional theory (DFT), the team investigated the energetics of silver substitution to form $Au_{22}Ag_3$ structures by evaluating 176 possible atomic arrangements for incorporating silver into the structure and determining the most stable configuration. Experimental optical and electrochemical measurements confirmed DFT predictions, showing that alloying with silver increased the lowest unoccupied molecular orbital energy for the cluster, introduced new features in its absorbance spectrum, and forbade some optical transitions. Described in April 18 issue of the highly regarded *Journal of Physical Chemistry C*, the work sheds new light on how the electronic structure of these small clusters can be systematically tuned to improve catalytic reactivity.

Computer Model Predicts Mechanical Properties of Advanced Molybdenum-based Alloys

As part of an NETL-administered grant under the University Coal Research Program, a project team at the University of Missouri–Kansas City has developed an *ab initio* molecular dynamic model to obtain thermo-mechanical properties of alloys proposed for the molybdenum-silicon-boron ternary system. The calculated coefficient of thermal expansion, thermal expansion anisotropy, and elastic constants agree well with empirical results. The method enables researchers to arrive at a theoretical assessment of advanced molybdenum-based alloy properties for temperatures up to 2,000 Kelvin.

NETL Method Enhances Chemical Looping Gasifier Kinetics

NETL researchers demonstrated that, when operating a bench-scale calcium oxide (CaO)-calcium carbonate ($CaCO_3$) chemical looping gasification reactor, adding a small amount of potassium hydroxide (KOH) can increase the steam-coal gasification kinetics 4-fold compared to using CaO alone, and 10-fold compared to no CaO or KOH. Using two different coal types and temperatures between 700 °C and 900 °C, the researchers studied the effect of these dual-functioning catalyst capture agents on syngas composition, the steam-coal gasification kinetic rate, and the capture of carbon dioxide (CO_2) and hydrogen sulfide (H_2S). The composition of the dry syngas from the gasifier was roughly 20% methane, 70% hydrogen, and 10% other species for a CaO/C molar ratio of 0.5. Since the CaO and KOH species also capture H_2S and hydrogen chloride that may be in the feedstock, the process has potential for converting high-sulfur coals or chlorine-containing wastes, such as municipal solid waste, into syngas to generate electricity with near-zero emissions of acid gases and greenhouse gases. Multi-cycle studies, in which the $CaCO_3$ was heated to 900 °C to regenerate the CaO, showed that the increased steam-coal gasification kinetics rates for both CaO and CaO+KOH persisted even after six gasification-regeneration cycles. The work is slated for publication in an upcoming issue of the American Chemical Society journal *Energy & Fuels*.

NETL Model Accounts for Particle Clustering in Gasifiers

NETL researchers have developed, for the first time, a model that incorporates a variable specularity coefficient (a boundary condition parameter) to improve mixing predictions in fluid-particle flow systems by capturing the clustering phenomenon that occurs at the particle-wall boundary and by responding to dynamic changes in gasifiers. Described in the American Institute of Chemical Engineers publication *AIChE Journal*, the new model provides a physically meaningful and direct way to estimate boundary condition parameters without increasing computational costs and will increase the fidelity of modeling results for transport integrated gasification.

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