NETL's Ultra-Clean Fuels Focus Area: an Overview

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Introduction

The Ultra-Clean Fuels (UCF) focus area is involved in conducting the enabling science to provide the 21st century transportation systems with ultra-clean transportation fuels. The primary objectives of the UCF Focus Area are to take advantage of advances in computational chemistry computational chemistry, develop novel pathways to sulfur removal, develop advanced analytical techniques, develop improvements in separation science, and devise novel synthetic routes.

The following tasks are included in the UCF focus area: computational chemistry, advanced materials research, advanced analytical techniques, advanced hydrogen separations, and catalysis and reactor engineering.

The purpose of this paper is to present an overview of the UCF Focus Area.

Discussion

Computational Chemistry

Computational Chemistry utilizes advances in high speed computing to use simulation and modeling for understanding molecular processes and advancing technology. Molecular modeling is a powerful and rapidly developing suite of computational tools for understanding macroscopic phenomena in terms of molecular level events and properties. Molecular and materials modeling makes use of quantum chemical (electronic structure) and statistical mechanical methods to accurately describe the behavior of matter from a molecular viewpoint. The computational work of this group generates insight into the molecular level processes that control the outcome of experimental processes. Application of these methods to processes that use catalysts is particularly challenging, but has enormous promise.

In general, work will be conducted by both computations and complementary experimental efforts i.e. molecular modeling of hydrogen, hydrocarbon, and xenon adsorption on carbon nanotubes will be performed and comparison will be made with complementary experiments carried out at NETL. Simulations of chemisorption of hydrogen on carbon nanotubes will be performed and results will be compared with recent in-house experiments. Quantum mechanical electronic structure calculations will be carried out to model the formation of carbide deposits on iron and nickel surfaces and to elucidate the reaction mechanisms for hydrodesulfurization (HDS) of liquid fuels by heterogeneous catalysts.

The long-term goals of this work can be divided into two broad areas, the first being adsorption and reaction of gases on carbon nanotubes, and the second being chemisorption and reactions on metal surfaces. The fundamental difference between these two areas is in the nature of the surfaces under investigation. Other areas of research include F-T wax cracking, hydrogenation of aromatics, heteroatom removal, catalyst design, and carbonization reactions.

These goals can be achieved by employing optimized catalysts and procedures. The design of these catalysts and procedures would be based on a full understanding of the elementary chemical processes involved including both the control of the electronic properties of various active sites and of the interactions of different molecular species with such sites assisted by various types of promoters.

Advanced Materials Research

The advent of new forms of carbon such as single- and multi-walled carbon nanotubes opens possibilities for fuels-related applications. These carbons are unique porous materials with properties that lend themselves to uses as adsorbents, gas storage media, and catalyst supports. Since their discovery in 1991 [1], there has been an explosion of interest in nanotubes, but their properties in relation to fuels applications have still not yet been well defined. For example, conflicting reports about their hydrogen storage capacity have been made; some optimistic, others pessimistic. (For a review see [2]). Their large potential to play a role in enabling technology for future fuels makes intense investigation of these materials wise. Past work on this project entailed the development of methodology for the use of a novel instrument, the pulse mass analyzer, to determine isotherms for hydrogen, methane, and other gases and liquids on nanotubes or other materials [3,4]. In addition to measuring adsorption isotherms, this versatile instrument opens the possibility to study the kinetics of carbon growth on catalysts [5]. Full exploitation of its capabilities can provide information of the growth, adsorption properties, and destruction of novel carbon forms. Theoretical studies [6,7] have been of considerable help in guiding these experiments and interpreting their results [8]. Other carbon products in addition to nanotubes will also be explored. Coal-derived pitches have been used as an inexpensive starting material for carbon fibers. Expanded use of carbon fibers would result if production costs could be reduced. Tailoring the reactive properties of coal-derived pitches presents a possible route to cheaper high-performance fibers, but this will require deeper knowledge of the chemistry of formation of isotropic and anisotropic mesophase. Complimentary experimental and theoretical studies are planned to improve the process.

Advanced Analytical Techniques

This research initiative supports the efforts toward the design of novel methods for removing sulfur from fuels by developing advanced analytical techniques for sulfur analysis as part of the ultra-clean fuels focus area. The presence of sulfur in petroleum products such as gasoline, diesel fuel, and jet fuel adversely affects the performance and lifetime of current automobile emission control catalysts. Sulfur in fuels is the main contributor to environmental acid rain products, and by-products of sulfur-containing fuels also pose human health threats because of their toxic and mutagenic properties. Sulfur compounds also have adverse affects on the performance and lifetime of catalysts designed to reduce emissions of particulate matter and oxides of nitrogen. These concerns have resulted in the legislative lowering of the allowable levels of sulfur in fuels. This lowering, in turn, has necessitated the development of removal strategies in order for the fuels produced from the refining process to meet these stringent requirements.

Traditional methods of desulfurization, such as hydrotreating, are not capable of removing those sulfur compounds that have lower reactivity [9-12]. To meet the removal efficiency desired, new methods and technologies for sulfur removal are being designed. By developing the capabilities for determining the presence and concentration of different classes of organo-sulfur compounds, or of individual compounds within the larger classes, these sulfur removal strategies can be evaluated, developed, and optimized toward more complete removal of sulfur from the fuels.

The removal of sulfur from fuels has been linked to other fuel properties, such as lubricity, thermal storage, and compatibility with...
rings and seals currently used as engine components [13]. Many questions remain about the way that removing the sulfur-containing molecules affects the fuel quality and performance. Therefore, not only is the accurate determination of sulfur-containing compounds in fuels important for design and evaluation of desulfurization processes, but it is also a key in establishing functional relationships between sulfur compounds present and the fuel’s performance. In this light, the analytical development component of this task will be developed to both identify individual sulfur components and determine their concentration, especially at the trace levels where their presence or removal may begin to affect other fuel properties.

Advanced Hydrogen Separations

The Advanced Hydrogen Separations Technologies effort investigates the development, modeling, and verification of novel hydrogen membrane reactor concepts. Hydrogen can be produced from natural gas or other fossil fuel feedstocks. However, improving upon current methods for hydrogen separation from other gases remains a key issue, both for the large-scale production of hydrogen as in a refinery or Vision 21 plant environment, and for the small-scale purification of hydrogen as in fuel cell powered vehicles. Hydrogen separation membrane development, and its deployment in membrane reactor technology, has the potential for significant advances in hydrogen production and purification.

The development of advanced hydrogen separation membranes has the potential for profound improvements in efficiency for the separation and purification of hydrogen. The ideal membrane material would be low cost, highly selective, highly permeable, easily machined or formed, inert, and stable under severe operating conditions. Although such a membrane does not currently exist, there are materials and fabrication techniques that can produce membranes that possess several of these qualities. Hydrogen transport may take place through different types of materials—porous materials, diffusion-type membranes, and ion-transport membranes. Ceramic materials have the potential for low cost, high strength and chemical inertness, but are not easily formed, machined, and integrated into an otherwise metallic infrastructure. Some metals, such as palladium, possess both high selectivity and good permeability, but are easily poisoned and so expensive as to be impractical except in small, specialty applications. Composite materials offer some of the best qualities of their various component materials, but represent an increased manufacturing cost, complexity of fabrication, and potential for defects.

The long-term goal of this task is to produce novel prototypes for hydrogen separation membranes, either via collaboration or direct NETL in-house efforts. Specifically, two types of membranes are sought. One is a highly robust membrane capable of separating hydrogen from gasification feed streams at severe conditions of temperature (900°C) and pressure (up to 400 psi), while possessing chemical resistance to carbon monoxide, sulfur-containing compounds, ammonia, and other impurities. The second application is for membranes in “intermediate” severity conditions, such as those found in refinery processes. These include temperatures up to 500°C, with pressure drops and impurity tolerance dependent on the specific process.

Research efforts include:

- Hydrogen membrane development.
- Hydrogen membrane flux measurements
- Membrane reactor concepts.
- Sorption-based hydrogen separation concepts.
- Computational modeling.

Catalysis and Reactor Engineering

The objective of the Catalysis and Reactor Engineering Team is to explore experimental advancements in catalytic processes and reactor design for the production of fuels and chemicals from a variety of sources. Each Task investigates specific aspects of the advanced technologies for the production of ultra-clean fuels. Areas of interest will range from feedstock generation, reaction mechanisms, direct methane conversion, enhancements for improved Fischer-Tropsch (FT) performance, production of hydrogen and/or syngas from hydrocarbon feedstocks, fuels evaluation and upgrading, and the formation, dissociation, and conversion of methane hydrates.

One key area of research is the conversion of methane, the principle component of natural gas. It has been estimated that the world’s supply of natural gas will be sufficient to supply the demand well into the next century [14]. Lately, most of the near-term projected use of natural gas is for replacement of other fossil fuels in the generation of electricity. However, the supplies of natural gas can also be used for conversion to chemicals and transportation fuels. At present, the most probable scenario for the conversion of natural gas, in remote areas such as Alaska, is by partial oxidation of the methane by an ion-transport membrane reactor to produce syngas, followed by Fischer-Tropsch technology to produce liquids. Another possible route is the photocatalytic conversion of methane to methanol, under mild conditions, using light, water, and a semiconductor photocatalyst. Research is focusing on both the conversion of methane dissolved in water and methane contained within methane hydrates.

Another area of research is to overcome problems with current reforming processes. The reforming of fossil fuels (both liquid and gaseous) is an important process to help transform the transportation system from dependence on internal combustion engines to fuel cells. The problems with current reforming technologies are high operating temperatures and the quantity of carbon monoxide (CO) produced. Carbon monoxide acts as a poison upon contact with the proton exchange membrane (PEM) fuel cell (Pt based) catalyst. In an effort to reduce the CO produced, water is introduced with the fuel to convert the CO by the water-gas-shift (WGS) reaction. The objective of our research is to reduce the quantity of carbon monoxide produced during reforming to near-zero levels without the need for the water-gas-shift (WGS) reaction.

The conversion of natural gas into clean liquid fuels requires the use of cobalt-based Fischer Tropsch catalysts. Despite a great deal of research on these materials, the exact conditions to which the catalyst is exposed after reduction in hydrogen, and before it is fully on-line, have not been systematically studied in the open literature. These conditions include temperature, gas composition, and time. The specific relationships among these variables have a dramatic and irreversible effect on the activity, selectivity, and lifetime of the working catalyst. By conducting a systematic study of the activation of these catalysts, the changes in the cobalt metal that lead to optimal product yields and minimal deactivation rates can be identified.

Research into the physical properties and conversion of the methane contained within the methane hydrate molecule is an integral part of the Catalysis and Reactor Engineering Team. Methane hydrates have the potential of providing the U.S. with a supply of methane well into the next millennium. They occur naturally in deep-ocean and permafrost areas.

Many of the physical properties of methane hydrates are not well understood. One of these properties is the transport of methane within the hydrate [15]. Research planned in FY-02 will address this and other physical property issues with the aid of the larger hydrate reactor.

The photocatalytic conversion of the hydrates is based on research invented at NETL [16,17]. This research has applications in
the utilization of the methane contained in the vast hydrate deposits and as a solution to hydrate plugs that form in oil and gas pipelines.

Methane hydrates offer potential for the storage of natural gas. One volume of methane hydrates has the ability to store 180 volumes of methane at STP. [18] This ability of hydrates to contain vast quantities of methane opens the use of hydrates as a storage medium for natural gas. By use of methane hydrates, natural gas could be stored in a solid form at relatively moderate temperatures. Methane hydrates could also be used for the transport of stranded natural gas. By conversion of the natural gas into hydrates, transport to market of the solid hydrate is much more feasible than either pressurized liquefied natural gas tankers. In order to utilize hydrates as a storage medium for natural gas, the quantity of natural gas within the hydrate must be maximized.

Conclusions
The Ultra-Clean Fuels Focus Area at NETL has identified several issues that require advanced research to provide the 21st century transportation systems with ultra-clean transportation fuels. Specific Tasks were developed to address these issues and the research at NETL is striving to address the issues.

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